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Angular Momentum Partitioning in the Dissociation of Diatomic Molecules

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Abstract. We discuss recent experiments that study the transfer of angular momentum from a projectile to the residual target in collisions between the simple diatomic molecules H_2 and N_2 and spin-polarized electrons or circularly-polarized photons. We observe the fluorescence of both the atomic fragments and excited molecular states, and measure the circular polarization fraction of this light, P_3. The incident electron energies range from 10 to 100 eV; the incident photon energies from 33 to 38 eV.

Keywords: angular momentum; spin polarization; circular polarization; molecular dissociation
PACS: 33.15.Vb; 33.80.Gj; 34.30.+h; 34.80.Ht; 34.80.Nz

INTRODUCTION

An important problem in atomic collisions is the distribution, or partitioning, of angular momentum in an excited or ionized atomic target produced by photon or electron bombardment [1]. A complete picture of the angular momentum dynamics must include the ionized or scattered electrons as well [2]. An interesting extension of this problem involves molecular targets, which have the additional complication of rotational angular momentum. One experimental approach to the general problem of angular momentum dynamics in such collisions is to use incident photon or electron beams that are spin polarized, and to detect the polarization of the fluorescence emitted by the target or its fragments following the collision. The advent of third-generation light sources and GaAs polarized electron sources has made such experiments much easier. Earlier experiments had used unpolarized electrons and detected the polarization (both circular and linear) of emitted light in coincidence with the scattered electron [3,4], or used linearly-polarized incident light and detected linear polarization of the subsequent molecular or atomic fluorescence[5-7]. We report here the results of several recent experiments done by our group and others which have begun to elucidate how angular momentum, inserted into the collision complex by the use of either polarized electrons or photons, is distributed in a collision with a simple

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diatomic molecule or molecular ion. We will concentrate on the measurement of P_3, the circular polarization fraction (or Stokes parameter), as a direct measure of the angular momentum transferred along a specific axis to the target by the incident polarized particle.

EXPERIMENTS WITH ELECTRONS

A particularly simple example of angular momentum transfer in the electron-impact excitation of atoms is one in which a longitudinally-polarized electron excites, via exchange, an upper state of the atom which subsequently emits a photon that is circularly polarized along the axis of the incident electron. Ultimately, for an atom to emit circularly-polarized light, its *orbital* angular momentum must have a magnetic dipole along the direction of photon emission. The incident electron spin provides this through the atom's internal spin-orbit coupling. An example of this occurs in the exchange excitation of the 1s3p 3^3P state of He. For 100% incident electron spin polarization, the emitted photon in the 2^3S-3^3P 389 nm transition has a P_3 of 50% near threshold [8]. Similar angular momentum transfer has been observed in a variety of atomic systems [9,10].

Problems arise with molecules, however. The Münster group bombarded N_2 in its singlet closed-shell ground state with beams of polarized electrons, and measured P_3 of the resultant $C^3\Pi_u$ – $B^3\Pi_g$ 337 nm fluorescence [11]. The excitation of a triplet state with light targets guarantees that exchange excitation, and thus angular momentum transfer, has occurred. Within their statistical uncertainty of 2×10^{-3}, however, they found P_3 to be nil at all the incident electron energies they investigated (see Figure 1).

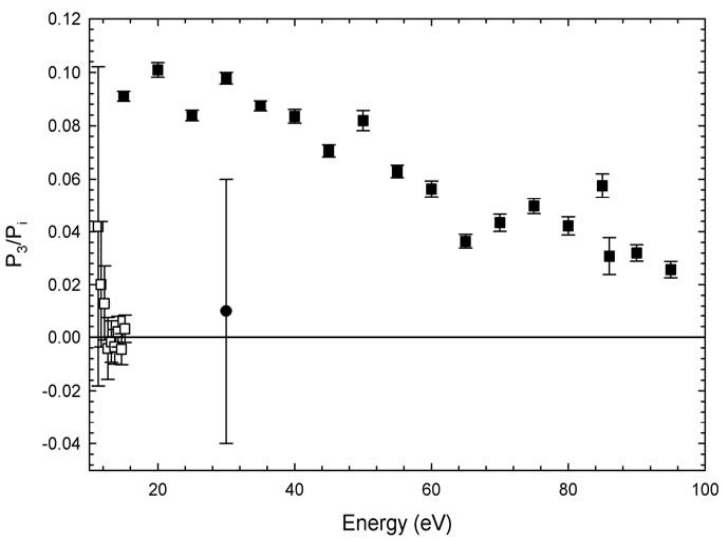

FIGURE 1. Circular polarization fraction P_3 normalized to incident electron polarization *vs.* incident electron energy. Open squares: data of ref. 11; solid circle: measurement with N_2 target and 388 nm filter (see text); solid squares: data of ref. 12 taken with a 600 ± 5nm filter.

