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Ultrashort Cross-Correlation in the Middle Infrared: A Novel Approach to Standoff Detection

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Ultrashort Cross-Correlation in the Middle Infrared: A Novel Approach to Standoff Detection

by

William "Conner" Thomas

A DISSERTATION

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The Graduate College at the University of Nebraska
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Lasers are a common tool in standoff detection because of their small divergence, large amount of power, and multiple wavelengths available for optical interaction. Optical signatures of targets can be composed of but are not limited to absorption, fluorescence, backscatter, polarization manipulation, and plasma spectra. This work was an investigation of a new signature phenomenon: Dispersion of middle infrared ultrashort laser pulses through gas and vapor phase molecules. Vibrational and rovibrational absorption lines of molecular species affect the spectral phase and spectral amplitude of ultrashort light pulses leading an inititally gaussian temporal profile to become distorted. This dissertation is an exploration of these temporal signatures for various concentrations of $H_2O$, $CO_2$, $CH_4$, $CF_4$, and dimethyl methylphosphonate which is a common simulant for the nerve agent, Sarin. By tuning the wavelength to a rovibrational resonance, unique temporal signatures were observed for each molecule. Experimental results were corroborated by simulations based on gas spectra and the Kramers-Kronig transformation. This is one of the few times that this phenomenon has been reported for non-atmospheric molecules.

A novel improvement in the signal-to-noise ratio of the ultrashort pulse signatures was developed by measuring the cross-correlated four-wave-mixing output with an amplified photodiode and lock-in amplifier. Principal component analysis was used to successfully discriminate the optical signatures. The signatures did not have a linear relationship with respect to molecular concentration as in other laser-based standoff techniques. Therefore, the MATLAB regression learner toolbox was used to trend the
data for quantitative prediction. Sensitivity of the proposed technique was analyzed in comparison to the state-of-the-art.
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DEDICATION

This dissertation is dedicated to Hoyle and Juanita Thomas.
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**CWA**: chemical warfare agent
**DMMP**: dimethyl methylphosphonate
**LOD**: limit of detection
**FTIR**: Fourier transform infrared spectroscopy
**QCL**: quantum cascade laser
**TDLAS**: tunable diode laser absorption spectroscopy
**PCA**: principal component analysis
**mid-IR**: middle infrared
**CW**: continuous wave
**SHG**: second harmonic generation
**SFG**: sum frequency generation
**WLG**: white light generation
**THG**: third harmonic generation
**SPM**: self-phase modulation
**XPM**: cross-phase modulation
**BBO**: beta barium borate
**OPA**: optical parametric amplification/optical parametric amplifier
**DFG**: difference frequency generation/difference frequency generator
**FWM**: four-wave mixing
**OFID**: optical free induction decay
SNR: signal-to-noise ratio
LSF: least squares fit
NIOSH: National Institute for Occupational Safety & Health
LBO: lithium triborate
QWP: quarter wave plate
XFROG: cross-correlated frequency resolved optical gating
ECBC: Edgewood chemical & biological center
LICC: lock-in cross-correlation
HITRAN: high-resolution transmission molecular absorption database
NIST: National Institute of Standards & Technology
FWHM: full-width at half-maximum
IMS: ion mobility spectrometry
SAW: surface acoustic wave
LPAS: laser photoacoustic spectroscopy
Chapter 1

Introduction

Chemical, biological, and explosives terrorist attacks can be disseminated in the form of vapors, aerosols, and surface powders. Detection methods that are optimal for one dissemination form may not be effective for another. For example, a detector may be suitable for chemical vapor detection but cannot logistically detect explosive powders. This introductory chapter will discuss current point and standoff detection methods with a focus on chemical detection. Chemical warfare agent (CWA) detectors are typically designed to provide early detection and subsequent warning alarms. Wynn et al. call this the "left of boom" concept in their laser-based explosives detection paper. Detectors can vary in affordability, portability, response time, sensitivity, and selectivity. As of 2013, there are no all-encompassing solutions for CWA detection because of the different dissemination methods including: liquid on surfaces, vapors, aerosols, and contamination of water sources. A detection method with high sensitivity and selectivity will lead to a low probability of false positives and false negatives.

The two common methods of CWA detection are standoff and point detectors. Point detectors are typically inexpensive devices that need to be immersed in the chemical vapor or come in contact with the liquid sample to initiate an alarm. Standoff detectors can be active (laser-based) or passive (background thermal radiation) and are

\[1\textsuperscript{With the addition of a few standoff detection of explosive powders and bio-aerosols.}\]
ideal for keeping operators safe and can scan areas up to a kilometer away. Point detectors typically have an advantage over standoff in monitoring capabilities due to their direct contact with the chemical analytes. However, they are limited to a smaller areas for which they can provide effective information and may be limited in response/recovery times due to the adsorption and desorption interactions.

1.1 Point detection

Colorimetric, ion mobility spectrometry (IMS), surface acoustic wave (SAW), and flame photometry sensors have all been developed as commercially available point detectors. Chemical sensors based on changes in mass uptake, conductivity, electrochemical behavior, and fluorescence are still in the fundamental research phase. Pushkarsky et al. used infrared absorption with a $CO_2$ laser as an excitation source and photo-acoustic microphone detector to perform laser photo-acoustic spectroscopy (LPAS). Their work uses a least squares fit spectral decomposition algorithm to predict CWA simulat concentrations in chemically cluttered environments. Their algorithm will be described in Chap. 6. A couple of examples of point detector limits of detection (LOD's) and response times are shown in Table 1.1.

<table>
<thead>
<tr>
<th></th>
<th>Colorimetric</th>
<th>IMS</th>
<th>SAW</th>
<th>Flame photometry</th>
<th>LPAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>response time</td>
<td>13 min</td>
<td>N/A</td>
<td>60 sec</td>
<td>2 sec</td>
<td>60 sec</td>
</tr>
<tr>
<td>LOD (ppb)</td>
<td>0.8726</td>
<td>15</td>
<td>87.26</td>
<td>1.75</td>
<td>5.8</td>
</tr>
</tbody>
</table>

1.2 Standoff detection

Laser-based standoff detectors utilize the infrared, THz, or Raman signatures of molecules to collect retro-reflected or backscattered data for local detection and data
analysis. The ability to cast laser light across large distances gives the standoff technique an advantage over point detectors in large-area applications. The LOD’s for retro-reflected standoff detectors are typically an average of the total absorption coefficient over the entire pathlength. Standoff detectors that rely on scattered signals contain the added benefit of not needing to “pitch” a retro-reflector downfield in order to obtain a signal. Therefore, scattering-based standoff detectors have the advantage in “on-the-fly” scenarios. Retro-reflected standoff detectors may be better suited as stationary detection equipment.

1.2.1 Infrared spectroscopy standoff

Three passive Fourier transform infrared (FTIR) standoff detectors that are commercially available are the remote sensing chemical agent alarm,\(^3\) the Bruker RapidPLUS,\(^5\) and the Block engineering PORTHOS.\(^1\) The passive FTIR standoff detectors do not require a laser source and offer some of the best portability and operational simplicity on the market. Block engineering also has an active tunable quantum cascade laser (QCL)-based retro-reflected standoff detection system called LaserWarn.\(^6,11,20\) Frish et al. discuss the use of tunable diode laser absorption spectroscopy (TDLAS) in long standoff aerial applications with telescope transceivers to collect scattered laser light from surface topography.\(^7\) Hunter et al. are exploring new infrared absorption spectroscopic signatures by exciting the molecules with a microwave preparatory pulse prior to infrared absorption.\(^21\) The LOD’s of standoff detectors based on infrared absorption are dependent on the chemical cloud length and, thus, the pathlength-integrated concentration is the important metric. LOD’s and other detection performance merits of the aforementioned infrared spectroscopy-based standoff detectors are shown in Table 1.2. The path-integrated concentration (units of ppm-m) is used for comparison between the technologies.
Table 1.2: Standoff detection merits.5–8

<table>
<thead>
<tr>
<th></th>
<th>RapidPLUS</th>
<th>LaserWarn</th>
<th>TDLAS (Frish et al.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>response time</td>
<td>50 ms</td>
<td>2 s</td>
<td>N/A</td>
</tr>
<tr>
<td>receiver style</td>
<td>passive (background thermal)</td>
<td>retroreflected</td>
<td>backscatter</td>
</tr>
<tr>
<td>LOD (ppm-m)</td>
<td>100</td>
<td>2.6 (16.25)</td>
<td>10,000</td>
</tr>
<tr>
<td>LOD chemical</td>
<td>$NH_3$</td>
<td>$Sarin (CH_4)$</td>
<td>$CH_4$</td>
</tr>
<tr>
<td>standoff distance</td>
<td>$&gt;5$ km</td>
<td>$&gt;1$ km</td>
<td>2 km</td>
</tr>
</tbody>
</table>

1.2.2 Raman standoff

Brady et al. developed a multiplexed coherent anti-stokes raman scattering standoff detector.22 The anti-stokes scattering cross-section is increased by overlapping a narrowband femtosecond pulse with a supercontinuum-broadened pulse on the sample which causes the Raman process to be coherent. In lieu of detection limits, four CWA simulants were discriminated using a principal component analysis (PCA) clustering plot. Each simulant was discriminated well despite having overlapping spectral characteristics. Ortiz-Rivera et al. developed a telescope collection system to perform remote Raman scattering experiments on various CWA simulants from a 6.6 meter standoff distance.23

1.2.3 Bio-aerosols and explosives standoff

Biological warfare agents can be in the form of spores, toxins, vegetative bacteria, or viruses.24 Polarization-resolved lidar backscattering and laser-induced fluorescence methods have been successfully used to discriminate such agents.24 Schmitt et al. used a least squares fit to discriminate between bio-agents and non-bio-agents (dust, smoke, fog, etc.).25

Standoff detection of explosives is challenging due to the low vapor pressure of solid powders.13 To increase the vapor pressure to a measurable concentration, photodissociation (or photofragmentation) techniques have been used to excite, fragment, and vaporize powdered explosives as a pre-treatment. After the powders are
treated with the initial pulse, laser-induced fluorescence, middle infrared (mid-IR) spectroscopy, or other techniques can be applied. Laser induced breakdown spectroscopy can also be used to discriminate chemical agents, biological agents, and explosives with PCA.

1.3 Ultrashort mid-IR pulse propagation effects for chemical warfare agent detection

The various spectroscopic methods discussed in the previous section demonstrate unique responses to different molecules. These unique responses, or signatures, are used in conjunction with statistical data processing to form the basis for standoff detection. The response of mid-IR ultrashort pulses to CWA simulants has not yet been explored. The propagation effects of mid-IR ultrashort pulses through atmospheric vapors have been explored by Lanin et al., Coddington et al., and Hammond et al. Initially Gaussian pulses in time become distorted through a series of shifts in spectral phase intimately tied to the absorption and dispersion characteristics of the molecules. As a result, the measured ultrashort pulses have unique signatures in the time domain. Because of the uniqueness of the atmospheric molecular signatures in the previous works based on this technique, it was hypothesized that the technique would provide new information about CWA simulants leading to a higher selectivity than with the signatures of continuous-wave (CW) absorption and Raman spectra. Measurements of mid-IR ultrashort temporal signatures transmitted through non-atmospheric molecules are shown for the first time in this dissertation. Detailed studies of mid-IR wavelengths and temporal measurement ranges were performed for various concentrations of $CH_4$, $CF_4$, and dimethyl methylphosphonate (DMMP). DMMP is a common chemical warfare agent simulant with a similar chemical structure to sarin (GB).
1.4 **Scope/organization of this dissertation**

The content of this dissertation is outlined as follows:

1. Theory

   Chapter 2 is a theoretical chapter outlines the physics and mathematics related to the propagation and measurement of ultrashort laser pulses in the mid-IR. The spectral representation of ultrashort pulses is introduced and studies are performed on the effects of spectral phase. The spectral phase can have profound effects on the time-domain propagation which is shown through the inverse Fourier transform. Nonlinear optics plays a crucial role in both the generation and measurement of ultrashort mid-IR pulses. Ultrashort pulses in the mid-IR are generated through optical parametric amplification (OPA) and difference frequency generation (DFG) of a fundamental beam from a Ti:Sapphire oscillator+amplifier system. Four-wave-mixing (FWM) is utilized in the ultrashort pulse measurement scheme of this dissertation. The FWM process is performed in air rather than a traditional nonlinear optical crystal. Efficient FWM with a large phase-matching bandwidth is possible inside of an ultrashort laser filament which arises from a combination of plasma defocusing and Kerr self-focusing. A quantum description of the rovibrational motion of molecules is also outlined to introduce the fundamental principles of spectroscopy. The eigenstates of the Schrödinger equation solution are what lead to the absorption resonance wavelength of each molecule. Doppler and collisional effects of the molecular ensembles cause spectral line broadening and consequently shorter excited state lifetimes. Finally, a dephasing mechanism called optical free induction decay (OFID) is discussed. OFID has a profound effect on the time-dependent polarization density of the light-matter interaction and thus how the ultrashort pulse behaves in the measurements of this dissertation.
2. Experimental

The experimental setup used to generate mid-IR ultrashort pulses, the gas cell used to introduce controlled vapor concentrations, and the FWM ultrashort pulse measurement scheme developed by Lanin et al. is discussed in Chapter 3. The pulse measurement results are shown as a function of wavelength to identify the resonance mid-IR wavelength. After determining the mid-IR wavelength with the most unique response to the molecule of interest, results are shown as a function of concentration.

3. Simulation

The pulse propagation effects through various concentrations of molecular species are simulated in Chapter 4. Spectral absorption information is imported from the high-resolution transmission (HITRAN) and National Institute of Standards and Technology (NIST) databases and a Kramers-Kronig transformation is used to compute the real part of the refractive index. The simulation results are juxtaposed with the experimental results for various gas concentrations, mid-IR wavelengths, and scan ranges.

4. Increasing sensitivity

The pulse measurement approach developed by Lanin et al. was modified to increase the signal-to-noise ratio (SNR) of the temporal pulse measurement in Chapter 5. The improved results are juxtaposed with the previous cross-correlated frequency resolved optical gating (XFROG) measurements for comparison. The new results were collected in a much more consistent manner which improved the repeatability between measurements under the same conditions.

5. Detection

Statistical data processing techniques are required to translate optical signatures from an experimental observation to a detection technique which is the focus of
Chapter 6. This chapter demonstrates that PCA is an effective method for discriminating the measured optical signatures. This chapter also describes the linear least squares fit (LSF) data processing technique used by standoff detectors based on linear infrared absorption signatures. The LSF technique fails, however, for the proposed ultrashort pulse signatures because there is a nonlinear behavior of the temporal peaks as a function of gas concentration. Thus, the MATLAB regression toolbox is used to identify a regression technique that fits the experimental data.

6. Comparing to industry standards

The feasibility of the proposed detection technique compared to the current state-of-the-art is discussed in Chapter 7. This dissertation was performed at a technology-readiness-level of fundamental research. The next steps in the project are to identify the meaningful concentrations that CWA simulants need to be detected at and determine if the proposed technique can offer high selectivity. The standardized concentration and dosage criteria developed by the National Institute for Occupational Safety and Health (NIOSH) are outlined. The results of this dissertation are analyzed in comparison to the detection limits that are necessary to make the technology effective.
Chapter 2

Theory

2.1 Spectral representation of ultrashort pulses: Electric field & spectral intensity

The notation in this section follows Rick Trebino’s book, "Frequency Resolved Optical Gating: The Measurement of Ultrashort Laser Pulses." The time-domain electric field of an ultrashort laser pulse is represented by a uniform plane wave:

\[ E(t) \propto \frac{1}{2} \sqrt{I(t)} \exp \{j[\omega_0 t - \phi(t)]\} \]  

(2.1)

where \( I(t) \) represents the intensity, and \( \phi(t) \) represents the temporal phase. A Gaussian is commonly used to represent the pulse envelope:

\[ |E(t)| = E_0 \exp \left[ -2ln(2) \left( \frac{t}{\tau_{FWHM}} \right)^2 \right] \]  

(2.2)
The Fourier transform of Eq. 2.1 yields the spectral representation of an ultrashort laser pulse:

\[
\tilde{E}(\omega) = \frac{1}{2} \sqrt{S(\omega - \omega_0)} \exp \{-j[\varphi(\omega - \omega_0)]\} + \frac{1}{2} \sqrt{S(-\omega - \omega_0)} \exp \{+j[\varphi(-\omega - \omega_0)]\}
\]

(2.3)

where \(S(\omega)\) and \(\varphi(\omega)\) are the frequency domain equivalents of intensity and phase. They are called the spectrum and spectral phase, respectively. The second term in Eq. 2.3 is typically neglected because it represents negative frequencies. The Fourier transform of Eq. 2.1 with a Gaussian magnitude (Eq. 2.2) is represented as:

\[
|\tilde{E}(\omega)| = 0.602 \tau_{FWHM} \sqrt{2\pi} \exp \left[-\frac{(0.602\tau)^2(\omega - \omega_0)^2}{2}\right]
\]

(2.4)

Thus, the frequency representation of the ultrashort pulse electric field is also a Gaussian. The group delay of an ultrashort pulse is the derivative of spectral phase with respect to angular frequency:

\[
t_{gr}(\omega) = \frac{d\varphi}{d\omega}
\]

(2.5)

The usefulness of the group delay concept will become more evident in the examples worked out in section 2.1.2. The instantaneous frequency gives insight into the frequency of the waveform at any instant in time:

\[
\omega_{\text{inst}}(t) = \omega_0 - \frac{d\phi}{dt}
\]

(2.6)

### 2.1.1 Index of refraction & spectral phase

Materials are characterized by their complex index of refraction,

\[
\tilde{n}(\omega) = n(\omega) + j\kappa(\omega).
\]

The transfer function of the frequency domain electric field
traveling through an arbitrary medium of length $z$ is given by:

$$\tilde{E}_{\text{out}}(\omega) = \tilde{E}_{\text{in}}(\omega) \exp \left[ -\frac{\kappa(\omega) z}{2} \right] \exp \left[ -j \frac{\omega}{c} n(\omega) z \right]$$  \hspace{1cm} (2.7)

Modeling laser-matter interaction is much easier in the frequency domain compared to the convolution required in the time domain.

In continuous-wave optics, choosing the right material for a transmissive optic preserves the quality of the light used in an experiment. The situation is much different for ultrashort pulses. Even if the material is highly transmissive and the spectral amplitude is maintained, the changes in spectral phase can distort the temporal characteristics of the pulse. Changes in spectral phase from passing through media is called dispersion and comes from the imaginary component of Eq. (2.7). The Taylor series expansion of the imaginary components is how material dispersion properties are classified:

$$\varphi(\omega) = \varphi_0 + \varphi_1 \frac{\omega - \omega_0}{1!} + \varphi_2 \frac{(\omega - \omega_0)^2}{2!} + \ldots$$  \hspace{1cm} (2.8)

$\varphi_1 = \left. \frac{d\varphi}{d\omega} \right|_{\omega=\omega_0}$ is called group delay and $\varphi_2 = \left. \frac{d^2\varphi}{d\omega^2} \right|_{\omega=\omega_0}$ is called group-delay dispersion.

