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“Atomic Processes in High Energy Density Plasmas," Summaries of FY 1997 Research in the Chemical Sciences

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Summaries of FY 1997 Research in the Chemical Sciences

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences

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PREFACE

This summary book is published annually to provide information on research supported by the Department of Energy's Division of Chemical Sciences, which is one of four Divisions of the Office of Basic Energy Sciences in the Office of Energy Research.

These summaries provide the scientific and technical public, as well as the legislative and executive branches of the Government, information, either generally or in some depth, about the Chemical Sciences program. Areas of research supported are indicated in the Disciplines Indes (page 173) and in the summaries themselves. Energy technologies that may be advanced by use of the basic knowledge generated in this program are included in the Technologies Indes (page 177) and are often referenced in the summaries.

Scientists interested in proposing research for support will find the publication useful for gauging the scope of the present basic research program and its relationship to their interests. Proposals that expand this scope may also be considered or directed to more appropriate offices. The primary goal of the research summarized here is to add significantly to the knowledge base in which existing and future energy technologies can evolve efficiently and safely. Scientific excellence is a major criterion applied in the selection of research supported by the Division of Chemical Sciences. Another important consideration is advancing science that will produce new information related to energy use and its environmental impacts.

The program takes place in several different kinds of organizations. About one-third of the projects are at DOE laboratories and the rest mostly at universities, with a small number of projects at industrial laboratories. In DOE laboratories, much of the research utilizes special unique facilities which, in some instances, are national user facilities. These are described in a special section of this publication.

Questions about the detail of an individual project may be directed to the investigators involved or the persons in charge at DOE laboratories (who are identified at appropriate places in this publication). Other questions about the program may be directed to the appropriate program manager, team leader or the Division Director.

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Division of Chemical Sciences
Office of Basic Energy Sciences

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PROGRAM DESCRIPTIONS

The objective of this program is to expand, through support of basic research, knowledge of various areas of chemistry, physics and chemical engineering with a goal of contributing to new or improved processes for developing and using domestic energy resources in an efficient and environmentally sound manner. Each team of the Division of Chemical Sciences, Fundamental Interactions and Molecular Processes, is divided into programs that cover the various disciplines. Disciplinary areas where research is supported include atomic, molecular, and optical physics; physical, inorganic, and organic chemistry; chemical energy, chemical physics; photochemistry; radiation chemistry; analytical chemistry; separations science; heavy element chemistry; chemical engineering sciences; and advanced battery research. However, traditional disciplinary boundaries should not be considered barriers, and multi-disciplinary efforts are encouraged. In addition, the program supports several major scientific user facilities. The following summaries describe the programs.

Fundamental Interactions Team
(KC-03-01)

Photochemical and Radiation Sciences
(KC-03-01-01)

The Photochemical and Radiation Sciences program consists of research on the interactions of radiation with matter. Emphasis is placed on exploration of fundamental photochemical processes aimed at the capture and conversion of solar energy. The solar photochemistry research encompasses organic and inorganic photochemistry, electron and energy transfer in homogeneous and heterogeneous media, photocatalysis, and photoelectrochemistry. The photosynthetic reaction center is studied as a model for design of efficient photoinduced charge separation in biomimetic/photocatalytic assemblies. The radiation chemistry research is concerned with the chemical effects produced by absorption of energy from ionizing radiation. Electron pulse radiolysis techniques provide information on the nature of transient intermediates, kinetics, and mechanisms of chemical reactions in the condensed phase.

Chemical Physics
(KC-03-01-02)

The Chemical Physics program supports research on fundamental molecular processes related to the mission of the Department in the areas of combustion, catalysis, and environmental restoration. Specific areas of emphasis include gas phase chemical reaction theory, experimental dynamics and spectroscopy, thermodynamics of reaction intermediates, chemical kinetics and reaction mechanisms at high temperatures in the gas phase and at surfaces, combustion diagnostics, and chemical dynamics and kinetics at surfaces and with metal and semiconductor clusters.

A major user-oriented facility, the Combustion Research Facility at Sandia National Laboratories, California, is supported by this program. This facility offers the use of advanced instrumentation and computation to interested combustion scientists from industry, universities, and national laboratories.

Atomic, Molecular, and Optical Physics
(KC-03-01-03)

The Atomic, Molecular, and Optical Physics program supports experimental and theoretical studies relevant to energy technologies. These include studies of atoms and atomic ion structures, energy levels and lifetimes of quantum states, and of transport and exchange processes associated with energy and momentum transfer. These studies seek to obtain the most accurate and complete fundamental knowledge of the properties and interactions of photons, electrons, atoms, and ions. Relatively high energy atomic physics research involving atoms stripped of all or almost all electrons and of atoms and ions in which electrons are promoted to upper energy levels provide basic information to assist fusion energy development. The study of processes that lead to the production of coherent radiation and its statistical manifestations in atomic physics are included. Research on the manipulation of atoms with coherent photon fields, on the behavior of plasmas generated by intense laser beams, and on the physics of low-temperature plasmas relevant to materials processing is also supported.

Facility Operations
(KC-03-01-04)

DOE operates large scientific facilities for the benefit of the scientific community. Major user facilities permit forefront research to be conducted in areas important to DOE by scientists from industry and universities in addition to DOE contractors/grantees. Operating support for these expensive, unique facilities that are open to all qualified researchers is provided by DOE. Many of the facilities are user oriented. The five operated by the Chemical Sciences Division are the following: the Combustion Research Facility (CRF) at Sandia, Livermore; the High Flux Isotope Reactor (HFIR) and the Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory; the Stanford Synchrotron Radiation Laboratory (SSRL); and, shared with the Material Sciences Division, the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. They represent research resources for the general scientific community, and qualified scientists not associated with the host laboratory are encouraged to make use of them. However, any activity that can be carried out at commercially available laboratories is not appropriate for these DOE-supported facilities. The process by which an off-site scientist can use a facility is discussed in each summary. Other facilities described in the “Special Facilities in the Chemical Sciences Division” section are also available for use through collaboration with staff scientists. The names of individuals to contact for further information and technical data on available instrumentation at each facility are described.

Molecular Processes Team (KC-03-02)

Chemical Energy
(KC-03-02-01)

The Chemical Energy program includes basic chemistry research related to chemical transformations or conversions which are fundamental to new or existing concepts of energy production and storage. Of particular interest are those research activities with the objectives of understanding the chemical aspects of (1) catalysis, both heterogeneous and homogeneous; (2) the chemistry of fossil resources, particularly coal, including characterization and transformation; (3) the conversion of biomass and related cellulosic wastes; and (4) the chemistry of precursors to advanced materials. The disciplines of organic, organometallic, inorganic, physical, thermo- and electrochemistry are central to these programs. The emphasis is on understanding the fundamental chemical principles underlying the new and developing technologies and on innovative chemical research with potential for new energy concepts.

Separations and Analysis
(KC-03-02-02)

The separations part of the program supports basic research focused on obtaining an improved understanding of the molecular basis for physical and chemical separations. The research seeks to elucidate fundamental chemical phenomena which have broad implications for separation science rather than to develop specific processes. The analysis part of the program supports research on understanding phenomena underpinning analytical methods to provide the basis for improving sensitivity, reliability, and/or productivity of analytical determinations. Investigation of chemical and physical principles which can lead to entirely new methods or which elucidate the fundamentals of current separations or analytical techniques are encouraged. This program does not support instrument or process development. Research progress is reported quickly in the open literature so that those interested in specific applications can build on work supported herein.

Heavy Element Chemistry (KC-03-02-03)

The Heavy Element Chemistry program focuses on furthering the molecular level understanding of the chemistry of actinides and their fission products. This understanding provides a basis for the development of new technologies for the production, use, safe handling, storage, and disposal of nuclear materials. The program also serves to train scientists who can address these important activities and their environmental consequences with a broad understanding of the underlying chemistry. Areas of interest include but are not limited to: (1) aqueous and non-aqueous coordination chemistry, (2) solution and solid-state speciation and reactivity, (3) measurement of chemical and physical properties, (4) synthesis of actinide-containing materials, (5) chemical properties of the heaviest transactinide elements, and (6) advanced theoretical methods for the prediction of electronic and molecular structure and reactivity. Collaboration with the national laboratories is encouraged because of the special facilities required for handling radioactive materials.

Chemical Engineering Sciences (KC-03-02-04)

This program addresses energy aspects of chemically related engineering topics, including thermodynamics, turbulence related to combustion, and physical and chemical rate processes. Particular attention is given to experimental and theoretical aspects of phase equilibria, especially of mixtures, including supercritical phenomena, and to the physics of gas phase turbulence. Also included are fundamental studies of thermophysical and thermochemical properties. Emphasis is given to improving and/or developing the scientific base for engineering generalizations and their unifying theories.

The program also supports fundamental research in electrochemistry related to advanced batteries for areas critical to understanding the underlying limitations in the performance of non-automotive electrochemical energy storage systems. Areas of research include anode, cathode, and electrolyte systems and their interactions with emphasis on improvements in battery size, weight, life, and recharge cycles. Although both primary and secondary battery systems are considered, the greatest emphasis is placed on rechargeable (i.e., secondary) battery systems. The program covers a broad spectrum of research including fundamental studies of composite electrode structures, failure and degradation of active electrode materials, and thin film electrodes, electrolytes, and interfaces. Problems of electrode morphology, corrosion, electrolyte stability, and the transport properties of electrode and electrolyte materials and surface films are also addressed. Investigations in computational modeling and simulation of the underlying chemistry; including reactions, structure-function properties, interactions at critical interfaces, film formation, phase change effects on electrodes, and electrochemical characterization of crystalline and amorphous materials are also of interest.

LABORATORY ADMINISTRATION

Listed below, by laboratory and department or division, are persons who are or will be in charge of the Division of Chemical Sciences projects at DOE laboratories. These individuals are laboratory, department, or division administrators who can provide information about specific programs or refer inquiries to appropriate individuals.

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NATIONAL LABORATORIES

Photochemical and Radiation Sciences

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Fundamental Interactions Program

1. ***Raman Spectroscopy of Model Photosynthetic Systems***

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The objective of this project is to study heterogeneous electron transfer between different molecular assemblies at metal surfaces with the ultimate goal to prepare model photosynthetic systems. Monolayers and multilayers composed of donor acceptor species are fabricated by self-assembly and Langmuir-Blodgett techniques. The distinguishing feature of this project is the use of metal substrates as a means of enhancing different optical phenomena as well as photoinduced electron transfer. Such enhancement occurs due to excitation of the plasmon resonances on specially prepared metal surfaces or metal nanoparticles. The photoreduction of nitrite has been studied at roughened silver electrodes and a significant increase in yield is observed, as compared to smooth silver. Recently, a completely new concept was developed based on the coupling of the plasmon resonances of individual metal particles in highly organized two-dimensional arrays. The coupling produces nonradiative energy transfer between particles resulting in highly efficient light collection. Such substrates (termed Colloidal Metal Films) were successfully prepared using surface chemistry to immobilize small silver and gold particles on glass surfaces. Strong coupling between particles was observed to give rise to a blue shift in the plasmon resonance (exciton-like behavior). These systems will be employed as artificial antenna and will be coupled to different model photosynthetic systems in order to increase significantly their efficiency.

2. ***Photosynthetic Light Harvesting and Charge Separation***

Small, G.J.; Jankowiak, R.; Hayes, J.M. **$200,000**
515-294-3859
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gsmall@ameslab.gov

The major goal is a detailed physicochemical understanding of the efficient solar energy conversion processes of plants and photosynthetic organisms. Focus is on the two most important processes: ultrafast (picosecond or faster) excitation energy transfer within the antenna network of protein-chlorophyll complexes and the primary photochemical event of charge separation which occurs in the reaction center. Advanced frequency- and time-domain spectroscopies are essential for understanding these processes. This program uses laser-spectral hole burning spectroscopies. To understand excitation energy transfer and charge separation, several key issues are being addressed. They are: the nature of excited electronic states of coupled chlorophylls bound to protein; the effects of the protein on the electronic structure of chlorophylls; the effects of structural disorder of proteins on excitation energy transfer and charge separation; and characterization of protein and chlorophyll vibrational motions which mediate excitation energy transfer and charge separation. These problems are investigated using a unique facility which combines hole burning with high pressure (10,000 atm) and electric fields. The responses of biological systems to external perturbations such as pressure provide insights on the mechanistic aspects of their transport properties. Theoretical efforts are directed towards understanding how photosynthetic systems carry out efficient excitation energy transfer and charge separation in the presence of structural disorder.

3. ***Ultrafast Spectroscopy and Energy Transfer***

Struve, W.S.; Savikhin, S. **$220,000**
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Femtosecond laser spectroscopy is applied to studies of ultrafast electronic energy transfer and charge separation in natural and artificial photosynthetic systems. The goal is a full understanding of the primary processes and structure-function relationships in natural systems, in order to facilitate design of biomimetic systems. Recent experiments have dealt with energy transfers in light-harvesting antennas from purple photosynthetic bacteria, bacteriochlorophyll-protein complexes from the green bacterium *Chlorobium tepidum* and oligomeric bacteriochlorophyll antennae in light-harvesting chlorosomes from green bacteria. The sequence of level-to-level energy transfers was recently mapped in the structurally well characterized Fenna-Matthews-Olson (FMO) antenna complex from green photosynthetic bacteria—a major milestone in the study of structure-function relationships in strongly coupled antennas. The kinetics of energy transfers within the B808-866 antenna of the green bacterium *Chloroflexus aurantiacus* was recently determined; this complex shows surprising parallels with the much-studied B800-850 antennas of purple bacteria, which are not otherwise closely related to *Cf. aurantiacus*. Planned experiments include kinetic studies of genetically altered FMO complexes (e.g., with systematic deletions of bacteriochlorophyll pigments), in order to identify the roles of specific pigments in the level relaxation scheme of this prototypical antenna.

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Chemistry Division

4. *Time-Domain Molecular Structure Determination in Photoinduced Electron Transfer Processes*

Chen, L.X.; Thurnauer, M.C.; **$70,000** Operating
Wasielewski, M.R. **$200,000** Equipment
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The objective of this research is to correlate the molecular structures of reaction intermediates in photoinduced electron transfer processes with reaction mechanisms using time-domain X-ray absorption spectroscopy (TDXAS). The structures of photochemical reaction intermediates are important in determining the factors that control reactions, such as the vibrational modes that are strongly coupled with electron transfer, the energy barriers of the reaction, and the potential surfaces of the intermediates. The TDXAS experiments are to be conducted at the Advanced Photon Source in a new TDXAS facility currently under construction. This experimental facility will implement "pump-probe" X-ray absorption spectroscopy (XAS) to monitor structural changes. The XAS spectra of a particular intermediate state of electron donor-acceptor molecules will be collected at an optimal delay time after the laser pulse that initiates the reaction. The structural information obtained from TDXAS experiments combined with dynamics information from other spectroscopic techniques will enhance our understanding of photoinduced electron transfer and will create new research opportunities in solar energy conversion and storage.

5. *Electron Transfer and Energy Conversion*

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This project seeks knowledge related to photochemical conversion of solar energy and safe disposal of nuclear waste materials. Four scientific areas are the focus of the program: the mechanisms of electron transfer reactions, the nature and reactions of excited radical ions, the reactions of NO_x radicals, and the effects of interfaces on these reactions. Each area is studied by combinations of three techniques: electron pulse radiolysis, ab initio computation, and laser photoexcitation. Intramolecular electron transfer rates are measured which enable separate evaluation of the distance dependence of electronic couplings and solvent reorganization energies, coupled to examination of computed electronic couplings as functions of distance. Radical ions are studied which have excited states capable of driving photochemistry, including photochemical energy storage. While the majority of radical ions have short-lived (<< 100 ps) excited state lifetimes, the radical anion of benzoquinone was found to have a 60 ns excited state lifetime due to a forbidden transition. Redox equilibria are being measured of nitrate radical dianion and results compared with ab initio calculations of the corresponding electron affinity and solvation energies. Charge carriers, generated by ionizing radiation in small colloidal particles, were found to exit the particles and appear in the surrounding solution. The latter studies interface closely with more applied efforts aimed toward understanding and stabilization of nuclear waste in storage tanks.

6. *Hierarchical Photosynthetic Systems for Photochemical Energy Conversion*

Thurnauer, M.C.; Tiede, D.M.; **$699,000**
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This program investigates mechanisms of coupling ultrafast photoinduced charge separation to the production of chemical and electrochemical products. Natural photosynthesis is being studied as an example of a photochemical system in which ultrafast photophysical processes are nearly optimally linked to chemical energy conversion. The natural systems have a hierarchical design, consisting of discrete chemical subsystems that break up photosynthesis into a sequence of individual photochemical and chemical reaction steps. This program examines how linkages between different photosynthetic subsystems are achieved and delivers strategies for the design of novel, hierarchal artificial systems for enhanced photochemical energy conversion. The biological systems under investigation include the bacterial photosynthetic reaction center protein, and the photosystems I and II from algae and plants. Surface-modified, semiconductor colloid photocatalysts are being synthesized and investigated as models of synthetic hierarchical photochemical systems. Time-resolved EPR (pulsed and CW) and neutron and X-ray diffraction experimental techniques and theoretical modeling are being developed to investigate structure and photochemical activity in hierarchical photochemical systems. Notable contributions from this program have been the resolution of structures and sequences of electron transfer events in natural photosynthesis, and, following from this, the design and synthesis of surface-modified semiconductor colloids that exhibit photoinduced sequential electron transfer steps leading to charge separation.

7. *Stable Isotope Labeling of Photosynthetic Materials and Structural Analysis*

Tiede, D.M. **$65,000**
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This project produces photosynthetic materials enriched with nonnatural, stable isotopes that offer unique opportunities for structural and photochemical analyses of complex natural and synthetic photochemical systems using magnetic resonance and neutron scattering techniques. A central problem for unraveling mechanisms for solar energy conversion lies in detecting photochemistry and structure of individual components buried within larger molecular arrays. The isotopically labeled materials produced by this program provide an elegant, non-perturbative solution to this problem. Primary emphasis is on the production of 99.7% deuterium-enriched algae and photosynthetic bacteria. Deuteration greatly simplifies the electron paramagnetic properties of free-radical intermediates produced by light-induced chemistry. Neutron scattering experiments also benefit from deuteration by amplifying the coherent neutron scattering signal from the labeled molecules and suppressing incoherent scattering. These features are being exploited for the determination of photochemistry and structure in natural photosynthesis using new, high-resolution, state-of-the-art pulsed and CW magnetic resonance spectroscopies and neutron scattering techniques. In addition, the photosynthetic materials are being used as sources for the isolation of fully deuterated chlorophylls, bacteriochlorophylls, chlorins, quinones, carotenoids, and lipids. These compounds are used for the reconstitution of selectively labeled natural photosynthetic assemblies and for the synthesis of artificial assemblies with selected isotopic composition. This program is providing new materials for probing the components, structure, and mechanisms of charge separation as performed by natural and artificial photosynthetic systems.

8. Reactive Intermediates in the Condensed Phase: Radiation and Photochemistry
Trifunac, A.D.; Bartels, D.M.; **$1,772,000**
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An understanding of reaction dynamics and overall chemistry of the short-lived species that are created when energetic radiation interacts with matter is important to many fields of chemical research and to many uses of radiation. The knowledge developed in the course of this research is applicable to diverse areas of technology, such as polymer processing and treatment of hazardous wastes, and to questions relating to long-term radioactive waste storage. Recent studies include an examination of the role of solvation in controlling reactivity of charged species. Novel ultrafast studies of water photoionization have provided new insights into the energetics of ionization. A new chemistry of excited ions is being examined; highly excited aromatic radical cations accept electrons from the solvent in a process termed hole injection. Solid state studies of ions provide insights into the control of ion chemistry and have led to the development of new methods for the study of catalytic effects of acidic zeolites. Reactions of hydrogen atoms in silica glasses, in noble gas fluids, and in aqueous solutions are being examined, providing insights into the radiolytic defect formation. These studies are being carried out using unique real-time tools, including a picosecond linear accelerator; a Van de Graaff accelerator; and femtosecond, picosecond, and nanosecond UV lasers coupled to specialized detection equipment.

9. Molecular Systems for Photochemical Energy Conversion and Storage
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In this project, molecular systems consisting of organized arrays of energy and electron donor and acceptor molecules are synthesized and studied with the goal of producing new, fundamental approaches to the efficient conversion of light energy into chemical energy. A variety of spectroscopic techniques, including femtosecond optical spectroscopy and time-resolved magnetic resonance, are being applied to these problems. The focus of current research includes preparation of the first chemical systems that precisely mimic the electron transfer and spin dynamics that are exhibited only by natural photosynthetic energy conversion proteins. This work yields important information regarding how the structure of a chemical system can be optimized for efficient energy conversion. New rod-like charge separation molecules are being studied in which light can be used to control the distance over which the initial charge separation events occur. These molecules are being used to develop nanostructures for use in energy conversion applications. New structures are being examined that test whether molecular arrays may act as conduits for long distance transport of photogenerated charges to storage sites. Critical mechanistic issues of fundamental importance regarding the role of the surrounding medium and donor-acceptor electronic structure in controlling rates of charge separation and recombination are also being studied.

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Porphyrins are nature's choice catalysts. They mediate a remarkable spectrum of bioenergetic reactions ranging from photosynthetic solar energy transduction to conversion of carbon dioxide into fuel. This program seeks to understand the common chemistry that controls these multifaceted (photo)catalytic reactions and aims to develop synthetic systems that duplicate the efficiency and selectivity of biological systems. Recent work has focused on structural control of the photophysical and chemical properties of porphyrins, prompted by the mounting evidence of conformational distortions and flexibility observed in crystallographic determinations of photosynthetic antenna, reaction centers, and heme proteins. Results with synthetic porphyrins demonstrate that simple molecular engineering can readily alter the architecture of the porphyrins and, thereby, significantly modulate their physicochemical properties. Besides providing insights into the consequences of nonplanar conformations in vivo, the synthetic work has opened attractively simple avenues into entirely new classes of porphyrins with dramatically altered (photo)physical and chemical properties. The facile introduction of multiple substituents on the periphery of porphyrins results in multiconformational landscapes that cause major changes in optical, redox, radical, and excited state properties. For example, simple modifications of substituents can change excited state lifetimes by three orders of magnitude. These results establish the acute sensitivity of porphyrins to structural motifs found in photosynthetic and heme proteins and, in addition, demonstrate that synthetic porphyrins can be molecularly tailored to exhibit specific dark and excited state properties.

11. Electrochemistry and Photoelectrochemistry
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The objective of this research is to provide new insights into the mechanisms of electrochemical and photoelectrochemical phenomena. Electron-transfer is a key element of these phenomena. A novel methodology has been developed, the laser-induced temperature-jump method, which has provided a unique tool for the measurement of fast interfacial electron transfer (time resolution approaching one nanosecond). Recent experimental studies have focused on the measurement of electron transfer rates between an electrode and a tethered redox moiety. For the first time it has been shown that there are significant differences in the rate constants and the distance dependencies of the rate constants for saturated and unsaturated tethers and that these differences are consistent with theoretical predictions. Another facet of this program is theoretical analyses and computer simulations of a broad range of electrochemical and photoelectrochemical systems which may be generally described as electron transfer coupled with homogeneous chemical reactions.

Chemistry Department

12. Thermal, Photo-, and Radiation-Induced Reactions in Condensed Media
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This program addresses issues fundamental to the efficient capture and storage of light energy: excited-state formation, chemistry, and photophysics; energy transduction by electron-transfer reactions; and energy storage through chemical transformations. Theoretical and experimental efforts are elucidating the factors controlling excited-state lifetimes and electron-transfer rates; the roles of electronic configuration, donor/acceptor separation, bridging groups, nuclear-configuration and free-energy changes; as well as the role of solvent dynamics, which are being investigated through studies of transition-metal complexes and other donor/acceptor systems. Electron pulse radiolysis and flash photolysis techniques are being used to generate and characterize transient species important in solar energy conversion, including the preparation and properties of transition-metal complexes in unusual oxidation states and their ability to bind and activate small molecules, and to determine bimolecular and intramolecular electron-transfer rates. The properties and reactions of electrons and other ions in dielectric fluids are being studied utilizing both X-ray and high energy electron sources. The long-term storage of solar energy as fuels or valuable chemicals requires efficient coupling of light absorption and chemical transformation processes. Mechanistic studies of systems which couple photoinduced electron-transfer processes to the bond-forming reactions required in the photogeneration of hydrogen and the photoreduction of carbon dioxide are a major focus. New efforts focus on photochemical and mechanistic studies of organometallics in water.

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Structural Biology Division

13. Chemistry with Near-Infrared Photons
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The objective of this project is to establish new concepts that allow the use of long-wavelength visible and near-infrared light for the synthesis of important chemicals and fuels. This is motivated by the fact that the energy-rich part of the solar spectrum lies at long wavelengths. Over the past few years we have established a new concept for highly selective partial oxidation of small alkanes, alkenes, and aromatics by molecular oxygen to organic building blocks and industrial intermediates using visible light. Reactions are conducted in room temperature zeolites without the need for solvent or sensitizer. The method exploits the high electrostatic fields in the vicinity of exchangeable alkali or alkaline-earth ions, and the high concentration of collisional reactant pairs that can be formed inside the zeolite. Most recent examples include the conversion of ethane to acetaldehyde, and of propane to acetone without byproduct. The key role of photoinduced hydrocarbon-oxygen charge-transfer has been established by rapid-scan FT-infrared spectroscopy of the reaction and by optical spectroscopy of reactant mixtures loaded into translucent monolayers of large NaY crystals. Time-resolved step-scan FT-infrared spectroscopy with 10 nanosecond resolution has been developed for mechanistic studies. Nano and microsecond infrared spectra of excited molecules and transient radicals in zeolites have been recorded for the first time.

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Center for Basic Science

14. Interfacial Photochemical Processes: Dye-Sensitized Nanocrystalline Semiconductor Electrodes
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The objective of this research is to establish a basic understanding of charge transport and interfacial phenomena governing the performance of dye-sensitized nanocrystalline semiconductor solar cells. The specific focus of the current work is on dye-sensitized nanocrystalline TiO_2 electrodes. Major issues being addressed include the underlying cause for the photovoltage and for the improved performance resulting from chemically modifying the TiO_2 surface, the mechanism and kinetics of charge recombination at the solid/redox electrolyte interface, the position of the conduction-band edge potential, and the effect of the nanoporous structure on the mass transport of redox species in the solution phase. Detailed information on most of these phenomena is being obtained by using a nonstationary technique, which monitors the photovoltage response to the modulation of light intensity. The theoretical framework for application of this technique to dye-sensitized nanocrystalline semiconductor electrodes is being developed.

15. *Photoconversion Processes in Liquid Crystal Porphyrin Films and Other Molecular Semiconductors*

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Fundamental aspects of photoconversion processes in molecular semiconductors are being explored and compared to natural photosynthetic systems. Recent measurements show that singlet excitons are transferred further and faster in polycrystalline perylene diimide films than in the photosynthetic light-harvesting systems. The results suggest that excitons may be delocalized over a number of molecules and that coherent energy transfer plays a role in exciton motion. The perylene diimide films are some of the best artificial light-harvesting systems yet discovered. Quenching of excitons via interfacial electron transfer, a key step in photocurrent generation, has been studied using a number of different quenching films. Steady state and time-resolved luminescence measurements led to the postulate that the effective interfacial contact area between the perylene film and most quenchers was substantially less than the geometrical contact area. Support for this postulate was recently achieved by nanoscale measurements using a near field scanning optical microscope. Exciton dynamics and interfacial electron transfer processes are currently being studied in highly ordered films of liquid crystalline perylene diimides. These studies will contribute to our understanding of natural photosynthesis and to the ultimate development of organic-based solar energy conversion systems.

16. *Synthesis and Characterization of Novel III-IV and II-VI Semiconductor Quantum Dot Structures for Solar Photochemical Conversion*

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The photochemical and photophysical properties of quantum dot (QD) structures are being investigated for solar photochemical conversion. Colloidal quantum dots of InP with diameters ranging from 20 to 80 Å were synthesized as well-crystallized nanoparticles with bulk zinc blende structure; p-type ($InP:Zn=10^3:1$) and n-type ($InP:S=10^3:1$) QDs were also synthesized, as well-crystallized particles. Colloidal solutions of InP quantum dots show excitonic features in their absorption spectra. The spread in QD diameters is about 10%. The photoluminescence of InP preparations showed highly efficient band-edge photoluminescence with the quantum yield of about 60% at 10 K after etching the particles with hydrogen fluoride. Global PL spectra show a broad band which shifts to higher energy with decreasing QD size. Resonant photoluminescence and excitation spectra (PLE) show several transitions close to the band edge energy. The Stokes shifts, obtained through fluorescence line narrowing and PLE experiments, are size dependent and increase from 6 to 16 meV as the particle size decreases from 45 to 26 Å. InP QD close packed films can be prepared with short range hexagonal packing. A close packed solid shows long-range energy transfer from smaller to larger particles. Photoinduced electron transfer from InP QDs to SnO_2, TiO_2, and ZnO has also been observed.

17. *Carrier Dynamics and Quantization Effects in Photoelectrochemistry*

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The kinetics of photoinduced electron transfer at semiconductor-liquid interfaces, for both macroscopic and size-quantized structures, and for both minority and majority electron transfer processes, is being investigated both theoretically and experimentally. Three semiconductor-liquid redox systems have been analyzed theoretically using new, rigorous ab initio calculations, which treat, for the first time, the full electronic structure of the coupled semiconductor-solvent-redox system. Experimental studies of photoinduced minority electron transfer dynamics are being conducted in the nanosecond to femtosecond time scales using transient photoluminescence spectroscopy based on upconversion and time-correlated single photon counting. Experimental studies of majority electron transfer in the dark are being conducted using impedance spectroscopy and current-voltage characteristics under depletion conditions. The results for majority and minority electron transfer kinetics are being compared to theory. Studies are also being made of the electron cooling and electron transfer dynamics in InP quantum dots in the form of colloidal solutions, three-dimensional quantum dot superlattice arrays, and as quantum dots sensitizers of nanostructured TiO_2 films.

18. *Fundamental Studies of Electron Injection Dynamics at Dye-Sensitized Nanostructured Semiconductors in Photochemical Solar Cells*

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The time for electron injection from a Ru-based dye molecule Ru(4,4'-dicarboxy-2,2'-bipyridine)$_2$(NCS)$_2$] adsorbed on nanostructured TiO_2 films into the TiO_2 conduction band is being investigated in the femtosecond time regime using femtosecond transient absorption spectroscopy. Initial results indicate that the injection time into the TiO_2 conduction band is less than 125 fs, followed by a trapping time of 4 ps. However, measurements of the dye in blank electrolyte indicate that the excited dye itself exhibits some long-lived near-infrared absorption, which complicates the interpretation of the results under normal cell operating conditions. Complementary results obtained by other researchers operating under ultrahigh vacuum conditions have helped to clarify our results under ambient conditions. This project is part of an integrated effort of basic and applied research to develop and evaluate the potential of photochemical (i.e., dye-sensitized semiconductor) solar cells as a new and viable photovoltaic technology. The basic research contained in this project will underpin the applied/ development effort.

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Radiation Laboratory

19. Radical Reaction Mechanisms in Solution

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In this project chemical reaction mechanisms are studied which are initiated by or involve free radicals. These basic studies are a prerequisite for the optimization and control of radical reaction systems. The investigations rely on time-resolved radiation chemical techniques (pulse radiolysis) using optical and electron spin resonance spectroscopic (ESR) detection and are complemented by photochemistry, steady-state radiolysis, electrochemistry, and analytical methods. One focus has been on halogenated peroxyl radicals which are able to act as one- and two-electron oxidants. Applying pulse radiolysis, experimental evidence has now been found for a radical adduct previously proposed as an intermediate in the two-electron mechanism. Other recent accomplishments include the triplet-sensitized oxidation of the dipeptide threonyl-methionine as a model for the complex kinetics of peroxynitrite oxidations, and the experimental establishment of the complete material balance in the radical-induced degradation of several halogenated organic acids. The latter results have a bearing on environmental cleanup procedures using radiation chemical and electron beam techniques. Radical scavenging by iodine in irradiated normal alkanes (up to dodecane) indicated a general 1:3 ratio for the loss of hydrogen from primary and secondary positions, respectively. The first chemical dosimeter for in situ ESR has been developed and calibrated.

20. Sulfur-Centered and Other Heteroatom-Based Organic Radicals

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This project is concerned with properties of radicals derived from heteroatom-containing organic compounds with focus on species with the radical site located at the heteroatom itself. Emphasis is on sulfur-organic molecules in view of their general significance in the biosphere. The effects of charge and spin localization, the influence of electron-donating or -withdrawing groups, free electron pairs, and structural parameters are of fundamental importance for the stability and reactivity of such radicals. To conduct a systematic and comparative evaluation of significant physico-chemical parameters investigations have been extended to other organic molecules with Group V (N, P), Group VI (O, Se, Te), and Group VII (F, Cl, Br, I) heteroatoms. A major effort is directed towards the characterization of odd-electron bonded species in which antibonding electrons exert a bond-weakening effect on existing or newly formed bonds. These studies have a fundamental implication on the understanding of bond formation and breakage. Measurements of vibrational frequencies of several $2\sigma/1\sigma^*$ three-electron bonded radical cations by time-resolved resonance Raman pulse radiolysis are in excellent agreement with high-level calculations. Advances have been made in the understanding of protonation kinetics and sites in heteroatom-centered radicals, and in electron transfer and decarboxylation mechanisms in amino acids and peptides.

21. Structure and Chemical Properties of Radiation-Produced Intermediates

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Highly reactive free radical and molecular excited state intermediates produced by radiolysis or photolysis are studied to determine their often unusual structures and bonding characteristics and to relate these to the chemical properties, kinetics, and mechanisms of the reactions they undergo. Time-resolved experimental approaches include resonance Raman spectroscopy, electron spin resonance, and microwave absorption, which are complemented by theoretical calculations of electronic structure. In recent work, studies of phenoxyl radicals have revealed a solvent-dependent zwitterionic component in the structure and a precise relationship between the rate of radical formation and pH in the hydroxyl radical oxidation of phenols. In the strongly exothermic reaction between hydrated electron and phenoxyl radical, the triplet state of the initial encounter pair has been shown to be energetically below the singlet. An extreme acid form of π-H^+ bonded semiquinone radical, the electron transport agent in photosynthesis, has been observed. The accuracy of highly efficient density functional methods for spin density determination has been calibrated by comparison to definitive atomic results obtained from highly-correlated coupled-cluster calculations with an extrapolation technique employing systematic sequences of basis sets. New charge separation reactions have been found with 2,2'-biphenol, where the triplet state transfers an electron to fumarate, and with 1,4,5,8-naphthalene tetracarboxylate, where a triplet state molecule transfers an electron to a ground state molecule.

22. *Mechanisms of Redox Processes in Coordination Compounds*

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The dynamics of excited- and ground-state redox reactions of coordination complexes are being investigated under magnetic inductions of up to 9 Tesla (90 kilogauss). The Zeeman mechanism, spin-orbit coupling and hyperfine coupling, among other perturbations to the Hamiltonian, are being unraveled by comparing several series of compounds of the transition metal ions Ni(III), Co(II), and Mn(II). The photochemical reactivity of coordination complexes in excited states not directly accessible from the ground electronic state (phantom states) is studied by these sequential excitations which provide means of measuring quantum yields and relaxation kinetics. The catalysis of the O_2 oxidation of SO_3^{2-} by Co(III) complexes has been investigated. The dimethylglyoxymate of Co(III) is a good thermal catalyst for this reaction. A newly prepared compound, $Co(Me_6\text{-}[14]dieneN_4)(SO_3)^+$, cannot catalyze the thermal reaction but is an efficient photocatalyst. The mechanisms of these reactions are being investigated. Radiolytic one- and two-electron oxidation of 2,7,12,17-tetrapropylporphycene (H_2TPrPc) and its Fe, Co, Ni, Cu, and Sn complexes in CH_2Cl_2, CCl_4 and 2-propanol solutions produced the π-radical cation and thence, in aprotic solvents, the stable dication. Oxidation of Co(II) and Ni(II) porphycenes produced unusual, stable Co(III) and Ni(III) products due to the influence of the macrocycle. Since oxidation of Ni(II) porphyrins yields only transient Ni(III) complexes or π-radical cations, the stabilizing difference is the macrocycle.

23. *Photochemical and Photoelectrochemical Processes for Energy Conversion*

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Photoresponse of large-bandgap semiconductors such as SnO_2, TiO_2 and ZnO have been extended into the visible with surface modification using novel sensitizers such as organic dyes, ruthenium(II) polypyridyl complexes, and fullerene derivatives. The mechanistic and kinetic details of interfacial charge-transfer processes are investigated by probing the excited state and redox behavior of these sensitizers. Composite nanoparticles composed of two or more semiconductors (e.g., SnO_2/TiO_2 and SnO_2/CdS) or metal-capped semiconductors (e.g., Au/CdS) are also being sensitized with organic dyes to achieve charge rectification and suppress the back electron transfer process. Photoelectrochemical, microwave conductivity, and spectroelectrochemical measurements of dye-modified semiconductor films are being carried out to understand the charge transport properties and loss of charge carriers at the grain boundaries. Redox properties, excited states, and associated reaction kinetics of fullerenes and functionalized fullerene derivatives are significantly impacted by the size and shape of the fullerene core (C_{60}, C_{70}, etc.), the nature of the functionalizing addends (electroactive, photoactive, hydrophilic, etc.), and the number of functionalizing groups (mono-adduct, bis-adduct, etc.). This class of compounds is subjected to a wide range of radiation-chemical and photochemical measurements to investigate intramolecular electron and energy transfer processes.

24. *Heavy Ion Radiolysis and Track Structure*

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Experimental and theoretical techniques are being used to provide basic knowledge in order to better predict the variation of radiation damage with different types of ionizing particles. Single photon counting studies on the heavy ion radiolysis of liquid benzene show that the decrease in yield of the dimer excited state with increasing linear energy transfer can be well correlated with the increase in molecular hydrogen formation and suggests that excited states participate significantly in the chemistry occurring in heavy particle tracks with important consequences in liquid hydrocarbons and polymers. Reconciliation of the time resolved yields of the hydrated electron with scavenger concentration dependent studies represents a significant solution to a long-standing problem in radiation chemistry and paves the way for more accurate models of water radiolysis. Monte Carlo track simulation methods utilizing these findings are in excellent agreement with measured yields of the radical and molecular products of water radiolysis with fast electrons and are giving invaluable details on the track structure of lower energy electrons. The first realistic deterministic diffusion-kinetic model of liquid hydrocarbons has given new insight on the initial distribution of cations, and it will further aid in the construction of more accurate Monte Carlo track codes.

25. *Radiation Chemistry Data Center*

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Radiation chemical and complementary photochemical studies provide a wealth of numerical chemical property data on free radicals and excited state species. The reaction rate constants and reactive intermediate yields obtained in these studies are being compiled, evaluated, collected into databases, and disseminated via the World Wide Web. This timely kinetic data is used by engineers and scientist as input to calculations modeling systems involving free radical intermediates. A World Wide Web-based current awareness service has been instituted to help chemists, biologists, and engineers keep abreast of primary literature references in these fields. An active search capability for bibliographic and chemical property data on the World Wide Web at http://www.allen.rad.nd.edu has been added to facilitate easy user access. A revision of the NDRL/NIST Solution Kinetics Database is underway.

Chemical Physics

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Fundamental Interactions Program

26. Chemical Theory
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The central focus of this research is the theoretical description of the structure and dynamics of metal clusters. The goal is to determine the relationship between the structure and reactivity of clusters. Close connection is made to the experimental program of Riley and coworkers (at Argonne National Lab) which addresses many of the same questions. This research has utilized non-self-consistent semiempirical density functional electronic structure theory, i.e., a corrected effective medium (CEM) method. Now, the effort is directed toward discovery and testing of new variational one-electron density functional methods which would provide further information on electronic structure and would also allow calculations on large systems. In particular, the CEM method is being extended in two novel ways: (1) use of a linear combination of atomic densities with the fractions determined by minimization of the energy; and (2) inclusion of an explicit first order perturbation correction for non-additive atomic densities. These two describe charge transfer and weakly directional bonding, and thus may also allow the treatment of metals with open structures, oxides, and mixed metals. Two other projects involve kinetics and traditional ab initio electronic structure. The first analyzes the kinetics and non-equilibrium structures associated with irreversible or far-from-equilibrium adsorption and catalytic reaction processes on solid surfaces. The second calculates potential energy surfaces for combustion-related gas phase reactions and metal catalysis-related reactions using multiconfiguration self-consistent field methods.

27. Molecular Beam Photoionization and Photodissociation Studies of Molecules, Clusters, and Radicals
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The goals of this program are (1) to obtain accurate thermochemical data, such as ionization energies (IEs) and bond dissociation energies, for neutral polyatomic molecules, radicals, and their ions; (2) to study the UV and VUV photoionization and photodissociation dynamics of molecules and radicals; and (3) to investigate the reaction dynamics and mechanisms of fast radical-molecule reactions. One current focus is on the studies of organosulfur radicals and transition metal carbonyl compounds and their fragments. Oxidation of organosulfur compounds, which are emitted to the atmosphere due to the incomplete combustion of coal and oil, ultimately lead to the formation of SO_2 and acid rain. The study of the UV and VUV photochemistry of organosulfur species is relevant to the modeling of atmospheric sulfur chemistry cycles. The energetic and reactivity studies of transition metal carbonyl species are motivated by attempts to understand their catalytic abilities. We have recently expanded to include studies of oxygen-containing hydrocarbon radicals. In the past year, we have obtained reliable energetic data for the CH_2CH_2SH, CH_3SO, C_6H_5, and C_6H_5CO radicals. We have also determined highly accurate IEs for CH_3SH and CH_3CH_2SH using laser photoelectron spectroscopy.

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Chemistry Division

28. Metal Cluster Chemistry Research
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This program comprises experimental and theoretical studies of the chemical and physical properties of clusters of catalytically active transition metals. The goal is to understand how cluster structure depends on cluster size, and how cluster properties depend on structure, thereby providing a better understanding of surface chemistry and heterogeneous catalysis. Experimentally, the reactivity of clusters with small molecules is investigated by measuring absolute reaction rate constants and adsorbate binding energies, and by determining product compositions, the nature of adsorbate binding sites, and cluster geometrical structure. Complementary laser spectroscopic studies combine size-specific infrared techniques with threshold photoionization measurements to study the characteristic vibrational spectra and adsorbate-induced ionization potential shifts of selected cluster-adsorbate systems. The theoretical effort involves studies of stable and metastable structural forms and electronic properties of clusters, cluster phases and phase changes, thermal stability and fragmentation, reactive and nonreactive cluster-molecule interactions, etc. Both single-component and two-component (alloy) clusters are investigated using existing and newly developed semiempirical potentials and ab initio approaches. The goal is to understand cluster properties and the mechanisms defining them in terms of the nature of the interatomic forces.

29. Photoionization-Photoelectron Research
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This program focuses on the investigation of reactive intermediates in combustion and other energy-producing processes, and on key species involved in subsequent atmospheric chemistry, using the photoionization mass-spectrometric method and its derivatives (TPES, PEPICO, ZEKE, MATI). The technical capabilities of this program have been recently enhanced by the addition of pulsed laser-based experiments. The ephemeral species of interest are produced in situ using selected techniques (abstraction reactions, discharges, on-line synthesis, pyrolysis, laser photodissociation, etc.). The primary motivation of our research is to provide accurate and reliable thermochemical data and spectroscopic and structural details that are crucial in comprehending pertinent chemical reactions. In addition, we endeavor to extract useful generalities and insights into the nature of chemical bonds or of the dynamical processes accompanying photoionization. The desired level of detail is unraveled by combining suitable experimental techniques with subsequent data analysis using novel fitting methods. Our recent measurements on CF_3OH, CF_2O, and CF_3-containing species addressed several important open questions regarding the environmental soundness of the latest generation of refrigerants. Other measurements, such as those on C_2H_5O and CH_3O isomers, CH_nS (n=1-3), and HNCX and NCX, (X=O, S), have provided valuable new data related to combustion of hydrocarbons, alcohols, and sulfur-containing fuels, and to the industrially important $RAPRENO_x$ process. Our experimental results also play a very important role in testing the most sophisticated ab initio calculations, which are beginning to achieve near-chemical accuracy for small molecules.

30. *Chemical Dynamics in the Gas Phase*
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The program mission is to characterize the gas-phase chemical reactivity of small molecules and radicals, especially those involved in combustion, by a combination of both theory and experiment. The experimental effort involves high-temperature reaction rate studies by UV absorption in two shock tubes and low-temperature product distribution studies by IR absorption in a flow tube. A companion data analysis effort has expanded the use of sensitivity coefficients and error propagation in accounting for secondary chemistry. Recent measurements have included the dissociation rate constants of chlorofluorocarbons (CFCs) and their alternates, the HCN product distributions from CN attack on alkanes, and the reactions of methyl radicals with themselves and with oxygen. The theoretical effort involves large-scale studies to complement the above measurements and others done outside the group. Associated methods development emphasizes the efficient exploitation of advanced computers, especially massively parallel ones. Recent theoretical activity has included electronic structure studies of potential energy surfaces, classical and quantum dynamics studies of reactivity on those surfaces, hierarchical studies for the assignment of highly excited spectra, and low dimensional manifold studies for the simplification of coupled kinetic equations. The close coupling between theory and experiment brings a unique combination of expertise to bear on problems of chemical reactivity.

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Applied Science

31. *Combustion Kinetics and Reaction Pathways*
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The objectives of this basic research project are to further the understanding of the kinetics of combustion-related reactions and the thermodynamics and reaction dynamics of the compounds and transient species involved. This work provides fundamental information to other researchers such as theorists (who need reliable experimental data with which to test their calculations) and modelers (who study practical problems like fuel oxidation, pollutant formation and destruction, flame suppression, and waste chemical incineration.) Specific interest is focused on: (1) determining absolute rate coefficients for gas phase reactions; (2) identifying pathways for multichannel reactions; and (3) studying the photoionization and thermochemistry of a wide variety of compounds and radicals. For kinetics studies, the project features a shock tube to obtain reliable kinetic measurements over a wide range in temperature (800 K to 2500 K). For thermodynamics and reaction dynamics studies, a discharge flow-photoionization mass spectrometer apparatus is employed in determining primary products from multichannel reactions and in performing photoionization studies on reactants, free radicals, and stable reaction products. The mass spectrometer apparatus was designed to be operated on beamline U-11 of the National Synchrotron Light Source and thus take advantage of high intensity, tunable vacuum ultraviolet light to achieve high detection sensitivity and selectivity in monitoring a wide variety of free radicals that may be readily generated in the flow tube reactor.

32. *Gas-Phase Molecular Dynamics*
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Research in this program explores the energetics, dynamics, and kinetics of chemical reactions resulting from molecular collisions in the gas phase. We are interested in the microscopic factors affecting the structure, dynamics, and reactivity of short-lived intermediates, such as free radicals, in gas-phase reactions important in combustion chemistry. A significant aspect of this work is the study of radical-radical reaction kinetics. Molecular species are studied using both experimental and theoretical tools including high-resolution spectroscopic probes, time-of-flight mass spectrometry, and time-dependent quantum wavepacket calculations. The goal of the work is a fundamental understanding of the transient species involved in chemical processes related to combustion chemistry. The research carried out in this program is part of the effort of the Center for Spectroscopy in Molecular Science within the BNL Chemistry Department.

33. *Photoinduced Molecular Dynamics in the Gas and Condensed Phases*
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The goal of this program is to elucidate the dynamics of photoinduced fragmentation processes of molecules in the gas phase and on surfaces through the use of state- and energy-resolved spectroscopies. Particular emphasis is placed on systems or processes that provide information on the spectroscopy and dynamics of chemical intermediates which are important in combustion and surface catalytic reactions. Coherent VUV and ultra-fast laser sources are used to induce photoionization, photodissociation, surface desorption, and intramolecular motion, the dynamics of which are probed by state- and/or energy-resolved photoelectron and photoion methods. Dissociation and ionization measurements at high laser intensities investigate the response of molecules to intense fields well beyond the perturbative regime which introduces new selectivity and "field-induced" fragmentation pathways. Further studies of the effects of well characterized fields on simple, isolated systems are also under investigation with the ultimate goal of optimal control of physical and chemical processes. The mechanisms for photodesorption and photofragmentation of molecules chemisorbed on metal surfaces are being explored through the use of state-resolved VUV probes of the desorbed fragments. Laser-induced, bimolecular reactions are also being pursued in an effort to probe the transition state dynamics of surface reactions that lead to gas-phase products. The research in this program is part of interdisciplinary efforts within the BNL Chemistry Department represented by the Catalysis and Interfacial Chemistry group and the Center for Spectroscopy in Molecular Science.

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Chemical Sciences Division

34. *Energy Transfer and Structural Studies of Molecules on Surfaces*
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The goal of this research is to study the dynamics of excited electronic states on surfaces, at interfaces, and in condensed phases and to develop new laser techniques for studying these dynamics. The research program is both theoretical and experimental in character, and includes nonlinear optical and ultrafast laser techniques in addition to a variety of standard surface science tools for characterizing surfaces and adsorbate-surface interactions. Recent work has centered on developing and applying femtosecond two-photon photoemission to study the dynamics of electrons at metal-polymer and magnetic interfaces. The ultrathin layers under study range from 0.4 to 4 nm in thickness. The results of this program have a direct bearing on high-speed technological devices and materials, the fundamental physics of two-dimensional systems, and on other problems of general interest such as surface photochemistry and optical processes at interfaces.

35. *Chemical Dynamics*
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The objectives of this program are to develop the basic knowledge and understanding of the mechanisms and dynamics of elementary chemical reactions that have a major impact on combustion and advanced energy production technologies. Recent emphasis has been to determine the structure and chemical behavior of reactive free radicals and highly excited polyatomic molecules, and to provide microscopic details of primary dissociation and bimolecular processes. These objectives are achieved with a strongly coupled experimental and theoretical-computational approach, using emerging technologies. Dynamical studies use advanced molecular beam and laser methods including photofragmentation translational spectroscopy, ion imaging, and fast-beam photodissociation techniques. Kinetics studies employ IR laser flash kinetic spectroscopy, IR-UV double resonance, and high-resolution UV-VUV laser spectroscopy. New theoretical methods and models are developed both to provide insight into chemical reactivity and the dynamics of reactive processes, and to provide more accurate and efficient means of calculating reaction rates and molecular structures. Current studies include crossed-beam reaction dynamics and photochemistry with emphasis on processes involving reactive hydrocarbon radicals and carbon atoms. Studies continue to probe the structure and dynamics of the chemical transition state and the microscopic mechanisms of primary chemical processes. New studies take advantage of the Chemical Dynamics Beamline recently commissioned at the Advanced Light Source, providing greatly enhanced experimental capability for studies of primary photochemical and photoionization processes and reaction dynamics.

36. *Physical Chemistry with Emphasis on Thermodynamic Properties*
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The object of this project is the measurement and the theoretical calculation of the thermodynamic and related properties of novel or prototype systems. Recently, the emphasis has been on ionic fluids under near-critical or supercritical conditions. Binary fluids have been selected and measured that model a pure ionic fluid but have critical points at experimentally accessible temperatures. Critical exponents have been determined by phase equilibria and light scattering methods. Recent results show a clear crossover from Ising to classical (mean field) exponents as the temperature moves away from the critical point. Other recent research has included a comprehensive equation of state for the important system $CaCl_2$-H_2O in the range 523 K to 900 K. A new theoretical basis was developed for this equation based on mixtures of dipole (H_2O) and quadrupole ($CaCl_2$) molecules for which Monte Carlo calculations were made. This represented a good first approximation that was refined by small semi-empirical adjustment terms. Other recent research includes a comprehensive equation of state for NaOH-H_2O extending to pure liquid NaOH. Investigations often involve collaboration with Lawrence Livermore National Laboratory (LLNL), Oak Ridge National Laboratory (ORNL), or the United States Geological Survey (USGS).

Environmental Energy Technologies Division

37. Combustion Chemistry
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In order to understand and optimize combustion processes we address fundamental issues of chemical reactivity in combustion systems at both the microscopic and macroscopic levels. Combustion processes are governed by chemical kinetics, energy transfer, transport, fluid mechanics, and the complex interactions between these. Pathways for energy movement and competition between the pathways determine reaction rates, product yields, and product energy distributions. The theme of our research is to bring new advances in computing, particularly parallel computing, to the study of these computationally intensive combustion problems. Our current activities are concerned with: 1) developing models of combustion processes with complex and realistic flow fields that include detailed chemical mechanisms; 2) developing tools to quantify model sensitivity and uncertainty; 3) using functional sensitivity analysis to explore relationships between dynamic observables and the potential energy surface structure significant in scattering and rate coefficient calculations; and 4) calculating rate coefficients.

38. Mechanism and Detailed Modeling of Soot Formation
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The project focuses on fundamental aspects of physical and chemical phenomena critical to the development of predictive models of soot formation in combustion of hydrocarbon fuels. The proposed work includes theoretical and numerical studies of gas-phase chemistry of gaseous soot particle precursors, soot particle surface processes, and particle aggregation into fractal objects. For the surface growth, principal types of reactions—those determining soot particle growth and oxidation—will be investigated using quantum-chemical, transition-state-theory, and kinetic Monte Carlo simulations, thus providing a sterically resolved analysis of the soot surface growth and oxidation kinetics. The surface will be modeled as a graphitic-type edge, comprising either a single aromatic sheet or multiple aromatic layers. Particle aggregation will be studied via stochastic simulations. An ensemble of spherical particles, with a prescribed distribution, will undergo collisions and simultaneously with that particle growth by surface deposition. The objective of these simulations is twofold: first, to investigate the physical nature of transition from spherical to fractal growth and the factors affecting this transition, and second, on the basis of the results collected in the stochastic simulations to develop a simple mathematical model that captures the essential physics and yet computationally affordable for applications with computational combustion codes.

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Division of Applied Physics

39. Chemical Kinetics Modeling
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This project emphasizes numerical modeling of chemical kinetics of combustion. Combustion modeling applications in both practical combustion systems and in controlled laboratory experiments are included. Elementary reaction rate parameters are combined into reaction mechanisms, which then describe reaction of the fuels being studied. Detailed sensitivity analyses are used to identify those reaction rates and product species distributions to which the results are most sensitive and therefore warrant the greatest attention from other experimental and theoretical research programs. Experimental data from a variety of environments validate the reaction mechanisms, including results from laminar flames, shock tubes, flow systems, detonations, and even internal combustion engines. Particular attention will be given to oxidation of hydrocarbons at relatively low temperature and corresponding influences on ignition, and to formation and combustion of aromatic species leading to soot production.

Pacific Northwest National Laboratory
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Environmental Molecular Sciences Laboratory

40. Chemical Structure and Dynamics
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The Chemical Structure and Dynamics program responds to the need for a fundamental molecular-level understanding of chemistry at environmental interfaces by providing insight into condensed-phase chemistry and developing and validating ab initio theories. There are three primary program elements: (1) Interfacial Chemistry, with a special focus on water-oxide interfaces; (2) High-Energy Processes at Environmental Interfaces; and (3) Understanding the Condensed

Phase Through Cluster Models, recognizing atomic and molecular clusters as a form of matter whose properties lie outside the realm of general chemical experimental science, and that both provide a quantitative basis for comparison with theory and are also the source of a microscopic understanding of the condensed phase. The approach includes (1) synthesis of unique and well-characterized surfaces and interfaces by controlled deposition of atoms, molecules, and clusters using molecular-beam epitaxy; (2) characterization of surfaces and interfaces by atomic-resolution surface mapping (e.g., scanning tunneling microscopy) and near-field optical microscopy, in addition to various state-of-the-art surface science and optical spectroscopic methods combined with molecular scattering and diffusion studies; (3) synthesis of atomic and molecular clusters that mimic the structures of surface sites and of solvated species in solutions and at interfaces; (4) laser methods for studying atoms and molecules with time resolution sufficient to measure chemical dynamics in real time; and (5) direct photon and/or electron excitation of surfaces, interfaces, and molecules to model chemical processes important in mixed waste storage (radiolysis) and in the energetic destruction of wastes.

41. Molecular Theory and Modeling
Dunning, T.H.; Garrett, B.C.; **$2,500,000**
Corrales, L.R.; Dang, L.X.; Feller, D.F.;
McCarthy, M.I.; Palmer, B.J.; Peterson, K.A.;
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The molecular theory and modeling project is designed to increase understanding of molecular processes important in environmental chemistry. The project integrates ab initio studies of fundamental molecular processes in model systems (e.g., clusters) with modeling of the complex molecular systems found in the environment. Four research areas are emphasized: (1) properties (e.g., structure and energetics) and processes (e.g., solvation, association, reaction) for aqueous clusters and solutions containing inorganic species (e.g., metal and radionuclide ions) and organic species (e.g., chlorinated hydrocarbon), including studies of aqueous-vapor and liquid-liquid interfaces; (2) structure and energetics of ion-ligand complexes (such as metal ions with crown ethers) and the dynamics of complex formation in aqueous solutions, including studies of factors influencing selectivity and efficiency (e.g., ligand design, solvation); (3) properties of aqueous-mineral interfaces that control the binding of ions and molecules to soil minerals and the dynamics of molecular processes at these interfaces, including adsorbate kinetics and solvent and adsorbate structure at the interface; (4) properties of amorphous materials that control their dissolution (e.g., by water) and degradation (e.g., by radiolysis), including the structure and thermodynamics of bulk materials, surfaces, and interfaces with other phases. This knowledge will further the development of new processes for the separation of metals from liquid wastes, the construction of reliable models of contaminant transport and transformation in soils and groundwater, and the assessment of amorphous materials proposed for long-term isolation of radionuclides.

Sandia National Laboratories
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Combustion Research Facility

42. Turbulent Reacting Flow Research
Barlow, R.S.; Schefer, R.W.; **$1,300,000**
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This experimental and computational research project is directed toward an increased understanding of the coupling between chemical kinetics and turbulent mixing in reacting flows. Current research efforts address fundamental issues, such as differential diffusion; unsteady strain and flame curvature; the influence of heat release on the scalar dissipation field; geometric properties of turbulent premixed flames; and the role of turbulence-chemistry interactions in pollutants formation. Quantitative techniques for simultaneous imaging of velocity and multiple scalars are used to determine the spatial structure of turbulent reaction zones. Direct numerical simulations, where all scales of fluid motion are computed, reveal fundamental aspects of reacting flow. Simulations with detailed chemical kinetic mechanisms are combined with experiments on two-dimensional vortex-flame interactions to investigate hydrocarbon flame response to unsteady flow-induced strain rate and curvature. Recent focus of computational work has included migration to massively parallel architectures, and stiff time-integration techniques to enhance computational efficiency. The influence of turbulent mixing on thermochemical states is determined by simultaneous point measurements of NO, OH, CO, the major species, temperature, and mixture fraction. These detailed multiscalar data reveal instantaneous relationships among scalars and constitute a unique basis for evaluation and refinement of turbulent combustion models.

43. Chemical Dynamics and Kinetics
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The goal of this research is to understand the details of fundamental chemical processes that occur in combustion. Experiments in chemical kinetics use approaches such as laser-photolysis/laser-induced fluorescence, laser-photolysis/long-path IR absorption, and high-temperature shock-tube measurements. Recent systems of interest have included the reactive systems CH + CO, O_2, acetylene and Cl + hydrocarbons, as well as the collisional quenching of electronically excited OH. These experimental studies are aided by quantum chemical and statistical theoretical calculations. Experiments in chemical dynamics emphasize collecting data for elementary processes and individual molecules resolved to a quantum-state level. Techniques utilized include ion imaging of unimolecular and bimolecular reactions, femtosecond time-resolved approaches (transient absorption, photoelectron spectroscopy, and stimulated Raman scattering), and linear and nonlinear laser spectroscopies. Recent applications have included ion-imaging studies of the product angular distributions of the H atom and H_2 fragments from the multiphoton excitation of methane. Femtosecond time-resolved studies using photoelectron spectroscopy have focused on the investigation of internal conversion dynamics in conjugated polyenes. Recent spectroscopic studies have emphasized the application and development of LIF, two-color resonant four-wave mixing and laser-induced grating techniques for molecular spectroscopy and photodissociation dynamics, with application to the important HCO, CH_2CHO, and HCCO radicals.

44. *Novel Laser Facility for Basic Research in Optical Diagnostics*

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Continued progress in developing quantitative optical diagnostics requires an increasingly detailed understanding of collisional phenomena. We are constructing an innovative system of high-repetition rate, short-pulse lasers optimized for excite/probe studies of collisional processes. The lasers will be highly configurable with respect to pulse widths and output wavelengths, and will offer near-transform-limited pulse widths in the range 10-140 ps and at ~2 ns. Using a frequency-doubled distributed feedback dye laser we have recently obtained tunable transform-limited pulses at 285 nm (100 ps pulse width, 0.2 cm^{-1} bandwidth, 0.6 mJ pulse energy). The lasers will allow us to: 1) study state-resolved rotational-vibrational energy transfer over a wide range of temperatures for a variety of subject species and foreign-gas colliders; 2) measure mass transport properties, energy transfer, and reorienting collisions in transient species using novel laser-induced grating techniques; 3) measure electronic quenching rates of species with short upper-state lifetimes; and 4) develop new picosecond-pulse diagnostic techniques that are less sensitive to collisional effects than conventional methods. These capabilities will have a significant impact on the advancement of optical diagnostic techniques such as CARS, LIF, degenerate four-wave mixing (DFWM) and absorption spectroscopy through enhanced understanding of collisional processes, leading to more quantitative diagnostics modeling. The availability of sub-nanosecond pulses will allow basic studies to be conducted under combustion-like conditions. In addition, the lasers will provide powerful new capabilities when applied directly as diagnostics tools. The system will be located in a dedicated laboratory available for collaborative experiments by external users and Combustion Research Facility staff. External researchers will benefit from the facility in two ways: through improved diagnostics codes and scientific publications available from the CRF, and through use of the equipment during visits. Interested researchers should consult the section on CRF user facilities elsewhere on this site.

45. *Combustion Research Facility (CRF) Diagnostics Research: Nonlinear and Cavity Ringdown Spectroscopy*

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This project involves the development, support, and application of nonlinear spectroscopic diagnostics for Combustion Research Facility programs. Emphasis is on coherent anti-Stokes Raman spectroscopy (CARS), resonant four-wave mixing techniques, and cavity ringdown spectroscopy for measurements in reacting gases. CARS is a relatively mature technique that provides spatially and temporally precise measurements of temperature and major species concentrations. Degenerate four-wave mixing (DFWM) has recently emerged as a coherent diagnostic roughly similar to CARS but offering greater sensitivity for trace species detection. Cavity ringdown spectroscopy is a laser absorption technique that provides greatly enhanced sensitivity compared to conventional methods. The DFWM work is focused on investigations of fundamental issues involved in quantitative applications of DFWM. Topics include experimental studies of isolated DFWM line shapes and intensities as influenced by collisional and Doppler broadening, electronic quenching, predissociation, thermal-grating generation, and laser saturation effects. High-resolution pulsed laser systems, in both the ultraviolet (UV) and infrared (IR) wavelength regions, are used for detailed spectral studies. The experimental results are compared to theoretical calculations, leading to quantitative but simpler models for spectral analysis software. Computer codes for analyzing CARS and DFWM spectra are being developed and made available to diagnostics and combustion researchers. Polyatomic molecules in flames and discharges have been detected by exciting IR transitions using DFWM and cavity ringdown techniques. The use of IR excitation here is new, and will dramatically increase the number of species detectable by these methods. A technique for measuring the methyl radical, a transient polyatomic species important in combustion and diamond film growth, has been developed based on DFWM with UV excitation. Current work is aimed at further quantifying a method of detecting carbon monoxide by two-photon-excited laser-induced fluorescence (LIF) via the B-X system (two 230-nm photons). Cross sections for photo-ionization, two-photon excitation, and collisional broadening are being measured in a high-resolution Doppler-free experiment. Time-resolved measurements of species- and temperature-dependent LIF quenching rates of the CO B state are also planned. The results will be incorporated in a simulation and fitting code available to interested researchers.

46. *Flame Chemistry: Modeling and Experiments*

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This research program represents an integrated effort to understand the chemistry of combustion both qualitatively and quantitatively through the development of predictive mathematical models. There are three aspects of the program: (1) the mathematical modeling of flame experiments and other macroscopic experiments where chemistry is a critical factor, (2) the theoretical prediction of rate coefficients and product distributions of critical elementary reactions using a combination of statistical and dynamical methods in conjunction with ab initio potential energy surfaces, and (3) low-pressure flame experiments in which laser-induced florescence and mass spectrometry are the principal diagnostic tools. The focus of the research is on combustion-generated pollutants (nitrogen oxides, soot and its precursors, and other air toxics) and on limit phenomena in combustion (flammability limits, extinction limits, etc.)

47. Combustion Research Facility (CRF) Diagnostics Research: Novel Techniques and Strategies
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The research goals of this project include the conception and development of novel laser-based diagnostic techniques for Combustion Research Facility programs. New techniques involving ultrafast phenomena, wave-mixing, and thermo-acoustic scattering as well as new strategies in planar laser-induced fluorescence (PLIF) and resonant multiphoton excitation are being actively pursued. Frequency-resolved optical gating techniques provide full characterization of single ultrashort laser pulses. These new capabilities and recently developed ultrashort-pulse lasers are being exploited further to develop transient absorption and time-domain resonant wave-mixing combustion diagnostics for measurements of temperature, pressure, and relative concentrations. Investigations of thermo-acoustic scattering processes, exposed in degenerate four-wave-mixing research, are being pursued for potential application as diagnostics of velocity, viscosity, temperature, and concentration. Time-resolved PLIF for quantitative two-dimensional measurements are limited by low signal strengths and a strong sensitivity to quenching processes. Studies of collisional energy transfer and quenching processes are leading to predictive models of quenching cross sections for molecules such as NO and OH. Results from these and other fundamental studies, combined with new laser or camera technologies, are providing new capabilities to combustion researchers.

Atomic, Molecular, and Optical Physics

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Physics Division

48. Accelerator Based Atomic Physics
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This program is focused on precision measurements which test many-body relativistic atomic-structure calculations. The current concentration is on helium-like ions with nuclear charge Z in the intermediate range of 20-40. Here, electron-electron correlations (dominant at low-Z) and relativistic effects (dominant at high-Z) are simultaneously important, and the competition between these contributions is an important theoretical problem at the present time. Recent work is a comprehensive study of forbidden transitions in helium-like ions and features the introduction of new experimental techniques such as the coincidence method for measurements of two-photon transition probabilities and the two-foil method for measuring the lifetimes of very short-lived states. Another area of concentration is precision spectroscopy within the n=2 shells of few-electron ions where a disagreement between theory and experiment for the n=2 He-like energy levels was resolved. Future efforts will include studies of the spectral distribution of emission in two-photon decay and spectroscopy of multi-electron, highly-charged ions. The work is conducted at the ATLAS heavy-ion accelerator at Argonne and the heavy-ion synchrotron SIS in Germany. Together these facilities provide access to all charge states of all elements.

49. Synchrotron Radiation Based Atomic Physics
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The primary goal of this effort is to establish a fundamental understanding of X-ray interactions with atoms and molecules. These studies of photoprocesses in prototypical systems in the hard X-ray range provide a fundamental basis for the X-ray diagnostics used in other disciplines (e.g., Compton scattering studies of electron momentum distributions in materials, Raman scattering studies of electronic band structure, X-ray diffraction studies of large molecules and core-hole shifts in complex chemical environments). In addition, systematic precision measurements of X-ray photoprocesses in free atoms, as is possible at the Advanced Photon Source (APS), test, guide, and stimulate current theoretical developments in atomic physics (e.g., relativistic many-body and S-matrix scattering theories). During FY1997, a dedicated endstation has been commissioned and the first two experiments in X-ray scattering at the APS were completed: (1) X-ray scattering beyond the impulse approximation, (2) Resonant Raman scattering near threshold. The latter experiment commissioned the first major instrumentation project, a general purpose X-ray spectrometer, by obtaining a complete set of data showing the evolution from resonant Raman scattering to characteristic fluorescence as the excitation energy was stepped across a deep inner shell threshold where interference in the scattering channels should be observable. An ion-electron imaging apparatus with 4π collection efficiency is under development to make detailed measurements of the dynamics of ionization processes.

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Chemical Sciences Division

50. *Pair Production Processes in Relativistic Heavy Ion Collisions*
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Cross sections for electron capture, ionization, capture from pair production, and free pair production for 0.96 GeV/nucleon U 92+ and 0.405-1.3 GeV/nucleon La 57+ , and 10.8 GeV/ nucleon Au 79+ projectile ions incident on Au, Ag, and Cu targets have been measured. The cross sections for ionization, capture of a target electron, capture from pair production, and free pair production were analyzed as a function of collision energy, projectile and target atomic numbers. In the 1-GeV/nucleon energy range, the capture cross section of an electron from the target (sum of nonradiative and radiative electron capture) decreases almost as γ^{-3} (γ is the Lorentz factor), while the cross section for capturing an electron from the negative energy continuum (capture from pair production) increases almost as $\ln^2\gamma$. In the 10 GeV/nucleon energy range, the cross section for capturing an electron from the vacuum or capturing an electron from the target becomes comparable. At higher energies (10.8 GeV/n) for which capture from pair production is dominated by perturbative contributions, theoretical predictions of the cross sections come very close to the measured values. An experiment will be performed at the LBNL's Advanced Light Source to investigate double photoionization. The study of the correlation and interference between the two-ejected electrons (one from the negative continuum and the other from the K-shell) will give access to unique and fundamental information on the interactions of the electrons of a high-Z atom with the vacuum and the process of creation of matter. In this type of experiments, atomic physics is expected to bring new and fundamental knowledge in particle and high energy physics.

51. *Atomic Physics*
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This program provides detailed experimental descriptions of the structure and interactions of atomic and molecular systems to stimulate and challenge theoretical understanding. The program exploits the ability of two state-of-the art electron cyclotron resonance (ECR) ion sources at LBNL to produce intense, highly charged, continuous ion beams for the conduct of low energy ion-atom and ion-molecule collision studies. Recent activity includes determination of the complex amplitudes, and their scattering angle dependences, for excited substates produced in multiple electron transfer collisions, differential momentum distributions of the products of ion collisions with He atoms, and systematics of the production and fragmentation of highly charged C_{60} ions by slow multiply charged ion impact. A portion of the program includes collaborative efforts with colleagues from outside LBNL; e.g., novel studies of the photoionization of He and other target atoms at the LBNL Advanced Light Source, and X-ray emission following multiple electron capture by slow highly charged ion collisions with neutral fullerenes.

Physics Division

52. *Search for the Electric Dipole Moment of the Electron*
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An elementary particle can possess an electric dipole moment (EDM) only by virtue of an interaction that violates parity (P) and time reversal (T) invariance. The possible existence of an electron EDM, d_e, is an issue of great current interest in connection with the unsolved problem of CP violation. The present experimental upper limit on d_e is $4\text{x}10^{-27}$ e-cm. This was obtained using ^{205}Tl in an atomic beam magnetic resonance experiment employing separated oscillating fields, laser optical pumping for state selection and analysis, and a very intense electric field. Since arriving at these results, a new version of the experiment has been prepared which makes use of the same general method but has important modifications as follows: (1) In addition to ^{205}Tl beams, ^{23}Na atomic beams are used which are generated in the same ovens and collimated by the same slits. The sodium is ideal for calibration purposes because it is even more sensitive than thallium to a variety of systematic effects, but exhibits essentially no true EDM effect. (2) A new electric field assembly has been constructed which permits simultaneous comparison of two beams of thallium (and at the same time two beams of sodium) in equal and opposite electric fields. This feature sharply reduces a major contribution to noise that limited the precision of the previous result. In addition, a number of other significant improvements have been made, including the installation of photodiode detectors with high quantum efficiency and low noise, and the acquisition of a single-mode titanium sapphire laser to drive the thallium optical pumping transitions. Evolution of hydrogen gas from ovens when the sodium and thallium beams are operated at full intensity has forced a delay of several months. It has been determined that the hydrogen originates from NaOH which reacts with Na at high temperatures to form NaH and NaO. The sodium hydride then dissociates to form H_2. Sodium hydroxide was formed on otherwise pure sodium because of insufficient care in the loading and transfer of sodium when the vacuum system was open to the atmosphere. Steps have been taken to eliminate this problem and collection of EDM data is proceeding.

53. High-Energy Atomic Physics
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The goals of the High Energy Atomic Physics program at LBNL include achieving an experimental understanding of charge changing collisions at relativistic energies including capture from pair production which directly affects the operation of RHIC. Recent results include measurement of charge changing cross sections, including electron capture from pair production by Au projectiles at 10.8 GeV/nucleon. In a separate effort, atomic structure and collision measurements on francium using laser trapping and cooling of francium obtained from a radioactive source were initiated. Future activities include extending capture from pairs to higher energies and to particles heavier than electrons.

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Physics and Space Technology

54. Spectroscopy and Collision Studies with Highly Charged Ions Produced by Electron Beam Ion Traps
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The project focuses on the spectroscopy and interactions of highly charged ions produced in the LLNL Electron Beam Ion Traps (EBITs), which produce stationary ions up to fully stripped uranium. Studies of electron interactions provide benchmarks for distorted-wave and close-coupling calculations and for refining modeling calculations of spectral diagnostics used in ICF and MFE research. Current efforts center on the magnetic sublevel populations of helium-like ions generated by electron-impact excitation and dielectronic recombination processes that result in polarized line emission. Moreover, highly accurate measurements of the transition energies of few-electron high-Z ions are performed, which include the hyperfine splitting of hydrogenic $^{185}\mathrm{Re}^{74+}$ and $^{187}\mathrm{Re}^{74+}$ and of lithium-like $^{209}\mathrm{Bi}^{80+}$. These provide definitive assessments of the accuracy of nuclear magnetization (Bohr-Weisskopf effect) and QED calculations on a level that clearly demonstrates theoretical inadequacies. The capability of measuring radiative lifetimes of highly charged ions in regimes inaccessible to traditional sources was demonstrated by a determination of the 1.65-fs radiative lifetime of the resonance transition in Cs^{45+}. Laser cooling has been demonstrated successfully in the RETRAP project by cooling Be^+ ions needed for sympathetic cooling of the highly charged ions to less than 2 K, setting the stage for experiments with highly charged ion plasmas.

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Physics Division

55. Accelerator Atomic Physics
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The project objective is to achieve a detailed understanding of the interactions of high-energy, multiply-charged ions with gas and solid targets, and with electrons. The ORNL facilities used for this research are the EN Tandem Accelerator and the Holifield Radioactive Ion Beam Facility (HRIBF). A unique feature of the EN Tandem Facility is the Elbek high resolution magnetic spectrograph. This is coupled with a target recoil momentum spectrometer to allow complete energy disposition studies. A second unique feature, the von Hamos position sensitive crystal X-ray spectrometer, permits efficient high resolution measurements of X-rays from both projectiles and targets. Studies of differences in X-ray spectra from gas and solid targets are being pursued to determine electron refilling rates in solids for highly charged argon target recoil ions (subsurface neutralization of hollow atoms). Electrons contained in a crystal channel can be quantitatively treated as a dense electron gas target. A swift ion passing through the channel can be excited by collisional excitation, by dielectronic processes, or by resonant coherent excitation in which the periodicity of the crystal lattice provides an oscillator, which can separately excite specific m-states of the moving ions. X-rays are measured to determine survival of these states against secondary electron impact ionization. At CERN in Geneva, lead beams at energies of 33 TeV are used to study electron capture from the negative continuum and ionization of the one-electron ions formed, lepton pair production cross sections, and precise total energy loss. In collaboration with Swedish scientists, experiments have been performed at the Stockholm Heavy Ion Storage Ring to measure dissociative recombination between electrons and various molecular ions, e.g., HeH^+ and $\mathrm{CH}_5{}^+$.

56. Collisions of Low-Energy Multiply Charged Ions
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In this activity, multicharged ion interactions with atoms, molecules, and surfaces are studied at the lowest attainable energies. At such energies, the stored electronic potential energy of the multicharged ions dominates the total interaction energy, and inelastic collisions depend strongly on the detailed quasi-molecular potentials of the interacting systems. Emphasis is currently on merged-beam measurements of absolute electron-capture and ionization cross sections in the energy range from 0.01 to 1000 eV/amu, to provide benchmark data for the evaluation of theoretical approaches under development for this still poorly characterized energy regime, as well as to investigate low-collision-energy phenomena such as orbiting resonances and other cross section enhancements arising from trafectory effects. Experimental studies of the neutralization of multicharged ions during grazing interactions with metal, semiconductor, and insulator surfaces are also being carried out. The current focus is on measurements of the angular and charge state distributions of scattered ions, as well as the characterization of the energy and angular distributions of ejected electrons, in order to better understand the detailed mechanisms by which the multicharged ions' potential energy is dissipated during their interaction with the surface.

