ULTRABROAD FEMTOSECOND PULSES FOR COHERENT ANTI-STOKES RAMAN SCATTERING SPECTROSCOPY

Bу

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ABSTRACT

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This dissertation focus on the use of sub-ten femtosecond pulses applied to coherent anti-Stokes Raman scattering spectroscopy. The use of such a broadbandwidth pulse coupled with adaptive pulse shaping has provided a method to impulsively excite all vibrational modes within the bandwidth of the pulse. Furthermore, this method using only a single beam eliminates many of the experimental difficulties associated with the typical multi-beam CARS methods.

The generation of supercontinuum has allowed for high energy, amplified pulses to reach the same time duration/bandwidth as lower energy femtosecond oscillators. This significant increase in pulse energy has allowed the single-beam CARS method to be extended beyond microspectrocopy, which requires the tight focusing conditions afforded by a microscope objective in order to reach the necessary pulse energy. This extension has opened single-beam CARS to fields such as remote sensing and combustion diagnostics. This dissertation presents the evolution of single-beam CARS in the context of these fields.

Remote sensing is demonstrated at distances of 12 m for solids, liquids, and gases in a retro reflective set-up with signal to noise levels high enough for molecular identification. Single shot measurements are also made, along with direct backscatter measurements.

CARS gas phase measurements are made on several atmospheric gases, as well as mixtures of gases. Mode-selective CARS excitation is used to excite a single Raman mode, creating a contrast mechanism that allows for direct visualization of a CO₂ jet. Several gases were also measured in various pressure regimes to determine the number density relationship.

Lastly, the group velocity dispersion of several combustion gases was measured to illustrate the temporal broadening that occurs when femtosecond pulses propagate in combustion environments. The ability to manipulate the axial resolution of a nonlinear optical process when using adaptive pulse shaping is also discussed.

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KEY TO SYMBOLS AND ABBREVIATIONS

α	a parameter used to define the amplitude of the sine function
BPS	binary phase shaping
CARS	coherent anti-Stokes Raman Scattering
СРА	chirped pulse amplification
δ	a parameter used to define the phase of the sine function
E	electric field
φ(ω)	phase (as a function of frequency)
f(ω)	reference phase used in MIIPS
FROG	frequency-resolved-optical-gating
FWHM	full-width-at-half-maximum
GVD	group velocity dispersion
IR	infrared
L	propagation length
LC-SLM	liquid crystal spatial light modulator
LN	liquid nitrogen
MII	multiphoton intrapulse interference
MIIPS	multiphoton intrapulse interference phase scan
$\eta(\Omega_R)$	normalized excitation efficiency spectra
ñ	complex index of refraction
PCF	photonic crystal fiber
SHG	second-harmonic generation
SLM	spatial light modulator

SPIDER	spectral phase interferometery for direct electric-field reconstruction
SRS	stimulated Raman scattering
Ti:Sa	titanium:sapphire
TL	transform-limited
UV	ultraviolet
ω	frequency
$\Omega_{\rm R}$	Raman transition

Introduction

Ten femtoseconds, the time it takes light to travel 3.0x10⁻⁶ m, is the approximant width of a human hair. This is also the same time scale on which the atoms that compose molecules twist, turn, wiggle, and if provided with enough energy, break apart. This short time scale, where the electric field is present, is the defining characteristic of femtosecond lasers. As the field is present for such a short time, it allows power densities greater that 10¹² W/cm² to be reached by the focusing of amplified femtosecond pulses. This high power density is sufficient to induce nonlinear optical effects, such as second harmonic generation, two photon fluorescence, molecular ionization, and other various nonlinear spectroscopies. One of these spectroscopies, coherent anti-Stokes Raman scattering (CARS), is the focus of this dissertation.

The first chapter is written to provide insight into the concepts and characteristics of femtosecond pulses that make them such a unique and powerful experimental tool. It also discusses the experimental apparatuses that are critical for the production of amplified femtosecond pulses and the manipulation of spectral phase, amplitude, and polarization.

The second chapter discusses the fundamental concepts behind Raman spectroscopy and the correlation between traditional Raman spectroscopy and CARS. Furthermore, this chapter discusses some of the typical CARS methods and their applications. The single-beam CARS method is also introduced.

Chapter three highlights the adaptation of the single-beam CARS method from microspectroscopy to performing CARS measurements at distances >10 m. This chapter also examines CARS measurements on mixtures of gases and liquids.

The fourth chapter presents mode selective single-beam CARS on gas phase molecules based upon Binary Phase pulse shaping (BPS). BPS uses a broadbandwidth pulse to excite only a single Raman mode, rather than impulsively excite all modes within the bandwidth of the pulse.

Chapter five focuses on examining several different methods of performing mode selective excitation applied to the single-beam CARS methodology. The theory, in the context of multiphoton intrapulse interference (MII), and application of double chirped pulses, sinusoidal modulation, and BPS are highlighted through the use autocorrelation and CARS measurements.

The last chapter discusses the use of a broadbandwidth pulse to measure the dispersion of gases that are related to combustion. As the use of femtosecond-laser sources for the diagnostics of combustion and reacting-flow environments becomes more common, detailed knowledge of optical dispersive properties of the medium interacting with the laser beams is required. Here, the second-order and third-order dispersion values within the 700–900 nm range are reported, along with the pressure dependence of the chromatic dispersion. The effect of dispersion on axial resolution when applied to nonlinear spectroscopy with ultrabroadband pulses is also discussed.

Chapter 1

Concepts and Experimental Tools

This first chapter discusses the critical concepts and various experimental tools that are used in the work presented in this dissertation. In particular, ultrashort laser pulses, femtosecond laser systems, and pulse shaping are highlighted.

1.1 Ultrashort laser pulses and spectral phase

Lasers are typically thought of as narrowband, monochromatic light sources. However, ultrashort lasers, particularly those with pulse durations on the order of femtoseconds, are composed of numerous optical frequencies. Ultrashort pulses are ideal for inducing non-linear optical processes due to the short time duration, resulting in very high peak powers.

An ultrashort pulse is simply an oscillating electric field, $\varepsilon(t)$. This field cannot be monitored electronically due to the short time duration. This results in measurements that are typically performed in the frequency domain. $\varepsilon(t)$ can be Fourier transformed to get $\tilde{\varepsilon}(\omega)$, which describes the field in the frequency domain. A practical definition for $\tilde{\varepsilon}(\omega)$ is as follows:

$$\tilde{\varepsilon}(\omega) = A(\omega) \exp[i\varphi(\omega)]$$
 (1.1)

 $A(\omega)$ is the spectral amplitude and $\varphi(\omega)$ is the spectral phase that contribute to the pulse shape. As the spectral domain is the most common, ultrashort pulses can be represented by:

$$S(\omega) \propto |\tilde{\varepsilon}(\omega)|^2$$
 (1.2)

which can be easily measured using a spectrometer. However, the spectral phase is much more difficult to measure. The combination of spectral amplitude and phase is all the information that is needed to completely characterize an ultrashort pulse.

The spectral phase is simply the relative phase of each of the frequency components. Non-linear optical processes induced by ultrashort pulse are highly sensitive to the spectral phase of the ultrashort pulse. To achieve the shortest pulse duration, the spectral phase of the laser pulse must be a flat function. When an ultrashort pulse achieves the shortest possible duration, it is said to be transform limited (TL).

Spectral phase distortions arise from different frequencies of the laser pulse experiencing different refractive indices as the pulse propagates.¹ This results in different frequencies traveling with different velocities. Optical components such as lenses, windows, or cuvettes all induce phase distortions. Nearly all materials induce a distortion that is quadratic in nature along with several higher order distortions. Optical prism and grating compressors have been designed to correct for quadratic distortions, but do not correct for higher order distortions. In fact, these compressors often introduce additional higher order distortions. The impact of the phase distortions are best see by the examination of a non-linear optical process. Second harmonic generation (SHG) will be used to illustrate the effect of various phase distortions. The SHG can be defined as:

$$S(2\omega) = \left| \int E^2(t) \exp[i\omega t) dt \right|^2 \tag{1.3}$$

The effect of various phase distortions on SHG and time duration of an ultrashort (10 fs) pulse are highlighted in Fig. 1.1. Linear phases are not examined as they have no effect on the second harmonic and, and simply shift the pulse in the time domain.



Figure 1.1. The effect of spectral phase on temporal intensity of the pulse (second column) and second harmonic spectrum (third column). The first column shows fundamental spectrum (solid line) and the applied phase (dashed line). a) Corresponds to quadratic phase distortion, b) is for cubic phase distortion, and c) is for sinusoidal phase modulation. In columns two and three, the solid line corresponds to TL pulses and the dashed corresponds to applied phase distortion.