### 2.1.2 Inverse Fourier transform: Time-domain representation

Each point on the ordinate of an $\tilde{E}(\omega)$ plot represents a plane wave in the time domain with amplitude given by $|\tilde{E}(\omega)|$ and phase given by $\varphi(\omega) = -\arctan \{ \Im \{ \tilde{E}(\omega) \} / \Re \{ \tilde{E}(\omega) \} \}$. Thus, the time domain electric field is reconstructed by a summation of complex exponentials:

$$E(t) = \sum_{i=0}^{\infty} |\tilde{E}(\omega_i)| \exp \left\{ -j [\omega_i t + \varphi(\omega_i)] \right\}$$  \hspace{1cm} (2.9)

In the following paragraphs, this inverse Fourier technique is applied to fields with various orders of spectral phase (Eq. 2.8) to study their effects on temporal pulse distortion.
First-order spectral phase (group delay) causes a shift in time. A simulation of group delay is shown in Fig. 2.1 where $S(\omega)$ is defined with $\delta f_{FWHM} = 0.02\, fs^{-1}$, $f_0 = 0.375\, fs^{-1}$, and $\varphi_1 = -14.5\, fs$. The group delay, $t_g$, of a linearly sloped $\varphi(\omega)$ is a constant $-14.5\, fs$ which indicates that all the frequencies are in phase at $-14.5\, fs$. The results from applying Eq. 2.9 verify the temporal offset.

![Simulation of first-order spectral phase](image)

Figure 2.1: Simulation of first-order spectral phase.1

Second-order spectral phase (group delay dispersion or linear chirp) causes the frequencies that make up an ultrashort pulse to arrive at different times. An example of positive linear chirp is demonstrated in Fig. 2.2 where $S(\omega)$ is defined with $\delta f_{FWHM} = 0.07\, fs^{-1}$, $f_0 = 0.375\, fs^{-1}$, and $\varphi_2 = -40\, rad \cdot fs^2$. The group delay is linearly sloped with frequency because the spectral phase is quadratic. The positive linear slope indicates that the smaller (red) frequencies arrive prior to the larger (blue) frequencies.
Third-order spectral phase causes interference of large and small frequencies that form beat patterns in the time domain. This characteristic is common amongst all odd-ordered harmonics of the spectral phase (Eq. 2.8). An example of third-order spectral phase is demonstrated in Fig. 2.3 where $\delta f_{FWHM} = 0.02 \text{fs}^{-1}$, $f_0 = 0.375 \text{fs}^{-1}$, and $\varphi_3 = 1500 \text{rad} \cdot \text{fs}^3$. The group delay is quadratic which indicates that there are red and blue frequency components arriving at the same time and leads to the beat pattern seen in Fig. 2.3b,c.

This section investigated how spectral phase can distort ultrashort optical pulses which is an inevitable effect when using transmissive optics in experiments. The Taylor expansion of the spectral phase term takes place of the imaginary exponential in the plane wave propagation term of Eq. 2.7. Therefore, the index of refraction can replace the spectral phase. The spectral phase representation is, however, a convenient formality when representing optics used in experiments. This concept will become important
when considering gas-phase media in Sec. 2.4.6. Gas-phase media can absorb at certain frequencies as well as affect the phase. Thus, $\kappa$ will no longer be zero like the models used in this section.

## 2.2 Nonlinear optics

The polarization vector is commonly used to model the linear response of a material to an applied electric field:

$$P = \epsilon_0 \chi E = Np$$  \hspace{1cm} (2.10)

where $\chi$ is the linear susceptibility, $N$ is the number density of dipole moments, and $p$ represents a dipole moment induced by $E$. In a simple Lorentz model, the dipole moment serves as the restoring force proportional to the displacement: $p = -ex$. The
polarization is proportional to the electric field and the material response is linear in this analogue of Hooke's law. When the restoring force behaves like an anharmonic oscillator, the polarization is no longer linearly proportional to the electric field and the system becomes nonlinear. Anharmonic behavior typically starts to occur when the electric field becomes comparable to the strength of interatomic fields \((10^5 - 10^8 V/m)\).\(^{35}\) A quadratic or cubic response of the polarization to an applied electric field are the most common nonlinear behaviors encountered. This is represented in a Taylor series expansion of the polarization vector:

\[
P = \epsilon_0 \chi E + 2dE^2 + 4\chi^{(3)}E^3 + \ldots
\]  

(2.11)

where \(d\) is the second-order nonlinear coefficient and \(\chi^{(3)}\) is the third-order susceptibility. Non-centrosymmetric media is required in order to have a non-vanishing \(d\) term but all media has a finite \(\chi^{(3)}\). The wave equation must also include the nonlinear polarization term:

\[
\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2} = \mu_0 \frac{\partial^2 (\epsilon_0 \chi E + P_{NL})}{\partial t^2} = \Sigma
\]

(2.12)

which simplifies to a simpler form that represents the nonlinear polarization as the source term that radiates in a linear medium of refractive index \(n\):

\[
\nabla^2 E - \frac{1}{v^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P_{NL}}{\partial t^2} = \Sigma
\]

(2.13)

The nonlinear polarization induced in the material by the input electric field becomes the source of a different wave propagating with a different frequency.
### 2.2.1 Second harmonic generation

Consider the electric field of a single wave:

\[
E(t) = Re\{E(\omega) \exp(j\omega t)\} = \frac{1}{2}[E(\omega) \exp(j\omega t) + E^*(\omega) \exp(-j\omega t)]
\]  

(2.14)

The second-order nonlinear polarization induced in a medium is given by:

\[
P_{NL}(t) = 2dE^2 = 2d\frac{1}{4}[E(\omega)^2 \exp(2j\omega t) + 2E(\omega)E^*(\omega) + E^*(\omega)^2 \exp(-j2\omega t)]
\]

(2.15a)

\[
= P_{NL}(0) + Re\{P_{NL}(2\omega) \exp(j2\omega t)\}
\]

(2.15b)

\[
= dE(\omega)E^*(\omega) + Re\{dE(\omega)^2 \exp(j2\omega t)\}
\]

(2.15c)

Each nonlinear polarization term acts as a source in the wave equation and new waves are generated inside the medium. The second term in Eq. 2.15c generates a second-harmonic wave:

\[
\Sigma(2\omega) = 4\mu_0\omega^2 dE(\omega)^2
\]

(2.16)

Neglecting pump depletion and any phase mismatch, the intensity of the generated wave increases proportionally to the square of the distance \(z^2\) travelled in the medium. Phase-matching is an important requirement for nonlinear optical interactions and is discussed below in Sec. 2.2.4.

### 2.2.2 Pockels effect

A Pockels cell has the ability to control crystal anisotropy with an applied voltage. Consider a DC electric field in addition to an optical wave:

\[
E(t) = E(0) + Re\{E(\omega) \exp(j\omega t)\}
\]

(2.17)
The nonlinear polarization induced in the medium will have three components:

\[
P_{NL}(t) = 2dE^2 = P_{NL}(0) + Re\{P_{NL}(\omega) \exp(j\omega t)\} + Re\{P_{NL}(2\omega) \exp(j2\omega t)\} \tag{2.18a}
\]

\[
P_{NL}(t) = d[2E(0)^2 + |E(\omega)|^2] + Re\{4dE(0)E(\omega) \exp(j\omega t)\} + Re\{P_{NL}(2\omega) \exp(j2\omega t)\} \tag{2.18b}
\]

If the optical electric field is much smaller than the applied DC field, the third term in Eq. 2.18b can be ignored. The middle term in Eq. 2.18b creates a change in the index of refraction of the medium:

\[
\Delta n = \frac{2d}{n\epsilon_0} E(0)
\]

which can be modulated by the strength of the applied voltage across the crystal.

### 2.2.3 Three-wave mixing: Optical parametric amplification and difference frequency generation

Consider two optical waves at different frequencies entering a crystal:

\[
E(t) = Re\{E(\omega) \exp(j\omega t)\} + Re\{E(2\omega) \exp(j2\omega t)\} \tag{2.20}
\]

The nonlinear polarization induced in the crystal contains components at the second harmonic of each wave, the sum frequency, and difference frequency:

\[
P_{NL}(t) = 2dE^2 = P_{NL}(0) + P_{NL}(2\omega_1) + P_{NL}(2\omega_2) + P_{NL}(\omega_+) + P_{NL}(\omega_-) \tag{2.21a}
\]

\[
P_{NL}(0) = d[|E(\omega_1)|^2 + |E(\omega_2)|^2] \tag{2.21b}
\]

\[
P_{NL}(\omega_1) = dE(\omega_1)E(\omega_1) \tag{2.21c}
\]

\[
P_{NL}(2\omega_2) = dE(\omega_2)E(\omega_2) \tag{2.21d}
\]
\[ P_{NL}(\omega_+) = 2dE(\omega_1)E(\omega_2) \]  
\[ P_{NL}(\omega_-) = 2dE(\omega_1)E^*(\omega_2) \]

Eq. 2.21f represents DFG. A longer wavelength photon is generated by mixing two photons with shorter wavelengths. OPA is a special case of Eq. 2.21f. Parametric amplification involves \( \omega_1 \) (pump) and \( \omega_2 \) (signal) interacting such that \( \omega_2 \) increases in energy. As a result, \( \omega_- \) (idler) is created. 2.21f

### 2.2.4 Phase-matching

As discussed above in Eqs. 2.21b-f, there are numerous modalities of three-wave mixing. All of these interactions cannot occur at the same time. Phase-matching is a requirement for efficient generation and is the criterion used to select the preferable nonlinear interaction or necessary material to use. In the case of sum-frequency generation (SFG), the matching of wave vectors depends on the index of refraction:

\[ P_{NL}(\omega_3) = 2dE(\omega_1)E(\omega_2) = 2dA_1A_2 \exp(-jk_3 \cdot r) \]  
\[ \omega_1 + \omega_2 = \omega_3 \]  
\[ k_1 + k_2 = k_3 \]  
\[ n_1\omega_1 + n_2\omega_2 = n_3\omega_3 \]

Naturally, materials are dispersive which makes finding a suitable material for phase-matching difficult. The most common way to achieve phase-matching is by taking advantage of birefringent crystals. In practice, crystals are cut to a certain angle with respect to the optical axis or their temperature is controlled. Type I phase matching involves signal and idler beams with the same polarization and type II phase-matching involves orthogonal polarizations. An example of type II phase-matching for second
harmonic generation (SHG) is demonstrated in Fig. 2.4. The ideal crystal cut in this example is approximately 20°.

Now consider an OPA process in which a continuum of frequencies ($\omega_2$'s in Eq. 2.21f) are available for amplification. The amplified frequency will depend on the crystal angle that satisfies the collinear phase-matching condition:

$$\omega_+ n_+ = \omega_1 n_1 - \omega_2 n_2$$  \hspace{1cm} (2.23)

The amplified signal beam has a tunable frequency controlled completely by the crystal angle. For any set of frequencies that satisfy $\omega_+ = \omega_1 - \omega_2$, the process can be visualized similar to Fig. 2.4. The blue curve represents the sum of two wave vectors, $\omega_+ n_+ + \omega_2 n_2$, and the yellow curve represents the wave vector of the pump, $\omega_1 n_1$. Efficient parametric amplification occurs at the intersection of the two curves. The optimal crystal angle shifts for each set of frequencies chosen. A similar phase-matching procedure is followed for OPA and DFG processes.
Another method of achieving phase-matching is to use a non-collinear beam geometry. The non-collinear phase-matching conditions for SFG are as follows:

\[ \omega_1 + \omega_2 = \omega_3 \]  
(2.24a)

\[ \omega_1 n_1 \cos \theta_1 + \omega_2 n_2 \cos \theta_2 = \omega_3 n_3 \]  
(2.24b)

where \( \theta_1 \) and \( \theta_2 \) are defined with respect to \( \theta_3 = 0 \). Non-collinear phase-matching is used in applications where collinear geometries are hard to produce.

The limiting factor of nonlinear optical generation is the phase mismatch. Finite mismatch results in generation only being efficient over a certain distance called the coherence length:

\[ L_c = \frac{2\pi}{|\Delta k|} \]  
(2.25)

The generated intensity follows a \( \text{sinc}^2(\Delta kL) \) trend.

### 2.2.5 Four wave mixing

Third-order nonlinear interactions occur in materials with large \( \chi^{(3)} \) properties. Consider an electric field with three optical waves incident on a material:

\[ E(t) = Re\{E(\omega_1) \exp(j\omega_1 t)\} + Re\{E(\omega_2) \exp(j\omega_2 t)\} + Re\{E(\omega_3) \exp(j\omega_3 t)\} \]  
(2.26)

The nonlinear polarization induced in the material contains numerous components:

\[ P_{NL}(t) = \frac{1}{8} \chi^{(3)} \sum_{q,r,l=\pm1,\pm2,\pm3} E(\omega_q)E(\omega_r)E(\omega_l) \exp[j(\omega_q + \omega_r + \omega_l)t] \]  
(2.27)

Of particular interest in this dissertation is the degenerate pump difference frequency four-wave mixing:

\[ P_{NL}(2\omega_1 - \omega_3) = 3\chi^{(3)}E^2(\omega_1)E^*(\omega_3) \]  
(2.28)
In this dissertation, $\omega_1$ represents the fundamental wavelength from the Ti:Sapphire amplifier, 790 nm, and $\omega_3$ represents the mid-IR pulses from the OPA+DFG system. The generated wavelength from Eq. 2.28 ranges between 410-470 nm depending on the mid-IR wavelength used.

### 2.3 Filamentation

The work in this section follows the book, "Femtosecond Laser Filamentation" by Chin. Nonlinear optical properties of filaments, in particular FWM, is used in this dissertation. A filament is formed when a laser pulse self-focuses in a transparent optical medium, generates a plasma, undergoes intensity clamping, and emerges as a white light laser pulse with conical emission of colored rings. A filament formed in air will typically leave behind a trail of fluorescent N$_2$ molecules that are tunnel ionized. The behavior of femtosecond laser filaments are conducive to a number of nonlinear optical phenomena relevant to this dissertation.

#### 2.3.1 Slice-by-slice view of a filament

Due to the plasma dynamics formed by the propagating laser pulse undergoing filamentation, the Gaussian spatial profile along the propagation axis is best considered in slices. Consider the center slice that contains the peak power first. The transverse profile is a radial Gaussian that will experience a nonlinear index of refraction from the third-order Kerr effect:

$$n = n_0 + n_2 I$$  \hspace{1cm} (2.29)

where $n_0$ is the refractive index of air, $n_2$ is the Kerr coefficient, and $I$ is the laser intensity. The nonlinear index will be highest at the core of the transverse profile and decay radially to $n_0$. The nonlinear refractive index results in a converging wavefront and is known as the Kerr lens effect. However, diffraction is naturally causing the laser beam
to diverge. The critical power for self-focusing is defined at the point where Kerr lensing and divergence cancel each other out exactly:

\[
P_c = \frac{3.77 \lambda^2}{8 n_0}
\]

(2.30)

where \(\lambda\) is the wavelength of the laser. Above \(P_c\), the laser will eventually converge to a high enough intensity that the \(N_2\) molecules are tunnel ionized and a plasma is formed. The plasma contributes to the index of refraction as follows:

\[
(\Delta n)_p = -\frac{4\pi e^2 N_e(t)}{2m_e \omega_0^2}
\]

(2.31)

where \(N_e\) is the electron density, \(m_e\) is the electron mass, and \(e\) is the electron charge. The laser beam begins to defocus when the electron density becomes high enough that \((\Delta n)_p\) exceeds \(n_2 I\). The minimum beam diameter is reached when Kerr self-focusing exactly balances the plasma defocusing. This phenomenon is known as intensity clamping and has an approximate value of \(5 \times 10^{13} \frac{W}{cm^2}\) in air. The location of self-focus of a collimated laser beam is given by:

\[
without a lens: z_f = \frac{0.367 k a_0^2}{\left\{\left(\frac{P}{P_c}\right)^\frac{3}{2} - 0.852\right\}^\frac{1}{2}}
\]

(2.32a)

\[
with a lens: \frac{1}{z_f'} = \frac{1}{z_f} + \frac{1}{f}
\]

(2.32b)

where \(k\) is the wavenumber and \(a_0\) is the \(\frac{1}{e^2}\) beam radius. Plasma densities at \(z_f'\) are higher when an external focusing optic is used but intensity clamping still occurs.

Each successive slice heading towards the front of the pulse will self-focus at a further distance than the main slice according to Eq. 2.32b because the power is decreasing. The gradual increase in \(z_f\) values from the center to front of the pulse map out a plasma column which makes up the filament. The slices of the latter half of the
pulse behave in a different way because they interact with the plasma left behind from the leading edge of the pulse.

### 2.3.2 Self-phase modulation, self-steepening, and white-light generation

The refractive index experiences Kerr and plasma effects that are a function of time:

\[
n(t) = n_0 + \Delta n(t) = n_0 + n_2 I(t) - \frac{4^2 N_e(t)}{2m_e \omega_0^2}
\]

(2.33)

A plane wave representation of the beam at self-focus becomes:

\[
F(z, t) = \exp\{j[\omega_0 t - \frac{\omega_0 n_0}{c} z - \frac{\omega_0 \Delta n(t)}{c} z]\}
= \exp\{j[\omega_0 t - \frac{\omega_0 n_0}{c} z + \int_0^t \Delta \omega dt]\}
\]

(2.34)

where \(\Delta \omega = -\frac{\omega_0}{c} z \frac{\partial \Delta n(t)}{\partial t}\). The extra phase term represents a change in the frequency content of the pulse spectrum and is caused by the plasma and Kerr effects of the pulse itself. The leading edge of the pulse does not experience a refractive index that has been modified by the plasma yet so the frequency is red-shifted:

\[
\Delta \omega = -\frac{\omega_0}{c} z \frac{n_2}{2} \frac{\partial I(leading\ edge)}{\partial t} < 0
\]

(2.35)

The back side of the pulse interacts with the plasma generated from the leading edge and center slice of the pulse. The frequency shift associated with the plasma dynamics is:

\[
\Delta \omega = \frac{2\pi z e^2}{cm_e \omega_0} \frac{\partial N_e(t)}{\partial t}
= \frac{2\pi z e^2 N_0 w}{cm_e \omega_0} I^m(t) > 0
\]

(2.36)

where \(N_0\) is the density of neutral air, \(w\) is the ionization cross-section, and \(m\) is related
to the ion yield. The result of the back side of the pulse interacting with the plasma is a frequency blue-shift. It can be concluded from Eq. 2.33 that \( n_{\text{back}} < n_{\text{center}} < n_{\text{front}} \) when the center slice is at self-focus (\( n = n_0 \) because \( n_2 I = (\Delta n)_p \)). Therefore the backside of the pulse is catching up to the front which causes a self-steepening effect. This effect also contributes to the blue-shift in pulse spectrum:

\[
\Delta \omega = -\frac{\omega_0 z}{c n_2} \frac{\partial I(\text{steep trailing edge})}{\partial t} > 0
\]

Thus the entire pulse spectrum contains blue- and red-shifts which is called continuum or white-light generation (WLG).

The plane wave approximation from above neglected the radial component of the wave vector. The electron density generated by the leading edge and center slice of the pulse also has a radial component, \( N_e(z, r) \). The trailing edge of the pulse will experience a \( \Delta k_r \hat{r} \propto \frac{\partial N_e}{\partial r} r \). This results in conical emissions of the blue-shifted wavelengths which create a unique conical pattern in experiments.