57. Theoretical Atomic Physics
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The atomic theory program studies the dynamics of strongly perturbed atomic systems which requires the development of new physical models and new mathematical and computational techniques. The program is intimately related to state-of-the-art experimental programs at ORNL and other laboratories. Particular attention is focused on both fundamental and complex systems which play a role in many branches of energy research such as collisions of ions with atoms, solids, and surfaces, as well as atoms subject to high-intensity electromagnetic radiation. Because of the nonperturbative nature characterizing these interactions, and the nonseparability and high dimensionality of the equations describing them, this project is computationally intensive and requires the development of efficient numerical algorithms and their implementation on high-performance computers. These studies are interdisciplinary as the methods developed provide a link between atomic, solid state, plasma sciences, and chemical sciences. Specifically, the time-dependent dynamics of atomic systems is investigated using quantum mechanical, semiclassical, and classical approaches. Efforts to develop and apply fully quantum treatments involve direct numerical solution of the Schrodinger equation on a lattice and coupled channels techniques. Partial support is also provided through this program for a joint appointment of a Distinguished Scientist/Professor at ORNL and the University of Tennessee, Knoxville.

Chemical Energy

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Processes and Techniques Program

58. Organometallic Complexes in Homogeneous Catalysis
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The aim of this research is to provide an understanding of the details of processes involving homogeneous and heterogeneous catalysis. One such process is the hydrodesulfurization (HDS) of petroleum feedstocks. From studies of model organometallic complexes of thiophene and related organosulfur compounds, it has been established that π-bonded thiophenes are activated to undergo reactions that lead to cleavage of the carbon-sulfur bonds in the thiophene. Such reactions on HDS catalyst surfaces would be expected to lead to desulfurization of the thiophene. To test this hypothesis, reactor studies of thiophene with deuterium over molybdenum-based catalysts were performed. The deuterium location in the butadiene product is consistent with activation of thiophene by π-bonding to metal sites on the catalyst surface. Future studies involve the development of new catalysts that are comprised of a homogeneous catalyst tethered to a supported metal catalyst. Initial investigations show that these combination catalysts have unusually high activities.

59. Chemical Kinetics and Reactivity of Transition Metal Complexes
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New catalytic reactions are being developed to learn what otherwise sluggish but important reactions can be made to occur, and to understand how they take place, with a goal of developing new processes. These reactions relate to environmentally-benign chemical processing and to selective oxidations. The effects of catalyst composition, reagent concentrations, structural variations, solvents, salts, etc. are being used to determine their mechanisms. A major target is selective oxidation, presently with hydrogen peroxide but with oxygen activation as a secondary goal. Methylrhenium trioxide (MTO), a soluble organometallic oxide, activates hydrogen peroxide for catalytic attack by a significant number of substrates. Sulfides, phosphines, styrenes, alkenes, alkynes, anilines, β-diketones and halide ions are among the molecules that can be efficiently oxygenated by the rhenium catalyst. The mechanism involves a peroxorhenium intermediate that contains an electrophilically activated peroxide chelated to rhenium. From these findings we postulated that a "carbene equivalent" might be able to engage in the catalytic transfer of a carbene unit, just as the peroxo complex transfers an "oxene" (i.e., an O atom). For example, it should be able to convert an alkene to a cyclopropane, analogous to the conversion of an alkene to an epoxide.

60. Fundamental Studies of Supported Metal Catalysts
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The fundamental processes occurring at the surface of heterogeneous catalysts are investigated by a combination of NMR with traditional techniques (kinetic studies, selective chemisorption, infrared spectroscopy). We are focused on catalysts that find numerous applications in the petroleum and chemical industries and in pollution control technology. Most of our effort in this area is concentrated on characterizing the surfaces of working catalysts, probing the chemisorption behavior and surface reaction of various molecules, and studying the synergistic effects of adding a second element; the second element can be another metal to form a bimetallic or it can be a promoter, poison or a support modifier. The other area of effort in our program is the application of new nuclear spin dynamics and new solid state NMR techniques. This program develops and applies solid-state NMR techniques to significant problems in catalysis and surface science as well as other areas in material science. Recent catalytic work has demonstrated the ability of solid state NMR to probe the kinetics of hydrogen chemisorption on supported metal catalysts. For example, it was found that small ruthenium particles (25% dispersion) had a sticking coefficient for hydrogen adsorption significantly higher than ruthenium single crystals. However, the introduction of Ag reduced the apparent sticking coefficient to the values seen on Ru(0001). It was postulated that Ag blocked edge and corner sites which are significantly more active than basal planes for hydrogen adsorption. Microcalorimetry studies of these same catalysts gave complementary information. Other recently completed work investigated CO and hydrogen adsorption on Rh_6/NaY catalysts via ^1H and ^{13}C NMR and microcalorimetry. Also, crotonaldehyde selective hydrogenation over Pt bimetallic catalysts was studied.

61. Spectroscopic and Phenomenological Studies of Catalysts and Advanced Materials
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This research project develops and applies transient techniques in solid-state NMR to probe the physics and chemistry of materials involved in heterogeneous catalysis, surface science, and materials science. One of the most recent achievements is the development of multiple quantum magic angle spinning (MQMAS) NMR with cross polarization (CP). This technique provides a new capability to the high resolution MQMAS NMR by allowing direct inference of the connectivities between atoms in the solid structure. CPMQMAS was used to discriminate between the fluorinated and nonfluorinated Al sites in $AlPO_4$ aluminophosphate, and to establish the exact location of H_2O in a hydrated AlPO-11. Another study used solid state NMR to investigate small Rh clusters that were produced by the oxidation and subsequent reduction of $Rh_6(CO)_{16}$/NaY. The combination of in situ ^1H NMR, ^{13}C MAS NMR, in situ FTIR, and volumetric adsorption of CO and H_2 provided unique insight into the structure of the catalyst itself and into the dynamics of catalytic processes. The project also includes studying the surface phenomena on larger particles dispersed on porous supports (e.g., monometallics and bimetallics, including poisons and promoters, on SiO_2, Al_2O_3, and zeolite supports).

62. Spectroscopic and Kinetic Characterization of Metal Oxide Catalysts
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We will continue to prepare and characterize thin films of multicomponent catalysts having specific structures and compositions. We will continue to explore the nature of the $MoO_3/NiMoO_4$ interface because of the relevance of the solid state chemistry to other catalyst systems and because of the high activity and selectivity associated with this material. Our primary methods of examination will be vibrational spectroscopy, X-ray diffraction, and electron microscopy.

New studies involving rapid detection laser Raman and FT-IR spectroscopies will be initiated which will allow us to examine catalysts under in situ conditions for very short time periods.

We will examine the differences in paraffin, olefin, and di-olefin feedstocks. A new series of multicomponent metal oxide catalysts will be investigated based on the combination of reducible and "non-reducible" metal oxides.

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Chemical Technology Division

63. Fluid Catalysis
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The Fluid Catalysis Program's activities in the area of catalytic chemistry in supercritical media are aimed at exploring the chemistry associated with the potential conversion of some key industrial homogeneous catalytic processes to more energy efficient and more environmentally benign supercritical ones. In this regard, the various processes designed to achieve the commercial hydroformylation of olefins comprise the largest scale use of homogeneous catalysts and are the subject of our current efforts in this area. Using in situ toroid NMR techniques, we have uncovered and quantified a variety of high-temperature concerted and free-radical processes that dominate the high-temperature chemistry of the cobalt carbonyl and tertiary phosphine modified cobalt catalyzed systems. Our efforts in the ceramic precursor area include: (1) the exploration of catalytic strategies for the synthesis of organometallic polymers that can be shaped by conventional polymer-forming methods and then pyrolyzed to yield three- dimensional ceramic objects that retain this shape and (2) the exploration of organometallic precursor processes that require our unique capabilities for spectroscopic characterizations at high pressures and temperatures. In research in the ceramic precursor area, we have invented the toroid cavity imager (R&D 100 Award, 1994) and the toroid cavity detector. Both devices show great promise in providing structural information for the characterization of advanced materials and for identifying and characterizing materials chemistry processes at elevated temperatures and pressures. Our research in the hydrocarbon activation area is aimed at achieving the controlled catalytic functionalization of methane and other hydrocarbons via activation of their C-H bonds. We have shown that metallophthalocyanines can be tuned (with fluorocarbon substituents) to achieve very high electrophilicities, which combined with their high thermal and oxidative stabilities, offer attractive possibilities for achieving selective hydrocarbon conversion.

Chemistry Division

64. *Argonne Premium Coal Sample Program*

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This program provides premium quality, uniform coal samples for fundamental research in coal science. All samples were prepared and are stored under nitrogen, and are packaged in amber glass vials to ensure sample integrity. Eight coals, ranging in rank from lignite to low volatile bituminous, are included in the program and are available to researchers. To date ~24,000 samples have been shipped to researchers all over the world. A users handbook is available and sample information, including bibliographic information for the ~700 papers published concerning work carried out with APCS samples, is also available via the WWW (http://www.anl.gov/PCS/pcshome.html). Information at this site is continuously updated.

65. *Characterization and Reactivity of Coals and Coal Macerals*

Winans, R.E.; Anderson, K.B.; *Dyrkacz, G.R.; Botto, R.E.;* *Carrado, K.A.; Hunt, J.E.* *630-252-7479* *630-252-9288 (FAX)* *rewinans@anl.gov*	**$2,054,000**

This program seeks to provide a comprehensive picture of the molecular structure of coal over a broad scale. An objective is to be able to predict the reactivity of the Argonne Premium Coals under a variety of conditions from models based on the fundamental information derived from this program and other studies. Because the heterogeneous nature of coal adversely influences its reactivity, we have been systematically studying physical methods for the separation of coal into its fundamental organic constituents (macerals). Further, chemical modification methods are coupled with structural and spectroscopic measurements, such as synchrotron X-ray spectroscopy and scattering, solid-state NMR spectroscopy and imaging, laser desorption time-of-flight mass spectrometry, high-resolution tandem mass spectrometry, and small angle neutron scattering, to probe coal structure, in particular, the large molecular building blocks. The chemistry of large molecules is a major focus, which has led to research on the synthesis and characterization of large-pore, layered clay catalysts for upgrading large, complex organic molecules. For the first time, the synthesis of clays has been followed by anomalous small angle X-ray scattering (ASAXS). To further advance this and other elements of the program, we are building the next generation ASAXS instrument at the ANL Advanced Photon Source. Pyrolysis high-resolution mass spectrometry results on Argonne Premium Coals suggest that aromatic clusters related to buckyballs are found in the higher rank coals. Finally, nitrogen-and oxygen-containing aromatic clusters appear to be derived from alkaloids.

66. *Development of a Facility at APS for Time-Resolved/ Anomalous Small Angle X-ray Scattering: Applications in Condensed Matter Research*

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The objective of this project is to construct a small angle X-ray scattering instrument on the undulator beamline (12-ID) of the Basic Energy Sciences Synchrotron Radiation Center (BESSRC) at the Advanced Photon Source (APS) that will offer unprecedented opportunities for studying static and dynamic atomic order in condensed phases and nanoscale materials. The high flux at the APS will enable time-resolved structural studies on dynamic systems using techniques that require high-energy resolution of the probing X-rays and high counting statistics. Anomalous small angle X-ray scattering, ASAXS, possible only after the advent of synchrotron sources, is a powerful method for structural resolution of materials in noncrystalline states. The high brilliance of the X rays from the undulators at APS will, for the first time, enable the full potential of both the time-resolved and anomalous scattering techniques to be realized in such areas as heterogeneous catalysis, ceramics, metallic glasses, organometallics, carbons, and photochemical energy conversion. The proposed ASAXS facility will offer new capabilities for measuring atomic order within macromolecular assemblies in disordered media on a length scale of 6-6000 Å. These capabilities will offer opportunities to resolve the structural basis for catalysis. Initial experiments will begin in August 1997.

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Chemistry Department

67. Catalysis: Reactivity and Structure
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The goal of this program is to provide an improved understanding of chemical catalysis by elucidating details of the fundamental properties of molecules, surfaces, and their reactions that are critical to catalysis. Reactivity-structure correlations are a key aspect of these studies. Complexities stemming from the inherent multi-component aspects of heterogeneous catalysis are explored using both ultra-high-vacuum surface science investigations of well-defined model systems, and powder diffraction and x-ray absorption studies of more “real-world” systems. In the former, emphasis is placed on understanding the effects of catalyst modifiers at a molecular level and on rationalizing the distinctive behaviors of bimetallic surfaces that simulate important industrial bimetallic catalysts. X-ray and ultraviolet photoelectron spectroscopies at the National Synchrotron Light Source (NSLS) are essential to this work. In the latter systems, time-resolved studies of the formation and transformations of zeolitic materials, supported metals, and metal oxides under catalytic reaction conditions are carried out using our improved X-ray diffraction/absorption facility at the X7B beamline at the NSLS. Our homogeneous catalysis efforts focus on detailed studies of the reactivity of transition metal hydride complexes. Kinetic and mechanistic studies of metal hydride complexes are designed to elucidate the factors that determine the rates and mechanisms of M-H bond cleavage and associated atom transfer reactions that are central to the participation of metal hydrides in catalysis. The knowledge gained from these studies is used to assist in the development of new catalytic reactions. New efforts will involve the synthesis of water-soluble metal hydrides and studies of their reactivity.

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Materials Science Division

68. Selective Conversion of Light Hydrocarbons to Chemicals and Fuels
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The U.S. chemical and fuel industries are major sources of industrial waste and significant consumers of energy. Considerable savings in energy, carbon dioxide emissions, and feedstock costs could be achieved by developing catalytic processes for the selective oxidative dehydrogenation of alkanes to alkenes and the selective oxidation of alkanes directly to products such as alcohols, ketones, epoxides, and carboxylic acids. Achieving these goals requires an understanding of the relationships between the structure and composition of the catalyst and its function. During the initial phase of this project, studies have been carried out on zirconia-supported vanadia catalysts for the oxidative dehydrogenation of propane to propene. High specific activity and propene selectivity in excess of 80% is achieved for vanadia loadings corresponding to about one monolayer of vanadia. The structure of the active phase of vanadia is currently being determined. Novel vanadosilicates have been synthesized and are currently being investigated for their catalytic activity.

Chemical Sciences Division

69. High-Energy Oxidizers and Delocalized-Electron Solids
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The aim of this work is the synthesis and characterization of new two- and three-dimensional solids that may be useful in electrical energy storage. Fluorides are emphasized because fluorine is highly electronegative, small, and lightweight; thus, high oxidation-state fluorides such as those of cobalt, nickel, copper, or silver have high oxidizing potential and low formula weights. Emphasis is placed on the thermodynamically unstable fluorides, which have sufficient kinetic stability to be easily stored. Such fluorides are not only powerful oxidizers, but the metal center in each is comparable in electronegativity to fluorine. It is probable, therefore, that some of the thermodynamically unstable fluorides will be metallic or even superconducting (like some copper oxide systems). Access to such fluorides is provided by salts of anions that are thermodynamically stable (e.g., NiF_6^{2-}). Kinetically stable, thermodynamically unstable fluorides, as reagents, can probably substitute for anodic oxidation processes (Simons process) for the preparation of fluorochemicals. Lithium cations in open-channel fluorides could provide ionic conductors stable to oxidation. New synthetic routes also provide access to ordered mixed rutile materials (e.g., $MnNiF_4$). These should be ferrimagnets. Other “rutile” systems such as MNF (isoelectronic with MO_2) like CrO_2, could be metallic.

70. Catalytic Conversion of C_1 Compounds
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The purpose of this program is to develop an understanding of the fundamental processes involved in the catalytic conversion of C_1 compounds such as carbon monoxide, carbon dioxide, methane, formaldehyde, and methanol to gaseous and liquid fuels. Attention is focused on defining factors that limit catalyst activity, selectivity, and resistance to deactivation, and the relationship between catalyst composition/structure and performance. In recent studies, the hydrogenation of CO and CO_2 has been investigated over Cu promoted with zirconia. Up to 25-fold increases in the methanol synthesis activity are observed. In situ infrared studies reveal that zirconia adsorbs CO_2 much more strongly than Cu. The resulting bicarbonate species then undergo hydrogenation to formate, methylenebisoxy, and methoxide species. Methanol is produced by hydrolysis of methoxide species. Current research is focused on altering the basicity of the promoter by forming mixed metal oxides in which one of the metals is Zr. The combustion of CH_4 over PdO has also been investigated. It is found that high activity requires the presence of a small amount of metallic Pd to activate CH_4.

71. Transition Metal Catalyzed Conversion of CO, NO, H_2 and Organic Molecules to Fuels and Petrochemicals

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The goals of this project are: (1) to develop new chemical reactions in which transition metals interact and chemically transform organic materials, (2) to understand how these reactions work, and (3) to apply this information to the development of new potentially useful chemical transformations. Several years ago a major discovery on this project was the first alkane-transition-metal C-H oxidative addition reaction (C-H activation). This involved the direct reaction of C-H bonds with an iridium center in the +1 oxidation state (Ir(I)). More recently, a series of Ir(III) C-H activating complexes has been discovered. Subsequent research has been directed at examining the scope and mechanism of these C-H activation reactions and working toward utilizing them in the conversion of alkanes to functionalized organic molecules. Recent activities on this project include (1) use of liquefied xenon and krypton as inert solvents for C-H activation; (2) design of experiments aimed at determining whether weak metal-noble gas and metal-alkane complexes intervene as intermediates in these processes; (3) exploratory studies on the extension of C-H activation methods to C-F activation; (4) improvement in the techniques utilized for flash kinetic studies aimed at directly measuring the rates of reaction of coordinatively unsaturated C-H activating intermediates with alkanes, including those allowing the measurement of rates in the picosecond time regime, and (5) utilizing the Ir(III) C-H activating systems in the synthesis of new novel organometallic materials, such as carbene and carbyne complexes.

72. Molecular Chemical Routes to New Materials With Tailored Properties

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Advanced solid-state materials with useful properties increasingly involve intricate three-dimensional networks, characterized by complex stoichiometries (e.g., in ceramic superconductors such as $HgBa_2Ca_2Cu_3O_{8+d}$) and/or metastable architectures (e.g., in zeolites). New generations of materials will undoubtedly result from chemically directed, low-temperature synthetic routes. Our approach involves use of synthesis, coordination chemistry, and condensation reactions to build novel three-dimensional networks. Primary targets have been oxide-based materials, which are built from tailored, oxygen-rich precursor molecules. This project involves synthesis and characterization of candidate precursor molecules, and then examination of chemical processes by which a metal oxide building block can be transferred to a growing network. Initial directions are based on the finding that metal complexes of the siloxide ligand $OSi(O^tBu)_3$ eliminate isobutylene and water cleanly at remarkably low temperatures (100-200°C) to form $M_xSi_yO_z$ materials. For example, $M[OSi(O^tBu)_3]_4$ (M=Zr, Hf) complexes undergo very clean conversions at about 100°C to homogeneous $MO_2{\bullet}4SiO_2$ materials. The chemistry of this network formation allows control over the growth of ZrO_2 nanoparticles at higher temperatures. Other precursors being examined include the Al/P oxide cluster $Al_4(O^iPr)_8[O_2P(O^tBu)_2]_4$ and the $[ZnO_2Si(O^tBu)_2]_\infty$ polymer. The low temperatures at which such conversions take place allow for the formation of networks in refluxing hydrocarbons, thereby offering an alternative to the sol-gel approach to thin films, porous ceramics, fibers, etc. (which usually employs alcohol solvents). Initial experiments also indicate that thermolyses of precursor molecules in the crystalline solid state can generate surprisingly ordered microstructures for the resulting oxide materials. Such observations are followed with attempts to add directionality to the network formation, via added templates or “ancillary” ligands in the precursor that might orient the condensation reactions. The ultimate goal of this research is to provide tailored materials with new and specific structural, electronic, optical, and/or catalytic properties.

73. Potentially Catalytic and Conducting Polyorganometallics

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Synthetic chemistry has reached the level of sophistication at which it is possible to plan and execute the creation of new structures following the principles of molecular architecture. This research has targeted for synthesis polyorganometallics, because they have great potential as catalysts for known or new organic transformations, and as building blocks for novel materials. It follows an interdisciplinary approach to the designed construction of polyorganometallic arrays, anchored rigidly on novel oligocyclopentadienyl π-ligands that enforce hitherto unprecedented metallic topologies, or bound to other, highly energetic hydrocarbon ligands with high C/H ratios. During the past year we have discovered that a cyclically conjugated hexaalkyne and its metal complexes undergo explosive decomposition to onion- and tube-like closed-shell carbon particles (“buckymaterials”), a fundamental finding that opens up a plethora of possibilities in materials catalysis. We have also exploited the reactivity of (fulvalene)$Cr_2(CO)_6$ as a catalyst in the 1,4-dihydrogenation of conjugated dienes, the potential of the novel penta(cyclopentadienyl)(cyclopentadienyl)$Mn(CO)_3$ as a matrix for hexametallic cluster construction, the ability of (cyclopentadienyl)iron(arene) sandwiches to function as electron-reservoir electrocatalysts in (fulvalene)dimetal zwitterion production, and the propensity of Ru, Co, and Ir systems to enter into novel modes of C-H activation. The aim of this work is to develop new chemistry for low-energy, efficient processes relevant to organic synthesis and to understand the mechanisms by which such processes occur.

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Physics and Space Technology Department

74. ***Plasma-Assisted Catalytic Reduction of NO$_x$***
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Electron-impact reactions in a non-thermal plasma creates a mix of reactive species that permits unique and diverse chemical reactions to be possible. The rich chemistry from the plasma provides an added dimension to allow more favorable pathways to some of the limiting steps encountered in conventional surface catalysis. Plasma-assisted catalysis (PAC) is an innovative method for improving the reduction of nitrogen oxides (NO$_x$) under conditions that normally make it difficult for known catalysts to function with high activity and durability. The goals of this project are to (1) explore the effects of a plasma on the NO$_x$ reduction activity and temperature operating window of various catalysts, and (2) develop a fundamental mechanistic understanding of the interaction between the gas-phase plasma chemistry and the heterogeneous chemistry on catalyst surfaces. PAC schemes based on direct NO$_x$ decomposition and selective catalytic reduction are being explored. The effects of plasma on the activity of transition metal-zeolites, metal-mixed metal oxides, single-metal oxides, and novel aerogel catalysts are being studied. If successful, the results of this project would have immediate utility in controlling NO$_x$ emissions from combustion and chemical manufacturing processes. More importantly, a revolutionary method for controlling surface catalysis would be established.

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Chemical Science and Technology Division

75. ***Transition Metal Mediated Reactions of Small Molecules***
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A primary goal is characterizing metal-dihydrogen and related sigma-bond complexes, and mapping out the reaction coordinate for cleavage of H-H, Si-H, Ge-H, etc., bonds on metal complexes. This oxidative addition process is a foundation of catalysis and many types of chemical/biochemical conversions. New highly electrophilic cationic complexes of the type $[Mn(CO)_xL_y]^+$ and $[Re(CO)_4L]^+$ (L = phosphine donor) are being developed for sigma bond coordination, possibly including methane activation towards liquid fuels. Low-interacting counteranions are necessary for these complexes, which contain agostic C-H interactions. These complexes will also be investigated for application in hydrogen isotope (e.g., tritium) separation, for which calculations and experiments show a sizable inverse equilibrium isotope effect (e.g., D_2 binds better than H_2). On analogy with silanes, germanes such as $PhGeH_3$ have been found to bind to $Mo(CO)L_4$ and will be further studied. These metal centers will also be studied for binding and activation of other small molecules, particularly pi-acceptors like nitrogen, ethylene, and sulfur dioxide to compare with sigma-bond activation.

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Basic Sciences Center

76. ***Basic Research in Synthesis and Catalysis***
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The major objectives of the research carried out by the Synthesis and Catalysis task are the synthesis and characterization of organometallic precursors for preparing semiconductor particles and thin films and the development of catalysts for the electrochemical reduction of CO_2 and CO to fuels and chemicals. The preparation of more efficient and lower cost semiconductor materials would have a significant impact on the cost and performance of photovoltaic devices. Research efforts are aimed at developing new precursors to thin films and semiconductor nanoparticles. Nanoparticles of CdTe and $Cu(In,Ga)Se_2$ have been synthesized and used to deposit photovoltaic thin films by a spray deposition process. Catalysts for electrochemical CO_2 and CO reduction would permit the conversion of electricity, which is the primary product of most renewable energy sources, to fuels. This would provide a new sustainable route to fuels. This research involves the synthesis and evaluation of new catalysts. These studies are guided by information derived from previous research that delineated important relationships between catalyst structure and catalyst performance.

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Chemical Technology Division

77. ***Kinetics of Enzyme-Catalyzed Processes***
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The objective of this program is the study of fundamental kinetics and enzyme catalysis of chloroplast reducing power related to fuels and chemicals production from renewable inorganic resources. Fundamental studies that probe the function of the cellulase enzyme components in relation to their structure are also being performed. Kinetic and mechanistic aspects of photosynthesis will be studied using a unique experimental approach. Areas of investigation include: (1) simultaneous light-driven production of hydrogen and oxygen; (2) separation of the two light reactions of photosynthesis; (3) construction of photosynthetic photoelectrochemical cells; and (4) precipitation of metallic catalysts on photosynthetic membranes. Absolute pulsed yields of hydrogen and oxygen from saturating single-turnover flashes of light have been measured in Photosystem I-deficient mutants of the green alga *Chlamydomonas reinhardtii*. The key result of these measurements is that the amount of hydrogen produced per single-turnover flash cannot be accounted for by the Z-scheme based on the measured amount of Photosystem I present in mutants (Fud26, for example.) Moreover, the measured stoichiometric ratio of hydrogen to oxygen compared to that of the Photosystem I to II ratio also conflicts with the Z-scheme. We have observed specific photosynthetic reactions that cannot be quantitatively accounted for by the Z-scheme, not of course that the Z-scheme is universally wrong. In nature these reactions may not occur at all or they may be a supplemental or parallel process working in tandem with the Z-scheme. The binding of cellobiohydrolase I to naturally-colored cotton fibers in the absence of catalysis does not result in any fiber disruption. Binding of cellulase components does not, therefore, precede hydrolysis. In other studies the kinetics of hydrogen production from glucose and other sugars has been studied. Glucose dehydrogenase possesses low specificity and oxidizes glucose, galactose, and xylose to hydrogen (in the presence of hydrogenase) and the corresponding sugar acids.

Chemical and Analytical Sciences Division

78. ***Organic Chemistry of Energy Resources***
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The objective of this program is to conduct basic research that provides new molecular level understanding of the organic chemical structure and reactivity of complex hydrocarbon materials from fossil and renewable resources such as coal, petroleum, oil shale, lignin, and biomass. The thermochemical reaction kinetics and mechanisms involved in processing these complex organic materials are being explored through the systematic investigation of well-designed model systems. Pyrolysis studies of model compounds for woody biomass are providing new insights into the significance of competing concerted and free-radical reaction mechanisms under flash pyrolysis conditions. The mechanisms associated with retrograde reactions of oxygen-containing functional groups in the pyrolysis and liquefaction of low rank coals are now being revealed through in-depth investigations of ether and carboxylic acid model compounds. Investigations of silica-immobilized and polymeric models are providing unprecedented insights into the impact of restricted mass transport on free-radical and ionic reaction pathways. Moreover, solid-state NMR methods are being developed for the structural analysis of heterogeneous, amorphous, organic solids such as coals, lignins, charcoals, graphites, and polymers. Derivatization with NMR-active isotopes is often employed to select a reactive structural sub-domain for spectroscopic analysis. Solid-state F-19 NMR, and triple resonance methods that utilize the C-13, F-19 dipolar interaction to provide nanoscale molecular structure information, are being investigated for a variety of fluorinated organic materials. The knowledge gained from this research will contribute to the scientific foundations required for the development of novel, environmentally responsible processes for the utilization of hydrocarbon resources.

79. ***Heterogeneous Catalysis Related to Energy Systems***
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The objective of this program is to develop a fundamental understanding of reactions occurring in emission control catalysis. Emphasis is placed upon studies of the interactions between catalytically active metals and reducible metal oxides and the manifestations of these interactions upon redox properties of the oxide support, the catalytic reduction of NO, and the oxidation of CO and small hydrocarbons. The approach is experimental and utilizes three dedicated UHV systems for laboratory and synchrotron based surface analytical techniques. In situ metal deposition and gas dosing permit control of the metal loading and gas exposure. A new apparatus is in development for interfacing a catalytic reactor with UHV and in situ surface characterization. Model catalysts composed of Rh supported upon single crystal and highly oriented cerium oxide have been used. Studies have focused on the surface properties of the ceria support, reducibility of the support by chemical and physical means, and characterization of the chemisorption of NO and the effects of Rh coverage and various pre-treatments upon NO decomposition. It is found that pre-reduction of the ceria by ion sputtering dramatically alters both the adsorption of NO on the ceria and the decomposition of NO on the Rh dosed support. This result exemplifies the synergism between support and metal in determining catalytic activity. Future work will be directed at identifying and understanding the factors which control the catalytic activity for NO decomposition in this and related systems.

80. ***Photolytic Transformations of Hazardous Organics in Multiphase Media***
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This research program emphasizes fundamental investigations into the influence of substrate chemical structure on the photochemistry and photophysics of sorbed hazardous organics. The primary goals of this research are to enhance a basic understanding of photochemical reactions occurring at industrially and environmentally important interfaces and to delineate the role of surface interactions in controlling the observed chemistry. Polycyclic aromatic hydrocarbon (PAH) photochemistry and photophysics have been the focal point of these studies. Product analysis, physical characterization of surfaces, and in situ spectroscopic techniques are the principal methods used in these investigations. Highly polar substrates, such as SiO_2, have been shown to dramatically affect the photochemistry of weakly interacting organics, as typified by unsubstituted PAHs. Contributions from electron transfer and singlet molecular oxygen mediated PAH photochemical oxidation pathways have been elucidated. Surface-sorbed water has been shown to exert significant influence on the reaction rates and product distributions observed for PAH photochemistry at the SiO_2/air interface. Among other benefits to be derived from this research are a better understanding of how molecular interactions influence chemical processes in heterogeneous media and how these factors control the environmental fate and residence times of PAHs and related anthropogenic materials.

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Materials and Chemical Sciences Department

81. ***Free-Radical Chemistry of Energy Utilization***
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This project develops kinetic, thermochemical, and theoretical information describing the reactions of organic and organometallic free radicals, particularly those involving sulfur, nitrogen, and oxygen important to hydrocarbon, lignin, and coal conversion. Kinetics of hydrogen transfer, molecular rearrangements and fragmentations are examined in studies using kinetic EPR and optical spectroscopy, laser photoacoustic spectroscopy, and product study competition kinetics. Select bond strengths of heteroatom-containing organic hydrocarbons are determined. Advanced ab initio calculations are employed to study novel hydrogen transfer and radical rearrangement reactions. Mechanisms of reactions of nanometer FeS particles with organic substrates leading to bond scission are investigated. Homolytic reactivity of bridging and terminal triosmium cluster hydrides and bimolybdenum-complexed sulfhydryl groups in reactions with organic radicals is under study. High pressure liquid NMR is applied to study metal-olefin bond formation and dissociation in reactions of organometallic complexes. Reaction of oxygen and nitrogen atoms with organic substrates leading to heteratomic biradicals and subsequent transformations are examined. Overall, the program develops novel approaches and properties of molecules supporting the development of new hydrocarbon utilization technologies.

Chemical Sciences Department

82. ***Theoretical Investigations of Heterogeneous Catalysis***
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The purpose of this research program is to develop and apply atomic level molecular and solid state theoretical methods to the study of catalytic processes occurring at the internal and external surfaces of metal oxides and zeolites. These studies provide information on the geometric and electronic structure of surface and surface adsorbate complexes, including the energetics of physisorption, chemisorption, and dissociative chemisorption events. Particular emphasis is placed on understanding the effect of topological and electronic defects, metal adatoms, and explicit size effects on the reactivity and selectivity of these materials. The complex geometric and electronic structure of transition metal oxides and substituted zeolites combined with the need to accurately predict the small energy changes associated with fundamental processes such as adsorption and desorption is a challenging task for the current generation of theoretical methods. Our approach to increasing the capabilities of solid state quantum mechanical methods that can efficiently describe the ground state properties of these compounds is based on the mathematical development of low order scaling methods that are designed to be implemented on large scale parallel computing systems. To this end we have developed a new all electron periodic Gaussian basis density functional approach that provides fully self-consistent solutions to the Kohn-Sham equations for systems periodic in 3-(crystals), 2-(surfaces), and 1-(polymers) dimension. This new method is implemented in the program GAPSS and is currently being used on large scale parallel computers to study several metal oxide and transition metal oxide systems. These studies strive to provide reliable information on quantities of importance which are difficult to obtain by experimental means. The specific systems being investigated are generally chosen jointly with our experimental collaborators to maximize the interplay between theory and experiment.

Environmental Molecular Sciences Laboratory

83. ***Fundamental Studies of Oxygen Storage Materials: Transient Effects on NO_x Reduction Kinetics and the Role of Aging on These Material Properties***
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The goal of this research is to fill a gap in the fundamental understanding of catalyst activity and durability with respect to the transient NO_x reduction performance in automotive catalytic converters. Our overall objective is to obtain detailed chemical kinetics data on idealized but well-characterized catalyst systems useful for understanding the important elementary converter reactions. A particular focus of the work will be on how the catalytic chemistry is affected by the oxygen uptake, storage, and release processes carried out by the oxygen storage material. The fundamental understanding of critical rate-determining processes in this complex system will provide insight into the material properties required for improved, more durable catalysts. For example, we will elucidate and quantify the mechanisms responsible for the improved performance with the use of ceria/zirconia mixtures relative to ceria alone formulations. The kinetic data to be obtained in this program will also be used for the further development of a full process model to describe the performance of an actual vehicle running the Federal Test Procedure (FTP). Ultimately, this detailed understanding will lead to the ability to model both the performance and durability of catalysts on actual vehicles. While this is a considerable challenge and clearly a long-term (>10-year) goal, there are a number of recent developments that have enabled considerable progress to be made in this area. This work is providing an excellent opportunity to couple the powerful fundamental research capabilities of Pacific Northwest National Laboratory with a currently ongoing applied research program at General Motors Research Laboratories.

Separations and Analysis

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Molecular Processes Program

84. *Analytical Separations and Chemical Analysis*
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Advances in many branches of science and technology depend on a steadily growing capability for chemical analysis. Capillary electrophoresis (CE) is emerging as the premiere technique for many types of analytical separation and analysis. For example, in terms of theoretical plates CE has approximately 50 times the separation power of liquid chromatography. In addition to devising CE methods for separation of complex mixtures of metal ions, a superior CE technique for separating and measuring neutral molecules is being developed. A new family of additives has been found for high-performance liquid chromatography (HPLC) that provides the chromatographer with a new parameter for improved selectivity and resolution of complex analytical samples. New resins and techniques for solid-phase extraction are resulting in major improvements for sample pretreatment, which has been identified as the slowest and most expensive step in the analytical process.

85. *Analytical Spectroscopy*
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The basic principles and practical aspects of several important methodologies for ultratrace analysis are studied in this project. Plasma sources for atomic spectroscopy and mass spectrometry are emphasized, particularly mechanistic and analytical investigations of the inductively coupled plasma (ICP). New directions in ICP mass spectrometry include basic studies of the sample introduction and ion extraction processes, development of instrumental methods for removing interferences, and the use of ICP-MS in conjunction with chromatographic separations for measurement of elemental speciation. These ICP studies have resulted in state-of-the-art analytical methodologies that are utilized extensively elsewhere in DOE and in the outside analytical community. New studies in ion trapping and ion formation in electrospray mass spectrometry are also being initiated.

86. *Chemical Analysis at Liquid-Solid Interfaces*
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This project explores novel approaches to the design, fabrication, and characterization of monomolecular and thin polymeric films at liquid-solid and gas-solid interfaces. Projects this year have entailed (1) the development of a nanoscale approach to the construction of compositionally patterned surfaces, (2) extending adhesion and friction force microscopy to the real-time monitoring of chemical and electrochemical surface transformations, and (3) probing solvent-monolayer interactions at such interfaces with infrared reflection and Raman spectroscopies and quartz crystal microbalances. The nanoscale patterning effort examines the use of an atomic force microscope tip to affect an acceleration in the rate of the base hydrolysis of ester terminated monolayers as a consequence of the mechanical interaction between the tip and outermost portion of the adlayer structure. The real-time monitoring studies are aimed at monitoring the heterogeneity of interfacial reactions at nanometer length scales. The in situ investigations employ infrared reflection and Raman spectroscopies, optical ellipsometry, electrochemistry, and contact angle measurements. The objective is to develop relationships that form a basis for correlations between the composition and molecular arrangement of organic interfaces with macroscopic physical and chemical properties (e.g., lubrication, catalysis, adhesion, and chemical analysis).

87. *Lasers in Analytical Chemistry*
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With the development of new energy technologies, materials problems, environmental pollution, and health effects present challenges to the analytical chemist. Several laser-based analytical techniques are being developed to gain unique insight into elemental, organic, and gaseous pollutants associated with energy utilization, to study chemical changes of ultrasmall samples, and to probe variations in the surface composition of materials. Areas emphasized are (1) studies of fundamental processes such as matrix-assisted laser desorption (MALD) and chromatographic retention; (2) liquid chromatographic and capillary electrophoretic determination of organic, inorganic, and biochemical species using more sensitive or more selective detectors; (3) laser-based mass spectrometric detection of large molecules deposited or adsorbed on surfaces of materials; and (4) real-time spectroscopic probes of chemical reactions down to the single-molecule limit.

Process and Techniques Program

88. Electrochemically Transformable Extraction Phases for the Separation of Critical Metal Ion Constituents and High Level Wastes
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The remediation of the large volumes of high level wastes (HLWs) in the DOE complex requires the separation of radioactive materials into high- and low-level waste streams. Remediation also mandates the minimization of HLW stream volumes to reduce long-term storage costs. This program explores the reversible electrochemical transformation of selective chelates tethered to carbon packings as a novel method for concentrating highly radioactive constituents in HLWs. The aim is to exploit the unique capabilities of a new series of metal-ion selective crown ethers (CEs) that incorporate redox transformable moieties like catechols and disulfides into the CE structure. Since the stability constants for metal ion binding are expected to be markedly affected by the redox transformation of such moieties, a new separation process can be envisioned in which a column can be switched between concentration and stripping modes by the respective reduction and oxidation of the immobilized chelate. This program assesses the range and scope of this new separation concept.

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Chemistry Division

89. Separations Science Related to Nuclear and Hydrometallurgical Technology
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The overall objective of this program is to develop new and improved reagents and separation processes applicable to problems in environmental remediation and waste management, and to elucidate the basic chemistry underlying these new reagents and processes. This program has four major subdivisions. First, the interactions between extractants and diluents are studied, with the goal of altering the extraction efficiency and selectivity that can be achieved with a given extractant and improving the physical properties of the system. In addition, the effect of stereoisomerism on metal ion recognition by macrocyclic polyethers is explored to determine the effect of ligand conformational changes on the strength and selectivity of metal complex formation. Also, new classes of multifunctional extractants that exhibit enhanced selectivity for certain metal ions are designed, synthesized, and characterized. Finally, aqueous-soluble molecules capable of serving as selective hosts for chelated metal ions and subsequently yielding a precipitate are pursued, with the goal of developing new separation schemes that combine molecular recognition and precipitation into a single operation. All of these studies are directed towards applications in nuclear and hydrometallurgical technology, among them, nuclear waste processing, actinide separations, and by-product recovery.

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Department of Applied Science
Chemical Sciences Division

90. Structure and Function in Electrochemistry
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The program focuses on the understanding of the relationship between the structure of an electrode surface and its function in an electrochemical process. It emphasizes in situ determination of the structure of an electrode surface with atomic resolution during the course of electrochemical reactions, determination of atomic and molecular monolayer structures and their phase behavior, as well as the identification of adsorbates, intermediates, and products with molecular specificity. In addition to providing insights into fundamental surface electrochemistry, electrocatalysis and chemistry and physics of adlayers on metal surfaces, the results will have potential applicability in electrochemical energy conversion, electroorganic synthesis, and electrochemical sensors. The work utilizes electrochemical, X-ray scattering (utilizing synchrotron radiation), Fourier transform infrared spectroscopy, and scanning tunneling microscopy techniques. The program is expected to identify the atomic geometry of active sites in some electrocatalytic reactions; to establish the correlation between the structure of a surface and its electrocatalytic activity; and to develop a more complete picture of the behavior of metal monolayers on electrode surfaces. Some generalization of the understanding of the ordering of adsorbates on metal surfaces and guidelines for prediction of electrocatalytic properties may also be expected.

91. *Microparticle Analysis by Laser Spectroscopy*
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Aerosol particles are present abundantly and ubiquitously in nature and in environments associated with many energy conversion systems, industrial processes, and health related areas as well. These microparticles need to be characterized by their physical state and chemical composition. In the past year, the hydration and phase transformation of microparticles composed of alkaline-earth metal nitrates have been investigated in the single-particle Raman-spectroscopy apparatus developed at BNL. In the levitation cell, a single microparticle is held in dynamic equilibrium with water vapor under controlled humidity conditions. Laser Raman and Mie resonance scattering techniques are used to probe the chemical and physical states before and after phase transformation. It is found that aqueous $Mg(NO_3)_2$, $Sr(NO_3)_2$ and $Ca(NO_3)_2$ droplets solidify to a metastable amorphous state that contains residual water persisting even in high vacuum. Raman spectra of the amorphous particles reveal that the nitrate ions form contact-ion pairs with the bivalent cations and that the residual water molecules possess very little, if any, hydrogen-bond characteristics. Thus, this research will not only continue to discover and elucidate heretofore unknown properties unique to microparticles, but also will provide the science and technology basis for advanced analytical techniques.

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Department of Chemistry

92. *Surface Ionization Mass Spectrometry*
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The elucidation of mechanisms for the formation of gas phase ions from high temperature inorganic condensed state matrices is the main thrust of this program. Ion emitters capable of being scaled up in intensity by several orders of magnitude are currently receiving the most activity. There are three features which are emerging as requirements; pre-synthesis of the ion which will migrate and vaporize, a stationary counter ion, and redox chemistry to satisfy the bonding requirements of the vacancy left after ion migration. The bonding requirements are currently receiving the most study. These new understandings led to the prediction and subsequent demonstration of a new high intensity iodide anion emitter. A new line of study will test the concept of storing ions on a surface via electrostatics. Ion optic modeling capabilities have been developed which led to last year's release of SIMION 6.0, and work continues on its enhancement.

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Environmental Energy Technologies Division

93. *Repetitively Pulsed Laser-Material Interactions for Chemical Analysis*
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The interaction of a high-powered pulsed laser beam with solid materials can be utilized in many applications within the DOE and U.S. industries, including environmental analysis, non-proliferation, materials, electronics, and medical. Importantly, the laser material interaction (LMI) is a powerful technology for chemical separations and analysis. A pulsed, high-powered laser beam ablates constituent elements from any sample material into the vapor phase, which can be analyzed by classical spectroscopic techniques. The term 'laser ablation' is commonly used to describe the more general 'laser material interaction.' However, the explosive laser material interaction is not fundamentally described. The word 'ablation' implies that a particular mechanism underlies the explosive interaction, which is not the case. The fundamental mechanisms underlying the interaction, such as mass ablation rate behavior and stoichiometric ablation must be understood for accurate and sensitive chemical analysis. This Basic Energy Sciences supported research endeavors to elucidate fundamental mechanisms of the laser-material interaction and to develop laser sampling capabilities for DOE needs in chemical separations and analysis. The research emphasizes the study of repetitively-pulsed laser material interactions at atmospheric pressure; the conditions that will be utilized in most chemical analysis applications. Atomic emission spectroscopic (AES) data from an inductively coupled plasma (ICP) demonstrate changes in the laser material interaction as a function of laser and material properties. ICP-AES is one of the only technologies for studying LMI at atmospheric pressure. Spectroscopic emission from the laser-induced surface plasma is studied to support the ICP-AES data. Piezoelectric sensors are used to study the propagation of acoustic waves induced in the material by the pulsed irradiation. Optical probe-beam deflection is employed to determine the onset of material removal and the formation of a laser initiated surface plasma. Fundamental mechanisms describing the laser material interaction are developed by drawing correlations between these acoustic, deflection, and atomic emission data. Improved capabilities for direct solid sample chemical analysis are reported to the DOE and scientific community through technical publications and conference meetings.

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Chemical Technology Division

94. *Chemical and Physical Principles in Multiphase Separations*

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This program comprises several fundamental studies that explore the use of electromagnetic fields to enhance the efficiency of multiphase separations processes. Experimental, theoretical, and computational methods are employed to investigate the effect of electromagnetic fields on transport processes in liquid-liquid, gas-liquid, and solid-liquid systems. This work will provide information necessary to devise novel means to dramatically improve transport rates in these systems, and thus will have widespread benefit for separations processes such as solvent extraction and distillation as well as applications in environmental and biotechnology areas. The areas of current focus are: (1) interface deformation and breakup, including electrostatic spraying (both “normal” and “inverse”), drop formation, drop oscillations, stretching liquid bridges, and drop impact; (2) interactions and coalescence of drops; (3) enhancement of transport processes through electrohydrodynamic flows, and (4) magnetic separations, including a fundamental analysis of high-gradient magnetic flocculation and filtration.

95. *Interactions of Solutes, Solvents, and Surfaces: Adsorption and Supercritical Extraction*

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The striking properties of solutions in supercritical solvents can be understood in terms of the underlying fluid microstructure and molecular interactions. Fundamental understanding of these properties is the aim of theoretical and experimental studies. Such solutions are important in novel separations technologies such as supercritical extraction and supercritical chromatography and in other technologies as well. Understanding of supercritical solutions has been extended to complex fluids of practical importance to industry—for example, solutions in supercritical water and solutions of polymers with supercritical solvents—using molecular simulation techniques. In addition, we are currently exploring inhomogeneous and non-equilibrium systems in supercritical solvents. We have also performed neutron scattering and X-ray scattering studies of polymers and of reverse micelles containing polymers in supercritical CO_2. A new X-ray pressure cell has been commissioned with improved diamond windows yielding tenfold improved transmission. Corollary applied studies currently focus on lipid extraction from fungal biomass and electrodispersion of aqueous media in supercritical CO_2.

96. *Chemistry of Actinides and Fission Products*

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Understanding the fundamental chemistry of the actinide and fission products is crucial in developing new separation technologies for these elements. The primary objectives of this task are to explore the speciation and chemistry of the actinide elements and their fission products in molten salts, aqueous solutions, and condensed phases through novel applications of spectroscopic and other methodologies; to elucidate photochemical reactions involving actinides in various media; and to investigate the fundamental principles leading to molecular recognition of actinides species in novel separation schemes. Current topics of pursuit are: (1) Lewis acid/base effects on the chemistry (redox and thermodynamics) of actinides in molten salts; (2) novel methods of tailoring solubilities of actinides in ionic melts and glasses; (3) application of imprinting technique to prepare actinide-imprinted sol-gel sorbents for selective separation and recognition of actinides; (4) investigation of interfacial uranyl photochemistry in sol-gel glasses; (5) U(V) photochemistry; (6) small angle scattering to determine zirconium and other tetravalent metal ion colloid growth chemistries.

Chemical and Analytical Sciences Division

97. *Mass Spectrometric Research in Inorganic Analysis*

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The goal of this research is to use mass spectrometry to investigate various inorganic systems and to extend the use of the discipline to areas previously closed to it. A glow discharge has been interfaced to an ion trap mass spectrometer to study gas-phase ion chemistry of inorganic species. Metal ion interactions and collision-induced dissociation are being explored. Several means of addressing molecular interferences are being studied. A pulsed glow discharge is being investigated as means of improving signal-to-noise. Reactive discharge gases are being used in fundamental studies aimed at elucidating the formation of rare species. It is hoped that a better understanding of plasma chemistry can be gained by, for example, closing various thermodynamic cycles. On-line pretreatment of samples prior to ICP analysis is being investigated to extend present capabilities. An ICP sector mass spectrometer with seven collectors is being evaluated for measurement of isotope ratios. In secondary ion mass spectrometry, our primary effort is directed toward understanding the relationship between the chemical composition of the sample and variations in instrumental bias that affect isotope ratio measurements. A model to predict isotopic bias as a function of chemical composition is being extended to three-component systems; a linear combination of the biases due to each end member has yielded promising results. Work in speciation of metals has continued in an effort to understand the alkylation chemistry that transforms innocuous inorganic forms of elements into toxic organometallic compounds.

98. Single-Photon Laser Photoionization of Oxygenated Compounds

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Research on laser photoionization (PI) in combination with tandem mass spectrometry is the focus of this work, with development of the speed, sensitivity, and specificity required for real-time measurement of oxygenated compounds in automotive exhaust being emphasized. Because ionization potentials (IP's) for many oxygenated and other organics are below 10.5 eV, single-photon ionization with coherent vacuum ultraviolet (118 nm, 10.5 eV) light should, with a few exceptions, be universal for these exhaust components. An apparatus for production of 118 nm radiation via third harmonic generation from 355 nm light has been designed and is in the fabrication stage. Subsequent compound identification via a single stage of mass spectrometry can be complicated since some exhaust components have identical molecular weights or overlapping peaks in their mass spectra. Thus, we are also investigating tandem mass spectrometry (MS/MS) to increase specificity of compound identification. More specifically, we have designed an optical system for interfacing the 118 nm radiation with a quadrupole ion trap mass spectrometer. Such mass spectrometers are intrinsically suited for use with pulsed ionization methods, such as laser PI, and are capable of executing ion manipulation operations for MS/MS and MSn experiments on the time scale (tens-hundreds of milliseconds) necessary for real-time emissions monitoring.

99. Advanced Spectroscopic Methods for Chemical Analysis

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Fundamental studies of the interaction of positrons with atoms and molecules are being pursued. Ionization mechanisms are totally different from those involving photons and electrons. Positronium production plays a key role, and it appears that positronium compounds occur as intermediates in certain reactions, such as the ionization of methyl alcohol, methyl chloride, methyl fluoride, and possibly certain alkanes, such as heptane. Ionization experiments using electrons have verified that the effects attributed to positronium compound formation are not spectrometry artifacts. In the course of studying the ionization of helium by positrons, the production of HeH+ was observed. When deuterium was substituted for hydrogen, HeD+ was generated. These results are important with respect to astrophysical research, suggesting that HeH+ and HeD+ may be produced in the Great Annihilator, located at the center of our galaxy. Positron spectrometry techniques have been applied to the study of automobile tires, resulting in techniques for rapidly detecting degradation. The above work has involved collaboration with Marquette University, Brookhaven National Laboratory, University College London, and the Electrotechnical Institute, Tsukuba, Japan.

100. Chemical and Structural Principles in Solvent Extraction

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Principles governing the recognition and separation of ions by molecular hosts in solvent extraction and ion exchange are under investigation. Crown ethers and calixarenes may be tailored to afford highly selective inclusion of ions and molecules and thereby offer exciting possibilities for novel separations. Deliberate design of such hosts can be achieved only through understanding how host-guest interactions depend upon host structure and solvent matrix. Toward this end, a holistic experimental approach is undertaken, involving organic synthesis, X-ray crystallography, distribution analysis, and multi-nuclear NMR spectroscopy. Synthesis efforts have recently focused on building a "superstructure" onto dibenzo-14-crown-4 ethers to accommodate ion-pair recognition, leading to a new focus on the role of the anion. Without the superstructure, sandwich formation with sodium ions relegates the anion to a second-sphere role with clear consequences for boosting selectivity for anions of low charge density, while superstructures interact with both cation and anion. By use of the program SXLSQI, equilibria in lithium extraction by alkylated 14-crown-4 ethers have been defined, revealing a structure-function relationship with ligand conformation and paving the way to improved ligand design. Structural results show that rigidification of 21- and 24-membered crown ethers by o-phenylene bridges modifies the nature of the cavity, improving selectivity toward large alkali metal ions.

101. Research, Development and Demonstration of Advanced Chemical Measurement Techniques

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The objective of this program is to utilize fundamental developments in optics, lasers, chemistry, and physics to develop new laser-based techniques to improve the sensitivity and/or specificity of chemical measurements. These techniques are applicable to a broad range of chemical measurement problems in fields encompassing environmental monitoring, process control, materials analysis, and biotechnology. Areas of research include ultrasensitive fluorescence detection, nonlinear optical processes, and microparticle optical processes. The effort addresses fundamental principles that must be understood to advance the area of single molecule detection in liquids. Microdroplet sampling is utilized to achieve picoliter to femtoliter probe volumes for the detection of single fluorescent molecules. These small probe volumes and the absence of diffusional losses have allowed detection of single chromophore molecules at high sensitivity ($S/N \approx 50$). In addition, cavity quantum electrodynamic effects and increased spontaneous emission rates for chromophores in microdroplets have been observed. These quantum optical effects will be exploited to further enhance detection sensitivity of the microdroplet approach.

Surface nonlinear optical probes will be used to study surface chemistry within the top monolayer of thin films during growth in chemical vapor deposition reactors. These probes are expected to assist understanding of materials growth mechanisms. A custom laser system is being constructed to advance the objectives of this program.

102. ***R & D in Secondary Ion Mass Spectrometry***
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This research concerns extending the applicability of secondary ion mass spectrometry (SIMS) by identifying the fundamental causes of barriers to applicability, characterizing these barriers, and then finding suitable methods to overcome them. For example, primary ion damage limits the utility of SIMS for mapping the distributions of organic compounds. In this work fullerene primary ions are used to perform simultaneous ionization and ablation of a damaged surface; raster of the fullerene ion beam permits imaging. Secondary ion yields from organic samples are typically 10X those obtained from cesium ion beams; effects of primary ion damage are also mitigated. Apparently molecular primary ions do not penetrate the surface as deeply as atomic ions. A greater fraction of the primary ion's energy is transferred at the surface, increasing the efficiency of secondary ionization and sputtering of damaged material. As another example, methods are being developed for imaging and isotope ratio measurement of targeted elements from geologic samples. Here, the historic barriers have included limited precision and reproducibility. These barriers arise from the peculiarities of the mass spectrometer. To overcome them, a mass spectrometer is used that permits simultaneous detection of isotopic ions and alternates measurement of an isotopic standard with measurements from the sample.

103. ***Mass Spectrometry Research for Organic Analysis***
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This research program is aimed at enhancing organic mass spectrometry as an analytical tool through pursuit of two major, and synergistic, objectives: (1) advance the understanding of the chemical and physical principles underlying the main components of all organic mass spectrometry experiments, namely, sample introduction, ionization, mass analysis, and ion detection; and (2) to use this improved understanding to develop new mass spectrometric methodology for fundamental and analytical applications. Four main areas of investigation are currently the focus of the research effort, viz., electrochemically-based sample handling/introduction methods; electrostatic spray ionization; gas-phase reactions of polyatomic multiply-charged ions; and quadrupole ion trap mass spectrometry. The sampling handling/introduction work is an exploration of novel electrochemical-based techniques for overcoming sample matrix effects, lowering detection levels, and improving detection specificity. Work with electrospray ionization and electrohydrodynamic ionization focuses on understanding the fundamental operational principles of these condensed-phase ion sources so as to widen their analysis figures of merit, such as ionization universality/selectively, dynamic range, and detection limits. Electrostatic spray ionization methods have made multiply-charged ions increasingly important. Ion chemistry studies are focused, therefore, on the unimolecular, ion/molecule, and ion/ion reactions of multiply-charged ions. Understanding the effects of experimental conditions on the internal energies of stored gaseous ions is a major theme in the quadrupole ion trap work. Ion heating and cooling are important phenomena in many quadrupole ion trap experiments. A theoretical model to follow changes in ion internal energies during the course of an ion trap experiment is being developed and refined. Enhanced analytical utility of ion trap collisional activation is expected to result from the detailed understanding of the chemical and physical processes inherent in resonance excitation of polyatomic ions. Furthermore, ion trap collisional activation is used as a slow heating method whereby both energetic and dynamic information on unimolecular decomposition of gaseous ions can be obtained. This capability can then be applied to the work on gaseous multiply-charged ions in which coulomb field effects on unimolecular, ion/molecule, and ion/ion reactions are being studied.

Pacific Northwest National Laboratory Richland, WA, 99352

Chemical Sciences Department

104. ***Fundamentals of Phase Partitioning in Supercritical Fluids***
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The objective of this program is to describe the molecular interactions underlying separations and chemistries in supercritical fluids. The scope of these studies spans the range from simple bi-molecular solute/solvent interactions to more complex multi-molecular clustering, ion-pair formation, chelation, and micellization phenomena. Molecular level studies in supercritical fluids will provide an improved understanding of both fluids and condensed-phase interactions by bridging the gap between the gaseous and liquid states. This program focuses on the fundamental chemistry that controls solute/solvent intermolecular interactions and the behavior of complex molecular assemblies in supercritical fluids through experimental and theoretical investigations. The experimental effort entails the use and expansion of various spectroscopic techniques such as NMR, FTIR, Raman, X-ray absorption (XAFS), and X-ray scattering (SAXS) for supercritical fluids. The experimental X-ray studies will be designed to exploit the brilliant X-rays available from the third-generation synchrotron facility at the newly commissioned Advanced Photon Source (ANL). The parallel theoretical effort involves molecular dynamics simulations describing the fundamental behavior of fluid solvents. Continued studies seek to characterize angstrom- to micron-sized molecular assemblies in supercritical fluids; e.g., alcohol aggregates, chelates, hydrated ions, and reverse micelles. Newly initiated investigations involve the study of the photophysics of organometallic ligand substitution and organometallic photochemical reactions using high-pressure NMR in addition to investigations of ion hydration and ion pairing in supercritical water and the solvation structure of metal chelates in supercritical carbon dioxide using XAFS spectroscopy. It is anticipated that this program will provide the basis for new and improved analytical separations and for larger scale separations and reactions needed in environmental remediation.

Materials and Chemical Sciences Department

105. ***Laser-Based Analytical Techniques***
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This program applies high-resolution laser-based spectroscopic methods to understanding fundamental processes which lead to the development of advanced analytical techniques. High-resolution methods offer unique capabilities for ultra-trace detection and isotopic analysis. Recent studies include the development of a diode-laser-based method of analysis for the environmentally important radioisotope strontium-90. Using Doppler-free double-resonance excitation, subfemtogram detection limits and isotopic selectivity greater that 10^{10} have been demonstrated. High-resolution studies are also used to investigate the dynamics and fundamental interactions in laser ablation sampling. A detailed understanding of the physico-chemical processes that occur during laser ablation are key to improving the performance and acceptance of laser ablation as a solids analysis tool. Our approach is to perform comprehensive spatially and temporally resolved measurements of neutral atomic, ionic, and particulate species produced in the laser ablation process. Comparison of temporal and spatial distributions for these species as a function of laser parameters will provide valuable insights into the basic processes leading to their formation. This will allow optimization of laser ablation parameters for a given application. Detailed measurements of atomic lineshapes and angle-resolved time-of-flight spectra provide information on the local environment, including parameters such as velocity distributions, charge densities, and the formation and propagation of shock waves. Understanding of the plume formation and evolution dynamics then allows the development of optimized high-resolution analysis methods. Multi-step resonant excitations, such as those developed for Sr-90, are being investigated for the reduction of Doppler broadening in the high-temperature environment of the laser ablation plume and will be compared to conventional thermal atomization sources for the ultra-trace detection of long-lived radionuclides.

Heavy Element Chemistry

Argonne National Laboratory
Argonne, IL, 60439

Chemistry Division

106. ***Heavy Element Chemistry Research***
Beitz, J.V.;Nash, K.L.; **$1,743,000**
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This program is developing an improved understanding of the fundamental chemical and physical properties that characterize the interaction of an f element with its surrounding environment. One goal is to understand the mechanisms by which the electronic properties of an f ion, including its redox behavior, are influenced by the materials in which they are contained. Basic knowledge obtained from these experiments will provide a predictive guide to the design of materials with predetermined electronic and cooperative properties. A second thrust area is determination of the electronic, magnetic, and nuclear properties of heavy elements using laser-based methods as well as theoretical modeling to attain crucial insight into important nuclear phenomena such as radiation damage. The understanding achieved is applied to fundamental and technological issues throughout the nuclear fuel cycle, for example, advancement of novel methods for early determination of leakage from uranium hexafluoride cylinders. A third area of investigation is the coordination chemistry of actinides, focusing on the interaction of metal ions with polydentate chelating agents in solution. These studies are revealing the interrelationship of the physical and chemical properties of complexes, ligand donor and structural characteristics, and solvation effects using spectroscopic, thermodynamic, kinetic, and structure determination techniques.

107. ***An Actinide Facility for Synchrotron Research in Molecular and Environmental Sciences***
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The purpose of the Actinide Facility is to make accessible, to experiments involving radioactive samples, the variety of state-of-the-art beamlines currently under construction at the Advanced Photon Source (APS). Funded by a DOE - Facilities Initiative, this user facility will provide technical and administrative support, including assistance with transport protocols, to both the user and the CAT staff. Hot-laboratory space will be provided in the Chemistry Division for simple chemical and physical manipulations of radioactive samples before and after experiments. In addition, there will be available specialty equipment, both in the form of safety monitoring devices to be used at the hutches at APS, and equipment necessary for performing experiments. One example will be a purpose-built portable glovebox that can be loaded in the hot laboratory, and used at the beamline to manipulate samples in the beam. This will be particularly important for experiments involving real-time chemistry. In addition to equipment, there will also be personnel available for consultation on both the experimental and safety aspects of the proposed experiments. This Facility is designed to address the needs of members of both the synchrotron and the actinide communities who wish to take advantage of the APS to conduct state-of-the-art experiments.

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Chemical Sciences Division

108. Actinide Chemistry
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Development of new technologies for the use, safe handling, storage, and disposal of actinide materials relies on further understanding of basic actinide chemistry and the availability of trained personnel. This research program is a comprehensive, multifaceted approach to actinide chemistry and to the training of students to address future issues. Research efforts include synthetic chemistry to develop new chemical reagents and actinide materials, characterization of their chemical and physical properties, and thermodynamic and kinetic studies of complex formation. Specific programs are the development of complexing agents that specifically sequester actinide ions for the decorporation of actinides in humans and for the separation of actinides in the environment. Extensive efforts are underway to prepare organometallic and coordination compounds of the f-block elements that show the differences and similarities among the f-elements and between the f- and d-transition series elements. Interpretation of optical and magnetic studies on actinide ions in ionic and molecular solids gives information about electronic properties as a function of atomic number. X-ray absorption fine structure techniques at SSRL are employed to investigate both the fundamental and environmental chemistry of transuranic and fission product materials. VUV/soft X-ray methodologies are being employed to study actinide materials at the ALS.

Nuclear Science Division

109. Chemistry of the Heaviest Elements
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The chemical properties of the heaviest elements are being investigated to explore the architecture of the periodic table of the elements at its furthest reaches and to compare their properties with those of their lighter homologs. Investigations of the dramatic changes in properties which occur in going from the actinides, which end with lawrencium (element 103), to the transactinides are especially important. Methods for studying the chemical properties of elements 102 through 106 are developed even though some of the half-lives are only seconds and only small numbers of atoms can be produced. Chemical separations of elements 102-105 have been used to determine their most stable oxidation states in aqueous solution, thus confirming their positions in the periodic table. Detailed studies of chemical properties of the heaviest elements have shown anomalous trends which cannot be predicted on the basis of simple extrapolations of known periodic table trends. It is important to extend these studies to even heavier elements and to compare the results with predictions of fully relativistic calculations. During FY-97 the volatilities of the bromides of Hf, Ta, and W were measured with the Heavy Element Volatility Instrument in preparation for measurement of the gas-phase properties of the bromides of elements 104, 105, and 106. As part of an international collaboration, the full range of automated liquid and gas-phase chemical separation systems were used to perform the first ever chemical studies of seaborgium (Sg, element 106) using the recently reported longer-lived isotopes of Sg. Sg was found to form anionic complexes in HNO_3/HF solutions, similar to its lighter homologs W and Mo, and unlike its pseudo-homolog U(VI). Sg was also found to form oxychlorides which are slightly less volatile than those of Mo and W formed under identical conditions.

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Chemical Science and Technology Division

110. Actinide Organometallic Chemistry
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Studies of the non-aqueous coordination and organometallic chemistry of the early actinides are being carried out in order to enhance understanding of the influence of geometry and coordination environment on the electronic structure and chemical reactivity of these elements in the absence of the effects of hydration. These investigations generate new insights into the nature of metal-ligand bonding in the actinide series, and often explain observed trends in the structures and relative reactivities of complexes. Recent investigations have concentrated on the study of early actinide complexes containing metal-ligand multiple bonds, including the structural chemistry and ligand redistribution reactions of uranyl alkoxide complexes, and the reactivity of actinide-imido complexes as a function of metal, oxidation state, and imido substituent. These reactions often suggest the involvement of f-orbitals in chemical bonding. High-valent organoimido complexes of uranium have demonstrated the capacity to activate H-H, Si-H, and C-H bonds. Multi-electron transfer reactions from low-valent precursors have also been exploited to either break bonds in substrates (e.g., the cleavage of azobenzene to generate the bisimido complex $(C_5Me_5)_2U(NPh)_2$)

or make bonds to generate coupled products (alkyne coupling). The latter reactions reveal important differences in the reactivity of uranium and thorium, likely as a result of the availability of higher oxidation states in uranium chemistry.

111. Actinide Chemistry in Near-Neutral Solutions

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The purpose of this work is to provide fundamental physicochemical knowledge pertinent to the behavior of plutonium and other light actinides under environmental and physiological near-neutral pH conditions, with potential practical applications in the areas of actinide reprocessing and purification, nuclear waste isolation and storage, and remediation of contaminated sites. The lighter actinides (U, Np, Pu, Am) constitute a long-term hazard because of their relatively high radioactivity and reasonably long half-lives. This past year significant advances were made in the application of molecular studies to environmental problems. The molecular and solid-state structure of $Pu(CO_3)_5^{6-}$ was determined using XRD and EXAFS spectroscopy. The solution UV-Vis-NIR, diffuse reflectance of single crystals, and EXAFS solution spectra show that the same limiting anion is present in both solution and the solid-state. The nature of this complex has been in debate for nearly two decades. With the limiting structure in hand, studies were initiated to determine the identities of the other more complex species, presumed to contain mixed hydroxo-carbonato units. It was also shown that the neptunium(V) cation can be completely encapsulated by crown ether ligands in aqueous solution to form the highly unusual cation of formula $NpO_2(18\text{-}C\text{-}6)^+$, with Np=O = 1.799(5), and Np-O = 2.589(9) Å. We will work to develop an understanding of the factors that control inner- versus outer-sphere complexation of actinyl ions by crown ether ligands.

112. Actinide Chemistry in Alkaline Radioactive Waste

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The purpose of this work is to determine the behavior of light actinides (U, Np, Pu, Am) under strongly alkaline conditions ($[OH^-$ = 2 - 14M) of relevance to radioactive wastes. Such knowledge is essential to understand and predict actinide solubility, sorption, phase separation in tanks, determine whether chemical separations are needed for waste treatment, for rational design and optimization of separations process, and the molecular level compatibility with the vitrification process. This past year saw significant advances in the application of structural studies towards understanding molecular level speciation under alkaline conditions. For example, while the uranyl(VI) ion will precipitate in highly alkaline solution to produce uranate salts, we find that neptunyl ions (V, VI, and even VII) are highly soluble in both 2.5 M LiOH and NaOH solutions. This suggests that Np will be much more soluble in tank wastes than previously thought, and may impact low-level waste streams at sites such as Hanford and Savannah River. Uranate precipitation could be prevented by using 3.5M TMA(OH) solutions. EXAFS spectroscopy in solution, and solid state single crystal X-ray diffraction revealed the $UO_2(OH)_4^{2-}$ anion with U=O = 1.826(7) and U-OH = 2.260(6) Å. Strong bonding of equatorial OH- ligands result in a lengthening of the U=O bond and a shift of 86 wavenumbers in the Raman-active nu_1 stretch to 784 wavenumbers. O-17 NMR spectroscopy on trans dioxo U(VI), Np(VI), and Np(VII) ions in 3.5 M hydroxide reveals an unprecedented chemical exchange between An=O and An-OH moieties. This was confirmed for U(VI) by Raman spectroscopy on O-18 enriched samples.

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Oak Ridge, TN, 37831-6375

Chemical and Analytical Science Division

114. Chemistry of Transuranium Elements and Compounds

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The program's objectives are to promote the fundamental chemistry, physics, and materials science of the actinides through systematic studies, which are relevant for advancing a diversity of technological interests (e.g., nuclear waste disposal, environment assessments/ behaviors, databases, transmutation concepts, etc.). These objectives are pursued through experimental studies, whose results are interpreted in terms of electronic configurations, the fundamental framework of the periodic table. Multiple scientific disciplines are used and collaborations with other laboratories and universities are employed frequently. The latter provide increased manpower, expertise and facilities, as well as promoting interest and training in this area of science. The principal areas of solid- and vapor-state study are: ambient and high-temperature X-ray diffraction; laser and high-temperature mass spectrometry; optical spectroscopy; high-pressure chemistry/ physics; and thermal analysis. Limited solution and colloidal chemistries are also pursued. Examples of recent efforts are: exploring the bonding behavior in actinide alloys and pnictides through high-pressure studies; laser ablation mass spectrometry studies (e.g., comparative actinide organometallic gas-phase reactions and vapor-state cluster chemistry); studies of Np alloy systems; and investigations of the fundamental science (oxidation state, local environment/ coordination, structural/bonding interactions, effects of radioactive decay, etc.) of actinides in selected glass and inorganic-ceramic matrices.

Stanford Linear Accelerator Center
Stanford, CA, 94309-0210

Stanford Synchrotron Radiation Laboratory

115. ***Controlled Clean Lab Enclosure for XAFS Studies of Radioactive and Toxic Samples on Beam Line 11 at the Stanford Synchrotron Radiation Laboratory***
Hodgson, K.O.; **$200,000** Equipment
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During the past few years, there has been increasing demand at the Stanford Synchrotron Radiation Laboratory by national laboratory and university scientists for beam time on high-flux, insertion-device beam lines to characterize the chemical forms (speciation) of radionuclides and toxic heavy metals in environmental samples. To help meet the needs in this new research area, DOE-BES-Chemical Sciences is funding a new wiggler beam line at SSRL (BL-11) devoted to molecular environmental science research. This new beam line is currently under construction and should be commissioned in 1998. An essential component of this new environmental sciences beam line is a controlled clean enclosure that will be built around the experimental hutch. This facility is required to permit safe sample handling, temporary storage, and XAFS spectroscopy studies on environmental samples containing radionuclides, particularly transuranics, and highly toxic or carcinogenic species. This project will provide the funding to construct this controlled experimental area on BL-11. Because this will be a permanent installation, with all the necessary equipment for radiation monitoring and safe sample handling and containment, it will also permit increased numbers of radioactive and toxic samples to be studied without the time-consuming and inefficient set-up and dismantling times now required on SSRL Beam Line 4-2, where XAFS studies of samples containing these elements are typically carried out. Various design features for this clean lab are being explored with members of the BL-11 Advisory Committee. When BL-11 and the controlled clean laboratory are completed, a major new synchrotron radiation facility for XAFS studies of radioactive and toxic elements in natural samples, man-made waste forms, and simplified synthetic analog systems will be available to the growing number of environmental science users at SSRL.

Chemical Engineering Sciences

Ames Laboratory
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Department of Materials Science and Engineering

116. ***Design and Processing of High Purity and Ultrafine Electrodes for High Performance Nickel/Metal Hydride Batteries***
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Rechargeable Ni/Cd products are currently on the edge of an outright ban or a heavy tax due to the extreme toxicity of Cd. The Ni/metal hydride (Ni/MH) rechargeable battery has emerged as one of the most promising environmentally acceptable substitutions for current Ni/Cd rechargeable batteries in nonautomotive applications for the consumer and industrial market. A key to realization of this potential lies in coupling of the development of both high performance positive and negative electrode materials with the development of efficient, well-controlled electrode processing approaches for each new electrode material. Another key is the close collaboration of a high level research team with a capable and aggressive manufacturer of Ni/MH batteries. This coupled development and industrial collaboration targets not only improved battery performance and effective manufacturability but also will promote a rapid transfer of materials and process research results from the laboratory to the manufacturing floor and marketplace. This program's focus includes the fundamental, systematic development of a significantly improved alloy composition (especially with respect to chemical and phase purity levels), processing, and electrode fabrication technique for the negative based on $LaNi_5$ intermetallic compounds. The objective of this work is to greatly reduce self-discharge and to double cycling life characteristics of this electrode material over the competing AB_2 compounds. The latest effort is concentrated on basic studies to develop suitable high pressure gas atomization technique for preparation of uniform spherical particulate with improved hydrogen absorption-desorption and mechanical characteristics. Also, focus is on development of a unique processing approach for the NiOOH positive electrode that will permit fabrication of new ultrafine pitch electrodes. Such an ultrafine pitch electrode with homogeneously dispersed particulate has the potential to increase the energy storage density by about 50%, thereby reducing size and weight of this new generation of Ni/MH batteries. This program is being carried with intimate contact between the Ames Laboratory and Harding Energy Systems Inc., an emerging domestic battery manufacturer.

Argonne National Laboratory
Argonne, IL, 60439

Chemical Technology

117. *A Fundamental Study of Lithium Polymer Electrolytes: Neutron and X-ray Scattering Experiments and Electronic Structure Calculations*

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This project is a complementary experimental and theoretical study of the structure, dynamics, and transport properties of lithium polymer electrolytes. The goal is to obtain a fundamental understanding of the ionic transport properties in these electrolytes in order to help optimize their performance in lithium secondary batteries. The experimental part of the study includes neutron scattering measurements at the Intense Pulsed Neutron Source at Argonne and X-ray scattering measurements at the Advanced Photon Source at Argonne. Application of scattering techniques to lithium polymer electrolytes will provide information on ion solvation and the attendant effects of ion pairing, which affect the ionic transport in these systems. The theoretical part of the project involves electronic structure calculations based on ab initio molecular orbital theory and density functional theory. These calculations are being used to investigate the ion-ion and ion-polymer interactions including reaction energies, barriers to cation migration, coordination numbers, and vibrational properties. The computational studies are providing accurate potentials for molecular dynamics simulations being carried out at the University of Minnesota. The calculations are being used to help interpret experimental data. At a later stage these methods will be used to study processes occurring at electrode/electrolyte interfaces in batteries.

118. *Ion Transport Properties*

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This program uses in situ magnetic resonance imaging to better define electrode-electrolyte interfaces and solid-state ion transport mechanisms. Special emphasis is placed on developing techniques that probe the micro-environment immediately adjacent to the electrode and not simply the properties of the bulk electrolyte. Work is conduced using a unique toroid cavity probe that was designed to simultaneously provide 2-μm distance resolution and NMR chemical shift information. The new imaging methodology is well suited for the in situ analysis of the chemical composition at the electrode-electrolyte interface, ion concentration gradients within solid state batteries, conformational dynamics of polymer electrolytes, and ion penetration depths within carbon insertion electrodes. Additionally, a new method for measuring diffusion coefficients has been developed. The method is based on NMR imaging and is capable of resolving different regions of the cell. For example, it is now feasible to explore the ionic mobility within the salt depletion zone that forms within a few micrometers of the cathode under normal battery operation. Furthermore, methods for probing the phase composition of polymer-electrolytes in the vicinity of the electrodes based on NMR spin relaxation time measurements are also being developed.

119. *Development of New Electrode Materials for Battery Applications: Synthesis, Characterization, and Modeling*

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This project focuses on the search for and characterization of novel or modified metal oxide electrodes for non-aqueous rechargeable lithium batteries. State-of-the-art metal oxide electrodes are limited by performance factors such as structural instability to lithium insertion/extraction reactions, particularly at the end of discharge/charge, and an instability to temperature rise effects. Furthermore, the capacity of metal oxide electrodes and cycle life of lithium batteries need to be improved. There is, therefore, a need to explore the possibility of developing alternative electrode materials for these batteries. This project, which is exploratory in nature, has two complementary tasks. The first is to search for novel or improved electrode materials (notably metal oxides) to optimize materials processing techniques and to characterize the materials in terms of their structural and electrochemical properties. Recent efforts have focused on the stabilization of the α-MnO_2 (hollandite-type) structure which is of interest for 3 V lithium batteries. The second task focuses on the modeling of materials using ab initio methods: theoretical calculations and modeling of vanadium oxides, (such as LiV_3O_8), and manganese oxides (such as α-MnO_2) have provided valuable insight into the structural behavior of materials during electrochemical discharge and charge. The project makes use of the extensive battery expertise that exists at Argonne National Laboratory and its unique facilities, such as the Intense Pulsed Neutron Source (IPNS), for undertaking detailed structure analyses of materials. Materials characterization also includes convergent-beam electron diffraction (CBED) and high-resolution transmission electron microscopy (HRTEM) techniques to provide "real-life" pictures of the structures of materials which cannot be obtained from "time-averaged" structural representations provided by X-ray or neutron diffraction techniques alone.