From Fig. 1.1, the effects of the phase distortions are dramatic. The quadratic phase distortion, or chirp as it commonly referred to, significantly increases the duration of the pulse in the time domain as well as reduces the intensity of the non-linear, second harmonic signal. This is contrasted with the third order, or cubic phase distortion, which actually generates a train of pulses in the time domain, while spectrally narrowing the second harmonic. Sinusodial phase modulation also results in the generation of a pulse train in the time domain and narrowing in the second harmonic signal. The ability to correct for phase distortions, regardless of the optical components, results in highly reproducible experimental data. The use of the Multiphoton Intrapulse Interference Phase Scan (MIIPS) method has demonstrated the ability to accurately correct for all orders of phase distortion. MIIPS will be discussed in more detail in the following chapter.

1.2 Femtosecond Laser Systems

More than a decade after the first experimental laser use, sub-picosecond pulses were generated using dyes as gain media.² Until the late 1980's and the arrival of solid state gain media, these dye-lasers were the primary source of ultrashort pulses, generating pulses as short at six fs.³ However, the use of solid state gain media, titanium-doped sapphire (Ti:Sa) in particular ended the dominance of dye lasers due to their ability to support broad gain bandwidths and provide long term stability.^{4,5} A Ti:Sa regenerative amplifier described in the following section was employed for the experiments presented in this dissertation.⁶

The regenerative amplifier is used for laser pulse amplification. Amplification is achieved by the pulse making multiple passes through a gain medium (Ti:Sa). In the regenerative amplifier, the Ti:Sa crystal is placed in an optical resonator with an optical switch that allows the pulse to exit after a desired number of passes through the gain medium. During this amplification process, the peak intensity of the pulse can become so high that it becomes possible to induce high order, non-linear effects that may distort the laser pulse or damage optical elements. To avoid this, a chirped pulse amplification (CPA) method is used.⁷ In CPA, pulses are temporally stretched, typically from femtoseconds to picoseconds, using a highly dispersive optical element before amplification. This results in a significant reduction in the peak intensity during amplification. The stretched pulses enter the amplification gain media where after several passes (4-50), the pulse energy increases by several orders of magnitude. After amplification, the pulses enter a compressor, typically built with a grating pair that recompress the pulses to a duration similar to before amplification (<100 fs), resulting in femtosecond laser pulses with very high peak intensities.⁸

The regenerative amplifier (Legend USP, Coherent), seeded by a Ti:Sa oscillator (Micra, Coherent), used for the experiments described in this dissertation is presented in Figure 1.2. This system produces pulses of ~35 fs with energies of ~1 mJ/pulse at a 1 kHz repetition rate.



Figure 1.2. Regenerative amplifier schematic. (a) Grating stretcher, which stretches the time duration of the seed pulse, (b) regenerative amplifier, (c) grating compressor where the amplified pulses are recompressed. F1: Faraday Isolator, G1 and G2 gratings, Pc1 and Pc2: Pockel cells.

1.3 Pulse Shapers

Pulse shapers are optical devices that allow for the user to control attributes of the laser pulse such as spectral phase, amplitude, or polarization. These can be designed in several ways with varying levels of complexity. For example, the use of optical components such as a grating or prism based compressor allows for the application of quadratic phase. However, more complex phase functions require the use of programmable pulse shapers. The use of programmable pulse shaping with ultrafast lasers covers a wide variety of applications ranging from pulse characterization^{9,10}, non-linear microscopy^{11,12}, to control of photochemical processes.^{13,14}

There are two separate approaches taken for the application of pulse shaping. The first is based upon manipulation in the time domain. This is typically done through the use of an acousto-optic device. In this device, a time dependent acoustic signal is driven in a crystal through which the laser pulse propagates. This allows for control of both the phase of the pulse and the amplitude.¹⁵ The second approach uses manipulation in the frequency domain, with Fourier-transform pulse shapers. Fouriertransform shapers work by applying a spatial mask to the spatially disperse frequency spectrum of the pulse.¹⁶ This allows for manipulation of individual frequencies of the laser pulse. This type of pulse shaping is used throughout the research that is decribed in this dissertation.

The pulse shaping apparatus highlighted in Figure 1.3 is the typical optical design of a frequency domain pulse shaper. It is constructed from two diffraction gratings and two lenses arranged in a "4-*f* configuration" and a spatial light modulator (SLM). The input beam is spectrally dispersed from the first diffraction grating (or prism) and is focused into a spectral disperse line by the first lens (or curved mirror). The focus of this lens is the Fourier plane, where the SLM is placed. After passing through the SLM, the frequency components of the beam are recombined, generating a single, collimated output beam. This arrangement is also known as a "zero dispersion pulse

compressor", due to the fact that if the SLM was removed, the output pulse would be identical to the input in terms of spectral phase.



Figure 1.3 Schematic of "4-*f*" pulse shaper, where each optical component is separated by the focal distance *f*. The input beam is spectral dispersed into frequency components and then focused by a lens. The SLM is place at the focal plane (Fourier plane). The SLM allows for individual manipulation of each frequency with respect to spectral phase, amplitude or polarization. After passing through the SLM the frequency components are recombined creating a shaped, collimated output.

The SLM used for the experiments performed in this dissertation uses liquid crystal technology (LC-SLM). This device is composed of a thin layer of nematic liquid crystals that are placed between two glass windows. The inside surface of the glass windows are coated with a thin, transparent material that is electrically conductive. This creates the SLM mask, which is composed of numerous pixels. When an electric field is applied to each pixel, the liquid crystal molecules rotate, which results in a change in refractive index for that pixel. Depending on the polarization of the input light, this change allows for the introduction of phase retardation, or polarization rotation.^{17,18} There are two different types of LC-SLM. One type is phase only, and the second type is phase and amplitude. In the phase only LC-SLM, a single mask is used, and the polarization of the input light is such that only phase retardation is introduced. In the LC-

SLM capable of phase and amplitude shaping, there are two liquid crystal masks. In this LC-SLM, the masks are oriented with perpendicular optical axes which are rotated 45 degrees from the polarization of the incoming light. These two masks, along with the combination of a polarizing optical device allow for the shaping of phase and amplitude; the polarizing optic can be removed, and phase and polarization shaping can be performed. The ability to vary transmission of light dependent on polarization is utilized for the calibration of the various LC-SLMs used.

In the work performed in this dissertation, a 128 pixel phase only LC-SLM (CRi) was used, along with a 640 pixel phase and amplitude shaper (CRi). The 128 pixel shaper was placed between the oscillator and the regenerative amplifier, the 640 pixel shaper was place after the regenerative amplifier. These shapers were configured in an alternate, fold geometry, highlighted in Figure 1.4.



Figure 1.4 Schematic of an all reflective, folded "4-*f*" pulse shaper. The output beam follows the same path as the input, but is vertically displaced. OM: Output mirror, CM: Curved mirror, FM: Folding mirror, and BM: Back mirror.

This folded, all reflective design was chosen because it reduces the amount of space needed for the shaping device, and it doubles the amount of phase retardation the LC-SLM can apply, since the beam passes through the device twice.

These pulse shaping devices were used for several applications discussed throughout this dissertation. Pulse shapers were used for pulse characterization and compression, the generation of phase and polarization mask the acquisition of coherent anti-Stokes Raman scattering (CARS) data, and for the application of phases to selectively excite individual CARS modes.

1.4 Multiphoton intrapulse interference phase scan (MIIPS)

For ultrashort pulses, the measurement and characterization of spectral phase distortions is essential. Accurate measurement and correction of phase distortions prevents any experimental ambiguity that may result from unknown phase distortions, making experimental results highly reproducible. This is particularly critical for sub 30 fs pulse durations. The use of multiphoton intrapulse interference phase scan (MIIPS), developed by the Dantus group¹⁹ provides a highly accurate method to both measure and correct spectral phase distortions.

There are several different approaches that have been used to perform pulse compression. These methods include the use of prism or grating compressors, which was the initial method of choice for pulse compression. In this method the SHG signal is observed as the compressor is adjusted to achieve an optimal SHG si,gnal. A second method for characterization involves the use of a computer controlled pulse shaper and

an optimization genetic algorithm. Here the integrated SHG signal provides feedback to the algorithm, which then modulates the phase applied by the pulse shaper in order to maximize the integrated SHG signal. The downfall of these methods is that they are limited by the noise level of the measurement. A very stable laser source will fluctuate on the order of 1-3%, which means that the pulse to pulse stability of the SHG is 2-6%. This level of noise is insufficient for measurements that require very accurate knowledge of the phase distortions.

Retrieving spectral phase using a method based upon autocorrelations and/or interferometery is a a third approach used to perform pulse compression. Frequency resolved optical gating (FROG)²⁰⁻²² and spectral phase interferometry for direct electic-field reconstruction (SPIDER)^{23,24} are two of these methods. Figure 1.5 is a cartoon demonstrating these approaches, along with the MIIPS method.



Figure 1.5 Cartoon of various pulse compression methods. (a) Prism/grating compressor, (b) Optimization algorithm using integrated SHG signal, (c) FROG/SPIDER characterization methods (d) MIIPS method.