### 2.3.3 Filamentation nonlinear optics

Third-order nonlinear optical processes are highly efficient in air-filaments due to a phenomenon called self-group-phase-locking which is specific to filaments. Cross-interaction causes generated and fundamental waves to propagate in the filament with relative phases that are locked together. The full theoretical treatment of self-group-phase-locking for third harmonic generation (THG) is covered in this section. The concept is also applicable to FWM in a filament which will be qualitatively discussed.
2.3.3.1 Third Harmonic Generation in a filament

The wave equation to model a nonlinear optical interaction using the slowly varying envelope approximation is defined as follows:

\[
\Delta_{\perp}A + 2jk_0\left[\frac{\partial A}{\partial z} + \frac{1}{v_g} \frac{\partial A}{\partial t}\right] - k_0^2 k^2 A - \frac{\omega^2}{c^2} A + j\alpha^2 A = -\frac{k_0^2}{\epsilon_0} P_{NL} \exp(-jk_0 z) \tag{2.38}
\]

where \(v_g\) is the group velocity, \(\alpha\) is the absorption coefficient, and \(A\) is the amplitude of \(E = A \exp(-j\omega_0 t - k_0 z)\). The nonlinear polarization, \(P^{(3)} = \epsilon_0 \chi^{(3)} E^3\) can be enumerated in a number of different ways:

\[
THG : P_{3\omega}^{(3)} = \frac{1}{8} \epsilon_0 \chi^{(3)} A_\omega^3 \exp[j(3k_\omega z - 3\omega_0 t)] \tag{2.39a}
\]

\[
SPM_\omega : P_\omega^{(3)} = \frac{3}{8} \epsilon_0 \chi^{(3)} |A_\omega|^2 A_\omega \exp[j(k_\omega z - \omega_0 t)] \tag{2.39b}
\]

\[
XPM_\omega : P_\omega^{(3)} = \frac{3}{4} \epsilon_0 \chi^{(3)} |A_{3\omega}|^2 A_\omega \exp[j(k_\omega z - \omega_0 t)] \tag{2.39c}
\]

\[
SPM_{3\omega} : P_{3\omega}^{(3)} = \frac{3}{8} \epsilon_0 \chi^{(3)} |A_{3\omega}|^2 A_{3\omega} \exp[j(k_3\omega z - 3\omega_0 t)] \tag{2.39d}
\]

\[
XPM_{3\omega} : P_{3\omega}^{(3)} = \frac{3}{4} \epsilon_0 \chi^{(3)} |A_\omega|^2 A_{3\omega} \exp[j(k_3\omega z - 3\omega_0 t)] \tag{2.39e}
\]

Recall that the index of refraction is related to the total polarization by

\[
n = \sqrt{\frac{\epsilon}{\epsilon_0}} = \sqrt{1 + \chi} = \sqrt{1 + \frac{P}{E}}. \quad \text{Therefore, the index of refraction of the fundamental beam is dictated by Eqs. 2.39b & 2.39c, while the index of the third harmonic follows Eqs. 2.39a, 2.39d, & 2.39e. Since the intensity of the fundamental beam is much stronger than the third harmonic, } n(\omega) \text{ is dominated by self-phase-modulation (SPM), while } n(3\omega) \text{ is dominated by cross-phase-modulation (XPM). The results for } n(\omega) \text{ and } n(3\omega) \text{ are found quantitatively by solution of Eq. 2.38 which is covered in Ref.}^{36} \text{ The results are as follows:}
\]

\[
n_\omega = n_{0,\omega} + \frac{3}{8} \chi^{(3)} [|A_\omega|^2 + 2|A_{3\omega}|^2 - |A_\omega||A_{3\omega}|] \tag{2.40a}
\]
\[ n_{3\omega} = n_{0,3\omega} + \frac{3}{8} \chi^{(3)} [ |A_{3\omega}|^2 + 2|A_{\omega}|^2 - \frac{|A_{\omega}|^3}{3|A_{3\omega}|} ] \]  

(2.40b)

where both indices are controlled by \(I_\omega\).

### 2.3.3.2 Four-wave-mixing in a filament

Self-group-phase-locking is possible for a FWM interaction as well. Theberge et al. used a Ti:sapphire laser system (800 nm) with an optical parametric amplifier (near-IR) to demonstrate FWM in filaments.\(^\text{37}\) Further information on the experimental setup used in this dissertation for FWM is discussed in Sec. 3.2. The FWM nonlinear polarizations using such a configuration are described by:

\[ FWM : P_{FWM}^{(3)} \propto |A_\omega|^2 A_{IR} \exp[j(k_{FWM}z - \omega_{FWM}t)] \]  

(2.41a)

\[ XPM_{FWM} : P_{FWM}^{(3)} \propto |A_\omega|^2 A_{FWM} \exp[j(k_{FWM}z - \omega_{FWM}t)] \]  

(2.41b)

\[ XPM_{IR} : P_{IR}^{(3)} \propto |A_\omega|^2 A_{IR} \exp[j(k_{IR}z - \omega_{IR}t)] \]  

(2.41c)

\[ FWM_{IR} : P_{IR}^{(3)} \propto |A_\omega|^2 A_{IR} \exp[j(k_{IR}z - \omega_{IR}t)] \]  

(2.41d)

where only the nonlinear polarizations controlled by the intensity of the fundamental, \(I_\omega\), are considered. The filamenting 800 nm beam controls the index of refraction and therefore phase of the infrared beam and generated FWM beam. The FWM interaction is self-group-phase-locked. Remarkably, the FWM conversion efficiency changes from \(10^{-5}\) at powers below \(P_c\), to greater than 30 % when the pump beam undergoes filamentation.\(^\text{36,37}\)

### 2.4 Vibrational & rovibrational spectroscopy

Molecules absorb mid-IR light at discrete wavelengths in order to reach excited vibrational states. The transition wavelengths are unique to molecule-specific properties
such as bond strength, bond length, and atomic masses. The vibrational energy states can be modeled as a solution to the Schrödinger equation for a simple harmonic oscillator. Rotational energy states are also discussed.

### 2.4.1 Harmonic oscillator & rigid rotor

The solution of the Schrödinger equations always requires the same procedure. First, the potential energy is defined so that the differential equation solution of $\psi$ can be found. The potential energy is defined from the classical mechanics analogue. The eigenstate energy can be solved for after applying boundary conditions to the solution of $\psi$. The eigenstate energy contains information about energy states and transition frequencies.

#### 2.4.1.1 Classical oscillator

A mass-spring dumbbell system can be simplified to a single mass connected to a rigid wall by use of the reduced mass:

$$
\mu = \frac{m_1 m_2}{m_1 + m_2}
$$

(2.42)

The differential equation of motion for the reduced mass system is solved as follows:

$$
DE : \mu \frac{d^2 x}{dt^2} + kx = 0
$$

(2.43a)

**General Solution**:

$$
\psi = b_1 \cos \sqrt{\frac{k}{\mu}} t + b_2 \sin \sqrt{\frac{k}{\mu}} t
$$

(2.43b)

**B.C.'s**:

$$
x(0) = 0, v(0) = v_0
$$

(2.43c)

**Specific Solution**:

$$
x(t) = \sqrt{\frac{k}{\mu}} v_0 \sin \sqrt{\frac{k}{\mu}} t
$$

(2.43d)
where \( k \) represents the spring constant from Hooke’s law. The system experiences simple harmonic motion with frequency \( \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \), potential energy \( \frac{1}{2} k x^2 \), and kinetic energy \( \frac{1}{2} \mu v^2 \).

### 2.4.1.2 Quantum oscillator

The Schrödinger equation with a Hooke’s law potential energy is as follows:

\[
-\frac{\hbar^2}{2\mu} \frac{d^2 \psi_n(x)}{dx^2} + \frac{k x^2}{2} \psi_n(x) = E_n \psi_n(x)
\]  

(2.44)

The solution of the wave function involves the Hermite polynomials:

\[
\psi_n(x) = A_n H_n(\alpha^{\frac{1}{2}} x) \exp\left(-\frac{\alpha x^2}{2}\right)
\]  

(2.45)

where \( \alpha = \sqrt{\frac{k}{\mu} \frac{\hbar^2}{\hbar^2}} \) and \( A_n = \frac{1}{\sqrt{2^n n!} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}} \). The eigenstate energy solution:

\[
E_n = \hbar \sqrt{\frac{k}{\mu}} \left( n + \frac{1}{2} \right)
\]  

(2.46)

results in the vibrational energy levels being quantized. The energy states are proportional to the square-root of the bond strength and inversely proportional to the square-root of the reduced mass.

### 2.4.1.3 Classical rotation

A reduced mass freely rotating on a rigid radial arm has a kinetic energy given by:

\[
E_{kin} = \frac{1}{2} \mu v^2 = \frac{1}{2} \mu (r \frac{d\theta}{dt})^2 = \frac{1}{2} \mu r^2 \omega^2 = \frac{1}{2} I \omega^2
\]  

(2.47)

where \( I \) is the moment of inertia. The energy can be more conveniently defined in terms of the angular momentum:

\[
E = \frac{p^2}{2\mu} = \frac{l^2}{2\mu r^2} = \frac{l^2}{2I}
\]  

(2.48)
Eq. 2.48 is the case for a tangential angular momentum, \( l = r \times p = rp \).

### 2.4.1.4 Quantum rotation

If vibrational and rotational motion are decoupled from one another, the Schrödinger equation solutions can be solved for separately:

\[
\hat{H}_{total} = \hat{H}_{vib}(\tau_{\text{internal}}) + \hat{H}_{rot}(\theta_{cm}, \phi_{cm})
\]

(2.49a)

\[
E_{total} = E_{vib}(\tau_{\text{internal}}) + E_{rot}(\theta_{cm}, \phi_{cm})
\]

(2.49b)

\[
\psi_{total} = \psi_{vib}(\tau_{\text{internal}}) + \psi_{rot}(\theta_{cm}, \phi_{cm})
\]

(2.49c)

The quantum rotor is allowed to freely rotate so the potential is \( V(\phi) = 0 \). The Schrödinger equation in polar coordinates is:

\[
\frac{-\hbar^2}{2\mu r_0^2} \frac{d^2 \Phi_n(\phi)}{d\phi^2} = E_n \Phi_n(\phi)
\]

(2.50)

which has a solution:

\[
\Phi_+(\phi) = A_+ \exp(i|m_l|\phi)
\]

(2.51a)

\[
\Phi_-(\phi) = A_- \exp(-i|m_l|\phi)
\]

(2.51b)

From the boundary condition \( \Phi(\phi + 2\pi) = \Phi(\phi) \), the eigenstate energy is attained:

\[
E_{m_l} = \frac{\hbar^2 m_l^2}{2I}
\]

(2.52)

When solving for the three-dimensional rigid rotor solution, spherical harmonic functions are necessary. The eigenstate energy solution is similar to Eq. 2.52:

\[
E_{m_l} = \frac{\hbar^2}{2I} l(l + 1)
\]

(2.53)
2.4.2 Boltzmann distributions

Thermally-populated excited states are important in the interpretation of absorption spectra. The Boltzmann distribution describes the ratio of population in upper state, $i$, compared to lower state, $j$:

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp\left[-\frac{j}{k_B T} (\epsilon_i - \epsilon_j)\right]$$  \hspace{1cm} (2.54)

The degeneracy of each state is represented by $g_{i,j}$ and $\epsilon_i - \epsilon_j$ represents the difference in energy between the states.

2.4.3 Selection rules

Selection rules restrict the states for which a transition is allowed in spectroscopy. The selection rules can be explained by modeling the light-matter interaction with a transition dipole moment. The transition moment contains a permanent and dynamic dipole moment. Polar molecules have a permanent, or unchanging, dipole moment. Vibrating molecules have electron interactions that result in a dynamic charge transfer and a dynamic dipole moment. The Taylor series expansion of the dipole moment is given by:

$$\mu_x(x_e + x(t)) = \mu_0 x_e + x(t) \left(\frac{d\mu_x}{dx}\right)_{x=0} + \ldots$$  \hspace{1cm} (2.55)

which mathematically describes both the permanent and dynamic components. The transition dipole moment expectation value is given by:

$$\mu_x^{mn} = \int \psi_m^*(x) \mu_x(x_e + x) \psi_n(x) dx$$  \hspace{1cm} (2.56)

needs to be nonzero for absorption to be allowed. By analysis of Eq. 2.54, it can be determined that only the ground vibrational state is significantly populated at room temperature. Plugging in the wave functions of the simple harmonic oscillator from Eq.
the transition dipole moment becomes:

\[
\mu_{x0}^m = A_m A_0 \mu_{0x} \int_{-\infty}^{\infty} H_m(\alpha \frac{1}{2} x) H_0(\alpha \frac{1}{2} x) \exp(-\alpha x^2) dx
\]

\[
+ A_m A_0 \left[ \left( \frac{d\mu_x}{dx} \right)_{x=0} \right] \int_{-\infty}^{\infty} H_m(\alpha \frac{1}{2} x) x H_0(\alpha \frac{1}{2} x) \exp(-\alpha x^2) dx
\]

where \(A\) is a normalization constant. The first term in Eq. 2.57 is equal to zero because wave functions are always orthogonal. The second term can be nonzero if the integrand is an even function. This forces \(H_m(\alpha \frac{1}{2} x)\) to be odd since \(H_0(\alpha \frac{1}{2} x)\) is even. Therefore the excited state in the vibrational transition must be odd. Further analysis shows that the area under the curve in the dynamic dipole moment integral cancels out if \(m \neq 1\). Therefore the only allowed transition for a simple harmonic oscillator is \(\Delta n = +1\).

Overtones transitions \(\Delta n = +1, +2, +3, \ldots\) are possible if the more-realistic Morse potential is used instead of Hooke’s law. However, overtones are weak in comparison to \(\Delta n = +1\). Experimentally, only one transition is observed for each vibrational mode of a molecule.

Transitions between rotational energy levels in a molecule also follow a set of selection rules. Recall that the rotational energy levels of a molecule are defined by Eq. 2.53. The energy levels are much more tightly spaced than vibrational levels. For example,

\[
\frac{\Delta E_{rot}}{\Delta E_{vib}} = \frac{b}{r_0^2 \sqrt{4}\mu} = 0.028 \text{ for } H_2O \text{ or } 0.00034 \text{ for } I_2.^{38}
\]

Unlike vibrational energy levels, rotational levels are not evenly spaced. When discussing rotational transitions, \(l\) in Eq. 2.53 is conventionally replaced by \(J\). The selection rules for a rotational transition are \(\Delta J = \pm 1\).

### 2.4.4 Rovibrations

A significant number of rotational excited states are thermally populated at room temperature according to Eq. 2.54. The Boltzmann ratio for population of an excited rotational state becomes

\[
\frac{n_J}{n_0} = (2J + 1) \exp\left[ -\frac{\hbar^2 J(J+1)}{2I_k T} \right]
\]

For small \(J\), the \(2J + 1\) term
dominates and the ratio grows. At large \( J \), the exponential decay dominates and the ratio tails off. Since \( n_J / n_0 \) represents the thermally populated rotational states and \( \Delta J = \pm 1 \) transitions are possible, there is an entire rotational manifold superimposed on a vibrational transition. If \( \Delta J = +1 \), the transition line is part of the R-branch and the \( \Delta J = -1 \) lines are called the P-branch. The P and R branches of \( \text{CO}_2 \) are depicted in Fig. 2.5. The inverted parabolic trend of both branches is directly related to the thermally-populated rotational states at room temperature.

![CO₂ P & R branch](image)

Figure 2.5: P & R branch from \( \text{CO}_2 \) rovibrational transitions. Inverse parabolic behavior is a result of thermally populated rotational states at room temperature.

### 2.4.5 Mathematical models of spectral lines

As discussed above, the rovibrational frequencies depend on intramolecular interactions. The shape of the line, as discussed in this section, depends on intermolecular interactions. The total transmittance of an optical beam through a gas media is defined by the Beer-Lambert law of transmittance:

\[
\tau_\nu = \exp(-\kappa_\nu x) = \exp\left(-\frac{qP_x}{kT} \sigma_\nu\right)
\]

(2.58)
where $\kappa_\nu$ is the absorption coefficient, $q$ is the volume mixing ratio, $P$ is the total gas pressure, $k$ is the Boltzmann constant, $x$ is the path length, $T$ is the temperature, and $\sigma_\nu$ is the absorption cross section. The spectral-dependent line shape and intensity is contained in the cross section which does not depend on concentration or path length. The cross section is further divided into the line intensity, $S_{ij}$, and the line shape, $f(\nu)$.

Absorption spectrums of gases usually contain a few hundred lines. Each individual line occupies a certain width because of natural widths (uncertainty principle), Doppler broadening, and pressure broadening. Doppler broadening, which is due to thermal motion of gas molecules and results in a Gaussian line shape, is described by:

$$f_{\text{Dopp}}(\nu) = \sqrt{\frac{\ln(2)}{\pi \alpha_{\text{Dopp}}^2}} \exp\left[-\frac{(\nu - \nu_{c,ij})^2 \ln(2)}{\alpha_{\text{Dopp}}^2}\right]$$

(2.59a)

$$\alpha_{\text{Dopp}} = \frac{\nu_{c,ij}}{c} \sqrt{\frac{2N_A k T \ln(2)}{10^{-3} W_g}}$$

(2.59b)

where $\alpha_{\text{Dopp}}$ represents the Gaussian half-width, $\nu_{c,ij}$ is the line center, and $W_g$ is the molar mass. Pressure broadening is a result of collisions between molecules which give the line a Lorentzian shape described by:

$$f_{\text{Lorentz}}(\nu) = \frac{1}{\pi} \frac{\gamma}{\gamma^2 + (\nu - \nu_{c,ij})^2}$$

(2.60a)

$$\gamma = \left(\frac{296}{T}\right)^{n_{\text{air}}} (\gamma_{\text{air}}(P_{\text{total}} - P_{\text{partial}} + \gamma_{\text{self}} P_{\text{partial}}))$$

(2.60b)

which contains a term from collisions with other molecules present ($\gamma_{\text{air}}$) and a self-collision term ($\gamma_{\text{self}}$). Doppler broadening typically dominates below 0.01 atm and pressure broadening dominates above 0.1 atm. The Voigt profile is a convolution of the two broadening mechanisms and is the most accurate description of line shapes, but it
requires an algorithmic solution. The Voigt profile is solved as follows:

\[ f_{\text{Voigt}}(\nu) = \frac{\ln(2)}{\sqrt{\pi} \alpha_D} \cdot \text{Voigt}(x, y) \]  

(2.61a)

\[ \text{Voigt}(x, y) = K(x, y) + jL(x, y) \]  

(2.61b)

\[ K(x, y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-\nu^2)}{y^2 + (x - \nu)^2} d\nu \]  

(2.61c)

\[ L(x, y) = \frac{1}{\pi} \int_{-\infty}^{\infty} (x - \nu) \exp(-\nu^2) \frac{d\nu}{y^2 + (x - \nu)^2} \]  

(2.61d)

where \( x = \frac{\ln(2)(\nu - \nu_{c,ij})}{\alpha_D} \) and \( y = \frac{\ln(2)\gamma}{\alpha_D} \). HITRAN uses the Voigt profile which simplifies to a Gaussian lineshape at low pressures and a Lorentzian at high pressures.\(^{39}\)

The line intensity for a transition between two states in a single molecule can be calculated as:

\[ S_{ij} = \frac{A_{ij}}{8\pi cv_i^2} \cdot g' \exp\left(-\frac{h\nu''}{kT}\right)(1 - \exp\left(-\frac{h\nu_{ij}}{kT}\right)) \cdot \frac{Q(T)}{Q(296)} \cdot \frac{1 - \exp\left(-\frac{h\nu_{ij}}{kT}\right)}{1 - \exp\left(-\frac{h\nu_{ij}}{k(296)}\right)} \]  

(2.62)

where \( A_{ij} \) is the Einstein coefficient, \( g' \) is the statistical weight of the upper state, \( E'' \) is the energy of the lower state, and \( Q(T) \) is the total internal partition sum.