Chemistry Division

120. *Template Mediated Synthesis of New Carbon Negative Electrodes*

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The overall goal of this program is to understand the chemistry and physics of the carbon anodes used in lithium secondary batteries. The approach is to design and prepare carbons with specific molecular properties. Inorganic templates such as pillared clays are being used to prepare molecularly porous, disordered carbons. New methods of preparing the clay organic complex are being explored to increase the carbon yield and enhance the carbons electrochemical properties. The carbons have been characterized by a number of methods, including small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), and synchrotron X-ray spectroscopy. Both SANS and SAXS data have shown that after removal of the pillared clays, the carbon sheets contain holes the size of the original pillars, and that the overall structure of the carbon resembles the clay. In electrochemical studies, these carbons exhibit high reversible capacities (up to 850 mAh/g) and coulombic efficiencies higher than 90%.

Materials Science Division

121. The Study of Electrochemical Interfaces Important to Energy Storage and Conversion Processes at the Advanced Photon Source

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The primary objective of this interdisciplinary research is the fundamental understanding of the solid/solution interfacial structure of materials important to energy storage and to energy conversion. The problem areas include electrocatalysis, surface morphology of metal deposition/dissolution, the intercalation/deintercalation mechanism, and the structure of the electric double layer. The final aim is to contribute seminal guidance to the development of improved energy storage/conversion materials with increased energy and power density and charge/discharge rate for a variety of battery and fuel cell systems. While we expect that the results of our investigation will provide impetus for technological developments, they will also be of fundamental scientific importance in the field of interfacial electrochemistry. The research program that we carry out couples in situ synchrotron-based X-ray measurements with electrochemical transient techniques and theoretical modeling. An example of our investigations is the study in real time of the actual and complete phenomena occurring in ultracapacitor storage devices. The ultracapacitor stores energy using several different phenomena restricted to the interface of the electrodes, such as the electrochemical double layer and the adsorption pseudocapacitance involving redox processes. All these phenomena can be observed at a third-generation-synchrotron facility such as the Advanced Photon Source.

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Department of Applied Science

122. Chemistry and Electrochemistry of Hydrogen Insertion Electrodes

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The purpose of this program is to elucidate the structural, thermodynamic, and other parameters that affect the stability, kinetics, and energy density of hydrogen insertion electrodes. It is primarily focused on multicomponent metal hydride electrodes and develops and applies in situ methods such as X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), X-ray tomography, magnetic susceptibility and scanning tunneling microscopy to determine the roles of various hydride phases and alloying elements in hydrogen storage and corrosion inhibition. In situ methods are complemented with ex situ studies employing XRD and neutron diffraction as well as electrochemical, thermodynamic, and metallurgical characterization of candidate materials. The information thus gained will be used to develop low-cost metal hydride electrodes having high cycle life, high discharge and charge rate capability, and improved energy densities.

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Chemical Sciences Division

123. Molecular Thermodynamics for Phase Equilibria in Mixtures

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Phase equilibria are required for design of efficient separation processes (e.g., polymer devolatilization or selective precipitation of a target protein from an aqueous protein mixture) in the chemical and related industries and for development of new chemical products and materials. In this context, “efficient” refers to optimum use of raw materials and to conservation of energy. Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all equilibria from experiment. Therefore, the objective of this research is the development of molecular thermodynamics for interpretation and correlation of reliable experimental data toward confident prediction of phase equilibria for chemical process and product design. The correlations are expressed through semi-theoretical, physicochemical models based on statistical and classical thermodynamics and on our own as well as published experimental data. Particular attention is given to those materials that may be useful for innovative low-energy-consuming separation processes such as polymers, gels, and polyelectrolyte systems with applications in chemical technology and biotechnology. However, attention is also devoted to conventional materials for applications in fuel technology and for proteins used in nutrition or pharmaceutics. Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work. Further, it requires simultaneous awareness of progress in molecular science and of realistic requirements for engineering application.

124. *Characterization of the Li—Electrolyte Interface*

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A detailed understanding of the reactions that occur between metallic Li and the individual molecular constituents of electrolytes used in Li batteries will be developed. Ultrahigh vacuum (UHV) deposition methods are used to prepare ultraclean Li surfaces of preferred orientation. Molecular films of solvent and/or solute molecules are deposited onto the clean surfaces in UHV at a very low temperature. The reaction between Li and the molecular films is followed using a combination of UHV surface analytical techniques, including Auger electron spectroscopy (AES), secondary ionization mass spectroscopy (SIMS), vacuum UV and X-ray photoelectron spectroscopy (UPES and XPS), and the recently developed variant of XPS termed photoelectron diffraction. The connection between films formed on Li in UHV and films formed at ambient temperature and pressure on Li in liquid electrolyte is made by the use of a common spectroscopy, ellipsometry. Using the fingerprint method, the ellipsometric signatures obtained in UHV for different surface layers having various known structures and compositions are used to identify the structure and composition of the film formed on the Li electrode in liquid electrolyte. Studies of tetrahydrofuran (THF) and propylene carbonate (PC) have been completed. The study of dimethylcarbonate (DMC) is in progress.

Energy and Environment Division

125. *Fundamental Studies of Materials and Processes in Rechargeable Lithium Batteries*

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Rechargeable lithium batteries are attractive for future hybrid electric vehicle applications because of the low equivalent weight and low electronegativity of lithium. However, large-sized (capacities greater than a few Ah) rechargeable lithium batteries have not been developed because of problems with rechargeability, safety, and cost. Fundamental problems associated with interfacial processes, sensitivity to overcharge and overdischarge, material stability, and electrolyte chemistry have prevented successful battery scale-up and commercialization. We propose to address these problems by carrying out fundamental studies of key interfacial processes at the positive electrode, cell overcharge chemistry, and cell materials. The in situ interfacial techniques of ellipsometry, Raman spectroscopy, and probe beam deflection will be used to study oxide stability and/or film formation at the positive electrode/electrolyte interface. These studies will be carried out on thin dense oxide films prepared via pulsed laser deposition (PLD) in a parallel project. Overcharge protection is a serious issue for lithium batteries, since overcharging shortens cell life and may cause internal shorting and/or gas evolution, resulting in dangerous runaway reactions. This problem is magnified for the multi-cell stacks used in high power applications. We are studying chemical additives which behave as redox shuttles to allow current to pass harmlessly through a cell after it has been fully charged. A useful additive must have a low equivalent weight, high diffusion coefficient, and appropriate redox chemistry. Additional concerns are stability towards other cell components, volatility, and toxicity.

126. *Application of Pulsed Laser Deposition to the Study of Rechargeable Battery Materials*

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The aim of this project is to study the performance-limiting phenomena of complex transition metal oxides of significance to rechargeable batteries and to suggest practical means for improving their performance and lifetime. Studies are carried out on thin dense pure oxide films prepared on electronically conductive and/or transparent substrates with the pulsed laser deposition (PLD) technique. PLD is particularly suited to the preparation of oxides with complex stoichiometry. Thin dense films of complex oxides such as $Li_xMn_2O_4$, $Li_xNi_{0.05}Mn_{1.95}O_4$, $La_{0.6}Ca_{0.4}CoO_3$, and $Bi_2Ru_2O_7$ have been prepared. These films are characterized with XRD, FTIR, SEM, and RBS. The FTIR spectra for $Li_xMn_2O_4$ films on Si substrates show two main peaks associated with the MnO_6 octahedra at 475 and 610 cm^{-1}. The spectra of these films show the temperature-induced Jahn-Teller distortion that has been studied by other techniques. This distortion is not observed with a nickel-doped film. $Li_xMn_2O_4$ films are electrochemically cycled over various voltage ranges to study the electrode processes during overcharge and overdischarge. When $Li_xMn_2O_4$ films are discharged below 3.5 V vs. Li/Li^+, the voltage required for charging on the next half-cycle is increased. In a parallel project, the behavior of the $Li_xMn_2O_4$/electrolyte interface is being studied with a variety of techniques using films prepared in this project.

127. *EXAFS and NMR Studies of Electrode Materials for Lithium Batteries*

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Manganese oxide materials are under development for use as the positive electrode for rechargeable, high-performance lithium cells. This project seeks to correlate the electrochemical performance of lithium insertion materials with the atomic and electronic structural changes that occur as a result of the insertion process. Major tools used in these studies are X-ray absorption spectroscopies and NMR spectroscopy, along with advanced electrochemical methods. The base material for this work is $Li_xMn_2O_4$(with 0.1<x<2.0). The XAS techniques of XANES, EXAFS, and K beta emission spectroscopy have shown that the inserted Li affects the electronic structure of the Mn to a significant degree, giving it an electronic square-planar structure when the atomic structure is in the tetragonal state for x>1. It has also been determined that the Mn is in the high-spin state in this material, providing confirmation that the Jahn-Teller distortion is the explanation for the cubic to tetragonal transformation for x>1. These studies are being extended to Li, Co, and Ni-substituted materials (replacement of Mn). These materials are of interest because of the observed improvement in capacity stability with cycling. The nickel-substituted lithium manganese spinels are currently being studied with variable temperature ^{7}Li nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), and SQUID (superconducting quantum interference device) magnetometry to elucidate the electronic structure and phase transitions of these materials. In addition, variable temperature ^{7}Li NMR studies will also be used to probe the lithium microscopic mobility in these materials. These approaches will also be applied in the coming year to the study of chromium-substituted and cycled electrode materials, starting with $Li_xMn_2O_4$ (0<x<=2).

128. Fundamental Characterization of Carbon-Based Materials for Electrochemical Systems
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The objective of this research is to develop an understanding of the relationship between the physicochemical properties of carbon-based materials and their electrochemical properties. Studies on catalytic etching of carbon surfaces to modify their surface properties for electrochemical reactions was completed. An effort was initiated to utilize semiconductor processing techniques involving spin-coating photoresist, photolithography, and carbonization to form micron-sized nanostructures for carbon electrodes. Photoresist of thickness about 10 microns was spin-coated on silicon wafers and carbonized at temperatures from 500-1100°C in an inert atmosphere. Preliminary analyses indicated that a disordered carbon structure was obtained, although smaller regions of more graphitic structure were also present. Electrochemical studies to characterize the carbon electrodes by redox reactions involving the ferri/ferrocyanide couple and oxygen reduction are underway. Cyclic voltammetry clearly shows that the electrochemical behavior of the carbon depends strongly on the carbonization temperature; improved performance is obtained with samples produced at higher temperature. Experiments have started to electropolymerize polypyrrole on the carbon surface to evaluate as positive electrodes for rechargeable batteries.

Environmental Energy Technologies Division

129. Turbulent Combustion
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The objective of this program is to investigate, primarily experimentally, the interaction and coupling between turbulence and combustion. As turbulent combustion processes are characterized by scalar and velocity fluctuations with time and length scales spanning several orders of magnitude, our approach is to gain a fundamental understanding through detailed investigation of idealized laboratory flames with flow and flame geometries amenable to theoretical analysis. The experiments are designed to allow detailed interrogation by laser diagnostics. The emphasis is on gaining a physical understanding of the coupled effects of turbulence and flame geometry on heat release, turbulent burning rate, stability limits, and flame extinction. Such knowledge is essential for the guiding the development of turbulent combustion theories. One primary effort is on investigating flames with moderate turbulence under which the chemical reaction rates are high compared to those of turbulence. The burning rate can be inferred from the flame wrinkles scales for direct comparison to turbulence scales. Our current focus is to investigate the relative effects of shear and non-shear turbulence. We are also studying flames with intense turbulence. Intense turbulent flames occur in practical systems where turbulence may alter the reaction rates, cause flame quenching, and affect the formation of pollutants. The use of planar laser-induced fluorescence techniques has provided statistical information on flame wrinkle scale and will show the effects of local flame quenching.

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Theoretical Division

130. Thermophysical Properties of Mixtures
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The thermophysical properties of mixtures of particles interacting through simple interaction potentials are evaluated, using both equilibrium Monte Carlo and molecular dynamics, as well as nonequilibrium molecular dynamics. The properties under investigation include the equation of state and transport properties, including mutual and self diffusion, shear and bulk viscosity, thermal conductivity, and thermal diffusion. Fundamental questions arising in the theory of fluids and fluid mixtures are addressed where numerical “experiments” are appropriate. Current research is concentrated on the phase diagram of hard-sphere mixtures having diameter ratios no greater than 0.2 and compositions in which the molecular volume of the two species are similar. Theoretical predictions of fluid phase demixing have been made for such mixtures in recent years, contradicting the conventional understanding arising from the Lebowitz solution to the Percus-Yevick integral equation. The Gibbs ensemble Monte Carlo method permits the study of the coexistence of disordered phases, but current implementations are inadequate to overcome the ergodic difficulties attendant upon the disparate hard-sphere interactions. Advanced methods have been development to permit the study of this mixture as well as others having large disparities in the interactions. While progress in these new methods has been significant, there remain ergodic difficulties associated with the need to effect Monte Carlo "moves" in which large changes in composition occur. We have, therefore, turned to the hard sphere fluid-solid phase transition to develop and test further algorithms which will enable the direct study of first-order phase transitions in dense systems. A generalization of the Gibbs ensemble method builds a "super"-realization from segments consisting of simple Gibbs-ensemble realizations initiated in the important regions of the phase-partition space of the system. Early results indicate that averages over this realization in fact describe the transition rather accurately. The extension of this method to the mixture problem and the demixing transition appears to be straightforward.

National Renewable Energy Laboratory Golden, CO, 80401

Center for Basic Sciences

131. ***High Efficiency Thin-Film Cathodes Based on Doped Vanadium and Manganese Oxide with Improved Microstructures***
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Stable, high-efficiency cathodes are critical for development of thin-film lithium rechargeable batteries. Although much work has been done investigating the electrochemical properties of various cathode materials (such as V_2O_5, V_6O_{13}, and $LiMn_2O_4$), further improvement of the cathode charging-capacity and lifetime can be achieved by improving the morphology and appropriate doping in these materials. Development of a cost-effective manufacturing technique is also necessary for large-scale applications. We have found that the vanadium oxide films prepared by plasma-enhanced chemical vapor deposition exhibit a high discharge capacity and are very stable, even after several hundred cycles. The charge capacity of the film is 390 mAh/g or 1209 mAh/cm^3 when cycled at C/1 rate. The capacity fade is only 0.036% per cycle over 200 cycles. The film deposition rate of PECVD process is more than 5 times higher than those of thermal evaporation. We propose to expand this promising technique to doped vanadium oxide ($V_{2-x}M_xO_5$ and $V_{6-x}M_xO_{13}$) and lithium manganese oxide films ($Li_xM_yMn_zO_n$) for lithium rechargeable battery applications, where M includes Co, Cr, Ni, V, W, Mo, etc. These films will be prepared by both plasma-enhanced chemical vapor deposition and sol-gel technology at low temperatures. Various factors which affect the performance, lifetime, and safety of these materials will also be investigated. Combination of the doping and appropriate microstructures generated by the low-temperature deposition methods will enhance the stability and charge capacity of the cathodes. The cost-effective preparation methods developed in this project will also help accelerate industry acceptance of this important technology.

Oak Ridge National Laboratory Oak Ridge, TN, 37831

Chemical and Analytical Sciences Division

132. ***Basic Aqueous Chemistry at High Temperatures and Pressures***
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The purpose of this program is the study of the aqueous chemistry of broad classes of solutes at high temperatures and pressures to provide understanding of basic principles governing chemical equilibria and the thermodynamic properties of electrolytes. The advancement of both experimental methods and new models for representation and prediction of behavior over extremes of temperature and pressure are important parts of the program. A number of unique but complementary techniques are used up to and beyond the critical temperature of water and its solutions. Current research uses: flow calorimetry, densimetry, isopiestic apparatus, electrochemical cells, electrical conductance apparatus, vapor-liquid partitioning cells, Raman spectroscopy, and solid-liquid equilibrium cells. Chemical equilibria under study are ionization, ion association, metal complexation, metal ion hydrolysis, solubilities, volatilities, and adsorption reactions. Reaction thermodynamic quantities and excess properties of electrolytes are of interest. New results are bridging the challenging transition from strong-to-weak electrolyte behavior, near critical "anomalous" behavior, and reaction behavior of new classes of ions and species. Models are being developed for describing variations of both standard state and excess thermodynamic quantities over wide ranges of temperature and pressure. Computer simulations relating our macroscopic observations to microscopic structure have been initiated. Initial work addresses ion pairing in the near critical region. Results of the overall program impact strongly the communities in basic solution chemistry, as well as hydrothermal geochemistry, steam generator technology, geothermal technology, environmental chemistry, and nuclear and hazardous waste disposal.

Solid State Division

133. ***Rechargeable Thin-Film Lithium Batteries***
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The purpose of this program is to conduct the research needed for further advancement and commercialization of thin-film lithium and lithium ion batteries developed at the Oak Ridge National Laboratory. These all-solid-state batteries are less than 15 micrometers thick, have high energy and power densities, and they can be cycled thousands of times. They can be fabricated on a variety of substrate materials in arbitrary shapes and to any required size large or small to meet the demands of specific applications. Thin-film lithium and lithium ion batteries have potentially numerous applications as small power supplies for consumer products and implantable medical devices, and for many applications, they can be integrated into electronic circuits at the chip carrier or the chip level. Recently, a significant increase in rate capability was demonstrated with Li-$LiCoO_2$ batteries having highly textured crystalline cathodes. For example, at a continuous discharge rate of 2 mA/cm^2, the batteries could deliver more than 0.1 mAh/cm^2 of charge between 4.2 V and 3.0 V. Several important issues addressed in this research are crucial to the commercialization of this technology. These include investigating the effects of deposition and processing conditions on the structure of cathode films and determining those conditions which optimize rate capability and cycle life, investigating the origin of capacity fading in crystalline and amorphous cathodes, determining cell performance as a function of temperature and discharge current density, and devising methods for fabricating multicell batteries. The program also includes studies of the possible use of the lithium phosphorus oxynitride (Lipon) electrolyte discovered at ORNL as a protective coating that could improve the performance of existing rechargeable lithium-solid polymer electrolyte and lithium-liquid electrolyte batteries. Part of this research is carried out under Cooperative Research and Development Agreements with commercial firms. Joint research is also conducted with groups at other national laboratories and universities.

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Combustion Research Facility

134. ***Analysis of Turbulent Reacting Flows***
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The goal of this project is to develop numerical simulation techniques for the understanding of reacting turbulent flows. The objective is to show the mechanisms of turbulent mixing and reaction and their effect upon combustion rate. A simulation of an expanding premixed flame in two dimensions has provided agreement with the enhanced flame speed observed in three-dimensional experiments. The hydrodynamic instability of a premixed flame generates flame surface at wavelengths large compared to the flame thickness. The resulting nonlinear growth creates a flame bulge between two flame cusps. This flame shape resembles a cycloid curve. These expanding flames acquire a speed which grows like the square-root of time; this power-law is thought to be determined by the cycloid geometry. The linear-eddy mixing model, unique in its representation of the distinct influences of convective stirring and molecular diffusion, reproduces many of the interactions between turbulence and molecular diffusion that are known to influence combustion processes. The model has yielded predictions of novel interactions that have been confirmed experimentally. Work in progress incorporates combustion chemistry into the model.

Exploratory Batteries Department

135. ***Doping of Lithium Manganese Oxide for Improved Battery Performance***
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Lithium manganese spinel compounds demonstrate considerable promise as cathodes in the next generation of rechargeable batteries due to their high specific capacity, long cycle life, and benign effect upon the environment. In order to evaluate potentially new cathode materials based on the $LiMn_2O_4$ spinel structure, we have used an atomistic theoretical approach. The atomic simulations employ an energy optimization of the crystal structure based on the summation of Coulombic, short-range repulsive, and van der Waals interactions. A minimum energy structure is obtained under the constraint of P1 symmetry and constant pressure conditions, thereby allowing all 56 atoms of the spinel unit cell and the cell parameters to relax while maintaining an isometric crystal. A shell model that accounts for electronic polarization is used to refine the model. Pure $LiMn_2O_4$ and various doped spinels were examined in this study in order to determine the lattice energy, unit cell volume, and the relative stability of the doped structures. We are studying the effect selected dopants have on the theoretical lattice parameter of spinels as a function of the ionic radii of the substituted metal ion and dopant amount. Having validated the model, we are developing structure/property relationships that impact cathode performance in rechargeable lithium battery systems. The doped lithium manganese dioxide materials were prepared at Sandia using a proprietary non-aqueous precipitation technique. Ti^{4+} and Nb^{5+} doped spinels exhibit significant unit cell expansion (and energy destabilization), while Al^{3+} and Co^{2+} doped compounds exhibit only slight unit cell contraction. Cathode performance will be intimately linked to lattice expansion and contraction upon lithiation and delithiation of the spinel. Molecular dynamics simulations are being used to compare the relative diffusion rates of lithium ions in these various structures. We are also measuring kinetic parameters in these materials by electrochemical impedance spectroscopy (EIS). A single EIS experiment can provide information on both electron transfer and diffusion limited reactions. Smaller diffusion constants are observed for doped materials with contracted unit cells.

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

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Department of Chemistry

136. ***Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion***
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The primary objective of the research is to gain fundamental understanding of the factors governing the efficiency of charge transfer and energy transfer processes in molecular systems of relevance to photochemical energy conversion. The major focus of the current investigation is the excited-state interaction between two aromatic chromophores that are brought together in close proximity by a short covalent linkage or by ground-state van der Waals (vdW) association. Aromatic-aromatic interactions involving the strong charge transfer forces and those involving the weaker vdW forces are investigated for covalently bonded diaryl compounds and vdW molecules using laser spectroscopy in supersonic free jets as well as in solution. Where appropriate, and feasible, quantum chemical methods are also used to gain theoretical understanding of the conformational dependence of charge and energy transfers.

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Department of Chemistry

137. ***Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids***
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The goal of this research is to evaluate the role of polar media in the mechanism of carotenoid radical cation and dication formation and decay and to determine the special properties of carotenoids bound to pigment-protein complexes in photosynthetic membranes that enable them to serve both as antennae and as photoprotective agents and as a possible component of electron transfer processes. Simultaneous electrochemical and electron spin resonance measurements, simultaneous electrochemical and optical measurements, and simultaneous electrochemical and resonant Raman measurements have been carried out. From these studies, the reason has been deduced for the observation of carotenoid radicals in some photosystems and not others. In the solid state, the energy of the cis isomers falls close enough to that of the all trans isomers that the solid host can stabilize higher energy cis isomers. All trans or cisoidal carotenoid radical cations can exist on solid supports and in solution. Semiempirical molecular orbital (RHF-INDO/SP) calculations of the canthaxanthin cation radical in solution are in excellent agreement with the electron nuclear double resonance measurements. The host matrix is being manipulated in such a manner as to understand the carotenoid function and to ultimately develop predictive mechanisms for directing the outcome of photochemical events.

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Department of Chemistry and Biochemistry

138. ***Supramolecular Structures for Photochemical Energy Conversion***
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Photosynthetic solar energy conversion is the ultimate energy source for essentially all life and is one of the most durable and efficient solar conversion “technologies.” The goal of this project is to synthesize artificial photosynthetic reaction centers that employ the basic chemistry and physics of photosynthesis to help meet energy needs. Specifically, the research involves the preparation and study of photochemically active multicomponent molecules that functionally mimic photosynthetic light harvesting, photoprotection from light-initiated singlet oxygen damage, and, most importantly, photoinduced multistep electron transfer to generate long-lived charge-separated states with a quantum yield close to unity. One current project involves the preparation of molecular triads and tetrads featuring new linkages between the donor and acceptor moieties that lead to ultrafast electron transfer both in fluid solution and in glassy solids at low temperature. Another investigation deals with new methods for the stabilization of charge separation through intramolecular proton transfer. Recently, we have expanded our mimicry of photosynthetic processes to include the conversion of intramolecular redox potential to chemical energy manifest as a proton potential gradient across a bilayer lipid membrane. This has been accomplished by the assembly of molecular triad-based artificial reaction centers and collateral quinones into a liposome-based model system that uses light energy to translocate protons across the bilayer. Upon excitation, electron transfer processes in the triad generate reduction potential near the outer surface of the bilayer and oxidation potential near the inner surface. In response to this vectorial redox potential gradient, a freely-diffusing quinone alternates between its oxidized and semiquinone forms to transport protons across the bilayer. These experiments demonstrate the conversion of light energy to transmembrane proton motive force in a purely synthetic, biomimetic system.

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Department of Chemistry

139. Photoinduced Electron Transfer in Ordered Macromolecular Assemblies
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Investigations involve the design and characterization of systems capable of photochemical charge separation involving electron donor and acceptor groups that are bound to polymer or biopolymer chains. Objectives of the research include the observation of the effects of polymer, peptide, or protein microenvironments on the efficiency and rate of electron transfer between groups that are separated by distances that can be controlled within a macromolecular domain. For these systems the (bio)polymer acts as a template or scaffolding for assembly of chromophores and photoactive species. Of special interest are systems capable of photoinduced electron transfer among groups covalently bound to peptide chains or within the domain of a peptide [alpha] helix. For use in these polymer-based arrays, a family of new chromophores based on the acridinium ion has been synthesized. On photoexcitation these structures engage in intramolecular charge separation within picoseconds of an excitation pulse. Decay of the electron transfer intermediates (the time scale for molecular "switching") is variable over at least four orders of magnitude, reaching the 10-nanosecond time domain. Domain-forming vinyl polymers and glasses are especially effective in extending the lifetime of charge separation. Current work also includes the synthesis of amphipathic helices that will potentially provide protein "bundles" for assembly of synthetic reaction centers. Methods that are employed in these investigations include peptide synthesis, laser flash photolysis and fast kinetics, fluorescence probes, circular dichroism, and molecular modeling. In these studies, emphasis is placed on the opportunities for construction of highly functionalized synthetic polymer materials in which reactive groups are held in relatively rigid arrays that provide controls at the molecular level of charge separation and photochemical energy storage. The work is important to the understanding of charge transport in both natural and biomimetic systems and the development of energy conversion devices based on reversible electron transfer.

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Department of Chemistry

140. Mechanistic Studies of Excited State Chemical Reactions
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Excited state redox reactions in homogeneous solution are being studied to test basic mechanisms of endergonic electron transfer processes and to optimize the factors governing rates and radical yields. The efficiency of primary energy conversion in such reactions depends on the avoidance of dissipative channels and on the difference in redox potential between ground and excited states. Both these factors may be profoundly modified by coupling proton and electron transfer, as in many biological redox systems. Such coupling may be structurally imposed by hydrogen-bonding electron donors or acceptors respectively to proton acceptors or donors. Thus, phenols H-bonded to pyridines become stronger reductants, and quinones H-bonded to alcohols become stronger oxidants. These specifically structured redox systems, properly related to the excited substrate, then permit increased control of both the dynamics and thermodynamics of the reaction, to favor efficient product formation. Our current program is now mainly concerned with the basic aspects of these effects. Voltammetric studies on ground-state H-bonded pairs as well as effects of deuteration and solvent variation are used to help interpret photochemical kinetic data in terms of coupled electron-proton mechanisms. Useful substrates are fullerenes and porphyrins, which provide a wide range of base strength and redox potential. Fundamental questions of detailed dynamics and relative phasing of electron and proton displacement are being approached in collaborative picosecond studies.

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Department of Chemistry

141. Interfacial Electron Transfer Kinetics at III-V Semiconductor Liquid Interfaces
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Semiconductor-based photoelectrochemical cells yield stable, efficient current-voltage properties at a considerably lower cost than solid-state devices. However, relatively little is known concerning the kinetics of charge transfer at semiconductor/liquid interfaces. In order to improve photoelectrochemical cells for solar energy conversion, a detailed understanding of such charge-transfer processes is necessary. Indium phosphide is an ideal candidate for such studies, because it has an optimal bandgap for solar energy applications and affords well-behaved current-voltage characteristics in non-aqueous solvents.

Charge-transfer rate constants have been measured for several n-InP/electrolyte systems exhibiting exchange currents dominated by electron transfer across the semiconductor/liquid interface and having energetics near optimal exoergicity. The experimentally determined rate constants ranged from 10^{-17} cm^4s^{-1} - 10^{16} cm^4s^{-1}, in close agreement with the theoretically expected maximum charge-transfer rate constant determined from a modification of Marcus' model for charge transfer at liquid-liquid interfaces. In addition, digital simulations are being performed to ascertain the excitation intensity and applied bias that would allow simultaneous determination of the surface recombination velocity and charge-transfer rate constant from experimental time-resolved photoluminescence decay spectra of n-InP photoelectrodes. Efforts have also been directed at obtaining charge-transfer rate constants for gallium phosphide electrodes in the presence of a homologous series of redox couples. With a bandgap considerably larger than the reorganization energy of most redox species, GaP should allow measurement of charge-transfer rate constants in the Marcus inverted region, in which the rate constant becomes inversely proportional to the driving force for charge transfer.

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Department of Chemistry

142. ***Theoretical Studies of Electron Transfer in the Photosynthetic Reaction Center***
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The structure, dynamics, and free energies pertaining to electron-transfer in complex systems are analyzed through large-scale numerical simulations and through analytical methods. The research on electron transfer is concerned with (1) the mechanisms of charge transfer in complex systems that include self-assembled structures; (2) derivation of analytical theories of electrostatics and solvation, tested by numerical simulation and used to explain measured free energetics for electron-transfer reactions; and (3) derivation of simplified quantum dynamical theories for electron transfer processes. These dynamical theories are done in concert with computer simulation studies and are used to interpret experimental observations and to suggest new experimental work.

143. ***Femtosecond Photoinduced Dynamics in Transition Metal Complexes: Probing the Elementary Processes of Excited-State Relaxation***
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This research involves the application of femtosecond time-resolved spectroscopy for studying the photoinduced dynamics of transition metal complexes. The overall goals are to understand at a fundamental level the nature of excited-state relaxation and energy and electron redistribution immediately following photon absorption but prior to excited-state thermalization. Tailored chemical synthesis is being coupled to these ultrafast studies in order to systematically examine the roles of electronic and geometric structure as well as solvation in influencing excited-state evolution. Preliminary results have revealed dynamics which are inconsistent with widely accepted models of excited-state behavior, suggesting that significant conceptual advances for understanding the photoinduced properties of molecular systems are possible.

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144. ***Energy and Charge Transfer Processes at Nanocrystalline Silicon Interfaces***
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This research concerns energy transfer quenching of nanocrystalline Si photoluminescence (PL) with solutions of organic aromatic molecules. Steady-state and time-resolved photoluminescence quenching by a series of substituted fused aromatic molecules have been measured as a function of Si nanocrystallite size by preparing porous Si samples with a range of emission spectral maxima. The effects of molecular triplet energy, molecular size, and the porous Si emission energy on PL quenching efficiency were probed. The quenching of PL adequately fits a dynamic Stern-Volmer quenching model. The rate of quenching increases with increasing exoergicity, and then levels off at higher exoergicities. The mechanism of quenching is attributed to highly nonadiabatic energy transfer from the porous Si excited state to the triplet levels of the quencher molecules. Reactions have also been investigated that involve the native hydride species on the porous silicon surface. Nonaqueous solutions of benzoquinone were found to react with the hydride-terminated surface of luminescent porous Si to generate a surface-bound para-hydroxylphenoxy (hydroquinone) species.

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Department of Chemistry

145. ***Exploring Energetics of Photoinduced Electron Transfer in Integral Membrane Proteins***
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The goal of this work is to understand better the primary events of photosynthesis for practical implementation. The three dimensional organization of the light-harvesting complexes (LHCs) and the photosynthetic reaction center (RC) of photosynthetic bacteria results in the assembly of an unusually symmetric array of bacteriochlorophyll (Bchl) molecules. The LHCs transfer incident light energy into the RC where conversion of energy into chemical potential occurs. In order to manipulate energy transfer and storage, a new genetic expression system has been developed in Rhodopseudomonas viridis. By using a special strain of viridis capable of producing the photosynthetic apparatus in the dark, large quantities of modified photosynthetic proteins of viridis are possible for the first time. Since the RC of Rhodopseudomonas viridis contains a bound cytochrome, a completely new set of electron transfer processes is now available for practical exploitation by site directed mutagenesis. The core light-harvesting complex (LH-I) of Rhodobacter sphaeroides yields stable Bchl radical cations, Bchl+, upon “forced” chemical oxidation. At room temperature, the LH-I exhibits an unusually narrow EPR linewidth. At 4.2 K the LH-I EPR linewidth broadens and becomes identical to that of the oxidized photosynthetic reaction center. This change in linewidth as a function of temperature is indicative of the electron transfer between the light harvesting Bchl molecules. Interestingly, this “forced” electron transfer within the light-harvesting antenna resembles processes in artificial photosynthesis and is quite different from the primary electron transfer on natural photosynthesis.

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Department of Chemistry

146. *Studies of Intramolecular Photoinduced Charge Separation and Donor-Acceptor Interactions in Transition-Metal-Based Molecular Assemblies*

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The primary goals of this research are to design, synthesize, and study the electron transfer and charge separation processes in transition metal-based molecular assemblies. The chemical systems under study are of two general types: ones which consist of a light-harvesting chromophore linked by conformationally flexible linkages to organic donor or acceptor moieties, and ones which consist of a metal-complex chromophore rigidly linked to a second metal complex which acts as the donor/acceptor. The two types of systems have been designed to probe different aspects of light-induced electron and energy transfer reactions. Through studies of these flexible systems, knowledge can be gained that will be of value in the design of practical solar conversion devices. Moreover, because they are conformationally flexible, the intramolecular motions in these assemblies can be exploited to separate charge and store energy. The rigidly linked metal complexes, which have well-defined structures, are excellent systems for studying the fundamental process of electron transfer. For example, these rigid systems have allowed for the first detailed studies which compare light-induced and thermal intramolecular electron transfer reactions for a single system.

147. *Electron Transfer Dynamics at Semiconductor Nanocluster Interfaces*

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This research program deals with the synthesis, characterization, and electron/hole dynamics in semiconductor nanoclusters. Specifically, the research focuses on electron transfer across the nanocluster/solution and nanocluster/solid interfaces. These electron transfer reactions are of importance in the development of photocatalysts. Most studies involve layered-metal chalcogenide semiconductors, such as MoS_2, WSe_2, PtS_2, etc. The interest in these systems is due to their great photostability. Dyes, electron donors and electron acceptors have been adsorbed on the nanocluster surfaces and the interfacial electron transfer rates measured by time-resolved optical spectroscopy. The dependence of these rates on the energetics, solvent polarity, and nature of the nanocluster trap states may be understood in terms of modern theories of electron transfer. Most of the research thus far has been on MoS_2 nanoclusters with adsorbed electron acceptors. These MoS_2 nanoclusters consist of a single S-Mo-S trilayer with diameters of 2.5-4.5 nm. Variation of the nanocluster size changes the extent of quantum confinement of the electron/hole pair, and thus the electron transfer energetics. The electron acceptors are substituted 2,2'-bipyridines, and the nature of substituents affects their reduction potentials. By varying the size of the nanocluster and the substituents on the electron acceptor, a wide range of electron transfer driving forces may be obtained. Marcus “normal” and “inverted” behavior of the electron transfer rates have been obtained. Further studies will include examining solvent effects and other electron transfer reactions.

148. *Studies of High Quantum Yield Sensitization Processes at Semiconductor Electrodes*

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Dye sensitization has the potential to increase the light utilization of large band gap semiconductors. The excited state of a dye molecule adsorbed onto the surface of the semiconductor electrode can inject electrons into the conduction band of an n-type semiconductor. These electrons can then be detected as energies less than the band gap of the semiconductor. The quantum yield for electrons collected per photon absorbed by the dye at single crystal oxide electrodes was always less than a few percent. The quantum yield per absorbed photon can approach 100% when two dimensional chalcogenides are used as photoelectrodes. Recently methods for increasing the surface area of SnS_2 photoelectrodes have been developed. By photoelectrochemically etching the surface in either acid or basic solutions, increases in the quantum yield for electron flow per incident photon have been obtained. The adsorption isotherm for methylene blue on etched and unetched surfaces has the same shape but shows an increase of 20 times more in the quantum yield. An in situ scanning tunneling microscopy (STM) method is being developed for detecting the position and energy levels of dye molecules adsorbed on these surfaces with molecular resolution. This is accomplished by modulating a light source at the wavelength of the dye absorption maximum and extracting the photoinduced contribution to the tunneling current via a lock-in amplifier. A simultaneous picture of photocurrent response and topography can then be obtained. Questions such as the state of dye aggregation on the surface and whether dye molecules are adsorbed on special sites could then be answered. The photo-STM technique has already been applied to semiconductor surfaces with bandgap light. Methods to produce organized layers of dye molecules on these surfaces are also being developed. Two dimensional layers of perylene dyes have been formed and imaged with the STM. Squarilium dyes have also been imaged in two dimensional molecular arrays. Sensitization of TiO_2 nanocrystalline films is being investigated. The influence of the morphology of the film is being studied by using template synthesis to pattern the nanocrystalline films.

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Department of Chemistry and Biochemistry

149. Charge Transfer Reactions at Semiconductor-Liquid and Liquid-Liquid Interfaces
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The goal of this research is understanding how solar energy can be utilized in photoelectrochemical cells (PECs) and facilitated transport membranes. Reactions of “hot” electrons that are created by light absorption in a semiconductor electrode have the potential to increase the energy conversion efficiency or to alter the product distribution in PECs. Current investigations involve studying the photoreduction of organobromide compounds in the presence of oxidized metallocenes. Rotating ring disk electrochemical methods are used to determine the products of the photoreduction reactions. These data can be used to infer relative rate constants for thermalized and “hot” electron reactions. The materials being investigated include p-InP and p-GaAs capped with $GaInP_2$. Photochemistry in membranes can allow chemical species to be transported against their concentration gradients. In principle, this process can be used in a variety of contexts ranging from environmental restoration to energy storage. Membranes that contain photochemically active carriers are prepared and characterized. Illumination of these membranes allows ions or molecules to be selectively separated and concentrated. A mathematical model based on molecular parameters (reaction rates, excited state lifetimes, diffusion coefficients, etc.) that describes this type of membrane process has been developed. This model will be used to guide subsequent experiments aimed at improving the selectivity, productivity and photoefficiency of photochemically controlled membrane transport.

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Department of Chemistry

150. Charge Generation and Separation at Liquid Interfaces
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We are currently using surface second harmonic (SHG) and sum frequency generation (SFG) detected femtosecond pump-probe experiments to monitor the electronic and orientational dynamics of solute molecules at air-liquid and liquid-liquid interfaces. Since a solute at the interface is in an environment different from either bulk, these dynamics can be different than in either solvent alone. We are pursuing SFG detected pump-probe experiments to monitor intramolecular photo-induced electron transfer at and across these interfaces. We have further developed the study micron sized particles in liquid suspension using SHG. While SHG is forbidden in bulk centrosymmetric media, the particle/liquid interface breaks the symmetry on a scale equal to the wavelength of light. This discovery has made SHG a powerful spectroscopic method for in situ investigation of the physical and chemical properties of polymer microspheres, emulsions, vesicles, semiconductor particles, and clay particles. We have demonstrated that SHG provides a new method for determining the interface electrostatic potential of charged microparticles. For example, the charged sulfate groups at the surface of 1 micron PSS microspheres polarize and orient bulk water molecules, which changes the SHG signal. The dependence of the SHG on electrolyte concentration gives an excellent fit to the Gouy-Chapman model of the interface electrostatic potential.

151. Theoretical Studies of Photoactive Systems: Electron Transfer, Energy Transport, and Optical Spectroscopy
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This project involves development of new theoretical methods for studying electron transfer and optical spectroscopy with particular applications to small semiconductor particles and long range electron transfer through intervening media. For semiconductor particles, an empirical pseudopotential model has been developed that predicts bandgaps to ~0.1eV as a function of particle size for a significant number of semiconductors, e.g., CdS, CdSe, Si, and GaP. For electron transfer, a Redfield relaxation model capable of treating multilevel electronic systems with intervening bridges has been developed, with an initial application to long distance electron transfer through a molecular bridge. A novel mechanism, virtually independent of distance, was obtained and possible relevance to electron transfer through a DNA bridge was discussed. Finally, ab initio electronic structure methods have been applied to the computation of electron transfer matrix elements. Using novel numerical methods, large systems are tractable (for example, two bacteriochlorophyll molecules) in modest CPU times on a single workstation, at the Hartree-Fock level. This approach will be applied to a variety of systems relevant to the DOE solar photochemistry program, such as molecule/solid electron transfer and transfer through various complex molecules. Future work will also include using ab initio methods to determine structures and electronic states at the surface of semiconductor particles.

152. Photo-CIDNP of Photosynthetic Reaction Centers
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Chemically Induced Dynamic Nuclear Polarization (CIDNP) is used to observe the nuclear magnetic resonance (NMR) spectra of ^{15}N-labeled photosynthetic reaction centers. In spectra collected during magic-angle spinning, nuclear polarization has been detected for the nitrogens in the tetrapyrroles of the bacteriochlorophyll special pair (“P’’), associated imidazoles, and the primary acceptor pheophytin (“I’’) that are far from Bolzmann equilibrium. The resulting NMR lines are emissive and 300 times the intensity of the thermally relaxed nuclei. The polarization is not observed if the quinones are present and preoxidized. The signals presumably result from a transient nonequilibrium mixing of the singlet and triplet states of the initially formed charge transfer pair, P^+I^-. Selectively labelled samples are used to assign the signals. Polarization is also observed for plant centers and for ^{13}C. We have determined that the mechanism by which polarization is developed is the radical pair mechanism, and have developed a simulation routine for the intensities of signals which gives good agreement with a broad collection of experimental data. Ongoing efforts are aimed at identifying lines associated with the monomeric bacteriochlorophyll.

Department of Electrical Engineering

153. Translational-Energy-Resolved Studies of Photogenerated Carrier-Induced Reactions on UHV Semiconductor Surfaces
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Recent work has been centered on experimental studies of the UV photodissociation of alkyl halides (R-X, with R = methyl, ethyl and propyl and X = Cl, Br, and I) on single crystal surfaces of GaAs (110) held under ultrahigh vacuum conditions. Angle-resolved photofragment time-of-flight (TOF) distributions and temperature programmed desorption (TPD) have been the primary tools used to elucidate the dynamics of the photofragmentation process and the post-irradiation chemistry of products trapped on the surface. Photofragmentation of methyl halide molecules, adsorbed at monolayer coverage on the surface, is found to occur through the dissociative electron attachment (DEA) of sub-vacuum level electrons created by substrate absorption. Angular distributions of methyl fragments ejected via this process are also found to be highly anisotropic with respect to the surface normal. This has been taken to reflect a tilted surface orientation of the CH_3-X bond in the adsorbed molecule; a result that is consistent with ab initio calculations and polarization dependent NEXAFS studies. More recently, detailed studies of the photodissociation of ethyl and n-propyl bromides on the GaAs (110) surface have revealed surprising differences in the dynamics of the ejected alkyl photofragments. Again, a surface mediated DEA process appears to be responsible for the rupture of the R-X bond, which, from the measured angular distribution of ejected fragments, is also tilted with respect to the surface normal. In contrast to the methyl bromide system, three dynamically distinct channels appear to be possible for the larger alkyl fragments generated by the DEA process. While some fragments appear to be directly ejected with high kinetic energies (similar to the methyl case), other fragments are ejected with distinctly lower energies and other fragments are trapped and become adsorbed on the surface. The low-energy fragments are also found to have an isotropic angular distribution, symmetric with respect to the surface normal (e.g., the isotropic ethyl fragment angular distribution varies as the cosine squared of the polar angle). This type of dynamical behavior evokes the direct and trapping-desorption channels sometimes observed in molecular beam scattering from surfaces. Measured angular and energy distributions are consistent with a model where the departing fragments experience a potential barrier exhibiting normal energy scaling. Gas phase measurements for the photofragmentation of the same alkyl halides show that less of the total available energy winds up in fragment translation as the size of the alkyl group is increased. A lowering of the nascent average velocity of ethyl and propyl fragments could explain why the slow and trapping channels emerge as the alkyl group size is increased. The trapping channel also provides a source of adsorbed ethyl and propyl fragments; the thermal chemistry of these fragments has been investigated using TPD. Further studies of the photodynamics of the alkyl halides has begun on the GaAs (100) surface. This surface can be prepared as a Ga-rich or As-rich surface with several reconstructions; we hope to assess the effect of surface binding sites and topography on the dynamics and post-irradiation chemistry.

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Department of Chemistry

154. Photoinduced Dipoles and Charge Pairs in Condensed Media
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The objective of this project is to understand photoinduced charge separation in liquids and solids composed of organic molecules. Fast displacement current measurements are used to follow the separation dynamics of photoinduced charged and dipolar species. The dipole moment technique has proved useful in the study of both intramolecular and intermolecular charge transfer. Current investigations include the solvent polarity dependence of intramolecular dipoles, exciplexes, contact and solvent-separated ion pairs. The excitation in the charge transfer band of the trans-stilbene/ fumaronitrile complex leads to unexpectedly large free ion yields corresponding to 1-1.5 nm of separation in initial thermalized ion pairs. Mechanistic aspects of exciplex association and dissociation and the degree of charge transfer in various exciplexes are being studied.

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School of Chemistry and Biochemistry

155. ***Time-Resolved Laser Studies of the Proton Pump Mechanism of Bacteriorhodopsin***

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There are two basic systems in nature that convert solar into chemical energy, chlorophyll-based system present in green plants and bacteriorhodopsin (bR) present in Halobacterium Salinarium. In both, solar energy is first converted into electric energy and then into chemical energy. The final step in the solar to electric energy conversion involves the formation of proton gradients. In chlorophyll, this involves electron pumps while in bR this involves proton pumps. The absorption of light by retinal in bR leads to very rapid (450 femtosecond) and specific (around C_{13}-C_{14} bond) isomerization. This leads to the separation of positive and negative charges, protein conformation changes, and finally to the pumping of protons from inside the cell to the membrane surface. This pump requires metal cations for its function. Our present research is focused on trying to answer two fundamental questions regarding the mechanisms of the conversion of solar to electric energy: (1) What are the molecular mechanisms by which the protein catalyzes the retinal photoisomerization and (2) What role do metal cations play in the proton pump? For the former research, femtosecond spectroscopy is used to study the structural changes of the retinal and its environment during the photoisomerization process. This study is carried out for bR and its mutants under different pH, ionic strength, and temperature conditions. In order to understand the function of the metal cations, their location in the protein needs to be elucidated. For this, binding, spectroscopic, and diffraction studies are being carried out in our laboratories as well as in collaboration with laboratories worldwide.

University of Houston Houston, TX, 77204

Department of Chemistry

156. ***Photoinduced Charge Separation in Microheterogeneous Media***

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This research focuses on molecular photoionization as well as photoinduced charge separation in colloidal titanium oxide particles in newly developed MCM-41 silica tube mesoporous materials, in aluminophosphate (AlPO-n) micro-porous materials, and in layered zirconium phosphate materials. In the MCM-41 and AlPO materials a transition metal ion electron acceptor center is built into the oxide framework. Encapsulated molecular electron acceptors with macrocyclic ligands will also be utilized. These novel systems give rise to quite long-lived photoinduced charge separation at room temperature. The photooxidized paramagnetic centers are used as probes to study their local environment in these systems by electron spin resonance and pulsed electron spin resonance. To assess and control the photoyield efficiencies, the interaction of the photoproduced centers with the internal walls of the silica tube materials will be deduced by electron spin echo spectrometry, in which weak nuclear modulation of magnetic nuclei in the walls is detected. The variable dimensions of the mesoporous MCM-41 silica tube materials, the microporous aluminophosphate materials, and the layered zirconium phosphate materials offer control for optimally locating the photoionizable molecules to enhance charge separation.

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Department of Chemistry

157. ***Electron Transfer Dynamics in Efficient Molecular Solar Cells***

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Regenerative solar cells based on dye sensitization of wide band gap semiconductors have recently experienced an order of magnitude increase in light-to-electrical energy conversion. Results in this laboratory and others have shown high efficiency and excellent stability, indicating an economically competitive approach to solar energy conversion. This remarkable breakthrough marks the first time that devices that operate on a molecular level are competitive with traditional solid state photovoltaics. The ability to control the fate of molecular excited states at semiconductor surfaces is key to improving solar cell performance. Recently, studies aimed toward this goal were initiated. Ruthenium and osmium polypyridyl compounds have been anchored to mesoporous nanocrystalline anatase films for light-to-electrical energy conversion. The osmium sensitizer displays less than half the photocurrent efficiency of the corresponding Ru(II)- based sensitizer. Spectroscopic studies indicate that the lower photocurrent efficiency is due to a more sluggish iodide oxidation rate. For surfaces that contain both Ru(II) and Os(II) sensitizers, energy transfer across the nanocrystalline semiconductor surface from Ru(II)* to Os(II) is observed under conditions where the Fermi energy is shifted toward the vacuum level. Shifting the Fermi level positive, with applied potential or electrolyte modification, results in efficient electron injection from both surface anchored sensitizers. The process is reversible and forms the basis for a charge-energy transfer switch. The results indicate that arrays of Ru(II) and Os(II) sensitizers can be used for efficient light-to-electrical energy conversion.

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Chemistry Department

158. ***Organized Photochemical Assemblies Based on Y-Zeolite Supports***

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The goals of this project involve the synthesis and photophysical characterization of zeolite-entrapped complexes of divalent ruthenium and functional molecular photoredox assemblies based on these sensitizers. Previously developed synthetic methods suitable for the preparation of adjacent-cage dyads, wherein two complexes are strongly coupled with respect to energy and electron transfer interactions, are being exploited to produce a number of structurally diverse assemblies. Recent work has been devoted to systems composed of bipyridine and bipyrazine complexes, while interest currently has shifted to complexes involving terpyridine and dipyridylpyrazine. Preliminary work has been initiated which suggests that transition metal complexes of the tetrapyrrole macrocycle, porphyrazine, can be constructed inside the supercages of Y-zeolite by the so-called “ship-in-the-bottle” approach, using dicyanopyridine as the monomeric precursor. Such complexes may serve as relatively low energy photosensitizers, which are also suitable as templates for construction of functional organized assemblies.

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Department of Chemistry

159. ***Magnetic Resonance Studies of Photoinduced Electron Transfer Reactions***

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Excited state electron transfer plays a central role in many photochemical reactions, including those that may find use in the conversion of solar energy. This project is concerned with the application of time-resolved Electron Paramagnetic Resonance (TREPR) in the study of photoinduced electron transfer reactions. With EPR, paramagnetic molecules can be identified, and their formation and decay can be monitored. TREPR spectra also give information on the spatial distribution of paramagnetic molecules in heterogeneous media. Research focuses on photoionization reactions in micellar solutions and subsequent capture of hydrated electrons (e_{sol}^-) by acceptor molecules. Of interest are: (1) the spin polarization with which the solvated electrons are born since this provides mechanistic information, and (2) the effect of the spatial distribution of donors and acceptors on efficiency of e_{sol}^- generation and rate of subsequent e_{sol}^- capture. The project is also concerned with photoinduced electron transfer at the surface of semiconductor particles. A TREPR study was made of the photoreduction of methylviologen (MV^{2+}) in a colloidal suspension of TiO_2. Also investigated was MV^{2+} reduction by TiO_2 using dye sensitization. There is a pronounced change in MV^+ formation kinetics upon going from the TiO_2 system to the TiO_2/dye system. Apparently, coverage of the particle surface by dye molecules can strongly inhibit electron transfer across the particle-solution interface.

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Department of Chemistry

160. ***Femtosecond Time-Resolved Experiments on the Solvated Electron and Intermolecular Charge Transfer in Solution***

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The photophysical properties of the solvated electron have been studied using a unique 25 fs transient absorption spectrometer. The technique involves three separate laser pulses. The first pulse generates solvated electrons, the second pulse excites the electron from the ground state to the first excited state, and the third pulse probes the dynamics of the ground state repopulation and the ground and excited state relaxation. The experimental data has resolved for the first time the

<300 fs dynamics of this key prototype for quantum dynamics in solution. These data allow for a rigorous experimental evaluation of recently published nonadiabatic quantum molecular dynamics simulations of the photophysics of the hydrated electron. The data exhibit a previously unresolved ultrafast components that are well-modeled by a combination of Gaussian (50-70 fs) and exponential (200 fs) decays which are both assigned to adiabatic solvation dynamics. The solvation dynamics are ~15% slower in D_2O.

161. The Photophysical Properties of Organic Liquids at High Excitation Energies

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Previous studies of the absolute efficiency of electronic energy transfer from cis-decalin excited at 161 nm to 2,5 -diphenyloxazole (PPO) have shown the existence of two intermediate states. At concentrations above ca. 0.001M, the normal fluorescing state of cis-decalin plays the dominant role in the transport mechanism, but at lower concentrations, another state, which is non-fluorescing, becomes more important. This other, so-called dark state, although produced in low yield (ca. 4%), is so much more efficient in transporting its energy to the PPO that at the lowest concentration thus far studied of 0.00001M, it has become about 60x more important than the fluorescing state and exhibits a transport efficiency (per dark state produced) of 0.03. This study is now continuing with measurements involving both other hydrocarbons as donors (e.g., benzene, p-xylene, cyclohexane, hexadecane, and squalane) and other acceptors (e.g., p-xylene and fluorene). Evidence for the dark state has appeared in all systems involving a saturated hydrocarbon as donor, whereas for aromatic donors, only the fluorescing state plays any role even at the lowest concentrations studied. The nature of the dark state in the saturated donor systems and the reason for its absence in the aromatic donor systems remains a mystery. In a separate study, the general theory of the hyperfine-driven spin evolution of a geminate pair of ions diffusively recombining has been found to predict the shapes and positions of observed resonances in the effect of a magnetic field on the quantum yield of geminate recombination fluorescence. Studies of these resonances began with observations on the recombination of isooctane cations with hexafluorobenzene anions generated by photoionization of the isooctane at 124 nm and is continuing with studies of anthracene cations (photoionized at 180 nm) recombining with either hexafluorobenzene or perfluorocyclobutane anions. Using a sensitive modulation technique, the shapes of some of the weaker resonances and the influence thereon of fluorocarbon concentration is being examined. Determination of the magnetic fields at which the resonances occur provides a simple technique for the determination of hyperfine constants of short-lived anions.

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Physical and Chemical Properties Division

162. Electron Transfer Reactions of Metalloporphyrins

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The pulse radiolysis technique is applied to the study of electron transfer processes involving metalloporphyrins. Reactive intermediates are produced in solution by electron pulse irradiation and the kinetics of their reactions are followed by time-resolved absorption spectrophotometry. Supportive product analyses are done with various techniques following γ-radiolysis or photolysis. The studies focus on the unique ability of pulse radiolysis to provide absolute rate constants for many fast reactions of metalloporphyrins, which permits evaluation of these strongly light absorbing molecules as sensitizers and intermediates in solar energy conversion. Metalloporphyrins react with free radicals via electron transfer, involving the ligand or the metal center, or via bonding to the metal, leading to a variety of chemical species whose behavior is also investigated. An important potential application of metalloporphyrins is as catalysts for reduction and binding of carbon dioxide. Several iron and cobalt porphyrins are shown to act as homogeneous catalysts for reduction of CO_2 to CO. The species involved in binding and reduction of CO_2 are investigated.

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Department of Chemistry

163. Biomimetic Porphyrin Light Harvesting Arrays

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A molecular building block approach is being used to prepare synthetic light-harvesting systems. In many studies in artificial photosynthesis, zinc porphyrins have been used as surrogates for magnesium porphyrins due to the greater ease of synthesis of the former. A new synthetic method provides facile access to the latter. The energy transfer dynamics of a ZnFb-porphyrin dimer has been compared to a MgFb-dimer (Fb = free base). The rate of energy transfer lifetime is essentially the same in each (25 ps), as is the extent of electronic communication. Similar rates were observed in star-shaped Zn_4Fb- or Mg_4Fb-pentamers. However, the longer inherent lifetime of the Mg- vs. Zn-porphyrin (9 vs. 2.2 ns) results in an increased yield of energy transfer (99.7% vs. 99.0%) in the MgFb-dimer or Mg_4Fb-pentamer. The longer lifetime with Mg compared with Zn stems from the lesser heavy atom effect and the commensurate decrease in competition from intersystem crossing. This work indicates that Mg-porphyrins have superior properties for light harvesting applications where a series of energy transfer steps occurs. These studies have been done in collaboration with Prof. David Bocian (UC-Riverside) and Prof. Dewey Holten (Washington U).

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Chemistry Department

164. Excited State Processes in Transition Metal Complexes. Redox Splitting in Soluble Polymers

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Polypyridyl complexes of Ru(II), Os(II), and Re(I) are being investigated for applications in photochemical energy conversion. They are stable, have well understood light absorption and excited state properties, and undergo facile electron and energy transfer. The background synthetic chemistry is being extended toward a number of targets including a family of black absorbers and near Infrared emitters. Transient vibrational spectroscopy, IR, and resonance Raman are being applied to the elucidation of excited state molecular and electronic structure. Synthetic procedures have also been developed for adding these polypyridyl complexes to soluble polymers, and for assembling the polymers on conducting substrates in device configurations. Photophysical studies on the resulting materials have demonstrated photoinduced electron or energy transfer on single polymeric strands. This has led to the design of efficient “antenna” polymers for collecting and storing visible light.

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Department of Chemistry

165. Dynamic Structural Studies of Light-Induced Charge Transfer in Strongly Interacting Systems

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This project involves (1) time-dependent scattering studies of vibrational structural changes accompanying chemically important photoredox processes; (2) collaborative studies of femtosecond charge-transfer kinetics in fully vibrationally characterized systems; (3) electronic Stark effect studies and resonant hyper-Rayleigh scattering studies of one-electron transfer distances and charge-transfer symmetry phenomena; (4) vibrationally resolved optical electron transfer studies; and 5) transient DC conductivity studies of photoinduced torsional coupling, transient delocalization, and enhanced charge separation efficiency. The objectives are to understand the fundamentals of light-induced electron transfer kinetics and dynamics in a way that will ultimately facilitate the broader design of molecule-based solar energy conversion systems.

166. Light-Driven Charge Separation in Face-to-Face Donor-Spacer-Acceptor Supramolecular Systems

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The objective of this project is to investigate the kinetics of charge separation and recombination in donor-spacer-acceptor systems of well-defined geometry in which the spacer is an aromatic molecule or an array of aromatic molecules. The unique feature of these systems is the location of the donor and acceptor on opposite faces of the aromatic spacer(s). The shortest distance for electron transfer in these molecules is through the aromatic spacer rather than the sigma-bonded framework connecting the donor and acceptor. Base pairing in duplex DNA provides a well-defined geometry in which the aromatic bases are held in a parallel stack. The distance dependence of photoinduced electron transfer in duplex DNA has been determined for a family of synthetic DNA hairpins in which a stilbene dicarboxamide forms a bridge connecting two oligonucleotide arms. Investigation of the fluorescence and transient absorption spectra of the stilbene chromophore in these hairpins establishes that no photoinduced electron transfer occurs for a hairpin which possesses six dA-dT base pairs. However, introduction of a single dG-dC base pair results in distance-dependent fluorescence quenching and the formation of the stilbene anion radical. Kinetic analysis suggests that duplex DNA is somewhat more effective than proteins as a medium for electron transfer, but does not function as a molecular wire.

167. Vibrational Dynamics in Photoinduced Electron Transfer

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Theory and experiment suggest that molecular vibrations and distortions are important controlling elements for electron transfer. The objectives of the project are to develop a new molecular understanding of electron transfer processes. The unique method of picosecond infrared absorption spectroscopy is being used to monitor electron transfer kinetics. The neutral pair created by a pulse of visible light in a charge transfer band has a rate of return electron transfer that is dependent on vibrational quantum number. The vibrational excitation in the ion pair formed after the electron transfer also is observable. An ion pair complex with a cobaltacenium cation and a vandium hexacarbonyl anion is being studied where vibrationally resolved electron transfer rates show a two-fold change in rate for each quantum of vibration in a CO stretching vibration. New molecules and calculations involve the vanadium hexacarbonyl anion and neutral because of its excellent spectroscopic properties. This molecular structure is amenable to detailed modeling so that quantum calculations of molecular structure and vibrations as well as electron transfer models are being developed to understand these results. Additional spectroscopic and kinetic measurements are being done on these and other molecules.

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Department of Chemistry

168. ***Energy and Electron Transfer Properties of Photochemical Assemblies in Zeolites***
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In designing artificial photosynthetic assemblies, the choice of molecules, their spatial arrangement, and their environment is fundamental to the success of the process as evidenced in nature. Zeolitic microporous frameworks are being investigated as a means to spatially arrange molecules for efficient energy and electron transfer processes. Progress in understanding the dynamics of electron transfer from photoexcited $Ru(bpy)_3^{2+}$ to methylviologen in neighboring cages. Using time-resolved diffuse reflectance spectroscopy, the back electron transfer from the reduced viologen radical to $Ru(bpy)_3^{3+}$ was shown to be reduced by three orders of magnitude as compared to the forward electron transfer. This significant lowering of the back electron transfer allows a competitive process of electron hopping between viologen molecules to occur, leading to charge migration away from $Ru(bpy)_3^{3+}$. The decrease in back electron transfer rate arises because the zeolite 7 Å window puts significant constraints on the orientation of the viologen radical, thereby limiting access to the Ru^{3+} t_{2g} orbital, the final destination of the electron. Now the challenge is to efficiently remove the photogenerated electron from the zeolite. The use of nanometer sized crystallites is being investigated for that purpose.

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Department of Chemistry and Biochemistry

169. ***Quinone Binding and Reduction in the Photosynthetic Reaction Center***
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A vast amount of experimental data makes photosynthetic reaction centers (RCs) the paradigm for biological energy transduction. Furthermore, an enormous number of synthetic structures modeling biological electron transfer (ET) incorporate components of the RC, but most models lack the exquisite selectivity and control of ET exhibited by RC proteins. Our work combines quantum chemical and molecular dynamics computations of quinone and semiquinone anion binding to bacterial photosynthetic RCs. Goals are to determine (1) the effect of RC protein modulation upon binding and electrochemistry of quinone electron aceptors; (2) the inhibition of ET through unfavorable thermodynamics and/or kinetics by protein induced effects on quinones; an (3) the thermodynamic and kinetic effect on ET through variance of quinone substituents or amino acid side chains. Insight gained here will pave the way for studies of subsequent quinone reduction steps in photosynthesis and quinone oxidation-reduction chemistry in other energy storage systems modeled upon the photosynthetic RC.

University of Oregon
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Department of Chemistry

170. ***Photochemical Water-Splitting Using Organometallic Oxides as Sensitizers***
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The project objective is to split water photochemically into hydrogen and oxygen using homogeneous organometallic catalysts. The catalysts studied are molybdocene oxide and tantalocene hydrido oxide. In each case, experiments show that the oxygen ligands are photochemically removed from the complexes, followed by oxidative addition of water. The fate of the oxide ligand has been investigated and it was determined that only trace amounts of oxygen formed. Metal oxides form as products in the reactions, and it is suggested that the oxygen reacts with the starting materials to form these oxides. Control experiments showed that the Mo-containing products of the photoreactions were indeed the same as those that form when oxygen reacts with the molybdocene oxide starting material. Attempts to sweep out the oxygen gas product before it could react with the starting material were unsuccessful, however. Following oxidative addition of water, the metal oxide complexes are regenerated, accompanied by the quantitative formation of hydrogen gas. A binuclear Mo complex with bridging oxo ligands was synthesized in order to investigate the possibility that a binuclear species was involved in the photochemical reaction. Irradiation of this complex, however, did not improve the yield of oxygen. Efforts will focus on finding organometallic sensitizers that are less oxygen sensitive and on elucidating the mechanism of the hydrogen producing reactions.

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Department of Chemistry

171. Electron Transfer Reactions in Microporous Solids

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This project uses microporous solids and surface assemblies as organizing media for light-induced electron and energy transfer reactions. The solid acts as “scaffolding” for redox-active and photoactive molecules, and also, in some cases, participates as an active component of the electron or energy transfer cascade. A new technique for exfoliating lamellar solids and restacking them on high surface area substrates is being used to prepare electron and energy transfer assemblies. Individual electroactive and photon harvesting polymer monolayers are separated by nanometer-thick sheets of oxide semiconductors or metal phosphates, and the kinetics of light-induced reactions are studied by flash photolysis techniques. This work is targeted at functional heterostructures, in particular photochemical proton pump and water splitting assemblies. In related work, alkali niobates and titanoniobates, which are wide-bandgap lamellar semiconductors, have been sensitized by ruthenium polypyridyl complexes. When loaded with interlamellar metal catalysts, these materials catalyze the photogeneration of hydrogen from water and non-sacrificial electron donors, such as iodide. Surface modification of these materials with polyelectrolytes increases the efficiency of charge separation and hydrogen evolution, and this strategy is now being applied to improving the efficiency of dye-sensitized titanium dioxide photoelectrochemical cells.

172. Polar Solvation, Dielectric Friction, and Electron Transfer

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This project focuses on understanding how polar solvents influence electron and other charge transfer processes in solution. Towards this end, both ultrafast laser spectroscopy and computer simulation techniques are employed in studies of simple intramolecular charge transfer reactions, as well as simple nonreactive dynamics. Current work has involved studies of (1) the time-dependence of solvation itself, (2) the effects of polar solvation dynamics on rotational motion (“dielectric friction”), and (3) the nature of the solvent effects on a particular class of intramolecular charge transfer reactions known as twisted intramolecular charge transfer, or TICT, reactions.

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Department of Chemistry

173. Evaluation of Electronic Coupling in Photoinduced Electron Transfer Reactions

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The primary objective of this project is to delineate the relative and absolute importance of the factors that determine the dimension of the electronic coupling matrix element (H_{ab}) for photoinduced and thermal charge recombination electron transfer processes. These studies are being carried out with several families of donor-spacer-acceptor (D-Sp-A) complexes that utilize electronically excited porphyrin donors and quinone acceptors. A key feature of this effort lies in the detailed focus on the role played by the tunneling medium in such reactions and the parameters that should affect the dimension of H_{ab} such as absolute donor-acceptor energetics, medium topology, and medium electronic structure. Experimental work in the progress focuses on probing the nature of charge tunneling interference phenomena as well as how medium band energetics, σ-π electronic coupling, π-manifold orientation, and medium excited electronic states establish the magnitude of H_{ab}. The fundamental information obtained in these studies will be useful in directing and controlling the electron and energy transfer processes essential to effective photoconversion. Recent work has utilized metal-mediated cross-coupling to enable the synthesis of conformationally rigid, porphyrin-based, cofacial D-Sp-A compounds. For example, electron transfer systems have been fabricated in which a porphyrin donor and a quinone acceptor are separated only by the sum of their van der Waals radii; these constructions provide the prototypes for a series of molecules designed to probe the nature of electronic coupling modulated through stacked π interactions as well as for new structural motifs designed to test mechanistic apects of ultrafast charge transfer. The unprecedented juxtaposition of porphyrin and quinone in these compounds is manifest in the unusual spectroscopic properties of such species. Similar experimental methodology permits the fabrication of other related complexes which will allow us to probe respectively electronic coupling as function of the spatial relationship of the donor and acceptor aromatic ring centroids as well as begin to address the issue of the distance dependence of photoinduced electron transfer and thermal charge recombination events in optimally stacked π orbital manifolds.

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Department of Chemistry

174. *Experimental Studies of Photoinduced Charge Carrier Processes at Semiconductor/Electrolyte Interfaces*

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This project probes charge relaxation and charge transfer processes at semiconductor-electrolyte interfaces. The formation of self-assembled monolayer films on semiconductor electrodes is used to provide surfaces with well-defined properties that can be controlled and reproducibly prepared. These films are used to study the distance dependence of interfacial electron transfer between aqueous electrolyte solutions and the InP. The electron transfer is monitored using photocurrent measurements. The distance dependence is determined by studying the photocurrent as a function of the length of the methylene chain in the alkanethiols. These investigations have used a freely diffusing redox species [$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$] in aqueous solution. The results show that electron transfer occurs by tunneling through the overlying self-assembled monolayer. The nature of the tunneling is being further explored by extending these studies to systems in which the energy structure of the semiconductor changes, such as Si. More recently, redox active layers have been prepared in order to circumvent some difficulties encountered in the study of insulating barriers and freely diffusing species. Two different types of redox functionality have been used in these latest investigations. First phenyl moieties were attached to the alkane chain and their influence on the surface recombination of charge carriers was observed. Second, ferrocene units were attached to the end of the alkanethiol film. The electron transfer rate between the InP surface and the ferrocene is being studied as a function of the alkyl chain length.

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Department of Chemistry

175. *Photochemistry of Platinum Group Element Complexes: Applications to Energy Conversion and Bond Activation*

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Complexes of platinum(II) and other d^8 metal ions containing diimine and dithiolate ligands are being investigated for their potential use as chromophores in the conversion of light-to-chemical energy. Previous studies of Pt diimine dithiolate complexes have shown that these solution emissive compounds have a directional charge transfer excited state involving a mixed Pt(d)/S(p) orbital as the filled donor function and a π^* orbital of the diimine as the acceptor function. The excited state properties of these complexes including emission energy, lifetime, redox potentials, electron transfer quenching rates and relaxation dynamics can be systematically tuned by ligand variation. Efforts of the past year have focused on the development of a supramolecular photochemical system for light-driven hydrogen generation. Such a system would consist of a platinum diimine dithiolate chromophore, a redox center capable of serving as a reductive quencher and a dark reaction catalyst for charge storage and promotion of the reaction of interest. The components are connected by ligand bridges. The simplest of these bridges is dipyridocatecholate (dpcat) which has been has been used to link two or more metal centers together. The degree of electronic coupling between the metal centers in these systems is being assessed and is important for determining the efficacy of dpcat bridges in promoting electron/hole creation and separation. A number of new polynuclear complexes have been made and are being characterized spectroscopically. Other ligand bridges have also been employed. The dark catalyst in the proposed systems will be either a noble metal colloid or a macrocyclic complex. Preliminary work has focused on the former. The use of Pt(diimine)(dithiolate) chromophores in the new multicomponent systems builds on the understanding that has been achieved regarding their luminescence and excited state properties.

176. *Photoinduced Electron Transfer Processes in Homogeneous and Microheterogeneous Solutions*

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This project comprises a study of light-induced electron transfer reactions in solution, the solid state, and thin films. It focuses on potentially useful net chemical conversions that can occur following single electron transfer quenching of excited states. Typically, these reactions are initiated by photoexcitation of visible or near ultraviolet light absorbing electron donors (or acceptors) and subsequent quenching by single electron transfer. In the cases examined in these studies either the acceptor or donor or both contain a potentially fragmentable bond. The compounds are stable as the even electron precursors and hence the fragmentation is only accessible in one or both of the photogenerated radical ions due to a drastic and selective reduction of bond dissociation energies in these species. Such a change in bond dissociation energies has been found to be quite general for a number of different species upon one electron oxidation or reduction. Donors that can fragment from their cation radicals include amines, diamines, aminoketones, aminoalcohols, and pinacols. Acceptors that can undergo corresponding fragmentations include organic halides, ethers, and esters. Polymeric systems containing photoexcitable acceptors and fragmentable donors that can be reacted in solid state, solution, and thin films have been designed, synthesized, and studied. Amphiphilic donors and acceptors that can be incorporated into various organized media are also under investigation. Co-fragmentation reactions involving excited pinacols reacting with various organic halides are also under investigation. In some cases, especially with oxygen present, the co-fragmentation reactions can include a chain process resulting in highly efficient generation of acid and potentially useful radicals.

Rutgers, The State University of New Jersey
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Department of Chemistry

177. Electron Transfer in Helical Constrained Peptides and Hydrogen Bonding Networks
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This project is an investigation of the electron mediating properties of peptide bonds, amino acid side chains, and hydrogen bonds in the control of long-range electron transfer in proteins. Well-defined, rigid peptides derivatized with redox active and/or photoactive metal donors and acceptors are covalently attached at the peptide terminals and amino acid side chains. The peptides chosen are designed to emphasize special features such as the number of peptide bonds, H-bonding networks, connectivity of redox centers to main chain and side chain of the peptide, as well as the overall distance separation between the donor and acceptor. Intramolecular electron transfer between the donors and acceptors is initiated by radiation and photochemical methods. Results of intramolecular electron transfer rates across a series of bridging peptides of the polyproline II helix type ($n \geq 4$) shows an unusually small distance dependence in comparison to saturated hydrocarbons of similar length. Interpretation of these results using current theoretical models of electron transfer theories is being carried out. Hydrogen-bonding networks are also implicated in electron transfer pathways in molecules with crosslinked helical peptides and guest-host assemblies. Current experiments are directed towards comparing these results to electron transfer rates across other peptide secondary structure motifs.

178. Electronic and Nuclear Factors in Intramolecular Charge and Excitation Transfer
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The objective of this work is to gain a detailed understanding of molecular model systems relevant to efficient conversion of light into electrochemical potential and to controlled transfer of electronic excitation. The contribution of virtual electronic states of disorganized fluctuating medium to the exchange coupling, as well as in a similar coupling through non-covalently bound walls separating donors and acceptors, are of particular interest. Experimental study of the importance of specific vibrational modes in promoting rapid intramolecular excitation transfer is the second area of current activity. In addition, the dynamics of solvation of photoinduced charge separated states in binary (polar/nonpolar) solvent mixtures is also being investigated. The experimental capabilities of the group include femtosecond fluorescence upconversion and picosecond resonance Raman measurements.

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179. Photoinduced Electron Transfer and Electronic Excitation Transport in Complex Systems
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A variety of experimental and theoretical studies have been performed which examine photoinduced electron transfer and electronic excitation transfer in complex molecular systems. Photoinduced electron transfer and geminate recombination have been examined in liquid solution as well as in micelle systems. Fluorescence mixing, time correlated single photon counting, and two color pump-probe experiments have been performed. The results have been compared to very detailed theoretical models of the molecular systems. Electronic excitation transport in polymer and micelle systems has been studied. Again, detailed theoretical treatments have been developed. Experimental results on forward electron transfer between N,N-dimethylaniline (DMA) and photoexcited octadecylrhodamine B (ODRB) on two normal micelles: dodecyltrimethylammonium bromide (DTAB) and Triton X-100 were obtained. These chromophores are located preferentially on the micelle surfaces. Fluorescence up-conversion and fluorescence yield experiments for forward electron transfer between DMA and photoexcited ODRB on micelle surfaces were performed. The data were analyzed using recent theoretical developments from this group, with particular emphasis placed on the role of diffusion. Inclusion of diffusion leads to extremely good fits for reasonable values of the forward transfer parameters. Analytical theory was developed, and Monte Carlo simulations were used to study electronic excitation transport (EET) among chromophores diffusing on the surface of spherical micelles. The effect of molecular diffusion on the experimental observables was analyzed for two cases, donor-trap (DT) and donor-donor (DD) EET. Analytical expressions are given for the time-dependent ensemble averaged survival probability of the excited donor in the DT case. The analytical theory agrees with simulations. Simulations were employed to study the DD problem. The importance of diffusion on the time dependence of EET was demonstrated.

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180. Studies of Radiation-Produced Radicals and Radical Ions
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The objective of this project is to characterize both the structure and reactivity of selected organic free radical and radical ion intermediates generated by irradiation of molecular systems. Of particular interest is the study of the radical ions that are generated in the primary chemical processes resulting from the absorption of high-energy radiation, since these charged species play an important role in the mechanisms of both radiation and photochemical effects. Current projects involve structural and reactivity studies of novel species including (a) 1,3- and 1,4-cycloalkanediyl radical cations where one electron is delocalized over two nonadjacent carbon centers, (b) twisted structures in olefin (1,2-diyl) radical cations, (c) bisallylic (5π electrons) radical cations involving through-space interactions, (d) distonic radical cations where spin and charge are separated in the same molecule, and (e) thermal and photoinduced rearrangements of radical cations in rigid matrices proceeding by hydrogen transfer, ring opening, ring closure, and sigmatropic shifts. Many of these thermal radical cation rearrangements can be interpreted in terms of the role of vibronic coupling between the ground state and the first excited state of the radical cation. Moreover, several radical cations are found to adopt a stable structure corresponding to the transition state for the rearrangement of the neutral molecule, suggesting that the potential-energy surface becomes inverted upon one-electron oxidation. There is also a special focus on the photochemistry of radical cations in the visible region of the solar spectrum, with emphasis on the role of orbital, configuration, and state symmetry in going from the photoexcited state of the reactant to the ground state of the product.