The MIIPS method works by applying a set of well defined reference phases, $-f(\omega)$, is applied to the pulses with an unknown phase distortion, $\varphi(\omega)$, while measuring a SHG spectra or other non-linear optical spectra. This results in a total second derivative of the phase being $\varphi(\omega)$ -f(ω). When $\varphi(\omega)$ -f(ω)=0, there will be a maximum in the SHG signal. By creating a grid in the second derivate space using $-f(\omega)$, the unknown phase $\varphi(\omega)$ can be mapped out. The simplest way to do this is to use a function in which the second derivative is a constant, which corresponds to a linear chirp function. This approach is shown in Figure 1.6 a). The unknown phase (solid line) is measured using the reference phases (horizontal dashed lines). When the reference phase intersects with the unknown phase a maximum is generated in the SHG signal as show in figure 1.6(b). This sample method can be applied using a sinusoidal reference phase and is shown in Figure 1.6 c) and 1.6 d). In each of these methods, the $\varphi''(\omega)$ is measured for the unknown and then double integrated to obtain $\varphi(\omega)$. The - $\varphi(\omega)$ is then introduced by the pulse shaper eliminating the phase distortion. The time to scan the reference phase is on the order of 10 to 30 seconds, and an interative routine can be used to obtain the best possible accuracy.



Figure 1.6 MIIPS principles. (a) The unknown phase (ϕ'') is mapped using a reference grid composed of linear chirp phases. (b) The SHG signal corresponding to the places where the reference phase and the unknown phase intersect. (c) Mapping the unknown phase using a sinusoidal reference phase. (d) The SHG signal corresponding to the intersection of the sinusoidal reference phase with the unknown phase.

Each of these methods are described in great detail elsewhere, but these methods are used experimentally thoughout this dissertation for measurement and correction of spectral phase distortions. This ensures the use of TL pulses and allows for highly accurate phase shaping to be performed.

1.5 Conclusions

This chapter has presented several key concepts related to the use of ultrafast laser pulses and phase shaping, including the effect of spectral phase on ultrashort pulses examined in second harmonic generation and in the time domain. The 4*f*- pulse

shaper is also described in detail regarding the set-up of the devices as well as the functionality. Multiphoton Intrapulse Interference Phase Scan (MIIPS) is also described with its application to phase measurement and correction.

Chapter 2

Coherent anti-Stokes Raman Scattering (CARS)

The majority of the work addressed in this dissertation involves or is related to coherent anti-Stokes Raman Scattering (CARS). CARS is a non-linear method that provides information analogues to that of Raman spectroscopy that provides rich spectroscopic information. An introduction to the basic theory of Raman spectroscopy will be given followed by a discussion of the principles of CARS and how it compares and contrasts with Raman spectroscopy. Lastly, several CARS methods will be highlighted to provide a frame of reference for the work discussed in chapters 3-6 of this dissertation.

2.1 Theory of Raman spectroscopy

The interaction of light with matter has long been a field of interest and study for the scientific community. When light interacts with a material, the material may absorbed, scattered, or not interact with the light. This interaction is the phenomena behind all spectroscopic methods, independent of wavelength. Raman spectroscopy is a scattering technique in which the light interacts with a molecule to distort the electron cloud surrounding the nuclei. This distortion, or induced polarization, creates a short lived, unstable virtual state from which photons are quickly reradiated. As Raman is a vibrational spectroscopy, molecular motion is required, so photons that only distort the electron cloud are scattered with small frequency changes or elastically scattered. This process is known as Rayleigh scatter, is the dominate process. However, if nuclear motion is induced an inelastic scattering occurs and energy may transfer from the photon to the molecule (Stokes) or from the molecule to the photon (anti-Stokes).²⁵⁻²⁷

This inelastic scatter results in a frequency shift in the scattered photon is known as the Raman process. Fig 2.1 highlights this process for a single vibration.



Figure 2.1 Energy level diagram of the Rayleigh and Raman scattering processes.

Molecular vibrations can result in a change in dipole moment or a change of polarization. Infrared absorption spectroscopy (IR) is highly sensitive to changes in dipole, while insensitive to changes in polarization, the opposite of Raman scattering. Therefore, vibrations which cause the largest change in the polarizability are those which produce the greatest Raman scattering. These are typically symmetric molecular vibrations. The number of vibrations that a molecule contains is 3N-5 for linear molecules and 3N-6 for all others, where N is the number of atoms. However, not all of these modes are Raman active. Some modes result in only in a change of dipole moment, others a change in polarizability, and some change both the dipole moment and polarization. To illustrate this CO₂, is examined in Fig 2.2. As CO₂ has three atoms, there are 4 vibrational modes: symmetric stretching, bending and asymmetric stretching. There are two degenerate bending modes, where the spectroscopic

signature is identical. Of these modes, the symmetric and an overtone of twice the bending mode are Raman active, while the bending mode and asymmetric stretch results in a change in the dipole moment making it active to infrared absorption.



Figure 2.2 Vibrational modes for CO₂: The symmetric stretch and overtone of twice the bending mode are Raman active, whereas the bending mode and asymmetric stretch are IR active.

While the modes for small molecules are easy to predict and to model it becomes much more complicated for large molecules. For example, toluene (C₇H₈) has 39 vibrational modes, far too many to approximate as was done for CO₂. This also makes in very time consuming to computational model each molecule to predict the Raman signal. Spectroscopists typically consider single vibrations and group frequency vibrations when using Raman for identification. Fig 2.3 illustrates the approximate position of Raman features for some of the more common vibrations. The solid, vertical lines represent the approximate range for the observation of the Raman response, while the stars indicate the position of the Raman response for gas phase molecules discussed later in this dissertation.



Figure 2.3 Single and group vibrations of peaks common to Raman scattering. The stars indicate the frequency of the Raman signal in gas phase molecules (CO₂, O₂, N₂)

While only vibrational Raman scattering has been discussed, rotational transitions are also commonly observed for gas phase measurements. For the work presented in the following chapters only vibrational scattering is examined.

2.2 Comparison of Raman and CARS

Raman spectroscopy is a linear spectroscopy and is typically performed with a single CW laser source. CARS is a nonlinear, four wave mixing process which traditionally requires three lasers beams. The first two beams, pump(E_P) and Stokes(E_S) serve to coherently drive the molecular vibrations, which are then probed by a third beam (E_{PR}) to generate the CARS signal ($E_{CARS} = E_P - E_S + E_{PR}$).²⁸⁻³¹ This is

highlighted in the energy level diagram, Fig 2.1. Taking this into consideration, the Raman signal can be approximated as $S_{Ram.}\alpha I_LN \times eff.$, where I_L is the laser intensity, N is the number density of the sample and *eff.* is the detection efficiency. The CARS response is proportional to $S_{CARS} \alpha N^2 I_{P/S}^2 I_{PR} \times eff.$, where N is the number density, $I_{P/S}$ is the intensity of the pump/Stokes component, I_{PR} is the intensity of the probe and *eff.* is the detection efficiency. From this we can see that in order to perform CARS spectroscopy high intensity pulses are desired. This makes pulsed laser sources the ideal choice.

While, experimentally CARS is more complex than traditional Raman spectroscopy, it has several advantages. First, the CARS signal is coherent and emerges as a directional beam, not scattered over free space as traditional Raman. This allows for a much higher efficiency in signal collection. Second, the CARS signal is blue shifted, making it free from background fluorescence which typically plagues Raman measurements. Third, CARS signals are typically orders of magnitude stronger that those of Raman. This enhancement of the CARS signal vs. Raman has been determined to be $\sim 10^5$. This significant enhancement is the result of phase-locked signal accumulation over the active sample volume.^{32,33}


Figure 2.4 Cartoon showing the signal accumulation over an active sample volume for a) CARS and b) Raman. Notice how the signal for CARS is phase-locked, compared to random for Raman. This phase-locked accumulation results in the large signal enhancement in CARS.

2.3 Resonant and Nonresonant contributions

For CARS the Raman response is due to the change in the third order polarization due to the pump, Stokes and probe pulses. This response contains both a resonant and a nonresonant portion. The nonresonant contribution is due to the instantaneous electronic response of the molecule, while the resonant response can be attributed to the Raman transitions of the molecule. In the frequency domain we can consider the third order polarization, $P^{(3)}(\omega)$ as follows:

$$P^{(3)}(\omega) = P_{NR}^{(3)}(\omega) + P_{R}^{(3)}(\omega)$$

However, the CARS response of the sample is proportional to $\left|P^{(3)}(\omega)\right|^2$, which

results in complex spectra due to the interference of the resonant Raman transactions and the nonresonant background. As a result, numerous methods have been developed with the goal of reducing or eliminating the nonresonant contribution. Figure 2.5 is a schematic diagram highlighting the different contributions to the CARS process.



Figure 2.5 Energy level diagrams for four wave mixing processes (ω_1/ω_2 ;red, ω_3 ; blue, and ω_4 ; orange a) resonant contribution to the CARS process and b) for nonresonant contributions. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.