To modify the existing line shapes and intensities for arbitrary temperatures and pressures, the pressure-dependent line center and temperature-dependent intensity must be taken into account. The line center will shift under the influence of non-atmospheric pressures according to:

\[ \nu_{c,ij} = \nu_{c0,ij} + \delta_{\text{air}} P_{\text{tot}} \]  

(2.63)

where \( \delta_{\text{air}} \) is the pressure shift with respect to atmospheric pressure. The line intensity is also affected by temperature according to:

\[ S_{ij} = S_{0,ij} \left(\frac{Q_{296}}{Q_T}\right) \cdot \frac{\exp\left(-\frac{h\nu''}{kT}\right)}{\exp\left(-\frac{h\nu''}{k(296)}\right)} \cdot \frac{1 - \exp\left(-\frac{h\nu_{ij}}{kT}\right)}{1 - \exp\left(-\frac{h\nu_{ij}}{k(296)}\right)} \]  

(2.64)
Notice that the Doppler (2.59b) and pressure-broadened (2.60b) halfwidths already take temperature into account.

### 2.4.6 Kramers-Kronig relations

As shown in Sec. 2.1.2, taking the inverse fourier transform of a Gaussian distribution of frequencies returns a Gaussian temporal pulse. Beer’s law indicates that a small linewidth spectral amplitude will be attenuated after passing through an absorbing medium. However, taking the inverse Fourier transform of the resulting spectrum will break the rules of causality. The spectral frequencies affected by the absorption process must also undergo dispersion. This implies that absorption and dispersion must be affected conjointly. The Kramers-Kronig formulations describe the ability to calculate the real part of the index of refraction if the imaginary part is known or vice versa:

\[
\begin{align*}
n(\omega) &= 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \kappa(\omega')}{\omega'^2 - \omega^2} d\omega' \\
&= \frac{w\omega}{\pi} \int_0^\infty \frac{n(\omega') - 1}{\omega'^2 - \omega^2} d\omega'
\end{align*}
\]  

(2.65a)

(2.65b)

### 2.5 Optical free induction decay

Absorption processes become much less intuitive when the pulse width is shorter than the material’s natural excited state lifetimes. The macroscopic polarization, \( P(t) \), can completely disappear even when the individual dipoles continue to oscillate at their natural frequency. This is attributed to an interference effect when the dipoles start to dephase after the initial pulse has passed. This process was described mathematically by Allen et al.\(^\text{42}\) and is discussed in the following sections.

The polarization density of a dipole collection with density \( \rho \) driven by an external
field of frequency $\omega$ is represented as follows:

$$P(t) = \rho x_0 \int Re\{(u + jv) \exp(j\omega t)\} g(\Delta') d\Delta'$$ (2.66)

where $e$ is the electron charge, $x_0$ is the dipole amplitude, $u$ & $v$ are the in-phase and in-quadrature components from the Rabi resonance solution, $g(\Delta')$ is the lineshape detuning function, and $\Delta = \omega - \omega_0$. For a Lorentzian-shaped detuning function,

$$g(\Delta') = \frac{\delta \omega}{\pi} \frac{1}{(\Delta'-\Delta)^2 + \delta \omega^2}$$,

the macroscopic polarization density can be simplified to:

$$P(t) = \rho x_0 Re\{(u_0 + jv_0) \exp[j(\omega + \Delta)t]\} \exp(-\frac{t}{T}) \exp(-\delta \omega t)$$ (2.67)

which exhibits two different rates of decay. The first rate, $\exp(-\frac{t}{T})$, is the natural lifetime of the homogeneous linewidth. The second decay rate, $\exp(-\delta \omega t)$, is a result of dephasing between individual dipoles oscillating at all frequencies in the inhomogeneous linewidth. All these dipoles oscillate in phase under the influence of an applied field but begin to return to their natural frequencies after the pulse. The total relaxation rate of the system includes both the natural and dephasing lifetimes:

$$\gamma^{-1} = \frac{1}{T} + \frac{1}{T^*}$$ (2.68)

This behavior is a well-known phenomenon in nuclear magnetic resonance as free induction decay. The optical analogue of free induction decay was discovered by the pioneering work of Brewer and Shoemaker. OFID was experimentally observed by exciting a two-level system of $NH_2D$ molecules with a $CO_2$ laser and then Stark-shifting the molecular system to switch it off-resonance. The $NH_2D$ molecules continued to radiate at 10.6 $\mu m$ after the switch following a $P(t) \propto \exp(-\frac{t}{T}) \exp[-(\frac{1}{2\tau} + 4y^2)^{\frac{1}{2}}]t$ trend, consistent with Eq. 2.67.

The macroscopic polarization becomes a source term for electromagnetic radiation
in the wave equation:

\[
\left( \frac{\partial^2}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) E(t, z) = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} P(t, z)
\]  \hspace{1cm} (2.69)

The in-phase and quadrature behavior of the radiated electric field can be separated by using the previous definition of the macroscopic polarization density (Eq. 2.66) in conjunction with the slowly varying envelope approximation:

\[
\begin{align*}
[k^2 - k_0^2] \xi &= 2\pi k_0^2 \rho e x_0 \int u g(\Delta') d\Delta' \\
2[k \frac{\partial}{\partial z} + k_0 \frac{\partial}{\partial t}] \xi &= 2\pi k_0^2 \rho e x_0 \int v g(\Delta') d\Delta'
\end{align*}
\]  \hspace{1cm} (2.70a, 2.70b)

The slowly varying envelope approximation assumes that \( \frac{\partial \xi}{\partial z} << k \xi, \frac{\partial \xi}{\partial t} << \omega \xi, \) and \( \frac{\partial u}{\partial z} << ku. \) Letting \( t \) be much larger than the relaxation times of the dipole ensemble simplifies Eqns. 2.70a & 2.70b to simpler forms:

\[
k^2 - k_0^2 = k_0^2 \frac{\omega_p^2}{2\omega} \int \frac{\Delta' g(\Delta') d\Delta'}{\Delta'^2 + T^{-2}}
\]  \hspace{1cm} (2.71a)

\[
\frac{\partial \xi}{\partial z} = -\frac{1}{2} \alpha_c \xi
\]  \hspace{1cm} (2.71b)

where \( \omega_p \) is the plasma frequency of the dielectric and \( \alpha_c \) is the familiar absorption coefficient from Beer’s law, which follows the same inhomogeneous broadening curve of \( P(t) \):

\[
\alpha_c = \frac{\omega_p^2}{2cT} \int \frac{g(\Delta')}{\Delta'^2 + T^{-2}} d\Delta'
\]  \hspace{1cm} (2.72)

To extend this analysis to pulses that are shorter than the relaxation times of the dipole ensemble requires the definition of the pulse area theorem:

\[
A(t, z) = \kappa \int_{-\infty}^t \xi(t', z) dt'
\]  \hspace{1cm} (2.73)
where $\kappa = \frac{e}{m \omega x_0}$. It can be shown with the analysis in Ref.\textsuperscript{42} that the change in pulse area with distance traveled in the dipole ensemble for times between $T^*$ and $T$ can be represented as follows:

$$2k \frac{\partial A}{\partial z} = - \int v_0 g(\Delta') \frac{\Delta'^2}{\Delta'^2 + T^{-2}} \frac{\sin \Delta'(\bar{t} - t_0)}{\Delta'}$$  \hspace{1cm} (2.74)

This new propagation equation involves the same Beer’s law trend observed in the long $t$ approximation (Eq. \textsuperscript{2.71b}) multiplied by an additional sinc function. This sinc function forces the pulse area, $A(t, z)$, to have negative portions. Thus, the total area of the pulse (related to the envelope and electric field) can trend towards zero while the dipole ensemble may still have significant energy $\propto A(t, z)^2$. The exponential decay of the electric field still abides by Beer’s law ($A(\bar{t}, z) = A(\bar{t}, z_0) \exp\left(-\frac{1}{2} \alpha_c (z - z_0)\right)$), while the pulse energy does not have to follow such strict guidelines. The work of Crisp et al.\textsuperscript{44} extends the use of the pulse area theorem to anomalous absorption of dipole ensembles for ultrashort pulse widths shorter than the inhomogeneous dephasing time, $T^*$. The radiated light from the induced macroscopic polarization radiates $180^\circ$ out of phase with the incident pulse field.$^{28,42,44}$ The phenomenon is demonstrated qualitatively in Fig. 2.6. The results from Crisp et al.\textsuperscript{44} indicate that the pulse area can decay to almost nothing while the energy in the pulse can still be large.

The OFID process outlined above describes the coherent radiative response of molecules after stimulated absorption. The molecular ensemble will radiate as long as the macroscopic polarization remains finite which follows in the wake of the initial ultrashort excitation pulse. The behavior will be demonstrated in the experimental chapters of this dissertation (Chap. 3, Chap. 5, Appendix A, & Appendix B) as a decaying tail of radiation following the excitation pulse. The observed response is not a stimulated emission process.
Behavior of $\pi$-shifted OFID radiation interfering with the incident pulse. The pulse area oscillates between positive and negative values when the pulse width is shorter than $T^*$ (the dephasing rate) of a medium.
Chapter 3

Experimental

3.1 Lasers & wavelength conversion

A Coherent, Inc. Legend Elite Duo HE+ chirped pulse amplifier was used as the laser source for this dissertation. The Legend produces an output pulse train with 10 mJ pulse energy, 35 fs pulse width, 790 nm central wavelength, and a repetition rate of 1 kHz. The amplified pulse train feeds a Light Conversion TOPAS-Prime where the wavelength is converted through OPA and noncollinear DFG (see Sec. 2.2.3) processes. The DFG output wavelength is tunable throughout the mid-IR (3-10 µm) which enables the study of laser interaction with rovibrational absorption bands of different gasses.

3.1.1 Legend Elite Duo HE+ ultrafast amplifier

The amplifier is seeded by a Vitara-S modelocked oscillator that generates an 85 MHz femtosecond pulse train centered at 790 nm. The average power of the oscillator is 600 mW which yields a pulse energy of approximately 7.06 nJ. The seed pulses from the oscillator are stretched to a pulse width greater than 35 ps prior to amplification to prevent damage to the Ti:Sapphire crystal from Kerr self-focusing. The amplifier has two stages; a regenerative amplifier and a single pass amplifier. The Ti:Sapphire crystals in
each amplifier are pumped by a Q-switched, Nd:YLF diode laser that is frequency doubled to 527 nm in a temperature phase-matched Lithium Triborate (LBO) crystal. After the seed laser pulses are stretched, they enter the z-fold regenerative amplifier cavity as shown in Fig. 3.1. The seed has vertical (s) polarization and reflects off the Brewster window. Most of the pulses in the train will not end up contributing to the output.

If the Pockels cells are off, the polarization is rotated by 90° after passing through the QWP twice. The horizontally (p) polarized pulse will pass through the Brewster window and Ti:S, bounce off M4, and through the Ti:S again. On the second double-pass through the quarter waveplate (QWP), its polarization returns to vertical (s) and gets dumped from the cavity by the Brewster window. This path is demonstrated in Fig. 3.2. However, if PC1 is activated after the seed makes its first double-pass through it, the pulse will remain horizontally (p) polarized each time it makes a double-pass through the QWP-PC1 combination. The pulse gets amplified (called the build-up) inside the z-fold cavity until PC2 is fired which forces the pulse to become vertically (s) polarized out of the amplifier cavity and sent to M5 by the polarizer. While the amplified pulse continues to build inside the cavity, subsequent seed pulses are immediately rejected by the Brewster window because their polarization remains vertical (s) after a double-pass through the active PC1 and QWP combination. The complete timing scheme is illustrated in Fig. 3.3.

The output power of the regenerative amplifier is 6 W at a 1 kHz repetition rate which means the pulse energy has been amplified to 6 mJ (close to 10⁶ amplification). After the regenerative cavity, the pulse train is amplified up to 12 mJ after a single pass through another Ti:S crystal. The pulses are then compressed back to 35 fs. Energy is lost in the compression process and the final output is around 10 mJ.

### 3.1.2 HE-Topas-Prime optical parametric amplifier

Parametric amplification is a specific application of three-wave mixing (Sec. 2.2.3) in which a weak signal beam of photons is amplified by a much stronger pump inside a
Figure 3.1: Z-fold regenerative amplifier cavity in the Legend Elite Duo HE+, Coherent Inc. M1-M5: ultrafast mirrors, PC1,2: Pockels cells, QWP: quarter waveplate, I1,2: iris, BW: Brewster window, Ti:S: titanium sapphire crystal, PL: pump lens, P: polarizer, PD: photodiode. The green beam indicates the 527 nm pump and the red beam indicates the seed femtosecond pulse train from the oscillator. Figure reprinted from the Coherent Legend Elite Duo instruction manual with permission from Coherent.

Figure 3.2: Z-fold regenerative amplifier cavity in the Legend Elite Duo HE+, Coherent Inc. The z-fold path of all seed pulses is shown in red. The orange arrow indicates the dumping of most of the seed pulses off the Brewster window. The blue arrow indicates the dumping of a fully amplified single pulse from the train after PC2 has fired. Figure reprinted from the Coherent Legend Elite Duo instruction manual with permission from Coherent.
Figure 3.3: Timing scheme for regenerative amplification, pulse amplification buildup, and Pockels cell triggers. Figure reprinted from the Coherent Legend Elite Duo instruction manual with permission from Coherent.
nonlinear crystal. An idler beam is generated at the difference frequency during the process. Approximately 85% of the amplified pulse train is sent into the OPA where weak signal beams are generated by WLG (Sec. 2.3.2) in a sapphire crystal and then amplified in a series of type II Beta Barium Borate (BBO) crystals.\textsuperscript{45-48} Wavelength tunability is achieved by the temporal overlap of the WLG signal photons relative to the pump beam and in a BBO crystal and through control of the BBO crystal angle.\textsuperscript{48} The signal and idler beams are tunable between 1.2-1.6 $\mu$m and 1.6-2.4 $\mu$m, respectively, with maximum output pulse energies shown in Fig. 3.4.

![Graph showing OPA output pulse energy](image)

Figure 3.4: OPA output pulse energy.

### 3.1.3 Non-collinear difference frequency generator

In the NDFG, the signal and idler beams are split by a dichroic mirror and then recombined in a AgGaS$_2$ crystal (Eksma optics, AGS-801H).\textsuperscript{45,47,49,50} The difference frequency beam is tunable between 2.5-11 $\mu$m with pulse energies shown in Fig 3.5. Wavelength tunability is achieved by changing the signal and idler wavelengths in.
addition to controlling the AgGaS\textsubscript{2} angle. Mid-IR wavelength tunability out to 20 $\mu$m is possible in a GaSe crystal but fresnel reflections result in post-pulses with substantial contrast ratios compared to the main pulse. This occurs because GaSe cannot be coated with an anti-reflective coating. The post-pulses contaminate the cross-correlation measurements, so the AgGaS\textsubscript{2} crystal was used for the studies reported in this dissertation.

![Figure 3.5: DFG output pulse energy. Pulse energies could be higher but an OD 0.4 filter was used on the signal and idler prior to the DFG crystal to prevent damage in the AgGaS\textsubscript{2}. The filter is removed at 8.5 $\mu$m which accounts for the discontinuity in pulse energy.](image.png)

3.1.3.1 NDFG bandwidth from Light Conversion

As discussed in Sec. 2.1.2, the pulse bandwidth plays a major role in the temporal behavior of the pulse. Most groups utilize a monochromator and HgCdTe detector to characterize DFG bandwidth.\textsuperscript{47,49–51} Petrov et al. measured an increase in the bandwidth ($\Delta \lambda$) as the wavelength was increased. In this dissertation, spectral widths were interpolated from data provided by Light Conversion as shown in Fig. 3.6.
Figure 3.6: Interpolated mid-IR bandwidths from data provided by Light Conversion.

### 3.2 Pulse characterization: four-wave-mixing XFROG

XFROG was used to measure the temporal characteristics of the tunable mid-IR pulses. After passing through a cell that contained the gas analytes (see Sec. 3.4), the mid-IR beam was recombined with the remaining 1.5 mJ of the amplified pulse train in a Ge wedged window (ThorLABS, WW91050). The two collinear beams were focused by a 90° off-axis silver-coated parabolic mirror (ThorLABS, MPD169-P01) so that a filament was formed. Broadband FWM in a filament is efficient at all DFG wavelengths because of the self-group-phase-locking discussed in Sec. 2.3.3.2. The mid-IR waveform was obtained by delaying the reference (790 nm pump) pulse train, filtering out the longer wavelengths, and reading only the FWM beam spectrum with a spectrometer. The entire experimental configuration is shown in Fig. 3.7. Generated FWM wavelengths range between 410-470 nm depending on the mid-IR wavelength used. An example of a mid-IR pulse waveform obtained by FWM XFROG when the mid-IR pulse is unaffected during propagation is shown in Fig. 3.8.
Figure 3.7: Experimental Setup.

3.3 LabVIEW program

FWM XFROG data collection was automated by incorporating mid-IR wavelength tuning (OPA crystal rotation, WLG seed delay, DFG crystal rotation), reference (790 nm pump) beam delay, and spectrometer acquisition into a LabVIEW program. The interface allows the user to select the desired wavelengths to use, temporal scan range, temporal scan resolution, and spectrometer integration time. In this dissertation, the central wavelength was tuned between $\lambda_c = 3 - 10 \mu m$ by increments of $\Delta \lambda = 0.5 \mu m$. The scan ranges were arbitrarily set to cover a range of timescales in which molecular temporal signature phenomena occurred. The ranges chosen were 2 ps (2 fs resolution), 8 ps (8 fs resolution), and 50 ps (50 fs resolution). The delay motor was stopped for each spectral acquisition to ensure that the computer queue did not affect the timing resolution or repeatability.
Figure 3.8: Off-resonance XFROG example.

3.4 Gas cell/vapor generation system

Significant concentrations of $CO_2$ (399 ppmv\textsuperscript{52}) and $H_2O$ are present in the atmosphere. Their presence affect the experimental XFROG results. Controlled concentrations of $CH_4$, $CF_4$, and DMMP were introduced into the mid-IR beam propagation path by using a Ramé Hart environmental chamber (100-07). The cell was reconditioned with 180x2 mm ZnSe windows (Crystran ZNSEP18-2) and brass fittings for
pressure gauge and gas tank integration. Temperature was controlled between 25-130 °C.

### 3.4.1 Theoretical Antoine

DMMP is a low-volatility liquid at room temperature. A cuvette of liquid DMMP\(^1\) was placed inside the gas cell out of the beam path. Temperature was increased to 130 °C by 10 °C increments to produce a controlled amount of vapor pressure. The vapor pressure versus temperature curve is well-known in physical chemistry as the Antoine equation. The Antoine equation for DMMP is well-described by Butrow et al.\(^2\) from the U.S. Army Edgewood chemical and biological center (ECBC). The vapor pressures produced in this dissertation were monitored with the pressure gauge attached to the cell and are shown in Fig. 3.9. The measured pressure increase was decomposed into two components: the vaporized DMMP according to the Antoine equation and the ideal gas law contribution. The experimental vapor pressure trends were fit in the MATLAB curve fitting toolbox after subtracting the ideal gas law component as shown in Fig. 3.10. The nominal values of DMMP vapor pressure are used throughout the rest of this dissertation because of the verified experimental fit. Appendix C demonstrates how to convert these partial pressures to volume concentration and these concentrations are compared to the state-of-the art in detection limits in Chap. 7.

\(CH_4\) and \(CF_4\) were also used to pressurize the gas cell at matching vapor pressures of Fig. 3.9. Pressure gauge resolution and high flow rates limited the minimum repeatable gas pressure to 0.224 PSI. The described experimental pressure sequences are shown in Table 3.1.

Table 3.1: Nominal Antoine vapor pressures of DMMP. Pressures in red indicate the pressure sequence used for \(CH_4\) & \(CF_4\).