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Department of Chemistry and Biochemistry

181. Interfacial Chemistry at the Chalcogenide Semiconductor/Electrolyte Junction

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This research involves two projects: (1) new electrosynthetic routes to the fabrication of chalcogenide semiconductors at support electrode surfaces; and (2) real-time in situ correlations of the interfacial chemistry and the electrical performance of a semiconductor electrode/ electrolyte junction. Proof-of-concept experiments have been completed and have opened a new route to the electrosynthesis of chalcogenide semiconductors that is based on a chemically-modified support electrode. Specifically, a sulfur-modified gold electrode is electroreduced in a medium containing a targeted metal ion (or ions) to yield immobilized metal sulfide particles at the gold surface. The utility of this approach for molecular-level ordering of the immobilized semiconductor particles and the role of the sulfur layer as a “template”is being investigated. A second topic is the development and use of new families of real-time/in situ probes for the characterization of semiconductor/electrolyte interfaces. These include the complementary probes, laser Raman spectroscopy, and electrochemical quartz crystal microgravimetry. A photoelectrochemical version of the latter technique has been developed to facilitate microgravimetry measurements on metal/semiconductor interfaces under illumination. Experiments have been completed on the growth and characterization of copper sulfide and copper indium sulfide layers. Composite photoelectrodes containing nanosized semiconductor particles in a nickel or polymer matrix have also been prepared and characterized. These materials exhibit high selectivity toward photo-oxidation of certain organic compounds. Finally, chemical modification of these nanocomposite photoelectrodes results in unusual photoeffects.

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Department of Chemistry

182. New Architectures for Integrated Photoelectrochemical Systems

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Chemically modified semiconductor surfaces are being studied mechanistically as sites for controlled photomediated oxidation and reduction reactions. New methods for synthetic manipulation of the surfaces are being explored, along with new methods for preparation and characterization of coordination polymers and solar light harvesting polymeric layers. These polymeric coatings are then associated with optically transparent electrodes, producing a multicomponent system that can be used to probe quantitative aspects of electrocatalysis, electrosorption, and chemisorption. The use of new polymerization methods for preparing rectifying mono- and bilayer electrode coatings are being explored, with the attainment of vectorial migration of excitons and electrons being an ultimate project goal.

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Department of Chemistry

183. Photochemical Studies of Two Component Organic Systems within the Restricted Spaces of Zeolites

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In this project it is proposed to establish that by confining reactants to a particularly shaped space, zeolites can direct reactions to specific products. Reactions to be investigated are initiated by light; where possible, by visible light. This strategy will have an impact on how fine chemicals are synthesized in the laboratory and in industry. One of the reactions investigated is the oxidation of olefins. Unprecedented selectivity has been observed when the reaction is carried out within the restricted spaces of a zeolite. The main reagent used in this reaction are abundantly available ‘air’ and ‘sunlight.’ The products are synthetically most useful alcohols. This reaction will be studied in great detail so that it can be developed into a 'clean' method to activate (functionalize) hydrocarbons. Another aspect of the research deals with generating and stabilizing highly reactive intermediates within zeolites. Intermediates such carbocations, cation radicals, carbenes are highly energy rich and they are considered to be very reactive and are established to live for less than a few microseconds in solution. It has been shown that radicals can be generated readily within zeolites and that they have a considerably long lifetime when encapsulated within the confined spaces of a zeolite. Future studies will be directed towards restraining the reactivity of energy-rich reactive species.

184. Photoinduced Energy and Electron Transfer Reactions in Light Harvesting Arrays of Transition Metal Complex Chromophores

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Ruthenium(II) diimine complexes have been shown to be particularly effective sensitizers for dye sensitized photoelectrochemical cells having nanocrystalline TiO_2 as a high surface area adsorbate for the dye. Our efforts have focused on (1) devising new light harvesting arrays capable of absorbing a higher fraction of incident photons per adsorbed molecule and (2) understanding and controlling excitation energy migration in multimetallic Ru(II) diimine complexes. Through systematic investigations of intramolecular energy transfer in bimetallic complexes, bridging diimine ligands (linked bis-2,2'-bipyridyl ligands) have been found which are capable of mediating energy migration between adjacent metal centers with 100% efficiency. In addition, simple synthetic strategies have been developed for preparing the most effective of these ligands. Using these ligands, arrays of chromophores can be prepared at interfaces via sequential reaction of complementary components in which coordinate covalent bonds are formed. Methods have been developed for synthesis of multimetallic arrays in which intact chromophoric centers are linked, thus avoiding problems associated with synthesizing sensitizers at the semiconductor-solution interface. This is achieved by preparing diimine complexes having phosphonic acid substituents and taking advantage of the exceedingly low solubility of various metal phosphonates. Light absorbing complexes can then be deposited in a stepwise fashion on a metal oxide semiconductor surface. It has been demonstrated that films of these complexes are electroactive and that films having at least three layers of complex are uniform and pinhole free on SnO_2.

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185. Investigations of Charge-Separation Processes in Metal Complexes

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The research is directed toward the elucidation of the excited states of metal complexes, particularly those materials that show promise for application in solar cells and as sensitizers for photochemical transformations. The principal emphasis is on platinum(II) and iridium(I) species, particularly those that tend to form excimers and extended chains. The role of dioxygen in energy degradation processes of rhodium(III) complexes is also under study. The principal tools are synthesis, absorption and emission spectroscopy at sub-77 K temperatures, and perturbation of excited states by magnetic fields (0 → 5T). Rhenium(I) complexes are also being investigated for possible use as photochemical sensitizers, and efficient injectors of electrons into nano-dispersed semiconductors. The use of both bi-and tri-metallic complexes as possible candidates for photochemical sensitizers is also being explored. The ultimate goal of the research is to arrive at a degree of understanding of the low-lying excited states in metal complexes such that substances having potential for commercial applications can be designed at the molecular level.

186. Membrane-Organized Chemical Photoredox Systems

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This research is designed to improve our conceptual understanding of reaction mechanisms in two general areas related to solar photoconversion: (1) catalysis of water oxidation to O_2 and (2) transmembrane separation of photoredox products across artificial bilayer membranes. Both areas are critical to developing membrane-based integrated chemical systems for photogeneration of fuels. The immediate objective in the catalysis studies is to identify the oxygen-evolving species formed by ruthenium μ-oxo dimers in the presence of strong oxidants. These studies entail structural analyses by resonance Raman and electron paramagnetic resonance methods, made in conjunction with steady-state kinetic measurements of O_2 evolution rates. The focus of the transmembrane product separation studies will be upon developing multifunctional molecules that can act both as oxidative quenchers of photoexcited dyes and as transmembrane cotransporters of electrons and protons. The conceptual basis for these studies is our recent demonstration that a prototypic compound, N-methyl-4-cyanopyridinium, can function as a highly efficient oxidative quencher/transmembrane charge carrier in vesicle-containing systems. Current research utilizing transient spectrophotometry is directed at determining the influence of the topographic location of the quencher with respect to the vesicle upon individual reaction steps. This location is altered by replacing the N-methyl substituent with n-alkyl chains of varying lengths. Studies designed to assess the prospects of using analogous compounds bearing weakly acidic ring substituents as electroneutral cyclic H^+/e^- cotransporters have also been initiated.

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Department of Biochemistry

187. ***Femtosecond Spectroscopy of Energy-Transfer Dynamics in Photosynthetic Antennas***
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Photosynthetic antennas are pigment/protein complexes that collect sunlight and pass the excitation energy on to a “reaction center” where, consequently, a chemical potential develops. This, in a nutshell, is how sunlight is stored. There are different kinds of antenna complexes in a given system and, in the purple photosynthetic bacteria, there are two major types of complexes; these have distinct absorption spectra in the near-infrared. The mode and mechanism of the transfer of the electronic excitation is being studied within and between the antenna complexes of the purple bacterium *Rhodobacter sphaeroides*. Excitation transfer is very fast, occuring in a trillionth of a second or less. In the experiment, a laser pulse lasting 50 femtoseconds or less excites one of the complexes selectively and the changes in the absorption spectrum are monitored as a function of time. The evolution of the absorption spectrum reveals details about the transfer of excitation from one type of complex to another. The knowledge gained from these experiments permits the postulation of the spatial and energetic arrangement of the antenna complexes in the photosynthetic membrane; this information is essential for fabricating efficient synthetic antenna systems.

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Department of Chemistry

188. ***Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates***
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This research project involves the investigation of models for aspects of the photoinduced transfer of charge, or the migration of energy between donor and acceptor transition metal-complexes. Research involves the design and synthesis of molecular systems to be used as mechanistic probes and the characterization of photochemical transients using very sensitive detection techniques. Work in progress varies from studies of the general problem of electronic coupling in donor-acceptor (D/A) systems to specific problems relating to the pathways for intramolecular back electron transfer in photoexcited transition metal donor-acceptor complexes. Considerable electronic coupling of donor and acceptor seems to be an important characteristic of polynuclear transition-metal complexes with CN^- or polypyridyl bridging groups, and the effects of this coupling are manifested in excited-state electron-transfer rates, ground-state spectroscopic behavior, and electrochemical behavior. In complexes for which the donor is (^{3}CT) Ru $(bpy)_3^{2+}$ and the acceptor is a covalently linked metal complex, the D/A centers usually behave reasonably independently. The systematic comparison of the properties of some homologous series of D/A complexes has indicated that: (1) there is an unusual shift to lower energies of the bridging cyanide stretching frequency; (2) there is mixing of CT states; (3) several symmetry issues are important. The shift of the CN-stretch is proportional to the D/A coupling, and symmetry dependent. A simple vibronic model accommodates most of the observations. Studies in progress are designed to examine implications of this model including the effects of vibronic coupling on back electron transfer rates.

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Department of Chemistry

189. ***Mixed-Metal, Multielectron Photocatalysts for Solar Energy Conversion***
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The fundamental chemical and photophysical behavior of platinum(II), rhenium(I), and ruthenium(II) complexes containing both chromophoric and spectator ligands are under investigation. Direct access to the triplet emitting state in a series of Pt(II) complexes containing C^C’,C^N and N^N’ and either bis (diphenylphophino)alkane or carbonyl ligands has been observed. The $Pt(C\hat{}C')(CO)_2$ molecule is unique, displaying monomolecular photophysical characteristics in dilute solution, but semiconductor photophysical properties in the solid state. The direction taken in ruthenium(II) chemistry revolves around newly synthesized ligands based on phenanthroline derivatives with the added dimension of new chemistry resulting upon coordination to ruthenium complexes. For example, coordinated 4,5-diazafluoren-9-one undergoes nucleophic attack resulting in newly derivatized ruthenium bipyridine complexes derivatized in the 3' position of the bipyridine ring. In the case of rhenium(I) chemistry, advantage is taken of the reactivity of the central carbon atom of diethylmalonate to synthesize ligands capable of forming bimetallic complexes. Advantage of the fact that one of the ligands, 2-pyridylpyrimidine (py-pm) has nonequivalent coordination sites, has been taken to prepare $[(phen)Re(CO)_3(py\text{-}pm)Re(CO)_3py]^{2+}$ which transfers energy from the “(phen)Re(CO)py-” fragment to the “-pypmRe$(CO)_3$” unit.

Chemical Physics

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Department of Chemistry

190. ***Spectroscopy and Energy Redistribution in Methanol***
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An integrated study of energy redistribution within energized methanol molecules has been initiated. Methanol is itself a combustion fuel and is produced as an energized intermediate in the combustion of other fuels. Previous work on methanol and other molecules showed that the redistribution of vibrational and rotational energy occurs on multiple timescales and is induced by multiple coupling mechanisms. The measurements under this project are in the frequency domain, and give information about relaxation timescales ranging from 100 fs to 10 ns. Three different frequency regions are studied in the range from 2800 cm^{-1} to 25,000 cm^{-1}. In the region of the C-H and O-H fundamentals, slit-jet absorption spectroscopy will be used; for the first overtone region, infrared double resonance spectroscopy, and for the higher overtones, a double resonance variant of infrared assisted photofragment spectroscopy. As energy is increased, the relevant interactions appear first as discrete perturbations, then as clumps of eigenstates, and finally as unresolvably dense contours. The more rigorous analysis possible in the lower energy ranges will quantify the coupling mechanisms and shed light on the complicated irreversible dynamics that occur at higher energies.

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Department of Chemistry

191. ***Electronic Structure and Reactivities of Transition Metal Clusters***
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The objective of this research is to seek answers to fundamental and intriguing questions pertinent to the electronic structure and reactivities of transition metal clusters. The geometries, binding energies, energy separations of excited states, ionization potentials, and other properties of clusters, including their reactivities, are theoretically computed as functions of cluster size. Theoretical studies on the dimers and trimers are focused on the energy separations (T_e) of several excited states and their spectroscopic constants (r_e, ω_e, μ_e). Computations on the potential energy surfaces are undertaken to shed light on the reactivity of these species. Spectroscopic constants of several low-lying electronic states of HfN, and PdC are computed, including spin-orbit effects. The observed spectra are too complex to explain without theoretical studies. Comparisons with observed spectra are made. Transition metal carbides such as Ta_2C_n, TaC_n, LaC_n, LaC_n^+, TaC_n^+, HfC_n, RhC_n, ScC_n for the values of n between 3 and 13 are studied. The geometries, binding energies, enegy separations of low-lying electronic states, are being computed. The geometries of these carbide clusters are being fully optimized. Geometries and energy separations of transition metal clusters such as Pd_5, W_4, Hf_4, Hf_3, Rh_3^+, Rh_4^+, Rh_5^+, are being computed using high-level relativistic ab initio methods. The potential energy surfaces of transition metal clusters with benzene and carbon monoxide (CO) are computed to gain insight into the nature of surface + Benzene/CO interactions. Specific reaction studies are Rh^++Benzene, Rh_2^++Benzene, Nb^++Benzene, Nb_2^++Benzene, Rh_3+CO, Ru+CO, Os+CO, W+CO and Mo+CO, which are investigated through computation of potential energy surfaces. These studies use complete active space MCSCF (CASSCF) followed by multireference configuration interaction (MRCI) computations that include several million configurations. Spin-orbit effects are included using the relativistic configuration interaction (RCI) method.

192. ***Generation, Detection and Characterization of Gas-Phase Transition-Metal Aggregates and Compounds***
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Elucidation of the microscopic steps of metal catalyzed chemistry is the goal of this project. The focus has been: (a) Characterization of the gas-phase products generated in the reaction titanium and yttrium vapor with alkanes because, for example, yttrium is known to catalyze carbon nanotube growth while titanium reacts to form highly stable metal carbon (met-cars) clusters; (b) Characterization of iridium and platinium metal-containing molecules generated in the reaction with alkanes, H_2S, NH_3, and N_2O. Physical properties used to test/develop theoretical models are determined using optical and microwave spectroscopy. The molecular beams of the samples are generated using a laser ablation/reaction source. Bond lengths, force constants, and dipole moments for PtX (X=C, N, O and S) and IrX (X=C and N) molecules have been determined. The observations were used to construct a simple, single configuration, molecular orbital correlation diagram. The polyatomic molecule YCC has been identified. The determined “T-shape” structure with Y loosely bound to the C-C moiety is proposed to be ideal for catalyzing nanotube growth. Attempts to identify other metal dicarbides proposed to be intermediates in the synthesis of nanotubes and met-cars are in progress.

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Department of Chemistry

193. Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distributions and Bonding

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The continued purpose of this research program is to obtain detailed experimental information on the different fundamental ways metals bond and activate organic molecules. Our approach is to directly probe the electronic interactions between metals and molecules with a wide variety of ionization spectroscopies and other techniques. The following have been accomplished during this year of the project: (a) We have examined the electronic communication between two metals as a function of the distance between the metals and the organic linkage between the metals. An example is two iron atoms linked by two fulvalene molecules, which represents an edge-shared biferrocene. Changes in the linkage cause changes in the electronic interactions according to distance and orbital symmetry interactions. (b) We have studied the influence of metal electron richness upon the interactions with acetylides. Metal-acetylides are implicated in many catalytic processes, and these complexes are also of interest for nonlinear optical properties. Metal dimer complexes display features with acetylides that are not evident from the study of metal monomer complexes. (c) We have studied the effects of sulfur coordination to metals, which is a common poisoning method in catalysis. Sulfur has a strong effect on the nature of the frontier electronic structure.

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Department of Chemistry and Biochemistry

194. High-Resolution Raman Spectroscopy of Complexes and Clusters in Molecular Beams

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The project objectives are two-fold. The first is to develop methods of nonlinear Raman spectroscopy for application in studies of sparse samples. The second is to apply such methods to structural and dynamical studies of species in ultracold supersonic molecular-beam samples. In the past year, we have progressed in three areas: (1) In the application of mass-selective ionization-detected stimulated Raman spectroscopy (IDSRS) at 0.03-cm^{-1} resolution to the study of intermolecular vibrations in molecular clusters. (2) In the characterization of the “pendular states” that arise from the interaction of an intense optical field with a species having an anisotropic polarizability tensor. (3) In the initiation of experiments employing a pulsed discharge source of free radicals and molecular ions. In the first area, we have measured intermolecular Raman spectra and characterized the intermolecular level structures of numerous molecular complexes and clusters, including naphthalene trimer, benzene-Ar, benzene-N_2, benzene-$(N_2)_2$, benzene-water, benzene-$water_2$, benzene dimer, and benzene trimer. In the second area, we have found that optical-field-induced pendular states are nearly ubiquitous in IDSRS on molecular clusters, and that, moreover, their presence is extremely useful in facilitating the assignment of such spectra. In the third area, we have recently completed the construction of a pulsed-discharge source of cold radicals and molecular ions. IDSRS experiments with this source aim toward developing a versatile, sensitive means by which to perform high-resolution ground-state spectroscopy on such species and complexes thereof.

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Department of Chemistry

195. Interactions of Highly Vibrationally Excited Molecules with Clean Metal Surfaces

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We have extended our studies of the reaction of hydrogen and deuterium on copper: $D_{2\,(g)} \rightarrow 2D_{ad}$. Study of this simple dissociative adsorption reaction represents one of the best opportunities to understand the microscopic atomic motions that are necessary for chemical transformation at a surface, in particular the effect of reactant alignment. These studies will aid in developing fundamental understanding of reactions similar to those in heterogeneous catalysis. The experiment is performed by making state-specific measurements of the products of the reverse desorption reaction, $2D_{ad} \rightarrow D_{2\,(g)}(v, J)$, using polarized laser light. The laser-based detection produces ions, whose velocity distribution is measured with field free time-of-flight. Using detailed balance, observation of preferred alignments of the desorbing $D_{2\,(g)}(v, J)$ are indicative of the state-specific and velocity dependent steric effect for the adsorption reaction. We have observed a marked dependence of the reaction probability on reactant alignment; dissociative adsorption favors broadside collisions. This gives direct experimental evidence that the transition state for this reaction has the molecular bond parallel to the surface normal. We also find that the probability to react depends strongly on the collision conditions; the steric preference nearly disappears for high kinetic energies and it is enhanced for rotationally excited molecules. This work gives the first experimental evidence that the dynamical conditions of a surface chemical reaction can profoundly influence the associated steric requirements.

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Department of Chemistry and The James Franck Institute

196. Chemical Reaction Dynamics of Combustion Intermediates and Products

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These studies develop our predictive ability for bimolecular and unimolecular reactions of combustion intermediates and products. The first experiments investigate the photolytic generation and reactivity of bimolecular reaction intermediates important in combustion, such as the HOCO intermediate of the $OH + CO \rightarrow H + CO_2$ reaction. The branching ratios between competing product channels is determined with photofragment velocity and angular distribution analysis in a crossed laser/molecular beam apparatus and the early reaction dynamics is probed with emission spectroscopy of the dissociating species. The final experiments probe how the relative orientation of the reactants in bimolecular reactions, like $H + O_2 \rightarrow OH + O$, which is a key rate limiting, chain branching step in combustion processes, can influence the reaction cross section. Orienting the diatomic reagent in analogous systems, $H + XY \rightarrow X + YH$, with respect to the velocity vector of the H atom reagent, allows us to investigate how the effective barrier changes with relative orientation and how nonadiabatic recrossing influences the reaction cross section.

197. Quantum Dynamics of Fast Chemical Reactions

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In this research, we want to determine accurate values of thermal rate constants and state-to-state cross sections for elementary bimolecular reactions in the gas phase, including photodissociation. We develop and use accurate and efficient quantum methods. The thermal rate constants have been calculated both from the quantum thermal averaged flux-flux correlation function (evaluated by diagonalizing the Hamiltonian in a three-body DVR) and from the cumulative reaction probability, N(E). Recently, we have developed methods that use only real square integrable representations on a finite (small) range in order to represent the continuum scattering processes. We have applied these to the photodissociation of van der Waals molecules and the UV photodissociation of a model for methyl mercaptan. Resonances of HCO for $J = 0, 1$, and 3 have been determined by these methods and will be used to examine the "strong collision assumption" of unimolecular reaction rate theory. An additional focus has been on the development of an exact "quantum transition state method" based on operator expressions for N(E). Time evolution of the "transition state wavepackets" only once yields their contributions to the cumulative reaction probability at all desired energies. Applications to the $H_2 + OH$ reaction in full 6-D yields excellent results. Initial state wavepacket methods have been used for the reverse reaction to determine state-to-state cross sections and the effect of initial vibrational energy on the reactivity of HOD with H to form either H_2 or HD.

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198. Laser Photoelectron Spectroscopy of Ions

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Our experimental program uses photoelectron spectroscopy to study the properties of negative ions and radicals. The essence of our experiment is to cross a 0.6 keV mass-selected ion beam (M^-) with the output of a CW laser, hν. The resultant detached photoelectrons with kinetic energy, KE, are energy analyzed by an electrostatic hemispherical analyzer. $M^- + h\nu \rightarrow M + e(KE)^-$ Analysis of the photoelectron spectra enables us to extract molecular electron affinities, vibrational frequencies, and electronic splittings of the final radical, M, as well as the relative molecular geometries of ions (M^-) and radicals (M). During the last year, the (CNN^-, $HCNN^-$) and the (NCN^-, $HNCN^-$) systems have been investigated. Recent results for diazomethyl radical and diazocarbene energetics are as follows (in kcal mol^{-1}, except as noted): $EA[HCNN] = 1.685 \pm 0.006$ eV; $\Delta_{acid}H_{298}[H\text{-}CHNN] = 372 \pm 2$; $D_0[H\text{-}CHNN] = 96 \pm 2$; $\Delta_f H_0[H_2CNN] = 65 \pm 1$; $\Delta_f H_0[HCNN] = 110 \pm 2$; $T_0[2A\ \ HCN] = 0.675 \pm 0.012$; $EA(CNN) = 1.771 \pm 0.010$ eV; $\Delta_{acid}H_{298}[(H\text{-}CNN] = 349 \pm 2$; $D_0[H\text{-}CNN] = 75 \pm 2$; $\Delta_f H_0[CNN] = 133 \pm 3$; $T_0[a\ \ CNN] = 0.846 \pm 0.014$ eV; $T_0[b\ \ CNN] = 1.325 \pm 0.015$ eV; $T_0[A\ \ CNN] = 2.957 \pm 0.001$ eV

199. Time-Resolved FTIR Emission Studies of Laser Photofragmentation and Radical Reactions

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Time-resolved Fourier transform infrared emission spectra are used to study dynamical processes of radical-radical reactions and radical-molecule collision events. The results of these studies are important for combustion processes. New studies involve the detailed investigation of a novel five-membered ring transition state in the reactions of O atoms with molecules such as ethyl iodide and propyl iodide, which forms HOI. Detailed spectroscopic information has been obtained to determine the vibrational distributions of the HOI product molecule for the first time. Radical-radical reactions of O atoms with ethyl and propyl radicals have been investigated through the product OH vibrational distributions. Inverted vibrational states suggest a direct abstraction mechanism. A jet-cooled source of molecules has been developed to study infrared emission from photofragments and reactions. The dynamics of NH_2 from the photodissociation of NH_3

has been explored under the highly compressed spectral condition of jet-cooling.

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200. Energy Partitioning in Elementary Gas-Phase Reactions
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This research aims to understand the detailed mechanism of the reactions of O(^{3}P) with unsaturated hydrocarbons and to measure the yields of the important channels. Recent findings are: (1) When O reacts with an alkyne, one product pair is an alkene and a vibrationally and rotationally cold CO. The explanation is that the system crosses from the initial triplet surface to the lower singlet surface on which a transient substituted ketene is formed and then dissociates with little torque on the CO. (2) OH radicals are products of the reactions of O(^{3}P) with alkenes but not ethylene or alkynes. The allylic C-H bond has a smaller bond energy than the α C-H bond of an alkylalkyne and a far smaller bond energy than a vinyl C-H bond. (3) A prominent reaction channel for O + C_2H_4 is the formation of a vinoxy radical, CH_2=CHO and an H atom. With propene and 1-butene, vinoxy is also produced. The H atom yield diminishes strongly as the sidechain lengthens because it is energetically more favorable to eject methyl or ethyl radicals with vinoxy. Isobutene does produce methylvinoxy. A cavity ring down spectrometer is being constructed to detect unstable intermediates such as HCO, HSO and CH_2.

201. Laser-Enhanced Chemical Reaction Studies
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This project employs extremely high resolution infrared diode lasers to study fundamental combustion and collision dynamics and photochemical reaction processes. High energy atoms, molecules, and chemically reactive radicals, produced by excimer laser photolysis or dye laser excitation, are used as reagents to investigate collisional excitation, collisional quenching, and chemical production of individual rotational and vibrational states of molecules. Translational energy recoil of the target molecules is determined by measuring the time dependent Doppler profile of the molecular infrared transitions. This experimental method has been used to probe the quenching step in the famous Lindemann unimolecular reaction model in which vibrationally hot molecules with chemically significant amounts of energy are cooled by collisions with a cold bath molecule. Loss of energy by these highly excited molecules has been found to proceed via both a short range repulsive and a long range attractive force mechanism. We have also extracted from our data for the first time the shape of the energy transfer probability distribution function P(E,E′), which gives the probability that a donor molecule with internal energy E will end up in a state of energy E′ due to a collision with a bath molecule. P(E,E′) is exceedingly valuable in a master equation analysis of unimolecular chemical reaction kinetic data, and it provides detailed information for testing both potential energy surfaces and computational techniques for theoretical investigations of collision and chemical dynamic processes. We have already detected significant differences between the P(E, E′) distributions for hexafluorobenzene and pyrazine excited to the same energy (40,000 cm^{-1}). The data obtained in all of these experiments are of fundamental as well as practical interest in testing theoretical computations based on approximate potential energy surfaces and in providing an improved understanding of combustion and atmospheric chemical processes.

202. Single-Collision Studies of Energy Transfer and Chemical Reaction
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This research project addresses the dynamics of chemical reactions that are important in combustion processes, or that serve as prototypes of important combustion reactions. Our current interest is in reactions of free radicals, such as H, CN, and OH, with alkanes and other fuel species. Of particular interest are the reactions of the radicals with vibrationally excited molecules. At the high temperatures of combustion media, vibrationally excited reagents can make important contributions to the reaction rates, but their reactions may be characterized by different dynamics or products than the reactions of the unexcited species. We do both experimental and computational studies. The experiments—state-to-state dynamics experiments under single-collision conditions—use a sequence of precisely timed nanosecond laser pulses to create the free radical reactant, to vibrationally excite the reactant molecule, and to detect the products and determine their energy distributions. The computational simulations are quasi-classical trajectory calculations. The state-to-state reactive cross sections that come from our experiments are used to provide a rigorous test of the accuracy of the computational simulations of the reactions. When validated by comparison with experimental results, the computational simulations provide insight about the dynamics of combustion reactions, and are used to develop models of these reactions that have predictive power.

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203. Studies of Combustion Reactions at the State-Resolved Differential Cross Section Level
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The techniques of product imaging and Rydberg atom time-of-flight measurement will be used to investigate several processes important to a fundamental understanding of combustion. The imaging technique produces a "snapshot" of the three-dimensional velocity distribution of a state-selected reaction product. The Rydberg time-of-flight technique provides a high-resolution spectrum of the translational energy distribution of reaction products. Research in three main areas is planned. First, the imaging technique will be used to measure vibrational-to-translational energy transfer from highly vibrationally excited molecules to an inert gas. This measurement is important to an understanding of the "fall-off" region for unimolecular and radical recombination reactions. Second, the energy disposal and, in one case, the differential cross section will be measured for several important combustion reactions. These include the $H + O_2 \rightarrow OH + O$ reaction, where the differential cross section will be measured by imaging the OH and O atom recoil; the $OH + CO \rightarrow CO_2 + H$ reaction, where the H atom Rydberg time-of-flight measurement will provide details about the energy disposal; the $OH + HCN \rightarrow H_2O + CN$ reaction, where laser-induced fluorescence of the CN will probe the dynamics; and the OH + allene reaction, where time-of-flight mass spectrometry will be used to identify and characterize the products. Finally, imaging and Doppler techniques will be used to investigate the photodissociation dynamics of the vinoxy and phenoxy radicals. The fundamental understanding at a detailed dynamical level of these processes will be useful for future interpretation, modelling, and manipulation of combustion chemistry.

Laboratory of Atomic and Solid State Physics

204. Dynamics of Surface Photochemistry
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This project seeks to understand the mechanisms and forces involved in elementary chemical reactions by studying the dynamics of surface photochemistry. Comparison of the data to theoretical modeling of femtosecond and nanosecond laser induced dynamical quantum processes on solid surfaces provided insights into the nature and the time scales involved in photon-induced bond breaking and formation of adsorbed molecules. The role of excited states and the efficiency of energy exchange between adsorbed species and the substrate were investigated by determining the range of travel of photoproducts on the surface by low temperature scanning tunneling microscopy (STM). The systems studied were O_2 adsorbed alone and coadsorbed with NO and CO on Pt(111). Translational energy distributions were obtained for all the photodesorbed molecules, and for NO internal state distributions were also measured. The reactants and products on the surface were imaged by the STM. These studies provide an understanding of energy related processes such as catalysis, combustion, and materials synthesis and processing. The use of light in initiating chemical reactions contributes to the exploration for efficient and environmentally sound processes for the utilization of energy resources.

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205. Theoretical Studies of Combustion Dynamics
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The objectives of this research project are the development and application of rigorous theoretical methods to describe dynamical processes of importance in gas-phase combustion. The focus of the research is on bimolecular and unimolecular reactions of importance in combustion.

An important theoretical approximation we have examined is the so-called J-shifting approximation. This is one approximation that appears in reduced dimensionality theories of reactive scattering, and which has been used by a number of groups. The approximation relates the reaction probability for non-zero total angular momentum to the one for zero total angular momentum. The latter is generally much easier to calculate than the former. Recently we have tested this approximation for reactions that proceed via resonances due to complex formation. (This class of reactions is ubiquitous in combustion.) Our tests have made use of a new, more powerful approximation that we have termed the Adiabatic Rotation Approximation. Tests on HCO and HOCO indicate that J-shifting using rotation constants corresponding to the equilibrium structure is more accurate than using rotation constants corresponding to the transition state. In addition, the nature of the Adiabatic Rotation Approximation permits a perturbation calculation to be done for shifts in resonance position and widths as a function of J and K (the projection quantum number of J on the symmetry axis) using the $J = 0$ complex eigenfunction. This approach appears to be a good candidate for next generation of approximation, replacing or augmenting J-shifting when that method is suspect.

206. *Kinetics of Elementary Processes Relevant to Incipient Soot Formation*
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Experimental and theoretical studies of elementary reactions relevant to the formation of aromatic and polycyclic aromatic hydrocarbons have been carried out. Two new experimental methods (FTIR spectrometry and pulsed laser photolysis/mass spectrometry, PLP/MS) have been employed, in addition to the ongoing cavity ringdown technique, to investigate the kinetics of C_6H_5 reactions covering 300-1000 K. Preliminary results for the $C_6H_5 + H_2$ reaction by the two new methods agree closely with those predicted by ab initio MO/TST calculations, which have also been applied to elucidate the mechanisms as well as to predict the rate constants for $C_2H_3 + O_2$, and the decomposition of C_6H_5 and C_6H_5O radicals. By PLP/MS, we have also determined the absolute rate constant for the recombination of C_6H_5 radicals over the temperature range of 300-500 K, $k = 1.4 \times 10^{13} \exp(-56/T)\ cm^3mole^{-1}s^{-1}$.

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Supercomputer Computations Research Institute

207. *Ab Initio Electronic Structure Studies of Pyrolytic Reactions*
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Reaction pathways that lead from simple precursors to large polycyclic aromatic hydrocarbons (PAHs) are the subject of our continuing theoretical research on pyrolytic processes. Accurate predictions of the C-C, C-H, and C-Cl bond dissociation energies (BDEs) in ethane and its (poly)chloro derivatives have been obtained from high-level G2 and G2MP2 electronic structure calculations. The trends observed in these BDEs explain the diverse behavior of polychlorinated ethanes under pyrolytic conditions. Studies of the benzyne to cyclopentadienylidene rearrangement, carried out in conjunction with the HF, MP2, QCISD, CCSD(T), and BLYP approximations, have provided important clues about the performance of various quantum-chemical approaches to modeling of high-temperature reactions that involve carbenes and highly strained molecules. The data gathered from these studies facilitate investigations of analogous rearrangements of large arynes. Such rearrangements constitute some of the many reaction channels that connect biaryls with pericondensed PAHs. Energetics and reaction barriers of these channels are currently being examined at the BLYP/6-311G** level of theory.

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Center for Computational Quantum Chemistry

208. *Theoretical Studies of Elementary Hydrocarbon Species and Their Reactions*
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High level quantum mechanical methods are now a significant source of specific predictions concerning molecular systems that may be very important, but inaccessible, to experiment. An important example is the study of molecular species and chemical reactions of fundamental importance in combustion processes. This research involves both the development of theoretical methods and their application to hydrocarbon chemisty. Quantum mechanical electronic structure methods, intermediate between extensive configuration interaction and high level perturbation theory, are being developed. Chemical reactions being studied in molecular detail include the dissociation of HNCO and ketene and the different aspects of the $C_2H_5 + O_2$ reaction.

Department of Chemistry

209. *Spectroscopy at Metal Cluster Surfaces*
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Microscopic clusters composed of a variety metals are produced and studied in a molecular beam environment. These same methods are used to produce metal complexes, which have small molecules physisorbed on the surface of metal cluster particles. Electronic spectroscopy is applied to these clusters to investigate the fundamentals of metal-metal and metal-adsorbate bonding. These studies produce vibrational frequencies and bond energies for metal clusters and their complexes. Recently studied systems include Cu-Li, Na-Ag, Au-K, Au-Na, Au-Ar, Cu-Kr, Ga-Ar, Ga-Kr, and Ga-Xe. Studies of larger clusters focus on the metal-carbon systems known as met-cars clusters. In these systems, the M_8C_{12} stoichiometry is formed preferentially, and a cage-like structure has been proposed to explain this preference. In the last few months, we have constructed a gas addition system to study chemisorption on the surface of met-car clusters. Additional studies have identified preferential formation of $M_{14}C_{13}$ clusters believed to have face-centered cubic structures. Recent progress in this area includes the first measurements of ionization potentials for M/C clusters (e.g., Ti_8C_{12}: IP=4.9 eV) and the preparation of new metal carbide clusters (silver, copper, iron). We have also recently prepared metal-C_{60} clusters for study of the interactions at the fullerene surface. The measurements of the fundamental interactions exhibited by all these different kinds of clusters are used to evaluate their potential as models for bulk surface chemistry and catalysis and to provide specific data on finite sized systems for the development of theory in this area.

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210. Kinetics of Combustion-Related Processes at High Temperature
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The main purpose of this project is the determination of rates and mechanisms for hydrocarbon pyrolysis and other reactions at high temperatures. Additional work involves both experiment and theory on energy transfer and its coupling with unimolecular rates. The measurements are made in a shock tube with two very high resolution laser diagnostic techniques: laser schlieren measurement of density gradients (net endothermic rate) and excimer laser flash absorption, which provide rate data with 0.1 microsecond resolution. Recent work includes a study of the decomposition of the aromatic azines. Studies of large-molecule dissociation at extreme temperatures, as in the retro-Diels Alder dissociation of cyclohexene, tetrahydropyridine, and norbornene, have provided the first observations of unimolecular falloff in such dissociations. The norbornene study also offered the first measurements of incubation times in a large-molecule dissociation. Additional work involved measurements of vibrational relaxation in large molecules; dissociation, isomerization, and aromatic formation in allene/propyne; and dissociation rates in a large number of halocarbons. A theoretical analysis of large anharmonic effects arising from facile isomerization (restricted internal rotations) on the rate of dissociation of unsaturated hydrides has been developed and applied to HCN, C_2H_2, and now to allene/propyne. Investigations of decomposition, isomerization, and incubation in the oxirane/acetaldehyde system, and dissociation, relaxation, and incubation in furan are underway.

University of Illinois at Urbana-Champaign
Urbana, IL, 61801

Department of Mechanical and Industrial Engineering

211. Investigation of Saturated Degenerate Four-Wave Mixing Spectroscopy for Quantitative Concentration Measurements
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A combined experimental and theoretical approach is used for the development and evaluation of strategies for quantitative degenerate four-wave mixing (DFWM) concentration measurements in flames. The DFWM process is investigated theoretically by solving the time-dependent density matrix questions by direct numerical integration. During the past year we have investigated the DFWM signal generation process for closely spaced resonance transitions, a theoretical study that has important implications for fitting DFWM spectral regions with overlapping transitions. We have obtained excellent agreement with detailed experimental lineshape measurements, and our calculations clearly show significant interference effects under conditions of high saturation. We have investigated theoretically the effects of level degeneracies (Zeeman states) on DFWM signal generation in the saturation regime. Collisional effects and different laser polarization schemes are being investigated using our degenerate-level DFWM code. We will investigate the effects of multi-frequency-mode laser radiation in the coming year and will conclude a study of DFWM signal generation in the forward phase-matching geometry. Experimentally, we are performing OH DFWM measurements in low pressure flames. The results of OH DFWM measurements over a wide range of flame pressures and stoichiometries will be compared with our theoretical calculations of DFWM signal levels, saturation intensities, and detection limits.

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Department of Chemistry

212. Investigations of Reactions and Spectroscopy of Radical Species Relevant to Combustion Reactions and Diagnostics
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Nonadiabatic effects, that is, the effect of interactions that couple electronic potential energy surfaces, play an essential role in combustion chemistry. Two classes of electronically nonadiabatic processes are under consideration, spin-conserving and spin-nonconserving electronically nonadiabatic processes. The mechanism of the spin-forbidden reaction $N(^4S) + CH_3(^2A') \rightarrow H_2 + HCN$ has been analyzed. This analysis, which demonstrates that the reaction procedes through an intermediate complex, methyl nitrene, will be used to guide the determination of the electronic structure data necessary for a prediction of the rate constant for this reaction. The interaction of the T_1 and S_0 states of ketene will be carried out with the aim of determining whether this interaction contributes to ketene photodissociation via surface hopping. The possible role of T_1 S_0 intersystem crossing in the reaction of ^3O + acetylene will also be considered. The geometric phase effect, induced by conical intersections, can have important implications for molecular reaction dynamics. A seam of C_{2v} conical intersections, relevant to the key combustion reaction $OH + H_2 \rightarrow H_2 + H_2O$, has been located. Studies of the energetics along paths surrounding these conical intersections indicate that the geometric phase effect will not have a significant impact on the ground state reaction at low translational energies. However, recently we have demonstrated that seams of conical intersections can exhibit branches not expected on the basis of symmetry arguments. The existence of such branches for this seam of conical intersections will be considered.

Massachusetts Institute of Technology Cambridge, MA, 02139

Department of Chemical Engineering

213. ***Aromatics Oxidation and Soot Formation in Flames***
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Aromatics oxidation and soot formation in low pressure one dimensional flames are being studied using molecular beam sampling with radical scavenging/cryotrapping and subsequent spectroscopic analyses. Identifications of stable and radical species, including fullerenes, soot structural characteristics, and net reaction rates calculated from concentration profiles, are used to test and to refine hypothesized reaction mechanisms. Benzene oxidation is being tested using measured concentration profiles of radicals (e.g., C_6H_5, C_6H_5O, and hopefully C_6H_7 and C_6H_4OH) and stable species present during benzene oxidation in flames. The research on soot formation is concerned with the particle inception or nucleation stage and the study of soot structure at all stages of growth in order to obtain mechanistic information from evidence of growth steps recorded in the structure of particles. The ultimate objective is to understand how nascent soot particles are formed from high molecular weight compounds, including the roles of planar and curved PAH and the relationship between soot and fullerenes. The objective of the research on fullerenes is to identify the range of fullerenes formed in flames, the nature of the precursor species, and the mechanisms and kinetics of the formation reactions.

Department of Chemistry

214. ***Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules***
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Studies of intramolecular vibrational redistribution (IVR) and unimolecular isomerization have focused on the acetylene molecule (C_2H_2) and have utilized the spectroscopic techniques of dispersed fluorescence (DF) and stimulated emission pumping (SEP). Sensitive and selective absorption-based spectroscopic techniques, suited for both detection and characterization, have also been under development. These techniques are based on the combination of magnetic rotation spectroscopy (MRS), which provides selectivity to the lowest rotational levels of free radicals, and frequency modulation (FM) spectroscopy. In a collaboration with T. Sears at Brookhaven National Laboratory, the $S_1 \rightarrow S_0$ transition of photolytically generated HCBr was recorded by transient FM spectroscopy. In a collaboration with E. Eyler at the University of Connecticut, the sideband phase and amplitude stability, on which the sensitivity of FM spectroscopy depends, was shown to be preserved when an FMed cw dye laser was pulse amplified and frequency tripled. The study of IVR in acetylene is based on a polyad model in which the initial stages of IVR are described by a few spectroscopically determined resonance parameters. The polyad model describes the frequency and intensity patterns in the spectrum and the rates and pathways for energy flow in a computationally simple form, which is explicitly scalable in E_{vib}. The model also guides selection of initial states, accessible via IR-UV-SEP, that are optimally coupled to dynamical features such as the acetylene-vinylidene isomerization coordinate. Despite severe overlap of polyad features in the DF spectrum of acetylene, it has proven possible to "unzip" the spectrum into separate polyads. This provides a quick survey of the unimolecular dynamics at energies where breakdown of the predicted polyad patterns would signal the onset of isomerization. A new pattern recognition technique (XCC, eXtended Cross Correlation) has been used to disentangle spectrally overlapping polyads that encode the early time dynamics on the S_0 $X\ ^1\Sigma_g$ surface. A unique feature of the XCC is that it reveals patterns without any advance knowledge of the form or even the existence of patterns. From the polyads, it is possible to determine the "deperturbed" energies of the "zero-order bright states" and the deperturbed Franck-Condon factors for transitions between vibrational levels of the S_1 state and the Franck-Condon bright zero-order states on the S_0 surface. The IVR rates and pathways that are encoded in the patterns within each polyad may be surveyed and explained as a function of excitation in the two Franck-Condon active normal modes, CC stretch, and trans-bend. All of the polyad patterns follow harmonic oscillator scaling rules. In addition to the sharp features associated with the polyads, there is a quasicontinuum background that is shown not to be due to collisional relaxation or Coriolis perturbations. An extensively tested and refined effective Hamiltonian model is capable of describing the dynamics of any conceivable initial excitation and should be useful in the formulation of schemes for externally controlling intramolecular dynamics.

University of Massachusetts at Amherst Amherst, MA, 01003-3110

Department of Chemical Engineering

215. ***Probing Flame Chemistry with MBMS, Theory, and Modeling***
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Elementary reactions in combustion are studied using molecular-beam mass spectrometry (MBMS) of free-radical and stable species in flames, ab initio calculations of thermochemistry and transition states, new kinetics from reaction theories, and tests of mechanisms using whole-flame modeling. The present focus is on oxidation and molecular-weight growth chemistry important in forming and destroying aromatic pollutants. Complete MBMS data sets have been mapped for the first time in high-temperature ethene flat flames, $\phi=0.75$ and $\phi=1.90$. We obtained new measurements of the kinetics for H and

OH + C_2H_4, C_2H_3 decomposition, and C_2H_3+O_2. With the BAC-MP4 method, we have calculated thermochemistry and rate constants for these reactions and reactions of CH_3CHO, CH_3CO, and CH_2CHO. Gas-solid boundary-condition effects in flame modeling have also been studied by modeling ignition and extinction of stagnation-point flows for H_2/O_2. C_2H_4/allene flames are now being mapped and modeled.

Department of Chemistry

216. Theory of the Reaction Dynamics of Small Molecules on Metal Surfaces
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Realistic quantum mechanical and quasi-classical models are used to examine the dynamics of some molecule-surface reactions important in catalysis. Studies have been made of Eley-Rideal processes in which gas phase H or D atoms react with adsorbed H, D, or Cl atoms. Fully quantum three-dimensional calculations have been implemented, based upon a flat-surface approximation, allowing for the determination of reaction cross sections and product translational and ro-vibrational state distributions. More recently, a detailed potential energy surface has been constructed for the H(g) + H/Cu(111) reaction by fitting to the results of density functional calculations. This was used in quasi-classical studies that included all six nuclear degrees of freedom, and both direct Eley-Rideal and hot-atom reaction dynamics were explored. Good agreement was found with experiment. The dynamics have been elucidated in terms of a competition between adsorbate-mediated trapping, corrugation-mediated trapping, and reaction. The dissociative adsorption of H_2 and CH_4 on metal surfaces is also being studied using 3D flat-surface quantum models. The effects of surface temperature and the ro-vibrational state of the molecule on dissociation are being examined.

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Atmospheric, Oceanic, and Space Sciences

217. Energy-Transfer Properties and Mechanisms
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This project studies the mechanisms and properties of energy transfer involving moderate-sized molecules. A fuller understanding of highly excited molecules is obtained through a combination of experiments and modeling. The aim is to develop a theoretical model for prediction of energy transfer properties. In the experiments, the excited molecules are monitored with various techniques, including time- and wavelength-resolved IR emission and resonance-enhanced multiphoton ionization. The disposal of energy in translational, rotational, and vibrational degrees of freedom is monitored as highly excited molecules are deactivated. In the modeling effort, collisional/reaction master equation formulations are developed and used to investigate how molecular energy transfer affects chemical reaction systems in combustion and in other systems that experience temperature and pressure extremes.

University of Minnesota
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Department of Chemistry

218. Variational Transition State Theory
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This project involves the development and application of variational transition state theory (VTST) and multidimensional semiclassical transmission coefficients for gas-phase reactions. The work involves new theoretical formulations and the development of practical techniques for applying the theory to various classes of transition states and for interfacing reaction-path dynamics calculations with electronic structure theory. We are also carrying out applications to specific reactions of interest for combustion or for testing theory applicable to combustion. We have developed new general strategies for obtaining potential energy surface information for reaction-path dynamics calculations, and we are developing practical methods that eliminate the need for fitting electronic structure data to analytic forms. The new methods are called direct dynamics. We have developed one approach to direct dynamics that we call interpolated variational transition state theory (IVTST). In this approach, we base the dynamics calculations on electronic structure data, including energies, gradients, and hessians, at the reactants, products, saddle point, and zero, one, or more additional points near the saddle point. We are currently improving this method. Another direct dynamics scheme is called VTST with interpolated corrections (VTST-IC) or dual-level direct dynamics or triple-slash (///) dynamics. This approach involves using straight direct dynamics with NDDO-SRP parameterization or a low-level ab initio calculation as a first step; in the second step, this is augmented by high-level data at selected geometries along the reaction path. The new techniques are being incorporated in our portable POLYRATE, MORATE, and GAUSSRATE programs.

National Institute of Standards and Technology, Gaithersburg
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Chemical Science and Technology Laboratory

219. Kinetics Database for Combustion Modeling
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The computer simulation of combustion processes provides a means of making optimum use of increasing capabilities in computational power and fundamental understanding to supplement physical testing. It can therefore have important influences on design and optimization of combustion devices for energy efficiency and pollution minimization. The key ingredient for taking advantage of this technology is the availability of a reliable database of chemical kinetic and thermodynamic information bearing on all the species, stable and unstable, that are formed in the course of the reaction. This project seeks to fulfill this need through the development of a database of evaluated and estimated chemical kinetic and thermodynamic information. The procedure has been to start with the simplest of hydrocarbons, methane, and then add increasingly complex and more realistic fuel molecules containing the functional groups that are the key to their reactivity and the basis for estimation. Thus, smaller saturated alkenes, alkynes, and aromatics have now been examined. An important aspect of this work is the examination of techniques for estimation. Much progress has now been made in developing an understanding of the limitations of the general procedures for extrapolation of data to the high temperatures required for combustion applications.

Optical Technology Division

220. Spectroscopic Investigation of the Vibrational Quasi-Continuum Arising from Internal Rotation of a Methyl Group
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This project studies the vibrational quasi-continuum in acetaldehyde, methanol, and related molecules because internal rotation is important in promoting intramolecular vibrational redistribution (IVR). It aims to understand: (1) torsional motion below and above the barrier, (2) traditional vibrational states, and (3) interactions involving levels with excitation of both kinds of motion. Two questions remaining in the torsion-rotation problem have been essentially solved this year. First, examination of least-squares fits of numerically generated data sets shows that traditional ideas concerning the number of determinable parameters in the torsion-rotation Hamiltonian must be modified. An algebraic study is in progress to gain a better understanding of the causes of these numerical results. Second, examination of the K dependent torsional overlap integrals arising in the rho axis method has led to a new proposal for the "best" definition of a torsional state when going from below to above the top of the barrier. The vibration-torsion-rotation formalism developed last year has not yet been applied because of problems remaining in attempts to use Gaussian 94 to determine Fourier expansion coefficients for the variation with internal rotation angle of various structural parameters and vibrational force constants.

University of Nevada, Reno
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Department of Chemistry

221. Thermochemistry of Hydrocarbon Radicals: Guided Ion Beam Studies
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Gas phase negative ion chemistry methods are used to measure enthalpies of formation of small organic radicals important in combustion processes. Using guided ion beam mass spectrometry, we measured threshold energies of endoergic proton transfer and hydrogen atom transfer reactions of hydrocarbon molecules with negative reagent ions. The measured threshold energies yield the RH bond dissociation energy of the corresponding neutral molecule, or equivalently, the enthalpy of formation of the R· organic radical. Using guided ion beam techniques to study endoergic reactions allows accurate determinations of RH bond dissociation energies for species that are not easily investigated by thermal ion and neutral kinetics techniques. Examples include extremely weak gas phase acids, such as saturated alkanes, polyacetylenes, and the differential RH bond dissociation energies at various positions in substituted aromatic and conjugated compounds. Systems to be investigated are radicals important in combustion processes, including, for example, acetylenic and aromatic hydrocarbon radicals that lead to formation of polycyclic aromatic hydrocarbons and soot.

University of New Orleans
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Department of Chemistry

222. Identification and Temporal Behavior of Radical Intermediates Formed during the Combustion and Pyrolysis of Gaseous Fuel
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We have extended our complementary shock tube studies of the thermal decompositions of the azines to include, in addition to pyrazine, pyrimidine and pyridine. The pyrolyses were investigated using laser Schlieren densitometric measurements, performed by Professor John Kiefer and his group at the University of Illinois at Chicago, and time-of-flight mass spectrometric determinations of the dynamic concentration profiles of reactants, products, and intermediates detected during the available observation times of 1 ms. The complementary experiments covered the temperature and total pressure ranges of 1600-2300 K and 150-350 Torr, respectively. A free radical chain reaction with initiation by ring C-H fission for all three azines is proposed. The measured C-H fission rates are compared and analyzed by RRKM theory. Barriers of 103 kcal/mol for pyrazine, 98 for pyrimidine, and 105 for pyridine were calculated, supporting values lower than the barrier for C-H fission in benzene, 112 kcal/mol. The lower barriers for the azines are explained by the additional contributions of azyl radical resonance structures due to the neighboring N-C interactions, which serve to further stabilize the azyl radicals. These results are related to the formation of various NO_x species produced during the combustion of heavy oils and coal.

New York University
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Department of Chemistry

223. ***Accurate Polyatomic Quantum Dynamics Studies of Combustion Reactions***

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Recent state-to-state quantum dynamics studies for H_2+ OH reaction in full dimensions show that the TD wavepacket method, using a single set of Jacobi coordinates, is inefficient for carrying out state-to-state dynamics studies for polyatomics. This led to our development of the reactant-product decoupling (RPD) approach for general state-to-state quantum dynamics studies for polyatomics. In the RPD approach, the calculation of the full-wavefunction is split into those of the reactant and product components. The calculation of the reactant component is independent of that of the product components through the use of absorbing potentials, and the calculation of the product component wavefunction involves only inelastic scattering. This general RPD approach is efficient to apply to more complex reactions with many arrangement channels and with long-range inelastic interactions. Numerical test studies of the RPD approach to three dimensional triatomic reactions demonstrated the efficiency and accuracy of the RPD approach to state-to-state dynamics studies. Application of the RPD approach to state-to-state quantum dynamics studies of a number of combustion reactions is in progress.

University of North Carolina at Chapel Hill
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Department of Chemistry

224. ***Modeling of Unimolecular Reaction Dynamics of Moderate-Sized Ionic Systems***

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The photoelectron photoion coincidence (PEPICO) technique and vuv laser methods with molecular beam cooled samples are utilized to investigate unimolecular dissociation dynamics of moderate sized, energy selected ions. Reactions with and without barriers in the exit channel, as well as non-adiabatic reactions, are investigated and analyzed with simple theoretical tools (ab initio MO calculations, RRKM with tunneling corrections, and VTST methods). The goal of these studies is to develop protocols for the use of simple theoretical tools for analyzing the rates of complex reactions such as those that occur in combustion reaction systems. In support of these studies, photoionization and pulsed field ionization studies of cold free radicals are undertaken at the chemical dynamics facility of the Advanced Light Source in order to determine the ionization energy and vibrational frequencies of the resulting ions. The experimental results supported by ab initio MO calculations yield geometries and energies of both neutral free radicals and their closed shell ions. Another approach to measuring free radical heats of formation is through the dissociative photoionization of clusters in which an internal H atom transfer leads to dissociation of a closed shell ion and a neutral free radical.

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Fargo, ND, 58105

Department of Chemistry

225. ***Infrared Laser Studies of the Combustion Chemistry of Nitrogen***

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The project under investigation is part of a broad effort to understand at a molecular level the detailed kinetics of combustion processes. The studies in our laboratory concentrate on radical-radical and radical-molecule chemical reactions that either form or destroy NO_x. Many of these reactions are important in NO_x control strategies such as thermal de-NO_x and NO-reburning. The emphasis is primarily on the quantitative determination of product branching ratios for reactions that have several possible channels, although we also measure total rate constants for some reactions when warranted. We use UV laser photolysis to inititiate these reactions, and infrared diode laser spectroscopy to probe reaction products. Some of the reactions recently studied and/or currently under study include $NH_2 + NO_2$, $HCO + NO_2$, and $CH + N_2O$, and reactions of CN and NCO with main group hydride molecules such as SiH_4 and GeH_4.

University of Oregon
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Department of Chemistry

226. *Dynamical Analysis of Highly Excited Molecular Spectra*
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A framework for analysis of highly excited vibrational states of polyatomic molecules is investigated using techniques of nonlinear dynamics, especially bifurcation theory. The goal is classification of the motions of molecules excited to the regime of chaotic dynamics, and determination of patterns resulting from these motions in experimental spectra. Several research areas are being investigated with application to species and methods of interest in combustion processes. The first is a method based on diabatic correlation diagrams applied to polyatomic spectra with chaotic dynamics, specifically, triatomics such as H_2O and larger molecules such as acetylene. For the triatomics, the critical points of an effective Hamiltonian used for fitting spectra are analyzed, giving the large-scale bifurcation structure of the molecular phase space. An assignment procedure using the bifurcation analysis, in tandem with the correlation diagram procedure, is being investigated. A more phenomenological extension to acetylene is being investigated, where the bifurcation structure is harder to obtain, and at present, unknown. The final research area, with application to experimental spectra of CS_2, is bifurcation and semiclassical quantum analysis of three degree-of-freedom systems with such strong coupling between the stretches that earlier methods of analysis of chaotic systems are inapplicable.

The Pennsylvania State University
University Park, PA, 16802

Department of Chemistry

227. *Metal Cluster Alloys and Oxides Elucidating Structural and Electronic Effects in Governing the Reactivity and Catalytic Role of Matter in Finite Dimensions*
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Despite the importance of catalysis in areas ranging from the production of energy to the control of pollutant emissions to improving the efficiency of various industrial processes, the ability to design catalysts with a high degree of selectivity and specificity is still in a stage of infancy. The current program is addressed to investigations intended to provide new insights into the physical basis for catalysis, including the influence of structure, composition, charge state, stoichiometry, and size on the individual reaction mechanisms. Clusters of metal oxides and carbides are model systems under study to: (1) determine the influence of oxidation- and charge-state on their reactivity, (2) elucidate the reaction kinetics with selected molecules, (3) determine thermochemical properties of the systems, and (4) study catalytic reactions which have counterparts to ion-molecule reactions. Investigations are directed to species involved in combustion processes (e.g., nitrogen oxides), as well as in the formation of higher hydrocarbon fuels from small organic molecules. During the past year, studies were conducted of the evolving stoichiometry of transition metal-oxygen clusters and related oxygen transfer reactions. Work on the nickel-oxide system revealed the role of stoichiometry and charge states in effecting the oxidation of NO to NO_2. Research on the spectroscopy of excess metal-containing magnesium- and calcium-oxide systems provided insight into the nature of the electronic states involved in these systems of catalytic character. Finally, in work involving metal-carbon clusters, investigations of the reactions of niobium and zirconium species were conducted, providing a new understanding of their oxidation.

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Department of Chemistry

228. *Collisional Energy Transfer of Highly Vibrationally Excited Molecules*
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A fast (~10 ns) state-of-the-art HgCdTe infrared detector has been used to measure the time-resolved FTIR emission spectrum of highly vibrationally excited NO_2 molecules as they are collisionally deactivated by room temperature NO_2 molecules with sub-collisional-period time resolution. The fast time-resolved emission spectra can be used to extract the instantaneous energy distribution of the ensemble of excited molecules during collisional quenching for the first time. It is found that the Gaussian function, often assumed for the energy distribution of highly vibrationally excited molecules during collisional quenching, is nearly identical to the experimental measurement. Time-resolved Fourier transform IR emission spectroscopy can also be used to monitor the population distribution of both the highly excited donor molecules and the energy receiving molecules during collisional quenching of highly vibrationally excited SO_2 by bath-gas molecule SF_6. The change of the SF_6 v_3=1 level population measured as a function of time is compared with that calculated based on the transition dipole coupling model with the transition dipole of highly excited SO_2 extracted from its IR emission spectra. The excellent agreement indicates that long range interaction through transition dipole coupling is responsible for the vibration-vibration energy transfer from the highly excited molecules.

229. Intermolecular Interactions of Hydroxyl Radicals on Reactive Potential Energy Surfaces
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This program is focused on characterizing the OH $X^2\pi + H_2$ potential energy surface via spectroscopic and dynamical studies of OH-H_2 entrance channel complexes. The OH-H_2 complexes are formed by stabilizing the reactive partners within a shallow well in the entrance valley to the $OH + H_2 \rightarrow H_2O + H$ reaction. Recently, infrared overtone spectroscopy has been used to examine the structural parameters of OH-H_2, including the relative orientation of the OH and H_2 partners within the complexes. The experimental spectrum agrees remarkably well with a fully ab initio infrared spectrum originating from the ground state of ortho-H_2-OH in a T-shaped OH-H_2 configuration. The infrared excitation also supplies sufficient energy to induce vibrational predissociation of OH-H_2, or to initiate reaction between the OH and H_2 partners. These processes are found to occur on a nanosecond time scale, as evidenced by the magnitude of depletions in IR-UV fluorescence depletion measurements. The quantum state selective infrared pumping of OH-H_2 should provide sufficient population transfer to allow the products of vibrational predissociation and/or reaction to be probed, and these experiments are currently underway in this laboratory.

University of Pittsburgh
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Department of Chemistry

230. Optical Imaging in Microstructures
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Our research is focused on developing the analytic capabilities of morphology-dependent stimulated Raman scattering (MDSRS) imaging. MDSRS uses the cavity modes, called MDRs, present in microstructures to enhance optical signals. Since different cavity modes occupy different regions in space, location-specific spectra can be generated. One key aspect to performing analytic imaging studies on “real” systems is determining if chemical and molecular structure variations contained within microstructures strongly influence MDSRS signal generation. We are currently preparing microstructures with known internal variations and doing MDSRS imaging experiments on these systems. We are measuring the resulting shifts in MDR wavelength and changes in MDR Q factor. These experiments will enable us to determine if it will be possible to do in situ imaging studies on complex systems such as combusting fuel droplets or biological cells.

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Department of Chemistry

231. Analysis of Forward and Inverse Problems in Chemical Dynamics and Spectroscopy
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This research is concerned with fundamental issues in molecular science, and practical solutions in chemical kinetics engineering problems. The first part of the research aims to develop and apply new algorithms to optimally draw on ab initio quantum chemistry calculations and available laboratory data in order to gain a quantitative understanding of the effect of molecular interactions on spectroscopic, dynamical, and kinetic events. Specifically, mathematical and numerical tools based on functional sensitivity analysis, inverse problem theory, and reproducing kernel theory have been developed for identifying the relationship between potential energy surfaces and observables (forward analysis), and for constructing physically acceptable potential energy surfaces from either laboratory data or ab initio calculations. Application of this methodology has led to an accurate potential surface for H_2O and the inversion of HCN pressure-broadening data to extract relaxation rates. The second part of the research aims to develop effective dimension reduction methods for constructing simplified, yet accurate, combustion models. Here, a recently formulated algebraic-based method, along with nonlinear perturbation theory, has been employed to develop rigorous and efficient nonlinear lumping schemes for combustion model simplification. Applications include significant model reduction for H_2 and CO combustion models.

Mechanical and Aerospace Engineering

232. Aromatic-Radical Oxidation Kinetics
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Elucidating the details of the combustion of the aromatic ring of monocyclic species, the key components in most fuels, is the major focus of this effort. Specific attention centers on the important aromatic oxidation intermediate, cyclopentadiene. The experimental study of pure homogeneous oxidation and pyrolysis of cyclopentadiene between 1100-1200 K and equivalence ratios between 0.6 to 1.6 has been completed. Cyclopentadiene combustion produces not only a large number of aliphatic unsaturated compounds, but also methane and aromatics, including naphthalene. The lack of observable stable intermediates, except for 3-cyclopentene-one in the composition-time profiles, obtained in the flow reactor has complicated the data interpetation and necessitated greater reliance on modeling to interpet the overall mechanism. Initial modelling used the SENKIN package, with the Emdee-Brezinsky-Glassman toluene model modified to include specific species found during cyclopentadiene oxidation by including reaction paths for the higher molecular weight species developed in this laboratory. This model consists of 155 species and 588 reactions, and is able to handle species formed up to methylnaphthalene. Although refinements are required, the model can predict the major experimental profiles quite well and even the minor species to within a order of magnitude.

233. ***Comprehensive Mechanisms for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis***
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This program addresses improving the understanding of combustion chemistry through experimental flow reactor studies in the temperature range 550-1200 K, the pressure range 0.3-20 atmospheres, and with characteristic reaction times from 0.02-3.0 seconds. Through the use of techniques based on elemental gradient-feature sensitivity and path analyses, computations are performed to obtain elementary rate information and to develop and study comprehensive chemical kinetic mechanisms. Elementary kinetic data are obtained from perturbation studies of the H_2/O_2 and $CO/H_2/$ oxidant reaction systems by small amounts of hydrocarbons and/or hydrocarbon oxygenates. Of special interest here are the reactions of HO_2 with other species. Reaction systems of interest include those for pyrolysis and oxidation of simple oxygenates (especially formaldehyde, acetaldehyde, and dimethyl ether), simple olefins (especially ethene and propene), and ethane. The research emphasizes the extension of the present knowledge, based on reaction mechanisms of these small molecules, to pressures and temperatures where the reaction of radicals with oxygen and the reactions involving RO_2 and HO_2 are important.

Purdue University
West Lafayette, IN, 47907-1393

Department of Chemistry

234. ***Multiresonant Spectroscopy and the High-Resolution Threshold Photoionization of Combustion Free Radicals***
Grant, E.R. **$109,000**
765-494-9006
765-496-2512 (FAX)
egrant@chem.purdue.edu

This project applies methods of multiresonant spectroscopy and rotationally resolved threshold photoionization to characterize the structure, thermochemistry, and intramolecular dynamics of highly excited neutrals and cations derived from combustion free radicals. The objectives of this work are: (1) To measure ionization potentials with wavenumber accuracy for a comprehensive set of polyatomic molecules of relevance to combustion modeling; (2) To determine vibrational structure for polyatomic cations as yet uncharacterized by ion absorption and fluorescence spectroscopy, including the study of anharmonic coupling and intramolecular vibrational relaxation at energies approaching thresholds for isomerization; (3) By threshold photoionization scans, referenced in double resonance to specific cation rovibrational states, to obtain information on originating-state rovibrational level structures useful for the development of neutral-species diagnostics; (4) To measure rotationally detailed state-to-state photoionization cross sections for comparison with theory; and (5) To spectroscopically study near-threshold electron-cation scattering dynamics of relevance—for example, to plasma processes such as dissociative recombination—by acquiring and analyzing rotationally resolved high-Rydberg spectra.

235. ***Probing Activated Chemical Reactions in Diacetylene and Vinylacetylene***
Zwier, T.S. **$85,000**
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The chemistry of metastable states of diacetylene (C_4H_2) and vinylacetylene (C_4H_4) are being explored using laser excitation in a small reaction tube or channel attached to a pulsed valve. Vacuum ultraviolet photoionization or resonant multiphoton ionization time-of-flight mass spectroscopy are being used to probe the molecular composition and spectroscopy of the products. Among the key products which have been identified by their ultraviolet spectroscopy and/or ionization thresholds are the following: (1) The aromatic products benzene and phenylacetylene are the dominant products of the reaction of C_4H_2* with 1,3-butadiene. (2) C_4H_2* reactions with alkenes produce hex-1-ene-3,5-diyne (C_6H_4) as an important product. (3) The C_4H_2* + C_4H_2 reaction produces both triacetylene (C_6H_2) and tetra-acetylene (C_8H_2).

Rice University
Houston, TX, 77005

Department of Chemistry

236. ***Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals***
Curl, R.F.; Glass, G.P. **$129,900**
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This research is directed at detecting, monitoring, and studying the chemical kinetic behavior by infrared absorption spectroscopy of small free radical species thought to be important intermediates in combustion. HCN and fulminic acid (HCNO) have been detected as products of the reaction of HCCN with NO. For the reaction of HCCN with O_2, HCN, hydrogen isocyanide (HNC), and CO_2 have been observed. Species searched for but not observed from either reaction include HNCO, HOCN, HCO, HONC, OH, and C_2H. The reaction of the propargyl radical (C_3H_3) with NO has been studied at total pressures ranging between 3 and 18 Torr, and over the temperature range, 195 - 475 K. The apparent second order rate constant determined for the reaction with NO varied significantly with total pressure at all temperatures studied. For example, at 295 K, the rate increased by a factor of 2.4 as the He buffer gas pressure was increased from 3 to 18 Torr. As the temperature is raised from 195 K, the rate constant at any given pressure initially decreases, reaching a minimum near 400 K and then increases again as the temperature is raised further. The K structure of the acetylenic CH stretch of propargyl radical has been assigned and analyzed.

University of Rochester
Rochester, NY, 14627

Department of Chemistry

237. ***Low-Energy Ion-Molecule Reactions and Chemiionization Kinetics***

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Crossed ion-beam—neutral beam reactive scattering experiments—are being performed with the goal of using product quantum state distributions, energy disposal measurements, and state-resolved angular distributions to extract dynamical information on collision mechanics and features of the potential surface mediating the reaction. Attention has been focused on hydrogen atom transfer reactions of O^- with D_2 and CH_4, where either complete or partial vibrational state resolution of the products has been accomplished. In the $O^- + D_2$ reaction, ab initio calculations have shown that non-collinear trajectories in the vicinity of the OD^-- D transient intermediate lead to electron detachment. Experiments in which the rotational excitation of the D_2 reagents is varied, thereby varying the bending motion in the vicinity of the OD^-- D species, are being planned to probe this critical region of the potential surface. The $O^- + CH_4$ reaction forming OH^- at a collision energy of 0.34 eV shows that the product is sharply backward scattered with significant vibrational excitation, with the products maintaining their vibrational excitation but becoming forward scattered with increasing collision energy. Backward scattering corresponds to collinear approach of incoming O^- along one of the C-H bonds, while forward scattering arises from abstraction of one of the off-axis hydrogens. The data show clear structure corresponding to excitation of the CH_3 umbrella bending vibration. A series of experiments on O^- with vibrationally excited molecules prepared by laser excitation is planned.

University of Southern California
Los Angeles, CA, 90089-0482

Department of Chemistry

238. ***Reactions of Atoms and Radicals Using Pulsed Molecular Beams***

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Unimolecular and bimolecular reactions of atoms and small radicals are studied in pulsed molecular beams. Exothermic and endothermic reactions of atomic carbon are examined using laser ablation of graphite. Endothermic hydrogen transfer reactions of $C(^3P)$ induced by translational energy with H_2, HCl, HBr, H_2S, CH_3OH, CH_3OD, C_2H_2 and CH_4 yield CH radicals. Center-of-mass collision energies with all species except H_2 peak at ~ 2 eV but can exceed 6 eV. The rotational distributions with all reactants are rather similar and can be fit to temperatures in the range 1500-2200 K. The spin-orbit and the Lambda-doublet ratios are statistical. Mechanisms are discussed using the detailed calculations available for the $C + H_2$ system, which indicate that an insertion route is open for these reactions with no or only a small barrier. The reaction with chloroform is a prototype of an exothermic system; it yields CCl products whose energy disposal agrees with the predictions of statistical theories. In preparation for studies of free radical decomposition, an ion imaging detector has been introduced into a crossed molecular beams TOF machine, incorporating ion optics optimized for high resolution. The hydroxymethyl radical has been prepared by the photoinitiated reaction of Cl and methanol.

239. ***The Stabilization Theory of Dynamics***

Taylor, H.S. **$67,500**
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This work is concerned with the development of a scaling method for assigning to each highly excited molecular vibrational level in the irregular part of a spectrum a classical region of phase space where, locally, the trajectory motion reflects the underlying dynamics. The classical structures, when quantized, will give approximately the level's dynamic assignment. The assignment will be extended upward from the regular region, where tori assignment is the rule, into the irregular region of mixed phase space, where structures as unstable short periodic orbits and broken resonant tori replace tori as the quantizing structures. The assignment theory will also be developed to start from experimental data fitted to algebraic resonant Hamiltonians eliminating the need for potential surfaces. A few applications will be made to new molecular cases such as HO_2, CS_2, and other systems that become of interest and have available the required potential energy surface or algebraic Hamiltonian.

240. Reactions of Small Molecular Systems
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The focus of this work is on complex reaction mechanisms of prototypical molecules and radicals that display phenomena important in combustion chemistry. In the case of NO_3, a detailed understanding is sought for the two unimolecular reaction pathways: $NO + O_2$ and $O + NO_2$, both separately and in competition with one another. This is a case of nearly identical energy thresholds and qualitatively different transition states (i.e., tight versus loose). For the $NO + O_2$ channel, which has a tight transition state, tunneling will also be examined. The main experimental tools are double-resonance and time-resolved pump-probe methods. Detecting NO_3 and NO via LIF. C_2H_2 experiments will examine the threshold region, specifically, the roles of intersystem crossings and reactions via zeroth-order triplet versus singlet surfaces. For the case of C_2HD, the H/D ratio provides a good diagnostic. In this case, H atoms are detected via 1+1 photoionization or by using the high-n Rydberg time-of-flight (HRTOF) method. With the latter, detailed product state distributions are obtained from the c.m. translational energy distributions, and high sensitivity and good resolution have been demonstrated. Photolytically prepared radicals such as C_2H are also examined.

Stanford University
Stanford, CA, 94305

Department of Mechanical Engineering

241. Spectroscopy and Kinetics of Combustion Gases at High Temperatures
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This program involves two complementary activities: (1) development and application of cw laser absorption methods for measurement of species concentrations and fundamental spectroscopic parameters at elevated temperatures; and (2) shock tube studies of reaction kinetics relevant to combustion. Species of interest in the spectroscopic portion of the research include OH, NH_2, H_2O, and CH_3. Recent shock tube studies of reaction kinetics have been focused on the reactions $H + O_2 (+M) \rightarrow HO_2 (+M)$, with M = Ar, N_2 and H_2O; $C_2H_6 (+M) \rightarrow 2\ CH_3 (+M)$, with M = Ar; and $NH_2 + NO \rightarrow$ products, including branching ratios.

State University of New York at Stony Brook
Stony Brook, NY, 11794

Department of Chemistry

242. Ionization Probes of Molecular Structure and Chemistry
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Ionization processes in intense, wavelength-tunable laser fields are being used in new spectroscopic techniques to investigate the structure and chemistry of ions and molecules. Resonant multiphoton ionization, laser threshold ionization spectroscopy, and photoinduced Rydberg ionization (PIRI) spectroscopy provide sensitive tools for detecting transient species and for examining the excited state structure and dynamics of molecules. These methods also provide means for the detection and identification of minute quantities of molecular species in difficult environments, such as the mixtures produced in combustion reactions. Newly developed primary tools are mass analyzed threshold ionization spectroscopy (MATI), providing high resolution ion vibrational spectra of selected molecules, and PIRI, giving access to the excited states of ions. In MATI, ion state energies are measured by ionizing highly excited neutral states near each ionization threshold with an electric field. In PIRI, the final ionization is accomplished by the absorption of a further photon. The ions produced in either method are sent through a mass spectrometer so the optical spectrum of each mass is obtained with high sensitivity and resolution. These techniques are being used to refine our knowledge of the properties of benzene and substituted benzenes, molecules which play an important role in many combustion processes.

University of Utah
Salt Lake City, UT, 84112

Department of Chemistry

243. Spectroscopy of Polyatomic Transition Metal Clusters and Unsaturated Transition Metal-Ligand Complexes
Morse, M.D. **$103,000**
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Electronic spectroscopy is used to investigate the chemical bonding and electronic structure of unsaturated transition metal-ligand complexes and polyatomic transition metal clusters. Laser ablation of a transition metal target in the throat of a supersonic expansion of helium containing 3% CH_4 is used to generate a variety of unsaturated metal-ligand species for study by resonant two-photon ionization spectroscopy. In studies of diatomic transition metal carbides, our spectra establish ground states of $\Omega = 3$ [presumably $^3\Delta_3$] for FeC, $\Omega = 0$ [presumably $^1\Sigma^+$] for NiC, $\Omega = 0$ [presumably $^3\Sigma^-$] for MoC, $\Omega =$

0 [$^1\Sigma^+$] for RuC, and $\Omega = 0$ [either $^1\Sigma^+$ or $^3\Sigma^-$] for PdC. Ground state bond lengths of 1.596, 1.631, 1.688, 1.608, and 1.712 Å are found for FeC, NiC, MoC, RuC, and PdC, respectively. We have also recorded electronic spectra of the organometallic radicals CrCCH, $CrCH_3$, $NiCH_3$, and NiC_2H_4. Excited state M-C stretching vibrational frequencies of 426 and 455 cm^{-1} have been measured for CrCCH and $NiCH_3$, and a ground state Cr-C stretching frequency has been measured to be 509 cm^{-1} in $CrCH_3$. Rotationally resolved spectra have been recorded for all four molecules and are now being analyzed.

244. Thermochemistry and Reactivity of Transition-Metal Clusters

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The objective of this project is to obtain information regarding the thermodynamic properties of transition metal clusters, their binding energies to various ligands, and their reactions by using a metal cluster guided ion beam mass spectrometer. Recent progress includes studies of the reactions of vanadium, chromium, and iron cluster ions with D_2, O_2, and CO_2. In the O_2 reactions, cluster dioxide product ions are formed efficiently in exothermic processes for all three metal systems examined. Less abundant are cluster monoxide product ions which are formed in endothermic reactions. To form such species more easily, reactions with CO_2 have been studied. CO_2 is a good donor of a single oxygen atom because of the strong CO bond energy. Analysis of the kinetic energy dependence of these reactions is complicated, but thermodynamic information about the binding energies of one and two oxygen atoms to the clusters can be obtained. The trends in this thermodynamic information provide clues regarding the geometric and electronic structures of the bare clusters. Good agreement between this thermochemistry and that for bulk phase metal interactions with O are also found.