2.4 Frequency Domain CARS methods

While, spectroscopic CARS methods have existed since the early 1970s, advances in ultrashort laser technology and availability have lead to resurgence in CARS applications. As a result, the evolution in ultrafast sources has lead to the development of a variety of methods for CARS spectroscopy.

The first approach makes use of two narrowband pulses (ps/ns). One of the pulses serves as the pump/probe while the other serves as the Stokes. This allows for acquisition of the CARS signal at a single frequency. To obtain a full spectrum the Stokes pulse must be scanned in frequency. Narrrowband CARS using picoseconds pulses has traditionally been the dominate method for CARS microscopy³⁴⁻³⁸ and as a diagnostic method for combustion and reacting flows.³⁹⁻⁴¹ For CARS microscopy the

intrinsic chemical selectivity afforded by narrowband CARS provides a high contrast ratio, without the need for labeling. Phospholipids are among the molecules most often targeted in cells, due to large signal they provide, that enables visualization of even a single lipid bilayer. The advances in narrowband CARS have allowed for microscopy to become a method that is capable of producing video rate images with sub-cellular resolution. This same narrowband approach has also been a choice method for diagnostic measurements of combustion and reacting flows due to the ability to extract temperature and species information. Methods to detect two or three species simultaneously have been developed along with those that allow for measurements to be made at high temperatures and pressures. This has resulted in narrowband CARS becoming the most widely used method in the diagnostics of combustion and reacting flow environments.

Another approach combines a narrowband source and a broadband (fs) source, in a method know as multiplex CARS.⁴²⁻⁴⁵ In this approach the narrowband source again serves as the pump/probe and the broadband as the Stokes. Rather than excitation at a single frequency, this allows for the acquisition of several frequencies, determined by the bandwidth of the Stokes pulse. This allows for spectroscopy to be performed without any wavelength tuning. However this method only provides a single photon pair for excitation at each frequency. Multiplex CARS has been primarily applied for microspectroscopy of biological samples. For these applications a photonic crystal fiber (PCF) pumped by a femtosecond oscillator is used to generate broadband supercontinuum with bandwidth in excess of 2500 cm⁻¹ to serve as the Stokes pulse.

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The pump and probe are typically generated from output of the oscillator, but are spectrally narrowed. Much like the narrowband method this method has evolved to collect video rate images with subcellular resolution, with the advantage of observing several Raman transitions simultaneously.

A third method that has evolved is a hybrid CARS. In hybrid CARS two broadband sources provides the pump and Stokes and a narrow band source is used to provide the probe. Like the multiplex approach this method provides signal at several frequencies, however as two broadband sources are used to provide the pump/Stokes, there are several frequency pairs. These frequency pairs result in much higher efficiency than the multiplex method as there are several photon pairs that contribute to the Raman response. One example which illustrates this method is the work by Scully, *et al.* In this work they use a hybrid CARS approach to identify bacterial endospores that are stimulants for hazardous materials such as anthrax.⁴⁶⁻⁴⁸ The ability of this method to cover a large portion of the fingerprint region (200-1800 cm⁻¹) allows a complex spectrum to be obtained which may contain several Raman transitions.

Figure 2.6 is a cartoon illustrating these three different methods used for frequency domain CARS. There are numerous adaptations of these methods, and the examples given are simply samples of the body of work that has been performed. However, some insight into these methods is necessary as a frame of reference of the CARS method used in this work.

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Figure 2.6 Schematic diagrams of frequency domain CARS methods. a) Narrowbeam CARS, b)Multiplex CAR, and c) Hybrid CARS.

One common characteristic for each of these approaches is the ability to delay the probe pulse in time with respect to the pump/Stokes. This allows for the non-resonant response to decay, and the CARS signal to be acquired nearly background free. However, these methods are not without limitations. First, the hybrid and multiplex method may not be capable of collecting a full spectrum, due the limited bandwidth of the pulses used. For the narrowbeam CARS method Ω_R must be tuned through various frequencies in order to require a full Raman spectrum. This is both time consuming, as well as, experimentally unfavorable due to the instabilities which may occur and the broad tuning range required to obtain a full spectrum. Secondly, as this method requires up to three individual beams, from two or three lasers sources, they must be overlapped both spatial and temporally. This makes this type of CARS measurements unpractical for applications which are highly turbulent and can cause the beams to wander, or require the beams travel large distances, such as a standoff detection application.

2.5 Single-beam CARS

Single-beam CARS represents a drastic shift in the schemes that for CARS spectroscopy, as these methods require multiple beams. The single-beam CARS makes use of a single broadband pulse to both provide the excitation and probe the system. This method was first demonstrated for microscopy by the group of Silberberg in 2002.⁴⁹ This initial work in 2002 used coherent control techniques, via pulse shaping in order to examine Raman transitions in the 400-800cm⁻¹ range. The spectral phase of the broadband pulse is modulated periodically, where the period of the oscillation matches the vibrational energy level of the sample. While this method does not provide a spectrum and requires different spectra phases to examine different transitions, it has shown that it is possible to eliminate the multibeam setups and perform CARS microscopy using a single-beam.

Single-beam CARS like all CARS methods has undergone numerous advances. Following the initial single-beam CARS work, the next step was to use a single pulse to acquire a CARS spectrum. This was again accomplished by the use of pulse shaping. For this work a pulse shaper capable of providing both phase and polarization modulation is used. The broadband pulse is shaped as two components, one to serve as the pump/Stokes, the other the probe. For the probe pulse, a narrow spectral region, typically corresponding to a couple of pixels on the SLM is selected. A spectral phase of 0 is applied to half of these pixels, while a phase of π is applied to the others. Additionally, the polarization of this narrow region is also rotated to be orthogonal to the

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polarization of the incoming beam. For the pump/Stokes component the polarization is maintained and a flat spectral phase is applied across the bandwidth of the pulse. The combination of both phase and polarization has been shown to nearly suppress the entire nonresonant contribution.⁵⁰⁻⁵³ A schematic of the spectral pulse shaping in the wavelength and time domain is shown in Fig 2.7.



Figure 2.7 Schematic illustrating the phase and polarization shaping method used for single-beam CARS and a representative CARS response. The right insets show a closer view of the probe region, and left inset shows temporal profile of the pump/Stoke and probe components.

This method allows for impulsive excitation of all Raman modes within the bandwidth of

the pump/Stokes pulse. This means that a fairly standard femtosecond oscillator

capable of producing 10 fs pulses would allow for impulsive excitation of approximately

2000 cm⁻¹. This allows for coverage of the entire fingerprint region, which is highly useful as it contains numerous Raman transitions.

In addition to the work by the group of Silberberg, the groups of Leone and Motzkus also developed various single-beam approaches for applications to CARS microscopy, based upon the single pulse approach utilizing pulse shaping. The group of Leone used different phase functions on the probe portion of the pulse to acquire a CARS spectra for each phase.⁵⁴⁻⁵⁷ The use of an imaging spectrometer also allows the collection of two polarizations (\pm 45 \Box), enabling simultaneous measurement of the real and imaginary components of the CARS signal. The imaging capabilities of this method were demonstrated on the imaging of 200 nanometer poly(methyl methacrylate) (PMMA) beads and the collection of chemical images of thin films containing PMMA and polystyrene.

The Motzkus group has taken a slightly different approach with the single beam method and works primarily in the time domain, rather than the frequency as well as use a heterodyne method where the CARS signal is mixed with a local oscillator field.⁵⁸⁻⁶¹ To achieve this a periodic phase function is used to create two pulses from a single broadband pulse. The first pulse serves as the pump/Stokes; the second serves as the probe. The time delay of the probe pulse is then scanned while the signal is measured as a function of delay. This signal can then be Fourier transformed from the time domain back to the frequency domain and the CARS data extracted. This same data processing method was also used with two pulses of two different colors. These pulses

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were created again by phase shaping. For theses pulses, a broadband pulse was split into two sections by the use of linear phase, which can shift the pulse forward or backward in time. These methods have been used to image microcapsules filled with 1,4-diiodobenzene and bromoform at attomole concentration levels.

2.6 Conclusions

While in existence since the early 1970's, spectroscopic CARS methods have advanced as rapidly as the laser technology that enables them. The laser-like directionality of the CARS signal, low signal absorption, spectral selectivity, and excellent spatial resolution provide an optical method that is flexible and robust enough for applications ranging from video rate microspectroscopy, combustion diagnostics, and remote sensing. This chapter has highlighted several typical CARS methods along with the underlying principles related to CARS and Raman spectroscopy.

Chapter 3

Single-beam CARS for Remote Sensing

As the previous chapter has discussed CARS in great detail, this chapter will focus on the authors' contribution to the field of single-beam CARS spectroscopy, particularly for the application to standoff or remote sensing. The following is reproduced with permission from H. Li, D. A. Harris, B. Xu, P. J. Wrzesinski, V. V. Lozovoy, and M. Dantus, Coherent mode-selective Raman excitation towards standoff detection," *Optics Express* **2008**, 16, 5499-5504. Copyright 2008. Optical Society of America.