<table>
<thead>
<tr>
<th>25 °C</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0130 PSI</td>
<td>0.0228</td>
<td>0.0442</td>
<td>0.0815</td>
<td>0.144</td>
<td>0.244</td>
<td>0.400</td>
<td>0.635</td>
<td>0.979</td>
<td>1.47</td>
<td>2.16</td>
<td>3.10</td>
</tr>
</tbody>
</table>
Figure 3.9: Measured gas cell pressures for the temperature sequence used to produce DMMP vapors. A wet cell refers to a cuvette of liquid DMMP sealed inside the chamber. A dry cell refers to the control data set that follows the ideal gas law curve. Experimental data points are compared to theoretical trends from ECBC.
Figure 3.10: Individual Antoine equation fits for sampled experimental pressures after removing the ideal gas law component. The average of these fits agrees well with Butrow et al.²
3.5 XFROG results vs. wavelength

This section contains the experimental XFROG data as a function of wavelength while gas pressure was held constant. The central wavelength was started at $\lambda_c = 3 \mu m$ and increased by $\Delta \lambda_c = 0.5 \mu m$ until it reached a final central wavelength of $\lambda_c = 10 \mu m$. This caused the mid-IR femtosecond pulse to move in and out of spectral resonance with molecules along the propagation path. The contour plot data is normalized by dividing the raw data by the maximum saturation value of the spectrometer and then the logarithm (base 1.2) is taken. This is changed to a logarithm of base 10 when comparing experimental data with simulations in Chap. 4. The results are discussed qualitatively in this section. Quantitative explanations of the observed data with simulation results are the motivation of Chapter 4.

XFROG results for an atmospheric propagation path of 296.5 cm are shown in Figs. 3.11, 3.12, 3.13, & 3.14. Unique temporal features in the data can be seen in all of the timescales under study. The most prominent features showed up when the wavelength was on resonance with $CO_2$ (4-4.5 $\mu m$) and $H_2O$ (5-8.5 $\mu m$). Unique recurrences at approximately 18 & 25 ps delays (with respected to the initial pulse) in the 4.5 $\mu m$ plot of Fig. 3.11 agree with those observed by Lanin et al. who attributed the recurrences to the P & R branches of $CO_2$. Water vapor even had an affect on wavelengths that were off-resonance (i.e. 9.5-10 $\mu m$) because of the high atmospheric humidity and spectral overlap with the side-bands of the mid-IR pulses. The decaying beat pulses of the 10 $\mu m$ plots at smaller temporal delays (observed in Fig. 3.14) are indicative of third-order spectral phase which was discussed in Sec. 2.1.2. The $\varphi_3$ term is much larger at longer mid-IR wavelengths when taking into account the dispersion of the ZnSe and Ge windows.

The rationality of choosing to saturate the main femtosecond pulse when displaying the XFROG signals is demonstrated by Figs. 3.11 & 3.12. The contrast ratios of the $^{23} \mu m$ is effectively the beginning of the DFG tuning range.
Figure 3.11: 50 ps scan range experimental XFROG data through a 20 % RH atmosphere.
Figure 3.12: 50 ps scan range experimental XFROG data similar to above without saturating the main pulse. Choosing not to saturate the main pulse reduces the SNR.
Figure 3.13: 8 ps scan range experimental XFROG data through a 20 % RH atmosphere.
Figure 3.14: 2 ps scan range experimental XFROG data through a 40% RH atmosphere.
molecular-specific recurrences compared to the main pulse are on the order of 100-1,000. Saturating the main femtosecond pulse gives the best signal-to-noise ratio of the observed phenomenon at the expense of aesthetics. The pulses in Fig. 3.11 were exposed to the same propagation path as Fig. 3.12 but exhibit much more prominent features due to the increased SNR.\textsuperscript{3}

There are visible post-pulses at every wavelength in Fig. 3.11 at time delays of 7 & 35 ps. These are artifacts of the experimental design and do not contribute to the molecular-specific signal. The difference between measurement artifacts and the molecular-dependent data is the sensitivity to the change in wavelength. Molecule-induced pulse behavior changes as $\lambda_c$ is tuned in and out of absorption resonances while measurement artifacts remain at the same recurrence location in time.

XFROG results for $CH_4$ at 2.16 PSI are shown in Figs. 3.15,3.16, & 3.17. The greatest contrasts in pulse behavior between the $CH_4$ and atmospheric results are when $\lambda_c = 3 - 3.5 \mu m$ corresponding to the C-H stretching mode. Recurrences specific to $CH_4$ appeared at periodic intervals of 4 ps and decreased in amplitude with each succession. The behavior is observed in the 50 ps (Fig. 3.15) plot.

XFROG results for $CF_4$ at 2.16 PSI are shown in Figs. 3.18,3.19, & 3.20. According to the data, $CF_4$ appears to modify the temporal behavior of the pulse on a much shorter timescale than $CH_4$. Significant contrast between atmospheric data and $CF_4$ data can be seen in the 2 ps scan range plots (Figs. 3.14 & 3.20, respectively) at wavelengths between $\lambda_c = 6 - 10 \mu m$. The $CF_4$-specific behavior is superposed with an $H_2O$ background because of the overlap in spectral absorption of the two molecules.

XFROG results for DMMP at 2.16 PSI are shown in Figs. 3.21,3.22, & 3.23. The mid-IR wavelengths that are significantly affected by the presence of DMMP are $\lambda_c = 3.5 \mu m$ & $\lambda_c = 10 \mu m$. As discussed in Sec. 3.1.3.1, the bandwidth at $\lambda_c = 10 \mu m$ has a large $\delta \lambda$ that encompasses many rovibrational bands of DMMP so unique behavior is also observed for

\textsuperscript{3}The difference between the two plots is better experimental alignment that results in a higher FWM efficiency.
Figure 3.15: 50 ps scan range experimental XFROG data through an 8 cm path of 2.16 PSI $CH_4$ in addition to 288 cm atmosphere.
Figure 3.16: 8 ps scan range experimental XFROG data through an 8 cm path of 2.16 PSI $CH_4$ in addition to 288 cm atmosphere.
Figure 3.17: 2 ps scan range experimental XFROG data through an 8 cm path of 2.16 PSI $CH_4$ in addition to 288 cm atmosphere.
Figure 3.18: 50 ps scan range experimental XFROG data through an 8 cm path of 2.16 PSI $CF_4$ in addition to 288 cm atmosphere.
Figure 3.19: 8 ps scan range experimental XFROG data through an 8 cm path of 2.16 PSI $CF_4$ in addition to 288 cm atmosphere.
Figure 3.20: 2 ps scan range experimental XFROG data through an 8 cm path of 2.16 PSI CF₄ in addition to 288 cm atmosphere.
wavelengths other than 10 \( \mu m \). The distinctive features are most evident on the 2 ps (Fig. 3.23) and 8 ps (Fig. 3.22) timescales.

Experimental XFROG data from an empty 120 °C cell is shown in Fig. 3.24 to verify that the temporal propagation effects observed in Fig. 3.23 were a result of DMMP vapor and not just the temperature change. There is a clear distinction in the pulse propagation effects between a gas cell at room temperature versus elevated temperature. However, the pulse responses to DMMP vapor in Figs. 3.23 & 3.22 remain completely unique.
Figure 3.21: 50 ps scan range experimental XFROG data through an 8 cm path of 2.1597 PSI DMMP in addition to 288 cm atmosphere.
Figure 3.22: 8 ps scan range experimental XFROG data through an 8 cm path of 2.1597 PSI DMMP in addition to 288 cm atmosphere.
Figure 3.23: 2 ps scan range experimental XFROG data through an 8 cm path of 2.1597 PSI DMMP in addition to 288 cm atmosphere.
Figure 3.24: 2 ps scan range experimental XFROG data through an 8 cm path of 120°C atmosphere in addition to 288 cm atmosphere.
3.6 **XFROG results vs. partial pressure**

In the previous section, the mid-IR central wavelengths that provided the most unique XFROG response were identified for different gases. XFROG pulse measurements at these resonance wavelengths are plotted as a function of gas partial pressure in this section. The plots illustrate how the pulses behave as a function of concentration.

The resonance mid-IR wavelength of $CH_4$ is $\lambda_c = 3.5 \mu m$. XFROG results for those wavelengths versus $CH_4$ partial pressure are shown in Figs. 3.25 & 3.26, respectively. The periodic recurrences with 4 ps spacing that are visible in Figs. 3.15 are also present in Figs. 3.25 & 3.26. The amplitudes of the recurrences increase as the pressure increases.

Pulses measured after propagation through $CF_4$ were chemically cluttered by the presence and spectral overlap of $H_2O$ in the atmospheric absorption window. Since the pulse measurements were distorted in a broad range between 6-10 $\mu m$, the uncluttered 10 $\mu m$ wavelength is the easiest wavelength to see contrast between $CF_4$ and atmosphere XFROG data. However, Figs. 3.27 (8 ps) & 3.28 (2 ps) show the XFROG results versus $CF_4$ partial pressure at $\lambda_c = 8 \mu m$ to emphasize the unique pulse behavior despite the chemically-cluttered background. The contrast between low and high partial pressures are most-evident on the 2 ps timescale.

Pulses with $\lambda_c = 10 \mu m$ show the most unique response to DMMP. XFROG pulse measurements through DMMP vapor as a function of DMMP partial pressure are shown in Figs. 3.29 & 3.30. Unlike the peaks in the $CH_4$ data, the temporal peaks in the DMMP data seem to grow and then decay as vapor concentration increases. Subtle changes in the behavior are even observable for the smaller vapor pressures for the 2 ps scan range in Fig. 3.30. This observation is particularly useful for detection. The same measurements were performed with elevated temperature of an empty gas cell (no DMMP) to verify that the pulse response to DMMP is unique to the molecular vapor and
Figure 3.25: $\lambda_c = 3\mu m$ XFROG pulse measurements versus $CH_4$ partial pressure. 50 ps scan range.
Figure 3.26: $\lambda_c = 3.5 \, \mu m$ XFROG pulse measurements versus $CH_4$ partial pressure. 50 ps scan range.
Figure 3.27: $\lambda_c = 8 \mu m$ XFROG pulse measurements versus $CF_4$ partial pressure. 8 ps scan range.
Figure 3.28: $\lambda_c = 8 \mu m$ XFROG pulse measurements versus $CF_4$ partial pressure. 2 ps scan range.
not temperature. These results can be found in Appendix A Figs. A.20 & A.28.

3.7 Identifying unique XFROG signatures for chemical detection

The unique response of mid-IR femtosecond pulses to gas concentrations presented in this chapter can be used as an active signature. The novel signatures, or fingerprints, are explored in this dissertation as a possibility to supersede the industrial standards of standoff detection. The raw data must be transformed into a concentration prediction (regression) or species prediction (classification) in order to compete with the state-of-the-art in industry. This involves some matrix algebra concepts that will be investigated in Chap. 6. Chemical clutter provides a challenge to detection limits regardless of the signature used. Fig. 3.20 is a good example of chemical clutter for the temporal propagation signatures investigated in this dissertation. Competing signatures are present in the temporal pulse measurement because of the spectral overlap between $CF_4$ & $H_2O$. Chemical clutter is difficult to deconvolve and affects detection limits regardless of the detection signature used (femtosecond pulse propagation, absorption spectra, Raman lines, etc.).

One of the most critical parameters of the data presented thus far is the SNR. If the strength of the signal is low, certain features can easily be covered by the noise floor. The SNR is effectively dependent on the output FWM power which depends on both input beam peak powers, the overlap of the input beams at focus, and the nonlinear efficiency of the filament (Sec. 2.3.3.2). A more controllable parameter of the SNR is the spectrometer CCD integration times. Increased integration time leads to a higher SNR at the expense of a longer data acquisition time. Accurate regression and classification using matrix algebra (Chap. 6) requires a constant SNR or a normalization technique.

The rest of the collected XFROG data is shown in the appendix. In summary, the
Figure 3.29: $\lambda_c = 10 \, \mu m$ XFROG pulse measurements versus DMMP partial pressure. 8 ps scan range.
Figure 3.30: $\lambda_c = 10 \mu m$ XFROG pulse measurements versus DMMP partial pressure. 2 ps scan range.
data was an exploration of the gas signatures to be used in the proposed novel modality of standoff detection. The signatures of non-atmospheric molecules were shown for the first time. An in-depth analysis of the appendix data shows that the phenomenon is repeatable under constant propagation conditions but the magnitude of the signal is inconsistent due to changes in alignment and the lack of a normalization procedure. Inconsistent signal magnitudes cause problems in developing a trend of the data for regression. These issues are addressed in the Chap. 5 and the conclusion of this dissertation. Chapter 5 improves upon the XFROG pulse measurement technique of this chapter and contains data that is more repeatable.
Chapter 4

Simulation

The pioneering FWM XFROG work of Lanin et al. simulates the XFROG traces using analytical equations to represent the $\pi$-shifted polarization response of $CO_2$ and $H_2O$ with exponential decay curves similar to Eq. 2.67. They retrieve the complex index of refraction by computing the real and imaginary components of the Fourier transform of $E(z,t)$. The simulations performed in this dissertation were performed in a backwards manner compared to Lanin et al. The partial pressure-dependent imaginary part of the index, $\kappa$, was retrieved for the series of gases used in this dissertation from the HITRAN and NIST databases. Then, a Kramers-Kronig transformation was used to compute the real part of the index, $n$. After applying the plane wave propagation path $\propto \exp(jk_0\tilde{n}z)$, the inverse Fourier transform was taken using Eq. 2.9. This method of simulating OFID phenomena has been done many times in the literature to simulate OFID signals in THz time-domain spectroscopy experiments and near-IR ultrashort pulse propagation with exceptional accuracy. Harde et al. describe that the most accurate way of describing OFID is with the use of the Maxwell-Bloch equations but that the equations reduce to linear dispersion theory in the low intensity limit.

1Coddington et al. use a similar equation to simulate OFID in $H^{13}C^{14}N$ in an experiment involving frequency combs.
4.1 Modeling equations

Middle infrared pulse representation in the wavelength domain (Fig. 3.6) was converted to an angular frequency representation using $\omega_0 = \frac{2\pi c}{\lambda}$ and $\delta\omega = \frac{c\delta\lambda}{\lambda^2}$. Linear chirp was added to the equations to account for the dispersion through the ZnSe cell windows and Ge beam combiner. The wavelength-dependent second order phase term, $\varphi_2$, was interpreted from Tokmakoff’s reference of mid-IR dispersion in optical materials through 4 mm of ZnSe and 5 mm of Ge. The estimated values are shown in Table 4.1.2 Surprisingly, $\varphi_2$ through ZnSe becomes negative at longer mid-IR wavelengths and ends up compensating for some of the positive chirp effects in Ge. This indicates why the experimentally measured pulse lengths (Chap. 3) are shorter at longer mid-IR wavelengths. The spectral representation of the pulse was also modified by the three different path lengths prior to FWM: pre-cell ($z_1 = 200$ cm), cell ($z_2 = 8.5$ cm), and post-cell ($z_3 = 88$ cm):

$$E(\omega)_{out} = E(\omega)_0 \exp(jk_0\tilde{n}_{at}z_1) \exp(jk_0\tilde{n}_{cell}z_2) \exp(jk_0\tilde{n}_{at}z_3)$$ (4.1)

where $E(\omega)_0 = \exp[-2\ln(2)(\frac{\omega-\omega_0}{\delta\omega})^2] \exp[j\varphi_2(\omega-\omega_0)^2]$ and $\tilde{n} = n - j\kappa$. The transfer function (Eq. 4.1) models the interaction with gas molecules along the beam propagation path. Absorptive portions of the spectra undergo $\pi$ phase-shifts, dispersion, and interference to create a distorted signature waveform. The time-domain signature is attained by taking the inverse Fourier transform (Eq. 2.9) of Eq. 4.1 and a $\delta\lambda = 10$ nm bandwidth gaussian function is applied along the ordinate to represent the spectral content of the XFROG measurement.

The simulation results are extremely sensitive to the bandwidth, $\Delta\omega$, of the mid-IR pulse. As mentioned earlier (Sec. 3.1.3.1), spectral bandwidth in this dissertation was interpolated from the NDFG manufacturer data. The ramifications of using this $^2\varphi_3$ was not included in the simulations.
Table 4.1: Estimated values of the wavelength-dependent linear chirp, $\varphi_2$, through 4 mm ZnSe and 5 mm Ge.

<table>
<thead>
<tr>
<th>$\lambda_c$ ((\mu m))</th>
<th>$\varphi_2$</th>
<th>$\lambda_c$ ((\mu m))</th>
<th>$\varphi_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$60 \times 10^2 f s^2$</td>
<td>7</td>
<td>$12.5 \times 10^2 f s^2$</td>
</tr>
<tr>
<td>3.5</td>
<td>$60 \times 10^2 f s^2$</td>
<td>7.5</td>
<td>$5 \times 10^2 f s^2$</td>
</tr>
<tr>
<td>4</td>
<td>$50 \times 10^2 f s^2$</td>
<td>8</td>
<td>$-5 \times 10^2 f s^2$</td>
</tr>
<tr>
<td>4.5</td>
<td>$40 \times 10^2 f s^2$</td>
<td>8.5</td>
<td>$-10 \times 10^2 f s^2$</td>
</tr>
<tr>
<td>5</td>
<td>$37.5 \times 10^2 f s^2$</td>
<td>9</td>
<td>$-20 \times 10^2 f s^2$</td>
</tr>
<tr>
<td>5.5</td>
<td>$30 \times 10^2 f s^2$</td>
<td>9.5</td>
<td>$-27.5 \times 10^2 f s^2$</td>
</tr>
<tr>
<td>6</td>
<td>$25 \times 10^2 f s^2$</td>
<td>10</td>
<td>$-35 \times 10^2 f s^2$</td>
</tr>
<tr>
<td>6.5</td>
<td>$17.5 \times 10^2 f s^2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Approximation instead of measuring the bandwidth experimentally are discussed in detail in Appendix D. The largest source of error between experiment and simulation shown below can be explained by the error in approximating the spectral bandwidth of the simulation.

4.2 Kramers-Kronig transformation of HITRAN data

Spectral resolution of the frequency-domain representation is important for the simulation to accurately depict experimental results. Sufficient spectral resolution is obtained when all of the HITRAN data linewidths are accurately represented. A study of the spectral resolution is shown in Fig. 4.1, where the real part of the refractive index is computed from the Kramers-Kronig relations.

4.3 Model verification studies

Both simulation and experimental data are normalized. The experimental data is normalized by dividing the data by the maximum (saturation) value of spectrometer counts and the simulation is normalized by dividing the data by the maximum value after taking the inverse Fourier transform. The logarithm (base 10) is taken of both.
Figure 4.1: Study of the spectral resolution of HITRAN data and subsequent Kramers-Kronig transformation. (a) shows the entire HITRAN spectrum of a 50% relative humidity atmosphere. (b) is a close-up of the CO$_2$ P & R branches in the spectrum from (a). (c) shows the complex index of refraction for an individual peak at a 0.01 cm$^{-1}$ resolution, (d & e) show the same peak with 0.1 cm$^{-1}$ and 1 cm$^{-1}$ resolutions, respectively.

Experimental colorscales range from -3 (blue) to 0 (red). All simulation colorscales range from -5 (blue) to 0 (red).
4.3.1 CO₂ example

The simulation results for the CO₂ P and R branch using the resolutions defined in Fig. 4.1 are compared to the experimental XFROG data in Fig. 4.2 for a resonance mid-IR wavelength of $\lambda_c = 4.5 \mu m$. The study demonstrated that importing the HITRAN data with both 0.01 cm$^{-1}$ and 0.05 cm$^{-1}$ resolution was sufficient enough to give an accurate simulation of the experimental results. The rest of the simulations in this dissertation use a 0.01 cm$^{-1}$ resolution.

An important constraint in the experimental measurement is the noise floor. The noise floor is elucidated by decreasing the minimum value of the colorscale as shown in Fig. 4.3. Increasing the experimental SNR can prevent this loss of signature to the noise.