University of Virginia
Charlottesville, VA, 22901

Department of Chemistry

245. Photon and Electron Stimulated Surface Dynamics of Single Molecules

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804-924-3710 (FAX)
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The aim of this project is to initiate fundamentally new studies of the surface dynamics of individual molecules. The photochemical and electrochemical dynamics of single molecules are being examined using our newly built scanning tunneling microscope (STM) at surface temperatures sufficiently low (≤ 40 K) that adsorbate thermal diffusion is quenched. The ability to study individual events occurring for molecules absorbed at specific surface sites or next to coadsorbed molecules with specific relative stereochemical geometries can provide us with dynamical information that is unattainable from conventional studies involving ensembles of molecules. Specific goals are to examine, at the level of individual molecules: (1) the photodissociation dynamics of adsorbates whose photofragments remain trapped on the surface, (2) the dynamics of localized adsorbate chemistry induced by electrons emitted from the STM tip, (3) bimolecular photoreactions between coadsorbed molecules with prearranged relative stereochemistry. The research should improve our fundamental understanding of surface chemistry and the technological prospects for spatially localized processing of materials by photons from focused laser beams and electrons emitted from STM tips. Initial experiments have shown that photoinduced dissociative electron attachment of methylbromide on Pt(111) produces hot Br atoms, which directly abstract surface Pt atoms to leave monatomic vacancies behind.

University of Wisconsin at Madison
Madison, WI, 53706

Department of Chemistry

246. Vibrational State Control of Photodissociation

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The fundamental and practical importance of highly vibrationally excited molecules in combustion processes, atmospheric chemistry, plasmas, and a host of other environments motivates their detailed experimental investigation. This research uses a combination of laser excitation to prepare highly vibrationally excited molecules with single-quantum-state resolution, and spectroscopic detection to monitor the excited molecule or its decomposition product, in studies of the unimolecular reaction, photodissociation, and bimolecular reaction dynamics of vibrationally energized molecules. A collection of state preparation and detection techniques gives these measurements broad scope. The excitation approaches are vibrational overtone excitation, stimulated emission pumping, and stimulated Raman excitation, and the detection methods are UV and VUV laser-induced fluorescence and laser-induced grating spectroscopy. By selectively preparing vibrational states and subsequently dissociating or reacting them, these experiments explore normally inaccessible regions of both the ground and electronically excited potential energy surfaces. These approaches have even achieved laser control of the course of a chemical reaction. The experiments provide new insights into the structure and dynamics of vibrationally excited molecules, which play an important role in fundamentally and practically important processes.

247. Spectroscopy Studies of Methyl Group Internal Rotation and of Organic Free Radical Vibration

Weisshaar, J.C. **$93,000**
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The goal of this work is to develop techniques for measuring vibrational spectra of polyatomic neutral free radicals. Such spectra can provide in situ probes of radical concentrations, as well as fundamental insights useful in modeling of combustion reaction dynamics. An important unsolved problem which we are addressing is the effect of nearby radical centers on the barrier to methyl group internal rotation. Statistical modeling of chemical reactions requires good intuition about whether internal rotation is nearly free or hindered, since the density of rovibrational states is very sensitive to the internal rotation barrier. Yet we know next to nothing experimentally about how radical centers affect such barriers. We plan to use stimulated emission pumping (SEP) in combination with ab initio electronic structure theory to attack this problem. Fluorescent radicals of current interest are methyl-substituted vinoxy radicals and benzyl radicals.

Atomic, Molecular, and Optical Physics

California Institute of Technology Pasadena, CA, 91125

Division of Physics, Mathematics, and Astronomy

248. Spectroscopy with Nonclassical Light
Kimble, H.J. **$150,000**
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Radiative interactions of simple atomic systems with light, which is manifestly quantum or nonclassical in its characteristics, are investigated. Examples of nonclassical radiative fields include squeezed states of light and states that exhibit photon antibunching and sub-Poissonian photon statistics. Frequency tunable sources of such fields are being developed in the laboratory with the objective of exploring a variety of applications in atomic spectroscopy. From the perspective of quantitative spectroscopic analysis, squeezed light offers the potential for enhanced sensitivity beyond the usual quantum limit set by the vacuum fluctuations of the electromagnetic field (the so called coherent-state or shot-noise limit). However, in addition to the possibility for improved measurement sensitivity, the coupling of atoms to squeezed, antibunched, or sub-Poissonian fields should lead to fundamentally new atomic radiative processes relevant to diverse problems in optical physics, including resonance fluorescence and laser operation. Apart from the scientific objectives, the research program should make important contributions to a number of areas of technological significance, including spectroscopic detection of weakly absorbing or transient species and frequency metrology for optical fields separated by terahertz intervals.

Department of Chemistry

249. Electron Collisions in Processing Plasmas
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This work seeks to develop methods which produce reliable estimates for electron-molecule scattering cross sections for energies below about 50 eV, characteristic of plasmas used for material preparation in the electronics industry. Work is directed toward creating scalable computational methods that exploit the most advanced parallel computers to treat the largest polyatomic molecules possible; understanding the dynamics of collisions with polyatomic molecules, including resonant scattering, vibrational excitation, electronic excitation, attachment, and ionizaiton; and producing basic data that will be useful in applications, notably simulation of the plasmas used in semiconductor fabrication. The capabilities of an existing parallel electron-molecule scattering program will be extended to allow multiconfiguration target wave functions for both ground and excited electronic states of the molecule, and a new treatment of target polarization effects in very-low-energy scattering will be implemented. The accuracy of the calculated cross sections, and their influence on plasma properties, will be evaluated via numerical simulations. Work will be conducted in collaboration with the Intel Computer-Aided Design department and with the plasma modeling effort at Syracuse University.

California State University, Fullerton Fullerton, CA, 92834

Department of Physics

250. Few-Body Coulomb Systems
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This project aims to advance the fundamental description of interacting charged particles, in particular, of few body Coulomb systems composed of negative electrons and the positive ions they are attached to. The objective has been to better enable computer assisted science by blending basic theoretical understanding with key laboratory studies. Advances in bright, high-energy light sources have promoted double photoionization as a fundamental technique for studying the few-body Coulomb problem, including double escape near threshold. A Wannier description of the unstable equilibria in the few-body potential to include non-zero total angular momentum was made. A key element is the electron-pair center-of-mass momentum, which is fully represented by the momentum of the recoiling ion. General and Wannier-theory predictions for recoil-ion angular distributions were found to be in fair agreement with recent experimental observations. In a related project, antiproton impact ionization of hydrogen near threshold was analyzed and results showed that the dynamical instability is displaced from the potential saddle. The threshold law for fundamental Coulomb instabilities was derived, and negative ion probes for their observation were considered.

Clark Atlanta University
Atlanta, GA, 30314

Center for Theoretical Studies of Physical Systems and Department of Physics

251. ***Studies of Photon and Electron Interactions with Atoms and Ions***

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Electron and photon interactions with ground and excited atoms, ions, and molecules of importance in lasers, astrophysical, and laboratory fusion plasmas, are studied to understand the underlying physics, and the results are used to guide both theory and measurements. Two new theoretical methodologies have been developed for small-angle electron differential cross sections (DCS) for optically allowed transitions in atoms, ions, and molecules and have been used successfully. They provide a stringent test of both theory and experiment, and are utilized to help measurements and calculations obtain reliable small-angle, particularly at zero degree, DCS for optically allowed transitions. The first method is a dispersion relation for the electron DCS in the momentum transfer squared, K^2, at fixed energy E, which leads to a complex angular momentum Regge pole representation. This description, which embeds the more reliable large scattering angular measurements, allows an accurate extrapolation of the generalized oscillator strength (GOS) down to $K^2 = 0$, yielding the optical oscillator strength (OOS). This method has been employed to justify the successful universal extrapolation method. The second method is the recently developed theory of the GOS for forward electron scattering for optically allowed transitions in atoms, molecules, and ions. The method provides a unique path to reach the OOS at $K^2 = 0$ without traversing the nonphysical region. These methods are currently being used to study small-angle electron DCS for many transitions. They reveal that many DCS near zero scattering angles are poorly known, suggesting a need for careful investigations. The R-matrix method is used with extensive configuration interaction target wave functions that account for correlation and core-polarization effects. It is used to calculate integral and differential cross sections. Detailed multistate phototoinization calculations are performed for ground and innershell excited states to investigate and understand recent predictions and experimental measurements demonstrating strong enhancement of shake-up satellites and many-electron effects in sodium and potassium.

Colorado State University
Fort Collins, CO, 80523

Department of Physics

252. ***Ion/Excited-Atom Collision Studies with a Rydberg Target and a CO_2 Laser***

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Experiments now in progress study collisions between ions of various charges, obtained from the CRYEBIS ion source at Kansas State University, and highly excited neutral atoms, in the form of a “Rydberg target” formed by CW laser excitation of an Rb atomic beam. Completed experiments have studied (1) the total charge transfer cross section for ions of various charges and velocities incident on an n=10 Rydberg target, and (2) the product state energy distribution for singly charged ions at 0.1 a.u. velocity. Now in progress are experiments studying the product state energy distribution versus ion charge and velocity. The energy distribution studies are carried out using a Doppler-tuned CO_2 laser to probe the relative population of atoms (or ions) of one particular binding energy, as the Rydberg target binding energy is varied.

University of Colorado
Boulder, CO, 80309

Department Physics

253. ***Physics of Correlated Systems***

Greene, C.H. **$104,000**
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This project develops a quantum mechanical description of correlations for many different systems in atomic physics. The focus is on correlations, otherwise termed the coupling or nonseparability of different degrees of freedom, because these are responsible for all forms of energy transfer from one type of motion into another. Recent experiments on Bose-Einstein condensed alkali atoms have sparked an effort to unravel the many-body physics. Efforts have explained the remarkable double condensate, in which rubidium atoms in two different internal spin states are condensed in the same trap and can exchange energy back and forth. Exploration of the behavior of open-shell atomic systems in regimes that are not readily handled by conventional theoretical methods based on an independent electron approximation is being continued. This year, a major effort was completed to interpret new experiments on high lying neon doubly-excited states in an energy range that has severely challenged theoretical methods. The computational demands led to the introduction of a new approach to the solution of the corresponding variational equations. Progress was also made on the photodetachment of negative ions, which pose a greater challenge than neutrals owing to the stronger electron-electron interactions.

University of Connecticut
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Department of Physics

254. Experiments in Ultracold Collisions
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Laser-cooled atoms are being used to investigate atomic collisions at temperatures below 1 mK. Interest in these ultracold collisions stems from the large collisional deBroglie wavelength, the dominant role played by the long-range interatomic potentials, and the fact that the collision time can exceed the excited-state lifetime. Applications of laser cooling (e.g., Bose-Einstein condensation) generally require high density, where inelastic collisions can be a significant loss mechanism. Understanding and/or control of these collisions is important for future progress. In our experiments, diode lasers are used to confine rubidium atoms at high density in a laser trap. Inelastic collisions are observed by measuring the loss rate of atoms from the trap. The dependence of the trap-loss collision rate on trap parameters has been investigated in detail and suppression of inelastic collisions by “shielding” the atoms with laser light has been demonstrated. A cooperative effect caused by collisional flux enhancement was observed using two separate lasers to induce collisions. This effect has been used to follow ultracold collisions in real time. Due to the low collisional velocity and the long range of the atomic interactions, the collision time can exceed 10^{-7} s. Collisions involving the highly-excited 5D level of Rb, populated with efficient pulsed excitation, are also being investigated.

Cornell University
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School of Applied and Engineering Physics

255. Interactions of Highly Charged Ions with Atoms at keV Energies
Kostroun, V.O. **$318,000**
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Low energy, multiply charged ions react very strongly with atoms, molecules, or surfaces. At hyperthermal energies, (few eV to hundreds of eV), the dominant reaction is electron transfer from target to ion. True one electron transfer is state selective, and could be used to determine the atomic composition of surface layers. The objective of this research is to use the high reactivity of low energy, multiply charged ions and state selectivity of the electron capture process to form nanometer thick oxide and nitride layers on a semiconductor substrate and to study their atomic composition. This work has shown that a 1300 eV beam of N^{4+} at an incident angle of 2^o to a Si(111) surface comes off mostly as N^{3+}, while at 8500 eV mostly as N, or fully neutralized projectiles, as commonly expected. The angular width of the N^{3+} peak is 1^o, the width of the primary N^{4+} beam, and the angular distributions of scattered projectiles that have gained two and three electrons are 4-6 times broader. This would suggest that true one electron transfer to the projectile took place in a single collision with a surface O or Si atom. From an energy gain measurement, it should now be possible to identify the target atom.

Harvard University
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Harvard-Smithsonian Center for Astrophysics

256. Theoretical Investigations of Atomic Collisions
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Collisions at ultralow temperatures are under investigation as a source of information about the interactions between atoms at large distances and between atoms and surfaces at large distances. Methods for producing ultracold molecules are being explored. Calculations are in progress on threshold laws for vibrational quenching of hydrogen, lithium, and sodium molecules. A new procedure for incorporating the effects of correlation in multiple ionization events has been developed and tested on the single and double photoionization of helium and the negative hydrogen ion.

Kansas State University
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Department of Physics

257. Atomic Physics of Strongly Correlated Systems
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This research program focuses on the physics of strongly correlated atomic systems. The hyperspherical method is being developed for studying three-electron atomic systems, with the main emphasis on doubly and triply excited states. New numerical schemes are being developed such that the adiabatic potential curves for any symmetry can be calculated for any three-electron systems. The first goal is to show that there are no bound states or resonances for doubly negatively charged atomic hydrogen. For doubly excited states, the goal is to develop a hyperspherical close coupling method to obtain accurate positions and widths and photoabsorption cross sections. For triply excited states, the goal is to analyze the correlation patterns of these states in order to find new classification schemes. The method will also be developed for three-valence electron systems such that optical spectra and low-lying resonances can be analyzed. In ion-atom collisions, the close coupling method using two-center atomic orbitals will be used to perform calculations for collision systems in which the experimentalists are interested. The focus will be on the detailed partial cross sections to individual final states, as well as differential cross sections. The collision system of protons with helium will be further examined with a larger extended basis set following the scheme developed last year.

258. *Atomic Physics with Highly Charged Ions*

Richard, P.; Ben-Itzhak, I.; Bhalla, C.P.; **$1,855,000**
Carnes, K.D.; Cocke, C.L.; DePaola, B.D.;
Gray, T.J.; Hagmann, S.; Legg, J.C.;
Lin, C.D.; Stockli, M.P.; Thumm, U.
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The primary goal of the project is to understand at the most basic level binary collisions involving highly charged ions and individual targets and to provide conceptual frameworks and descriptions useful in understanding interactions of highly charged ions with matter in more complex situations. The facilities used include: (a) a cryogenic electron beam ion source (CRYEBIS) capable of delivering highly charged ions up to bare argon and Xe^{46+} at velocities between 0.1 and 2.0 a.u., (b) a tandem-LINAC accelerator delivering fast beams with specific energies up to 4 MeV/u in charge states up to, for example, hydrogen-like chlorine, and (c) an ion-ion collision facility. The targets used include neutral gases, ions, Rydberg atoms, clusters, and solid surfaces. The nine main areas of research are electron production in ion-atom collisions, quasi-free electron-ion processes in ion-atom collisions, single and double electronic transitions in ion-atom collisions, collisions with and production of Rydberg atoms and ions, ion-ion collisions, ion-molecule collisions, ion-surface and ion-C_{60} interactions, synchrotron radiation studies of atoms using cold-target recoil momentum spectroscopy (COLTRIMS), and ion-atom collision theory. Two areas of emerging research are: (1) the discovery of new symmetries in low-energy ionization of atoms by slow projectiles performed with COLTRIMS coupled with electron momentum imaging; and (2) the discovery of narrow electron jets in the forward and backward directions of electron spectra from swift ion-solid collisions. These jets of electrons with a 2.5^o half-angle divergence are interpreted in terms of the channeling of electrons in the plasma-like wake of the projectile tracks in carbon foils. Color images of the data demonstrating these effects can be viewed on the J R Macdonald Laboratory home page at www.phys.ksu.edu/area/jrm/ under “Emerging Research.”

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Department of Physics and Astronomy

259. *Coherent Excitation of Autoionizing Resonances*

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Atomic ionization by electron impact is being investigated by (e,2e) spectroscopy. Experiments with a cadmium target have observed interference effects between partial waves of differing multipolarity. Pairs of (e,2e) energy spectra are measured at three carefully chosen ejected-electron directions in the energy range dominated by autoionization via Cd $4d^95s^25p$. Interference effects are enhanced by taking the sum and difference of the spectral pairs. A comprehensive set of spectra have been obtained for an incident electron beam energy of 150 eV and scattering angles between 2° and 18°, which covers the range of momentum transfer 0.2 to 1 au. The experimental results have been compared with a plane wave Born approximation calculation. It is found that the calculated monopole and quadrupole phases (relative to the dipole) are incorrect by $+/-\pi/4$ at small momentum transfer; in fact, a simple constant correction to these phases appears to be valid over the entire momentum transfer range investigated. The relative Born magnitudes are extremely good for the spectral pair taken along the momentum-transfer axis, but are extremely bad for the other two chosen directions. With increasing scattering angle, a reduction in the $4d^95s^25p\ {}^3P_1/{}^1P_1$ intensity ratio in the sum spectra is observed, probably due to an increase in exchange scattering. At the largest momentum transfer, previously unobserved $4d^95s^25p$ J=3 autoionizing levels are seen. A second (e,2e) spectrometer has been configured for similar interference experiments on helium autoionizing levels.

260. *The Dynamics of Weakly-Bound States in Collisions and Fields*

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The dynamics of atomic Rydberg states in time-dependent external fields and in ion-atom collisions are investigated using theory. Dynamical processes involving Rydberg atoms are central problems of plasma physics, but are difficult to predict quantitatively due to the large numbers of states coupled by any external field. A theory describing the mixing of nearly degenerate Rydberg states in ion-atom collisions is now complete and in good agreement with absolute experimental measurements; this theory is fully quantum mechanical and based on a Floquet analysis of the collision process. Classical studies of charge transfer reactions involving Rydberg targets are fueling new experimental investigations into the dynamics of electron capture. A study of multiphoton microwave spectroscopy of Rydberg states has resulted in a new formulation and understanding of Floquet theory, complementing decades of experimental work in the field. A conclusive demonstration of the utility of Floquet theory for the description of dynamics in half-cycle electromagnetic pulses is emerging from an analysis of recent experiments in which Rydberg atoms pass through a cavity containining a circularly polarized microwave field. Finally, new theoretical models of the experimental technique of selective field ionization are now in qualitative agreement with observations.

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Department of Physics

261. Hydrogen Atom and Molecule Collisions
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Collisions of excited atomic hydrogen with other atoms and ions are studied by emission spectroscopy in the infrared, visible, and vacuum ultraviolet by laser induced fluorescence and by theoretical work on atomic spectral line broadening. In addition to H_2, H_2^+, and H_3^+, the atom-atom systems considered are those with H in combination with C, N, and O, leading to the radicals CH, NH, and OH, with applications to combustion, astrophysics, plasma processes, and the basic physics of spectral line broadening. Work is in progress now on observations and theory of the shape of the Lyman-β line of atomic hydrogen with the development of a laser-produced plasma in the jet from a pulsed valve to permit observations in the windowless vacuum ultraviolet. Other experiments on a laser-produced plasma in a static cell are being used to study collisions of more than two hydrogen atoms, in order to understand the effects of many-body collisions on spectral line formation. The addition of O in very small quantities yields the OH^+ ion. Its reactions to produce OH, and the subsequent radiative dissociation into atomic O and H, are followed with spectroscopic diagnostics.

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Department of Physics

262. Theoretical Hyperfine Structure Constants and Lifetimes for Transition Metal Atoms and Ions
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Transition metal atoms are technologically important for plasma diagnostics, catalysis, deep level traps in semi-conductors, hydrogen storage, and astrophysics. The large correlation and substantial relativistic effects which determine their electronic energy levels are subjects of this work. Wavelengths calculated for the unusual M1 $3d^4$ $^5D_3$ to $^5D_2$ transition differ by 5% from measurements made on Xe^{32+}, Ba^{4+}, Nd^{38+}, and Ga^{42+}. This transition is unusual because its wavelength was found to be independent of nuclear charge. The discrepancy has been reduced to below 2%; the major corrections are due to magnetic Breit and correlation effects. The presence of second order hyperfine structure effects in the La I $5d^2$ 6s ^2G levels was confirmed and accurate values calculated. Work on lifetimes of La II and Cs II is continuing. Resonance f-values for Kr I are being studied using relativistic many body perturbation theory to determine which of the conflicting experimental results are accurate.

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Department of Electrical Engineering and Computer Science

263. Atomic Processes in High Energy Density Plasmas
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Several important plasma atomic processes are studied in a controlled manner. These studies are enabled by the recent invention of ultrashort-pulse-duration lasers, which produce plasmas with independently controllable parameters. One such process is continuum lowering, which arises in dense plasmas when the excited states of an ion are perturbed by the close proximity of neighboring ions. Our study of this process addresses a basic question: how does the degree of ionization depend on the ambient plasma density? Continuum lowering—by affecting the degree of ionization—also ultimately determines the collisional ionization rate. It is thus fundamental to our understanding of dense plasmas, such as those used in material processing, laser-ablation for thin-film deposition, x-ray lasers, inertial confinement fusion, and astrophysics. Recently, it was found that bound states, which are observable in low density plasmas, disappear at high density. XUV absorption and emission spectroscopy with simultaneously high-spectral (sub-angstrom), temporal (sub-picosecond), and spatial (sub-micron) resolution are used to make these observations. This is accomplished by coupling an ultrashort-duration laser-produced continuum-x-ray source with an x-ray imaging spectrometer and a jitter-free x-ray streak camera. The experimental results are compared with the predictions of current theoretical models (Debye-Huckel, Stewart-Pyatt, and ion sphere) by means of computer simulation and analysis.

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Department of Physics and Astronomy

264. Dynamics of Few-Body Atomic Processes
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This project is concerned with elucidating the dynamics of few-body atomic processes. Single and multiphoton detachment studies are conducted of negative ions, particularly the negative alkali metal ions, using eigenchannel R-matrix methods. A major goal is to determine the role of high doubly-excited, two-electron states below high excitation thresholds on such processes. This role will be determined by detailed analyses of resonance energies, two-electron state density plots, resonant and non-resonant cross section components, etc. Contrasts and similarities between negative ion spectra will also be determined and compared to that of the prototypical 3-body Coulomb system, H$^-$. Long-range interactions between alkali metal atoms that are relevant to experimental studies of such atoms in traps are also being studied.

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Department of Physics

265. Energetic Photon and Electron Interactions with Positive Ions
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This project involves complementary experimental investigations of inner-shelll excitation and ionization of multiply charged positive ions by energetic beams of electrons and photons. Absolute electron-impact ionization cross-section measurements are being carried out at the multicharged ion research facility at the University of Nevada/Reno using a new crossed-beams apparatus based on the “animated-beams” technique. Ion beams are produced by a 14.4 GHz electron-cyclotron-resonance (ECR) ion source. A high-efficiency electron spectrometer is being developed to detect and energy-analyze ejected electrons for the first time from such collisions. The photoionization measurements will be conducted at the Advanced Light Source, for which an experimental end-station is being designed and constructed for the new undulator beamline 10.0. This collinear-beams apparatus will facilitate absolute photoionization cross section measurements for both negative and positive ions, including multiply charged ions to be produced by a permanent-magnet ECR ion source. A common objective of these synergistic electron and photon impact experiments is a deeper understanding of the complex multielectron interactions that govern charge-changing processes involving ions in high-temperature environments, such as those occurring in stellar, x-ray-laser, and thermonuclear fusion plasmas.

266. Screening Resonances in Plasmas
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The interaction potential between atomic ions and electrons in plasmas has consistently been modified to include short-range order and dynamical screening effects introduced by neighboring ions and fast electrons. These modifications determine one-electron properties (e.g., spectral lines which serve as key quantities in plasma diagnostics) as well as more-electron properties (e.g., dielectronic recombination rates which account for plasma losses). So far, the applications have been restricted to the usual Debye-Hückel theory which has been used to extend standard and non-standard atomic structure programs. Furthermore, the approach to screening has been generalized to encompass also dynamic screening effects in order to account for ion motions. The approach allows the simultaneous evaluation of level broadening and continuum threshold lowering. Basic features of line broadening have been incorporated into the theory, while line splitting (due to deviations of the immediate ion environment from sphericity) is presently being programmed. Calculations for the important case of a hydrogen plasma exhibit an unexpectedly high abundance of negative hydrogen ions in a variety of plasma conditions and even the possibility of excited states of this ion. The main focus of this study, the occurrence and stability of the negative hydrogen ion in plasmas, has so far been of interest for astrophysical plasmas, this ion being the main contributor to the opacity of white dwarf stars and one of the main contributors to the opacity of the solar chromosphere. The present findings indicate, however, that the opacity of a broader range of plasmas may be affected also; e.g., laboratory plasmas and, possibly, even fusion plasmas.

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Department of Physics and Astronomy

267. H$^-$ Spectroscopy
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Studies continue on the spectroscopy of the negative ion of hydrogen. Earlier work on this project was done on the 800 MeV H$^-$ beam at LAMPF using laser beams Doppler-shifted into the vacuum ultraviolet. More recent measurements are concerned with EPD (excess photon detachment) processes in H$^-$ using a 35 keV beam at Los Alamos. Observation of the lowest singlet D resonance in H$^-$ in absorption of two photons by the ground state demonstrated the feasibility of using nonlinear photoexcitation to access other dipole-forbidden states in this ion. In a related measurement demonstrating the feasibility of non-resonant EPD, a seeded YAG 1.06 pulsed laser beam was focused on the H$^-$ beam and the energy spectrum of the detached electrons observed. Two electron energy groups, separated by the energy of a single light quantum, are observed in the photodetachment continuum. From the angular distributions, the ratio of D to S wave production is deduced. The most recent measurement repeated the D resonance study using deuterium, allowing us to observe, for the first time, an isotopic shift in the energy of the resonance, exhibiting directly the nature of the electron-electron correlation. Further work is anticipated in collaboration with a Danish group at Aarhus.

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Department of Physics

268. Atomic Structure of Highly-Charged Ions
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Atomic properties of multiply-charged ions are investigated using excitation of energetic heavy-ion beams. Spectroscopy of excited atomic transitions is applied from the visible to the extreme ultraviolet wavelength regions to provide accurate atomic structure and transition rate data in selected highly ionized atoms. High resolution position-sensitive detection has been introduced for measurements in the extreme ultraviolet region. The detailed structures of Rydberg states in highly charged beryllium-like ions are measured as a test of long-range electron-ion interactions. The measurements are supported by multiconfiguration Dirac-Fock calculations and by many-body perturbation theory. Additional studies of high-angular-momentum Rydberg transitions are being performed to establish reference wavelengths and improve the accuracy of ionization energies in highly charged systems. Precision wavelength measurements in highly charged few-electron ions are underway as tests of the most accurate relativistic atomic structure calculations. Lifetime measurements for allowed and forbidden transitions in highly-charged ions are also being performed. Precision lifetime measurements in laser-excited alkali atoms have been initiated to establish the accuracy of relativistic atomic many-body theory in many-electron systems.

269. Precision Measurements of Atomic Lifetimes in Alkali Like Systems
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This project focuses on precision measurements of excited state lifetimes in neutral alkali and alkali-like charged systems. Scientists in astrophysics, geophysics, and plasma fusion depend on such lifetime measurements as means for calibrating relative values of oscillator strengths. These atoms also provide the simplest open shell systems for detailed comparisons between experiment and theory. Lifetime measurements also provide a means for testing atomic wavefunctions at large radii to extract correlation and polarization effects which have an increasing influence along the alkali-like isoelectronic sequences. The goal of this project is to address these needs experimentally and provide tests for atomic theory. An apparatus has been constructed for measuring atomic lifetimes by laser-excitation of a fast-atomic beam. This approach is extremely versatile and can be applied to a wide variety of atomic systems. The experiments are being carried out in the new Atomic Physics Accelerator Laboratory at Notre Dame (APALaND).

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Department of Physics

270. Electron Transfer, Ionization, and Excitation in Atomic Collisions
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The processes of electron transfer, ionization, and excitation in intermediate-and high-energy ion-atom and ion-molecule collisions are studied theoretically. Calculations of electron transfer and ionization in collisions of bare ions, H^+ to N^{7+}, with $C^{5+}(1s)$ have been performed over the energy range 125-1,000 keV/amu using a coupled-channel approach with Sturmian pseudostates to account for the strong interaction among the various channels. This work is motivated partly by the need to explain α-particle losses in the Tokamak Fusion Test Reactor. Double excitation of helium atoms in collisions with protons has also been studied using this approach. Accurate strong-potential Born-type calculations, including initial channel distortion, have been performed for 2s, 2p to 1s and 1s to 2s, 2p electron transfers by protons on target atoms (C, Ne, and Ar) at 0.1-20 MeV energies. Very limited work on these processes has been carried out. Lastly, the exact second-order Born approach has been applied to electron transfer in collisions of protons with spatially oriented hydrogen molecular ions at collision energies in the range of 0.5 to 10 MeV. Interference effects deriving from the two target nuclei have been studied.

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Department of Physics and Engineering Physics

271. Molecular Structure and Collisional Dissociation
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Electron collision techniques are used to probe the structure and the collisionally induced break-up of various technologically important species. Work during the past project year focused on ionization and dissociative ionization studies of SiH_4, and the free radicals SiH_x and on NH_x (x=1-3). This work is motivated (1) by data needs for fundamental processes in low-temperature plasmas and the further development and quantitative interpretation of plasma diagnostics techniques (e.g., threshold ionization mass spectrometry) and (2) by fundamental aspects (comparison of measured data with calculations and establishment of scaling laws and data trends for targets of similar structure). A special aspect of this research was to contrast the ionization behavior of halogen-containing vs. hydrogen-containing molecules and radicals. Because of the unique ionization properties of the halogen-containing species, future work will focus entirely on systematic studis of various compounds containing Cl and F. In terms of ionization cross section calculations, work continued on the extension of semi-empirical and semi-classical methods to calculate cross sections for the multiple ionization of atoms by electron impact, and for the ionization of molecules and free radicals.

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272. Behavior of Two-Electron Atoms in a Radiation Field

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This project is a theoretical study of the interaction of an atomic system with a synchrotron or laser radiation field. The focus is on atomic systems containing two electrons, i.e., the helium atom and the negative hydrogen ion. Particularly interest is in exploring the correlation between the two electrons, and how this is influenced by the radiation field. Recently, total rates of decay of the negative hydrogen ion, in both the perturbative and nonperturbative regimes, were calculated accurately using basis functions expressed in perimetric coordinates. These coordinates are ideally suited to highly correlated systems, but, since they mix the independent coordinates of the two electrons, perimetric coordinates do not facilitate the calculation of partial rates. Nevertheless, attempts are being made to develop a tractable method for calculating partial rates using perimetric coordinates, and use it to calculate rates for two-electron escape from the negative hydrogen ion by one and two photons. The study of two-electron escape is challenging not only because of the importance of electron-electron correlation but also because the boundary conditions for two-electron escape are complicated.

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Department of Physics and Astronomy

273. The Production and Destruction of Metastable Negative Ions

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The structure of few-electron atomic negative ions and the manner in which they interact with other particles via photodetachment and collisional detachment processes are investigated. The primary motivation for the work is to gain an improved understanding of the role played by correlated electron motion in atomic structure. The results also find practical application in the diagnostics of low temperature laboratory and astrophysical plasmas. A crossed laser-ion beam apparatus is used to make energy- and angle-resolved measurements of the electrons ejected in photodetachment. The photoelectron spectra provide information on electron affinities, asymmetry parameters, and cross sections. A recent experiment on the excited negative ion of carbon, for example, yielded cross sections and asymmetry parameters associated with photodetachment from both the ground and excited states. In other experiments with this apparatus, resonance structures in zero-degree detached electron spectra arising from ion-atom collisions have been studied. Highly sensitive spectroscopic measurements on the helium and lithium negative ions, made using a high resolution collinear laser-ion beam apparatus that employs state selective atom detection, have revealed many new resonances arising from the autodetaching decay of highly correlated doubly excited states.

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274. State-to-State Energy Transfer in Atomic Collisions

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Experiments studying the radiative collision $Xe + Cl_2 + 2h\nu \rightarrow Xe^+ + Cl_2^-$ at high pressures have been used to measure a more accurate potential for XeCl*(B) produced by breakup of the triatomic reaction complex. Fully quantal calculations are used to model the bound-free and bound-bound fluorescence of XeCl*(B). By comparing the spectra with results of the model, a more accurate potential was obtained. Measurements of state-to-state energy transfer rates for Xe (5d,5d′,6d) states in collisions with other rare gases have been completed. These results are relevant to kinetic models of excimer lasers and the nuclear pumped, infrared xenon laser. In many previous experiments, strong coupling to these states through avoided crossings with Xe (6p, 6p′, 7p) were suggested, but not confirmed, because the dynamics of Xe(nd) could only be indirectly observed. Experiments were initiated to study the cluster ions and radicals formed in high pressure discharges using Raman induced Kerr effect spectrosopy.

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275. Negative Ion-Atom Collisions
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This research project concentrates on the measurement of cross sections for various scattering processes in few-electron, negative ion-atom collision systems in order to understand the physics of ion-atom collisions at intermediate energies. This research effort has recently been expanded to include singly-charged, positive ion projectiles so that comparisons can be made of similar processes for positive and negative ion projectiles of the same species colliding with the target atoms. The primary experiments in progress this year include absolute cross section measurements of target excitation and ionization in the $H^{+,-}$+He collision systems. In addition to the primary experiments listed above, a series of collaborative experiments on photodetachment were conducted this past year in which angular distributions of the photoelectrons were measured for Al^-, Si^-, P^-, C^-, Fe^-, and V^-.

276. Semiempirical Studies of Atomic Structure
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The structure of heavy and highly ionized atoms is studied through the use of experimental measurements, data-based semiempirical systematizations, and theoretical calculations. Properties such as transition probabilities, energy levels, fine structure splittings, electric polarizabilities, and ionization potentials are determined through time-resolved fast ion beam measurements, and are combined with wavelength data obtained from conventional light sources as well as laser- and tokamak-produced plasmas and astrophysical sources. As examples, during the past year lifetime measurements have been performed for Tl II, Tl III, Bi II, Cd III, and In IV, which have applications to the interpretation of isotopic abundance anomalies observed in peculiar stars through Hubble Space Telescope spectra, and in K II, which has applications in the development of XUV lasers. Branching ratio determinations have been made for Pb I and Bi II, and both branching ratios and electric dipole polarizabilities have been determined for Au I, Hg II, Tl III, Pb IV, and Bi V. New methods have been developed that accurately account for relativistic and intermediate coupling effects in data-based isoelectronic systematizations, which have been applied to obtain reliable predictions for line strengths of the higher ions in the Be and Pb sequences. New methods have also been developed to test and enhance the precision with which lifetimes can be extracted from measured decay curves.

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277. Dynamics of Multielectron Systems Interacting with Matter and Light
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The general theme of this project in atomic collisions is interdependency of electrons in atomic systems. Specifically, the dynamics of electron correlation are studied by examining reactions in which electron correlation is dominant. These phenomena occur in few electron transitions in fast collisions of photons and charged projectiles with atoms and molecules. Using synchrotron radiation, one may observe both single and double ionization of simple atomic systems. Calculations are done using configuration interactions specifying the nature of electron correlation in terms of initial and final state correlation. Two and few electron transitions are also studied in interactions of atoms and simple molecules with charged projectiles. Two-center correlation is studied in systems in which projectile electrons interact with target electrons. Using first order perturbation theory, it was possible to relate cross sections for charged particle impact to Compton scattering by photons. These relations are now being tested experimentally and are providing an emerging picture of mechanisms for the dynamics of electron correlation. A more complete description of these and other methods is included in *Electron Correlation Dynamics in Atomic Collisions*, published by Cambridge University Press in 1997.

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278. Theoretical Studies of Atomic Transitions
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Atomic structure calculations are being performed for properties associated with energy transfer mechanisms in atoms. Properties of particular interest are energy levels, transition probabilities, autoionization rates, and photoionization cross-sections. Recent interests examined were the nuclear effects of hyperfine interaction and isotope shifts on transition energies and decay processes that may be hyperfine induced. The GRASP92 relativistic atomic structure package is being modified for large scale computation using MPI on the T3E, a massive parallel processing computer. Through the use of independently optimized wave functions, accurate transition probabilities, both allowed and spin-forbidden, will be determined for lines in complex spectra, particularly those of astrophysical interest.

Recent results include E1, E2, M1, M2 transitions from the ground state of Be-like and Mg-like systems and the evaluation of the nuclear quadrupole moment of isotope 45 of Scandium. The parallel codes will be used to study properties of heavy elements where relativistic correlation is critical for a proper description of the wave function.

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Department of Physics

279. ***Studies of Autoionizing States Relevant to Dielectronic Recombination***

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Configuration interacton is important in many contexts in atoms and molecules; among them are autoionization, its inverse, dielectronic recombination, and intramolecular vibrational energy redistribution. Such processes are both intrinsically interesting and of practical importance. For example, dielectronic recombination occurs in both fusion and astrophysical plasmas. This program is focused on configuration interaction in atoms. The experimental approach employed involves multistep laser excitation of alkaline earth atoms. In one set of experiments, Ba atoms were excited with a femtosecond laser to a band of bound Rydberg states perturbed by a doubly excited valence state, forming a coherent superposition of these states. The evolution of the superposition was observed with a second, delayed femtosecond laser pulse. Either of two wavelengths were used for the second pulse; one detected the Rydberg states and the other the valence state. The population was observed to oscillate back and forth between the two configurations at a rate equal to the strength of the configuration interaction, and the populations in the Rydberg and valence states were found to be complementary. Coherent oscillation between configurations has been proposed for control of chemical reactions.

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280. ***Correlated Charge-Changing Ion-Atom Collisions***

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Experimental investigations of atomic interactions in collisions of few-electron ions with neutral gas targets or electrons are conducted. Interactions involving excitation, ionization, and charge transfer (capture) are studied. The primary emphasis of this work is the study of two-electron processes, and, in particular, determination of the importance of the electron-electron interaction (i.e., electron correlation) in giving rise to various collision phenomena. This work centers around three general areas of investigation: (1) continuum-electron emission, especially electrons emitted along the beam direction which travel with the beam velocity (so-called "cusp" electrons), (2) double ionization of helium by structured ions (i.e., partially stripped ions) and ions undergoing electron capture or loss, and (3) resonant recombination of atomic ions, involving either dielectronic recombination (DR) or resonant transfer excitation (RTE). Specific collision processes are isolated and identified using coincidence techniques in which projectile charge-changing events are associated with electrons, recoiling target ions, or X rays. Measurements are conducted using accelerators at Western Michigan University, the Hahn-Meitner-Institute (Berlin, Germany), Kansas State University, and GANIL (Caen, France).

281. ***Near Threshold Excitation and Ionization of Atoms and Molecules***

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The primary emphasis of this research is to probe and identify many-body effects in atoms and molecules associated with electron correlations at an unprecedented level of detail. Special attention is given to phenomena near thresholds since there electron-electron correlation are the strongest. The aim is to study these fundamental aspects by using photoexcitation and photoionization processes. This is achieved by conducting high resolution measurements on atoms and molecules, including laser excited open-shell atoms, using photoelectron spectrometry coupled with high brightness and high resolution from the Advanced Light Source. New results have been obtained for studies involving (1) doubly excited states in Ne, (2) angle resolved Auger Resonant spectroscopy to study the angular distribution of the Ar $2p_{3/2,1/2} \rightarrow$ 4s, 3d, 4d decay spectrum, (3) inner-shell photoexcitation of HCl, and (4) photoexcitation studies in hollow lithium. Future activities include photoexcitation and ionization of molecular Cl_2, photofragmentation of H_2, ratio of double to single ionization of H_2^{++}/H_2^{+}, and continuation of photoexcitation studies of laser excited targets.

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282. ***Amplitude Modulation of Atomic Wavefunctions***

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This project uses a novel laser-excitation method in conjunction with the electron-electron interaction in a multi-electron atom to modulate the electronic wavefunction of a single electron within an excited atom.

Using this method, many bits of digital information can be stored within a single atom. This project will provide experimental confirmation of this process. Methods will be investigated to retrieve the stored information, and the limits of the information storage capacity will be defined. These novel wavefunctions are expected to have significant effects on other radiative processes, which should be important for the development of new coherent radiation sources. Current progress includes the development and characterization of a high-power, short-pulse blue laser for excitation of strontium, and the development of picosecond electric field pulses for Rydberg state analysis. Initial, low-power experiments have shown that the atom recognizes laser pulse timing. The first high-power experiments in barium have now shown that the excitation can be accomplished with at least 60% efficiency. The latest experiments have also shown that electron angular distributions may be useful for retrieving state information. Future experiments will center on modulating Rydberg states of strontium, where the wavefunction modulation process should be easier to detect.

283. Negative Ion Detachment Cross Sections
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The purpose of this experimental research project is to develop an understanding of the collisional dynamics for systems where negative and positive ions collide with atoms or molecules in the gas phase and with atoms which may be adsorbed on a well-characterized metallic surface. Two-body collision cross sections are measured in the gas phase experiments. Surface experiments seek to examine the role of an oxide layer in sputtering secondary electrons and negative ions from surfaces such as Al, Mo, and Ag. The collision energies for each of these experiments range from a few electron volts up to about 0.5 keV. In the gas phase experiments, cross sections for collisional and associative electron detachment, charge transfer, and negative ion-molecule reactions are determined for a variety of reactants. The absolute electron- and negative ion sputtering yields are determined in the surface experiments, along with the kinetic energy spectra of each sputtered species as a function of oxygen coverage on the surface. In both cases, the fundamental microscopic measurements are ultimately used as input for modeling macroscopic gaseous discharges or plasmas where the cross sections for gas phase collisions and the yields for surface collisions determine the equilibrium concentrations.

Chemical Energy

University of Arizona
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Department of Chemistry

284. A Model Approach to Hydrodenitrogenation Catalysis
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One major goal of petroleum hydrotreating is the catalytic removal of sulfur-, nitrogen-, and oxygen-containing impurities from assorted feedstocks. Although sulfur contaminants are present in higher concentrations than nitrogen or oxygen, declining crude oil quality is associated, in part, with increasing concentrations of organonitrogen compounds, lending a new urgency to improving hydrodenitrogenation (HDN) technologies. We are continuing our studies of soluble model compounds that undergo HDN reactions, such as heterocycle hydrogenation and C-N bond cleavage. Current studies of pyridine and its derivatives have demonstrated the following: (1) We have isolated and structurally characterized an elusive intermediate in a pyridine degradation sequence, viz., a monomeric metallapyridine complex. The conversion of this intermediate to the thermodynamic degradation product, a metallapyridine dimer, has been demonstrated. (2) An unexpected 4+1 addition of nitriles to the diene ligand in butadiene complexes of tantalum has been discovered that proceeds through an intermediate metallacycloimine rearranging to a cyclopentenylimido product. Juxtaposition of this metallacycloimine → cyclopentenylimido rearrangement with the hydride-induced C-N bond scission in η^{-2} pyridine complexes we described previously has allowed us to develop a theory for how quinoline undergoes denitrogenation in its conversion to indene. This unusual 4+1 addition appears to be driven by the formation of the strong metal-nitrogen multiple bond in the cyclopentenylimido species. These results offer new insights into fundamental HDN reactions and may eventually place the development of new catalysts on a more rational basis.

Boston College
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Chemistry Department

285. High-Temperature Chemistry of Aromatic Hydrocarbons
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This work focuses on the fundamental molecular processes involved in the rearrangements and interconversions of polycyclic aromatic hydrocarbons (PAHs) under conditions of thermal activation. An understanding of such processes in well-designed molecular systems provides insights into the more complex processes of combustion, the formation of soot, carcinogens, and fullerenes in flames and smoke, and the uncatalyzed gasification and liquefaction of coal, inter alia. This year we have found the first example of an ethynyl group migration from one benzene ring to another. Two 30-carbon bowl-shaped PAHs related to fullerenes have been found among the pyrolysis products of other hydrocarbons, and all three of the dicyclopentapyrenes that we synthesized two years ago have now been identified among the PAHs formed in flames (collaboration with Jack Howard, MIT). The electron affinity of corannulene in the gas phase has been measured (collaboration with Graham Cooks, Purdue), and the conversion of corannulene to C_{60} at high temperatures has been achieved (collaboration with Harry Kroto, Sussex). The long-range objectives of this research are to uncover all the principal reaction channels available to PAHs at high temperatures and to establish the factors that determine which channels will be followed in varying circumstances.

California Institute of Technology
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Department of Chemistry

286. ***Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds***

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The objectives of this research program are (1) to discover new types of chemical transformations between hydrocarbons and transition-metal compounds; (2) to investigate their mechanisms; and (3) to explore the possibilities of coupling these transformations with others to catalyze chemical reactions for the preparation of fuels, commodity chemicals, and polymeric materials. A current focus is the catalytic polymerization of olefins. New and superior polymers with different microstructures and new homo-block copolymers could be made from the same readily available monomers if sufficient control over the Ziegler-Natta catalytic process could be achieved. C_2-symmetric yttrocene derivatives with linked cyclopentadienyl ligands have been prepared. The alkyl and hydride derivatives function as well-defined, single component, isospecific alpha olefin polymerization catalysts well suited to mechanistic investigations. A ligand capable of affording only one enantiomer of a chiral catalyst has been synthesized. The absolute facial preferences for olefin insertion into Y-H and Y-C bonds has been established for a chiral, highly deuterated olefin using NMR methods. Recently a new class of metallocene catalysts has been developed that produce highly syndiotactic poly alpha-olefins. The mechanism of stereocontrol is under study. A modified version allows the preparation of polypropylenes with tacticities varying from isotactic to syndiotactic.

University of California, Davis
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Department of Chemical Engineering and Materials Science

287. ***Effects of Supports on Metal Complexes and Clusters: Structure and Catalysis***

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The research is a fundamental investigation of the effects of supports on the structure and catalytic properties of metal complexes and clusters. The metals are Rh, Ir, and Pt. The supports are MgO, γ-Al_2O_3, and zeolite LTL. The former are used as high-area powders and as ultrathin layers on metal single crystals. Like the oxides, the zeolite is basic, incorporating K^+ exchange ions. With precursors such as $[Ir(CO)_2(acac)]$, metal subcarbonyls such as $[Ir(CO)_3(OMg)_3]$ are formed (where the braces around MgO denote groups terminating the MgO). With precursors such as $[HIr_4(CO)_{11}]^-$, supported clusters such as Ir_4 and Ir_6 are formed. The supported species are being characterized structurally with IR, EXAFS, and NMR spectroscopies, TPD, H_2 chemisorption, and imaging methods and tested as catalysts for ethylene hydroformylation, toluene hydrogenation, and n-butane hydrogenolysis. The goals are to determine how the support structure and composition affect the structures of the well-defined supported metal complexes and clusters and their reactivities and catalytic properties. For example, tetrairidium clusters on MgO were oxidized to give iridium oxide clusters of nearly four atoms each, and these were reduced in H_2 to give back Ir_4. These latter clusters on MgO catalyze toluene hydrogenation, and the catalytic reaction rate depends only slightly on the MgO surface hydroxyl content. X-ray absorption near-edge data, among others, suggest that the supported clusters bear positive charges, which account (in part) for the large difference in catalytic activities between the clusters and supported metallic particles of the same metal.

University of California, Irvine
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Department of Chemistry

288. ***Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes***

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The goal of this study is to develop the chemistry of yttrium and the 14 lanthanide metals, a series of affordable heavy metals that are readily available in the United States, so (a) they can be efficiently incorporated into compounds useful in energy-saving practical devices that depend on their special optical and magnetic properties and (b) their special chemistry can be utilized in the conversions of low-value chemical starting materials to more valuable substances. Complexes containing strongly bound alkoxide, aryloxide, carboxylate, and arylamide ligands have been synthesized to provide stable, soluble compounds that can be converted to catalytically active species or to useful materials precursors. Industrially convenient syntheses of these compounds directly from the metal have been developed. Considerable effort has been devoted to europium due to its special luminescent properties. Polymetallic and heteropolymetallic europium complexes, containing as many as eight metals, have been obtained, which may be useful precursors to practical materials requiring homogeneity on a molecular level. A rationale has been proposed to explain the polymetallic chemistry observed and this is being tested in new syntheses. Lanthanide compounds useful in organic transformations and in polymerizations are being examined to help optimize their reactivity.

University of California, Riverside
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Department of Chemistry

289. ***Study of the Surface Chemistry of Hydrocarbon Radicals and of Carbonium Ions on Metal Oxide Surfaces***
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This project focuses on the development of two separate directions related to the characterization of the surface chemistry of hydrocarbons on metal oxide surfaces. In the first, the oxidation of nickel to nickel oxide films is being investigated. This year the thin NiO films grown by oxidation of Ni(110) surfaces were characterized under ultrahigh vacuum by low-energy electron diffraction (LEED), x-ray photoelectron (XPS), Auger (AES) and ion scattering (ISS) spectroscopies as well as by CO temperature-programmed desorption (TPD) titrations. In particular, the effect of introducing defects via Ar ion irradiation at room temperature was compared with the results from partially oxidized ordered Ni(110) surfaces. CO TPD proved to be a very useful local probe for the investigation of defective NiO surfaces, and revealed that Ar ion irradiation of thin NiO films leads to the formation of Ni-O phases similar to those found during the early oxidation stages of this surface. The second direction of this project has been to study the conversion of alkyl groups chemisorbed on the oxide surfaces prepared as described above. On clean nickel, alkyl species decompose via a combination of beta-hydride and reductive elimination steps to yield a mixture of alkanes and alkenes, and fully oxidized surfaces lose most of their activity and only promote total oxidation reactions. Interestingly, though, low oxygen precoverages were found to induce some conversion of 2-propyl iodide to acetone, a partial oxidation product. The experimental results obtained so far suggest that alkyl halides first adsorb and dissociate on the nickel atoms, forming the desired alkyl groups, which then migrate to the oxygen functionality and form alkoxy groups around 200 K; the alkoxides finally dehydrogenate via a beta-hydride elimination step above 300 K to produce the ketone.

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Department of Chemical and Nuclear Engineering

290. ***Alkane Catalysis on Group VIII Transition Metal Surfaces: Initial Activation and Subsequent Surface Reactivity***
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Our research objective is to quantify the activation of various alkane species on several transition metal surfaces, including Ru(001) and Ir(110). We have measured the initial probabilities of precursor-mediated dissociative chemisorption of c-$C_3H_6$and c-C_3D_6 on Ru(001) at surface temperatures from 400 to 1100 K. The measured activation energies for both c-C_3H_6 and c-C_3D_6 are 9470±120 cal/mol with respect to the bottom of the physically adsorbed well. The chemisorption occurs via C-C rather than C-H bond cleavage at all temperatures studied, as judged by the lack of a kinetic isotope effect. The preferred reaction pathway of C-C bond cleavage is a consequence of the ring strain present in molecular cyclobutane. We have also employed molecular beam techniques to investigate the initial probability of direct dissociative chemisorption, P_d, and the intrinsic trapping probability, ξ, as a function of beam translational energy, E_i, from 1.5 to 59 kcal/mol. Measurable (≥ 0.02) initial probabilities of direct dissociative chemisorption increase nearly linearly with E_i, approaching P_d=0.48 at E_i=52 kcal/mol for C_3H_8 and $(CH_3)_2CD_2$ and P_d=0.44 at E_i=59 kcal/mol for C_3D_8. The lack of a kinetic isotope effect for the direct chemisorption of $(CH_3)_2CD_2$ relative to C_3H_8 indicates that 1° C-H bond cleavage dominates over 2° C-H bond cleavage during the direct chemisorption of propane on Ir(110).

Department of Chemistry

291. ***Studies Relevant to the Catalytic Activation of Carbon Monoxide***
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This research is concerned with quantitative investigations of reactions relevant to the homogeneous catalytic activation of carbon monoxide, other C_1 compounds and hydrocarbons. Over the past year, our focus has been on the use of time resolved techniques to prepare and to investigate the spectra and dynamics of organometallic intermediates relevant to the activation of hydrocarbon C-H bonds and to the formation of carbon-carbon bonds via CO migratory insertion into metal-alkyl bonds. The latter studies have been directed toward elucidating the mechanisms of CO insertion into metal-alkyl bonds, a key step in catalytic schemes for carbonylations of various organic substrates. Initial attention has been on model manganese(I) and iron(II) compounds, and these studies have been extended to cobalt and to rhodium systems of the type used in commercial hydroformylation catalysts. The C-H activation studies have been mostly concerned with the reactions of unsaturated complexes $RhClL_2$ with various hydrocarbons as well as with CO and other ligands. The goals are to delineate the chemical principles relevant to the activity and selectivity of molecular catalysts for activating hydrocarbons and C_1 compounds, such as CO. Understanding such fundamental processes provides the guidelines for designing efficient and environmentally friendly applications of energy and chemical feedstocks.

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Department of Chemical Engineering

292. Effects of Dopants on the Acidic Properties of Oxide Aerogels

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Research progress has been made along two fronts. In order to understand the effect of either oxide or anionic dopants on the acidic properties of oxides, we have added a range of dopants, including silica, phosphate, and tungstate, to zirconia aerogels. The dopants were introduced, either individually or in combination, into zirconia by preparation methods, such as one-step sol-gel synthesis and incipient wetness impregnation. Characterization of the resultant materials with a set of chemical probes, namely, isomerizations of alkanes and base adsorption, provided new information on the preparation-structure-property relationship in modified zirconias. For zirconia-tungstate materials in particular, our results showed that preparation method affected the activation behavior but not the active species in n-butane isomerization. Work has also begun on the preparation of alumina aerogels by a sol-gel process that used a sub-stoichiometric amount of water. Preliminary data indicated that the sintering and crystallization behavior of alumina can be affected by dopant(s) choice, amount, and location. The next step is to develop effective strategies for controlling the textural and chemical properties of doped aluminas.

Colorado State University
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Department of Chemistry

293. Polyoxoanion-Stabilized Transition Metal Nanoclusters: Soluble Analogs of Heterogeneous Catalysts

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Studies are continuing on the new type of metal-particle catalyst, polyoxoanion and tetrabutylammonium-stabilized transition-metal nanoclusters, discovered via our DOE grant. The long-term goal is to gather the fundamental and practical knowledge necessary to construct a paradigm covering the catalytic applications of this new subclass of catalyst material. Most recently we have focused on understanding the mechanisms of formation of the nanoclusters, how so-called "magic number" nanoclusters are formed, and how to control nanocluster size—and thereby catalytic properties—in, for example, "structure-sensitive" reactions. Work with especially Ir(0) and Rh(0) nanoclusters has led to a new, apparently broadly applicable mechanism of nucleation and growth for nanoclusters formed under hydrogen. In addition, solution catalytic studies show that the polyoxoanion and tetrabutylammonium stabilization makes the nanoclusters of longer lifetime than any previous, non-polymer-protected metal particle. Overall, the results to date argue that such nanoclusters have potential to become "soluble analogs of heterogeneous catalysts."

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Department of Chemistry and Biochemistry

294. Syntheses and Reactions of Pyrrole and Indole Complexes

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The objectives of the project are (1) to synthesize new transition metal pyrrole, indole, and indoline complexes and (2) to investigate how the metal ion coordination affects the reactivity of the heterocycles. The work may provide a basis for understanding mechanistic features of the hydrodenitrogenation catalysts. New indoline complexes of ruthenium have been synthesized and structurally characterized, and their acid base properties have been studied. The new complexes include examples of both σ and π coordinated indoline ligands, and have the formulas $[(\text{cymene})Ru(\eta^6\text{-indoline})](OTf)_2$, 1, and $[(\text{cymene})Ru(\eta^1\text{-N-indoline})(CH_3CN)_2](OTf)_2$, 2. Complexes 1 and 2 were each titrated in aqueous solution to determine the pK_a value of the neutral indoline ligand. The value of 9.7 that was determined for the η^6-coordinated ligand in 1 indicates that the coordinated ligand is significantly more acidic than free indoline. The pK_a value for the η^1

indoline ligand in 2 was found to be 5.5. This value is similar to that of the free indolinium ion. Deprotonation of 2 with triethylamine in the presence of an alkene leads to further rapid dehydrogenation of the indoline ligand and the formation of free indole and the alkane. Further mechanistic work is in progress. Hydrogen transfer from indoline has been catalyzed by metal complexes previously, but the mechanistic features of the metal-indoline intermediates have not been previously established.

Columbia University
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Department of Chemistry

295. ***Diosmacycloalkanes as Models for the Formation of Hydrocarbons from Surface Methylenes***

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We have prepared $(C_5Ph_5)Cr(CO)_3$, a known stable metalloradical that should be useful for controlling radical polymerizations. We have protonated the reduced (anionic) form of this metalloradical with HCl, and prepared the corresponding hydride. Transfer of a hydrogen atom from this hydride complex to trityl radicals is very slow. We have prepared diosmacyclobutanes from strained olefins, such as norbornene and cyclobutene. We will now assess (1) the effect of ring strain on the relative binding affinities and (2) the potential for strained diosmacyclobutanes to cleave C-C and Os-Os bonds to form tethered alkylidene complexes: $(CO)_4Os{=}CHR\text{-}RHC{=}Os(CO)_4$.

296. ***Model Studies in Hydrocarbon Oxidation***

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Our recent research has centered on studies designed to provide information that is relevant to the activation of C-H bonds and the oxidation of organic substrates. Specific attention has been given to electron-rich trimethylphosphine complexes of molybdenum and tungsten, namely $M(PMe_3)_6$ and $M(PMe_3)_4X_2$ (X = F, Cl, Br, I). Previous DOE-sponsored research has demonstrated that $W(PMe_3)_6$ is capable of selective intramolecular C-H bond activation of phenol to give a novel four-membered oxametallacycle, $W(PMe_3)_4(OC_6H_4)H_2$. In contrast, $Mo(PMe_3)_6$ reacts with phenol to give the tetrakis(phenoxy) complex $Mo(PMe_3)_2(OPh)_4$, rather than a product derived from C-H bond activation. A further illustration of the difference in C-H activating abilities of tungsten versus molybdenum is provided by the reactions with 2,4,6-trimethylphenol: the tungsten system yields a metallacycle as result of C-H bond activation whereas the molybdenum system yields only an aryloxy-hydride complex $Mo(PMe_3)_4(OC_6H_2Me_3)H$. Mechanistic studies demonstrate that the reason for isolating $Mo(PMe_3)_4(OC_6H_2Me_3)H$ is thermodynamic in origin (i.e., the molybdenum center is kinetically capable of reacting with a C-H bond but that the energy required to break the C-H bond is not compensated by the formation of Mo-C and Mo-H bonds). We have also demonstrated similar differences in the ability of six-coordinate $M(PMe_3)_4X_2$ (X = F, Cl, Br, I) complexes to oxidatively add H_2; thus, the tungsten system exhibits a greater propensity to give the corresponding $M(PMe_3)_4H_2X_2$ complex and observation that reflects the greater strength of W-H versus Mo-H bonds. As part of this work, we have also demonstrated that the fluoride ligand in the molybdenum complex $Mo(PMe_3)_4H_2F_2$ can partake in a hydrogen bonding interaction with HF, thereby generating a stable bifluoride complex, $Mo(PMe_3)_4H_2F(FHF)$.

University of Connecticut
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Department of Chemistry

297. ***Synthetic Todorokite: Preparation, Characterization, and Applications***

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The goals of this project are to prepare mixed valent manganese oxides such as new microporous octahedral molecular sieve (OMS) and octahedral layered (OL) materials, manganese oxide mesoporous structures (MOMS), and pillared octahedral layered (POL) materials; to characterize these systems to determine structural, compositional, thermal, electronic, surface, acid-base, and optical properties; and to optimize the catalytic properties of OMS, OL, MOMS, and POL materials in CO oxidation, oxidative dehydrogenation of cyclohexane, and selective oxidations of large bulky hydrocarbons such as norbornene, and α-terpineol. Sol-gel, reflux, hydrothermal, phase transfer, and controlled hydrolysis syntheses are in progress. Small angle neutron scattering of gels in order to study early stages of crystal growth, calorimetry studies, and catalytic studies will be done in collaboration with researchers at Argonne National Laboratory, UC Davis, ADL, and DuPont, respectively. Battery studies of lithium containing OMS, OL, MOMS, and POL materials and giant magnetoresistance studies aimed at developing novel sensors will be pursued. Photoassisted catalytic oxidations of indoor air pollutants using amorphous manganese oxide materials will be done in collaboration with researchers at United Technologies Research Center.

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Center for Catalytic Science and Technology, Department of Chemical Engineering

298. Experimental and Theoretical Studies of Surface Oxametallacycle Chemistry

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Oxametallacycles (a.k.a. metallaoxetanes) are reactive intermediates with structures such as -OCH_2CH_2-, with the terminal O and C atoms coordinated to one or more metal atoms. They have been proposed as crucial intermediates in a variety of homogeneously and heterogeneously catalyzed reactions, including selective olefin oxidation and epoxidation processes, carbonylation and decarbonylation chemistry, insertion of other unsaturated functions, and metathetical reactions. Prior to this research, the sole extant examples of the isolation of such complexes were in homogeneous media (e.g., in organometallic chemistry in solution and matrix isolation experiments trapping gaseous species). We have produced the first example of a stable oxametallacycle intermediate on a metal surface, synthesizing this species from iodoethanol on silver. We have verified the existence of this cyclic surface intermediate by vibrational spectroscopy. Complementary theoretical studies using Density Functional Theory help to assign the vibrational spectrum and provide insights into the selectivities of oxametallacycle formation and conversion on different transition metals. By building connections between homogeneous and heterogeneous catalysis, and between experiment and theory, our aim is to establish new principles of surface organic reactions and to further the development of new catalysts and processes for synthesis of oxygen-containing fuels and chemicals.

Department of Chemical Engineering

299. Carbogenic Molecular Sieves for Reaction and Separation by Design: A Novel Approach to Shape Selective Super Base, Super Acid and Catalytic Membranes

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Carbogenic molecular sieves (CMS) provide a novel approach to shape selectivity in catalysis. It is for these reasons that we have begun research into two very promising areas of research with CMS - strong base catalysis and supported CMS membranes for reaction and separation. Cesium is the most electropositive element (Electronegativities: Pauling = 0.79, Sanderson = 0.69, Allred-Rochow = 0.86). It can be intercalated in graphite and is active for a number of base-catalyzed reactions. These materials are pyrophoric and exfoliate readily. For these reasons, we sought to investigate the properties and behavior of cesium entrapped within CMS. Cs(0) as the atomic vapor was transported into CMS at 300°C and <0.1 torr. Cesium levels from 5 to >40 wt% have been attained. The Cs/CMS materials do NOT react violently with air; they have EPR resonance intensities well above those of the CMS alone; XPS binding energies are much closer to the metal than to the univalent cation, and although not visible (HRTEM) Cs is plentiful (EDX). Reaction in water produces dihydrogen. Heating to 500°C under dynamic vacuum does NOT lead to desorption of the cesium. Work is underway to characterize CMS and Cs/CMS using synchotron radiation. In the isomerization of 1-butene the equilibrium cis/trans ratio is 0.3 at 25°C. Using Cs/CMS catalyst at 0°C, a cis-to-trans ratio of more than 9.1 and a rate constant, 0.07/s/g is obtained. CMS membranes can be prepared on a porous 316 stainless steel as a 10 microns thickness layer. STM analysis shows the CMS surface is flat (±10 nanometers in the z-axis), and irregular rows of carbon atoms separated by about 5 Å are visible. Truly molecular sieving transport with activation energies for He, Ar, N_2, and SF_6 of 2.5, 10, 12, 18 kcal/mol is noted. The transition between molecular sieving and surface flow regimes is under investigation along with structural characterizations of the nanoporosity.

Department of Chemistry and Biochemistry

300. Oxidation Catalysis with Tris(pyrazolyl)borate Metal Complexes

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This project involves the development of catalysts for the oxidation of organic substrates using dioxygen as the source of the oxygen. In particular, the approach involves coordination and symmetric cleavage of the O_2 molecule into two reactive metal-oxo moieties by hindered tris(pyrazolyl)borate complexes of late transition metals. The feasibility of this scheme has been previously demonstrated using a set of cobalt complexes. In the initial phase of the research the mechanism of the cobalt mediated stoichiometric reaction will be elucidated in detail, and some reactions of the cobalt system [$Tp^{t\text{-}Bu,Me}Co$, $Tp^{t\text{-}Bu,Me}$ = hydridotris(3-t-butyl-5-methylpyrazolyl)borate] related to oxidation catalysis will be investigated. Building on this, the metal complexes will be modified to facilitate catalytic turnover. To this end the ligands must be "hardened" against oxidative degradation. This will be done by appropriate substitution of the ligand and/or the metal. In the long term, catalytic oxidations of various substrates as well as the design of ligands for regio- and stereo-selective oxidations will be investigated.

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Department of Chemistry

301. Bimetallic Complexes as Methanol Oxidation Catalysts
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The project involves preparation of bimetallic Pt/Ru and Pt/Mo complexes as catalysts for the electrooxidation of methanol. The currently accepted mechanisms for methanol oxidation at Pt/Ru anodes involve C-H activation at Pt and "active oxygen transfer" from Ru. Since these reactions are known individually for mononuclear complexes, the catalysts are designed to mimic the anode behavior. Design features of the complexes include bridging ligands such as 1,10-phenanthrolinedione or bidentate phosphines to prevent dissociation of the metal centers, low-valent starting materials that allow a series of oxidation states for each metal to be generated during oxidation studies, and incorporation of ligands that are relevant to the methanol oxidation process. During this project period, a series of binuclear complexes has been prepared by substitution for the chloride ligands of $(PPh_3)_2Pt(O,O'\text{-PhD-N,N}')Ru(PPh_3)_2Cl_2$. Cyclic voltammograms of the complexes exhibit the two ligand-centered waves of phenanthrolinedione (irreversible quinone/semiquinone and reversible semiquinone/catecholate), as well as the Ru (III/II) wave. The position of the Ru (III/II) wave with respect to the ligand waves is dependent on the nature of the substituting ligand L. The electrochemistry of these complexes in the presence of methanol is being investigated.

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Department of Chemistry

302. Model Microcrystalline Mixed-Metal Oxides for Partial Oxidation and Desulfurization
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The broad objective of this proposal is to investigate how the constituents of bimetallic materials function in hydrocarbon oxidation, an extremely important catalytic process. We are specifically interested in the roles of oxygen in different types of coordination environment and how the morphology and electronic properties of the constituents of a bimetallic material affect chemical reactivity. Our recent work has shown that Mo=O sites are not necessary for either oxidation of methyl radicals to methoxy or for alcohol reaction on oxidized Mo(110), addressing a long-standing controversy in the catalysis literature. At the same time, our work on mixed Co-O-Mo phases has demonstrated that the reactions of alcohols can be qualitatively modified by changes in surface structure and electronic properties. In particular, recent scanning tunneling microscopy studies show that three-dimensional Co islands form upon heating Co deposited on oxidized Mo(110). These islands have different chemical properties than a uniform Co layer deposited either on clean or oxidized Mo(110). Currently, we are investigating the relationship between surface morphology and reactivity in these systems.

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Department of Chemistry

303. Electron Transfer Activation of Coordinated Thiophene
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The presence of organic sulfur, nitrogen, and organometallic compounds in fossil fuels poses very serious environmental and engineering challenges. The most effective method for addressing these problems is through hydrotreating processes (e.g., HDS, HDN, HDM). This project has the objective of obtaining fundamental chemical information on these processes so they can be better understood and can be improved, leading to more efficient use of resources and cleaner energy technologies. Current experiments focus on HDS pathways that involve electron transfer to a metal-thiophene ensemble followed by protonation (i.e., the so-called heterolytic activation process). The stereochemistry and energetics for individual steps are examined for model systems based on well-defined metal complexes. A newer area of research focuses on metal-contaminated fossil fuels that require the use of hydrodemetallation catalysis. In this effort, the binding and activation of metalloporphyrin complexes are being examined. Parallel studies are conducted on phthalocyanines.

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Department of Chemistry

304. Chemical Principles Relevant to Materials Precursor Design and Synthesis
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A new method of making mixed valence metal alkoxides has been devised, which has enabled us to study the CVD of $Sn(II)Sn(IV)(OR)_6$. We have also discovered a reaction that converts lead oxo/alkoxides to heterometallic oxo/alkoxides. CVD studies reveal that electropositive

Zr is the "fate" of oxide present in the precursor, but a $Pb(II)_3Sn(IV)O(OR)_{10}$ species gives 2 Pb, Sn, and PbO; this contrathermodynamic product demonstrates kinetic control of the CVD product.

305. *Generation and Characterization of Cross-Conjugated Bi- and Polyradicals*

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Potential candidates for magnetic organic materials will be generated by addition of vinylidenes to various olefins. A wide variety of vinylidenes and olefins are under investigation. As an example, addition of adamantylidene to adamantofulvene produces dimers of the m-xylylene biradical. Confirmation of the structures of these by generation of m-xylylene from aromatic precursors is in progress. It is possible that some of the reactions under investigation are related to the formation of buckminsterfullerene in soots. Routes to other candidates for organic magnets in which high symmetry results in self-assembly to create magnetic domains in the solid state are being pursued. The experimental work is supported by a concerted computational effort where questions of the three-dimensional geometry of these interesting species might be answered.

306. *Alkoxide Ligands in Organometallic Chemistry and Catalysis*

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Alkoxide and related aryloxide and siloxide ligands are hard π-donor ligands and complement the now traditional soft π-acceptor ligands, such as tertiary phosphines, carbonyls, and π-hydrocarbyl ligands. We are using the former with hard metals, such as early transition elements, lanthanides, and group 2 and 3 main group elements, such as ancillary ligands, for the development of a new field of organometallic chemistry. Current areas of research include (1) the development of selective hydrogenation cataylsts for conjugated dienes employing $W_2(OR)_6$ compounds; (2) the use of bidentate and tridentate diols and triols to impose specific coordination geometries at the metal atoms; (3) studies of opening of sulfur, nitrogen, and oxygen-containing aromatic rings as models for steps in HDS, HDN, and HDO catalysis; and (4) the development of single site metal alkoxide catalysts for the ring-opening of epoxides and strained cyclic esters.

307. *A Model Approach to Vanadium Involvement in Crude Oil Refining*

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The project is directed toward characterizing the initial fate of crude oil vanadyl impurities under the reducing and sulfur-rich conditions of industrial hydrodemetallation (HDM) and hydrodesulfurization (HDS) processes. The impurities are ultimately converted to insoluble vanadium sulfides (primarily V_2S_3 and V_3S_4), which lower the activity of, and eventually poison, the Mo heterogeneous catalyst. Recent work has concentrated on detailed characterization of various V/S clusters that represent models for intermediate stages of V sulfide polymer growth. A number of di- and trinuclear species have been prepared and studied by a range of techniques, including x-ray crystallography, VT magnetic susceptibility measurements, VT ^{1}H NMR studies, and EHT MO calculations. Selected complexes under study include $[V_3Cl_6(SCH_2CH_2S)_3]_{3-}$, $[V_2(SCH_2CH_2S)_4]_{z-}$ (z=1 or 2), and $[V_xO_y(pyt)_z]$ (pyt=pyridine-2-thiolate), which represent models of small V species adsorbed on the surface of the growing V_2S_3/V_3S_4 phases. The V/pyt complexes have been investigated by EI mass spectrometry, the observed MS fragmentation patterns (C-S and C-N bond cleavage) being employed as a model system for the fragmentation pathways of organovanadium impurities during the high temperature conditions of crude oil refining. The work has most recently been extended to include a variety of V/O/carboxylate clusters; the latter organic functionality is common in crude oils. A number of tetranuclear and pentanuclear species have been prepared and characterized by crystallographic and physical methods, including magnetochemistry. Aggregation methodology has been developed for the stepwise conversion of mononuclear vanadyl species to penta-, ennea-, and pentadecanuclear products, and all these species have undergone detailed characterization. The reaction of such species with H_2S is also being investigated as a model system for V sulfide polymer formation under refining conditions.

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Department of Chemistry

308. *Synthesis and Chemistry of Cationic d^0 Metal Alkyl Complexes*

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The objective of this research is to design and synthesize new types of electrophilic organometallic complexes for use in fundamental studies of olefin polymerization and C-H activation chemistry and for exploitation in catalysis. Earlier studies of $Cp_{p2}Zr(R)(L)^+$ complexes identified the key features required for high insertion reactivity in early metal systems: an electrophilic metal center, a d^o metal electron configuration, and one or more vacant (or virtual) coordination sites cis to the M-R ligand. Current work is directed to the development of new classes of cationic early metal alkyls, which incorporate these features in non-Cp_2M ligand environments. A series of Zr and Hf alkyl complexes $(N_4\text{-macrocycle})M(R)_2$ (R = CH_3, CH_2Ph, CH_2SiMe_3), containing dianionic tetra-aza macrocycles (N_4-macrocycle = Me_8-taa, Me_4-taen) in place of Cp ligands, has been prepared. The pockets of these macrocycles are too small to accommodate the large group 4 metal ions, so the metal sits out of the N_4-plane and cis structures are imposed. Base-stabilized cations [*cis*-$(N_4\text{-macrocycle})M(R)(L)][BPh_4]$ (L = THF, RCN, PMe_2Ph), and base-free cationic systems $[(N_4\text{-macrocycle})M(R)][B(C_6F_5)_4]$, have been prepared by protonolysis routes. The base-free systems are moderately active ethylene polymerization catalysts. One example, (Me_8-taa)$Hf(CH_3)$+, also undergoes clean single insertion of vinyltrimethylsilane and clean double insertion of dimethylacetylene. Ortho C-H activation of 2-methylpyridine and vinyl C-H activation of 2-vinylpyridine have also been observed with these cationic systems. Cationic alkyls based on tetradentate Schiff base ligands, e.g., (F_6-acen)Zr(R)+, have been prepared more recently. These systems are active olefin polymerization catalysts in the presence of AIR_3 cocatalysts. Chiral analogues catalyze the stereoselective polymerization of propylene to isotactic polypropylene. Current efforts are focused on more highly electron-withdrawing chelating ligands, which should maximize the electrophilicity of the metal center in these systems and thus increase reactivity. Additionally, studies of other ligand systems, including bidentate O,N donors and chiral chelating bis-amide ligands are being pursued. Most recently, cationic aluminum alkyl complexes of general type [(amidinate)AlR][A] have been prepared and shown to be active for ethylene polymerization. These results show that the catalyst design principles developed for metallocene catalysts can be extended to a wide range of transition metal and main group element systems.

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Department of Chemistry

309. ***Homogeneous Models of Ammoxidation Catalysis***
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The hexamolybdate cluster $[Mo_6O_{19}]_{2-}$ displays an MoO_6 coordination environment conspicuously similar to that within the ammoxidation catalyst component MoO_3, and our attention continues to focus on the preparation and study of organoimido derivatives of the hexamolybdate as structural and reactivity models for key nitrogenous surface species that have been proposed as intermediates in industrial ammoxidation chemistry. By applying a combination of electrochemical, structural, and multinuclear NMR spectroscopic methods, we have established that substitution of organoimido groups for oxo ligands within the hexamolybdate causes a progressive buildup of electron density that accumulates at the remaining terminal and bridging oxo sites in these derivatives. This finding provides important insights for understanding the hydrogen abstraction chemistry that accompanies the redox events in ammoxidation. We are initiating theoretical investigations parallel to our chemical studies and are now engaged in the synthesis of organoimido derivatives of other polyoxometalate clusters in which enhanced oxidation ability can be expected.

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Department of Chemical Engineering

310. ***Molecular Structures and Reactivity of Mixed Metal Oxide Monolayer Catalysts***
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Metal oxide monolayer catalysts, supported metal oxide catalysts possessing the active metal oxide components as a surface phase, find extensive applications in the energy industries of petroleum refining, pollution control from power generation plants, and automotive pollution control. To help bridge the knowledge gap between model and industrial metal oxide monolayer catalysts, a fundamental research program will address the relationships between the molecular structures and surface acidity and the molecular structures and surface redox chemistry of mixed metal oxide monolayer catalysts. For the fundamental surface acidity portion of the research program, the alumina-supported tungsten oxide system will be the focus of the investigation, and, for the fundamental surface redox chemistry portion of the research program, the alumina-supported vanadium oxide system will be the focus. The influence of secondary metal oxides upon the molecular structures and reactivity of these systems will be investigated. The molecular structures will be primarily determined with in situ Raman spectroscopy, but complementary structural spectroscopies (solid state nuclear magnetic resonance [NMR] and extended X-ray absorption fine structure [EXAFS] and X-ray absorption near-edge structure [XANES]) will also be applied. The surface chemistry will be probed by surface acidity and surface redox measurements. This fundamental information should allow better understanding of the synergistic interactions that occur in mixed surface metal oxides.