A similar, more crude measurement was recently made in our lab, in which we used an interference filter with a bandpass of 388±5 nm. This filter isolates light from the $A^3\Sigma_u^+ - X^1\Sigma_g^+$, $C^3\Pi_u - B^3\Pi_g$, $A^3\Sigma_u^+ - X^1\Sigma_g^+$, $C^3\Pi_u - B^3\Pi_g$, and $C'^3\Pi_u - B^3\Pi_g$ transitions in N_2, and the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ transitions in N_2^+. Since the N_2 transitions involve triplet states, and the N_2^+ excited state is a doublet, exchange collisions dominate the production of the light we observe. Nonetheless, as with the Münster data, we find P_3 to be consistent with zero (Fig. 1).

We can start to understand these data by remembering the relevant time scales for molecular processes. The impact excitation occurs in times of the order of 10^{-16}s, whereas N_2 rotational motion occurs on a scale of ~10^{-13}s, with fluorescence lifetimes being more typically 10^{-8}s. The spin-orbit coupling time for excited states of N_2, i.e., the time required for the electron to "spin-up" the orbital angular momentum of the excited state, is ~10^{-13}s. Thus while the N_2 target develops an orbital orientation over the course of several rotational periods, its internuclear axis subsequently rotates thousands of times before it decays, causing its orbital orientation to be essentially randomized in space. Thus P_3 is nil.

One can, however, expect that an exchange collision followed by a prompt dissociation of the molecule would result in atomic fragments with a non-zero expectation value of spin along the incoming electron axis. The atomic "memory" of this spin direction would not be lost. Thus it should be possible to investigate angular momentum transfer to the molecular fragments by investigating the circular polarization of atomic fluorescence. Using this idea, our group and the Perth group

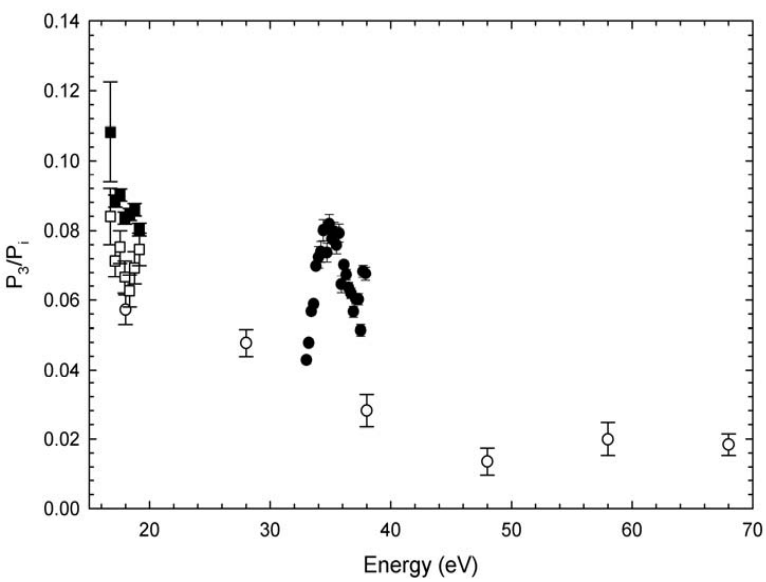

FIGURE 2. P_3 of Hα (656 nm) atomic fluorescence, normalized to the incident photon or electron polarization P_i, *vs.* incident electron or photon energy. Photon results are also divided by two to take into account the different angular momentum deposited by electrons vs. photons. Solid and open squares: electron data of ref. 13 with different incident electron polarizations; open circles: electron data of ref. 12; solid circles: photon data of this work.

have measured P_3 of H(n=3), Hα (656 nm) fluorescence resulting from electron-impact dissociation of H_2 [12,13]. These data are shown in Figure 2. Not surprisingly, significant polarizations near the n=3 production threshold of ~17 eV are apparent in these data, with a slow drop off as the electron energy increases.

It is instructive to compare these polarization values with those resulting from the direct impact excitation of atoms by polarized electrons. To do this, we define a "spin transfer efficiency," *T*, equal to the initial spin polarization of the excited system divided by the electron spin polarization, P_e. Thus, if we excited a pure molecular triplet state by exchange, $T = 2/3$ [1]. Following dissociation, we assume that the atomic 3s, 3p, and 3d states all have equal spin polarization *T'*, and that this polarization is completely coupled to the orbital angular momentum in the case of the 3p and 3d states, while we ignore hyperfine depolarization [12]. Taking into account the branching ratio between Hα and Lyα radiation (see Figure 3), assuming that light from the 3s state is unpolarized, and using published data for the relative production cross sections for 3s, 3p, and 3d states as the result of electron impact dissociation of H_2 [14], we can infer a threshold value of $T' = 0.37$. Assuming that all three n=3 initial populations are equal, $T' = 0.47$. These values are surprisingly comparable to those for direct excitation of, e.g., alkali atoms, from Na ($T = 0.25$) to Cs ($T = 0.45$) [15].