As discussed above and in Appendix D, error in the bandwidth can lead to misrepresentation of the measured XFROG signatures. A study on the effect that bandwidth has on the simulation results is shown in Fig. 4.4.⁴ Many groups use homemade mid-IR monochromators to alleviate this problem.²⁸,⁵⁰

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³More details found in Appendices D & E
Figure 4.2: (a) Experimental XFROG measurement compared to simulations using imported HITRAN data with (b-d) 0.01 cm$^{-1}$, 0.05 cm$^{-1}$, and 0.5 cm$^{-1}$ resolutions, respectively.

Figure 4.3: (a) Experimental XFROG data with colorscale reduced to show the noise floor. (b) The simulation does not have this noise. This demonstrates the missing information that is buried in the experimental noise floor.
Figure 4.4: (a) Experimental XFROG data of the $\lambda_c = 4.5 \mu m CO_2$ resonance. (b) Simulation using a $\delta \lambda$ of half the interpolated value of Fig. 3.6, (c) simulation using the interpolated value of $\delta \lambda$, and (d) simulation using twice the interpolated value of $\delta \lambda$. 
4.3.2 Lorentz decay

The inverse Fourier transform of a Lorentzian function is a decaying exponential with a decay rate that depends on the width of the spectral lines. A study of the pulse behavior in time as a function of Lorentzian half-width is shown in Fig. 4.5. The thicker (thinner) linewidths demonstrate a faster (slower) decay and narrower (broader) temporal peaks.

4.3.3 Five peak model

A model involving five equally distributed Lorentzian peaks was also used to provide insight into the temporal signatures of pulses through gas spectra of various shapes. The equation used to represent the five peak model is represented by:

$$\tilde{L} = A\frac{\Gamma}{(\omega - \omega_0)} - j\Gamma + 0.6A\frac{\Gamma}{(\omega - \omega_1)} - j\Gamma + 0.2A\frac{\Gamma}{(\omega - \omega_2)} - j\Gamma + 0.6A\frac{\Gamma}{(\omega - \omega_3)} - j\Gamma + 0.2A\frac{\Gamma}{(\omega - \omega_4)} - j\Gamma$$  (4.2)

where $A = 10^{-4}, \omega_1 = \omega_0 + \Delta \omega, \omega_2 = \omega_0 + 2\Delta \omega, \omega_3 = \omega_0 - \Delta \omega, \text{ and } \omega_4 = \omega_0 - 2\Delta \omega$.

The five peak model inverse Fourier transforms are studied as a function of Lorentzian linewidth (Fig. 4.6), Lorentzian spacing (Fig. 4.7), and what happens when the Lorentzian lines are only at the wings or center of the spectral representation of the ultrashort pulse (Fig. 4.8).
Figure 4.5: Lorentzian spectra (b,d,f) and inverse Fourier transforms (a,c,e). Lorentzian linewidths studied between (a,b): 0.01δλ, (c,d): 0.001δλ, (e,f): 0.0001δλ
Figure 4.6: Lorentzian linewidth study for the 5 peak model for different values of $\Gamma = (a,b) \frac{\Delta \lambda}{100}$, (c,d) $\frac{\Delta \lambda}{1000}$, and (e,f) $\frac{\Delta \lambda}{10000}$. (a,c,e) are the corresponding inverse Fourier transforms. Spacing held constant at $\Delta \lambda = 0.25 \mu m$. 
Figure 4.7: 5 peak model for different values of spacing between lines where $\Delta \lambda = (a,b)$ 0.15\(\mu\)m, (c,d) 0.25\(\mu\)m, and (e,f) 0.05\(\mu\)m. (a,c,e) are the corresponding inverse Fourier transforms. $\Gamma$ held constant at $\frac{\delta \lambda}{10,000}$. 
Figure 4.8: Study of the pulse behavior when the Lorentzian peaks are located at different locations of the pulse spectrum. $\Gamma = \frac{\delta \lambda}{10,000}$ for all peaks.
4.4 Experimental, simulation, spectra (ESS)

Figures containing the experiment, simulation, and spectra (ESS) are used to analyze the agreement between theoretical and experimental results in this section. The layout of an ESS figure is shown Fig. 4.9. Data normalization procedures and logarithmic colorscales are the same as discussed above. The following sections include ESS figures as a function of mid-IR central wavelength at fixed concentration and then as a function of concentration at fixed mid-IR central wavelength. The simulations are in good agreement with the experiments for the most part. Discrepancies between the two are most visible on the shorter (2 ps) timescale. The discrepancies arise from a combination of the mid-IR bandwidth (\(\delta \lambda\)) being an approximation, ignoring the temperature effects of the DMMP spectral lines (see Sec. 2.4.5), error in the interpretation of linear chirp values, or ignoring the nonlinear chirp (\(\phi_3\)) effects of the transmissive Ge and ZnSe optics in the system.

Figure 4.9: Example layout of an ESS figure using \(CH_4\) at 2.16 PSI, \(\lambda_c = 3.5 \mu m\), and a 50 ps scan range. The complex index of refraction inside the cell and outside the cell (atmosphere) are distinguished in the spectra plot.

The ESS figures are repeated in Appendix E for a simulation full-width at half-max (FWHM) scaled by 1.665 compared to the simulation FWHM used in this chapter. The reasoning for this scaling can be found in Appendix D. The larger bandwidth simulations do a better job of representing the experimental data of \(CF_4\) where there is major disagreement in this chapter. However, the larger bandwidth simulations of DMMP are
worse than shown in this chapter. This is most likely because AgGaS$_2$ stops transmitting at $\lambda > 11 \mu m$ which would cause the mid-IR spectrum to become non-Gaussian. In addition, the larger bandwidth results are worse for the $CH_4$ simulation because it appears to encompass the $CO_2$ signature in addition to the $CH_4$ signature. This indicates that the simulation bandwidth is too large because only the $CH_4$ signature is visible in the experimental data. While the studies of Appendices D & E aid in the discussion of simulation error in this dissertation, experimental measurement of the mid-IR spectra is needed.
Figure 4.10: ESS figure for atmosphere at 20% relative humidity. Scan range is 50 ps.
Figure 4.11: ESS figure for $CH_4$ at 2.16 PSI. Scan range is 50 ps.
Figure 4.12: ESS figure for $CF_4$ at 2.16 PSI. Scan range is 2 ps. There is a significant amount of error in this simulation that can be explained better by $\delta \omega = 1.665 \delta \omega$. See Appendix E.
Figure 4.13: ESS figure for DMMP at 2.16 PSI. Scan range is 8 ps.
Figure 4.14: ESS figure for DMMP at 2.16 PSI. Scan range is 2 ps.
Figure 4.15: ESS figure for $CH_4$ as a function of concentration. $\lambda_c = 3.5 \mu m$. Scan range is 50 ps.
Figure 4.16: ESS figure for $CF_4$ as a function of concentration. $\lambda_c = 8 \mu m$. Scan range is 2 ps. There is a significant amount of error in this simulation that can be explained better by $\delta \omega = 1.665 \delta \omega$. See Appendix E.
Figure 4.17: ESS figure for DMMP as a function of concentration. $\lambda_c = 10 \mu m$. Scan range is 8 ps.
Figure 4.18: ESS figure for DMMP as a function of concentration. $\lambda_c = 10 \mu m$. Scan range is 2 ps.
Chapter 5

Increasing sensitivity

In this chapter, an amplified silicon photodetector (Newport, 2001-FS-M) was used in place of the spectrometer that was used to measure the FWM spectrum in the XFROG scheme. The photodiode signal was fed into a lock-in amplifier (Ametek Signal Recovery 7270) for a phase-sensitive measurement. The lock-in cross-correlation (LICC) pulse measurements had a much higher SNR compared to the XFROG data and the repeatability of LICC measurements improved.\(^1\) In order to focus on the uniqueness of the DMMP signature compared to other molecules, LICC data was only collected at a mid-IR wavelength of \(\lambda_c = 10 \, \mu m\). In addition, the partial pressures are converted to pathlength-integrated volume concentrations, which is more typical when comparing detection limits.

5.1 Lock-in amplifier basics

A lock-in amplifier can be used to greatly enhance the SNR in an experiment. In this experiment, a reference signal and photodiode signal are fed into the lock-in amplifier. The reference signal is the 1 kHz square-wave from the back of the signal delay generator.

\(^1\)The improved repeatability was a result of more attention being paid to consistent experimental alignment and FWM efficiency.
box of the Legend Elite Duo. The photodiode signal is also at 1 kHz and can be approximated as a square wave with a small duty cycle. The Fourier series of the photodiode pulse train can be represented as:

\[
x(t) = \sum_{k=-\infty}^{+\infty} a_k \exp(jk\omega_0 t)
\]

where \(a_k\) follows a sinc function that is dependent on the duty cycle as seen in Fig. 5.1. The reference square wave is converted into an internal sine wave within the lock-in amplifier and is multiplied by one of the harmonics (Fourier coefficients) of the input photodiode signal, \(\omega_{sig}\). The first harmonic, \(a_1\), gives the largest voltage. After

---

Figure 5.1: Fourier coefficients of the photodiode pulse train approximated as a low duty cycle square wave.
multiplication:

\[ V_{out} = V_{sig}V_{ref}\sin(\omega_{sig}t + \theta_{sig})\sin(\omega_{ref}t + \theta_{ref}) \]
\[ = \frac{1}{2}V_{sig}V_{ref}\cos([\omega_{sig} - \omega_{ref}] + \theta_{sig} - \theta_{ref}) \]
\[ - \frac{1}{2}V_{sig}V_{ref}\cos([\omega_{sig} + \omega_{ref}]t + \theta_{sig} + \theta_{ref}) \quad (5.2) \]

and then a low pass filter is applied to get rid of the sum-frequency term. The difference frequency component of the output voltage is DC if the signal frequency matches the reference. High frequency noise is filtered out but the frequency-referenced signal is not. In addition, the reference phase can be tuned to match the signal frequency.

### 5.2 Comparing LICC data to previous XFROG data

A comparison between the LICC method and XFROG method is shown in Fig. 5.2.\(^2\) The LICC method has both a higher signal strength and lower noise floor. Small signatures from \(H_2O\) affect the side-bands of \(\lambda_c = 10 \mu m\) that were previously buried in the noise of the XFROG signature but are clearly visible using the new method.

### 5.3 LICC data versus concentration

All of the LICC data in this chapter is plotted against the same partial pressure sequences from Table 3.1 converted to pathlength-integrated volume concentrations which are shown in Table 5.1. The conversion mathematics are shown in Appendix C. An example of the LICC measurements for each species with \(\lambda_c = 10 \mu m\) is shown as a function of concentration in Figs. 5.3, 5.4, & 5.5. Subsequent LICC measurements of mid-IR laser pulses exposed to the exact same propagation conditions are shown as videos in Appendix B. The extra care taken to control the experimental alignment and

\(^2\)The XFROG measurement is cross-sectioned at the peak FWM wavelength to convert the frequency-resolved signature into a 2-D time-dependent signature for comparison with LICC
Figure 5.2: Optical signature comparison between XFROG (left-hand column) and lock-in cross-correlation (right-hand column) measurement methods for a mid-IR pulse with $\lambda_c = 10 \mu m$. Measurements are compared through 131 ppm-m DMMP for a (a,b,c,d) linear ordinate scale and and (e,f) logarithmic ordinate scale. The concentration is changed to 13,236 ppm-m for comparison of a high concentration (g) XFROG signature and (h) lock-in signature on a logarithmic ordinate scale.
signal strength is demonstrated by the repeatability of the LICC measurements. The results are much more consistent than the XFROG data.³

Table 5.1: Volume concentration sequence used for each vapor species.

<table>
<thead>
<tr>
<th>vapor</th>
<th>concentration (ppm-m)</th>
<th>LICC's per concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATM</td>
<td>17,286</td>
<td>5</td>
</tr>
<tr>
<td>CH₄</td>
<td>1,386 ; 2,309 ; 3,695 ; 5,658 ; 8,487 ; 12,470 ; 17,897</td>
<td>10</td>
</tr>
<tr>
<td>CF₄</td>
<td>1,386 ; 2,309 ; 3,695 ; 5,658 ; 8,487 ; 12,470 ; 17,897</td>
<td>10</td>
</tr>
<tr>
<td>DMMP</td>
<td>75.1 ; 131 ; 242 ; 437 ; 723 ; 1,204 ; 1,950 ; 3,034 ; 4,521 ; 6,604 ; 9,457 ; 13,236</td>
<td>10</td>
</tr>
</tbody>
</table>

³The XFROG results could have also been this consistent with more experimental alignment consistency.
Figure 5.3: LICC results for CH$_4$ at $\lambda_c = 10 \mu m$ versus concentration.
Figure 5.4: LICC results for CF$_4$ at $\lambda_c = 10 \mu m$ versus concentration.
Figure 5.5: LICC results for DMMP at $\lambda_c = 10 \mu m$ versus concentration.
Chapter 6

Detection & discrimination

The art of laser-based active standoff detection involves taking a laser signature and post-processing the raw data to produce an accurate species and/or concentration prediction. In the following sections, PCA and nonlinear regression techniques are applied to the LICC data to demonstrate a proof-of-concept for automated discrimination and quantitative DMMP concentration prediction.

6.1 Principal component analysis

PCA is a type of clustering method that discriminates between data samples when multiple variables are measured for each sample. To discriminate molecules based on their LICC signatures, the measured variables are the signal amplitude at each discrete point in time and the samples are the species at any given concentration. The matrix of data can be set up as follows:

\[
X = \begin{bmatrix}
  t_{1,8fs} & t_{1,16fs} & \cdots & t_{1,8ps} \\
  t_{2,8fs} & t_{2,16fs} & \cdots & t_{2,8ps} \\
  \vdots & \vdots & \ddots & \vdots \\
  t_{n,8fs} & t_{n,16fs} & \cdots & t_{n,8ps}
\end{bmatrix}
\]  

(6.1)
where \( n \) represents the number of samples, each row represents the raw LICC signature, and \( X \) contains the entire collection of LICC measurements. The total amount of LICC signatures collected in the dissertation is listed in Table 5.1 (the remaining signatures are shown in Appendix B). More explicitly, there were 135 LICC measurements used for training and 130 LICC measurements used for testing, as shown in Table 6.1. However, the largest discrimination with PCA will occur when the LICC signatures are most unique so the largest concentrations of each molecule were chosen for this example.

Since each LICC signature represents a new species, \( n \) in Eq. 6.1 is the 20 samples chosen (5 \( CH_4 \) measurements at 17,897 ppm-m, 5 \( CF_4 \) measurements at 17,897 ppm-m, 5 DMMP measurements at 13,236 ppm-m, and 5 atmospheric measurements). The principal components are found by taking the eigen decomposition of the covariance matrix, \( X^T X \). The eigen vectors (denoted by \( W \)) represent the principal components, or loadings, and the corresponding eigen value represents the amount of variance that each principal component explains in the data. The dimensionality of the original set of Eq. 6.1 can be reduced by matrix multiplication of the original data set with a subset of \( W \).

The variances represented by the first two principal components of the 20 LICC measurements mentioned above are 44.8% and 32.4%, respectively. Therefore, 
\[
T = X W_2,
\]
projects the original data (20x1,000) onto the first two principal components (1,000x2) to give a (20x2) matrix of principal component scores, \( T \). The scores can also be obtained for the testing data set, \( X_{test} \), which was not used in the process of finding \( W \). The 2-D PCA results for this example are shown in Fig. 6.1.
Figure 6.1: Discrimination of vapor species from the first two principal components of LICC measurement data at the highest vapor concentrations (17,897 ppm-m for \( CH_4, CF_4 \) and 13,236 ppm-m for DMMP).
Table 6.1: PCA matrix.

<table>
<thead>
<tr>
<th>species</th>
<th>conc. (ppm-m) of LICC (1x1,000)</th>
<th>ATM 20 % RH</th>
<th>DMMP (ppm-m)</th>
<th>training</th>
<th>testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATM</td>
<td></td>
<td>0</td>
<td>5</td>
<td>0</td>
<td></td>
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<tr>
<td>CH₄</td>
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<td>0</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,309</td>
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<tr>
<td></td>
<td>8,487</td>
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<td>5</td>
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<tr>
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<td>5</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
6.2 Linear least squares fit

In the case of TDLAS or Raman signatures, the signatures are linearly dependent on the concentration and respective cross-sections. One of the methods to turn linear absorption spectra into a predicted concentration is called a least squares fit (LSF). A LSF decomposition of an absorption spectrum containing multiple species is performed as follows: For the measured absorbance at an individual wavelength:

$$A_{\lambda_j} \propto S_{\lambda_j} P_{\lambda_j} \alpha_{\lambda_j} \quad (6.2)$$

where $S_{\lambda_j}$ is the photodiode sensitivity ($\frac{A}{W}$), $P_{\lambda_j}$ is the laser power, and $\alpha_{\lambda_j}$ is the total absorbance at an individual wavelength. The absorbance can be decomposed into individual contributions from each species present:

$$\alpha_{\lambda_j} = \sum_{i=1}^{\text{#species}} q_i \sigma_{i,\lambda_j} \quad (6.3)$$

where $\sigma = \frac{P_x}{kT} \sigma_v$ from Eq. 2.58. With these definitions, the total absorption spectrum is as follows:

$$\alpha = \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{bmatrix} = \begin{bmatrix} \sigma_{\lambda_1,1} & \sigma_{\lambda_1,2} & \cdots & \sigma_{\lambda_1,M} \\ \sigma_{\lambda_2,1} & \sigma_{\lambda_2,2} & \cdots & \sigma_{\lambda_2,M} \\ \vdots & \vdots & \ddots & \vdots \\ \sigma_{\lambda_N,1} & \sigma_{\lambda_N,2} & \cdots & \sigma_{\lambda_N,M} \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_M \end{bmatrix} + \begin{bmatrix} n_1 \\ n_2 \\ \vdots \\ n_M \end{bmatrix} \quad (6.4)$$

It can be shown that an approximation of the concentrations, $q$, of each species can be found by taking $(\sigma_{i,\lambda_j}^T \sigma_{i,\lambda_j})^{-1} \sigma_{i,\lambda_j}^T \alpha$. The LSF estimation of species concentrations from
the measured absorption spectra has a final form:

\[
\begin{bmatrix}
q_1 \\
q_2 \\
\vdots \\
q_M
\end{bmatrix} = 
\begin{bmatrix}
\sigma_{\lambda_1,1} & \sigma_{\lambda_2,1} & \cdots & \sigma_{\lambda_N,1} \\
\sigma_{\lambda_1,2} & \sigma_{\lambda_2,2} & \cdots & \sigma_{\lambda_N,2} \\
\vdots & \vdots & \ddots & \vdots \\
\sigma_{\lambda_1,M} & \sigma_{\lambda_2,M} & \cdots & \sigma_{\lambda_N,M}
\end{bmatrix}
\begin{bmatrix}
\sigma_{\lambda_1,1} & \sigma_{\lambda_2,1} & \cdots & \sigma_{\lambda_N,1} \\
\sigma_{\lambda_1,2} & \sigma_{\lambda_2,2} & \cdots & \sigma_{\lambda_N,2} \\
\vdots & \vdots & \ddots & \vdots \\
\sigma_{\lambda_1,M} & \sigma_{\lambda_2,M} & \cdots & \sigma_{\lambda_N,M}
\end{bmatrix}^{-1}
\begin{bmatrix}
\sigma_{\lambda_1,1},1 & \sigma_{\lambda_2,1},1 & \cdots & \sigma_{\lambda_N,1},1 \\
\sigma_{\lambda_1,2},1 & \sigma_{\lambda_2,2},1 & \cdots & \sigma_{\lambda_N,2},1 \\
\vdots & \vdots & \ddots & \vdots \\
\sigma_{\lambda_1,M},1 & \sigma_{\lambda_2,M},1 & \cdots & \sigma_{\lambda_N,M},1
\end{bmatrix}
\begin{bmatrix}
\alpha_1 \\
\alpha_2 \\
\vdots \\
\alpha_N
\end{bmatrix}
\]

(6.5)

Qualitatively, this means that the detection algorithms can deconvolve chemical clutter by taking into account the uniqueness of each signature across the entire spectrum. There are a few stipulations required to make the LSF approximation a good one. The number of wavelengths used (N) must be greater than the number of species predicted (M) so that the matrix is overdetermined. The main restriction is that \(\alpha\) is linearly dependent on the predicted variables \(q\).