3.1 Single-beam CARS for Remote Sensing

Ultrashort pulses have made possible the development of powerful spectroscopic tools that rival conventional high-resolution approaches.⁶² Their ultra-broad bandwidth makes them ideal for impulsive excitation of vibrational modes, which evolve in time coherently. When pairs or trains of such pulses are used, large amplitude molecular motion can be achieved.^{63,64} These capabilities were recently combined to achieve single-beam coherent anti-Stokes Raman scattering microscopy,^{49,53,60,65} a modality that is sensitive to molecular composition. Here we present a method for remote sensing of films and residues located on solid targets tens of meters from the laser based on single-beam CARS. In contrast to its implementation in microscopy, this development requires amplified (six-orders of magnitude) ultra-broad bandwidth pulses.

tens of meters from the laser source. The resulting method is capable of selective vibrational mode excitation to provide molecular discrimination and to eliminate the non-resonant contribution. The single-beam CARS method eliminates the need for crossing three separate laser pulses (pump, Stokes, and probe) as used for arms-length identification of anthrax spores,^{46,48} making it more practical for standoff detection 50-100 m from the laser and detection unit.



Figure 3.1. a) Supercontinuum spectrum (grey) and the phase measured using MIIPS (dashed black). (b) Measured SHG spectra (black) from the compensated pulses (spectrometer limited at 300 nm). The experimental SHG spectrum has a bandwidth of 73nm (FWHM), which agrees well with simulations for transform-limited pulses based on the measured spectrum. The supercontinuum pulses were compressed to 4.8 fs by MIIPS phase compensation (see inset). (c) Residual phase on the laser after compensation.

3.2 Experimental Set-up

Femtosecond laser pulses from a Micra oscillator (Coherent) are shaped by a 4f

reflective pulse shaper using a 128-pixel phase-only programmable liquid crystal spatial

light modulator (SLM) (CRi). The shaped pulses are then amplified by a regenerative

amplifier (Legend USP, Coherent) and focused by a 1 meter focal length curved mirror into an argon-filled hollow waveguide that is 0.39 m long and has a 500 μ m inner diameter. By adjusting the incident laser power, argon pressure and chirp of the input laser pulse, a continuum broadened spectrum is generated.^{66,67} An argon pressure of 0.15 MPa with input pulse energy of 340 μ J is found to generate 200 μ J of hollow waveguide output from 750 to 870 nm. Optimum continuum generation is obtained when high-order dispersion is eliminated by the pulse shaper using multiphoton intrapulse interference phase scan (MIIPS)^{19,9} and a linear chirp of -500 fs² is then added to the input pulse. The broad bandwidth output laser beam is collimated by a 0.75 m focal length curved mirror and shaped by a second 4*f* pulse shaper with a 640pixel, phase and polarization SLM (CRi).

The supercontinuum output spectrum is shown in Fig. 3.1 a); the spectral phase of the output laser beam is measured and compensated by using remote MIIPS⁶⁸, as shown in Fig. 3.1 c). The compensated, 4.8 fs pulses, are found to generate very broad second harmonic generation (SHG) spectrum, shown in Fig. 3.1 b).

For the CARS measurements, wavelengths shorter than 765 nm are blocked at the Fourier plane of the pulse shaper. The laser beam is reflected by a beam splitter and loosely focused on the target 12 m away by a home-built Newtonian telescope consisting of a negative 0.2 m focal length lens and a 0.75 m focal length spherical curved mirror (see Fig. 3.2 a)). The energy at the sample is 10 μ J/pulse, and the beam diameter is 2 mm. This laser power is well below the damage threshold of all the samples studied. For most of the measurements presented here, a mirror is placed behind the sample to retro-reflect the CARS signal for detection through the same telescope. After the signal passes through a horizontal polarizer and a 740 nm low pass filter (Omega Optical), a compact QE65000 spectrometer (Ocean Optics) is used to record the CARS spectrum. For other measurements, we remove the mirror behind the target and applied liquid samples (toluene and *o*-xylene), which form a thin film, to a scattering surface.





Figure.3.2. Setup and performance of the single-beam CARS. a) The experimental setup. b) The spectrum, phase and polarization of components of the shaped laser pulse. The pump and Stokes (red) components have vertical polarization (y) while the probe (green) and CARS signal (blue) have horizontal polarization (x). The inset shows a diagram for the CARS process. c) Spectra of six consecutive single shot spectra of toluene collected at a standoff 12 m distance.

3.3 Pulse Shaping for Single-beam CARS

As previously mentioned, the second pulse shaper uses MIIPS to compensate the dispersion introduced by the hollow waveguide, telescope optics and propagation in air $(k'_{air} = 20.1 \text{ fs}^2/\text{m})^{69}$, ensuring transform-limited pulses at the target. It is also used to control the phase and polarization of different components of the laser pulse in a way that minimizes the non-resonant contribution and improves resolution. The non-resonant CARS signal increases with the bandwidth of the laser, which in our case is 1800 cm⁻¹. In order to reduce the considerable background in single-beam CARS microscopy Oron *et al.* use a π phase gate.⁵⁰ In other work, they have also introduced a polarization gate to the probe to further improve the resolution.⁵³ We incorporate both of these strategies in our approach. The probe pulse is defined by keeping 6 out of 640 pixels (about 1.5 nm bandwidth, centered at 770 nm) horizontally polarized while using the SLM to rotate the rest of the pulse to vertical polarization. A π phase gate (3 out of 640 pixels) is also used.

3.4 Results and Discussion: Neat Samples

Single shot spectra obtained from a liquid toluene sample are shown in Fig. 2(c) to illustrate the speed, reproducibility and sensitivity of the system. The single-beam

CARS spectra of several liquid, gaseous and solid state samples obtained at a distance of 12 m are shown in Fig. 3. For these spectra, the non-resonant broadbandwidth contribution is fitted and removed by subtraction. Figures 3.3 a) and 3.3 b) present CARS spectra for a number of liquid samples including different isomeric species, which are easily distinguishable by this technique. Spectra from carbon disulfide (CS₂), 1,2dichloroethane (C₂H₄Cl₂) and chloroform (CHCl₃) vapors (0.11 m sample path length with vapor pressures of 40, 12, and 21 kPa respectively) were also recorded, and are shown in Fig. 3.3 c). The spectra for several solids including polycarbonate, polystyrene and polymethyl methacrylate (PMMA) are displayed in Fig. 3.3 d). We have observed similar signal levels for condensed phase samples of 0.1 to 10 mm thickness, leading us to believe that the majority of signal generation occurs within a thin region of the sample where phase matching is satisfied.



Figure 3.3. Single-beam CARS spectra from liquid, gaseous and solid state samples. a) CARS spectra from liquid toluene, *o*-nitrotoluene and *m*-nitrotoluene; b) CARS spectra from liquid *ortho, meta and para-*xylene. c) CARS spectra from CS₂, CH₂Cl₂ and CHCl₃ vapors; d) CARS spectra from solid polycarbonate, polystyrene and PMMA.

To illustrate the necessity for compensation of phase distortions, the unprocessed CARS spectrum of *m*-xylene is presented in Fig. 3.4 a) before and after elimination of spectral phase distortion using MIIPS, which results in a significant (order of magnitude) increase in the CARS signal. Note that despite polarization shaping, the non-resonant contribution (broad feature spanning the whole spectrum) is more intense

than the resonant CARS features at 725 and 1000 cm⁻¹. The ability to isolate the desired signal from a complex chemical background is a critical requirement for molecular sensing. In particular, for CARS it is important to eliminate, as much as possible, contributions from the non-resonant contribution. These improvements are achieved by phase, amplitude and polarization shaping.