Department of Chemistry

311. ***Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane***
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Palladium metal displays a remarkable structure sensitivity under mild conditions for C-H bond activation and dissociative chemisorption of methane in the order Pd(679) > Pd(311) > Pd(111). Defects promote the more efficient classical chemical pathway, while methane cracking on the smooth (111) surface is dominated by a tunneling mechanism. Oxygen, a reaction component in partial oxidations of hydrocarbons, induces surface states in the Pd metal revealed by angle-resolved X-ray photoelectron diffraction (XPD) and found to extend into 2-5 subsurface layers. Lateral interactions of O adatoms with surface halogen promoters have also been found to extend over several Pd-Pd distances and analyzed in terms of mobile adsorbate compression model for O surrounded by ensembles of immobile Cl adatoms. In a systematic examination of chloro-hydrocarbon (Cl-HC) precursors to ordered-disordered surface Cl ensembles, C_2Cl_4 was found to dissociatively chemisorb on Pd(100) into well-ordered layers, in contrast to disordered overlayers from CH_2Cl_2. Accessibility of the Cl-C overlayers to O was determined for different molecular Cl-HC precursors. Alkali (Cs) overlayers on MoS_2(0001) partially transfer an electron into the sulfide conduction band (CB). Locality and energy dispersion of this electron were determined by XPD. Theoretical valence band (VB) calculations were used to interpret the XPS observations and to identify the crystal orbitals in the VB and CB regions. Reactions of the transferred electron with Cl_2, O_2, and H_2O were carried out, and the product species identified for O were peroxide and superoxide but not oxide species.

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Department of Chemistry

312. ***Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Models and Precursors for Fullerenes***

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The discovery of the fullerenes has provoked considerable interest in potential applications, including batteries, conductivity, catalysis, and hydrogen storage, among others. This program deals with the synthesis and chemistry of polynuclear aromatic hydrocarbons possessing carbon frameworks represented on the buckminsterfullerene [C_{60}] surface. These so-called “buckybowls” serve as fullerene models. The simplest example is corannulene, $C_{20}H_{10}$, the polar cap of buckminsterfullerene. However, corannulene undergoes rapid bowl-to-bowl inversion that lessens its utility as a fullerene model, and this program has sought “locked” bowl-shaped hydrocarbons: over 20 carbons and more than one five-membered ring (five-membered rings provide curvature). Goals include (1) the synthesis of new “fullerene-fragments,” (2) examination of the properties of these novel hydrocarbons, especially how large they must become before their properties become less PAH-like and more fullerene-like, and (3) the combination of fullerene-fragments to produce carbon cages. This program produced the first “locked” buckybowl (cyclopentacorannulene) and the first synthesis of a “semibuckminsterfullerene” ($C_{30}H_n$ corresponding to one-half of buckminsterfullerene). To date, two such hydrocarbons have been prepared. The synthesis of a $C_{32}H_{12}$ fragment was recently accomplished, and progress has been made toward the synthesis of $C_{46}H_{16}$. The latter hydrocarbon will represent the largest fullerene fragment produced yet (by ten carbons), if successful.

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Department of Chemistry

313. ***Metallocarboxylate Chemistry***

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Our goal is to provide a base of information that may assist in the development of catalyst systems that can convert CO_2 to useful C_1 or C_2 products. The special focus of this project is on the transition metal organometallic chemistry of carbon dioxide. The studies include the development of synthetic strategies leading to a variety of CO_2 complexes, spectral and structural characterizations of them, and explorations of their chemical reactions. During the past year, we have used transmetallation reactions of a CO_2-bridged rhenium-tin complex to generate new CO_2-bridged complexes having unusual structural types (including one with two bridging carbon dioxide ligands). Also, work has been initiated on a broad spectrum of ruthenium(II) polypyridyl complexes with carboxylate (-COOH, -COOR, and CO_2) ligands; such compounds are little known but often proposed as intermediates in catalytic reductions of CO_2. New complexes with bipyridyl, phenanthroline, and terpyridyl ligands, including some with mixed polypyridyl ligands, have been prepared and several have been structurally characterized.

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Department of Chemistry

314. ***High-Pressure Heterogeneous Catalysis in a Low-Pressure, Ultrahigh Vacuum Environment***

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The aim of this project is to carry out high-pressure, heterogeneous catalytic reactions in a low-pressure, ultrahigh vacuum environment. These studies have now become possible because of the culmination of several investigations in our laboratory over the last six years, resulting in the development of new physical processes and techniques: collision-induced absorption; collision-induced recombinative desorption; bulk vibrational spectroscopy; and the synthesis of adsorbed, reactive intermediates by translational and collision-induced activation. These new processes allow the simulation of a high-pressure environment while maintaining the single-collision conditions in which microscopic reaction steps and intermediates can be elucidated and detected by molecular beam scattering coupled with high-resolution electron energy loss spectroscopy. Results to date show that bulk H is the reactive species in the high pressure hydrogenation of ethylene, while both bulk H and surface bound H are reactive in the hydrogenation of acetylene. The different reactivities of surface H are the result of the presence of a second π orbital on acetylene to which the surface bound H is readily accessible.

315. ***Controlled Synthesis of Polyenes by Catalytic Methods***
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A way has been found to synthesize totally new polyenes in a controlled living fashion from dipropargyl derivatives employing well-characterized alkylidene complexes of the type $M(CHCMe_2R)(NAr)(OR')_2$ [M = Mo or W, R = Me or Ph, Ar = 2, 6 diisopropylphenyl, R′ = $OCMe_3$, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, or various phenoxides] as catalysts. Dipropargyl derivatives of the type $HC{\equiv}CCH_2XCH_2C{\equiv}CH$ (X = NR, O, $C(CO_2R)_2$, $SiMe_2$, and so forth) are cyclopolymerized to give soluble polyenes that contain either six-membered rings (head-to-tail cyclopolymerization) or five-membered rings (tail-to-tail cyclopolymerization). The reaction can be controlled by varying the solvent and the type of catalyst so that “dangling” chains resulting from simple insertion of one of the propargyl groups are absent. Addition of one of the acetylene bonds to an alkylidene to yield a new disubstituted alkylidene normally would essentially terminate polymerization, since the disubstituted alkylidene would not react readily with more terminal acetylene. This problem is avoided by the speed of the intramolecular cyclization reaction to give a five-membered ring and a new monosubstituted alkylidene. This new polymerization reaction will lead to a large number of new materials, since the conditions of polymerization are relatively mild (versus Ziegler-Natta conditions), and many functionalities are therefore tolerated. In addition to the synthesis of polyenes, we are investigating new catalysts for the living polymerization of ethylene and terminal olefins. These are noncyclopentadienyl-containing catalysts having two metal-amido bonds (see JACS, 3830 (1997)). The living characteristics allow, for the first time, the synthesis of block copolymers from ordinary olefins. We are investigating the generality and limitations of these living polymerization catalysts.

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Department of Chemical Engineering

316. ***Zeolite Characterization and Dynamics: The Effect on Molecular Transport and Catalyst Selectivity***
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Zeolitic materials are most often crystalline alumina-silicates with microporosity (less than 20Å) created by interconnected ring-like structures. These channels give sorbing molecules access to the intraparticle surface where chemisorption and reactions occur. Since the channels within the lattice are similar in size to sorbing molecules, the term “configurational diffusion” has been used to describe intraparticle transport. The limited size of the products for the reactions of hydrocarbons, selective sorption, and selectivity in isomerization and trans-alkylation reactions have been ascribed to this “shape selectivity.” This research focuses on three related aspects of zeolites: the mutual interactions between adsorbing molecules and the zeolite lattice, the nature of the pore structure of the zeolite characterized during adsorption, and the influence of extreme steric constraints on cracking and isomerization reactions for cycloalkanes. Earliest perceptions of the pore structure within a zeolite have depended on the visualization of the Si(Al)-oxygen crystalline bond network from X-ray diffraction (XRD) studies of the solid structure. Recent studies employing solids nuclear magnetic resonance (NMR) and in situ XRD have documented that the shape of the adsorbing pores can change on adsorption. More recently, detailed spectroscopic studies of adsorption and of adsorbing molecules have begun to provide a picture of the pore structure and the sorbing species during sorption. In situ infrared spectrometry (specifically far-FTIR) and thermal or gravimetric analyses (DTA and TGA) are also being employed to understand the dynamic configurational changes in the sorbing species and the energetics of these interactions. Several of these techniques have been developed in this research, and each is being used in concert to understand the effects of the interactions between adsorbing molecules, their transport, and their reactivity. Specifically, ^{29}Si, ^{129}Xe, and ^{15}N NMR are being employed in conjunction with high resolution adsorption, HRADS, with DTA-TGA, and with FTIR for the initial studies of the adsorption of C6 and C7 cycloalkanes within ten- and twelve-member ring zeolites. In addition, the rate of adsorption/diffusion is being quantified. The cracking and isomerization reaction of these cycloalkanes is being studied to understand the symbiotic relationship between dynamic pore/adsorbate interactions and the resultant reactions of these cycloalkanes.

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Department of Chemistry

317. ***Towards Computer Aided Catalyst Design: Three Effective Core Potential Studies of C-H Activation***
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We focused on development of better techniques for modeling metal chemistry. Three different methods were developed and validated to provide a set of tools for efficient analysis of catalytic reactions. Applications included selective methane activation by transition metal and lanthanide complexes, vanadium oxidation catalysts, and phosphine cyclometallation. The latter is an important catalyst degradation pathway, and calculations combined with previous work suggest routes to minimizing this process. In methane activation by electrophilic complexes, calculations suggested new, more potent catalysts through the use of “variable denticity” ligands. For vanadium complexes, we developed desktop methods for structural prediction. We now seek to combine these with techniques for spectroscopic prediction to probe transient active species in biological and industrial oxidation catalysts. The techniques developed in our lab are now being applied to the solution structure of catalysts and catalysis involving extended systems. A novel approach to modeling inorganic molecules was researched—artificial intelligence (AI). AI is competitive with quantum methods for structural and spectroscopic prediction and greatly superior for enthalpic data. The latter is significant, given the difficulties in calculation of reaction energetics using quantum methods and the importance of accurate determination of these quantities in computer-aided catalyst design.

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Department of Chemistry

318. The Role of Hydrogen in C-N, C-C, and C-S Bond Activation on Ni and Pt Surfaces
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Development of a more detailed understanding of hydrogen-induced reactions in absorbed organic molecules containing C-S, C-C, and C-N bonds on nickel and platinum single crystal surfaces remains our primary objective. We have used energetic forms of hydrogen to initiate bond activation in a series of adsorbed organics that do not react with coadsorbed hydrogen. This approach has resulted in a new understanding of the intermediates formed during bond activation and recent results suggest the reactivity trends observed are similar to those observed during higher pressure studies. For instance the mechanism for C-C bond activation in strained cycloalkanes with energetic forms of hydrogen is more complex and occurs at higher temperature on platinum relative to nickel. Atomic hydrogen has also been used to study C-N bond activation for the first time. C-N bond activation by gas phase atomic hydrogen in cyclohexylamine occurs 70 degrees below the reaction with coadsorbed hydrogen. C-S bond activation studies, focusing on benzenethiol and cyclohexanethiol, have shown coadsorbed hydrogen to be crucial to the stabilization and subsequent reaction of hydrocarbon fragments. In summary, the role of hydrogen has been explored in the reactions of C-C, C-N, and C-S bond containing organic molecules on Pt and Ni metal single crystals and has yielded fundamental new information regarding these important reaction systems. The work has been expanded to include fundamental studies of propane and propylene oxidation over platinum surfaces in cooperation with Ford Science Laboratory. Synchrotron-based studies in combination with surface science methods will be used to elucidate mechanisms of hydrocarbon oxidation over a broad range of temperatures and stoichiometries. Supporting work to evaluate calorimetric hydrocarbon sensors for improved monitoring and control of internal combustion engines will be conducted at Ford.

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Department of Chemical Engineering and Materials Science

319. Homogeneous—Heterogeneous Combustion: Chemical and Thermal Coupling
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The roles of homogeneous and heterogeneous reactions in catalytic oxidation processes are being studied experimentally and theoretically by measuring rates and concentration and temperature profiles near reacting surfaces and by calculating these profiles for known kinetics. Laser-induced fluorescence methods are being developed to measure the concentrations of free-radical intermediates near reacting surfaces for several combustion reactions on polycrystalline platinum and rhodium as functions of surface temperatures and reactant composition, pressure, and temperature. Concentrations of stable and radical intermediates with and without homogeneous reaction will be measured directly. Concentration and temperature profiles are also being calculated for various reaction processes and flow conditions. Of particular interest is the occurrence of multiple steady states and oscillations for various models of homogeneous-heterogeneous processes. Reaction rate expressions for individual surface and homogeneous reactions are used to simulate the experimentally observed behavior. Particular interest centers on the selectivity of partial oxidation reaction, such as production of CO and hydrogen from methane oxidation, olefins by oxidative dehydrogenation of alkanes, and oxygenates by oxygen addition to alkanes. The objective of this research is to understand the contributions of each type of reaction in practical situations in catalytic reactors and combustors in order to determine their implications in reactor selectivity for chemical synthesis and for pollution abatement.

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Department of Chemistry

320. Late Transition Metal Oxo, Imido, and Hydrazido/Dinitrogen Complexes
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This project involves the exploration of the chemistry of late-transition metal oxygen and nitrogen bonds and is of relevance to catalytic processes in chemical manufacturing, energy conversion, and pollution control. In our last report we described the synthesis and structural characterization of the unique dinitrogen complexes $[(LAu)_3N_2(AuL)_3]^{2+}$ (L = a phosphane) and their potential relevance to nitrogen fixation. Reductive protonation of these complexes yields ammonia and/or hydrazine. The relative yields of ammonia and hydrazine depend on L in a subtle way. Our initial efforts at elucidating the reductive protonation pathways have revealed that under the conditions where ammonia and hydrazine are formed reduction of $[(LAu)_3N_2(AuL)_3]^{2+}$ is slower than protonation and that derivatives that give high yields of ammonia have more stable protonation products. NMR experiments with ^{15}N-labeled compounds are underway and have already shown that $[(LAu)_3N_2(AuL)_3]^{2+}$ are structurally stable in solution (on the NMR time scale) and do not undergo exchange reactions with atmospheric N_2. A potential protonation product $[(LAu)_2HNNH(AuL)_2]^{2+}$ ($L = PBu^t_3$) has been isolated from the reaction of $[(LAu)_3O]^+$ and hydrazine and has been structurally characterized. Reductive protonation of this complex also gives ammonia and hydrazine.

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321. ***Electrically Stimulated Supported Metal Catalysts***
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This project is directed to the use of unconventional methods in heterogeneous catalysts in order to prevent some of the shortcomings that are encountered in present technology. The objective is to develop a novel experimental approach in which either local heating and/or electronic perturbations of the supported metal particles can be performed by an electrically stimulated technique. The localized heating concept should result in an enhancement of the efficiency of the reaction, since only those gas molecules that are very close to or in direct contact with the catalyst surface will be thermally excited. One of the ramifications of such a procedure would be that the rate of uncatalyzed reactions will be significantly decreased. Studies are being conducted using the decomposition of 1-butene to probe the carbon depositing characteristics of nickel, iron, and copper supported directly on carbon fibers and a corresponding set of experiments where the carbon fibers are coated with selected oxides prior to the incorporation of the metallic component. In a further portion of the project, the rudiments of the experimental approach described above are being extended to cover the behavior of systems where an applied electric field is utilized to electrically stimulate the catalytic action of metal particles dispersed on certain electronic ceramics. In addition to generating valuable fundamental knowledge about the catalytic action of the metals, this approach could open up new horizons for the exploitation of oxide supported metal particles.

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322. ***Mechanistic Studies of Transition Metal-Catalyzed Alternating Copolymerizations of Carbon Monoxide with Olefins***
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The basic objectives of this program are to elucidate the fundamental mechanisms of Pd(II)- and Ni(II)-catalyzed alternating copolymerizations of carbon monoxide with olefins and to develop and investigate new catalytic systems. Specifically, well-defined organometallic precursors that yield active catalysts systems are being investigated to determine the catalyst resting state, details of the carbon-carbon bond coupling processes, the kinetics of chain growth, and the modes of chain termination and chain transfer. Proposed transient intermediates are prepared through independent low-temperature synthesis to verify their involvement in the catalytic cycle. Extensive mechanistic investigations have been completed on the copolymerization of ethylene and carbon monoxide using $(phenanthroline)Pd(CH_3)(OEt_2)^+ BAr'^-_4$ ($Ar' = 3,5-(CF_3)_2C_6H_3^-$) as the initiators; most of these results have been recently published (*J. Am. Chem. Soc.* 1996, 118, 2436-2448). Similar studies have recently been completed using various substituted styrenes and carbon monoxide. A unique method involving bidentate ligand exchange at the metal center (without chain transfer!) has been developed for synthesis of stereoblock alternating copolymers of CO and styrenes. Mechanistic studies have established details of the exchange process and some of these results have been communicated (*J. Am. Chem. Soc.,* 1996, 118, 7219-7220). Much of our current efforts are focused on detailed mechanistic studies of ethylene-CO and α-olefin-CO copolymerizations using a series of Pd(II) complexes employing various bidentate phosphine ligands. The well-defined ether complexes $(P-P)Pd(CH_3)(OEt_2)^+ BAr'^-_4$, where $(P-P) = (C_6H_5)_2P-(CH_2)_n-P(C_6H_5)_2$ ($n = 2,3,4$), $(i-Pr)_2P(CH_2)_3P(i-Pr)_2$, and $(CH_3)_2P(CH_2)_2P(CH_3)_2$, are used as initiators. Important intermediates generated include the gamma-carbonyl chelate complexes, the acyl carbonyls, the alkyl carbonyls and the alkyl olefin complexes. The rates of migratory insertion in the latter two species have been studied and significant variations have been observed as a function of the structure of the bidentate phosphine ligand. In situ studies of the working catalyst systems are underway with the objective of elucidating the structure of the catalyst resting state(s) as a function of the structure of the phosphine and the relative concentrations of olefin and CO. New neutral catalyst systems containing anionic bidentate P-N ligands are being prepared and will be examined for copolymerization activity.

323. ***Bond Forming Reactions of Carbyne and Nitrene Complexes***
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Oxidation of an amido precursor complex with iodine in the presence of base yields a new tungsten nitrene complex with an ancillary alkyne ligand in the coordination sphere. Reactions of the cationic nitrene complex with nucleophiles can occur at the nitrogen atom to reform the amido complex or at the carbonyl ligand to form acyl derivatives. Studies of substituent effects for nitrene transfer from PhINTs to olefins with a copper catalyst have been completed. Results for forming aziridine rings are distinct from results involving cyclopropane formation from ethyldiazoacetate and styrene with the same catalyst recipe. An electrophilic mechanism based on copper(I) for the carbene transfer and a radical-like mechanism based on copper(II) for the nitrene transfer have been proposed. By combining two carbyne reagents, $Tp'(CO)_2MoCCl$ and deprotonated $Tp'(CO)_2WCCH_3$, dimers containing the CCH_2C linkage can be synthesized. The intermediate dianion formed by double deprotonation has a rare cumulene resonance form. One-electron oxidation of the anionic vinylidene complex leads to a coupling reaction to form a CCH_2CH_2C bridged dimer. Stepwise proton removal and subsequent oxidation first yields the CCH=CHC bridge that can then be converted to the parent C_4 bridge.

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324. ***Solid-State, Surface, and Catalytic Studies of Oxides***
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Multicomponent oxides are catalysts for a number of technologically important reactions, including selective conversion of low-priced saturated hydrocarbons by oxidation (selective oxidation) to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher value, and for the removal of nitrogen oxides, which are atmospheric pollutants from exhausts of lean-burn, gasoline, or diesel engines (lean NO_x conversion). The emphasis of this project is to identify the properties of oxidic catalysts that determine their catalytic properties in these reactions. In selective oxidation, it was found that modification of a silica-supported vanadium oxide catalyst with phosphorus resulted in significant increase in the selectivity for the formation of maleic anhydride in butane oxidation. Spectroscopic characterization of the samples suggested that the high selectivity could be correlated with the formation of vanadium metaphosphate, while the activity was due to the presence of V^{5+}, probably as vanadyl phosphate. However, the supported catalysts still have lower yield of maleic anhydride than the unsupported vanadyl pyrophosphate catalysts. In lean NO_x reduction with hydrocarbons, it was found that oxide catalysts containing highly dispersed transition metal ions in an inert matrix are effective catalysts for high temperature (>350°C) applications. Thus, Co supported on γ-alumina is more effective if the sample has been heated to a higher temperature to disperse the cobalt oxide into the support. These highly dispersed ions are more difficult to reduce. A similar observation was made on the alumina-supported Ag catalysts. The desirable catalytic properties could be explained on the basis of the inability of the catalyst to activate oxygen rapidly. Noble metal catalysts, particularly Pt, are the most active for lower temperature applications.

Department of Chemistry

325. ***Organometallic Adsorbates and Models Chemistry, Spectroscopy, and Catalysis***
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The project goal is to characterize and model chemisorptive processes responsible for dramatic enhancements in catalytic activity when actinide, lanthanide, and early transition element organometallic complexes are adsorbed on Lewis acidic surfaces. Surface chemistry is studied by chemical and spectroscopic probes, while catalytic properties are characterized by kinetic measurements, isotopic labeling, product stereochemistry, and spectroscopy. On Lewis acid supports, Cp_2MR_2 complexes (Cp = cyclopentadienyl-type ligand; M = Th, U, Zr; R = alkyl group) undergo R^- abstraction to yield highly electrophilic Cp_2MR^+ species, which are shown to be active catalytic centers by CPMAS NMR. Importantly, these species can be spectroscopically, structurally, and functionally modeled in solution by isolable Cp^2MR^+ X^- complexes, where X^- is a weakly coordinating fluoroarylborate or fluoroaluminate anion. The chemisorptive process as well as the pathway by which methylalumoxane, "$[Al(CH_3O]_n$" activates organo-group 4 complexes for industrial scale olefin polymerization processes can be modeled, hence better understood, using a variety of fluoroarylborane organo-Lewis acids as abstraction reagents. Finally, these catalysts can be employed to produce completely new types of functionalizable polyolefins via catalytic ring-opening processes in which exo-methylenecycloalkanes are opened to yield exo-methylene substituted polyethylenes.

326. ***Chemical Interactions in Multimetal-Zeolite Catalysts***
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The problem of changing the selectivity of Rh catalysts in CO hydrogenation from hydrocarbon production to synthesis of oxygenates by "promoting" the catalyst with manganese has been addressed. By using zeolite supported samples, it was possible to synthesize samples with identical Rh content but with the manganese being present either as Mn^{2+} ions or as MnO particles. It was found that, in the former case, the selectivity for oxygenates was = O; in the latter case a high yield of ethanol and ethyl acetate was obtained, suggesting that acetate ions are primary products. Spectroscopic characterization revealed that acetate ions on MnO are precursors of oxygenate products. The acetate ions can be formed either from syngas + CH_x groups migrating from Rh clusters to adjacent MnO particles or, in the absence of Rh, from syngas and $CHCl_3$. In the presence of Rh, the acetate ions are readily reduced with H_2 to ethanol. The catalyst promoter Mn thus acts as the cocatalyst MnO in a bifunctional mechanism. Parallel to this work the isomerization of butane over sulfated zirconia has been studied. It was found that this catalyst is not a superacid but that it catalyzes the formation of adsorbed C_8 intermediates, which subsequently undergo β-fission to iso-C_4 entities. Over deuterated catalysts, monodeuterated-isobutane is initially formed.

327. Mixed Cluster Chemistry of SO_2 and Polycarbides
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Current research focuses on reactions of SO_2 with heterometallic carbonyl clusters. The heterometallic butterfly carbide clusters with the general formula $[MFe_3(CO)_n\mu^4\text{-}C]^x$ [M = Fe, W, Cr, Rh, and Mn] react with an excess of SO_2 to give the known cluster $[Fe_3(CO)_7(\mu\text{-}SO_2)\mu^3\text{-}CCO]^{2-}$. Reaction of one equivalent of SO_2 with $[WFe_3(CO)_{13}\mu^4C]^{2-}$ gives a new mono-SO_2 product, $[Fe_3(CO)_8(SO_2)\mu^3CCO]^{2-}$ and $W(CO)_6$. $[WFe_3(CO)_{14}]^{2-}$ reacts with an equimolar amount of SO_2, producing $[Fe_3(CO)_7(SO_2)\mu^3S]^{2-}$ and $W(CO)_6$. All of the new compounds have been identified by IR, Raman, ^{13}C NMR, mass spectrometry, EDAX, and X-ray crystal structure. The heterometal plays an important but, as yet, undetermined role in these reactions.

328. In-Situ Characterization of Working Catalysts by Ultraviolet Resonance Raman Spectroscopy
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Resonance Raman spectroscopy measurements that utilize ultraviolet excitation will be used to study catalysts under reaction conditions that produce carbonaceous residues (coke). Ultraviolet excitation largely avoids the strong fluorescence that makes conventional Raman spectroscopy very difficult on coke covered catalysts. Experiments will be carried out to first clarify the strengths and limitations of the UV resonance Raman method and then perform in situ characterization of zeolite catalysts under the reaction conditions typical of hydrocarbon conversion where catalyst coking occurs. Simultaneous on-line GC analysis of conversion and product distributions will make it possible to correlate the results of in situ characterization with catalyst performance. The goals of this work are to elucidate the chemical reactions that lead to coke formation, to better understand the influence of zeolite properties and reaction conditions on coke formation, and to discover how the zeolite structure responds to reaction conditions and the presence of coke deposits.

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Department of Chemistry and Biochemistry

329. Transition Metal-Mediated Thermal and Photochemical Carbon Dioxide Activation
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The overall goals of this project are to elucidate the patterns of reactivity, both thermal and photochemical, of coordinated CO_2 and to develop catalytic processes based on these patterns. Our activities during the past year have been concentrated in three areas: (1) investigation of the Pd-catalyzed carboxylation of organotin compounds; (2) study of potential metal-mediated carboxylation of cyclopropanes; and (3) study of group 16 (O,S,Se,Te) atom additions of $Cp_2TaH(CO)$. Regarding (1), we have discovered that Pd(0) complexes catalyze the efficient carboxylation of allylstannanes by CO_2, producing allylcarboxylate-Sn esters. This reaction, whose scope and mechanism are under investigation, constitutes the first example of transition metal activation of main group M-C bonds towards carboxylation. For project (2), a potential means for inserting CO_2 into reactive C-C bonds, a number of cyclopropanes have been screened for reactivity with Pd(0) and Ni(0) complexes in the presence of CO_2. Since carboxylation products (e.g., lactones) have not yet been observed, more reactive complexes and cyclopropanes are now under investigation. Study (3), which seeks to model heterogenous CO sulfurization and oxidation, has led to the generation of labile X-atom transfer intermediates, tentatively assigned as $Cp_2TaH(CO)X$ and $Cp_2TaH(COX)$.

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Department of Chemical Engineering

330. Activity and Selectivity Enhancements in Liquid-Phase Reactions by Metal-Support Interactions
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The project objectives are to study metal-support interactions that have a pronounced influence on adsorption and catalytic behavior and to use these effects to alter hydrogenation reactions, such as those involved in fine chemicals production. In addition to determining kinetic behavior, emphasis is on characterizing adsorbed molecules as well as the chemical and physical states of the metal and support. A unique high-pressure, liquid-phase hydrogenation reactor system has been constructed and tested. Its design allows the continuous monitoring of hydrogen consumption via a mass flow sensor, thus providing real-time rate data to complement periodic GC analyses. A very thorough kinetic study of liquid-phase benzene hydrogenation over Pd catalysts established, using the Weisz criterion and the Madon-Boudart test, that both internal and external diffusional limitations were absent at stirring speeds above 500 rpm. Hydrogen solubility in the liquid, not hydrogen pressure, was shown to be the important kinetic driving force, indicating that solvent effects may be attributable to this factor rather than, or in addition to, dipolar interactions. A reaction model proposed previously in this program for the vapor-phase reaction fit all the data and gave consistent thermodynamic parameters. Having verified the absence of deactivation and contamination in this reactor, a more complicated reaction—citral hydrogenation over Pt— is now being studied. Also, initial results for liquid-phase acetic acid hydrogenation showed rates were too low over most metals in the pressure range safely achievable (1-55 atm); therefore, a vapor-phase study is underway. Early results show that Pt/titania (MSI) is much more active than Pt/silica and gives ethanol and ethylacetate as products, whereas Pt/ferric oxide gives acetaldehyde.

Department of Chemistry

331. Transition Metal-Mediated Transformations of Small Molecules

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Catalytic transformations by transition metals and their compounds are of fundamental scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands usually associated with such systems. The current research is focused on several transition metal-catalyzed polymerizations and copolymerizations. One important area of research is the alternating copolymerization of alkenes with carbon monoxide. The resultant polymers are of great current interest because of their superior mechanical properties and photodegradability and because they are precursors to a wide range of functionalized polymers. The principal research goals are (1) the design of living copolymerization systems that would allow the directed synthesis of block terpolymers involving the copolymerization of two different alkenes with carbon monoxide, as well as block polymers incorporating polyalkene and alkene-carbon monoxide blocks, (2) the synthesis of regiospecific, stereospecific, and, ultimately, chiral alternating alkene-carbon monoxide copolymers, and (3) the synthesis of alternating copolymers of functionalized alkenes with carbon monoxide. A second area of research that also involves the use of carbon monoxide as a monomer is the direct synthesis of (a) polycarbonates and polyoxalates from carbon monoxide and diols and (b) polysuccinates from carbon monoxide, alkenes, and diols. Finally, the design of novel catalytic systems for the homo- and copolymerizations of functional alkenes is being attempted.

Department of Materials Science and Engineering

332. Determination of the Distribution of Hydrogen in Coal by Fourier Transform Infrared (FTIR) Spectroscopy

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The purpose of this research is to determine the role of hydrogen-containing functional groups in coal. In the course of the last year, we have accomplished three things. First, we have developed a statistical mechanical model for coal treated as a densely cross-linked network. Second, we have used the results of this work to analyze the temperature dependence of the elastic modulus of swollen coal particles, demonstrating that the elastic response is primarily entropic.This means that coal must be a macromolecular network as opposed to an associated structure. Finally, we have found that there are correlation and connectivity effects that must be accounted for in treating macromolecule/solvent interactions, and we are presently incorporating these factors into our treatment of coal swelling.

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Department of Chemical Engineering

333. Studies of Metal-Oxide and Oxide-Oxide Interactions in Automotive Emissions-Control Catalysis

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Interactions between ceria and precious metals are critical for oxygen storage in automotive applications. Ceria provides oxygen under rich conditions and takes up oxygen under lean conditions, but is known to lose its properties after aging. We have demonstrated that this is, in part, due to the structure sensitivity of ceria, which affects its reducibility in a critical manner. Formation of mixed oxides with zirconia is also known to be beneficial for reasons that are not understood. We are presently examining the fundamental reasons behind how metals interact with ceria, what leads to the structure sensitivity of ceria, how zirconia stabilizes ceria, and how interactions with ceria affect reactions of interest. Our work includes steady-state kinetic measurements for various reactions, desorption kinetics, and TEM characterization of ceria films.

Department of Chemistry

334. Inorganic Polymers and Materials

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This project is focused on the development of new synthetic routes for the formation of technologically important solid state materials in processed forms. Current studies are conducted on the syntheses, properties, ceramic-conversion reactions, and applications of new boron and silicon based polymers, with a particular focus on the design of new hybrid polymeric precursors to SiNCB composites. Such composite materials have recently been shown to have exceptional high temperature and oxidative stabilities and have projected uses in gas turbine engines. Major achievements of the last year have included the design and synthesis of a range of new melt-spinnable polymeric precursors to both boron nitride and composite SiNCB ceramic fibers. The continued development of the fundamental synthetic methodology needed to produce new inorganic monomers and polymers is also a key component of this project.

335. Catalytic Hydrogenation of Carbon Monoxide

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Primary objectives for this program are focused on the development of new strategies for conversion of carbon monoxide and hydrocarbons into organic oxygenates at mild conditions of pressure and temperature. Emphasis is placed on designing transition metal complexes to obtain thermodynamic properties and mechanistic pathways that promote the formation and transformation of intermediates, which determine the rate and selectivity for substrate reactions. The initial observation that rhodium porphyrin complexes have the unusual thermodynamic capability to produce metalloformyl (M-CHO) species at low pressures of H_2 and CO has been utilized in guiding the design of metal complexes that manifest both the thermodynamic and kinetic properties necessary for catalytic CO hydrogenation. Production of formyl species from H_2 and CO has now been shown to be a general property for rhodium complexes of nitrogen donor macrocycles and has also recently been extended to complexes of nonmacrocyclic tetradentate ligands with both nitrogen and oxygen donors. Structurally flexible nonmacrocyclic ligand complexes manifest reaction pathways excluded to macrocyclic ligand species that are essential for selective CO hydrogenation to alcohols.The range of materials studied is currently being expanded to electron deficient ligands, ruthenium pyridyl complexes, and bimetallic species. New materials are also being designed to achieve simultaneous activation of CO and CH_4 to give organic formyl and acyl functional groups.

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Department of Chemical Engineering

336. Fundamental Aspects of Selective Reduction of NO_x and Low Temperature Methane Activation Catalyzed by Zeolites

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Medium pore-sized zeolites containing a wide variety of charge-compensating cations are active catalysts for selective reduction of NO by hydrocarbons and for low-temperature activation of CH_4 by NO. The objective of the proposed research is to develop a fundamental understanding of the surface chemistry that governs both of these chemical processes. Metal-loaded zeolites will be prepared by ion exchange under controlled conditions that will be systematically changed in order to vary the type and concentration of metal species. The catalysts are to be characterized by a variety of techniques, including FTIR, MAS-NMR, temperature-programmed reactions with probe molecules, and isotopic exchange reactions. Fundamental information regarding the individual steps involved in the reaction mechanism and which of these steps are rate limiting will be developed by isotopic transient investigations. The role of parameters, such as zeolite acidity, structure, and the reducibility of the charge-compensating cations, will be probed through reaction studies and catalyst characterization, and relationships will be developed between these catalyst properties and key reaction steps, such as the activation of methane. Moreover, the importance of components, such as H_3CNO_2 and NO_2, in forming an N-N bond in these systems will be investigated.

Department of Chemistry

337. Vibrational Spectroscopic Studies of Surface Chemical Interactions in Chemisorption and Catalysis

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Vibrational spectroscopy methods, coupled with electron and photon stimulation of surface species are being used to study surface reactions on model catalyst surfaces. Systems being studied include the thermal oxidation and photooxidation of adsorbed carbon monoxide, the activation of Rh catalytic centers on Al_2O_3 by uv light, and the librational behavior of small adsorbed molecules, such as CO and NH_3. In addition, the first stages of oxidation of a copper single crystal surface have been investigated to determine (by electron stimulated desorption) the location of the most favorable site within or at the edge of ..O-Cu-O... islands for oxidation reactions. Finally, the mobile precursor NH_3 species to chemisorption has been trapped and studied at 32 K.

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Department of Chemistry

338. *Novel Intrazeolite Metal-Oxo Catalysts and Alloy Clusters*

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The focus of this project is the design of novel catalysts based on transition metal chelate complexes and oxo species encapsulated in the cages of zeolites. We combine the catalytic activity of transition metal catalysts with the shape selectivity and well-defined pore structure of zeolite pores. The intrazeolite catalysts are being created via assembly of components inside the zeolite cages and via reactions of organometallic precursors with the intrazeolite surface, primarily with hydroxyl groups, to anchor and stabilize the metal complexes. A new class of intrazeolite manganese triazacyclononane-type chelate complexes has been developed, and their activity in highly selective olefin epoxidation and other reactions has been demonstrated. We have also substantially improved the activity of such complexes in homogeneous catalysis, compared to previous work. Asymmetric, zeolite-encapsulated epoxidation catalysts based on Mn-salen systems have been constructed. Chiral epoxidation of olefins, such as methyl styrenes with enantiomeric excess of about 80%, has been demonstrated with these catalysts. Finally, molybdenum-oxo, vanadyl, and trioxorhenium species have been grafted into zeolite cages. Significant catalytic activity, including selective olefin epoxidation, has been observed in several of these systems. Characterization of the intrazeolite systems includes EXAFS (extended X-ray absorption fine structure) spectroscopy, utilizing synchrotron radiation, in situ FT-IR coupled to thermodesorption, UV-NIR, and ESR spectroscopies.

339. *Catalytic Arene Hydrogenation Using Early Transition Metal Hydride Compounds*

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During the last year, a concerted effort has been focused on gaining a better understanding of the mechanism of arene hydrogenation catalyzed by Group 5 metal hydride compounds. Most of this work has focused on the formation and reactivity of cycloalkene and cyclohexadiene derivatives of Nb and Ta (possible intermediates in arene hydrogenation). The kinetics of the hydrogenation of aryl-phosphines (e.g., PPh_3, $RPPh_2$), etc., by niobium aryloxide systems has been studied and successfully modeled. A mechanistically significant result is the observation of saturation behaviour with hydrogen pressure. Further detailed studies of this effect are underway. The mechanism of olefin and alkyne hydrogenation by $[Ta(OAr)_2(Cl)(H)_2(PMe_2Ph)_2]$(OAr=2,6-diphenylphenoxide) has been studied.

340. *Fundamental Studies of Reactive Intermediates in Homogeneous Catalysis*

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Mass spectrometry and gas-phase ion chemistry techniques are employed to investigate the thermodynamics and intrinsic reactivity of organic and organometallic models for reactive intermediates in combustion and homogeneous catalysis. A new flowing afterglow - guided ion beam apparatus has been constructed for use in determining accurate metal-ligand bond dissociation energies by means of energy-resolved collision induced dissociation. We have also completed the development of an electrospray ionization source for the flowing afterglow apparatus, which provides a means to transfer massive, multiply-charged transition metal complexes from polar solution to the gas phase. Current studies include an investigation of the gas-phase photoreaction and collision-induced dissociation of transition metal polypyridal complexes, including $Ru^{2+}(bipy)_3$, $Ru^{2+}(bipy)_2(pyr)_2$ and $Fe^{2+}(bipy)_3$, (bipy=2,2'-bipyridine; pyr = pyridine). We are also investigating the influence of transition metal coordination on the thermochemical properties of hydrocarbon ligands. The C-H bond dissociation energies, gas-phase acidities, and radical electron affinities have been measured for ferrocene and ferrocenium cation, as well as for selected cyclopentadienyl- and arene-metal carbonyl complexes. The gas-phase reactivity of transition metal containing organic radicals and diradicals has also been explored, with the ultimate aim of developing new types of organometallic reagents.

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Department of Chemistry

341. *I. Metal Carbonyl - Hydrosilane Reactions and Hydrosilation Catalysis; II. Catalytically Relevant Chemistry of (η^5-Indenyl)Ru Alkyl Complexes.*

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The reactivity of $(CO)_5$ MnY (Y = H, CH_3, and CH_2Ph) towards hydrosilanes (e.g., Me_2PhSiH, Ph_2SiH_2) has been studied under thermal and photochemical conditions. $(CO)_5$ MnH proved to be relatively unreactive; $(CO)_5$ $MnCH_2Ph$ cleanly produced $(CO)_5$ $MnSiR_3$ plus $PhCH_2OSiR_3$; and $(CO)_5$ $MnCH_3$ generated, depending upon reaction conditions, mixtures containing $EtOSiR_3$, $EtSiR_3$ (up to 30% each). Mechanistic studies on the origin of $EtOSiR_3$ and $EtSiR_3$ are consistent with hydrosilane promoting alkyl-CO migration, hydrosilation of the acetyl ligand, and, for $EtSiR_3$, deoxygenation of a siloxyethyl ligand. The major manganese-containing material remaining after treatment of $(CO)_5$ $MnCH_3$ with excess hydrosilane has been formulated as $(CO)_4Mn(H)(SiR_3)_2$; its catalytic properties are under study. $[(cod)Rh(acetate)]_2$ and related Rh(I) compounds

$[L_2Rh(O_2CR)]_x$ serve as unusually facile hydrosilation catalyst precursors. Our prototype catalytic system, $[(cod)Rh(acetate)]_2$ and $PhSiH_2$ in benzene, efficiently hydrosilates ethyl acetate to its silyl acetal (ca. 90%/30 minutes). Under comparable conditions, $(PPh_3)(CO)_4MnCOCH_3$ catalytically transforms ethyl acetate to diethylether (95%). $(CO)_5$ MnI, thus far, is the most efficient precatalyst for hydrosilation-then-deoxygenation of metallocarboxylic acids, esters, and silyl esters: $Cp^*(CO)(L)MCO_2R$ (M = Fe, Re; L = CO, NO; R = H, Me, SiR_3). These reactions afford $Cp^*(CO)(L)MCH_2OSiR_3$ as the major, if not exclusive, organometallic product. All of the catalyst systems mentioned are being evaluated for their efficacy and for mechanistic insight in the hydrosilation-then-deoxygenation of formic acid, formate esters, and formate silyl esters. Studies on the synthetic chemistry of indenyl ruthenium alkyl complexes $(Ind)Ru(CO)_2R$ (R = Me-hexyl) and their carbonylation reactions have been finished for the linear alkyl complexes. Samples of pure branched (secondary) compounds [e.g., $(Ind)Ru(CO)_2CH(CH_3)CH_2CH_2CH_3$], which are required for mechanistic studies on the (indenyl ligand) carbonylation-promoted alkyl ligand isomerization, remain elusive.

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342. *Dimensional Effects in Controlled Structures Support Catalysts Derived from Layered Synthetic Microstructures (LSMs)*

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A new class of supported catalysts has been produced, using solid-state fabrication techniques typical of the microelectronics industry. Deposition of alternating, nanometer thick layers of catalyst and support on an inert wafer, followed by etching perpendicular to the flat surfaces to reveal only the edges of the layers, provides a catalyst surface in the form of nanometer-wide, micrometer-long lines (the edge of a thin plate). These layered synthetic microstructures (LSMs), with Ni and silica as catalyst and support, duplicate the size effect ("structure sensitivity") that is observed during ethane hydrogenolysis on traditional silica supported Ni clusters of nanometer "diameter." In principle, any catalyst/support system can be manufactured so that the catalyst and support are uniform in size and geometry with arbitrary nanometer dimensions. Surface studies can be carried out on a totally accessible surface and one that behaves catalytically like a supported cluster. The objective of this research is to develop this new structure as a tool for understanding supported catalysts. LSMs (Ni/SIO_2) will be fabricated by using ion milling to provide higher catalyst surface areas per unit wafer area. Other supports will be studied (Al_2O_3 carbon, MgO, and silica-alumina). The Ni/SIO_2 LSMs will be tested using other structure-sensitive and structure-insensitive catalytic reactions. These include the reaction of CO and H_2 that show a rate maximum with 4 nanometer clusters; cyclopropane hydrogenation exhibits shows a rate maximum with 2 nanometer clusters; and benzene hydrogenation that is unresolved. Characterization will be carried out concurrently. TEM can be used to examine the edge array, Auger analysis will provide a spatially averaged composition, and both STM (AFM) and TPD will be used. Fabrication of Pt based LSMs will be carried out. Platinum catalyzed reactions that would be candidates for study include hydrogen plus oxygen at 273 K, since in excess hydrogen the rate is structure sensitive, while in excess oxygen it is insensitive; the hydrogenation of cyclohexene, which is structure insensitive; and skeletal isomerization of methylcyclopentane, which exhibits selectivity changes (rather than rate changes) with cluster size greater than 2 nanometers.

Department of Chemistry

343. *Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds*

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This project investigates the use of homogeneous transition metal complexes for the cleavage of C-H, C-C, and C-F bonds. Earlier studies of homogeneous C-H bond activation demonstrated that the reactive fragment $[(C_5Me_5)Rh(PMe_3)]$ reacts with a variety of alkanes and arenes to give C-H oxidative addition products, and with fused polycyclic hydrocarbons to give η^2 complexes and/or C-H bond activation products. The project has now been expanded to include C-C and C-F bond activation. Reaction of this same fragment with biphenylene results in aryl-aryl bond cleavage and the formation of rhodium biaryl complex, via initial aromatic C-H bond oxidative addition, followed by intramolecular rearrangement to the C-C inserted product. $(C_5Me_5)Rh(PMe_3)H_2$ serves as a homogeneous catalyst for the hydrogenolysis of the aryl-aryl bond of biphenylene, giving biphenyl. C-C cleavage reactions of biphenylene have also been observed with other rhodium and cobalt complexes. Reaction of $(C_5Me_5)Rh(PMe_3)H_2$with perfluoroarenes has been found to give C-F bond cleavage products of the type $(C_5Me_5)Rh(PMe_3)(aryl_F)H$ plus HF. Mechanistic studies of this reaction indicate that the reaction is catalytic in fluoride ion and that deprotonation of the dihydride complex is followed by nucleophilic aromatic substitution on the perfluoroarene. The ejected fluoride ion then continues the cycle. The C-C cleavage has been extended in a catalytic fashion to Pt and Pd complexes. $Pt(PEt_3)_3$ reacts with biphenylene to give the insertion adduct $Pt(PEt_3)_2$(2,2'-biphenyl). Further reaction with biphenylene cleaves a second C-C bond via a Pt(IV) intermediate and then reductively eliminates a C-C bond to generate a nine-membered metallacycle. A second reductive elimination produces another new C-C bond to generate free tetraphenylene and a $Pt(PEt_3)_2$ fragment, which reacts with more biphenylene to continue the cycle. Studies with the Pd system show similar intermediates of much higher reactivity. Reactions of the related metal fragment tris-(3,5-dimethyltrispyrazolyl)borate [Tp'Rh(CNR) where R = neopentyl] also show C-H activation reactions with of a variety of alkanes and can C-C activate biphenylene and cyclopropane.

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Department of Chemistry

344. Carbon-Hydrogen Bond Functionalization Catalyzed by Transition-Metal Systems

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A primary focus of this project is the development of homogeneous catalysts for the conversion of alkanes to the corresponding alkenes. $[Rh(PMe_3)_2Cl]_2$ and complexes $Rh(PMe_3)_2ClL$ have been discovered to catalyze efficient thermal (non-photochemical) alkane transfer-dehydrogenation under dihydrogen atmosphere. Apparently, the role of H_2 is to add to the complexes, which then dissociate to yield $H_2Rh(PMe_3)_2Cl$, which then reacts with hydrogen-acceptors to give the fragment $Rh(PMe_3)_2Cl$; the latter then reacts with alkanes. More recently, the first example of an efficient thermochemical homogeneous "acceptorless" alkane dehydrogenation catalyst was discovered: $Ir(PCP)H_2$ [PCP = η^3-2,6-$(t\text{-}Bu)_2C_6H_3$, a "pincer" ligand]. Refluxing alkane (cyclooctane, cyclodecane) solutions of the catalyst afford high turnover numbers of the corresponding alkenes. Rh(PCP) is much less effective than Ir(PCP), in contrast with the $M(PR_3)_2Cl$ fragments, where Rh is more effective than Ir. Ab initio calculations prove very useful in understanding this contrast: H_2 addition to Ir(PCP) is predicted to be thermodynamically similar to addition to $Rh(PR_3)_2Cl$, whereas addition to Rh(PCP) is much less exothermic and addition to $Ir(PR_3)_2Cl$ is much more so. The development of improved pincer-ligand catalysts is currently underway. A second objective of this project is the development of metal carbonyl catalysts for the deoxygenation of organoelement oxides using CO. Several such catalyst systems have been discovered and in all cases mechanistic studies have revealed an unanticipated pattern: the reaction proceeds via substitution of a ligand (either phosphine or halide) by CO to give a less electron-rich carbonyl. Although present in very minor concentration, the substitution product is the key species that reacts (via nucleophilic attack at CO and loss of CO_2) to deoxygenate the substrate (e.g., R_2SeO, R_3NO, R_3AsO).

Department of Physics and Astronomy

345. Morphological Instability in Model Thin Film Catalysts: Structure, Reactivity and Electronic Properties

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Our work focuses on the relation between surface structure and reactivity in model bimetallic catalysts (i.e., ultrathin films of metals on metals). We concentrate on atomically rough, morphologically "unstable" single crystal surfaces, such as bcc (111) and fcc (210); these undergo extensive reconstruction and faceting, when covered by monolayer films of or other adsorbates, upon annealing to elevated temperatures. There are three interrelated aspects to our program: structure of bimetallic surfaces, surface reactivity, and electronic properties, as follows: (1) The structures of film-covered W(111) and W(112) surfaces are studied using low energy electron diffraction (LEED) and ultrahigh vacuum scanning tunneling microscopy (UHV STM). We obtain atomically resolved images of Pd-induced (211) pyramidal facets on the (111) substrate and have found that S induces sub-nanometer scale faceted structures with long-range periodicity. (2) A structure sensitive reaction, cyclization of acetylene to make benzene, is studied using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS); we find that a monolayer film of Pd/W(112) is more active for this reaction than multilayer Pd. (3) Synchrotron radiation studies of many metals on W(111) have revealed correlations between interface W4f core level shifts and the heats of metal adsorption.

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Department of Chemical Engineering

346. New Heterogeneous Catalysts for Selective Reduction of NO_x Emissions to Improve Vehicular Transportation

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The objective of this project is the rational identification of new heterogeneous catalysts for the removal of nitrogen oxides (NO_x) from automobile tailpipe emissions through their selective catalytic reduction by hydrocarbons (hydrocarbon-SCR) under excess oxygen ("lean") conditions. The research focuses on platinum-based catalysts due to their high activity and hydrothermal stability. Kinetic studies with propylene (C_3H_6) as the reducing agent were conducted over 0.8 wt.% Pt/Al_2O_3 and Pt/SiO_2 catalysts and indicate the presence of two kinetically distinct regions at temperatures above and below the temperature of maximum NO reduction. The activation of propylene is kinetically significant in the low temperature region. Nitrous oxide (N_2O) selectivities are significantly different in the two regions and are primarily affected by the amount of propylene available. The kinetic studies were complemented by microcalorimetric and in situ FTIR studies over the same catalysts in an attempt to identify the surface species formed during the course of the reaction and study their reactivities. The results indicate the presence of cyanide and isocyanate species adsorbed on Pt, which are believed to be active reaction intermediates.

Department of Chemistry and Biochemistry

347. Studies of the Transformations of Sulfur Containing Heterocycles by Transition Metal Cluster Compounds

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Recent studies have focused on the activation of three- and four-membered strained ring heterocycles, containing sulfur and selenium, by polynuclear metal carbonyl complexes. The principal objective is to develop catalysts for the formation of polythio- and polyselenoether macrocycles by ring opening cyclooligmerization reactions of these precursors. Goals include synthesis of new macrocycles and the development of more efficient routes to known ones and then investigating their potential to serve as ligands for transition metals. Studies include determination of the mechanisms of the cyclooligomerization reactions. The ligand behavior of the macrocycles is being investigated by x-ray crystallographic characterizations of the metal complexes.

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Department of Chemistry

348. Chemistry of Bimetallic and Alloy Surfaces

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The objectives of our research are to determine the reactivity of well-defined Pt-Sn alloy surfaces, clarify the role of a second metal in altering surface chemistry and catalysis on Pt bimetallic and alloy surfaces, and develop general principles for understanding the reactivity and selectivity of bimetallic and alloy catalysts. The surfaces studied are primarily the stable, ordered surface alloys of Sn with Pt, Ni, and Rh that can be prepared by the controlled vapor deposition of Sn onto single crystal metal substrates. We use ALISS and XPD to probe the structure of the surface, and TPD and HREELS to study adsorption and reactions. Alloyed Sn on Pt(111) reduces the adsorption energies in the order alkynes > aromatics > alkenes > alkanes, and we find that pure-Pt three-fold hollow sites are important for strong chemisorption. The sticking coefficients and saturation coverages of hydrocarbons on Pt-Sn alloys illustrate the influence of a modifier precursor state in controlling the adsorption kinetics and that reaction ensembles for hydrocarbon dehydrogenation are quite small (<5 Pt atoms). On these alloys we have recently characterized oxidation and thermal reduction using O_3 and NO_2, used methyl nitrite to produce methoxy intermediates, and studied the interactions of H atoms. We are also measuring activation energies for dissociative chemisorption and determining catalytic reaction kinetics over these surfaces at higher (1-760 torr) pressures.

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Department of Chemical Engineering

349. The Dynamics of Adsorption on Clean and Adsorbate-Modified Transition Metal Surfaces

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The objectives of this research are (1) to determine the probabilities of both dissociative and nondissociative adsorption of alkanes on clean and adsorbate-covered surfaces, (2) to gain an understanding of the molecular dynamics of the adsorption process via experiments and molecular dynamics simulations, and (3) to clarify the role of precursor states in adsorption. Model metal surfaces are studied under highly controlled conditions in ultrahigh vacuum to reveal the dynamical features of the adsorption process. Molecular beams of gases are directed at these surfaces and the dependence of the adsorption probabilities for reactive and/or nonreactive adsorption are measured directly. Stochastic simulations are combined with the experiments related to nondissociative adsorption to gain insight into the energy exchange processes that lead to trapping and adsorption. Recent focus has been on the dynamical aspects of the adsorption of higher molecular weight alkanes on catalytically important surfaces. We have shown that neopentane dissociatively adsorbs by both precursor-mediated and direct collisional activation on Pt(111). Comparison of the reaction probabilities on Pt(111) surfaces with varying defect densities suggest that the active sites for dissociation via the precursor-mediated channel is associated with defects. Using pairwise additive methyl-platinum potentials determined from fitting the dependence of the adsorption probability of ethane on Pt(111) on the incident energy and angle, the adsorption probabilities and the energy scaling determined experimentally for neopentane on Pt(111) were reasonably well predicted by simulations. Comparisons with butanes with differing structure are underway.

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Department of Chemistry

350. Photochemistry of Intermolecular C-H Bond Activation Reactions

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The project has involved measuring absolute quantum efficiencies for the intermolecular C-H bond activation reactions of $(HBPz'_3)Rh(CO)_2$ (Pz' = 3,5-dimethylpyrazolyl) and $CpRh(CO)_2$ (Cp = cyclopentadienyl) in solution. In each case, the quantum efficiencies have been determined by spectroscopically monitoring the photoconversion of the dicarbonyl complex to the alkyl (or silyl) hydido product. A kinetic procedure has been developed that enables complicated photochemical reactions to be studied quantitatively and that accounts for the changing amounts of inner filter effects during these photoprocesses. Consequently, this method has made it possible to obtain absolute quantum efficiencies of intermolecular C-H bond activation in various hydrocarbon solutions for the first time. The results illustrate that in either system the quantum efficiencies are higher in the alkanes compared to the aromatic solvents. The differences in the quantum efficiencies have been related to the overall photochemical reaction mechanisms; however, they are found to be influenced predominantly by nonradiative relaxation processes from the excited states in these complexes.

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Department of Chemistry

351. Mechanistic Examination of Organometallic Electron-Transfer Reactions

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The goal of this research is to provide mechanistic understanding of organometallic reactions important to catalysis. In the past year we have continued to examine one- and two-electron processes in organometallic reactions, including discovery of a proton-transfer catalyzed substitution reaction analogous to the electron-transfer catalyzed substitution reactions. However, electron transfer reagents failed to activate inert complexes for catalytic hydrogenation and hydroformylation such that we reexamined the one case in the literature where electron transfer activated an inert complex $[W(CO)_3(CH_3CN)_3]$ for polymerization of an alkyne. There is only an acceleration by a factor of four in polymerization with the electron transfer reagent (Cp_2Fe^+). We consider this to be insufficient to pursue. We have expanded our research to include studies related to catalysis by organometallic complexes in water. Sulfonated phosphine ligands coordinated to metal complexes impart solubility in water to the complexes. We are using complexes trans-$Ir(CO)(Cl)L_2$ [L=PPh_2(m-$C_6H_4SO_3K$) or P(m-$C_6H_4SO_3Na)_3$] to examine the effect of water as a solvent on reactions with H_2 and CO. Reactions with H_2 are much more affected by water than reactions with CO. Such differences may influence catalytic reactions, such as hydroformylation.

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Department of Chemistry

352. Correlations Between Surface Structure and Catalytic Activity/Selectivity

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The project objective is to address those issues that are keys to understanding the relationship between surface structure and catalytic activity/selectivity. Of primary concern are those questions related to the origins of the enhanced catalytic properties of mixed-metal catalysts and the critical active site requirements for molecular synthesis and rearrangement. The experimental approach utilizes a microcatalytic reactor contiguous to a surface analysis system, an arrangement that allows in vacuo transfer of the catalyst from one chamber to the other. Surface techniques being used include Auger (AES), UV and X-ray photoemission spectroscopy (UPS and XPS), ion scattering spectroscopy (ISS), temperature programmed desorption (TPD), low energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), infrared reflection-absorption spectroscopy (IRAS), and scanning probe microscopies (STM/AFM). Currently, the preparation, characterization, and determination of the catalytic properties of ultrathin metal and metal oxide films are being explored. Specifically, the program is proceeding toward three goals: (1) the study of the unique catalytic properties of ultrathin metal films; (2) the investigation of the critical ensemble size requirements for principal catalytic reaction types; and (3) the modeling of supported catalysts using ultrathin planar oxide surfaces.

353. Solid-State NMR Studies of Zeolite Acidity

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We have elucidated roles for solvent effects in zeolite catalysts, an effect that we call solvent-enhanced solid acidity (SENSA). Coadsorption of species with high dielectric but low proton affinity results in higher effective acid strength, as reflected in probe molecule studies as well as the formation of reactive charged species (oxonium ions). Hydrogen bonding between zeolite acid sites and many organic adsorbates has been characterized in great detail through a combination of NMR, infrared, and theoretical methods. A solid acid catalyst on the threshold of superacid strength was characterized by various means. The theoretical work described above was carried out in collaboration with Dr. John Nicholas at Pacific Northwest National Laboratory.

354. Catalysts and Mechanisms in Synthesis Reactions
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The objective of this research is to understand the role of surface-generated gas-phase radicals in the catalytic oxidation of hydrocarbons, with emphasis on the conversion of methane to more useful chemicals and fuels. Matrix isolation electron spin resonance (MIESR), variable ionization energy mass spectrometry (VIEMS), and laser-induced fluorescence (LIF) methods have been used to detect radicals that emanate from or react with metal oxide surfaces during a catalytic reaction. The detection of methyl radicals using the MIESR system has been effective in establishing the mechanism by which methane and ethylene react to form propylene. The technique has been used to demonstrate that methyl radicals react with adsorbed ethylene to form propyl radicals, which rapidly lose a hydrogen atom. The VIEMS system has been used to follow the role of methyl radicals formed over Ba/MgO catalysts during the selective catalytic reduction of nitric oxide to N_2. It has also been demonstrated, using LIF, that water and oxygen react over strongly basic oxides, such as lanthanum oxide, to form hydroxyl radicals in the temperature range 1200 to 1350 K. The hydroxyl radicals are believed to be formed by the abstraction of hydrogen atoms from water at reactive surface oxygen ions. These radicals may play an important role in catalytic combustion, although methane competes with water for active centers on the surface.

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Department of Chemical Engineering

355. Catalytic Hydrocarbon Reactions over Supported Metal Oxides
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The research program focuses on the catalysis of hydrodesulfurization (HDS) over molybdenum-based catalysts. We seek to understand the catalytic features/sites that control hydrogenation, hydrogenolysis, and isomerization during HDS. Unpromoted silica-supported molybdenum oxides and molybdenum sulfides are studied. Model catalyst systems are prepared from organometallic precursors or cluster compounds to generate supported structures that feature Mo(II) and Mo(IV) cations that are isolated or in ensembles and that have either Mo-O or Mo-S bonds. Conventional MoS_2 catalysts, which contain both edge and rim sites, are studied. Finally, single-layer MoS_2 structures will be prepared from 2H-MoS_2 powder so that the model systems can be compared against a disulfide catalyst that only involves rim sites. Catalytic reactions for thiophenes and dibenzothiophenes are studied over the various catalysts. Vapor phase, atmospheric pressure and liquid phase, high pressure conditions are employed in the kinetic and reaction path studies. Oxidation states are determined using X-ray photoelectron spectroscopy. X-ray crystallography, atomic force microscopy, and electron microscopy are used to characterize and follow changes in the MoS_2 structures.

Department of Chemistry

356. Morphological Aspects of Surface Reactions
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Our work examines substrate morphology and fragments synthesized on surfaces, using thermal, electron, and photon activation techniques. Our goal is to acquire fundamental descriptions of heterogeneous chemical processes at gas-solid interfaces in selected systems that have controlled and characterizable morphology, are of catalytic significance, and are relevant to DOE missions. Preparation and kinetic characterization of intermediates lie at the heart of our program. Electron-induced activation of cyclopropane on Pt(111) results in the formation of 4- and 5-membered metallacycles, a trimethylene species bound on each end to one Pt atom and two Pt atoms, respectively. The metallacyclobutane forms methane and ethylene, and the metallacyclopentane forms propylene or propane if surface hydrogen is present. An η^3-allyl intermediate has been identified spectroscopically in the decomposition of metallacyclopentanes, derived from both electron irradiated cyclopropane and thermal decomposition of 1-chloro-3-iodopropane and from thermal decomposition of allyl bromide. We have kinetically characterized these hydrocarbon fragments, and studied the effects of coadsorbed bromine atoms, carbon monoxide, and carbon on the kinetics of their decomposition. Characterization of the thermal reactions of 3-bromocyclohexene on Pt(111) has been completed. A π-allylic C_6H_9 species has been identified spectroscopically and is important in the dehydrogenation of cyclic C_6 hydrocarbons to benzene.

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Department of Chemical Engineering

357. The Preparation and Catalytic Applications of Silica, Alumina and Zirconia Supported Thermally Resistant Mono and Bimetallic Catalysts
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A new generation of thermally resistant supported metal catalysts prepared by the sol-gel method is currently under development. These catalysts derive their superior thermal properties by minimizing sintering processes that occur by surface diffusion. Because surface diffusion is substantially decreased when metal particle size is matched to the average pore diameter of the support, synthetic procedures aimed at attaining this match are under study. The resultant materials are being tested in the combustion of propane and methane, the dehydrogenation of n-butane, and the hydroisomerization of n-butane by superacid solid catalysts. Catalyst deactivation studies are being performed, using a wide variety of in situ spectroscopic techniques. The synthesis of catalytic ceramic membrane reactors to study dehydrogenation reactions is under study. It is anticipated that the separation and dehydrogenation properties of platinum and palladium can synergistically be used to improve olefin yields by shifting the position of equilibrium. The catalytic membrane reactor devices will be prepared by using the slip casting method.

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Department of Chemistry

358. Ligand Intermediates in Metal-Catalyzed Reactions
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The first goal of this project is the synthesis, isolation, and characterization of homogeneous transition metal complexes containing ligand types (-CHO, -CHOH, $-CH_2OH$, -C, $=CH_2$,-$H_2C=O$,-OCHO, - OCH_2R, CO_2, etc.) intermediate in C_1/C_2 catalytic reactions. A second goal entails the characterization of ligand intermediates in other important feedstock conversions and the identification of new types of binding modes and bond activation processes. A third, new goal involves the development of catalysts that can be immobilized in fluorocarbon solvents. Mechanistic understanding of key steps and insight for the design of new catalysts is sought. The following topics are under active investigation: (1) the synthesis, structure, electronic properties, and reactivity of complexes that contain unsupported and supported C_2, C_3, and C_xN linkages spanning two metals or clusters; (2) C-H bond activation reactions of aromatic nitrogen heterocycles, such as pyrrole, and new HDN processes; (3) hydrogenation and hydrosilylation reactions with Rh(I) catalysts bearing fluorinated phosphine ligands; (4) the immobilization of catalysts and reagents in fluorocarbon solvents; and (5) mechanistic studies of oxidative additions in fluorocarbon solvents.

359. Carbon-13 NMR of Solid-State Hydrocarbons and Related Substances
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The objective of this project is the development of new nuclear magnetic resonance (NMR) techniques to study solid organic materials to gain structural and chemical information on model compounds and naturally occurring samples. The most important recent achievements have been (1) the development of new spatial correlation techniques to measure ^{13}C chemical shift tensors in single crystals; (2) improved theoretical methods for the calculation of shielding tensors; (3) developing a new magic angle slow turning (MAT) method of obtaining two-dimensional solid-state NMR spectra of powdered samples, where the isotropic shift is projected along one axis and the tensor powder patterns along the second axis, and a method for importing resolution into the evolution dimension of multidimensional NMR spectra; (4) extending the theoretical and experimental shift tensor work to nitrogen-containing species; and (5) construction and utilization of a high pressure NMR sample cell for observing hydrocarbons dissolved in supercritical fluid CO_2. The single crystal correlation techniques completely characterize all six terms of the chemical shift tensor and its orientation in the molecular frame. The accuracy of the single crystal methods is sufficiently high that it may be used along with quantum mechanical methods to refine crystal structures of fused aromatic hydrocarbons. Considerable progress has been made in dealing with the single crystals of sufficient size to obtain high quality data in a reasonable period of time. A new icosahedral flipper probe has recently been constructed that has significantly reduced the size requirements for single crystals (e.g., 14 mg) on a 400 MHz spectrometer. Theoretical calculations have been extended to a wide range of polycondensed aromatic hydrocarbons and a number of corresponding heterocyclic (O, N, S) species. A major effort has recently been mounted to obtain ^{15}N chemical shift tensor data on heterocyclic compounds. Enriched compounds were initially employed for studying powder patterns in compounds containing one and two nitrogen atoms. Powder pattern experiments carried out at high (400 MHz) have demonstrated that it is possible to obtain chemical shift tensor data at the natural abundance level on model compounds that have been doped with stable free radicals. The ^{13}C shift tensor data on model compounds have been extremely valuable in interpreting the MAT data obtained on several coal samples, and the ^{15}N data will be evaluated to determine its value in identifying the types of nitrogen species present in coals. Use of supercritical fluid solvents is rapidly gaining importance in problems of environmental cleanup and as a method for providing alternative cleaning solvents for a variety of industrial and commercial uses. NMR shift and spin relaxation data provide details on the important solute-solvent interactions.

Virginia Polytechnic Institute and State University
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Department of Chemical Engineering

360. Influence of Surface Defects and Local Structure on Chemisorption Properties and Oxidation Reactions over Metal-Oxide Surfaces
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The purpose of the project is to examine the effect of surface defects (primarily oxygen vacancies) and local structure on catalytic oxidation reactions over metal oxide materials. The $SnO_2(110)$ surface is being investigated because of the flexibility allowed in controlling surface cation coordination numbers, oxidation states, and the selective introduction of two different types of surface oxygen vacancies. Previous work on the heterolytic dissociation and oxidation of alcohols and organic acids has demonstrated the relationship between the acidity of surface cations and the activity for these oxidation "probe" reactions. Current work is aimed at understanding the role of crystallographically and coordinatively different surface oxygen anions in oxygen insertion reactions over $SnO_2(110)$. The oxidation of surface methyl groups generated by the adsorption of methyl iodide is currently being investigated. In addition, BF_3 is being tested as a Lewis acid probe molecule for characterizing surface oxygen anions with different local geometries and coordination numbers. Work to characterize surface defects with STM is continuing, while the geometry and electronic structure of surface defects (oxygen vacancies) is explored with density functional calculations.

361. Bimetallic Oxycarbides and Oxynitrides: A New Class of Hydrogenation Catalysts

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The project deals with the investigation of a new class of catalytic materials, bimetallic oxynitrides (M_I-M_{II}-O-N, where M_I, M_{II}=Mo, V, W, and Nb) that show promise as hydroprocessing catalysts. They were synthesized by nitriding bimetallic oxide precursors with ammonia gas via a temperature-programmed reaction technique. The oxide precursors were prepared by conventional solid state reaction between two appropriate monometallic oxides. X-ray diffraction studies showed single-phase materials in a face-centered cubic metal arrangement. The catalysts were characterized by using physisorption and chemisorption techniques, and were found to have high surface areas and CO chemisorption values. The hydroprocessing reactions studied were hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation (HDO) of model compounds at 3.1 MPa and 643 K. The activities of the catalysts were compared to a commercial Ni-Mo-S/Al_2O_3 catalyst under similar conditions. Among the bimetallic oxynitrides tested, the V-Mo-O-N exhibited the highest activity, surpassing the HDN activity of the commercial Ni-Mo-S/Al_2O_3 catalyst. X-ray photoelectron spectroscopic studies on the spent catalysts indicated that they are tolerant to sulfur.

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Department of Chemical Engineering

362. Structure-Property Relationships for Binary Metal Oxide Catalysts

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Alkali and alkaline earth oxides, both alone and on supports, are recognized as solid base catalysts. However, very little is known about these materials despite their potential for many industrially important reactions. This project explores solid base structure-property relationships determined by a variety of methods. Over the past year, strontium and rubidium were supported on a variety of carriers, including magnesia, silica, alumina, titania, and carbon, by impregnation and decomposition of acetate precursors at 773 K. These supported samples were characterized by surface area measurements, stepwise temperature-programmed desorption of carbon dioxide, and activity for the catalytic decomposition of 2-propanol. In some cases, infrared and X-ray absorption spectroscopy were used to identify surface species. Results from these techniques indicate that strontium and rubidium supported on silica form weakly basic surface silicate phases that have low activity for 2-propanol dehydrogenation. On alumina and titania, strontium acetate decomposed to form supported basic carbonates that were moderately active for 2-propanol dehydrogenation. Except for Rb/MgO, none of the rubidium-loaded samples contained surface carbonates as detected by IR spectroscopy after pretreatment at 773 K. For the Rb catalysts, the overall rate of acetone formation from 2-propanol correlated with the ranking of support basicity evaluated from the Sanderson intermediate electronegativity principle. These results suggest that strongly basic alkali-containing catalysts should utilize basic carriers to minimize alkali-support interactions that lower base strength.

Department of Materials Science and Engineering

363. Understanding and Controlling Metal-Support Interactions in Nanocrystalline Bimetallic Catalysts

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Supported metal catalysts are vital for control of automobile emissions and to the chemical and petroleum industries. Issues, such as loss of surface area due to the migration and coalescence of metal crystallites during service, thermal degradation of the support material or metal crystallites, the role of the support-metal interface and the segregation behavior of the metal crystallites, are all critical to the functionality of the catalysts. The purpose of this research is to use high-resolution transmission electron microscope (HRTEM) techniques to analyze, understand, and control the atomic and electronic structure, chemical composition, segregation behavior, wettability, thermal stability, and catalytic properties of bimetallic nanocrystalline catalysts as a function of alloy composition and substrate reactivity. A field-emission gun HRTEM, equipped with an energy-dispersive X-ray spectrometer and Gatan imaging filter, will be used to image the atomic structures of nanocrystalline bimetallic alloys on different substrates with 0.14nm spatial resolution and simultaneously determine the chemical compositions and electronic properties of the crystals and support-crystallite interface with 0.5nm spatial resolution. This research will provide a fundamental understanding of phenomena, such as (1) the effect of support reactivity on the atomic structure, morphology, and stability of bimetallic catalyst crystallites, (2) the effect of support reactivity on the surface and interfacial segregation behavior of bimetallic crystallites, (3) the effect of crystallite size on the morphology and segregation behavior of bimetallic particles, (4) the mechanisms and kinetics of nanocrystalline particle sintering as a function of alloy composition, substrate reactivity, and temperature, and (5) the effect of all of the above on the resulting catalytic properties and stability of bimetallic crystallites.

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Department of Chemistry

364. ***Oxide-Supported Metal Catalysts: Factors Controlling Particle Size and Chemisorption/Catalytic Properties***
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Many catalysts for energy technology consist of transition metal particles attached to oxide supports. Interactions at the interface between the metal and the oxide dictate the metal particle morphology, which in turn controls catalytic activity and selectivity, yet these interactions are poorly understood. These experiments aim to clarify the geometric, dynamic, and energetic factors that control the microstructure of the metal/oxide interface and to rationalize the interplay between this microstructure and chemical reactivity. Specifically, they are designed to determine how the number, dimensions, and structure of metal particles are influenced by oxide surface structure and defect density, the choice of metal, temperature, coadsorbed chlorine and hydrogen, and high-pressure gases. The chemisorption and catalytic properties of vapor-deposited, ultrathin metal islands and isolated metal adatoms are studied, as well as the dependence of these upon the characteristics of the underlying oxide surface. Recently, we have shown how the atomic structure of the oxide surface influences metal particle morphology, both for Cu on ZnO and Au on titania. Measuring the influence of flux and substrate temperature on particle morphology clarified the energetic barriers involved in metal atom migration on the oxide.

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Department of Chemical Engineering

365. ***Thermodynamic and Kinetic Aspects of Surface Acidity***
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During the past year, our research has involved butane isomerization over sulfated zirconia, butane isomerization over H-mordenite, and butene isomerization over ferrierite. The objectives of our work are to understand the factors that control the type and strength of acid sites on surfaces and to quantify the kinetic aspects of the catalytic cycles in which these acid sites participate. We have found that olefins (produced at levels from 1 to 100 ppm over an upstream Pt/Sn catalyst) have a strong promotional effect on the activity for butane isomerization of solid acid catalysts, most likely by increasing the surface concentration of reactive intermediates. By comparing the effect of C4 olefins on butane isomerization over H-mordenite and sulfated zirconia, we are elucidating the unique properties of sulfated zirconia (e.g., redox properties) that lead to its high activity for butane isomerization at low temperatures. For example, the rate of butane isomerization over H-mordenite becomes very slow when the concentration of olefins in the feed is decreased to lower than 10 ppm, whereas the rate of isomerization over sulfated zirconia remains high at these low olefin levels. Furthermore, the rate of butane isomerization is about one order of magnitude faster over sulfated zirconia compared to H-mordenite at comparable olefin levels. In addition, we are developing an understanding of the relation between acid strength and catalyst selectivity. In this respect, the selectivity for the isomerization of n-butene to isobutene over ferrierite increases as those acid sites that adsorb ammonia most strongly are blocked by carbonaceous deposits formed under reaction conditions.

Department of Chemistry

366. ***Mechanistic Studies at the Interface Between Organometallic Chemistry and Homogeneous Catalysis***
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Several different projects at the interface between organometallic chemistry and homogeneous catalysis are being pursued. All are designed to give increased understanding of the mechanisms of the reactions involved. (1) Hydroformylation with Chelating Diphosphines with Wide Natural Bite Angles Near 120°. A correlation between high regioselectivity for straight chain aldehydes and wide natural bite angle of chelating diphosphine ligands has been found in rhodium catalyzed hydroformylation. Attempts to explain this selectivity with steric effects have failed and the role of electronic effects of chelating ligands are being investigated. Ligands designed to allow independent assessment of electronic effects at equatorial and apical sites are being synthesized. (2) Reductions Catalyzed by Metal Complexes with Both Hydridic and Acidic Hydrogens. Attempts to develop bimetallic catalysts having one acidic and one hydridic metal hydride have led to interesting new complexes but not to new catalysts. Shvo has described a remarkable catalytic system in which the key intermediate $(C_5Ph_4OH)Ru(CO)_2H$ has an electronically coupled acidic OH unit and a hydridic RuH unit. These catalysts are effective at reducing polar compounds, such as aldehydes and ketones. The mechanisms of homogeneous catalysis by these fascinating species are being studied in detail. (3) Cyclopentadienyl Ring Slippage to Access Reactive Sites. Studies of $IndRe(CO)_2(MeC \equiv CMe)$, initiated in a search for more labile metal-alkene complexes, led to the discovery of the first case in which unimolecular ring slippage is a rate-limiting process. Studies of this process should provide better understanding of ligand exchange processes that provide access to reactive sites.

367. *Mechanism and Design in Homogeneous Catalysis*
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The principal goals of this proposal are the design, synthesis, characterization, and use of new ligand structures for controlling selectivity at transition metal centers. One synthetic effort concerns (1) synthesis of novel chiral phosphite ligands containing aza-crown ether ligands, (2) demonstration of the ability of these ligands to coordinate to metal centers, (3) establishing the catalytic competence of complexes of these ligands in hydroformylation and hydrogenation reactions, (4) synthesis of a series of novel borate-functionalized chiral diphosphine ligands, and (5) demonstration that borate-functionalized diphosphines (2) ligate transition metal complexes that are catalytically active in hydrogenation reactions. We have demonstrated that chiral aza-crown ether ligands can be readily synthesized, that these ligands form effective hydroformylation catalysts with catalyst precursors, such as $Rh(acac)(CO)_2$, that these catalysts show significantly enhanced acitivity for the hydroformylation of allylammonium salts relative to simple phosphites, and that the hydroformylation products are enantiomerically enriched. We have also found that these catalysts demonstrate unusual phase separation behavior that may be exploited in simplified catalyst separation/recycling schemes. Recently we have extended the ligand design to ferrocenyl-based diphosphines containing aza-crown ether functional groups. Our other synthetic effort concerns the synthesis of borate-functionalized diphosphines (2) based on ferrocene. We now have both racemic and resolved versions of these novel diphosphines in hand, as well as crystallographic structures for several variations of these ligands. We have demonstrated that these ligands bind to Pt and Rh complexes to yield clean compounds. The rhodium complexes are catalytically active toward alkene hydrogenation. Our examinations of the influence of secondary interactions suggest minor directing effects for the the catalytic hydrogenation of allylic borates. In the area of mechanistic chemistry, we have made significant progress in combined experimental and computational studies of the detailed mechanism of dihydrogen activation in catalytic asymmetric hydrogenation. Our results suggest that oxidative addition via molecular H_2 complexes is the most likely pathway for H_2 activation. For iridium analogues of the common rhodium-based catalysts, we have demonstrated that diastereomeric dihydrides undergo facile interconversion at moderate temperatures (-45°C) by a mechanism that does not involve dissociation of H_2. Numerous kinetic and spectroscopic probes indicate remarkably facile dynamics of the hydride ligands that include (1) rapid intramolecular exchange with C-H bonds, (2) diastereomer exchange, and (3) rapid intermolecular exchange. The absolute stereochemistry and quantitative three-dimensional solution structures have been determined by low-temperature NMR methods.