### 6.3 Training a regression model

For the concentration prediction equation, Eq. 6.5, to work on the LICC data presented in Figs. 5.3, 5.4, & 5.5, the pulse amplitude at each discrete point in time must be a linear function with respect to concentration, \(q\). The LICC behavior with respect to \(q\) is clearly nonlinear since the peaks in the data rise, fall, and shift in time. Therefore, more complicated regression techniques were pursued using the MATLAB regression learner application. The application was run with the data from Appendix B represented compactly in Table 6.1. Linear regression models, regression trees, support vector machines, and Gaussian process regression models were studied to find the best fit to
the DMMP LICC data. The regression technique that predicted the concentration of DMMP with the lowest RMSE was the squared exponential Gaussian process regression model. The model pressure predictions for the training and testing data sets of Table 6.1 are shown in Fig. 6.2. PCA was used in conjunction with the regression model and the coefficients are shown in Fig. 6.3. Error in the PCA discriminant analysis and error in Figure 6.2: DMMP concentration predictions of LICC signatures using the trained squared exponential GPR model with (a) no PCA and (b) 5-component PCA. The first 135 predictions are on the training data set while the final 130 predictions are for the testing data set.

the Gaussian process regression model could be decreased by normalizing the data prior to supervised learning and by increasing the number of pulse measurement samples used in training. Reducing the prediction error is directly related to the sensitivity and selectivity of the detector. The implications of being able to predict an unknown concentration from a raw pulse signature alone are profound. A LabVIEW program can be written with the regression model embedded to predict concentration based on LICC measurements.
Figure 6.3: Principal component loadings used in the regression model to predict concentration from a LICC signature.
Chapter 7

Comparing to industry standards

This dissertation has reported molecular vapor-sensitive ultrashort mid-IR pulse propagation signatures that have never been shown before. This chapter analyzes the merit of the idea to use these signatures for detection.

7.1 Exposure limits

The proposed standoff detection modality in this dissertation has focused on gas- and vapor-phase analytes with DMMP as the primary target. Since DMMP is used as a sarin simulant, knowledge of sarin toxicity is required because the detection limits have to be lower than the harmful exposure limits. A standard merit for dosage is the $\text{LC}_{t_{50}}$ value which is the lethal (L) concentration (C) that will kill 50% of those exposed for a time (t). The units of $\text{LC}_{t_{50}}$ are typically represented by $\frac{mg}{m^3} \cdot min$ but $ppm \cdot min$ could be used. The IDLH level is defined as the minimum concentration at which a person will undergo permanent adverse health effects after 30 minute exposure. The IDLH and $\text{LC}_{t_{50}}$ levels of sarin (GB) are 30 $ppb$ and 100 $\frac{mg}{m^3} \cdot min$ (equivalently 17.5 $ppm \cdot min$), respectively. Detection limits below the IDLH and $\text{LC}_{t_{50}}$ levels are desirable to keep civilians and military personnel safe.
7.2 State-of-the-art: Block engineering

The LOD’s for the previously described (Chap. 1) LaserWarn standoff detection system manufactured by Block engineering are used as an example to compare with the proposed LICC system.\textsuperscript{6,10–12} Their detection limits are typically defined for very long pathlengths up to 250 m which would increase the total absorbance by close to three orders of magnitude compared to the 8 cm cell used in this dissertation. Block’s LOD’s\textsuperscript{10} are shown in Table 7.1 along with some calculations to relate their numbers to the pressures used in previous chapters (see Appendix C).

Table 7.1: LOD’s for Block engineering’s LaserWarn open-path standoff detection system.\textsuperscript{6,10–12} Values in \textcolor{blue}{blue} indicate calculations to match the pathlength of a Herriott cell. Values in \textcolor{red}{red} indicate calculations to match the 8 cm gas cell used in this dissertation.

<table>
<thead>
<tr>
<th>chemical</th>
<th>LOD (ppb)</th>
<th>distance (m)</th>
<th>LOD @ 10.4 m (ppb)</th>
<th>LOD @ 10.4 m (PSI)</th>
<th>LOD @ 8 cm (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>65</td>
<td>250</td>
<td>1,513</td>
<td>2.22·10$^{-5}$</td>
<td>0.000289</td>
</tr>
<tr>
<td>Sarin</td>
<td>26</td>
<td>100</td>
<td>250</td>
<td>3.67·10$^{-6}$</td>
<td>0.000478</td>
</tr>
</tbody>
</table>

7.3 How does the proposed LICC detector compare?

The LICC detector proposed in this dissertation still has complications that need to be overcome in comparison to successful industrial products. The sensitivity, response time, cost, weight, and ruggedness all need to be considered as the technology readiness level shifts from basic research to feasibility analysis. The LOD was not defined for the proposed LICC detector but preliminary work on quantitative prediction and qualitative classification demonstrated that LICC signatures need to be studied at lower concentrations. The response time of the LICC acquisition needs to be substantially improved. The current response time is close to four minutes due to the stopping and starting of the motor for the acquisition at each discrete time delay. This is compared to the real-time (2 sec) response time of the LaserWarn system. In addition, the cost and
size of the ultrafast mid-IR laser source used in this work is prohibitively large and is not designed to handle rugged conditions or mechanical shock. Solutions to these problems are offered in the conclusion.
Chapter 8

Conclusion

8.1 Future work

8.1.1 Normalize signal power

The most important improvement that could be made to the prediction accuracy of the regression model is to implement a normalization procedure as discussed in previous chapters. Fluctuations in overall signal strength that are independent of gas concentration lead to error in the supervised learning process. A normalization procedure can account for these day-to-day changes in overall signal amplitude. Measuring the initial FWM pulse with a photodiode prior to the introduction of gas is a possible solution for an accurate calibration technique. An optical density filter would need to be used to keep the detector from being saturated by the fundamental pulse signal during the calibration steps.

8.1.2 Increase the signal-to-noise ratio

The experimental noise floor can limit the observable signal as demonstrated in Chapter 5. There is still room to reduce the noise in the lock-in amplifier signal because the photodetector is silicon-based. Silicon has a higher responsivity at 790 nm (0.35 A/W)
than 410 nm (0.125 A/W). Shortpass cutoff filters were used in front of the detector to attenuate the fundamental beam but it was still affecting the measurement.\(^1\) SNR could be further improved by using a GaP photodiode which is unresponsive to wavelengths longer than 550 nm and has a peak responsivity at 400 nm.

The signal amplitude could also be improved by a couple of other methods. The FWM efficiency was not studied in detail in this dissertation. However, Théberge et al. observed close to 30 % FWM efficiency inside the filament. The FWM efficiency could be optimized by choice of focal length and polarization. The Ge optic used to make the mid-IR and fundamental beams collinear is not ideal because of the relatively low (33 %) reflectivity at the fundamental beam wavelength. A custom dichroic mirror would improve the final FWM energy.

### 8.1.3 Background subtraction

It was shown in the LICC data that chemical clutter from \(H_2O\) in the atmosphere can affect the \(\lambda_c = 10 \mu m\) pulse measurements. The wings of the large bandwidth 10 \(\mu m\) pulse extend into the water absorption window even though the central wavelength is in the atmospheric transmission window. As a result, the regression model builds principal component coefficients that have to fit the chemical clutter. A background subtraction could focus the principal component coefficients on the concentration dependent signature and not the chemical clutter. An example of a background subtracted LICC DMMP data set is shown in Fig. 8.1.

---

\(^1\)A finite signal was observed on the lock-in amplifier if the laser shutter was open and a beam block was used to block the fundamental beam far from the photodetector. The signal was substantially attenuated when the laser shutter was closed. Therefore, the photodiode is still measuring some scattering from around the room that contributes to the noise floor.
Figure 8.1: DMMP LICC data at $\lambda_c = 10 \mu m$ with background subtracted in reference to the room temperature vapor pressure scan. 8 ps scan range.
8.1.4 Use of the entire surface plot data for regression

There are certain signatures in the XFROG data (Chap. 3) where distinct temporal signatures show up at two or more FWM wavelengths. For example, consider the red-shifted tail to the left of the 3.1008 PSI signature of DMMP in Fig. 3.30. This behavior could be a result of the pulse being chirped or it could actually be a unique fingerprint of DMMP. Incorporating the extra dimension into a regression model could be challenging but helpful if future signatures are observed with spectral uniqueness in addition to temporal uniqueness.

8.1.5 Multi-wavelength regression

Regression techniques were applied to the $\lambda_c = 10 \mu m$ data in this dissertation. However, other wavelengths demonstrate molecular signatures as well. Both 10 and 3.5 $\mu m$ show unique behavior in response to DMMP as was shown in Fig. 3.30. A statistical approach using more mid-IR $\lambda_c$’s could be used to improve the prediction accuracy of the regression model.

8.1.6 Improved detector response time

An idea to improve the time that each pulse measurement takes is to constantly acquire spectra/photodiode signals as the delay stage moves at a constant velocity. This is called the velocity XFROG scheme. The XFROG/LICC data could be recreated with a temporal resolution of $\Delta t = \frac{\Delta x}{c} = \frac{v_{\text{stage}} t_{\text{integration}}}{c}$ where $v_{\text{stage}}$ is the motor velocity and $t_{\text{integration}}$ is the detector integration time. The computer queue and stack would need to be overridden in the LabVIEW program in this scenario to eliminate possible timing errors associated with the computer processor that are not related to the data collection.

Another idea to improve the pulse measurement rate is similar to a single-shot FROG. A single-shot FROG uses a line-focus and angled pulse geometrical overlap in the
nonlinear crystal to replace the mechanical delay stage. The idea for a single-shot cross-correlation would be to angle the mid-IR beam into a line-focused fundamental beam. The temporal dependence of the distorted mid-IR pulse would be converted to a spatial dependence of the generated FWM beam and read out by a CCD camera. This idea is dependent on filament FWM being possible in a slightly non-collinear geometry. Otherwise, a crystal that satisfies the phase-matching conditions would have to be used.

8.1.7 System miniaturization

Surface plasmon designs have been used in recent literature to enhance nonlinear optical interactions. Zhang et al. demonstrated an enhancement of optical parametric amplification experimentally with $\text{BaTiO}_3 – \text{Au – SiO}_2$ nanoparticle complexes. These advancements could replace tabletop sources used in the lab with something much smaller. This could potentially decrease costs, weight and improve robustness.

8.1.8 Uniqueness compared to other large molecules

A constraint to the proposed detection modality is the uniqueness of each molecular signature as more molecules are added to the library. It was demonstrated in Chapter 4 how molecules with large linewidths have shorter signatures. If other large molecules have signature behavior similar to DMMP, the detection method could have selectivity issues. Pursuit of the ideas outlined in this future works section could lead to better control of the signatures and higher-resolution analysis when comparing molecules with similar signatures. The infrared spectra of molecules have many overlapping features but the phenomenon has lead to successful standoff detectors. Therefore, the proposed detection modality is promising.
8.2 Concluding remarks

The propagation effects of ultrashort mid-IR laser pulses through non-atmospheric molecules was demonstrated for the first time. Higher signal-to-noise ratios were achieved by modifying the XFROG approach developed by Lanin et al.\textsuperscript{28} to a cross-correlation technique using a lock-in amplifier. The signatures obtained using this technique displayed a nonlinear behavior versus concentration which eliminated the use of the LSF technique. Instead, the signatures were calibrated using supervised learning of a gaussian process regression model with principal component analysis. The molecular concentrations used in this dissertation were not low enough to meet IDLH standards for CWA detection. Suggestions for equipment improvement and studies that could improve the sensitivity of the proposed standoff detection method were discussed. Unique ultrashort optical signatures were demonstrated for $CH_4$, $CF_4$, and DMMP.
References


Block Engineering. Wide Area Detection of Chemical Threats.


Yingqiang Zhao, Junhui He, Mingqing Yang, Shi Gao, Guomin Zuo, Chunxiao Yan, and Zhenxing Cheng. Single crystal WO(3) nanoflakes as quartz crystal


Appendix A

XFROG repeatability

This section contains all of the XFROG data collected in this dissertation as a collection of videos versus increasing partial pressure. Each frame contains XFROG experimental data versus all wavelengths (3 – 10 µm) at a particular concentration. The frame rate is 1 Hz.
50 ps: Atmosphere

Figure A.1: 50 ps scan range atmospheric data set 1.
Figure A.2: 50 ps scan range atmospheric data set 2.
50 ps: Atmosphere

Figure A.3: 50 ps scan range atmospheric data set 3.
Figure A.4: 50 ps scan range atmospheric data set 4.
Figure A.5: 50 ps scan range atmospheric data set 5.
**50 ps:** $CH_4$

**Figure A.6:** 50 ps scan range $CH_4$ data set 1. Linked to video: (CH4-8-23-50psVID.wmv, 1.036 MB)
Figure A.7: 50 ps scan range $CH_4$ data set 2. Linked to video: (CH4-12-17-50psVID.wmv, 1.176 MB)
Figure A.8: 50 ps scan range $CF_4$ data set 1. Linked to video: (CF4-12-20-50psVID.wmv, 1.037 MB)
Figure A.9: 50 ps scan range $CF_4$ data set 2. Linked to video: (CF4-12-26-50psVID.wmv, 1.197 MB)
Figure A.10: 50 ps scan range DMMP data set 1. Linked to video: (DMMP-9-14-50psVID.wmv, 1.762 MB)
Figure A.11: 50 ps scan range DMMP data set 2. Linked to video: (DMMP-10-29-50psVID.wmv, 2.801 MB)
50 ps: Ideal Gas Law

Figure A.12: 50 ps scan range ideal gas law. Linked to video: (IGL-50psVID.wmv, 1.941 MB)
8 ps: Atmosphere

Figure A.13: 8 ps scan range atmospheric data set.
8 ps: $CH_4$

Figure A.14: 8 ps scan range $CH_4$ data set. Linked to video: (CH4-12-13-8psVID.wmv, 1.636 MB)
Figure A.15: 8 ps scan range $CF_4$ data set. Linked to video: (CF4-12-19-8psVID.wmv, 1.476 MB)
Figure A.16: 8 ps scan range DMMP data set 1. Linked to video: (DMMP-9-11-8psVID.wmv, 2.201 MB)
Figure A.17: 8 ps scan range DMMP data set 2. Linked to video: (DMMP-10-01-8psVID.wmv, 2.261 MB)
Figure A.18: 8 ps scan range DMMP data set 3. Linked to video: (DMMP-10-08-8psVID.wmv, 3.101 MB)
Figure A.19: 8 ps scan range DMMP data set 4. Linked to video: (DMMP-10-22-8psVID.wmv, 2.881 MB)
Figure A.20: 8 ps scan range Ideal Gas Law data set. Linked to video: (IGL-8psVID.wmv, 2.341 MB)
2 ps: Atmosphere

Figure A.21: 2 ps scan range atmospheric data set.
2 ps: $CH_4$

Figure A.22: 2 ps scan range $CH_4$ data set. Linked to video: (CH4-12-18-2psVID.wmv, 1.377 MB)
2 ps: \( CF_4 \)

Figure A.23: 2 ps scan range \( CF_4 \) data set. Linked to video: (CF4-12-19-2psVID.wmv, 1.796 MB)
Figure A.24: 2 ps scan range DMMP data set 1. Linked to video: (DMMP-920-2psVID.wmv, 2.641 MB)
Figure A.25: 2 ps scan range DMMP data set 2. Linked to video: (DMMP-9-20(2)-2psVID.wmv, 2.481 MB)
Figure A.26: 2 ps scan range DMMP data set 3. Linked to video: (DMMP-10-09-2psVID.wmv, 3.221 MB)
Figure A.27: 2 ps scan range DMMP data set 4. Linked to video: (DMMP-10-23-2psVID.wmv, 3.221 MB)
2 ps: Ideal Gas Law

Figure A.28: 2 ps scan range Ideal Gas Law data set. Linked to video: (IGL-2psVID.wmv, 2.641 MB)
Appendix B

LICC repeatability

This section contains all of the LICC data of Chapter 5. The mid-IR wavelength is fixed at $\lambda_c = 10 \, \mu m$, the scan range is 8 ps, and each plot contains the LICC pulse measurement as a function of partial pressure. Each subsequent figure is a repeated measurement to monitor repeatability of the data. The first figure for each molecule is hyperlinked to a video containing increased concentration at each frame. Changes in $CF_4$ signatures at high concentrations are most likely due to slight pressure leaks in the gas cell that reduced the $CF_4$ partial pressure. This was a non-issue with DMMP because any slight loss in pressure was replaced by new vapor from the cuvette.
Figure B.1: \( CH_4 \) LICC training data set 1. \( \lambda_c = 10\ \mu m \). 8 ps scan range. Linked to video: (CH4log.wmv, 1.859 MB)
Figure B.2: \( \text{CH}_4 \) LICC training data set 2. \( \lambda_c = 10 \mu \text{m} \). 8 ps scan range.
Figure B.3: $CH_4$ LICC training data set 3. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.4: $CH_4$ LICC training data set 4. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.5: $CH_4$ LICC training data set 5. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.6: $CH_4$ LICC predicting data set 1. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.7: $CH_4\ \text{LICC predicting data set 2. } \lambda_c = 10\ \mu m.\ \text{8 ps scan range.}$
Figure B.8: $CH_4$ LICC predicting data set 3. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.9: $CH_4$ LICC predicting data set 4. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.10: $CH_4$ LICC predicting data set 5. $\lambda_c = 10\, \mu m$. 8 ps scan range.
Figure B.11: $CF_4$ LICC training data set 1. $\lambda_c = 10 \mu m$. 8 ps scan range. Linked to video: (CF4log.wmv, 1.879 MB)
Figure B.12: $CF_4$ LICC training data set 2. $\lambda_c = 10 \, \mu m$. 8 ps scan range.
Figure B.13: $CF_4$ LICC training data set 3. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.14: $CF_4$ LICC training data set 4. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.15: $CF_4$ LICC training data set 5. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.16: $CF_4$ LICC predicting data set 1. $\lambda_c = 10 \, \mu m$. 8 ps scan range.
Figure B.17: \( CF_4 \) LICC predicting data set 2. \( \lambda_c = 10 \mu m \). 8 ps scan range.
Figure B.18: $CF_4$ LICC predicting data set 3. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.19: $CF_4$ LICC predicting data set 4. $\lambda_c = 10 \, \mu m$. 8 ps scan range.
Figure B.20: $CF_4$ LICCC predicting data set 5. $\lambda_c = 10 \, \mu m$. 8 ps scan range.
DMMP sets 1-10

Figure B.21: DMMP LICC training data set 1. $\lambda_c = 10 \mu m$. 8 ps scan range. Linked to video: (DMMPlog.wmv, 1.939 MB)
Figure B.22: DMMP LICC training data set 2. $\lambda_c = 10 \, \mu m$. 8 ps scan range.
Figure B.23: DMMP LICC training data set 3. $\lambda_c = 10 \mu m$, 8 ps scan range.
Figure B.24: DMMP LICC training data set 4. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.25: DMMP LICC training data set 5. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.26: DMMP LICC predicting data set 1. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.27: DMMP LICC predicting data set 2. $\lambda_c = 10\,\mu m$. 8 ps scan range.
Figure B.28: DMMP LICC predicting data set 3. $\lambda_c = 10\, \mu m$. 8 ps scan range.
Figure B.29: DMMP LICC predicting data set 4. $\lambda_c = 10 \mu m$. 8 ps scan range.
Figure B.30: DMMP LICC predicting data set 5. $\lambda_c = 10 \, \mu m$. 8 ps scan range.
Appendix C

Volume mixing ratio calculations

C.1 What is ppmv?