3.5 Results and Discussion: Selective Excitation and Backscatter

In addition to affecting the non-resonant signal, spectral phase can also provide a method for achieving molecular selectivity. Silberberg and coworkers used a sinusoidal phase function to control the single-beam, broad bandwidth CARS process and achieved molecular selectivity.⁵² Also, maximum intrapulse interference can be used to achieve selectivity in nonlinear optical processes using binary phase functions.^{70,71} When using binary phases, the laser pulse spectrum is partitioned into discrete regions, each receiving a phase retardation value of zero or π . The CARS signal at each frequency Ω is given by the sum of discrete contributions from all the frequencies in the pulse whose difference is Ω according to the equation: $E(\Omega) = \Sigma \omega E(\omega) E^*(\omega - \Omega)$, where the electric field E can only take the value of (+1) when the phase is zero and (-1) when the phase is π The goal becomes finding the binary phase function that causes the sum to reach a maximum for the desired Ω , and zero elsewhere. Fortunately, this problem has been solved in the field of mathematics. The type of functions that we are looking for are known as Galois fields⁷², or minimum correlation

sequences.⁷³ Pseudorandom binary sequences have been used to create pulse

trains^{63,74} and to control nonlinear optical processes.⁷¹

Figure. 3.4



Figure. 3.4 Single-beam CARS illustration of sensitivity and discrimination against background signals. a) Unprocessed spectra of *m*-xylene collected at a standoff 12 m distance with (black) and without (red) phase distortion compensation using MIIPS; note the presence of a large nonresonant contribution (compared to the resonant signal) in both cases. b) The red phase is designed to optimize excitation of the v₁ breathing mode at 725 cm⁻¹ and the blue phase is designed to optimize excitation of v₁₂ in-plane bending mode at 1000 cm⁻¹. The lower panel shows the calculated temporal profiles corresponding to red and blue phases. c) Unprocessed CARS spectra from *m*-xylene with two specially designed binary phases. Note that the nonresonant contribution is successfully suppressed eliminating the need for data processing. The designed binary phases control the ratio between the two Raman peaks with an overall two order-of-magnitude discrimination from 7:1 to 1:12. d) Integrated intensity for different binary phases (optimized for different Raman shifts) applied in the pulse shaper.

Here, we use optimal discrimination based on Galois fields synthesized using binary phase functions to achieve selective excitation of individual vibrational modes, and at the same time eliminate the non-resonant contribution. One of the reasons why the non-resonant signal is greatly reduced is that the complex binary spectral phase causes the creation of a train of pulses in the time domain (see Fig. 3.4 b)). The temporal profiles of the pulses corresponding to red and blue binary phases show oscillation periods ~46 fs and ~33 fs, which match the vibration frequency of v_{1} breathing and v $_{12}$ in-plane bending modes of *m*-xylene, respectively. By spreading the peak intensity of the ultrashort pulse into several sub-pulses, the non-resonant contribution is essentially eliminated. This type of pulse shaping allows for CARS data to be collected with high selectivity despite the ultrabroad bandwidth. The unprocessed spectra in Fig. 3.4 c) show selective excitation of the v $_1$ or v $_{12}$ modes of *m*-xylene⁷⁵, with the elimination of non-resonant contribution. We point out that selective vibrational excitation of two different molecules in a mixture was reported recently using feedback

controlled optimization in a three beams (two colors) setup with a special crossed-beam geometry.⁷⁶ Frequency selective excitation, as shown here, gives single-beam CARS a means to discriminate between different compounds in a complex mixture, making it ideal for applications in complex environments. By collecting the integrated CARS signal for each binary phase, single-beam CARS spectroscopy can be achieved without a spectrometer, as shown in Fig. 3.4 d).

Up to this point, the data obtained made use of a mirror placed behind the sample to retroreflect the CARS signal. In Fig. 3.5, we show data obtained from backscattered signal. For this experiment, we apply a drop of toluene or o-xylene on a surface covered with transparent polymer beads. The signal is collected by imaging the surface on the detection fiber placed at an arms-length distance. The characteristic Raman signatures can be easily identified. As we contemplate the application of this method to standoff detection of explosives at 50-100 m, we plan to increase the energy per pulse from 10 µJ to 100 µJ, increase the diameter of the telescope used for excitation and signal collection, and to use a photon counting, spectrally dispersed signal detector. Overall, we expect these changes should result in up to three orders of magnitude increase in signal. By using the time-gated detector, we will be able to obtain time-of-arrival information of the CARS signal and to further discriminate against ambient light. With these enhancements, we believe that this approach will have a significant impact in the standoff detection of films and residues located on solid targets which scatter or reflect the incident light.



Figure 3.5 Single-beam CARS spectra with back scatter signal detection. a) Unprocessed spectrum of *o*-xylene. b) Processed spectra of *o*-xylene and toluene.

3.6 Results and Discussion: Mixtures and Concentration measurements.

The following section contains excerpts which are reproduced in part with permission from H. Li, D. A. Harris, B. Xu, P. J. Wrzesinski, V. V. Lozovoy, and M. Dantus, Coherent mode-selective Raman excitation towards standoff detection," *Optics Express* **2008**, 16, 5499-5504. Copyright 2008. Optical Society of America.

In addition to the measurement of neat samples, mixtures of liquids and gas samples were also examined. A binary mixture of molecular isomers, *o*-xylene and *p*xylene, was studied at various concentration ratios ranging from 50:50 to 1:99 volume to volume. These measurements were made using the standoff detection set-up described previously. Figure 3.6 a) displays the CARS spectra for both molecules in the 50:50 mixture, while Fig.3.6 b) displays the 1:99 ratio.



Figure 3.6. CARS measurements of *o*-xylene and *p*-xylene mixture; a) is a 50:50 mixture, b) is a 1:99 mixture.

In Fig. 3.7, the relative intensity of the o-xylene (735 cm⁻¹) with respect to *p*-xylene (825 cm⁻¹) is plotted as a function of o-xylene concentrations ranging from 1-10% on a double logarithmic scale. The linear fit results in a slope of ~1.4. The CARS response should result in a value of 2.0 for the slope, while the non-resonant should result in a value of 1.0. The 1.4 value suggest that the measured CARS response is not purely resonant and contains some interference from the non-resonant contribution to the signal.



Figure 3.7. Double logarithmic plot of the relative CARS intensity for o-xylene and p-xylene as a function of o-xylene concentration.

In addition to performing measurements on liquid samples, several gas phase samples were examined. The experimental set-up varied slightly in that the experiments were made using a pressure cell for the various gases and the CARS signal collected in transmission mode. The experimental setup for the gas phase measurements is highlighted in Fig. 3.8.



Figure 3.8 Schematic diagram of the single-beam CARS instrument for detection of gasphase measurements.

Two different gases were examined: nitrogen, with a single resonance at 2330 cm⁻¹, and carbon dioxide, with two resonances at 1285 and 1388 cm⁻¹. Nitrogen was first examined as a function of pressure, up to 8 bar. These plots are shown in Fig 3.9. For each data point, the intensity of the CARS signal for nitrogen was integrated over a narrow spectral region. Fig. 3.9 a) displays the range for pressures up to 2 bar, while b) displays the pressures from 2-8 bar for nitrogen.



Figure 3.9. Nitrogen CARS signal as a function of pressure. Symbols represent the data points, while the solid lines are the power curves, fit to the data. Each plot contains three sets of data, illustrating the reproducibility of the measurements.

The CARS signal dependence on number density was also examined in CO2. These

measurements were performed under the same conditions as the nitrogen experiments.

Each vibrational mode, 1285 cm⁻¹ (B in Fig. 3.10) and 1388 cm⁻¹ (A in Fig. 3.10), is

plotted as a function of pressure and fit with a power curve as shown in Fig 3.10.



Figure 3.10. Carbon dioxide CARS signal as a function of pressure. Symbols represent the data points, while the solid lines are the power curves, fit to the data. In the low pressure regime for nitrogen, the CARS signal depends on the number density squared, as one would expect; however, for the higher pressure region (2-8 bar), the CARS signal is linearly dependant on the number density. In carbon dioxide, the signal from each mode does not show the expected number density relationship, with a saturation point appearing around 5 bar. The saturation effects and non-quadratic dependence may be due to nonlinear optical effects such as self-phase modulation or additional multiphoton processes, collisional line mixing⁷⁷, pressure effects on the coupling constants between the CO₂ Fermi resonances⁷⁸, saturation of the Raman transitions, or interference between the resonant and nonresonant responses.⁷⁹

3.7 Conclusions

Single-beam CARS using amplified femtosecond pulses has demonstrated its ability to be in several different fields. The additional energy provided by the amplified pulses allows for the single-beam method to be readily extended to distances much larger than those of the initial microspectroscopy applications. The ability to operate at larger distances along with the additional advantages provided by the single-beam CARS method highlight the applicability of this method for remote sensing. Additionally, this method has demonstrated the feasibility to be used for gas phase measurements, particularly those which may be of interest for the diagnostics of combustion processes or reacting flows.

Chapter 4

Selective Excitation of Gas Phase Molecules

This chapter expands upon the previous work and focuses on the theory and an methodology for selective excitation. In particular, this work highlights the application of binary phase shaping (BPS) for selective excitation of gas phase molecules. The application to gas phase molecules is significant in that CARS methods are one of the primary methods for the diagnostic of combustion processes.⁸⁰⁻⁸⁵ The following It is reproduced with permission from P. Wrzesinski, D. Pestov, V. V. Lozovoy, B. Xu, S. Roy, J. R. Gord, and M. Dantus, "Binary phase shaping for selective single-beam CARS spectroscopy and imaging of gas-phase molecules", *Journal of Raman Spectroscopy* **2011**, 43, 393-398 Copyright (C) 2010 John Wiley & Sons, Ltd.