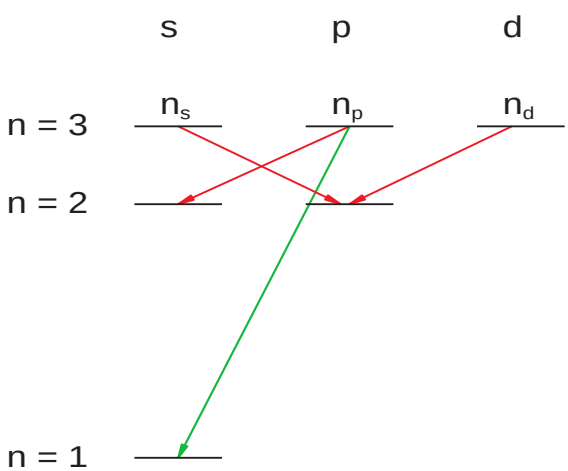

FIGURE 3. Grotrian diagram of the first three energy levels of the H atom. The circular polarization we observe is due to transitions from the 3p and 3d states; photons from the 3s state are unpolarized. In the calculations of T', initial populations of the n=3 states are taken from ref. 14. Only ~1/7th of the 3p states decay to the 2s state; the rest decay via Lyα emission.

EXPERIMENTS WITH PHOTONS

We can learn more about how angular momentum is distributed in a dissociating molecular complex by using circularly-polarized incident photons to provide the dissociation energy. This method has the advantage that a full ħ of angular momentum is dumped into the target, as opposed to ħ/2 for electrons. Moreover, spin-orbit coupling is not needed to convert spin to orbital orientation; the coupling between the photon and the orbital angular momentum of the molecule is direct. In a recent experiment done at the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory, we have measured Hα P_3 values when light with energy between 33 and 38 eV was used to dissociate H_2. The linearly-polarized synchrotron radiation was turned into circularly-polarized light by passage through a four-reflection quarter-wave retarder [2]. These data are shown in Figure 2. They have been divided by two to account for the larger amount of angular momentum carried by the photons, and adjusted to correspond to photon emission directly along the incident photon axis. Interestingly, the P_3 values produced by the incident photons are comparable to the results for electron bombardment, even though the angular momentum coupling is much more efficient. It is important to keep in mind, however, that the internal molecular spin-orbit coupling, while serving to *produce* orbital orientation in the case of electron bombardment, acts only to reduce it (by spinning up the electrons at the expense of orbital angular momentum) in the case of photon bombardment.

POLARIZED MOLECULAR FLUORESCENCE

Upon closer examination, the simple model of rotational destruction of polarization for excited molecular fluorescence fails. We used a broad (600±5 nm) interference filter to monitor fluorescence in the Fulcher band of H_2 excited by polarized electron impact. These results are shown in Figure 1 together with the N_2 and N_2^+ data. Our

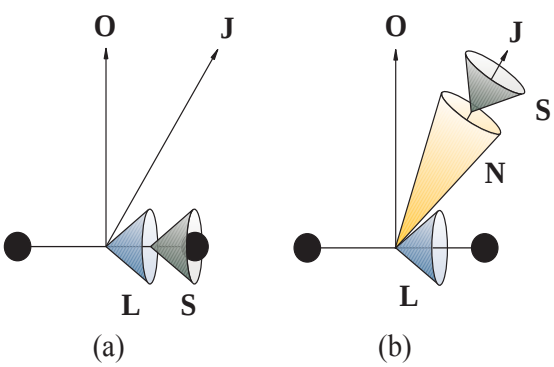

FIGURE 4. Hund's cases a) and b). The nuclear rotational angular momentum is **O**; total molecular angular momentum = **J**. In the case of H_2, **L** + **O** = **N**.

600 nm filter passes light which is due to a variety of H_2 transitions; we estimate that approximately 94% of the transmitted intensity is due to emission by triplet states which can, in principle, produce circularly-polarized light. Naively, one might expect that H_2 fluorescence would be suppressed even more than that of N_2, since, classically speaking, the H_2 molecule at a given temperature rotates somewhat more rapidly than does a nitrogen molecule, while both have comparable fluorescence lifetimes. This neglects the relative strength of the couplings between the various angular momenta in the molecule, however. Nitrogen is a Hund's case a) molecule, in which the spin is essentially coupled directly to the internuclear axis (see Figure 4). This is because the spin-orbit coupling time is comparable to the internuclear rotational period, $\sim 10^{-13}$s. Hydrogen, on the other hand, is a Hund's case b) molecule, meaning that the spin is much more loosely tied to the internuclear axis. While its rotational period is still $\sim 10^{-13}$ s, its spin-orbit coupling time is closer to $\sim 10^{-10}$s. Thus hydrogen can retain a better "memory" of the initial spin direction [12]. We have investigated several other transitions in molecular hydrogen, and find them to be polarized as well, although with generally lower polarization than that shown in Figure 1. Clearly a systematic study of this problem, with wavelength selection for specific vibrational and rotational levels is warranted.

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