University of Wisconsin at Milwaukee
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Department of Chemistry

368. *Aluminum Coordination and Active Catalytic Sites in Aluminas, Y Zeolites, and Pillared Clays*
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Progress has been made in four areas: (1) The REDOR technique that had been applied to the study of Bronsted sites through the $^{1}H(NH_4^{+}) \rightarrow ^{29}Si$ excitation has been extended to the study of the Lewis sites in zeolite extraframework alumina particles and in transition alumina. It has revealed an important feature: a Lewis site is made from a pair of aluminum with coordinations IV and V, separated by a distance of about 3 Å. (2) By combining infrared spectroscopy and proton NMR of chemisorbed NH_3, the absolute number of Lewis sites and of Bronsted sites has been determined for a large variety of Y, ZSM-5, and mordenite zeolites with different degree of dealumination. (3) These determinations have explained the rapid deactivation of the isomerization of n-pentane with decreasing fluorination of USY. (4) In the domain of acid catalysis and catalysts, we have succeeded in the synthesis of sulfated and phosphated mesoporous zirconia with t-plot surface area in excess of 500 m^2/g.

369. *An Investigation of Molybdenum and Molybdenum Oxide Catalyzed Hydrocarbon Formation Reactions*
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It has been shown earlier that an MoO_2 model of oxide olefin metathesis catalysts mimics the activity and selectivity of alumina-supported catalysts rather well below ≈650 K and provides a good model for this system. It is found that the model oxide and metal catalysts are covered with large amounts of carbon; following reaction and restart reactions indicates that catalysis proceeds in the presence of these layers. Raman and, more recently, infrared analyses of the layers indicate that they consist of both hydrocarbons and graphitic carbon. A portion of the carbonaceous layer can be removed at ≈600 K by hydrogen (5 torr); the activation energy for this reaction is ≈6.5 kcal/mol. It was shown, using reflection-absorption infrared spectroscopy, that ethylidyne formed on palladium (111) is present under high pressures (up to 1 torr) of gas-phase ethylene. The spectral linewidth increased with ethylene pressure, an effect ascribed to a loss of order of this layer due to the high pressure of gas. One possible explanation for this effect is that ethylene can adsorb onto the surface between the ethylidynes. It is also found that hydrocarbon conversion rates are accelerated, both for olefin metathesis and palladium-catalyzed acetylene cyclotrimerization, if hydrogen is added to the reaction mixture, even though hydrogen is not required for the reaction. This is ascribed to the removal of the carbonaceous layer by hydrogen. Palladium catalyzes acetylene hydrogenation to ethylene where the hydrogen reaction order is 1.04 at 300 K, which increases with increasing temperature. This is modeled by assuming that the role of hydrogen is both to act as reactant and to create catalytic sites by removal of the hydrocarbon. The model MoO_2 catalyst turns out to be very unreactive in ultrahigh vacuum. However, oxygen overlayers on molybdenum effect their catalytic metathesis activity, so that the chemistry of alkenes (ethylene, propylene, and 2-butene) have been studied on oxygen-covered Mo(100) surfaces. These are found to hydrogenate to form alkanes, thermally decompose to form carbon and evolve hydrogen, and also to react to form methane. In the case of ethylene, this latter reaction is proposed to take place via a direct carbon-carbon double bond cleavage, forming CH_2 species that can react with hydrogen to yield methane. It is proposed that both propylene and 2-butene react in a similar dissociative way to yield carbenes, in the case of propylene, to yield methylidene and ethylidene; and for 2-butene, two ethylidenes. It is shown, by grafting iodine-containing precursors, that ethylidene thermally decomposes to yield methane. Both photoelectron spectroscopic evidence and the fact that no other hydrocarbon products are detected, as well as examining the chemistry of surfaces species deposited by thermally decomposing iodohydrocarbons, suggest that the carbenes are formed by alkene dissociation rather than via other pathways. It is also proposed that the high-temperature metathesis reaction pathway (above 650 K) proceeds via recombination of the carbene fragments so that the product's distribution from ethylene is well described by a Shultz-Flory distribution; and the products formed from propylene can be rationalized, using a copolymerization model, where higher hydrocarbons are formed from carbenes and methyl carbenes. Initial work has been carried out to synthesize more realistic model metathesis catalysts by reacting molybdenum hexacarbonyl with planar alumina substrates in ultrahigh vacuum. It is found that carbonyls adsorbed at low temperatures desorb intact. Higher temperature adsorption results in complete carbonyl decomposition and the formation of a surface carbide. This suggests that the removal of the first CO in the carbonyl is rate limiting and, once decarbonylation is initiated, the remaining carbonyls are removed very rapidly. Heating the carbide-covered surface to ≈1300 K removes all surface carbon and desorbs CO. It is shown, by synthesizing an oxide substrate using isotopically labelled oxygen, that the carbon reacts with the alumina substrate. The carbide can be reformed by reaction with ethylene.

Yale University
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Department of Chemical Engineering

370. *Mesoporous Molecular Sieves (MCM-41) as Catalysts and Catalyst Supports*

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A series of vanadium containing mesoporous molecular sieves of the MCM-41 type has been synthesized systematically varying the pore size and metal loading. The uniform mesoporous structure was confirmed by X-ray diffraction and physisorption. To obtain information on the local structure of incorporated vanadium, a series of vanadium model compounds with well-defined local symmetry were characterized, together with V-MCM-41, by DR UV-visible, ^{51}V solid state NMR, and X-ray absorption spectroscopies. The UV absorption edge energy may be correlated with the domain size (local symmetry) represented by the average bond length. Based on this principle and NMR and XANES results, it is deduced that the vanadium is incorporated into the framework of hydrated and dehydrated samples occupied in mostly isolated tetrahedral sites, and a small portion of octahedral sites involving water coordination are observed in hydrated samples with larger pore size. An XAFS analysis provides quantitative information on localization of vanadium and agrees with the other results. Based on these results, a model of possible local structure of V^{5+} centers is proposed. These catalysts are active for the gas phase, air oxidation of methanol to formaldehyde and the liquid phase peroxide oxidation of cyclohexene to cyclohexenyl hydroperoxide. Both reactions are sensitive to pore size of the V-MCM-41 and the rate passes through a maximum at about 30Å as this parameter is varied.

371. *Pd Catalysts for Use in Vehicular Applications*

Pfefferle, L.D. **$435,000**
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Pd-based catalysts are being widely developed for new automotive applications. Pd poses particular challenges for these applications because its physical and chemical state changes with temperature and reactant environment over the range of conditions experienced in vehicular applications. In this research, we are studying the behavior of Pd-based catalysts, including interactions with a range of supports, dopants, and contaminants under typical vehicular reaction conditions. A technique based on UV-visible reflectance spectroscopy is being developed to monitor chemical state and particle size of the catalyst under reaction conditions. A variety of high-temperature supports are being used, including low- and high-surface-area aluminas, lanthanum aluminates, and metal supports derived from superalloys. Noble metal catalysts are often promoted with CeO_2, but the performance of the CeO_2 is affected by changes in catalyst state induced by the reaction environment. We have been studying the changes in Pd catalysts supported on alumina-coated gold TEM grids under cycled reaction conditions. Conditions are observed where both Pd and PdO coexist on the surface and reoxidation of the reduced Pd does not appear to occur through a shrinking core type mechanism. This was expected from the large lattice mismatch between Pd and PdO and will be confirmed by in situ STM experiments of Pd oxidation with Prof. Altman, also at Yale. This work has important consequences for understanding the reactivity of these catalysts. In other results, poisoning of hydrocarbon oxidation by water was found to be a strong function of the support. This may help us minimize the effect by support modification. Pd aluminate formation was observed under a range of reaction conditions.

Department of Chemistry

372. *Catalytic Oxidation of Hydrocarbons by Binuclear Fe Complexes*

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This project is investigating the ability of synthetic non-heme iron model systems to catalyze the oxidation of alkane and arene molecules, including the conversion of methane and ethane to methanol and ethanol, respectively. We have shown that simple binuclear ferrous iron complexes are capable of catalyzing the heterolytic decomposition of peracids and oxidizing (75-4500 turnover number) unactivated alkanes, alkenes, arenes, and sulfides in the presence of oxygen atom donor molecules, such as iodosylbenzene or dimethylaniline N-oxide. The catalytic oxidation of alkanes show almost exclusively alcohol production with very little ketone formation. Substrate oxidation studies indicate a C-H tertiary:secondary:primary preference of 230:45:1, indicating that the non-heme iron based intermediate is more reactive than the better characterized heme-based high valent iron-oxo species. The observed retention of stereochemistry (≥ 98%) observed during the catalytic oxidation of the tertiary C-H bond of cis- and trans-decalin suggests that the reaction is not proceeding through a freely diffusing hydroxyl radical species, a result consistent with our isotopic labeling studies which show that product oxygen arises from the oxygen atom donor molecule and not molecular oxygen. This conclusion is also consistent with temperature-dependent product distributions for the oxidation of adamantane, which show a change in C-H bond preference from tertiary:secondary alcohol ratios of 4.5:1 at 20°C to 1:40 at -40°C, indicating substrate shape selectivity and a metal-based oxidant. Finally, these studies have allowed the identification of an intermediate species, stabilized at low (-80°C) temperatures, that is capable of stoichiometric oxidation of substrates, including alkanes. This intermediate is characterized by an electronic spectrum that is very similar to intermediate Q, the putative reactive species of methane monooxygenase. Detailed mechanistic and spectroscopic characterization of these systems are underway as are efforts to generate the iron-based oxidant with other O-atom donor molecules, peroxides, and dioxygen, the latter reagent allowing the direct utilization of dioxygen in the oxidation of hydrocarbons.

373. *Some C-X Bond Cleavage Chemistry*

Crabtree, R.H. **$98,000**
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The CF bond-breaking chemistry has continued to provide striking new results. We now find that the extremely inert global warming gas CF_4 can be quantitatively destroyed by a series of inorganic materials related to sodium oxalate to give carbon and metal fluoride. In other work, we find that salts, such as magnesium anthracene, can defluorinate perfluoroalkanes with very high efficiency. A related system involves magnesium metal and rare earth salts of ytterbium and samarium that show interesting selectivity and, we hope, can be made catalytic. These new reactions are of considerable mechanistic and practical interest and we are following them up in the current grant period. In the same period, we published a number of full papers on our previous DOE-supported problem, alkane activation, including some theoretical work in JACS in collaboration with Per Siegbahn (Stockholm).

374. *Catalysis with Low Valent Transition Metal Amides, Thiolates, and Alkoxides and Applications to Polymer Synthesis*

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In the past year, four projects have been pursued under DOE support in my laboratory. The first project involves the formation of C-N bonds at a transition metal center by reductive elimination and includes extensive studies of the kinetic and electronic aspects of this reaction. Reductive eliminations are important elementary reactions in a variety of catalytic cycles, including future hydrocarbon functionalization processes. The second project involves a detailed mechanistic and thermodynamic evaluation of alkylamine N-H activation by palladium complexes, which is important for the future development of hydrocarbon amination processes, as well as for the catalytic formation of amines from halogenated hydrocarbons. The third project includes the synthesis of triarylamine dendrimers. The synthesis of aryleneamine analogs of polyaniline will help to understand and improve this conducting polymer, while triarylamines are important in conductive, ferromagnetic, and light-harvesting materials because of their ability to be oxidized to stable aminium ions. The fourth project involves the synthesis of modified polyanilines by the palladium-catalyzed reaction of either m- or o-phenylene diamine with 4,4'-dibromobenzophenone. The resulting materials are clearly polymeric by GPC analysis and display well-resolved ^1H and ^{13}C NMR spectra.

Separations and Analysis

The University of Alabama
Tuscaloosa, AL, 35487-0336

Department of Chemistry

375. *Clean Solvent Extraction Using Polyethylene Glycol-Based Aqueous Biphasic Systems*

Rogers, R.D. ***$311,000***
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Aqueous biphasic systems (ABS) consist of two immiscible aqueous phases formed when certain water soluble polymers are combined with one another or with certain inorganic salts in specific concentrations. As two-phase systems they are suitable for carrying out liquid/liquid separations, and since the major component in each of the two phases is water, a liquid/liquid extraction technology can be envisioned which completely eliminates the use of volatile organic compounds. In this project period, we have made progress toward predicting organic solute partitioning both for small model compounds and for larger dye molecules. Protocols have been developed which allow controlled, but rapid partitioning data to be obtained for dyes and molecular species at a range of tie-line lengths. The partitioning has also been examined in polypropylene/polyethylene glycol ABS and in sodium chloride media. The results obtained thus far for dye molecules, indicates that partitioning is closely related to the number of benzyl groups in the dye molecule and thus, most likely are also related to free energies of hydration or hydrophobic surface area. Tracer scale studies with small molecules (benzene, chlorobenzene, and salicylic acid) also support this view. Adsorption studies with the analogous aqueous biphasic extraction chromatographic (ABEC) resins are in progress. Additional work in progress includes testing the predictive tools obtained for dye molecules on the removal of color from textile mill effluent.

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Department of Chemistry

376. Raman Spectroscopy of Reversed-Phase Liquid Chromatographic Alkylsilane Stationary Phases on Thin Silica Films

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Reversed-phase liquid chromatography (RPLC) is the most popular mode of liquid chromatography used today. The stationary phase used for RPLC typically consists of silica gel onto which an alkylsilane layer has been covalently bound. Despite intense effort, a fundamental understanding of the molecular basis of the separation process has not been achieved. This program uses Raman spectroscopy to characterize RPLC alkylsilane stationary phases at the molecular level. Stationary phase supports currently being explored include a sol-gel ultrathin silica layer supported on a Ag substrate to enhance the Raman scattering, organically-modified sol-gel thin films, and commercially available silica-based RPLC stationary phases. During the past year, efforts to further characterize commercially available stationary phases have resulted in acquisition of Raman spectra from a range of such materials. Quite significantly, the spectral data clearly indicate that the octadecyl chains in low-coverage octadecylsilane stationary phases exist in a disordered state. Temperature studies indicate that these chains can be ordered by subjecting the stationary phase to liquid nitrogen temperatures. This observation further suggests that the octadecyl chains in these stationary phase materials are in close enough proximity on the surface to form crystalline alkyl domains. Effects of exposure to solvent and solutes are underway. Similar studies on all three types of stationary phases under investigation are continuing.

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Department of Chemical Engineering

377. Interfacial Chemistry in Solvent Extraction Systems

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The microscopic interfaces—i.e., association microstructures—in acidic organophosphorus extraction systems associated with Na^+, Co^{2+}, Ni^{2+}, Zn^{2+}, and UO_2^{2+} are being systematically investigated using various physicochemical, spectroscopic, and scattering techniques in order to resolve the physicochemical nature and structure of reversed micelles of metal-extractant complexes, the thermodynamics of the formation and growth of reversed micelles, the effect of organic phase additives on the structure of reversed micelles, and the relationship between reversed micellar structure and selectivity. A new structural model—the “open water-channel” mode—for reversed micelles and a quantitative model that relates the extractability and selectivity to the size of reversed micelles in solvent extraction systems have been proposed and are being experimentally verified. Advanced laser techniques (SLLS, LIF, FRAP) are being utilized to characterize the properties, structure, and dynamics of extractant-laden liquid-liquid interfaces. A study of the permeation of metal-extractant species, in particular, association microstructures, is being initiated using a state-of-the-art surface force apparatus in order to examine interfacial/transport phenomena within supported liquid membranes (SLMs). This innovative research program will make significant contributions to the science and technology of liquid-liquid extraction and supported liquid membranes.

Brigham Young University
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Department of Chemistry and Biochemistry

378. Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport

Lamb, J.D.; Bradshaw, J.S.; **$101,558**
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The cation selectivity of macrocyclic ligands such as crown ethers and cryptands is applied to making metal cation separations in hydrophobic liquid membranes and other chemical separations systems. Potential macrocyclic ligand carriers are designed and synthesized, then screened for cation binding characteristics using potentiometric titration, solvent extraction, calorimetry, NMR, and X-ray crystal structure determinations. Macrocycles which demonstrate potential for separations are then incorporated into liquid membrane systems. Focus is placed on the synthesis and characterization of new proton ionizable macrocycles that permit coupling of cation transport to the reverse flux of protons. Phenol- and hydroxyquinoline-substituted aza-crown ethers are currently emphasized. State-of-the-art molecular mechanics modeling techniques are used in the design phase of the project. Current focus is being given to a new type of polymer inclusion membrane for stable, long-term separations. Investigation is also under way on a novel method for mixing aqueous and nonaqueous phases in solvent extraction. This method exploits the unusual behavior of some hydrophobic solvents that coalesce with the water phase upon heating, then separate on cooling. Selective extractions of metal cations using macrocyclic extractants can be carried out rapidly by this method.

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Department of Chemistry

379. Generation of the Photoacoustic Effect Through Chemical Reaction
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The current research focuses on three main areas concerned with the photoacoustic effect: generation of sound waves by molecular volume changes, chemical reactions associated with the photoacoustic effect, and nonlinear wave generation produced by the photoacoustic effect in carbon suspensions. With regard to the first of these, we have found that when pulsed laser radiation is absorbed by carbon particles in a suspension, chemical reactions take place at the particle surfaces, giving rise to what has been called the "giant" photoacoustic effect. Experiments are being done on systems that undergo physical and chemical changes on irradiation parallel to those that take place in carbon suspensions in order to investigate further the consequences of a tentative theory that has been developed. In the second area, experiments are being carried out where chemical reactions are initiated by irradiating suspensions of lampblack with the output of a Q-switched, Nd:YAG laser. The gaseous and solution phase reaction products are analyzed using standard techniques. In the third research area, experimental and theoretical work is being conducted to study what might be called "nonlinear photoacoustics," the production of large-amplitude sound waves by the photoacoustic effect in carbon suspensions.

University of California, Santa Barbara
Santa Barbara, CA 93106-5130

Materials Research Laboratory

380. Halocarbon Separations with Zeolitic Materials
Cheetham, A.K.; Mellot, C.F.; Chihara, K. **$385,000**
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Several environmental pressures are driving the need to develop a better understanding of separation processes involving halocarbons. The focus of this project is on the adsorption and separation of common chlorocarbon ground-water contaminants, in particular chloroform, trichloroethylene (TCE), and perchloroethylene (PCE), using zeolites. Aluminosilicate and siliceous zeolites offer a range of potential advantages over other media, such as activated carbons. Our progress to date includes: (1) Development of a forcefield describing interactions between chlorocarbons and zeolites. Short-range non-bonding and long-range electrostatic interactions, as well guest-guest interactions, are considered. (2) Use of this forcefield in Monte Carlo simulations for estimating heats of adsorption in some prototypic systems; e.g., investigating the influence of structure type, Si/Al ratio, cation type, and sorbate loading. (3) Calorimetric determinations of the heats of adsorption of chloroform and TCE in faujasite-type zeolites (with Myers, Penn). These results are now providing a validation of our forcefield. (4) Inelastic neutron scattering studies of the vibrational properties of chloroform in NaY (with Eckert, LANL); these measurements underline the importance of hydrogen bonding between the sorbate and the framework. (5) Preliminary neutron diffraction studies for locating adsorbed TCE and PCE in NaY (with Vogt, BNL).

Carnegie Institution of Washington
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Geophysical Laboratory

381. High-Pressure Synchrotron Infrared Spectroscopy: An Integrated and Dedicated Facility at the NSLS
Hemley, R.J., Mao, H.K. **$200,000** Equipment
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A synchrotron facility, dedicated to high-pressure infrared and micro-infrared spectroscopy, is being developed. The facility consists of a versatile and dedicated high-pressure beam line capable of a broad range of measurements from the far-infrared to the visible spectrum at the U2A beam line of the National Synchrotron Light Source (NSLS). This new facility has a significantly higher IR brightness, particularly at long wavelengths, in comparison to the existing, partially dedicated beam line (U2B). A new FT-IR is being installed at the beam line, along with a recently completed high-pressure (long working distance) microscope and a commercial, high-magnification infrared microscope for 1-bar and low-pressure samples. With the existing high-pressure x-ray facility at the NSLS, the new instrumentation will permit synchrotron IR, synchrotron x-ray, and optical experiments on the same high-pressure samples. Systematic high-pressure measurements addressing a range of problems in condensed-matter physics and chemistry, Earth and planetary science, and materials science will be performed. These studies include high-pressure studies of dense hydrogen and related planetary materials; minerals of the Earth's crust, mantle, and core; geochemical reactions; glasses and melts; surfaces and interfaces; whole-rock samples; and new high-pressure technological materials.

Colorado School of Mines
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Chemical Engineering and Petroleum Refining

382. A Mechanistic Study of Molecular Sieving Inorganic Membranes for Gas Separation
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The objectives of this research are to investigate selective transport mechanisms in microporous, inorganic membranes and to examine the effects of membrane microstructure and surface chemistry on separation performance. In the past year, we have applied our fundamental understanding of transport in micropores to the measurement of component fugacities in fluid mixtures and to the development of a new inorganic membrane that provides "reverse selectivity." Reverse selectivity simply means that the membrane permeates heavy hydrocarbons such as isobutane preferentially over lighter, smaller compounds such as hydrogen or methane. This process could be of great commercial value in the commercial separation of natural gas liquids. A reverse selective membrane would allow the separation of these very valuable products from a natural gas stream, leaving the methane behind at pipeline pressures. No recompression of the methane would be needed. Given the very high selectivity of the silica hollow fiber membranes we have been studying for small penetrants (He, H_2, CO_2) over much larger penetrants such as isobutane, we have constructed a "fugacity meter" which we used to directly measure the fugacity of smaller molecules in mixtures with larger molecules. In collaboration with another DOE-BES investigator, Prof. James F. Ely, data were obtained for mixtures of CO_2 and isobutane.

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Chemistry; Soil Science; Earth Resources

383. A Multinuclear Magnetic Resonance Study of the Interactions of Pollutants with Major Soil Components
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This project is providing detailed information on the fundamental chemical-physical behaviors of certain organic contaminants with clays and humic materials. Chemical and physical behavior are being studied via state-of-the-art nuclear magnetic resonance (NMR) experiments on solid and aqueous-solution samples (mainly the former, to date). The specific tasks of this project include (1) to generate, or update and refine, the chemical-structural and NMR data bases of the specific clays and humics chosen for study; (2) elucidation of the behaviors of individual pollutants with these specific humics and clays; (3) study of the fundamental interactions in clay-humic "complexes"; (4) elucidation of pollutant mobility and diffusion in the specific humic and clay systems; (5) chemical structural characterization of ternary systems (pollutant-humic-clay); and (6) exploratory studies of pollutant/whole-soil systems. Results of this kind of study are needed in the long term for development of reliable and versatile soil-groundwater models of pollution. Second-year actively focussed on (a) fully characterizing via ^{13}C NMR the organic soil components (humic acid, fulvic acid and humin), (b) detailed NMR characterization of the photochemical decomposition of trichloroethylene adsorbed on clay, (c) a detailed NMR study of chemical tranformations in the co-contamination system, benzene/carbon tetrachloride/clay, (d) the hydrogen-bonding/acid-base interactions of acetone adsorbed on silica and other soil components, and (e) ^2H NMR lineshape analysis of motion in certain organic pollutants (benzene, trichloroethylene, acetone) adsorbed on soil components. Computer analysis of the ^2H data in terms of mtional models continues.

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Laboratory of Atomic and Solid State Physics, Clark Hall

384. Pixel Array Detector for Time-Resolved X-Ray Science
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The goal of this project is to develop, test, and install a silicon-based Pixel Array Detector (PAD) for x-ray applications at synchrotron radiation sources. At present, there are no existing detectors capable of recording successive x-ray images at the megahertz rates made possible by sources such as the Advanced Photon Source. The PAD is designed to fill this need and is intended for time-resolved applications such as Laue and conventional crystallography of proteins and other biological macromolecules, crack propagation and materials failure, and phase transition studies. In a PAD, each pixel has its own signal conditioning and storage electronics, so all pixels operate in parallel. A small scale prototype PAD has been fabricated and tested and performs to specification. A larger PAD (100x100) pixels is now in the fabrication stage. The 100x100 format will be used to determine the scale-up problems which must be solved before a full scale mosaic PAD (e.g., 1000x1000) can be built.

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Department of Chemistry and Biochemistry

385. Surface-Induced Dissociation Studies of Complex Ions Using Electrospray Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
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This research seeks to use the integrating characteristics of the Fourier Transform Ion Cyclotron Resonance mass spectrometer (FTICR) to elucidate fundamental mechanisms of surface-induced dissociation (SID) of large molecules. This process holds promise for providing a reliable and reproducible method for controlled fragmentation of large polymeric molecular ions, but detailed mechanisms are not now understood. The work will use well-characterized Langmuir-Blodgett layers as target surfaces, innovative ion collection methods, and FTICR mass spectrometry for fragment analysis. Strict control of the target surface will be ensured, and ion collection and analysis methods will capture all fragmentation products of the impact. Model compounds will be used to define the energy transfer excitation function and to determine the limits for the applicability of standard dissociation models to large molecules. This effort will also incorporate a new approach to graduate education that exploits collaborative partnerships between the University, the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory, and two industrial firms, the Finnegan and DuPont corporations.

386. Linear and Nonlinear Spectroscopic Probing of Solute Interactions with Chemically Modified Silica Surface
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This project involves the investigation of thin polymer films on nanoporous silica as new materials for potential applications in chromatography, capillary electrophoresis, solid-phase extraction, waste water recovery, and surface protection. Living radical polymerization to reactants covalently bonded to surfaces enables controlled growth of uniformly thin polymer films. Size-exclusion chromatography reveals that the pores remain intact after polymerization. The films are being studied with respect to the reaction parameters that control polydispersity, the applicability to different functional groups, and the feasibility of creating bilayers with a hydrophobic inner layer to protect the surface and a hydrophilic outer layer to provide the desired functionality. Characterization of these new materials is being accomplished by atomic force microscopy, electrostatic force microscopy, solid-state NMR spectroscopy, optical microscopy, infrared and fluorescence spectroscopy, in addition to chemical separations.

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Department of Chemistry

387. Fluorescence Lifetime in Chemical Analysis: The Next Generation
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This work investigates fluorescence lifetime measurement and its use to extract physical and chemical information in biochemical, clinical and environmental systems. Current research follows two directions that originate from the introduction of commercial, multiharmonic Fourier transform (MHF) technology, which allows frequency-domain acquisition of complete lifetime profiles in a single measurement that takes only a fraction of a second. First, in the new technique of Total Lifetime Distribution Analysis (TLDA), the MHF enables rapid characterization of complex samples with unprecedented sensitivity and detail—sensitivity derives from use of the entire sample emission in the lifetime measurement, and detail derives from self-modeling data analysis using the Maximum Entropy Method (MEM) to fully exploit the responsiveness of fluorescence lifetime to the chemical composition and dynamic molecular interactions of a sample. Recently, TLDA has been used to probe bacteria. Second, the introduction of the MHF for rapid, on-the-fly detection of fluorescence lifetime in capillary electrophoresis (CE) increases accuracy and peak resolution of fluorescence detection without compromising the speed and small sample size requirements that make CE so valuable. CE has been interfaced with the MHF and the potential for multiplex detection in biological analysis is under investigation.

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Department of Chemistry

388. The Glow Discharge as an Atomization and Ionization Source

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This research project explores the fundamental and potentially applied aspects of the microsecond glow discharge (GD). Research to date has shown that the high power delivered into the short duty cycle of the pulsed discharge creates an advantageous analytical environment. Not only is more atomic sputtering produced, but enhanced excitation and ionization are also observed. In this manner, the low-power GD can become an intermittent high-power discharge. Using detection systems keyed to the pulse frequency, improved signal intensities and S/N ratios are found. The project focuses primarily on time of flight (TOF) mass spectrometry, which permits optimum coupling of a periodic source with a similarly periodic spectra accumulation. Background signals of discharge gases can be decoupled from the sputtered atom signals. The effect of the pulsed discharge on plasma chemistry and reduced level of polyatomic species will be investigated. GD atomic emission is also of direct interest, given the high optical intensities obtained with the pulsed discharge. A 30-channel direct reader was recently acquired so that various species in the plasma can be monitored. This involves the use of a Grimm type source, so planned work will examine the differences between a conventional glow discharge and the Grimm configuration when used with a microsecond pulsed source.

389. Development of Laser-Excited Atomic Fluorescence and Ionization Spectrometric Methods

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The goal of this research program is to develop laser excited fluorescence and ionization methods for practical ultratrace elemental analysis in a wide variety of matrices. This is being done through fundamental studies of atomization processes, with the aim of developing optimum atom reservoirs for practical analysis; studies of laser excitation processes with the aim of enhancing our understanding of the dynamics of atom and ion populations in these reservoirs, and finding efficient single and multi-step excitation schemes for many elements; and studies of techniques for photon and ion detection with the aim of improved analytical performance. Projects include studies of laser excited atomic fluorescence and absorption in laser breakdown plasmas and electrothermal atomizers, laser shadowgraph and electrical probe diagnostics of laser breakdown plasmas, multi-step resonance ionization spectroscopy of mercury and the evaluation of a laser breakdown-glow discharge spectrochemical emission source.

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Department of Chemistry

390. New High-Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission and Mass Spectrometry

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This research follows a multifaceted approach, from theory to practice, to the investigation and development of novel helium plasmas, sample introduction systems, and diagnostic techniques for atomic spectrometry and mass spectrometry. Four major sets of research programs are being conducted that each include a number of discrete but complementary projects. The first program is concerned with investigation of atmospheric-pressure helium inductively coupled plasmas (He ICPs) that are suitable for atomization and ionization of elements, especially those possessing high ionization energies, for the purpose of enhancing the detecting powers for a number of elements. The second program includes simulation and computer modeling of He ICPs. The aim is to ease the hunt for new helium plasmas by predicting their structure and fundamental and analytical properties, without incurring the enormous cost for extensive experimental studies. The third program involves spectroscopic imaging and diagnostic studies of plasma discharges to instantly visualize their prevailing structures, to quantify key fundamental properties, and to verify predictions by mathematical models. The fourth program entails development and characterization of new, low-cost, low-sample consumption nebulization devices. These efforts collectively offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation, environmental pollution, biomedicine, and nutrition.

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Department of Chemistry

391. Molecular Aspects of Transport in Thin Films of Controlled Architecture

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Localized vibrational spectroscopy is being coupled with measurements of plasmon surface polaritons (PSPB9s) in Ag- or Au-supported ultrathin ($d \leq 35$ nm) organized molecular assemblies exposed to organic penetrants, with an especial emphasis on understanding the role of film defects on macroscopic properties. Since defects likely control a wide variety of technically important properties of the films, understanding their structure, dynamics, and how they mediate transport in the assembly is critical. Measurements of shifts in PSP resonances are exquisitely senstive, ultimately permitting changes in film thickness as small as $\Delta d \leq 0.01$ nm to be detected. An example of these studies targets the uv-induced photooxidation of alkanethiolates on Au. These films, which serve as models for organic coatings, are subject to attack by O_3 generated in situ on the thiolate head group to generate sulfonates which are readily removed in polar solvents.

Kansas State University
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Department of Chemistry

392. Multidimensional Hadamard Transform Spectrometry: A New Analytical Technique
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Multidimensional spectrometry is defined in terms of three spatial dimensions (x_i, y_i, z_i) and one spectral dimension (wavelength, λ_j or frequency, v_j). The x_i and y_i or surface coordinates are accessed via a stationary two-dimensional (2-D) Hadamard encoding mask, and the z_i or depth coordinate arises from using a photoacoustic detection system for depth profiling by optical modulation and phase-sensitive detection. Measurements utilizing two-dimensional and three-dimensional spectrometry are in print. Results for this program's first images and spectra from four-dimensional spectrometry are in press. Present efforts are focused on enhancement of capabilities for performing various multidimensional spectrometries. A multiwavelength acoustic-optic tunable filter (AOTF) for the spectral dimension is in its final testing. A new moving 2-D Hadamard encoding mask as a potential replacement for the stationary 2-D Hadamard encoding mask for the two surface dimensions has been obtained and is now being evaluated. Decoding the multiwavelength AOTF results by Hadamard methods gives a multiplex advantage in the spectral dimension. Using the multiwavelength AOTF without decoding will provide a multiplication advantage in images without spectral separation. The moving mask with completely open windows will allow access to any spectral region where appropriate sources, spectral separators, and detectors are available.

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Department of Chemistry

393. Perforated Monolayers
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This program is aimed at preparing new classes of synthetic membranes that can be used to separate small gaseous molecules on the basis of their size, shape, and polarity. The general approach is to fabricate composite membranes from "perforated monolayers" (i.e., monolayers that are assembled from "porous" surfactants) plus highly permeable cast film made from poly[1-(trimethylsilyl)-1-propyne] (PTMSP). Recent studies that have been carried out, using amide oxime-based calix[6]arenes plus PTSMP support material, have led to the synthesis of "the world's thinnest membrane separator" for helium and nitrogen; i.e., one that is ca. 40 angstroms in thickness. These studies have also revealed the importance of using surfactants, which are sufficiently large in diameter such that they can span individual pores on the surface of PTMSP, for producing relatively defect-free Langmuir-Blodgett films.

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Department of Chemistry

394. Novel Micellar and Calixarene Derivatives for Selective Luminescence Measurements
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Research for this funding period has focused on continued studies of calixarenes as host molecules for analytical measurements. As reported in last year's report, several novel chiral calixarenes have been synthesized by use of a novel synthetic scheme developed on this program. Some of these calixarenes are being used as pseudophases in capillary electrophoresis to achieve selective chiral separations. These chiral calix(4)arene derivatives, when combined with electrokinetic capillary chromatography, have produced enantioseparation of three binaphthyl derivatives at pH values below 7. The structures of the calixarene derivatives and the buffer pH were found to be important factors in the chiral separations. Even more selective chiral separations are achieved when these chiral pseudophases are used in combination with achiral micellar media such as sodium dodecyl sulphate. Currently the general utility of these new chiral selectors is being examined for other chiral separations in capillary electrophoresis.

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Department of Chemistry

395. Direct Examination of Separation Processes in Chromatography by Laser-Induced Fluorescence

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Much of the present knowledge of chromatographic separation processes has been obtained from experimental data and theoretical models that reflect the macroscopic behavior of solute zones. Because the separation ultimately arises through the migration and interaction of individual molecules; however, a more detailed understanding is necessary to guide future improvements in chromatographic performance. This research program is concerned with two technological advances that enable this challenge to be addressed from a unique and promising new perspective. First, a novel detection system has been developed in our laboratory that allows the examination of separation processes in situ as the solute traverses the chromatographic column. This system employs laser-induced fluorescence detectors to measure the solute zone profile at several distinct points along an optically transparent column. By effectively isolating the regions of interest, this system enables an accurate measure of kinetic, thermodynamic, and hydrodynamic processes that was not previously possible. Second, a three-dimensional stochastic computer simulation has been developed and validated which provides a more detailed understanding of mass transport processes in chromatographic separations. In this simulation, the migration of individual molecules is established through diffusion and convection within a fluid phase that is in contact with a surface. Molecular interaction and, hence, retention may arise by partitioning into permeable surfaces or by adsorption at solid surfaces. The molecular distribution and the corresponding zone profile may be examined and characterized by means of statistical moments at any specified time or spatial position during the simulation. This simulation provides the opportunity to perform hypothetical experiments and to make observations that may not be possible in a real chromatographic system. During the present grant period, these advances in experiment and theory have been used to characterize the kinetics of solute distribution between the fluid and surface phases. The experimental studies were performed using octadecylsilica, the most common stationary phase for liquid chromatography. The rate constants for a homologous series of model solutes were determined as a function of temperature in the range from 10 to 70°C, pressure in the range from 400 to 4463 psi, and mobile-phase composition. The experimental rate constants correlate well with values predicted by the stochastic computer simulation for a partition mechanism under diffusion-limited conditions. From these results, it is apparent that kinetic processes are a significant contribution to zone broadening and must be minimized in order to improve chromatographic performance.

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Department of Chemistry

396. A New Class of Macrocyclic Chiral Selectors for Stereochemical Analysis

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Halocarbons are usually separated using gas-liquid chromatography (GLC) using relatively long columns. Most of the more volatile chlorofluorocarbons can be better resolved by gas-solid chromatography (GSC), however, some of these compounds react with highly active stationary phases. Particularly reactive are the replacement chlorofluorocarbons that are not fully halogenated or fluorine substituted. A new, less-active GSC stationary phase was found to be sufficiently inert to effectively separate the lower molecular weight chlorofluorocarbons, in addition to the large, more polar halocarbons. These GSC columns also were used for analyses of the halocarbon content of refrigerator insulation. It was found that percent levels of specific halocarbons remained in the insulation decades after it was manufactured. Consequently, the destruction and disposal of old refrigerators could release significant quantities of halocarbons to the atmosphere. Commercial halocarbon preparations were sometimes found to contain signficant quantities of other halocarbon impurities. Among the more prevalent chiral monoterpenoid compounds in conifers are α-pinene, β-pinene, and smaller amounts of camphene and limonene. The most prevalent chiral monoterpenoid compounds in fossilized resin (referred to as amber in this paper) appear to be borneol, isoborneol, and camphene. Most of these compounds have easily measured enantiomeric excesses. The borneol and isoborneol in some amber samples have pronounced enantiomeric excesses despite the fact that they are tens of millions of years old. The enantiomeric ratios of the monoterpenoids in different ambers vary tremendously and often are distinct. However, in any single amber sample, the stereochemistry (absolute configuration) of the excess monoterpenoid enantiomers appears to be identical. The camphene in amber may be a secondary reaction product formed over time, possibly from the dehydration of borneol. Although a compound’s original stereochemistry can be preserved, it also may diminish with the number and type of chemical transformations over geological time. The monoterpene enantiomeric ratios in modern conifer resins vary tremendously. Future stereochemical studies are outlined that could provide the data necessary for more exact geochemical interpretations and possibly for obtaining pertinent paleobiological information.

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Department of Chemistry

397. Solid-State Voltammetry and Sensors in Gases and Other Nonionic Media

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This project is based on using microelectrode voltammetry for design and application of quantitative electrochemical transport and kinetics experiments to semi-solid and solid redox phases. The experiments include transport and electron transfer reactions of electron donor/acceptor solutes and surfaces in polymeric solvents and liquid crystalline phases. The goals of this project include (1) developing the necessary miniaturized electrode methodologies, cells, and requisite theory for quantitative voltammetry in rigid media, (2) exploring important characteristics of homogeneous and heterogeneous electron transfer reaction dynamics in rigid environments, in particular how the dynamics of "outer sphere" redox couples respond to rigidification of their surroundings, (3) exploring polymer-phase transport, including polymer-in-polymer diffusion of redox-labelled poly-ethers, anisotropic transport in liquid crystalline phases and polymers, and coupling between slow diffusion and homogeneous electron transfers, and (4) learning to dynamically manipulate diffusion rates of redox sites within polymer electrolytes so as to fashion ultrathin, electrically conducting mixed valent layers by freezing the concentration gradients that are electrolytically generated at electrodes. A film containing serial frozen gradients was recently used to demonstrate a molecular light-emitting diode-like behavior.

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School of Chemical Engineering

398. Fundamentals of Electric Field-Enhanced Multiphase Separations

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Motivated by the fact that the use of electric fields offers a powerful means for enhancing the efficiency of and reducing waste generation in separations, this research is focused on improving the understanding of the dispersion of one phase into another phase in the presence of an electric field. In diverse applications, including separations, atomization coating, and ink-jet printing, the creation of a dispersed phase entails forming drops from a nozzle. Drop formation involves the generation, stretching, and breakup of liquid threads. Current emphasis of the program is on the dynamics and rupture of liquid threads of pure and surfactant-laden liquids. A convenient means for studying the dynamics of liquid threads is through the use of a liquid bridge, which is formed by capturing a volume of the drop liquid between two circular rods. The liquid bridge is then stretched by separating the rods from one another at a constant velocity. The evolution in time of the bridge profile and the rupture of the interface are investigated theoretically and experimentally. Theoretical analyses are relying on a two-pronged effort in which slender-jet equations are utilized on the one hand, and the full transient-free boundary problem governing bridge response is solved on the other hand. For pure liquids, initial attention is focused on the dynamics of bridges of insulating and conducting liquids subject to axial and perpendicular electric fields. For surfactant-laden liquids, the case of insoluble surfactants is being considered first.

Department of Chemistry

399. Ion Trap Mass Spectrometry: Ion Motion, Reactions, and Applications

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Quadrupole ion traps are analytical tools of increasing importance in a variety of chemically based areas of technology. This work aims at improving these instruments through an understanding of the motion of trapped ions. This understanding is being sought experimentally using tomography and theoretically using multi-particle simulation programs; the information is being used to develop new methods of manipulating trapped ions. In the past year we have developed a Windows version of the simulation program ITSIM, added advanced 3D graphics to the program, and improved the way it models ion/molecule collisions. We have simulated ion injection using a retarding dc pulse procedure, which should give high trapping efficiency for externally produced ions over a wide range of mass/charge ratios. We have simulated and then implemented a fourier transform non-destructive method of mass analysis in the trap and investigated the effects of operating parameters on its performance. We have made thermochemical measurements by examining the dissociation of cluster ions and introduced a new method of estimating heterolytic bond dissociation energies (e.g., the energy required for the reaction $NaCl \rightarrow Na^+ + Cl^-$). New methods of electrical cooling of ions, of controlling motion in the radial direction, and of using dc pulses for high resolution should continue the rapid advances being experienced in this eminently useful technology.

400. Reactions of Gaseous Metal Ions/Their Clusters in the Gas Phase Using Laser Ionization Fourier Transform Mass Spectrometry

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Powerful Fourier transform mass spectrometry methods developed in our laboratory are applied to obtain detailed kinetic, mechanistic and thermochemical information on a broad range of metal-containing ions. Some areas of current interest are summarized here: (1)

Theoretical calculations (HF, DFT, etc.) have been initiated to complement experimental studies. First examples include the species $Fe(CH_2O)^+$, $Fe(CH_2S)^+$ and MCF_3^+ (M = first row transition metals, Ca, Al). Theory helps explain the dramatic differences of reactivity seen for the first two ions, and corroborates the experimental evidence that MCF_3^+ is really the ion-dipole complex CoF^+—F_2C. (2) It was shown that metastable ion lifetimes and unimolecular dissociation rate constants for $(ML^+)^*$ species (M = Cr, Mn; L = benzene, acetone) can be obtained by applying a novel continuous ejection technique with FTMS. In addition, bond dissociation energies are derived from RRKM modeling. (3) Infrared multiphoton dissociation (IRMPD) studies continued with the investigation of two isomers, M(1,3-butadiene) and $M(C_2H_2)(C_2H_4)^+$ (M = Fe, Co, and Ni). The observation of four products for $CoC_4H_6^+$ is surprising and suggests a fortuitous balance of several factors.

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Howard P. Isermann Department of Chemical Engineering

401. Chemical Interactions between Protein Molecules and Polymer Membrane Materials

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Measurements of the intermolecular forces between a model protein (hen egg-white lysozyme, Lz) and a surface-modified polysulfone film using the Surface Forces Apparatus (SFA) were correlated with ultrafiltration measurements using the same model protein and a similarly modified polysulfone membrane (above the pI, below the pI and at the pI (11.00) of the protein). Low-temperature plasma was used to activate the polymer film and membrane in order to graft monomers of 2-hydroxyethyl methacrylate (HEMA) onto the surface, rendering them hydrophilic. Attractive interactions were diminished significantly with the HEMA-modified membranes as compared to the unmodified relatively hydrophobic membranes. Similar results were found for the ultrafiltration experiments where the effect on filtration due to protein adsorption was significantly reduced for the modified hydrophilic surface. Simple linear correlations were obtained relating the interactive energies to the various fluxes measured during the filtration experiments. The correlations imply that both protein-protein and protein-polymer interactions are important during ultrafiltration. Therefore, either altering the chemistry of the polymer surface or the solution conditions could lead to a minimization of fouling for a specific protein/polymer combination. A manuscript is in preparation describing this new work.

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Department of Geological and Environmental Sciences

402. Detectors and Other Instrumentation for Research in Environmental Chemistry and Heterogeneous Catalysis at the Stanford Synchrotron Radiation Laboratory

Brown, G.E., Jr.; Hedman, B.; **$217,000** Equipment
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This effort will acquire state-of-the-art x-ray detectors and other related instrumentation required for x-ray absorption spectroscopy (XAS) studies of metal cations and oxyanions in complex, heterogeneous samples of relevance to environmental chemistry and heterogeneous catalysis at the Stanford Synchrotron Radiation Laboratory (SSRL). These detectors will be used to study chemical reactions on metal oxide surfaces used as catalyst supports or common in the Earth's near-surface environment. The coverage of cations or oxyanions on these surfaces is often much lower than one monolayer, thus XAS studies on high-flux synchrotron x-ray beam lines are required, as are very sensitive x-ray detectors. SSRL is currently constructing a new 26-pole wiggler beam line that will provide about an order of magnitude higher flux than the wiggler beam lines commonly used for XAS studies of environmental samples or catalyst supports. Completion of this new beamline is scheduled for early 1999. To take full advantage of this new beamline facility, a new state-of-the art, high-sensitivity, high-throughput x-ray detector is also needed, as are a new ion chamber detector and other related equipment. Tests conducted on newly developed detection systems indicate a possible sensitivity improvement of a factor of 10 over existing detectors. Detection limits are expected to be less than 0.1 monolayer on surfaces and less than 10 ppm for dilute elements in bulk samples. A vacuum-compatible detector for soft X-ray measurements will also be installed, and a new grazing-incidence XAS apparatus for enhanced surface sensitivity will be designed.

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Department of Chemistry

403. Determination of Solvation Kinetics in Supercritical Fluids

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This research program is directed toward several key aspects of supercritical fluid science and technology. The goals/subprojects are as follows: (1) Understanding the effects of neat and entrainer-modified supercritical fluids on solute-fluid dynamics; (2) Determining the effect of fluid density on the disposition of energy between a dissolved solute and the fluid bath; (3) Probing the effects of continuous phase density on the internal dynamics of novel reverse micelles formed in supercritical carbon dioxide; (4) Quantifying the behavior of polymer tail-tail dynamics and radii of gyration at infinite dilution in supercritical carbon dioxide vs. fluid density; (5) Determining the effects of carbon dioxide on molten polymer; (6) Quantifying solute-solute synergism and the origin of such; (7) Investigating local density and composition surrounding a solute at an interface and its influences on extraction and separation processes in supercritical fluid science and technology. Modern ns/ps (and now fs) in situ optical spectroscopy are used in this work. To date, this work has helped to better define and quantify how solvation occurs in supercritical fluid systems and how one can tailor a supercritical fluid for a particular "solvent" need. Overall, this work is continuing to provide an advanced molecular-level view of the unique chemistry of supercritical fluids and how a supercritical fluid can be used to control reactions and solute conformation.

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Department of Physics

404. Enhancement of the Microscopy Facilities at the National Synchrotron Light Source X1A Beam Line

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The project is designed to open important new capabilities at the microscopy stations on the National Synchrotron Light Source soft X-ray undulator beamline X1A. Both the Scanning Transmission X-ray Microscope, STXM, and the Scanning Photoemission Microscope, SPEM, use zone plates to form microprobes for imaging with elemental and chemical specificity. STXM is designed to study primarily biological and other organic specimens at 50 nanometer or better resolution. SPEM is designed to study surfaces at 150 nanometer or better resolution. Both instruments can take spectra from small specimen areas—absorption spectra on STXM, photoelectron spectra on SPEM. STXM is in the process of being made vacuum compatible to extend XANES microscopy capabilities to the nitrogen and oxygen edges, where even small amounts of residual air interfere with imaging and spectroscopy. At the same time, the computer and software system are being brought up-to-date. The stage is being rebuilt using a new design for accurate linearity and orthogonality of the axes. SPEM will also have its stage rebuilt to improve reliability and reproducibility. Its computer/data acquisition/software system will be replaced with one that is compatible with STXM for improved speed, flexibility, and economy.

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Department of Chemistry

405. Polymer-Based Separations, Synthesis and Application of Polymers for Ionic and Molecular Recognition

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Research during the current period has resulted in the preparation of several new ion-chelating polymers. A new resin has been prepared where chelating diphosphonic acid groups are grafted on to a silica support. These groups have a high affinity for actinide ions from acidic solutions, allowing for its application to mixed waste treatment. The new resin would be useful in cases where it is desirable to leave the actinides on the resin and treat it as a solid waste since replacing an organic with an inorganic matrix avoids the generation of gases due to radiolytic degradation of the organic polymer. A high capacity bifunctional sulfonate / monophosphonate ion exchange resin was also synthesized. It was found that the bifunctional resin complexes far higher levels of Eu(III) from 0.5 M and 1M nitric acid solutions, even in the presence of 0.4M sodium nitrate, than the monofunctional phosphonic acid resin. The results are consistent with the hypothesis that the sulfonic acid ligand provides an access mechanism for the metal ions into the polymer by hydrating the matrix and preventing collapse of the micropores in high ionic strength solutions, thus allowing for rapid complexation by the selective phosphonic acid ligands. Two new bifunctional resins, with anion and cation exchange ligands bonded to the same polymer backbone, were synthesized and studied. The new resins contain diphosphonic acid groups bonded to a polystyrene matix along with anion exchange groups as either tetraalkylammonium ligands or quaternary pyridinium ligands. The resins rapidly complex actinide cations, as well as pertechnetate and Se(IV) anions,from acidic solution.

406. Study of the Homogeneity of the Packing Density of Chromatographic Columns and its Effects on Column Performance

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During the packing of chromatographic columns, consolidation of the bed takes place to an important extent. Because of the friction of the bed against the column wall during consolidation, the local stress varies systematically across the column. This causes the formation of a nonhomogeneous bed, with significant radial changes of the packing density and of any property (porosity, permeability, efficiency, retention, saturation capacity) which is related to this packing density. We have measured simultaneously the local elution profiles in a dozen locations of the exit frit of a 2" i.d column. The local velocity is typically 3-4% higher and the column efficiency 50-100% higher in the central core region than close to the wall. The results are the same for analytical (i.d., 4.6 mm) and intermediate (i.d., 7-9 mm) columns. Pulsed field gradient NMR shows that the axial dispersion coefficient is much lower, hence the column efficiency is higher than measured from chromatograms recorded with on-line detectors. The nonhomogeneous distribution of the local velocity is the cause of this efficiency loss. The aim of this research is to understand the phenomena that take place during column packing, the mechanism of bed consolidation and improve column efficiency.

407. Fundamental and Instrumental Development of Capillary Electrokinetic Separation Techniques for Energy Applications

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This research program is dedicated to the development of capillary electrokinetic separation techniques for energy related applications and is directed at (1) developing a fundamental understanding of pertinent separation and band dispersion mechanisms and (2) developing and refining instrumentation and instrumental approaches for these techniques. (1) The fundamental work focuses on studies involving highly ordered assemblies as running buffer additives. These additives include macrocyclic compounds such as cyclodextrins (CDs) and calixarenes, micelles, and soluble (entangled) polymers and are employed in electrophoretic (e.g., capillary electrophoresis, CE) and/or electrochromatographic (e.g., micellar electrokinetic capillary chromatography, MECC) modes of separation. A dual-CD phase (charged and neutral) form of capillary electrochromatography (cyclodextrin distribution capillary electrochromatography, CDCE) has been demonstrated that offers advantages over the more established MECC technique. Since the CDs used in the CDCE technique effect solute retention independently, it is anticipated that molecular modeling techniques will permit the computational development of “designer” CDCE separation systems (simple-to-complex combinations of commercially available CDs) that meet many separation challenges. A class of macrocyclic phenolic compounds (calixarenes) have also shown some promise as reagents for CE separations. The mechanisms by which DNA restriction fragments migrate, disperse, and interact with proteins in size-selective CE separations employing entangled polymers as running buffer additives are also being studied (using novel instrumentation; see below). (2) Instrumental work includes the development of an instrumental configuration that permits rapid and reproducible translation of the detection zone along a CE capillary. This instrumentation has resulted in improvements in both separation and detection performance and facilitated certain fundamental studies. A prominent area of research involves the development of separation-based fiberoptic sensors (SBFOSs). Basically, the SBFOS is a single fiberoptic, single buffer reservoir (the sample constitutes the other reservoir) device that is usually operated in a frontal mode of separation. The introduction of CE methodologies into sensing provides a unique and powerful element of selectivity for remote analyses and should offer unparalleled versatility and reusability. Several prototype SBFOSs have been fabricated and evaluated for measurements of fluorescent dyes and toxins in CE and MECC modes of separation, respectively. Incremental improvements in the design and function of the SBFOS are being implemented. In particular, a sensor is being developed that will permit zonal operation and active delivery of running buffer to the sample side of the sensor. Initially, this type of SBFOS will be employed for measurements of metal ions based on the on-column formation of fluorescent complexes.

Texas A & M University
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Department of Chemistry

408. Development of Laser-Ion Beam Photodissociation Methods

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This research program focuses on developmental mass spectrometry. Acitvities include studies of laser ionization mass spectrometry, especially matrix-assisted laser desorption ionization (MALDI), unimolecular and bimolecular reaction chemistry of gas-phase ionic species, laser-ion beam photodissociation methods to probe dissociation reactions of highly activated ions, laser-ion beam photodissociation of multiple-charged ions formed by electrospray ionization (ESI), and the development of high performance time-of-flight (TOF) mass spectrometry instrumentation for basic and applied research. In addition, the developmental mass spectrometry efforts are actively coupled to important chemical and biological areas through collaborative research projects. High priority is given to collaborations that couple important, difficult, chemical and biological problems that challenge edge-of-the-envelope mass spectrometry technologies and methodologies. Over the past year, this work has developed high resolution (>10,000 at m/z up to 6,000 daltons) and accurate mass measurements (errors < ppm and 10-25 ppm up to m/z 30,000) of large biological molecules by using MALDI-TOF. Deveolped methods are now being used quite effectively for identification and characterization of proteins. Liquid chromatography (LC)-TOF and LC-tandem TOF mass spectrometry methods are also being explored for performing complete protein sequencing of unknown proteins. The instrument under development for this project is an ESI-TOF that can be used for tandem MS. To date, the major focus of the sequencing efforts have utilized metastable ion (MI) mass spectra obtained by using post-source decay (PSD) focusing; however, MI-PSD spectra often times do not contain sufficient numbers of fragment ions to provide complete sequence information. Consequently, methods such as collision-induced dissociation (CID) and photodissociation are being used to fragment the analyte ions and enhance the versatility of the tandem TOF method. These latter studies require extensive investigation of fundamental issues of photoexcitation and dissociation of highly activated species for experimental optimization and to facilitate experiment design.

Texas Tech University
Lubbock, TX, 79409

Department of Chemistry and Biochemistry

409. ***Metal Ion Complexation by Proton-Ionizable Lariat Ethers and Their Polymers***
Bartsch, R.A. **$95,000**
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Crown ethers with pendent proton-ionizable groups are novel reagents for the separation of metal ions by solvent extraction and liquid membrane transport processes. The study of metal ion complexation by cyclic polyethers which possess pendent, proton-ionizable functions (i.e., proton-ionizable lariat ethers) continues. The current research effort involves synthesis of new mono-ionizable lariat ether complexing agents in which the terminal acid group is N-(R′)sulfonyl carboxamide. Preliminary studies have shown that the acidity of this new proton-ionizable group may be altered markedly by variation of the R′ group. Thus the acidity of the proton-ionizable group may be 'tuned'. Initial studies have demonstrated that chelating agents with this new proton-ionizable function possess higher selectivity in competitive solvent extraction of alkali metal cations than do analogous lariat ether carboxylic acids and phosphonic acid monoethyl esters. Ligands which contain two N-(R′)sulfonyl carboxamide groups are being prepared for evaluation as complexants for divalent metal ions. Structures of the new ligands and their metal ion complexes are being investigated in solution by NMR spectroscopy and in the solid state by X-ray diffraction. The metal ion separation properties of the new proton ionizable lariat ethers are being evaluated in solvent extraction systems and in transport across polymer inclusion membranes.

University of Texas at Austin
Austin, TX, 78712

Department of Chemical Engineering

410. ***Carbon Dioxide Based Solvents for Waste Minimization***
Johnston, K.P. **$382,000**
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This work seeks to develop environmentally benign carbon dioxide-based solvent formulations to replace toxic organic solvents for chemical processing. CO_2-based solvents offer exciting new opportunities in chemical manufacturing involving heterogeneous reactions (including polymerization); solvent-free coatings; extraction of heavy metals, including radioactive compounds from soils and wastewater; polymer processing; and separations processes, including cleaning and purification. Surfactants for microemulsions, emulsions, and latexes are being designed. This year, surfactants for the water-CO_2 interface have been studied. Fundamental studies of the interfacial tension are being used to understand complementary studies of the formation and stability of emulsions. The emulsion particle size, stability, critical flocculation density, and the reversibility of flocculation are being measured in situ by light scattering to understand the mechanism of steric stabilization in supercritical fluids. The mechanisms of stabilization and destabilization of these colloids are being characterized with lattice fluid self-consistent field theory and computer simulation to interpret the experimental results and to plan new experiments. With theory and simulation, we are studying the adsorption of surfactant, the conformation of the stabilizer group of the surfactant, and the interaction between dispersed phase droplets.

411. ***Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications***
Koros, W.; Paul, D. **$90,999**
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Currently, convenient solution-based processing of polymers allows production of economical asymmetric membranes with thin (1000 Å) selective layers. Such membranes have, in fact, revolutionized many separation applications for economically important gas pairs like oxygen/nitrogen, hydrogen/nitrogen and carbon dioxide/methane. Recently, limitations have been identified that limit the selectivity achievable with conveniently soluble polymers. Eliminating these limitations will increase the range of application of membrane technology. Analysis of the deficiencies of conventional membrane materials suggested an approach to greatly improve their properties while maintaining compatibility with current commercial formation equipment and processes. This work is based on materials with the potential to provide both entropic and energetically selective size and shape separation of the important gas pairs mentioned above. An additional reactive step is introduced in the material formation process to achieve the necessary rigidity for optimum membrane properties. Thermal and chemical treatments that can be implemented with relative simplicity are being investigated. This project seeks to continue to expand on past experience in tailoring properties while beginning to explore secondary steps to achieve truly superior separation properties.

University of Utah
Salt Lake City, UT, 84112

Department of Chemistry

412. ***Spectroscopic Characterization of Intermediates in the Iron Catalyzed Activation of Alkanes***
Eyring, E.M. **$86,000**
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A principal focus of this research is the observation of hypervalent iron species in liquid solutions. The primary experimental tool for examining these sample systems is a Bruker purge bench, step-scan, infrared spectrophotometer. Experiments require a stopped-flow rapid-mixing device that is interfaced with the IR spectrophotometer. The apparatus has been assembled and transient intermediates have been observed for a test system. Parallel visible spectroscopic studies are on-going of tuna fish myoglobin and other proteins trapped in sol-gel matrices that are bathed in supercritical carbon dioxide containing a variety of substrates. Experiments include laser flash photolysis and stopped-flow spectrophotometric experiments carried out at pressures ranging from atmospheric pressure (0.1MPa) up to 100MPa. The resulting values of the activation volume are used to delineate reaction mechanisms. These experiments are yielding autoxidation rate constants and reaction mechanisms for oxygen binding proteins. Studies of peroxidases trapped in sol-gel matrices continue. These systems are of potential interest for clean-up of soils contaminated with noxious organic compounds.

413. *Time-Resolved Analytical Methods for Liquid/Solid Interfaces*

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Many chemical phenomena that occur at boundaries between insulating solids and liquids (adsorption, partition, monolayer self-assembly, catalysis, and chemical reactions) are critical to energy-related analytical chemistry. These phenomena are central to developing chromatographic methods, solid-phase extraction, immobilized analytical reagents, and optical sensors. The goal of this program is to develop surface-sensitive spectroscopies by which chemical kinetics at liquid/solid interfaces can be observed on timescales from nanoseconds to seconds. Temperature-jump relaxation measurements are used to probe adsorption/desorption kinetics at liquid/solid interfaces; kinetic barriers to adsorption of molecular ions onto alkylated silica surfaces are being investigated. Surface-enhanced Raman spectroscopy is being used to study adsorption and binding to silica surfaces, deposited as thin layers over silver- and gold-island films that enhance the Raman scattering of interfacial species. The dielectric-overcoated metal island film technology is being extended to hydrophobic surfaces prepared by binding of siloxane ligands to gold-colloid films; these surfaces are being used to investigate the kinetics of surfactant adsorption to hydrophobic surfaces from aqueous solution. Further applications in studies of protein adsorption kinetics are planned. A fiber-optic Raman probe is also being developed for direct probing of metal ion complexation to ligands attached to porous silica; this probe will allow “on-column” detection of complexed species as they are retained on the silica surface. The transport of neutral molecules and ions within the pores of porous silica, which affects the efficiency of heterogeneous catalysis and chromatographic processes, is being studied on a microsecond time-scale by quenching of phosphorescence from probe molecules immobilized on the silica surface.

Department of Metallurgical Engineering

414. *Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species*

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Froth flotation is one of the most important examples of applied surface chemistry, and this separation technology is used in the food, petroleum, pulp-paper, and mineral industries. Several novel experimental techniques, such as in situ Fourier transform infrared (FTIR) internal reflection spectroscopy (IRS) with reactive internal reflection elements, multichannel laser Raman spectroscopy, nonequilibrium laser-Doppler electrophoresis, and atomic force microscopy for surface force measurements, are being developed and/or used to analyze surfactant adsorption phenomena at mineral/water interfaces and to describe the impact of adsorption phenomena on the hydrophobic character of the surface. The nonsulfide flotation research includes the soluble salt, semisoluble salt, and insoluble oxide mineral systems. In the case of soluble salt minerals, significant contribution has been made to predict the surface charge of alkali halides by considering partial hydration of surface lattice ions. Also, atomic force microscopy in concert with FTIR/IRS techniques is currently being used to investigate the influence of the structure of interfacial water on the electrokinetic behavior of fluoride salts. Also, short-range interparticle forces responsible for the adsorption of surfactant colloids in soluble salt flotation have been explained on this basis. Significant progress has been made in understanding the nature of the forces responsible for heterocoagulation of oppositely charged particles at high ionic strengths by measuring interparticle forces using atomic force microscopy. These experimental results are now being explained based on the interfacial polar interaction theory. In the category of semisoluble salt minerals, carboxylic acid adsorption by fluorite, calcite, and apatite minerals is being examined by FTIR/IRS and referenced to the characteristics of transferred Langmuir-Blodgett films. The spectral data obtained are being used to obtain information concerning a variety of interfacial phenomena, including the structure of the adsorbed molecules, adsorption kinetics, adsorption state, and conformational and orientational order. Progress continues to be made in spectroscopic characterization of interfacial water at both hydrophilic and hydrophobic surfaces by depth profiling using in situ FTIR/IRS. The results obtained from this research program will provide the basis for the design of new reagent schedules to improve flotation separation efficiency and to promote energy conservation.

Virginia Commonwealth University
Richmond, VA, 23284

Department of Chemistry

415. ***Selective Methods for Quantification of Target Species in Complex Mixtures***
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The quantification of specific compounds in complex mixtures is a common goal in many analytical methods. Here, two experimental approaches are coupled with chemometric data analysis methods to explore the possibility of obtaining reliable, quantitative results subsequent to chromatographic separations. The first approach is liquid chromatography coupled with UV-visible diode array and mass spectral detection for the analysis of polyaromatic hydrocarbons, metabolites, and pesticide residues. Quantification will be achieved by using methods such as alternating least squares, direct trilinear decomposition, and neural networks. Standard addition methods can be used for calibration. In the second experimental approach, thin-layer chromatography will be used to separate the analytes, and the kinetics of a subsequent derivatization reaction will be used to resolve and quantify the species of interest on the thin-layer plates. This novel approach has been applied successfully for the analysis of amino acids, and the trilinear decomposition method has given satisfactory results for the quantitative resolution of the severely overlapped amino acids, glutamine and glycine. Chemiluminescent-detection approaches based on these principles are also being investigated.

Washington State University
Pullman, WA, 99164

Department of Physics and Materials Science

416. ***UV Laser-Surface Interactions Relevant to Analytic Spectroscopy of Wide Bandgap Materials***
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This research emphasizes basic studies of the laser desorption and ablation of materials, in particular those with bandgaps which exceed the photon energies of the incident light. The mechanisms of emission and formation of ground state and excited neutral species, ±ions, and free electrons are probed using time resolved optical spectroscopy, time resolved absorption spectroscopy, photoluminescence, charged particle energy analysis, and angular distribution measurements. We examine the role and production of absorption centers in the form of point defects and determine their role in (a) photodesorption processes, (b) heating and vaporization, and (c) plasma formation. Current studies involve careful time and spatial determinations of particle densities of the desorbed particles as a function of the state of the surface and near surface of single crystal ionic solids. The latter includes quantifying defect densities, the rate of production of surface defects with particle bombardment and mechanical stimulation, modeling the role of anion vacancies in photostimulated emission of ionic species. Recently, we have concentrated on developing and experimentally proving a new model of fluorescent plume formation at low laser fluences that contradicts many previously proposed mechanisms based on inverse bremsstrahlung as a necessary electron heating mechanism. We show that coupling of positive ions, photoelectrons, and thermally emitted neutrals leads to the necessary energies and excitations, as verified by experiment. A number of studies are underway on laser interactions with inorganic solids containing covalently bonded anions which photodecompose. The latter include nitrates, carbonates, and phosphates with a number of cations such as alkali and alkaline earth metals. We are showing that photodecomposition of the oxyanion controls and strongly increases the coupling of UV laser light to these materials, thus generating highly non-linear responses.

University of Wyoming
Laramie, WY, 82071

Department of Chemistry

417. ***Solid-Matrix Luminescence Analysis***
Hurtubise, R.J. **$95,000**
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The major goal of this project is the development of a fundamental understanding of the physicochemical interactions and photophysical properties for the room-temperature fluorescence and phosphorescence of aromatic compounds in solid matrices. Glucose, trehalose, sodium acetate, and different types of filter paper are used. Polycyclic aromatic hydrocarbons and other compounds are selectively removed from water with silicone treated filter paper, and the isolated compounds are characterized by their solid-matrix fluorescence and phosphorescence. Solid-matrix luminescence data are acquired for luminescent food toxins in carbohydrate glasses. Phosphorescence intensities and lifetime data are obtained as a function of temperature, and a variety of photophysical parameters are calculated from these data. For example, calculated activation energies are correlated with low frequency vibrational modes and rotational relaxation of functional groups in the solid matrices. Phosphorescence decay data and confocal laser scanning microscopy are employed in studying the heterogeneity of the distribution of NaI in glucose glasses. A new form of solid-matrix luminescence spectrometry is being developed in which the vibronic modes of the excited triplet state of phosphors are detected by combining infrared and luminescence spectrometry.

Heavy Element Chemistry

Colorado State University
Fort Collins, CO, 80523

Department of Chemistry

418. A Study of New Actinide Zintl Ion Materials
Dorhout, P.K. **$77,039**
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The specific goals of this project are to explore the chemistry of Zintl ion building blocks for the rational synthesis of new actinide materials. This study, a two-part project, will focus on the following interrelated tasks: (A) Synthesis of new actinide-metal Zintl phase materials. Another poorly characterized area of chemistry is the area of actinide (hereafter, An) ternary and quaternary chalcogenide and chalcopnictide compounds. The class of compounds that will be studied will be those compounds related to the actinide phosphates, carbonates, and other metallates, based not on oxide chemistry, but on heavier chalcogenide chemistry. There are no known thio or seleno analogs, for example, to uranyl phosphates, a large class of uranium compounds. The ternary and quaternary phase regions of the actinide-main group-chalcogenides will be explored, and a rational synthetic methodology will be developed that will lead to a better understanding of actinide materials chemistry. (B) Development of synthetic methods for directed synthesis. Initial experiments will explore the chemistry of Zintl ions under molten salt and salt-mediated low-temperature metathesis reactions. Each of these is a proven synthetic medium in its own right in lanthanide, actinide, and chalcogenide chemistry. Rational synthesis of materials incorporating heteroatomic Zintl ions as reactants has not really been explored in these media. As part of the synthetic program introduced above, the potential for rational materials synthesis within these solvent systems will be examined. Update information about the progress of this project will be published on our web site: http://www.chm.colostate.edu/pkd

Florida State University
Tallahassee, FL, 32306

Department of Chemistry

419. Research in Actinide Chemistry
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This research emphasizes basic studies of the behavior in solution of the actinide elements and of the chemically related lanthanide elements. A primary goal is an increased understanding of the principles governing the chemical behavior of the f-elements with a variety of complexing ligands, both organic and inorganic. The systems are chosen because the data may also be of direct value for modeling calculations of the behavior of actinides in environmental and waste repository systems or in improved separation schemes of these elements. Primary emphasis is on the thermodynamic, kinetic, and spectroscopic (absorption, luminescence, and NMR) studies of the complexation and redox reactions of the actinides. For example, humic acid binding to actinides in the III, IV, V, and VI oxidation states was shown to be very rapid, while dissociation is much slower. The kinetics and the binding constants of actinide complexation for different sized fractions of humics are being investigated by radiotracer and spectroscopic techniques. Actinide complexation thermodynamics and hydrolysis is being studied by potentiometry and calorimetry from 5 to 70°C. Actinide binding to large, soluble anionic polyoxometallates (e.g., $H_2P_2W_{12}O_{48-12}$) is being investigated to test surface complexation models for clay and colloid systems. Syntheses of various ligands with properties that could provide some unique complexation to various actinides are underway to evaluate their value in actinide separations.

University of New Mexico
Albuquerque, NM, 87131

Department of Chemistry

420. Preorganized and Immobilized Ligands for Metal Ion Separations
Paine, R.T. **$116,000**
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rtpaine@unm.edu

The objectives of this project are to (1) design and synthesize new families of organic ligands capable of selective chelation with d- and f- block metal ions present in nuclear and industrial waste streams, (2) study the coordination properties of the new ligands and delineation of the structural details of the complexes formed in order to improve the redesign and synthesis of enhanced metal ion chelators, and (3) prepare solid phase, immobilized chelators suitable for practical applications in separations. Two classes of chelate systems are under examination: multidentate phosphonopyridine N-oxides and aminophosphonates. In the former group, both aqueous soluble and chloroform soluble ligands have been prepared, and metal ion coordination chemistry has revealed several key features that control metal ion binding. Significant effort is applied to the synthesis of substituent modified ligands that will have enhanced solubility in hydrocarbon solvents. A notable advance in the last year centers on the isolation and structural characterization of a plutonium complex of one trifunctional ligand. The structural results confirm a tridentate coordination mode. Radiochemical extraction studies with Am in nitric and hydrochloric acid solutions have shown that one of these ligands is a highly selective and powerful liquid-liquid extractant. In the case of the aminophosphonates, new water soluble reagents have been generated and the small molecule chemistry has now been extended to include the formation of phosphono substituted polyamines and amine dendrimers. Possible applications for the dendritic polyamino-phosphonates are being sought in new colloid separations.

The Ohio State University
Columbus, OH, 43210

Department of Chemistry

421. ***The Electronic Structure of Heavy-Element Complexes***
Bursten, B.E. **$73,499**
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This project focuses on the use of advanced theoretical methods to calculate the electronic structure of organoactinide and related coordination complexes of the actinide and trans-actinide elements. The principal methodologies currently employed are fully relativistic and quasi-relativistic density functional methods with relativistic effective core potentials. Significant progress was made during the past year. First, the relativistic effective core potentials for trans-actinide elements through Element 118 were published. These potentials have been used to investigate the electronic structure of molecules of these elements. Second, continuing studies of the structure, bonding, and reactivity of actinide-containing molecules, particularly organometallics and binary actinide fluorides, have been conducted. Systems currently under investigation include an extensive series of sandwich compounds of the type $(\eta^n—C_nH_n)_2An$ (An = Th, Pa, U, Np, Pu, Am; n = 6, 7, 8). Studies of organoactinide chemistry have been expanded by examining those factors that lead to linear and bent AnL_2 moieties, and the electronic structure effects on the reaction chemistry of these systems will be addressed. The series of binary uranium fluorides UF_n, n = 1 - 6 has also been studied. Excellent success has been achieved in the calculation of vibrational frequencies and structures of these fundamental molecules.

Chemical Engineering Sciences

Arizona State University
Tempe, AZ, 85287

Department of Chemistry

422. ***Novel Electrolytes for Rechargeable Alkali Batteries***
Angell, C.A.; Xu, K. **$137,000**
602-965-7217 **(14 months)**
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Recent progress of our original program on novel electrolytes is focused on the development of new solvents with excellent stability in wide potential ranges on the surface of composite electrodes. When ether and carbonate structural units, which are universally present in traditional electrolyte solvents, are replaced with new polar groups by means of chemical tailoring, the new solvents show anodic decomposition potential as high as 5.8 V vs. Li^+/Li couple on composite cathode material. With further synthetic modification, the solvents are also stable in the lithium intercalation potential range (ca. 0.5~0.0 V vs. Li^+/Li couple on graphite surface, hence a lithium ion battery based on graphite anode and a high-voltage cathode can be assembled. The combination of the above anodic and cathodic merits makes a higher energy density Li^+-ion battery system possible. Currently, the efforts are being made to polymerize this brand new electrolyte solvent.

California Institute of Technology
Pasadena, CA, 91125

Department of Materials Science

423. ***Design of Metal Hydride Alloys for Battery Electrodes with High Cycle Lifetimes***
Fultz, B.; Ratnakumar, B.V. **$122,000**
818-395-2170 **(14 months)**
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This program is addressing basic questions that underlie the design of new metal hydride alloys for service as negative electrodes in nickel-metal hydride battery cells. Ternary solutes from the groups IIIB, IVB, VB of the periodic table are being substituted for Ni in $LaNi_5$ in a systematic way and in dilute amounts to preserve the single-phase $CaCu_5$ -type crystal structure. We are correlating the thermochemical properties of the solute atoms to their effects on the cyclic lifetime of the metal hydride electrodes, both during electrochemical cycling and during gas-phase cycling. The microstructural changes resulting from the degradation processes of the electrodes are being analyzed by x-ray diffractometry and transmission electron microscopy. Effects of these solutes on differential volume expansion between α and β hydride phases, and hydriding-induced lattice strains are also being used to test ideas about the mechanisms of electrode deterioration. Additional studies of engineering importance for metal hydride electrodes include measurements of kinetic properties of hydrogen absorption in different alloys. Finally, the retention of storage capacity during cycling, as well as practical performance parameters, are being evaluated on prototype batteries fabricated by commercial practice with our most promising Sn and Ge substituted alloys.

University of California, San Diego
La Jolla, CA, 92093

Department of Applied Mechanics and Engineering Sciences

424. ***Premixed Turbulent Combustion***
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libby@ames.ucsd.edu

This project is primarily concerned with flames in stagnating turbulence. Such flames are rich in problems of fundamental interest;

e.g., the extinction of turbulent flames under high rates of strain. As a consequence, there are five or six laboratories in Western Europe and several in the United States carrying out relevant experiments. Although our effort is primarily theoretical, we pay close attention to experimental results coming from these laboratories. In addition we have carried out and published in the Proceedings of the Twenty-Fifth Symposium (International) on Combustion the results of our own experiment on turbulent flames in impinging streams. Our principal focus during the past year has been on a Reynolds stress formulation for such flames. This configuration is the most widely studied experimentally, but to date there has been no satisfactory theoretical treatment of them. Although totally convincing solutions have not to date been obtained, several important findings have resulted from this effort. In particular, we have shown that the calculated mean axial velocity is in excellent agreement with data despite highly inaccurate predictions for the Reynolds stresses. The implications are that the mean velocities are determined by the mean pressure and that the Reynolds stresses are to be calculated in a known mean velocity field. In addition, we have found that the models for pressure-rate-of-strain effects derived for constant density flows must be altered to account for the variations of density associated with heat release. This effort is continuing. During the past contract year we have published three journal articles related to analyses of highly idealized flames in a channel, of laminar Couette flow involving premixed combustion, and of the extinction of premixed turbulent flames under nonisenthalpic conditions.