4.1 Selective Excitation

Selective excitation of Raman modes facilitates nonresonant-background suppression in the single-beam CARS scheme. Importantly, it also allows for elimination of multi-channel acquisition of CARS spectra, which is difficult to integrate with high-speed laser beam scanning for imaging applications. Sinusoidal phase modulation, though conceptually simple, provides a fairly low degree of signal rejection at off-resonant Raman frequencies. Better contrast is expected for linearly chirped pulses that have been utilized extensively in multi-beam CARS setups.⁸⁶⁻⁸⁸ Another attractive alternative, discussed in this work, is pseudorandom binary sequences. Using pseudorandom binary phase shaping (BPS), we have demonstrated previously high-

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contrast excitation selectivity for second-harmonic generation (SHG), two-photon excited fluorescence, and stimulated Raman scattering.⁷¹ We have also applied BPS for mode-selective CARS with liquid samples.⁸⁹ Here we extend it to selective excitation of gas-phase molecules. In particular, we use pseudorandom BPS for selective excitation of O₂ (~1550 cm⁻¹) and N₂ (~2330 cm⁻¹) vibrations in ambient air. We also show independent excitation of CO₂ Fermi dyads at ~1280 cm⁻¹ and ~1380 cm⁻¹ in gas-phase CO₂ and CO₂/N₂ mixtures. Finally, we demonstrate selective single-beam CARS imaging of CO₂ gas jet.

4.2 Binary Phase Shaping for Selective Single-Beam CARS

Coherent vibrations of a molecular ensemble in CARS are established through the nonlinear interaction with the optical field. The excitation efficiency is, therefore, dependent on both the amplitude and the relative phase of contributing spectral components, or rather on multiphoton intrapulse interference (MII) since the excitation is impulsive.⁹⁰ The coherence amplitude at some wavenumber Ω_R is proportional to

$$E^{(0)}(\Omega_R) \equiv \int_{0}^{+\infty} E(\Omega + \Omega_R) E^*(\Omega) d\Omega, \qquad (4.1)$$

where $E(\Omega) \equiv |E(\Omega)| \cdot \exp(i\varphi(\Omega)) \propto \sqrt{S(\Omega)} \cdot \exp(i\varphi(\Omega))$ is a complex spectral amplitude of the field at wavenumber Ω , determined by the spectral field intensity $S(\Omega)$ and phase $\varphi(\Omega)$. Since the pulse shaper operates with a finite number of independent channels, it is insightful to rewrite Eqn. (4.1) for a mesh of N equidistantly spaced points between

$$\Omega_{\min}^{ps} \text{ and } \Omega_{\max}^{ps} :$$

$$E_n^{(0)} \equiv \sum_{m=0}^{N-n-1} E_{m+n} E_m^* \propto \sum_{m=0}^{N-n-1} \sqrt{S_{m+n} S_m} \cdot \exp(i(\varphi_{m+n} - \varphi_m)),$$

$$n = 0 \text{ K } N - 1.$$
(4.2)

The notations used are:

$$E_{j}^{(0)} = E^{(0)}(j\Delta\Omega_{N}), \quad E_{j} \equiv E(\Omega_{j}), \quad S_{j} \equiv S(\Omega_{j}), \quad \varphi_{j} \equiv \varphi(\Omega_{j}),$$

$$\Omega_{j} = \Omega_{\min}^{ps} + j \cdot \Delta\Omega_{N}, \quad \Delta\Omega_{N} = (\Omega_{\max}^{ps} - \Omega_{\min}^{ps})/(N-1), \quad j = 0 \text{K } N-1.$$
(4.3)

If we now limit the phase values to 0 or π (more generally, to two values offset by π)

and assume that the spectral intensity within the $[\Omega_{\min}^{ps}, \Omega_{\max}^{ps}]$ -interval remains constant, we find that the electric field $\{E_j\}$, subject to proper normalization, can be presented as a sequence of values +1 and -1. Since all such sequences of length *M* form a mathematical object known as a Galois field $GF(2^M)$, the problem of selective excitation can be linked to the number-theory problem of finding sequences of numbers +1 and -1 with minimal autocorrelation. Indeed, for every given Raman shift $\Omega_R^{j0} \equiv j_0 \cdot \Delta \Omega_N$, the excitation efficiency is determined by $E_{j0}^{(0)}$ from Eqn. (4.2), *i.e.*, by

correlation of $\{E_j\}$ and $\{E_{j+j_0}\}$. When the binary sequence is repeated after $\Omega_R^{j_0}$,

 $E_{j}^{(0)}$ would have a maximum at $j = j_{0}$. The use of a minimal-autocorrelation sequence to modulate the phase, however, ensures that the excitation at nearby frequencies is suppressed.

Following the considerations above, the phase mask across the pump-Stokes part of the spectrum is built as follows; see the diagrams in Fig. 4.1. We first assign the minimal, Ω_{\min}^{ps} , and maximal, Ω_{\max}^{ps} , wavenumbers of the pump-Stokes band and compare its bandwidth, $\Delta \Omega^{ps} \equiv \Omega_{\max}^{ps} - \Omega_{\min}^{ps}$, with $2\Omega_R$, where Ω_R is the selected wavenumber. Here we assume that the pump-Stokes bandwidth $\Delta \Omega^{ps}$ exceeds Ω_R , *i.e.*, the transition can be excited impulsively. If $\Delta \Omega^{ps} < 2\Omega_R$, as shown in Fig. 4.1 a), the chosen



4.1. Selective excitation of Raman-active vibrational modes via BPS: a) binary phase mask design for $\Delta\Omega^{PS} < 2\Omega_R$; b) binary phase mask design for $\Delta\Omega^{PS} \ge 2\Omega_R$. Here

 $\Delta\Omega^{ps}$ is the bandwidth of the pump-Stokes part of the laser spectrum; Ω_R is the transition Raman shift.

pseudorandom sequence is stretched over a ($\Delta \Omega^{ps} - \Omega_R$)-wide interval, from Ω_{max}^{ps} down to $\Omega_{\min}^{ps} + \Omega_R$, and then repeated between $\Omega_{\max}^{ps} - \Omega_R$ and Ω_{\min}^{ps} , with translational symmetry relative to the first interval. The interval between Ω_{max}^{ps} - Ω_R and $\Omega_{\min}^{ps} + \Omega_R$, which does not contribute towards excitation at Ω_R , is filled with a high-frequency random binary phase to suppress the background contribution from this part of the spectrum. If $\Delta \Omega^{PS} \ge 2\Omega_R$ (see Fig. 4.1 b)), the Galois sequence is stretched over Ω_R and encoded from Ω_{max}^{ps} to $\Omega_{max}^{ps} - \Omega_R$, and then from $\Omega_{max}^{ps} - \Omega_R$ down to $\Omega_{\text{max}}^{ps} - 2\Omega_R$. The left-over SLM pixels are again filled with a high-frequency random binary phase. In principle, one can put in as many sequence copies as can fit in $\Delta\Omega^{ps}$, *i.e.* more than two. The extra copies, however, will contribute to higher harmonics of Ω_R as well. At last, it is worthwhile to note here that Galois sequences are best suited for shaping of flat-top laser spectra. Their minimal-autocorrelation property implies equally weighted contribution from every term in a sequence, which is not quite the case for the spectrum provided by our laser source. In practice, it results in inferior background suppression when compared to the optimal case.

To retrieve CARS spectra, we use a polarization-shaping technique.^{53,89} The polarization of a narrow band on the blue side of the laser spectrum (polarization P_x in Fig. 4.2 a), four SLM pixels wide) is rotated by 90° relative to the remaining spectrum. The polarizer in the acquisition arm is also set along this polarization. Only CARS photons with polarization P_x are detected. The intense P_y-polarized signal, overwhelmed by the nonresonant background produced by the pump-Stokes component and having poor spectral resolution, is rejected. We also encode a π -phase step across the P_x-polarized band when acquiring multi-mode CARS spectra, as shown in Fig. 4.2 b). The π step is used to minimize the time overlap between the P_y-polarized pump-Stokes and P_x-polarized probe parts, mitigating the contribution due to the instantaneous electronic response.



Figure 4.2 Phase-and-polarization shaping for multi-mode and selective single-beam CARS measurements. a) Polarization mask encoded onto the laser spectrum, shown on the background by the gray line; b) Phase mask for multi-mode CARS measurements, when all Raman modes within the laser bandwidth are excited. c,d) Pseudorandom phase masks used for selective single-beam CARS from O_2 (1550 cm⁻¹) and N_2 (2330 cm⁻¹), respectively.

Two examples of selective-excitation phase masks, based on a 37-bit Galois sequence, are shown in Figs. 2 c) and 2 d). The phase mask in Fig. 2 c) is designed to excite the O₂ vibrational mode at ~1550 cm⁻¹. For the given experimental parameters, the condition $\Delta\Omega^{Ps} \ge 2\Omega_R$ is fulfilled; therefore, the Galois binary sequence is stretched over 1550 cm⁻¹, and its two copies are stacked together next to the probe band. The pseudorandom phase mask in Fig. 2 d) targets the N₂ Raman transition at ~2330 cm⁻¹. Here $\Delta\Omega^{Ps} < 2\Omega_R$ and the two sequence copies are separated by a random binary modulation.