Consider a gas mixture at fixed temperature, pressure, and volume. The volumetric concentration of any component in a gas mixture is the ratio of volume occupied by that component to the total volume:

\[
\frac{V_{\text{partial}}}{V_{\text{total}}} = \frac{n_{\text{par}}RT}{P_{\text{tot}}} = \frac{n_{\text{par}}}{n_{\text{tot}}} = \frac{P_{\text{par}}V}{P_{\text{tot}}V} = \frac{P_{\text{par}}}{P_{\text{tot}}} \quad (C.1)
\]

Therefore, the volumetric concentration is equivalent to the molar ratio and the pressure ratio of the gas component to the total mixture.

C.2 Observable pressure

The experimental observable of the vapor pressure in this dissertation is the pressure gauge reading attached to the fixed volume gas cell. The partial pressure of the gas introduced to the cell via vaporization (from the liquid cuvette) or via the valve inlet
is represented as:

\[ P_{\text{partial}} = P_{\text{total}} - P_{\text{air}} = P_{\text{measured}} - (1 \text{ atm}) \frac{T_2}{T_1} = P_{\text{measured}} - (14.70 \text{ PSI}) \frac{T_2}{T_1} \]  \hspace{1cm} (C.2)

which is the difference between the measured total pressure and the ideal gas temperature increase of the atmosphere (N\(_2\), O\(_2\), H\(_2\)O, CO\(_2\), etc.).

### C.3 Calculation of ppmv for \(CH_4\), \(CF_4\), and DMMP for this dissertation

Since the DMMP partial pressures are vaporized at temperatures greater than 298 K, the partial pressure ratio of Eq. C.1 cannot be used to calculate ppmv. Instead, the molar volume must be considered. An example from Sun et al.’s "Detection Technologies for Chemical Warfare Agents and Toxic Vapors" is used for clarification. The example calculates the ppmv from 1.33 \(\frac{mg}{m^3}\) of Tabun (GA) at standard temperature and pressure:

\[
\text{Concentration (ppmv)} = \frac{\text{Molarity}_{\text{GA}}}{\text{Molarity}_{\text{air}}} \times \frac{8.205 \times 10^{-5} \text{ m}^3\text{-atm}}{\text{mol-K}} \left(298K\right) \frac{1 \text{ atm}}{\text{mol}} \]

\[
= 8.20 \times 10^{-6} \frac{\text{mol}}{m^3} \frac{1m^3}{40.9\text{mol}}
\]

\[
= 2 \times 10^{-6}
\]

\[
= 0.2 \text{ppm}
\]

Therefore, the Molarity (\(\frac{\text{mol}}{m^3}\)) is calculated for each vapor in the sequence of Table 3.1 and then divided by the Molarity of air at standard temperature and pressure to obtain the ppmv sequences of Table 5.1. Note that standard temperature and pressure are used to represent the concentrations because that resembles a realistic detection scenario. Even though the concentration (ppmv) is different inside the gas cell at elevated temperature,
the Molarity is constant. The Molarity is what affects the absorption coefficient, $\kappa_\nu$, in Eq. 2.58. Even though the measured partial pressure of DMMP was the same as for the other gases, the molarity (and thus concentration) was lower because the temperature was elevated. Here is an example for the concentration calculation of 2.16 PSI DMMP vaporized at 120°C:

$$Concentration(\text{ppmv}) = \frac{2.16 \text{ PSI} \times 0.068 \frac{\text{atm}}{\text{PSI}}}{0.0821 \frac{\text{L-atm}}{\text{mol-K}} (393.15 \text{K})} = 0.00428 \frac{\text{mol}}{\text{L}}$$

$$\times \frac{0.00456 \frac{\text{mol}}{\text{L}}}{0.0821 \frac{\text{L-atm}}{\text{mol-K}} (298.15 \text{K})} \times \frac{1 \text{atm}}{1 \text{atm}} = 0.105 \text{ ppmv}.$$

The pathlength-integrated concentration of 2.16 PSI DMMP at standard temperature and pressure is 111,620 ppm $\times$ 0.085 m $= 9,487$ ppm-m.
Appendix D

Optimizing NDFG spectral bandwidth in the simulation

Light Conversion has provided some data on the spectral width of the NDFG based on a 35 fs fundamental beam seeding the OPA. The spectral width could be represented as the FWHM or as the \( \frac{1}{e^2} \) width and could be used to represent either the intensity or electric field widths. Using the wrong representation could cause substantial error in the simulation results.

The simulation represents the spectral electric field using \( \delta \lambda = \lambda^2 \delta (cm^{-1}) \) or \( \delta \omega = 2\pi c \delta (cm^{-1}) = 2\pi c \frac{\delta \lambda}{\lambda} \) as the FWHM. If the spectral width is defined by Light Conversion from intensity measurements, the Gaussian representation of spectral intensity is \( I(\omega) = |E_0|^2 \exp((-4\ln(2)) \left(\frac{\omega-\omega_0}{\omega_{FWHM}}\right)^2) = |E_0|^2 \exp((-2.76(\frac{\omega-\omega_0}{\omega_{FWHM}})^2)) \). The Gaussian representation of a spectral electric field is \( E(\omega) = \sqrt{I(\omega)} = E_0 \exp((-\frac{2.76}{2} \left(\frac{\omega-\omega_0}{\omega_{FWHM}}\right)^2)) = E_0 \exp((-2.76(\frac{\omega-\omega_0}{\sqrt{2}\omega_{FWHM}})^2)) \). This indicates that the scaling factor between intensity and electric field representation of a \( \delta \omega_{FWHM} \) is \( \delta \omega_{FWHM,E} = \sqrt{2} \delta \omega_{FWHM,I} \). The electric field has a larger bandwidth than the bandwidth of the intensity from measurement. The scaling factor between the FWHM and the \( \frac{1}{e^2} \) width is \( \delta \omega_{FWHM} = 1.177 \delta \omega_{1/e^2} \). Therefore, there are four possible
representations of the FWHM of the spectral electric field that are shown in Table D.1.

Table D.1: Possible conversions to obtain $\delta \omega_{FWHM,E}$ from Light Conversion spectral widths.

<table>
<thead>
<tr>
<th>$\delta \omega_{LC}$</th>
<th>$\delta \omega_{FWHM,E}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{FWHM}$</td>
<td>$\delta \omega = \sqrt{2} \delta \omega_{LC} = 1.414 \delta \omega_{LC}$</td>
</tr>
<tr>
<td>$I_{1/e^2}$</td>
<td>$\delta \omega = 1.177 \sqrt{2} \delta \omega_{LC} = 1.665 \delta \omega_{LC}$</td>
</tr>
<tr>
<td>$E_{FWHM}$</td>
<td>$\delta \omega = \delta \omega_{LC}$</td>
</tr>
<tr>
<td>$E_{1/e^2}$</td>
<td>$\delta \omega = 1.177 \delta \omega_{LC}$</td>
</tr>
</tbody>
</table>

Most likely, the bandwidths were provided for the intensity spectra since intensity (not electric field) is measured in experiments. The above conversion values are studied for the ESS figures of atmospheric XFROG vs. $\lambda$, $CF_4$ LICC vs. concentration at $\lambda_c = 10 \mu m$, and DMMP LICC vs. concentration at $\lambda_c = 10 \mu m$. The shorter timescales may still experience some simulation error due to the approximation of the linear chirp through the transmissive optics and from neglecting the $\varphi_3$ nonlinear chirp. Three ESS figures for each converted $\delta \omega_{FWHM,E}$ term are shown for comparison using the same logarithmic scales discussed in Chap. 4.
D.1 Results for $\delta \omega = 1.414 \delta \omega_{LC}$

Figure D.1: Atmospheric XFROG ESS figure for $\delta \omega = 1.414 \delta \omega_{LC}$. 
Figure D.2: $\text{CF}_4$ LICC ESS for $\delta \omega = 1.414 \delta \omega_{LC}$. 
Figure D.3: DMMP LICC ESS for $\delta \omega = 1.414 \delta \omega_{LO}$. 

\[ \text{simulation} \]
D.2 Results for $\delta \omega = 1.665 \delta \omega_{LC}$

Figure D.4: Atmospheric XFROG ESS figure for $\delta \omega = 1.665 \delta \omega_{LC}$. 
Figure D.5: CF₄ LICC ESS for $\delta \omega = 1.665 \delta \omega_{LC}$.
Figure D.6: DMMP LICC ESS for $\delta \omega = 1.665 \delta \omega_{LO}$. 
D.3 Results for $\delta \omega = \delta \omega_{LC}$

Figure D.7: Atmospheric XFROG ESS figure for $\delta \omega = \delta \omega_{LC}$. 
Figure D.8: CF$_4$ LICC ESS for $\delta \omega = \delta \omega_{LC}$. 
Figure D.9: DMMP LICC ESS for $\delta \omega = \delta \omega_{OC}$. 
D.4 Results for $\delta \omega = 1.177 \delta \omega_{LC}$

Figure D.10: Atmospheric XFROG ESS figure for $\delta \omega = 1.177 \delta \omega_{LC}$. 
Figure D.11: CF$_3$ LICC ESS for $\delta \omega = 1.177 \delta \omega_{LC}$. 
Figure D.12: DMMP LICC ESS for $\delta \omega = 1.177 \delta \omega_{LC}$. 
Appendix E

Simulations reproduced with

$$\delta \omega = 1.665 \delta \omega_{LC}$$

E.1 Interpolated bandwidth

![Graph showing interpolated mid-IR bandwidths from Light Conversion data using $\delta \omega = 1.665 \delta \omega_{LC}$.

Figure E.1: Interpolated mid-IR bandwidths from Light Conversion data using $\delta \omega = 1.665 \delta \omega_{LC}$.}
Figure E.2: ESS figure for atmosphere at 20% relative humidity. Scan range is 50 ps.
Figure E.3: ESS figure for $CH_4$ at 2.16 PSI. Scan range is 50 ps.
Figure E.4: ESS figure for $CF_4$ at 2.16 PSI. Scan range is 2 ps.
Figure E.5: ESS figure for DMMP at 2.16 PSI. Scan range is 8 ps.
Figure E.6: ESS figure for DMMP at 2.16 PSI. Scan range is 2 ps.
E.3 ESS XFROG vs. partial pressure

Figure E.7: ESS figure for $CH_4$ as a function of concentration. $\lambda_c = 3.5 \mu m$. Scan range is 50 ps.
Figure E.8: ESS figure for $CF_4$ as a function of concentration. $\lambda_c = 8 \mu m$. Scan range is 2 ps.
Figure E.9: ESS figure for DMMP as a function of concentration. $\lambda_c = 10 \mu m$. Scan range is 8 ps.
Figure E.10: ESS figure for DMMP as a function of concentration. $\lambda_c = 10 \mu m$. Scan range is 2 ps.
Appendix F

MATLAB code

F.1 Spectral phase simulation

F.1.1 First-order spectral phase: A shift in time

```matlab
%compute Sw
FWHM = .02; %1/fs
wFWHM = 2*pi*FWHM;
f = linspace(.25,.5,10000); %1/fs
f0 = .375; %1/fs... 375 THz
w = 2*pi.*f;
w0 = 2*pi*f0;
%Phi0 = Phi2*w0^2;
%Phiw = (w-w0).^2.*Phi2;
Phi1 = 14.5;

S0 = 20; %a.u.
S = S0.*exp(-2*log(2)*((w-w0)/wFWHM).^2);
```
Ew = S.^5;

%compute It

%Sw -> Ew -> Et -> It for intensity vs. time only

Et_quick = zeros(length(w),length(t));

phiw = (w - w0).*Phi1;

PHI = zeros(1,length(w));

for i = 1:length(w)
    phi1 = w(i).*t;
    Et_quick(i,:) = Ew(i).*exp(-1i.*(phi1+phiw(i)));
    PHI(i) = -Phi1;
end

Et_quick = sum(Et_quick);

%phi(t) is referenced to the phase of an w0 wave

Et_quick_ref = exp(-1i.*w0.*t);

It = abs(Et_quick).^2;

%Normalize It

It = (It./max(It));

%compute actual Et

Et = .5*(It).^0.5.*exp(-1i*(winst.*t));

figure

set(gcf,'Units','inches','Position',[0 1 6 4])

p=panel();
p.pack(2,2);

%plot Sw
p(1,1).select();
yyaxis left
plot(f,PHI,f,S, 'LineWidth', 3)
hold on
ylabel('Delay (fs)')
xlabel('Frequency (1/fs)')

yyaxis right
plot(f,−phiw, 'LineWidth', 3)
ylabel('Spectral Phase (rad)')
title('S(\omega)')

xlim([0.25 0.5])
legend('group delay','spectrum','spec. phase')

phit = angle(Et_quick)−angle(Et_quick_ref);
dphit = zeros(1,length(t));
for j = 1:length(t)−1
dphit(j) = (phit(j+1)−phit(j))./((t(j+1)−t(j)));
end
finst = f0 − dphit./(2*pi);

%plot It
p(2,1).select();

yyaxis left
plot(t,It,t,finst, 'LineWidth', 3)
xlabel('time (fs)')
ylabel('f_i_n_s_t (1/fs)')

yyaxis right
plot(t,phit, 'LineWidth', 3)
ylabel('temporal phase (rad)')
ylim([-1 1])
title('\Im(t)')
legend('intensity','instant. freq.','temp. phase')

%plot Et
F.1.2 Second-order spectral phase: Linear chirp

%compute Sw

FWHM = .07; %1/fs
wFWHM = 2*pi*FWHM;
f = linspace(.1,.8,10000); %1/fs
f0 = .375; %1/fs... 375 THz
w = 2*pi.*f;
w0 = 2*pi*f0;
Phi2 = -40; %fs
%Phi0 = Phi2*w0^2;
Phiw = .5.*(w-w0).^2.+Phi2;
t_g = Phi2.*(w-w0);

S0 = max(t_g); % a.u.

S = S0.*exp(-2*log(2)*((w-w0)/wFWHM).^2);

Ew = S.^5;

% compute It

t = linspace(-50,50,10000); % fs

% Sw -> Ew -> Et -> It for intensity vs. time only

Et = zeros(length(w),length(t));

for i = 1:length(w)
    phi1 = w(i).*t;
    Et(i,:) = Ew(i).*exp(-i.*(phi1+Phiw(i)));
end

Et = sum(Et);

It = abs(Et).^2;

% Normalize It

It = (It./max(It));

Et_quick_ref = exp(-i*w0.*t);

phit = unwrap(angle(Et)-angle(Et_quick_ref));

dphit = zeros(1,length(t));

for j = 1:length(t)-1
    dphit(j) = (phit(j+1)-phit(j))./((t(j+1)-t(j)));
end

finst = f0 - dphit./(2*pi);

figure

set(gcf,'Units','inches','Position',[0 1 6 4])

p=panel();
p.pack(2,2);
%plot Sw
p(1,1).select();
yyaxis left
plot(f,-t_g,f,S,'g', 'LineWidth', 3)
hold on
ylabel('Delay (fs)')
xlabel('Frequency (1/fs)')

yyaxis right
plot(f,-Phiw,'r', 'LineWidth', 3)
ylabel('Spectral Phase (rad)')
title('S(\omega)')
xlim([0.1 0.7])
legend('group delay','spect. intensity','spec. phase')

%plot It
p(2,1).select();
yyaxis left
plot(t,It,t,finst, 'LineWidth', 3)
xlabel('time (fs)')
ylabel('f_i_n_s_t (1/fs)')

yyaxis right
plot(t,phit, 'LineWidth', 3)
ylabel('temporal phase (rad)')
title('\Im(t)')
legend('intensity','instant. freq.','temp. phase')

%plot Et
p(1,2).select();
Et = Et./max(Et);
plot(t,Et, 'LineWidth', 0.5)
xlabel('time (fs)')
ylabel('E (V/m)')
F.1.3 Third-order spectral phase: Nonlinear chirp

```matlab
% compute Sw
FWHM = .02; % 1/fs
wFWHM = 2*pi*FWHM;
f = linspace(.25,.5,10000); % 1/fs
f0 = .375; % 1/fs... 375 THz
w = 2*pi.*f;
w0 = 2*pi*f0;
% Phi0 = Phi2*w0^2;
% Phiw = (w-w0).^2.*Phi2;
Phi3 = 1500;
t_g = 1/2*Phi3.*(w-w0).^2;
S0 = max(abs(t_g)); % a.u.
S = S0.*exp(-2*log(2)*((w-w0)/wFWHM).^2);
Ew = S.^5;
```
%compute It

t = linspace(-50,100,10000); %fs

%Sw -> Ew -> Et -> It for intensity vs. time only
Et_quick = zeros(length(w),length(t));

phiwa = (w-w0).^3;
phiw = 1/6*Phi3.*phiwa;

for i = 1:length(w)
    Et_quick(i,:) = Ew(i).*exp(1i.*(w(i).*t-phiw(i)));
    %Et_quick(i,:) = S(i).*exp(1i*w(i).*t).*exp(-1i*phiw(i));
end
Et_quick = sum(Et_quick);

%phi(t) is referenced to the phase of an w0 wave
Et_quick_ref = exp(-1i.*w0.*t);
It = abs(Et_quick).^2;

%Normalize It
It = 35.*(It./max(It));

%compute actual Et
%Et = .5*(It).^5.*exp(-li*(winst.*t));

figure
set(gcf,'Units','inches','Position',[0 1 6 4])
p=panel();
p.pack(2,2);

%plot Sw
p(1,1).select();
yyaxis left
plot(f,t_g,f,S, 'LineWidth', 3)
hold on
ylabel('Delay (fs)')
xlabel('Frequency (1/fs)')
yyaxis right
plot(f,phiw, 'LineWidth', 3)
ylabel('Spectral Phase (rad)')
title('S(\omega)')
xlim([0.25 0.5])
legend('group delay','spect. intensity','spec. phase')

phit = unwrap(angle(Et_quick)−angle(Et_quick_ref));
dphit = zeros(1,length(t));
for j = 1:length(t)−1
dphit(j) = (phit(j+1)−phit(j))./((t(j+1)−t(j)));
end
finst = f0 − dphit./(2*pi);

%plot It
p(2,1).select();

yyaxis left
plot(t,It,t,finst, 'LineWidth', 3)
xlabel('time (fs)')
ylabel('f_inst (1/fs)')
ylim([-1 35])
yyaxis right
plot(t,phit, 'LineWidth', 3)
ylabel('temporal phase (rad)')
title('\Im(t)')
ylim([0 750])
legend('intensity','instant. freq.','temp. phase')
```matlab
% plot Et
p(1,2).select();
Et_quick = Et_quick./max(Et_quick);
plot(t,Et_quick, 'LineWidth', 0.5)
xlabel('time (fs)')
ylabel('E (V/m)')
title('E(t)')

p.de.margintop = 20;
p.de.marginleft = 28;
p.marginbottom = 12;
p.marginright = 14;
p.margintop = 8;
p(1,1).select();
set(gca,'fontsize',10)
p(1,2).select();
set(gca,'fontsize',10)
p(2,1).select();
set(gca,'fontsize',10)
```