Case Western Reserve University Cleveland, OH, 44106-7078

Department of Chemistry

425. Applications of In Situ and Ex Situ Spectroscopic Techniques for the Study of Electrode Materials with Relevance to Energy Generation and Energy Storage

Scherson, D.A. **$149,998**
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A. Potential-induced plastic deformations of nickel hydrous oxide electrodes in alkaline electrolytes: An in situ atomic force microscopy study

Dimensional changes of α-type nickel hydrous oxide, α-$Ni(OH)_2$(hyd), films electrodeposited on the basal plane of highly oriented pyrolytic graphite, HOPG(bp), electrodes, have been monitored by in situ by atomic force microscopy (AFM) in 1 M KOH as a function of the applied potential. Freshly prepared α-$Ni(OH)_2$(hyd) films were found to consist of conformal sections covered by large numbers of distinctly bright, globular-type features (0.25 µ average diameter), separated by sharply defined crevices. Upon oxidation, the width of the crevices, W_c, increased, whereas the distances between any two globular features, i and j, within a specific section, r_{ij}, decreased. A statistical analysis involving more than one hundred pairs of features from different sections of independent films showed that the relative decrease in r_{ij}, induced by the nominal full oxidation of the film, $r_{ij}(ox)/r_{ij}(red)$, is remarkably constant, 0.06 ± 0.01, and independent on the magnitude of r_{ij}. Plots of W_c obtained from linear AFM scans along an axis normal to the crevice as a function of the extent of oxidation of the films revealed, within the time scale of the experiments, a marked hysteresis between the oxidation and subsequent reduction process.

B. In situ x-ray absorption fine structure and optical reflectance studies of electrodeposited nickel hydrous oxide films in alkaline electrolytes

X-ray absorption fine structure (XAFS) and optical reflectance spectroscopy (RS) have been used to examine in situ electronic and structural aspects of nickel hydrous oxide, α-$Ni(OH)_2$(hyd), electrodes supported on gold in alkaline electrolytes as a function of their state of charge. The extended x-ray absorption fine structure (EXAFS) of α-$Ni(OH)_2$(hyd) electrodes in the uncharged (UC, or discharged) and overcharged (OC, or fully charged) states yielded, in each case, a single set of two distinct nearest neighbor shells, with distances, $d(Ni\text{-}O)_1$ = 2.05 ± 0.02 Å and $d(Ni\text{-}Ni)_1$ = 3.11 ± 0.02 Å for UC, and $d(Ni\text{-}O)_1$ = 1.87 ± 0.02 Å and $d(Ni\text{-}Ni)_1$ = 2.83 ± 0.02 Å for OC. The in situ EXAFS of films allowed to self-discharge following overcharge could be fit with contributions from both sets of shells, suggesting that only two types of nickel sites are sufficient to account for the redox chemistry of this material. These data, in addition to information derived both from quantitative x-ray absorption near edge structure (XANES) and optical RS in the visible range, indicate that the excess anodic charge (i.e., beyond the one-electron oxidation of Ni^{2+} sites) observed during the first oxidation of freshly prepared α-$Ni(OH)_2$(hyd) electrodes, may not be related to oxidation state changes involving nickel sites in the lattice, and, therefore, do not support the existence of nickel sites with a formal oxidation state higher than three for charged or overcharged electrodes in this media.

Colorado School of Mines Golden, CO, 80401

Department of Chemical Engineering and Petroleum Refining

426. Composition of Dependence of Fluid Thermophysical Properties Theory and Modeling

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The objective of this research is to develop high-accuracy predictive models that describe the physical property behavior of complex mixtures. The work is currently progressing along three fronts: (1) development of improved corresponding states models for asymmetric mixtures through reference fluid equation of state design and improved mixing rules; (2) investigation of the phenomenological behavior of the viscosity of molecular (e.g., structured) mixtures through nonequilibrium computer simulation techniques; and (3) development of ultrahigh accuracy equations of state for complex fluids and fluid mixtures through the use of stepwise regression and simulated annealing optimization. The ultimate goal of this research is to develop improved computer-based models for process design that provide accurate predictions of phase transitions and bulk-phase properties in systems that have large size and/or polarity differences. Current work is focused on improved predictive models for mixtures containing dissimilar species. Recent outputs include new high-accuracy equations of state for refrigerants and long chain hydrocarbons and a new, more accurate and versatile method of predicting shape factors for the extended corresponding states model.

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Department of Chemical Engineering

427. ***Study of Improved Methods for Predicting Chemical Equilibria***
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This project involves the study of computer-based molecular mechanics (or force field) techniques for accurate prediction of the thermodynamic properties of chemically reactive systems involving nontrivial molecules. Our studies have shown the power of the molecular-mechanics approach for such accurate predictive thermodynamics, relative to ab initio and semiempirical molecular orbital approaches. The molecular mechanics technique complements the ab initio and semiempirical approaches by being less demanding of computer power than the ab initio method, and capable of greater accuracy than the semiempirical technique for thermodynamic calculations. Software developed within this project is available through the Quantum Chemistry Program Exchange as programs QCPE 593 and QCMP 145. Our studies have involved both software development and supporting experimental studies for parameterizing the consistent force field employed. Most recently, these experimental studies have dealt with the d and l enantiomers of lactic acid. Simple techniques have been developed for isolating L(+) and racemic lactic acid crystals. Similar techniques have been employed in isolating several chiral enantiomers and determining their crystal structure and relative solution thermodynamics for future use in force field parameterization.

Department of Chemistry

428. ***Nanomaterials in Secondary Battery Research and Development***
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A critical parameter that affects the performance of Li-ion batteries at high discharge current is the particle size and shape of the Li-insertion material in the electrode. In an effort to study the effect of particle size and shape on rate performance, we have developed a novel method, called “template synthesis.” The advantage of template synthesis is that the diameter and aspect ratio of the Li-ion insertion material particles can be controlled at will. The objectives of this work are to explore the effect of particle size and shape on electrode rate capability. Our results to date show that, at high discharge currents, electrodes composed of nanoscopic cylinders of the Li-ion insertion material deliver higher capacity than thin-film electrodes of the same material. We have prepared nanotubular electrodes of $LiMn_2O_4$ and TiS_2. The $LiMn_2O_4$ nanotubes were nominally 200 nm in outside diameter with a wall thickness of ca. 50 nm. The tubules were attached to a Pt foil current collector such that they protruded from the foil like the bristles of a brush. A thin-film control electrode of $LiMn_2O_4$ was also prepared on Pt foil having the same mass of $LiMn_2O_4$ per cm^2 as the nanostructured electrode. The TiS_2 electrode was prepared by a different template synthesis technique so its morphology was slightly different. Template synthesis was used to prepare a microstructured current collector of Au tubules on Au foil. The current collector was then covered with a thin “skin” of TiS_2 by using chemical vapor deposition. The resulting electrode consisted of capped tubules of TiS_2 that were nominally 1 micron inside diameter with a wall thickness of ca. 360 nm covering the current collector of Au tubules and foil. Again, a thin film control electrode of the same mass of TiS_2 per cm^2 was prepared on Au foil. The rate capabilities of the nanostructured and thin film pairs were compared using constant current charge and discharge and cyclic voltammetric experiments. For both $LiMn_2O_4$ and TiS_2 electrodes, we found that the nanostructured electrode delivered 7 to 10 times more capacity than the thin film electrode in high current and high scan rate experiments. This work has shown that the greater surface area per mass of the template synthesized (nanoengineered) electrodes results in reduced current density and higher electrode capacity at high discharge currents.

Cornell University Ithaca, NY, 14853

School of Chemical Engineering

429. ***Simulation of Fluid Behavior in Well-Characterized Porous Materials***
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This work is developing new and rigorous theoretical and simulation methods for the study of the adsorption behavior of fluids in well-characterized porous materials. In particular, fluids in porous carbons, aluminosilicates (particularly MCM-41), aluminophosphates, and buckytubes are being studied. Simulations of carbon dioxide/methane and nitrogen/methane mixtures in zeolites have been carried out, and are being compared with experimental data; in both of these mixtures, inversion of selectivity has been found in certain materials. Both selective adsorption and melting/freezing studies have been made for a range of gases adsorbed in buckytubes and MCM-41. Freezing in these materials was found to depend strongly on the material (via the fluid-wall interactions) and on the adsorbed layer considered. In the case of buckytubes, an increase in freezing temperature was observed for the contact layer near the wall, whereas the freezing temperature was lowered for the adsorbate in the inner parts of the pore. Our studies of water adsorption on activated carbon have been extended to a more sophisticated model of the material, which includes the effects of oxygenated groups at edge sites on the graphite microcrystals, and incorporates the effect of pore size distribution. The results seem to be in good agreement with recent experimental data. We are also studying the freezing of water in these carbons and the behavior of water-hydrocarbon mixtures. The filling mechanism in such carbons is quite different for water than for simple fluids. In particular, filling occurs by the formation of clusters of water molecules about oxygenated surface sites, followed by a continuous filling. Capillary condensation does not occur when the density of such sites is appreciable.

430. Molecular Simulation of Phase Equilibria for Complex Fluids
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This project focuses on studies of phase equilibria for complex fluids using novel molecular simulation techniques. The long-range goal is development of improved modeling methods for rational design of efficient industrial chemical processes. Current research encompasses three main classes of systems, namely polymeric, surfactant, and ionic systems. A major recent methodological development has been the introduction of histogram reweighting Monte Carlo sampling methods. The methods allow significantly more accurate determination of phase coexistence properties than previously available techniques. They also can be used to locate critical points for strongly interacting fluids with high precision. We are presently applying these methods to polar and polarizable fluids, primitive electrolyte models, water, and lattice models for surfactants and polymers. For surfactant systems, the methods allow determination of aggregation properties in addition to transitions between structured phases. A related method, Hamiltonian-Scaling Monte Carlo, has been developed to allow determination of properties for a series of related models from a single simulation.

Department of Mechanical and Aerospace Engineering

431. Investigation of Non-Premixed Turbulent Combustion
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Turbulent combustion models are being used increasingly in industry to assist in the design of combustion equipment. The accuracy (and therefore usefulness) of these models depends on the how well turbulence-chemistry interactions are represented. PDF models, which are based on transport equations for the joint probability density function of fluid properties, have the great advantage of being able to treat chemical reaction exactly, without turbulence closure approximations. In this research project, PDF methods are being applied to non-premixed turbulent flames, which have been the subjects of extensive experimental studies. By comparing numerically-accurate model calculations with the experimental data, the capabilities and shortcomings of different sub-models are being determined. Calculations are in progress for the joint PDF of velocity, turbulence frequency, and 14 thermochemical variables, for piloted jet diffusion flames of methane. A skeletal mechanism for methane (consisting of 16 species and 41 reactions) is implemented efficiently using the method of “in situ adaptive tabulation” (ISAT).

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Department of Chemical Engineering

432. New Generation of Group Contribution and Equation-of-State Models
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To make intelligent, cost-effective decisions for the design of new chemical processes, for the development of synthetic fuels and other new technologies, and for estimating the environmental fate and bioaccumulation of chemicals, accurate methods of predicting and correlating thermodynamic properties and phase equilibria are needed. The research being conducted under this grant addresses this problem from three different directions. First, the Wong-Sandler mixing rules, which have greatly expanded the range of application of equations of state to highly nonideal mixtures, are being further developed to apply to collections of mixtures that previously could not be accurately described over large ranges of temperature and pressure. This includes hydrogen-containing mixtures and mixtures with strongly polar compounds. We are also considering complex phase behavior such as continuous and discontinuous critical lines, vapor-liquid-liquid and liquid-liquid equilibria. The second area of research is the use of ab initio molecular orbital calculations to compute the effect of hydrogen-bonding and other strong association phenomena. The results of these calculations have been incorporated into equations of state to reduce the number of adjustable parameters that must be used. This quantum mechanically-derived information is also being used in the development of a new generation of group contribution methods (improvement upon UNIFAC, ASOG, and similar methods) to provide more accurate prediction methods. Finally, we have completed a project which used computer simulation and statistical mechanical theory to develop a more accurate thermodynamic description of long chain hydrocarbons and polymers.

Georgia Institute of Technology
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School of Chemical Engineering

433. *Electrochemical Study of New, Room-Temperature, Molten Salt Electrolytes for Sodium/Metal Chloride Batteries*
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A novel approach to high-energy density, ambient temperature batteries involves the marriage of the high-temperature "Zebra" cell, which employs the Na/$NiCl_2$ couple at about 2.3 V with room-temperature melts, with electrochemical windows of 4.7 V. Electrolytes that show promise are room temperature molten salt mixtures made from: (1) inorganic solvents compounded with aluminum chloride ($AlCl_3$), buffered with NaCl, and (2) inorganic salt mixtures formed directly from solvents, along with $NaAlCl_4$. Electroanalytical and spectroscopic techniques will be used to identify the reaction products and parasitic reactions. The use of a quartz microbalance as an electrode support will allow measure of the change in mass with charge and discharge current; the amount of sodium plated and stripped is then directly calculable. The cathode in a Na/metal chloride battery has yet to be identified. The main criteria involved are: formation of a conductive (porous) chloride film, species which are insoluble in the melt, and rapid electrode kinetics, allowing high current densities. Recent work with polymer electrolytes suggest that intercalation of Na into a metal oxide may be successful here. Half-cell tests will be performed with all selected electrolytes, screened in the anode half-cell studies.

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Department of Chemical Engineering

434. *Computer Simulation of Osmosis and Reverse Osmosis in Solutions*
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Computer simulation studies are being carried out to study the phenomena of osmosis, reverse, and electro-osmosis in solutions. These studies have been carried out using a molecular dynamics method recently developed by us. Both aqueous and non-aqueous solutions are being investigated. Reverse osmosis is an energy-efficient separation technique widely used in the chemical industry. Our studies on aqueous electrolyte solutions, as well as methanolic solutions, have also suggested a new mechanism for reverse osmosis. It was previously thought that ions are prevented from crossing the semi-permeable membrane, despite their smaller size (compared to solvent), because of surface interactions between the membrane and the ions. Our work seems to suggest that solvent molecules strongly cluster around the ions, thus effectively increasing their size and preventing them from permeating the semi-permable membrane. We are also studying the phenomenon of electro-osmosis using molecular simulations. This will ultimately allow reverse osmosis separations to be carried out more efficiently. Our results have shown that electro-osmosis can be observed in non-ionic polar systems subjected to uniform electric fields. Previously, it was thought that since an external electric field only leads to a torque on polar molecules, it would not affect the reverse osmosis rate. The external field makes large clusters of polar molelcules less energetically favorable and this leads to a higher separation rate.

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Department of Chemical Engineering

435. *Prediction of Thermodynamic Properties of Complex Molecules*
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The goal of this research program is to improve our understanding of the factors that cause deviations from ideal behavior in complex fluids (i.e. molecules whose size, shape, or interaction energy cause them to behave differently from spherical, non-polar molecules). We are particularly interested in understanding the properties of mixtures of such molecules. Our program includes a combination of theory, molecular simulations, and experiments. We have developed a new model for non-random behavior behavior based on the Ono-Kondo theory for density gradients near an interface. We have applied this model to adsorption phenomena and to predicting mixture properties for highly non-ideal mixtures. This new model is more accurate than existing models (including NRTL, UNIQUAC, BGY, NRSF, and Wilson). It also is more general in that it can be used for one-, two-, and three-dimensional systems. We currently are working to extend this model to mixtures containing polymer molecules and to adsorption of polymers at surfaces.

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Institute for Physical Science and Technology

436. *Thermophysical Properties of Fluids and Fluid Mixtures*
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Critical fluctuations affect the thermodynamic and transport properties of fluids and fluid mixtures in a wide range of temperatures, densities and concentrations. We are developing a theory of crossover critical phenomena so as to obtain equations that incorporate the effects of the critical fluctuations on the thermodynamic and transport properties. First, we are continuing research on the crossover from Ising-like to mean-field critical behavior of one-component fluids. Using a general isomorphism approach, we are extending the theory to describe thermodynamic properties of simple and complex fluid mixtures. The method has been used to predict thermodynamic and transport properties of methane+n-hexane mixtures near critical endpoints. We are also applying the theory to describe thermodynamic properties of aqeous solutions of NaCl at high temperatures. We expect to extend the theory to also deal with crossover critical phenomena in polymer solutions.

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Department of Chemical Engineering

437. Studies in the Molecular Thermodynamics of Solid-Fluid Phase Equilibrium

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This research program involves development and applications of the molecular theory of solid-fluid phase equilibrium. The focus of the program is to improve our fundamental knowledge of how molecular interactions determine solid-fluid phase diagrams for pure components and for mixtures. Progress in this area is of long-term benefit to the needs of solid-fluid separations in the chemical industry and hydrocarbon processing in the petroleum and natural gas industries. We are extending our previous theoretical work on mixtures, which was successful for spherical molecules, to systems with more complex intermolecular forces. This will lead to predictions of, for example, the effect of anisotropic intermolecular forces on mixture phase diagrams and the stability of congruently melting substitutionally ordered solid solutions or compounds. We are also building on our prior work concerning the influence of molecular anisotropy on solid-fluid equilibrium in pure component systems by developing a treatment of molecular structure effects on solid-fluid phase diagrams of flexible chain molecules. This work focuses especially on the n-alkanes and the trends in their properties with chain length.

University of Minnesota
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Corrosion Research Center

438. Characterization of Insertion Electrodes in High-Energy Cell

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V_2O_5 xerogels are excellent hosts for Li^+ ions with an intercalation capacity of at least four Li^+ ions per mole of host. Organically modified gels (ormogels) of vanadium pentoxide show the same high capacity for intercalation of Li^+ ions, and the thermodynamic properties are also enhanced. The ormogels have been shown to host polyvalent cations at or near the same extent as Li^+ (i.e., 4 equivalents of Mg^{2+} and Al^{+3} and 3.6 equivalents of Zn^{+2}). The latter studies have been carried out on gels processed by supercritical drying to give aerogels. Other high surface area materials have been obtained by drying procedures that are continuous and avoid batch drying under supercritical conditions. The new processes are carried out under conditions of low surface tension and thus sacrifice small pores that collapse because of capillary forces. Surface areas up to 200 square meters per gram are achieved, with most of the area due to pores in the desired mesopore range. The same high intercalation capacities are maintained in the materials. Further research is being conducted to explore the rate of intercalation of both polyvalent and monovalent cations.

School of Physics and Astronomy

439. Modeling of Transport in Lithium Polymer Electrolytes for Battery Applications

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The goal of this research is to provide new insight into the mechanism of ionic conduction in Li polymer electrolytes and the electrolyte-electrode interface using a combination of new and powerful simulation techniques that have not previously been applied to these materials. A molecular dynamics model for amorphous polyethylene oxide has been developed, using a unique approach in which the model is developed by simulating a polymerization process, starting with liquid dimethyl ether. This has significant advantages over starting a molecular dynamics simulation in the crystalline phase. We are using the molecular dynamics model to evaluate solvation and hopping activation free energies for Li^+ ions and various anions. We have also developed algorithms for the direct evaluation of conductivity using this simulation. Structure predicted for the electrolyte from the molecular dynamics model is being tested by comparison with neutron scattering data obtained by Argonne collaborators. This output from the molecular dynamics studies is being used to construct models of the system at larger length and longer time scales appropriate to the transport problem and to evaluate various suggestions concerning the nature of the ionic transport in these electrolytes. To study the cathode-electrolyte interface, development of a tight binding molecular dynamics model of the cathode is planned.

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Department of Physics

440. *Long-Ranged Polymer Dynamic Behavior and Conductivity in Battery Polymer Electrolytes: Poly(ethylene oxide)/Salt Systems*

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In this project, light scattering—principally the noninvasive dynamic light scattering technique known as photon correlation spectroscopy—is being used to study relaxations of poly(ethylene oxide)(PEO) in the melt, both with and without lithium perchlorate. The purpose of this work is to reveal how relaxations, particularly long-ranged PEO relaxations in PEO solid polymer electrolytes, are related to lithium ion conductivity in these electrolyte systems. Following the project plan outlined in the FY 1995 project summary, the first phase study of the effects of lithium ions on PEO global behavior in methanol solutions has been completed and the results reported in the literature (P.A. Banka, et al; *Macromolecules*, vol. 29, pp. 3956-3959). The study of the effect of lithium ions on PEO coil internal motions is also progressing, but completion of this portion of the project awaits delivery of a satisfactory high molecular weight, narrow molecular weight distribution PEO sample. Significant progress has also been made on the second phase of the project dealing with melt PEO samples. We have now observed a well-defined, more-or-less monomodal, relatively fast relaxation in highly entangled melts, which is accompanied by a very slow relaxation associated with a visibly "grainy" structure in incompletely annealed samples. For melts of low molecular weight unentangled PEO, we observe a single, relatively faster relaxation with no graininess or associated slow relaxation. To better understand the nature of conductivity in SPEs, we are investigating the effects of lithium perchlorate on these relaxations and will compare the results both with those for poly(propylene oxide) melts and with conductivity data.

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Department of Physics and Astronomy

441. *Magnetic Resonance and X-Ray Absorption Studies of Materials for Advanced Batteries*

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Our program centers on spectroscopic analysis of materials important to high energy density secondary lithium battery development, using primarily magnetic resonance (NMR and EPR) and synchrotron x-ray absorption spectroscopy. Samples are provided by collaborators from universities in the U.S. and abroad, and from industrial and federal laboratories. Recent work includes: (1) We used ^{7}Li NMR and V K-edge x-ray absorption to characterize the structural environments of both the intercalated ion and the host in the $Li_xV_6O_{13}$ cathode system, leading to improved understanding of the phase behavior of this material as a function of Li concentration. (2) We have measured Fe K-edge near-edge and extended x-ray absorption spectra in situ on thin Li/polymer electrolyte/FeS_2 cells in various states of charge or discharge. Results show: (a) the structure changes reversibly with Li content; (b) intermediate iron-sulfur compounds may be present in partially discharged cells. (3) With high resolution NMR methods (magic angle spinning and proton decoupling), we have detected three distinct Li environments in disordered carbon anodes: (a) intercalated graphite-like; (b) ionic, corresponding to the irreversible surface layer formed by electrochemical reduction of the solvent; (c) a new species of relatively mobile Li apparently correlated with hydrogen-containing regions of the disordered carbon. (4) Using photoemission and LEED, we have examined the surface stability of VO_2 through the metal insulator transition.

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Department of Chemical Engineering

442. *Theoretical Treatment of the Bulk and Surface Properties of Fluids Containing Long, Flexible Molecules*

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This research program is designed to enhance understanding of the behavior of fluids and fluid mixtures containing chain-like molecules. The objective is to develop a theory that is capable of predicting the experimentally observed thermophysical properties, including phase equilibria and transport properties, of fluids and fluid mixtures containing chain-like molecules ranging in length from alkanes to polymers. Highlights of this year's accomplishments include: (1) the extension of the Generalized Flory Dimer theory to fluids containing heteronuclear chain molecules (block, alternating and random copolymers) that experience both attractions and repulsions, (2) simulation of the static and dynamic properties of large model systems of polymer networks, (3) simulation of the static and dynamic properties of mixtures of single- and double-tethered chain molecules at interfaces, and (4) the simulation of the sorption and diffusion of model penetrants into model polymer membranes (including facilitated transport membranes) in the presence of a chemical potential gradient. Work is continuing on extracting activity coefficients from the Generalized Flory Dimer theories, with the aim being to use this as a basis for developing a new group contribution approach to estimate the properties of mixtures when experimental data are unavailable.

443. Composite Polymer Electrolytes Using Fumed Silica Fillers in Low Molecular Weight Polyethylene Oxides: Synthesis, Rheology and Electrochemistry
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We continued our efforts to synthesize and develop a new class of highly processable composite polymer electrolyte systems for use in rechargeable lithium batteries. Based on surface-modified fumed silica and low molecular weight polyethylene oxide/glycols, this new approach have yielded the following desirable properties: (i) room temperature conductivities exceeding 10^{-3} S/cm, (ii) high mechanical strength with an elastic modulus similar to elastomers, (iii) shear thinning viscosity leading to easy processability, and, (iv) improved electrochemical stability with lithium. In addition, preliminary full-cell cycling tests show that the composite electrolyte functions well when using $LiCoO_2$ or $LiMn_2O_4$ as the cathode. The advantages of these systems are that while they are processable, they become self-supporting gels instantaneously following processing, and the mechanical properties can be tuned independently of the electrochemistry.

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Department of Chemical Engineering

444. Molecular and Polymeric Fluids in Microporous Media
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Experimental studies of transport in important microporous materials show that a significant resistance to mass transfer can be present at the surfaces of the nanoporous regions. These barriers may be caused by reconstruction effects at the free surfaces and can greatly modify the ability of a material to perform certain separations. Our work entails the application of computer simulation techniques and of molecular theory to a systematic study of surface barriers in carbon molecular sieves and zeolites, especially barriers due to highly localized pore-mouth resistances (on the order of a few Angstrom units). Preliminary studies prove that both types of techniques can be used effectively for the determination of surface mass transfer coefficients for simple, pure gases into models that mimic the slit pores believed to be characteristic of carbon molecular sieves. We are studying the effect of surface barriers on the transport of diatomics and light hydrocarbons into models for the same carbons and for silicalite. The effect of surface barriers on mixtures, in which a heavier component may block the transport of a lighter species, can lead to important insights into the mechanisms of kinetic separations.

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Center for Advanced Materials

445. Development of Novel Strategies for Enhancing the Cycle Life of Lithium Solid Polymer Electrolyte Batteries
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A wide range of substituted polyphosphazenes (PPZs)-based solid polymer electrolytes (SPEs) have been synthesized during the past four years of the project. The conductivities of SPEs formed from the PPZs+lithium triflate ($LiSO_3CF_3$) have been measured, and many are found to be greater than 10^{-5}S/cm at 25°C. Most importantly, we have established correlations between the substituent properties and the conductivity that will guide future synthetic efforts. We have also paid attention to the rheological properties of the polymers, with the goal of identifying systems that would not require crosslinking, because this adds an additional step in any manufacturing process and hence increases the cost. In parallel with the synthetic work outlined above, we have developed a combined impedance/dilatometry system for exploring the cycling performances of laminates that have been fabricated using the PPZs. By using Pt/SPE/Pt laminates, we have shown that the impedance of the system can be delineated into interfacial and bulk electrolyte components, as determined from the effect of pressure. Increasing pressure is found to decrease the interfacial resistance but to increase the bulk resistivity, with the latter being attributed to a decrease in the free volume. The cycling behavior of Li/SPE/Li has also been explored, in terms of changes in impedance and laminate thickness, as lithium (6 mA. hrs) is electrochemically pumped from one side to the other. We find no degradation (i.e., no increase in the impedance) as the system is cycled at a current density of 6 mA/cm^2 for more than 500 cycles, regardless of the pressure applied to the laminate, although a monotonic increase occurs in the thickness. Our findings suggest that, although irreversible changes occur at the Li/PPZ interface, they do not limit the cycle life performance, in contrast to other systems, where lithium “powdering” has been implicated in a sudden increase in cell (Li/SPE/IC) resistance and hence in failure. Our studies are now being extended to IC/PPZ/IC laminates, with the intercalation cathode (IC) employing MnO_2. Based on our impedance studies, we have derived a physical model for the lithium/PPZ interface that postulates interstitial conduction of Li^+ through a reaction product layer. A percolation model has also been developed for the intercalation cathode, which is now being used in conjunction with the anode model to describe the electrochemical properties of the batteries. We have also developed an Artificial Neural Network (ANN) for Li-ion batteries, based on data provided by NASA, with the goal of exploring whether such a model can be used to predict cycle life from short-term data. Finally, we have fabricated prototype batteries of the type Li/PPZ/TiS_2, which are found to have open circuit voltages of 2.8 - 3.02V.

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Department of Chemical Engineering

446. *Computational and Fundamental Studies in Metastable Liquids*

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The goal of this project is to gain fundamental understanding of the thermophysical properties of liquids outside of their range of thermodynamic stability. This knowledge is important in the prevention of vapor explosions in the metals processing, paper, and nuclear industries; the preservation of labile biochemicals; the inhibition of hydrate formation in natural gas pipelines; and cavitation in hydraulic machinery. We developed two new molecular simulation techniques for studying superheated liquids, in which voids larger than a critical size are prevented from forming. We studied the statistics of fluctuating void space in superheated liquids and its relationship to nucleation and cavitation. In our ongoing theoretical and computational investigation of the thermodynamics of network-forming liquids, and in particular of supercooled and glassy water, we have verified by direct computer simulation of phase coexistence that a model network-forming liquid that forms strong, orientation-dependent bonds, exhibits a first-order phase transition between two liquid phases at low temperatures. This is the first time that liquid-liquid immiscibility in a pure substance has been found using exact methods.

Rutgers, The State University of New Jersey
Piscataway, NJ, 08855

Ceramic and Materials Engineering

447. *Solid Electrolyte-Electrode Interfaces: Atomistic Behavior Analyzed via UHV-AFM, Surface Spectroscopies, and Computer Simulations*

Garofalini, S.H. **$125,000**
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UHV-AFM, STM, and XPS surface analyses and molecular dynamics computer simulations have been used to examine the structural and dynamic properties of the cathode/electrolyte interface in solid-state oxide thin-film batteries. Electrolytes include lithium-containing silicates, borates, phosphates, and phosphorous oxynitride ion conducting (IC) glasses; cathode/electrode materials include Li and V_2O_5 and WO_3. New UHV-AFM experiments using Force-Distance (FD) mode of analysis have been used to evaluate cathode-electrolyte glass interactions at the nanometer level (a nanobattery). Specifically, a clean and oxidized tungsten tip was brought in contact with a lithium borate electrolyte glass and a series of FD curves was evaluated as a function of applied voltage. Significant changes in the shape of the FD curves occurred as a function of bias, voltage, and time, consistent with the migration of Li ions between the glass and the tungsten oxide tip. The effect of cycling between tip and electrolyte glass was also studied. Computer simulations of the molecular details of Li transport across the glass/cathode interface showed an appropriate phase change and channel formation. Orientation of the cathode crystal significantly affected diffusion into the cathode, especially for the vanadia crystal.

University of South Carolina
Columbia, SC, 29208

Department of Chemical Engineering

448. *Synthesis, Characterization, and Testing of Novel Anode and Cathode Materials for Li-Ion Batteries*

White, R.E.; Popov, B.N.; **$204,000**
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This year several new cathode materials were synthesized: $LiMn_{2-y}Co_yO_4$, $LiMn_{2-y}Cr_yO_4$, CrO_x, and $LiCr_3O_x$. The effect of Co and Cr on the capacity fade of $LiMn_2O_4$ and $LiMn_2O_4$ was investigated. Cobalt and chromium doping in $LiMn_2O_4$ improved the cycling performance of the cathode due to the stabilization of the oxide spinel structure. This was observed for small quantities of doped Co or Cr. The optimum Co concentration in $Li_xCo_yMn_{2-y}O_4$ was found to be y = 1/6, and the optimum concentration of Cr in $LiCr_yMn_{2-y}O_4$ was found to be y = 0.1. These mixed oxide cathodes provided an overall capacity of 110 Ah/kg, with very small capacity fade with cycling. New CrO_x cathode material has been also synthesized with a capacity of 245 Ah/kg and a discharge voltage of 3.0 V. Also, Pd-graphite, Sn-graphite, and Ag-graphite composite anodes were synthesized. These anodes provided larger capacity than graphite alone. Electrochemical Impedance Spectroscopy (EIS) was used to determine the diffusion coefficient of Li ions in these anode materials.

Stanford University
Stanford, CA, 94305

Department of Chemical Engineering

449. *Fundamental Studies of Fluid Mechanics and Stability in Porous Media*

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This research project treats flow and transport problems in a variety of contexts of importance to energy recovery and utilization. Our work on porous media problems includes both macroscopic Darcy scale and pore scale flows. Current Darcy scale work addresses the issue of resonant interactions between the flows driven by fingering and by heterogeneities, respectively, which we are studying through a combination of analytical and numerical work. Theory indicates that the most effective resonance is a subharmonic one, in which the flow driven by fingering is enhanced through interaction with heterogeneity scales of twice the wave number of the fingering. Recent pore-scale work focuses on the propagation and instability of driven contact lines of elastic liquids. Perturbation theory for small Weissenberg numbers has shown how viscoelastic thin-film dynamics differs from the Newtonian case, with elasticity stabilizing the dynamic contact line against rivulet formation. The stabilization mechanism is related to the increased resistance to streamwise acceleration accompanying the rivulet formation. Recent experiments in our laboratory have corroborated these predictions. We are also concerned with mixing and drag reduction in viscoelastic fluids. Our recent theoretical studies have shown how elasticity can influence chaotic mixing. Current work is focused on understanding the mechanism of turbulent drag reduction in free shear layers through the use of polymer additives. These studies involve the use of large scale scientific computing.

State University of New York at Buffalo
Buffalo, NY, 14260-4200

Department of Chemical Engineering

450. *Molecular Simulation of Phase Coexistence, with Application to Ordered Phases*

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The aims of this research are the development of simulation tools that can be used by researchers in molecular thermodynamics, and the application of these tools to understand phase equilibria involving ordered phases, particularly solids. Presently the work is focused on three areas: (1) Methods for measuring the chemical potential. This is the most problematic part of the study of phase coexistence by molecular simulation. We are conducting a systematic, quantitative study of these methods with the goal of identifying which techniques are best, and how they are best implemented. One important result is the identification of entropy—as opposed to free energy—as a central quantity in understanding the various methods; (2) Solid-fluid phase diagrams of polydisperse hard spheres. Colloidal systems are known to form ordered, solid-like phases, and as a first approximation, the freezing of hard spheres can be used to understand the phenomenon. However, colloids are invariably polydisperse in size to some degree, and this polydispersity has significant consequences for the freezing transition. We have quantified the "terminal" polydispersity, above which solids cannot be formed, and are now working to characterize the high-density behavior; (3) Freezing in multisegment hard-sphere mixtures. When trying to predict the freezing transition of complex industial mixtures, it is important to know when solutions will be formed in the solid phase. In this work we examine freezing of simple model mixtures with the ultimate aim of developing and/or improving semi-empirical models of mixture freezing.

State University of New York at Stony Brook
Stony Brook, NY, 11794

Department of Chemistry

451. *Thermophysical Properties of Fluids and Fluid Mixtures*

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Theoretical research continues on the thermophysical properties of fluids using a statistical mechanical approach to do molecular modelling. Current emphasis is on the development of an integral equation for the pair correlation function, which will permit the prediction of structure and thermodynamics of a fluid model from its pair potential over the whole range of fluid temperature and density, with global accuracy heretofore unattainable from an integral-equation approximation. The approach has been tested on simple lattice-gas models and is now being developed for continuum fluids, starting with a pair potential with a hard core and Yukawa tail. The approach is also being extended to the replica Ornstein-Zernike integral equations that describe fluids in porous media that have irregular pore structure. Work also continues on the structure and thermodynamics of models of ionic fluids, including both weak and strong electrolytes, and on models of polymeric and polymerizing fluids. Over the last year, the ionic-fluid work has been focused upon understanding the nature of liquid-liquid and liquid-gas phase separation in a symmetric electrolyte close to a critical point. We are currently studying extensions to electrolytes showing charge asymmetry and/or marked size asymmetry between anions and cations.

University of Tennessee at Knoxville
Knoxville, TN, 37996

Department of Chemical Engineering

452. Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems

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The objective of this project is to develop fundamentally-based predictive theories for the thermodynamic properties and phase equilibria in mixed solvent electrolyte systems and supercritical aqueous solutions. During the current year, revised neutron scattering results on the structure of supercritical water [Soper et al., *J. Chem. Phys.* **106** 247-254 (1997)] have confirmed our earlier predictions of the structure of supercritical water [Cummings et al., *J. Chem. Phys.* **94** (1991) 5606-5621]. This was in contrast to the earlier neutron scattering results [Postorino et al., *Nature* **366** (1993) 668-670] which had suggested that our simulation results were inaccurate. We have continued development of a new intermolecular potential model for water that features polarizability and has the property that the isolated water molecule has the bare dipole moment of water (1.85D), unlike almost all other models for water. In the current stage of development, the model has a quadrupole moment in good agreement with the measured quadrupole moment, and via molecular simulation predicts the thermodynamic and structural properties of water (i.e., revised neutron scattering results) to a high degree of accuracy. We have completed the first molecular dynamics simulations of water/alcohol/tetrabutylammonium halide salt systems in order to probe the molecular basis of experimental measurements of phase equilibria and densities in alcohol/water/organic salt systems performed in our laboratory. Many of the simulation codes written in our group for this project have been developed to run on the massively parallel supercomputers in the Center for Computational Sciences at Oak Ridge National Laboratory.

Texas A & M University
College Station, TX, 77843-3402

Center for Electrochemical Systems and Hydrogen Research

453. Cell Components with Emphasis on Hydride Electrolytes for Nickel/Metal Hydride Batteries—Materials Research to Technology Development

Srinivasan, S.; Alexander, M.; **$118,500**
Gamboa-Aldeco, M.; Marrero, M.; **(14 months)**
Smith, D.; Soriaga, M.P.;
Visintin, A.; Zhang, W.
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The objectives of the research program in Phase 2 on this project are to (1) investigate hydriding/dehydriding on the alloys to examine whether inorganic additives to the electrolyte or metallic (electrocatalytic) coatings can enhance the charge/discharge behavior of metal hydride electrodes and have effects on the mechanisms of the hydriding/dehydriding reaction; (2) examine alloys with compositions other than AB_5-type, with the goals of improving the performance characteristics of hydride electrodes; and (3) significantly improve the specific energies of the positive electrode (nickel oxide) by incorporating other metallic ions that may make this reaction exceed one electron transfer (i.e., from $Ni^{2+} \rightarrow Ni^{3+}$ to Ni^{2+} to Ni^{3+x+} where $0 < x < 1$). The presence of zinc in the electrode improves the charge/discharge behavior of metal hydride electrodes. Fundamental studies using electrochemical, in situ, and ex situ electrochemical-XAS measurements (in collaboration with Drs. J. McBreen and S. Mukerjee at Brookhaven National Laboratory), and surface science techniques showed that the presence of zinc on the surface inhibits the oxidation of nickel and improves the kinetics of the hydriding reaction. Likewise, a palladium coating on the electrode accelerates the charge transfer step ($M + H_2O + e^- \rightarrow MH + OH^-$) in the hydriding reaction. A novel electrode (tip electrode), which uses only a small quantity of the active alloy, was developed and shown to be quite effective for determining electrode kinetic parameters for the hydriding/dehydriding reactions using electrochemical impedance spectroscopic techniques. Experiments are underway to investigate AB_2 alloys for hydride electrodes and elucidate their electrode kinetic behavior. A review article was prepared on the role of electronic, geometric, and surface properties of alloys for the hydriding/dehydriding reactions and was presented at the Montreal Meeting of the Electrochemical Society.

Tufts University
Medford, MA, 02155

Electro-Optics Technology Center

454. Reseach on Advanced Thin-Film Batteries

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The primary objective of the research is to develop affordable and safe prototype inorganic thin-film lithium-ion batteries that are more durable, have higher voltages, and have higher power and energy densities than can be obtained with commercially available rechargeable batteries. During the past year, the feasibility of serially depositing, series-connected high voltage thin film batteries has been demonstrated; namely, a 7-volt, 2-cell Li-ion LiCoO2/Lipon (Li3PO4:N)/C thin film battery was successfully deposited, and the (bulk density) Lipon layer was deposited by a production-worthy process (at a rate greater than 300 angstroms/minute). Additionally (1) a vacuum system is being retooled with electron and ion beam guns to allow us to deposit all the layers with improved properties by a production-worthy process; (2) a laser patterning technique is being developed which should eliminate masking with its attendant manufacturing and stress problems; and (3) density of states calculations have been made on small diameter single graphene sheets and suggest that layers of single C24 sheets might provide both a lower voltage and higher charge storage anode than conventional carbon (*J. Electrochem.* Soc. 143, L262 (Nov 1996)).

Utah State University
Logan, UT, 84322-0300

Department of Chemistry and Biochemistry

455. The Development of Conductive Diamond Thin Films as Advanced Battery Electrode Materials

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The research being conducted by our group is focused on developing conductive diamond thin films as new electrode materials for energy storage devices. The use of diamond in electrochemistry has only recently been reported, so little is known about the relationship between the film's physical, chemical, and electronic properties and the electrochemical performance. We are investigating the performance of boron-doped diamond thin films in the nickel hydroxide alkaline battery system. Possible advantages of using boron-doped diamond in this battery system include corrosion resistance, thermal stability, good conductivity, and morphological and microstructural stability. The research is progressing along three fronts: (1) examining the morphological and microstructural stability of the material in 15% KOH at high anodic current density; (2) developing viable deposition protocols that produce well adhering, electrochemically accessible active material adlayers on the film surface; and (3) long-term cycle testing of the active material adlayers at temperatures between 25 and 55°C. Diamond has been found to be dimensionally stable in 15% KOH at current densities as high as 0.5 amperes per centimeter ^{2} for periods of time up to 20 hours. Electrochemical AFM and Raman microprobe spectroscopy have revealed that no significant morphological or microstructural alterations occur under these harsh electrolysis conditions. Two multistep electrochemical deposition protocols have been developed that produce well-adhering and well-utilized active material on the diamond film surface. Important in these protocols is the electrochemical conditioning that is performed in 15% KOH at different stages during the deposition sequence. Active material deposits of up to 0.2 coulombs per centimeter ^{2} have been produced so far. Long-term cycle testing (6000 cycles) experiments in 15% KOH and at temperatures between 25 and 55°C have revealed that the active material deposits on diamond can be cycled between the charged and discharged states with little loss in capacity. In cases where lost capacity has been observed, the loss is usually less than 15% and occurs within the first 100 cycles at a given temperature. Potentiodynamic and galvanostatic electrochemical methods along with electrochemical AFM are being used to evaluate the electrochemical performance and the active material morphology, respectively, during cycle testing.

Yale University
New Haven, CT, 06520

Department of Mechanical Engineering

456. Computational and Experimental Study of Laminar Premixed and Diffusion Flames

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Our research has centered on an investigation of the effects of complex chemistry and detailed transport on the structure and extinction of hydrocarbon flames in coflowing axisymmetric configurations. We have pursued both computational and experimental aspects of the research in parallel. The computational work has focused on the application of accurate and efficient numerical methods for the solution of the boundary value problems describing the various reacting systems. Detailed experimental measurements have been performed on axisymmetric coflow flames using two-dimensional imaging techniques. Spontaneous Raman scattering and laser-induced fluorescence are used to measure the temperature, major and minor species profiles. Recent work has focused on the measurement and prediction of NO and CH profiles. Our goal is to obtain a more fundamental understanding of the important fluid dynamic and chemical interactions in these flames so that this information can be used effectively in combustion modeling.

SPECIAL FACILITIES

The special facilities described on the following pages are supported wholly or partly by the Division of Chemical Sciences. They represent an assembly of unique and/or expensive equipment that would be costly to develop elsewhere. They also represent research resources for the general Scientific community, and qualified scientists from laboratories outside the host laboratory are encouraged to make use of them. However, any activity that can be carried out through commercially available laboratories is not appropriate for these DOE-supported facilities.

The process by which an off-site scientist can use a facility is discussed in each facility summary. For the National Synchrotron Light Source, the Stanford Synchrotron Radiation Laboratory, and the Combustion Research Facility, see the section, "User Mode." For the remaining facilities, see "Collaborative Use," which describes the different procedures used at the individual facilities.

Each of the facility summaries also gives the names of individuals to contact for further information, a general description of the facility, and a list of technical data on the primary available instrumentation.

The Office of Basic Energy Sciences also supports other facilities not summarized here. Information concerning these can be obtained by contacting the Director of Materials Sciences, ER-13, U.S. Department of Energy, Germantown, MD 20874.

Budgets for the operation of those facilities specifically funded as Chemical Sciences Facilities (KC-03-01-04) are given below.

Location	Facility	Operating Funds
Brookhaven National Laboratory	National Synchrotron Light Source	$7,429,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	$24,923,000
	Radiochemical Engineering Development Center	$6,705,000
Sandia National Laboratories, California	Combustion Research Facility	$4,361,000
Stanford University	Stanford Synchrotron Radiation Laboratory	$13,947,000

PREMIUM COAL SAMPLE PROGRAM (KC-03-02-01)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne Premium Coal Sample (APCS) program provides premium quality, uniform coal samples for fundamental research in coal science. All samples were prepared and are stored under nitrogen, and are packaged in amber glass vials to ensure sample integrity. Eight coals, ranging in rank from lignite to low volatile bituminous, are included in the program and are available to researchers. To date ~24,000 samples have been shipped to researchers all over the world. A users handbook is available and sample information, including bibliographic information for the ~700 papers published concerning work carried out with APCS samples, is also available via the WWW (http://www.anl.gov/PCS/pcshome.html). Information at this site is continuously updated.

AVAILABILITY

Eight coal samples are available to research personnel at a nominal replacement cost. A limited quantity of large pieces, stored under similar inert conditions, is also available on special request.

PERSON TO CONTACT FOR INFORMATION

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Argonne National Laboratory
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#	Seam	State	C	H	O	S	Ash
1	Upper Freeport	PA	85.5	4.70	7.5	2.32	13.2
2	Wyodak-Anderson	WY	75.0	5.35	18.0	0.63	8.8
3	Illinois #6	IL	77.7	5.00	13.5	4.83	15.5
4	Pittsburgh #8	PA	83.2	5.32	8.8	2.19	9.2
5	Pocahontas #3	VA	91.1	4.44	2.5	0.66	4.8
6	Blind Canyon	UT	80.7	5.76	11.6	0.62	4.7
7	Lewiston-Stockton	WV	82.6	5.25	9.8	0.71	19.8
8	Beulah-Zap	ND	72.9	4.83	20.3	0.80	9.7

ARGONNE PULSE RADIOLYSIS FACILITY (KC-03-01-01)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne Pulse Radiolysis Facility has been and is being used for a wide variety of experiments. Although the accelerator was designed for chemical research, it has been used for a wide variety of experiments. Recent nonchemical experiments include the verification of radiation monitors under pulse conditions, the determination of cavity modes induced in cavities by a short pulse of electrons, the verification of the theory of wakefield acceleration, and the effect of high-energy electrons on material properties. For chemical experiments, the moderate energy of the electron accelerator (maximum energy of 21 MeV transient mode, 14 MeV steady state mode) generates transient species without excessive nuclear activation. The pulse width can be varied from 25 ps to 10 ms. In addition, a 5-ps pulse with the same peak current as the 25-ps pulse has been developed. In liquids, transient concentrations up to 20 mM can be generated with the 25-ps pulse and concentrations more than 10 mM can be generated with the longest pulse. Instrumentation for the measurement of chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. A 2-ps streak camera with custom software is available for fast emission measurements. Very high time resolution measurements that make use of the short pulse capability of the Linac can also be made. All data acquisition equipment is computer interfaced to provide accurate data reduction. Sample preparation and handling facilities are available for solids, and handling facilities are available for solid, liquid, and gaseous samples.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah Phone: (630)252-3471
Chemistry Division FAX: (630)252-4993
Argonne National Laboratory
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Argonne, IL 60439

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BROOKHAVEN PULSE RADIOLYSIS FACILITY (KC-03-01-01)

Chemistry Department
Brookhaven National Laboratory
Upton, NY 11973

The Brookhaven Pulse Radiolysis Facility is centered around a 10 MeV linear accelerator in which the electron pulse is produced by laser light impinging on a photocathode, in synchronization with the radio frequency. Pulse widths can be as short as 5 picoseconds. There are presently two experimental stations. At one station, 30 ps, 20 nanocoulomb pulses are available for optical and DC conductivity experiments with nanosecond resolution. The energy of the electrons permits high-pressure experiments. At the other station, 5 ps, 10 nanocoulomb pulses are available as well as a laser pulse synchronized to the electron pulse. A streak camera and a time-delay optical detection system will permit fluorescence and transient absorption measurements with 5 picosecond time resolution. The pulse radiolysis facility also includes a 2 MeV electron Van de Graaff with pulse lengths of 40 nanoseconds to several microseconds, equipped for UV/VIS/NIR transient absorption measurements. Specialized equipment is available for rapid preradiolysis-pulse mixing and for preirradiation of solutions for stopped-flow kinetics. Data acquisition is controlled by computer and programs are available for kinetic analyses.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

James F. Wishart Phone: (516)344-4327
Chemistry Department FAX: (516)344-5815
Brookhaven National Laboratory
Upton, NY 11973

e-mail: wishart1@bnl.gov

TECHNICAL DATA

10 Mev Facility	Electron Pulse	5 ps, 10 nanocoulomb 30 ps, 20 nanocoulomb
	Pulse Repetition Rate	single shot to 10 Hz
2 Mev Facility	Electron Pulse	40 ns, 20 nanocoulomb
	Pulse Repetition Rate	single shot to 200 Hz
	Optical Absorption Measurements	210 nm to 1.4 micron

NATIONAL SYNCHROTRON LIGHT SOURCE (KC-03-01-04)

Brookhaven National Laboratory
Building 725B, P.O. Box 5000
Upton, NY 11973-5000

The National Synchrotron Light Source (NSLS) is the largest facility in the U.S. dedicated to the production of synchrotron radiation. Funded by the Department of Energy as a user facility, construction on the NSLS began in 1977 with VUV Ring operation commencing in 1982 and X-Ray Ring operation in 1984. Since then, the facility has undergone a major four-year upgrade and is continually improved to take advantage of the latest technology in storage rings, beamline optics, and insertion devices.

The NSLS operates two electron storage rings producing high brightness synchrotron radiation in the infrared, visible, ultraviolet, and X-ray regions of the electromagnetic spectrum. Insertion devices installed in the straight sections of the rings provide radiation that is anywhere from one to several orders of magnitude brighter than the radiation from bending magnets. The VUV Ring operates at 800 MeV with a critical energy of 486 eV. It has 17 beam ports split into 25 experimental stations, or beamlines, and also supports two insertion devices. The X-Ray Ring operates at 2.5 GeV, 300 mA, with a critical energy of about 5 keV. It has a total of 30 beam ports split into 60 beamlines and currently supports 5 insertion devices: two undulators, a superconducting wiggler, and two hybrid wigglers. There are also a number of beamlines devoted to machine diagnostics and R&D. The NSLS facility has user laboratories and a wide range of research equipment for basic and applied studies in condensed matter, surface science, photochemistry and photophysics, lithography, crystallography, small-angle scattering, metallurgy, X-ray microscopy, topography, etc. Detailed information about beamline research programs, experimental apparatus, and optical configurations is available from the NSLS User Administration Office.

USER MODES

Approximately 2,300 scientists from more than 360 institutions came to the NSLS to perform research during 1996. The NSLS is a national user facility available without charge to university, industrial, national laboratory, and government users. In addition, a program is available to assist faculty/student research groups who have limited grant support and wish to defray travel expenses to the NSLS. Proprietary work can be done on a full cost recovery basis with the option to retain title to inventions resulting from research at the NSLS.

There are several ways of using NSLS experimental facilities. A large fraction of the beamlines have been designed and constructed by Participating Research Teams (PRTs). PRTs comprise one or more research teams from industry, universities, and other laboratories with large, long-range programs that have been approved by the NSLS Scientific Advisory Committee (SAC). The PRT members are given priority for up to 75% of their beamline's operational time, and their programs are reviewed by the SAC every three years. Peer-reviewed General User proposals are scheduled both on PRT beamlines and on beamlines built by the NSLS for the general community. The NSLS facility operates throughout the year, with beam time scheduled in four-month cycles. Deadlines for General User proposals are September 30, January 31, and May 31. Information about submitting research proposals, becoming a PRT, or applying for financial assistance may be obtained from the NSLS User Administration Office.

PERSON TO CONTACT FOR INFORMATION

Eva Z. Rothman, Phone: (516) 344-7114
User Administrator FAX: (516) 344-7206
NSLS Bldg. 725B
Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973-5000

e-mail: ezr@bnl.gov
See also World Wide Web at: http://www.nsls.bnl.gov/

NSLS TECHNICAL DATA*

STORAGE RINGS	**KEY FEATURES**
VUV	17 ports; E_c = 25.3 Å; 0.808 GeV electron energy
X-Ray	30 ports; E_c = 2.48 Å; 2.584 GeV electron energy

Research Area	**Wavelength Range (Å)**	**Energy Range (eV)**	**Number of Beamlines**
Absorption Spectroscopy	0.35 to 2480	5 to 35,000	24
Circular Dichroism	10.3 - 5904	2.1 - 1,200	2
High Pressure Physics	1 - 10,000 µm	0.124 - 1,240 meV	2
	WB[†]; 0.12-1.24	WB;10,000-100,000	2
High Q-Resolution Scattering	WB; 0.12 - 6.20	WB; 2,000 - 100,000	15
Imaging:			
Medical	WB; 0.12 - 1.24	WB; 10,000 - 100,000	2
Tomography	WB; 0.12 - 3.10	WB; 4,000 - 100,000	3
X-Ray Microprobe	WB; 0.12 - 3.10	WB; 4,000 - 100,000	3
X-Ray Microscopy/Holography	10 - 80	155 - 1,240	1
X-Ray Topography	WB; 0.41 - 3.10	WB; 4,000 - 30,000	2
Infrared Spectroscopy	1 - 10,000 µm	0.124 - 1,240 meV	2
Lithography	124 - 4133	3 - 100	1
Nuclear Physics	---	80 - 400 MeV	1
Photoemission Spectroscopy	2.10 - 6200	2 - 5,900	19
Photoionization	2.10 - 4133	3 - 5,900	3
Protein Crystallography	WB; 0.41 - 3.10	WB; 4,000 - 30,000	6
Radiometry	WB; 8.27 - 248	WB; 50 - 1,500	1
Small Angle Scattering:			
Biology	0.66 - 5.90	2,100 - 18,800	2
Materials Science	0.36 - 6.20	2,000 - 34,000	4
Small Molecule Crystallography:			
Powder	WB; 0.12 - 3.10	WB; 4,000 - 100,000	4
Single Crystal	0.21 - 6.20	2,000 - 59,400	7
Standing Waves	WB; 0.62 - 6.89	WB; 1,800 - 20,000	2
Surface Scattering/X-Ray Reflectivity	WB; 0.48 - 6.20	WB; 2,000 - 26,000	10
Time Resolved Fluorescence	1393 - 5904	2.1 - 8.9	1
UV Reflectometry	WB; 8.27 - 6200	WB; 2 - 1,500	2
X-Ray Emission Spectroscopy	2.48 - 50	248 - 5,000	2

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*From 1993 NSLS Users Manual - BNL 48724

[†] WB = White Beam

JAMES R. MACDONALD LABORATORY (KC-03-01-03)

Department of Physics
Kansas State University
Manhattan, KS 66506

The laboratory operates a 7-MV tandem accelerator, a 9-MV superconducting linear accelerator (LINAC) and a cryogenic electron beam ion source (CRYEBIS) for the study of ion-atom collisions with highly charged ions. The tandem can operate as a stand-alone accelerator with six dedicated beam lines. The LINAC is operated as a booster accelerator to the tandem. The tandem-LINAC combination has four beam lines available. The CRYEBIS is a stand-alone facility for studying collisions with bare ions at low velocity. An ion-ion collision facility using the CYREBIS and a new ECR ion source is also available. The laboratory has a variety of experimental apparatus for atomic physics research. These include recoil ion sources, Auger electron spectrometers, X-ray spectrometers, and a 45-inch-diameter scattering chamber. The laboratory is available to users who require the unique facilities of the laboratory for atomic collision experiments.

COLLABORATIVE USE

Interested users should obtain “Request for Proposal” forms for submitting proposals. The completed Request for Proposal forms should be submitted to the JRML Program Advisory Committee in care of the Laboratory Director by regular mail or by FAX.

PERSON TO CONTACT FOR INFORMATION

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TECHNICAL DATA

EN Tandem

Beams	Most elements
Terminal voltages	0.3 to 7MV
Output currents	Up to 10 μA, depending on the ion species and the charge state
Repetition rate	3-ns pulses at rates up to 4 MHz, or 12 MHz operation
Magnet limitations	ME/q2≤150

LINAC Booster

Acceleration field	9 MV
Resonators	Split-ring,superconducting Nb, operated at 97 MHz
Beam repetition rate	12 MHz with 75% of beam bunched
Mass limitation	M <100μ; due to injection energy

CRYEBIS

Beams	Up to bare ions of C, N, O, F, Ne, Al, and Ar. Up to Kr^{36+} and Xe^{47+}, Fe beams under development
Beam energy	A few to 200 keV/q<
Output currents	05 to 108 parts/s

NOTRE DAME PULSE RADIOLYSIS FACILITY (KC-03-01-01)

Notre Dame Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556-0579

The Notre Dame Pulse Radiolysis Facility is based on a 2-100 ns electron pulse from an 8-MeV linear accelerator. It is fully instrumented for computerized acquisition of optical and conductivity information on radiation chemical intermediates having lifetimes of 5 ns and longer. An excimer laser/dye laser combination is available for use at the pulse radiolysis facility for double-pulse experiments involving photolysis of radiolytic transients. Energies of ~400 mJ at 308 nm and ~50 mJ at various near-UV and visible wavelengths are available. For typical absorption studies, where one produces 10^{-5} M of intermediates, spectral and kinetic information can be obtained on species having extinction coefficients in excess of 100 $M^{-1}cm^{-1}$. Conductometric methods in aqueous solution cover the pH range of 3 to 11. Data are recorded digitally and stored in magnetically readable form for rapid off-line examination of spectral and kinetic details.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

PERSON TO CONTACT FOR INFORMATION

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Notre Dame, IN 46556

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TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	Workstation (DOS/Intel 486)
Pulse width	2-100 ns
Time resolution (RC)	2 ns
Pulse current	Up to 4 A
Repetition frequency	0.2 s^{-1}
Optical absorption measurements	
Spectral region	210 to 750 nm
Sensitivity	±0.00002 absorbance
Conductivity	
pH range	3 to 11
Sensitivity	±5 mhos/cm

HIGH FLUX ISOTOPE REACTOR (KC-03-01-04)

Research Reactors Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Since it began full-power operations in 1966, the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) has been one of the world's most powerful research reactors. A primary purpose of the HFIR is the production of ^{252}Cf and other transuranium isotopes for research, industrial, and medical applications. These materials are produced in the flux trap in the center of the HFIR fuel element where a working thermal-neutron flux of 2.5 x 10^{15} neutrons/(cm^{2}s) is available to irradiate the target material. Additional irradiation facilities are also provided in the beryllium reflector.

Beyond its contributions to isotope production, the HFIR also provides for a variety of irradiation tests and experiments that benefit from the exceptionally high neutron flux available. In the fuel element flux trap, a hydraulic rabbit tube provides access to the high thermal-neutron flux in the reactor for short-term irradiations, and other positions are ideal for fast-neutron irradiation-damage studies. A modification of the flux trap experimental facilities in 1986 has provided two locations in the maximum flux region that can accommodate instrumental capsules and engineering loops. The beryllium reflector contains numerous experimental facilities with thermal-neutron fluxes up to 1.0 x 10^{15} neutrons/(cm^{2}s). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by ORNL or other qualified users.

Another major use of the HFIR is for neutron-scattering experiments to reveal the structure and dynamics of a very wide range of materials. The reactor has four horizontal beam tubes with inner diameters of 10 cm that extend outward from the reactor core at the midplane of the reactor. Beam tube HB-2 extends radially from the reactor centerline, and beam tube HB-3, which extends tangentially from the core, is offset 34 cm from the reactor center. A third tube is aligned on a tangential line 39 cm from the reactor centerline with both ends extending outward from the reactor to allow for the installation of two individual facilities. The two ends of this tube are designated HB-1 and HB-4. A scattering block of beryllium has been placed at the centerline between beam tubes HB-1 and HB-4, effectively making them into two tangential tubes.

The neutron-scattering instruments installed on the horizontal beam tubes are used in fundamental studies of materials of interest to solid-state physicists, chemists, biologists, polymer scientists, metallurgists, and colloid scientists. These instruments are open to use by university and industrial researchers on the basis of scientific merit, and about 150 to 200 researchers use the experiment facilities at the HFIR each year.

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RADIOCHEMICAL ENGINEERING DEVELOPMENT CENTER (KC-03-01-04)

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The objective of the base program at the Radiochemical Engineering Development Center (REDC) is to supply transplutonium elements for use in research. The REDC is the distribution center for the DOE/ER heavy-element research program. Target rods are fabricated at REDC, irradiated in the High Flux Isotope Reactor (HFIR), and processed at REDC for separation, recovery, and purification of the heavy actinides up through ^{257}Fm. Since their construction in the mid-1960s, REDC and HFIR have provided the western world's supply of elements beyond curium (atomic number 96), either directly or by furnishing starting materials for further nuclear-synthesis reactions. The transuranium element isotopes produced in the REDC are used nationally and internationally to study the basic physics and chemistry of the transuranium elements. They are also being used in research and development, programs relating to environmental effects, biological effects, and waste isolation.

Similar radiochemical separations projects can be and are often carried out in the REDC for other DOE programs. Currently, transplutonium elements are being recovered from targets irradiated at Savannah River for Defense Programs. Also, ^{252}Cf portable neutron sources are prepared for a variety of radiography, activation analysis, and cancer treatment applications. A new Californium Users Facility has been established at the REDC that will allow users access to multimilligram quantities of ^{252}Cf yielding neutron fluxes of ~10^{11}n/s. REDC also conducts studies for waste management as directed. REDC facility management is under the direction of the Assistant Secretary for Nuclear Energy. Base funding is provided by the Office of Energy Research and is supplemented by other agencies when their projects are carried out.

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http://redc.ct.ornl.gov/default.htm

COMBUSTION RESEARCH FACILITY (KC-03-01-04)

Sandia National Laboratories, California
Livermore, CA 94551-0969

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flame processes, research in fundamental chemistry in combustion, as well as analytical studies of reacting turbulent flows. (These programs are individually described elsewhere in this publication.) The active program of visitors to the facility, including senior researchers, graduate students, and postdoctoral researchers supported through the Chemical Sciences Division, is described below.

Facility support, through the Chemical Sciences Division, includes operation and continued development of the CRF central lasers. Several are available. The tunable dye laser (Diana) is used by Sandia staff and visiting scientists for single-shot temperature, density, and species concentration measurements, and for two- and three-dimensional imaging of turbulent flames. A multipurpose laser system (Sirius) consists of a frequency-doubled Nd:YAG laser and a pulse-amplified ring dye laser. When the Nd:YAG laser is operated in single-axial mode in combination with the ring dye laser, the spectral resolution for CARS and other nonlinear spectroscopy experiments (performed in any of the CRF laboratories via the beam distribution system) is as small as a few thousandths of a wave number. Sirius is used also for CARS measurements in flames with large luminous backgrounds (e.g., heavily sooting flames laden with coal particles). A third central laser (Dyeblaster) consists of a frequency-doubled Nd:YAG laser and is used routinely to pump dye lasers in user laboratories throughout the CRF.

In addition, DOE/Energy Efficiency and Renewable Energy sponsors programs at the CRF in combustion technologies and materials processing by design, DOE/Fossil supports programs in coal combustion and related diagnostics development, DOE/BES Engineering Science supports advanced analysis of turbulent flows and DOE/BES Materials Sciences support programs in combustion-related materials research.

Complete facilities for resident and visiting researchers are available: offices for 60 staff, a meeting room accommodating 250 people, a laboratory building housing 24 independent experiments, special facility laser systems, a network of computer workstations, and access to supercomputers.

In specific instances, proprietary research can be carried out at the CRF. For this type of work, the DOE will be reimbursed on a full cost recovery basis for the use of all CRF resources. Details of a DOE Class Waiver for patent rights are available.

USER MODE

Qualified scientists are encouraged to take advantage of the specialized resources available at the CRF. Prospective participants should submit a brief proposal to the laboratory director. Criteria for selection include technical merit, the extent to which CRF facilities are used, overlap with DOE program objectives, and the availability of specific equipment.

In general, the CRF will host visiting scientists to use the special-purpose lasers, work with resident staff, make use of computers and codes, and set up experiments. Visitors pay for their own salary, travel, housing, meals, and other local expenses. Facility lasers, apparatus, technicians, instrumentation, computers, and support-group services are provided without charge for research that is not proprietary. Research results from nonproprietary projects are expected to be published and disseminated.

For scientists with active government contracts, support for CRF research often can be arranged on an informal basis with the contract manager. There are opportunities for faculty, postdoctoral scientists, and graduate students to obtain Sandia support for combustion-related research at CRF. Potential users may access the CRF Web page at http://www.ca.sandia.gov/CRF/.

TECHNICAL DATA

Equipment	Key features
Flashlamp-pumped, tunable dye laser high average power: 2-ms pulse length 5 J/Pulse, 5 Hz Tunable 440 to 620 nm 0.3-nm bandwidth	Long pulse, high energy,
Multipurpose pulsed laser system YAG lasers:	High peak power, high resolution double and tunable dye Single mode capability 10 to 500 mJ/pulse 10 to 29 ns/pulse
Low-pressure flames	10 torr to 1 atm Mass spectrometer sampling probe LIF detection of radicals
Atmospheric flames	Diffusion and premixed flames
Vertical turbulent diffusion flame	Open-circuit, induced-draft with tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow
Combustion bomb	Simulated constant-volume engine combustion
Internal combustion research devices	Highly repeatable environment for homogenous charge, diesel combustion, and pulse combustion studies
Experimental diagnostics research	Nonlinear optical spectroscopy laboratories
Turbulent flame structure laboratory	Rayleigh, Mie, and Raman 2-D imaging
Burner Engineering Research Laboratory	Firing rates from 1 kW to 3 MW, capabilities for air/fuel preheat, fuel gas recirculation, and humidification. Continuous monitoring of flue gas O_2, CH_4, CO_2, CO, NO, and NO_2. Optical diagnostics for particle and species concentrations and temperature.

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STANFORD SYNCHROTRON RADIATION LABORATORY (KC-03-01-04)

Stanford Synchrotron Radiation Laboratory
MS 69, P.O. Box 4349
Stanford, CA 94309-0210

The Stanford Synchrotron Radiation Laboratory (SSRL) is a national user facility which provides synchrotron radiation, a name given to X-rays or light produced electrons circulating in a storage ring at nearly the speed of light. These extremely bright X-rays can be used to investigate objects of atomic and molecular size, allowing a wide variety of research in basic and applied studies on the structure of matter. The facility, which provides 26 experimental stations on 22 beam ports as well as ancillary equipment, is used by researchers from industry, government laboratories, and universities in many areas, including the fields of biology, chemistry, molecular environmental science, geology, materials science, electrical engineering, chemical engineering, physics, astronomy, and medicine.

Vacuum Ultraviolet Studies (VUV)

Research utilizing VUV and soft X-ray radiation includes: (a) the determination of electronic states in metals, semiconductors, magnetic systems, superconductors and other materials; (b) properties of ultra-thin layers and a small clusters; (c) kinetic processes in a variety of materials; and (d) lithography and dynamic process of chemisorbed gases.

Structural Molecular Biology

X-rays are used for research in structural molecular biology including: (a) protein structures and functions through diffraction studies in the crystalline state; (b) structure and function of active sites in metalloproteins and metalloenzymes through X-ray absorption spectroscopy studies; (c) protein folding and structural changes in solution, including time-resolved, by small angle X-ray scattering. Specialized facilities for all three disciplines are available. A new high flux wiggler beam line has been dedicated for structural molecular biology research. One of the three stations is being routinely scheduled for users (crystallography), the second will soon complete commissioning (EXAFS), and the third (crystallography) will begin commissioning late in 1997.

Molecular Environmental Science

Synchrotron radiation methods, particularly X-ray absorption fine structure (XAFS) spectroscopy, have become crucial problem-solving tools in molecular environmental science (MES) because of their unique capabilities for characterizing the speciation of dilute metal ion contaminants in heterogeneous natural samples under in situ conditions and the unique information they provide on chemical processes in complex environmental systems. Recent MES research at SSRL includes (a) characterization of actinide contamination and transport in soils at DOE sites, (b) speciation of high-level radioactive waste in tanks and waste forms at DOE processing facilities including Hanford, Wash., (c) characterization of heavy metal contaminants and contaminant transport in soils and aquifers at industrial and mining sites in the United States, (d) phytoremediation, the use of plants to remediate metal ion contamination in soils and surface waters, and (e) investigations of fundamental molecular-scale processes at solid-liquid-gas interfaces that control the fate and transport of contaminants in soils and natural waters. SSRL provides technical support for MES users and is constructing a high-flux wiggler beamline (BL 11), that will be devoted to MES research. This new facility will be optimized for XAFS studies of dilute samples, and it will be equipped with a high throughput X-ray detector and a special experimental enclosure for safe, routine XAFS studies of radioactive and toxic materials.

X-Ray Studies of Condensed Matter

Research utilizing X rays for studies of condensed matter include the following areas: (a) structures of amorphous materials, catalysts, and environmentally interesting systems; (b) structures of and phase transitions in surfaces and thin surface layers; (c) kinetics of structural changes in materials; (d) chemical reactivities in the gas phase; (e) nuclear resonant scattering; and (f) fundamental X-ray scattering and absorption physics. A new beam line for environmentally-relevant studies is in the initial phases of construction.

Synchrotron Radiation Sources

Considerable research is also underway in the development of accelerators and devices inserted into the accelerators to produce more intense or brighter synchrotron radiation.

USER MODE

SSRL is currently used by approximately 1,100 scientists from over 169 U.S. and foreign-based institutions. Scientists gain access to the facility through a refereed proposal system. Proposals are due May 1 and October 1 each year. The booklet "User Guide" available from SSRL, contains information pertinent to proposal submittal. To date, 2,494 proposals for research have been received.

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See also World Wide Web at:
http://www-ssrl.slac.stanford.edu/

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS

SSRL presently has 26 experimental stations on 22 beam ports with 4 more stations under construction/commissioning.

	Horizontal Angular Acceptance (mrad)	Mirror Cut Off (keV)	Monochromator	Energy Range(keV)	Resolution $\Delta E/E$	Approximate Spot Size Hgt x Wdth (mm)	Instrumentation/ Special Capabilities
				INSERTION DEVICE STATIONS			
WIGGLER LINES - X-RAY							
End Stations							
4-2 (4 periods)							
Focused	2.0	10.2	Double Crystal	2400-10200	~5 x 10^{-4}	0.5 x 4.0	
Unfocused	1.0		Double Crystal	2400-45000	~10^{-4}	2.0 x 20.0	
4-2 SAXS	0.5-2.0	10.2	Double Crystal	2400-10200	~5 x 10^{-4}	0.5 x 4.0	SAXS Camera
	0.5-2.0	10.2	Multilayers	7000-10200	3 x 10^{-2}	0.5 x 4.0	SAXS Camera
6-2 (27 periods)							
Focused	2.3	22	Double Crystal	2050-21000	~5 x 10^{-4}	0.5 x 4.0	
Unfocused	1.0		Double Crystal	2050-32000	~10^{-4}	2.0 x 20.0	
7-2 (4 periods)							6-circle Diffractometer
Focused	2.0	10.2	Double Crystal	2400-10200	~5 x 10^{-4}	1.0 x 4.0	
Unfocused	1.0		Double Crystal	2400-45000	~10^{-4}	2.0 x 20.0	
9-2 (8 periods)				*Under Commissioning*			
Focused	2.0	23	Double Crystal	4000-23000			
White Light Laue	0.5			4000-45000			
10-2 (15 periods)							
Focused	2.3	22	Double Crystal	2400-21000	~5 x 10^{-4}	0.5 x 4.0	
Unfocused	1.0		Double Crystal	2400-40000	~10^{-4}	2.0 x 20.0	
10-2 Diffractometer							6-circle Diffractometer
11-2 (13 periods)				*Under Construction*			
Focused	~2	23	Double Crystal	4500-23000			
Unfocused	~1			4500-45000			

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS (CONT.)

	Horizontal Angular Acceptance (mrad)	Mirror Cut Off (keV)	Monochromator	Energy Range(keV)	Resolution $\Delta E/E$	Approximate Spot Size Hgt x Wdth (mm)	Instrumentation/ SpecialCapabilities
INSERTION DEVICE STATIONS Side Stations							
4-1	1.0		Double Crystal	2400-35000	~5 x 10^{-4}	2.0 x 20.0	
4-3							
Focused	1.0	Variable	Double Crystal	2400-15000	~10^{-4}	0.15 x 20.0	
Unfocused	1.0		Double Crystal	2400-35000	~10^{-4}	2.0 x 20.0	
7-1	1.0		Curved Crystal	6000-13000	~8 x 10^{-4}	0.6 x 3.0	30 cm Mar Detector
7-3	1.0		Double Crystal	2400-35000	~10^{-4}	2.0 x 20.0	
9-1	3.0	16	Curved Crystal	11500-13500	~5 x 10^{-4}	0.2 x 1.0	30 cm Mar Detector
9-3						*Under Commissioning*	
Focused	2.5	23	Double Crystal	4600-23000			
Unfocused	0.7		Double Crystal	4600-40000			
VUV/SOFT X-RAY STATIONS							
5-2 multi-undulator	1.5		4 Gratings	10-1000	1 x 10^{-3}	1 mm^2	Circular Polarization
5-3 multi-undulator	1.5		4 Gratings	20-250	1.0-2.0 x 10^{-3}	$\leq$ 1 mm^2	
5-4		NIM			*Under Construction*		
10-1 wiggler side station	2.0		6m SGM	250-1200	~2 x 10^{-4}	$\leq$ 0.1 mm^2	
			BENDING MAGNET STATIONS				
X-RAY							
1-4	2.0		Curved Crystal	6700-10800	4.0 x 10^{-3}	0.25 x 1.0	SAXS Camera
1-5	1.0		Double Crystal	5500-30000	~2 x 10^{-4}	2.0 x 17.0	CAD-4
1-5 ES2	1.0	14.5	Double Crystal	5500-14500	~2 x 10^{-4}	$\leq$ 1 mm^2	Fuji Imaging Plate
2-1 (Focused)	4.8	8.9	Double Crystal	2400-8900	~5 x 10^{-4}	2.0 x 6.0	
2-2	1.0		None	3200-40000		4.0 x 22.0	
2-3	1.0		Double Crystal	2400-30000	~5 x 10^{-4}	2.0 x 20.0	
VUV/SOFT X-RAY							
1-1	2.0		Grasshopper	24-1000	$\Delta\lambda$ = .05-2Å	1.0 x 1.0	*Commissioning*
1-2	4.0		6m TGM	8-180	~1 x 10^{-3}	0.1 x 0.5	
3-3	8-10	4.5	UHV Double Crystal (Jumbo)	800-4500	~5 x 10^{-4}	1.5 x 2.5	
3-4	0.6		Multilayer	0-3000	White or $\Delta\lambda/\lambda$ = .6%	2.0 x 8.0	Vacuum Diffractometer Litho. Expo. Station
8-1	12		6m TGM	8-180	~1 x 10^{-3}	$\leq$ 0.1 mm^2	
8-2	5.0		6m SGM	150-1000	~1 x 10^{-4}	$\leq$ 0.1 mm^2	Circular Polarization

FY 1997 EQUIPMENT FUNDS

Outlay funds of the Office of Basic Energy Sciences are divided among operating, equipment, and construction funds. Equipment funds are provided primarily to DOE laboratories. (Operating funds provided to other projects are used for all costs, including purchase of necessary equipment.) FY 1997 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	**Equipment Funds**
Ames Laboratory	$400,000*
Argonne National Laboratory	$2,820,000*
Brookhaven National Laboratory	$1,630,000
Idaho National Engineering Laboratory	$35,000
E.O. Lawrence Berkeley National Laboratory	$1,280,000
Lawrence Livermore National Laboratory	$120,000
Los Alamos National Laboratory	$105,000
National Renewable Energy Laboratory	$225,000
Notre Dame Radiation Laboratory	$350,000
Oak Ridge National Laboratory	$1,410,000*
Pacific Northwest National Laboratory	$815,000
Sandia National Laboratories California	$870,000
Stanford Synchrotron Radiation Laboratory	$1,045,000

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*In addition to the amounts shown, funds for General Purpose Equipment are provided to these laboratories. The amounts are $150,000 for Ames Laboratory, $2,000,000 for Argonne National Laboratory, and $4,300,000 for Oak Ridge National Laboratory.

DISCIPLINES INDEX

The numbered references below refer to abstract numbers, not page numbers.

TECHNOLOGIES INDEX

The numbered references below refer to abstract numbers, not page numbers.

INSTITUTION INDEX

This index lists the institutions responsible for the projects cited in this publication. The references below indicated abstracts numbers, not page numbers.

INVESTIGATOR INDEX

Investigators’ surnames are indexed in the form appearing in the citation. For projects with multiple investigators, each name is indexed. The references below indicate abstract numbers, not page numbers.

U.S. Department of Energy
Office of Basic Energy Sciences
Division of Chemical Sciences

1. Which of these best describes you?

   ☐ Current PI funded by BES CS ☐ Prospective PI in BES CS ☐ Congressional Staff
   ☐ DOE Technology Office Staff ☐ BES Program Staff ☐ Other (please specify) ____________________

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