Using this method, phases for selective excitation of the two Fermi dyads of CO₂, and the Raman modes of O₂ and N₂ were designed. The normalized excitation efficiency spectra $\eta(\Omega_R)$,

$$\eta(\Omega_R) = \left| E^{(0)}(\Omega_R) / E^{(0)}(0) \right|^2, \tag{4.4}$$

for each of the phases as well as for zero phase, which corresponds to a transform limited (TL) pulse, are shown in Fig. 4.3. From the figure it is clear that BPS is used most effectively when the condition $\Delta\Omega^{PS} < 2\Omega_R$ is fulfilled. When $\Delta\Omega^{PS} \ge 2\Omega_R$, BPS eliminates high-harmonic contributions at the expense of the inferior excitation strength. Raman-shift-dependent excitation efficiencies, both due the limited laser bandwidth and spectral phase shaping, contributes towards the strength of Raman peaks observed in CARS spectra. In principle, such dependences might be accounted for experimentally by the normalization of the CARS signal on the purely nonresonant response from a reference sample. To predict the measured CARS spectra or use those to retrieve relative concentrations of contributing species, however, one also needs to account for the timing between the pump-Stokes and probe fields, Raman cross sections of transitions being examined, and their coherence dephasing rates. This is currently under development, along with other possible methods to perform selective excitation in single-beam CARS.



Figure 4.3 Calculated excitation spectra, $\eta(\Omega_R)$, for a TL pulse (no phase modulation) and waveforms, produced by pseudorandom BPS for selective excitation at 1280 cm⁻¹, 1380 cm⁻¹, 1550 cm⁻¹, and 2330 cm⁻¹.

4.3 Experimental

The experiments were performed with a system based on a Ti:sapphire regenerative amplifier (Legend, Coherent Inc.); see Figure. 4.4. A pulse shaper (not shown) was installed between the oscillator (Micra, Coherent Inc.) and the amplifier to remove high-order phase distortion of laser pulses at the regenerative-amplifier output. The laser spectrum was then broadened through self-phase modulation in a hollow waveguide (HWG),⁹¹ constructed from a 39-cm-long glass capillary with a core
diameter of ~300 µm and filled with argon at ~2 bar. The HWG output bandwidth was optimized by varying the input power, pulse chirp, and argon pressure. The typical spectrum of a pulse reaching the sampled volume is shown in the inset of Fig. 4.4. The corresponding TL pulse duration is about 7 fs. Phase distortions of the pulse at the sample (primarily linear chirp of $\sim 2000 \text{ fs}^2$) were corrected via multiphoton intrapulse interference phase scan (MIIPS)¹⁰, performed with a 4f pulse shaper located after the HWG. The same shaper was used for polarization-and-phase shaping as discussed below. It had a dual-mask 640-pixel spatial light modulator (CRi SLM-640-D) at the Fourier plane, with the polarizer removed. The beam of shaped pulses was focused in ambient air or a gas pressure cell using a 75-cm-focal-length curved mirror. A concave metallic mirror with 25-cm focal length was used for imaging of the CO₂ jet. The generated CARS signal was separated from the input field using a 650-nm short-pass filter (Omega Optics) and a calcite polarizing cube (Newport), with the transmission axis set perpendicular to the polarization of the excitation photons. The filtered CARS photons were either focused into a high-resolution spectrograph with a LN-cooled CCD camera or fiber-coupled into a low-resolution Ocean Optics QE-65000 spectrometer. For imaging experiments, we used two motorized translation stages to shift the nozzle in the focal plane of the laser beam. Spectrally integrated CARS signal over 1460 cm⁻¹ was recorded as a function of the nozzle position.



Figure 4.4 Schematic diagram of single-beam CARS experimental setup. SLM, spatial light modulator. Inset: a typical pulse spectrum at the sample.

4.4 Results and Discussion

Selective excitation via BPS was examined with several different gases. Initial experiments were performed with ambient air, whose CARS spectrum is expected to have two strong Raman lines corresponding to vibrations of O_2 (~1550 cm⁻¹) and N_2 (~2330 cm⁻¹) molecules. The experimental multi-mode CARS spectrum (gray shadow in Fig. 5) indeed features a pronounced N_2 line. The O_2 line, however, is hidden by the remaining nonresonant contribution that rises at low wavenumbers. Selective excitation at 1550 cm⁻¹, using the phase mask from Fig. 4.2, mitigates the interfering background and makes the O_2 line obvious. The other pseudorandom phase mask highlights the N_2 vibrational mode. The slight offset of the spectra from zero is due to the electronic dark current of the LN-cooled CCD used for detection.



Figure 4.5 Selective single-beam CARS from O₂ and N₂ vibrations in ambient air.

Single-beam CARS measurements with a 1:1 N_2/CO_2 mixture in the pressure cell showed similar results. In the multi-mode CARS spectrum, the nonresonant background due to the instantaneous electronic response interferes with the two CO_2 signatures; see Fig. 6. The designed binary phase masks allow exciting all three Raman lines, including the N_2 line and CO_2 Fermi dyads at ~1280 cm⁻¹ and ~1380 cm⁻¹, independently. They also strongly suppress the nonresonant background.





The excitation selectivity contrast can be inferred from Fig. 4.7 a), where the CARS signal intensities at 1280 cm⁻¹, 1380 cm⁻¹ and over the entire spectral region (625-2125 cm⁻¹) from pure CO₂ gas at 1 atm are plotted as a function of the design parameter Ω_R .



Figure 4.7 Selective single-beam CARS of pure CO₂ at 1 atm. The target Raman shift Ω_R of the pseudorandom binary phase is tuned through the two resonances with CO₂ Fermi dyads at ~1280 cm⁻¹ and ~1380 cm⁻¹. CARS signal intensities at 1280 cm⁻¹, 1380 cm⁻¹, and integrated over 625-2125 cm as a function of Ω_R .

Several representative CARS spectra, acquired with Ocean Optics QE-65000 spectrometer while scanning Ω_R , are shown in Fig. 4.8. When the 1280-cm⁻¹ line is selectively excited, the ratio of CARS intensities between the 1280 cm⁻¹ and 1380 cm⁻¹ lines is 10:1. For selective excitation of the 1380cm⁻¹ CO₂ line, the ratio between the 1280 cm⁻¹ and 1380 cm⁻¹ lines is 1:24. When the CARS signal is not resolved

spectrally, the contrast is limited primarily by the cumulative nonresonant contribution reaching the detector.



Figure 4.8 Experimental CARS spectra acquired for Ω_R equal to 1200 cm⁻¹, 1280 cm⁻¹, 1330 cm⁻¹, 1380 cm⁻¹, and 1500 cm⁻¹ The multi-mode single-beam CARS spectrum of CO₂ (no BPS) is shown as a reference. The other CARS spectra are scaled in intensity by a factor of 6.

To emphasize the utility of selective BPS, we imaged a jet of CO₂ gas, flowing

out a narrow rectangular nozzle, with TL and shaped pulses. In both cases, a 0.6-by-2.2 mm region near the tip of the nozzle was scanned using 0.01 mm vertical steps and 0.05 mm horizontal steps. The spectrally integrated CARS signal from 1060-2520 cm⁻¹ was recorded at each position in the scan. The image obtained with TL pulses (see Fig. 4.9 a)) exhibits poor chemical contrast, which can be improved, however, by spectral

filtering of the CARS signal corresponding to the CO₂ lines or by post-processing of CARS spectra if those are available. Note that the CARS spectra over the observed range featured N₂ and O₂ lines from ambient air as well as comparable nonresonant contribution at lower wavenumbers (longer wavelengths). Selective excitation, implemented in Fig. 4.9 b) for 1280 cm⁻¹ Raman transition in CO₂, virtually eliminates the need for signal post-processing, favors single-channel detection, and allows for straightforward tuning between different Raman resonances. The image in Fig. 4.9 b) demonstrates excellent chemical contrast and reveals interesting dynamics of the turbulent CO₂ flow. In particular, the intensity modulation seen in the CO₂ flow is reproducible from image to image and is deemed to be characteristic of the imaged jet.



Figure 4.9 Imaging of a CO₂ gas jet with a) no BPS and b) BPS excitation at 1280 cm⁻¹.

4.5 Conclusions

We have extended the pseudorandom BPS technique, introduced elsewhere, to selective excitation of high-wavenumber molecular vibrational modes in the gas phase. In particular, we have used it to address Raman transitions of O₂ and N₂ in ambient air as well as CO₂ Fermi dyads in a 1:1 N₂/CO₂ mixture and pure CO₂ gas at atmospheric pressure. We have shown that pulse phase shaping using pseudorandom BPS allows for high-contrast selectivity and efficient nonresonant-background suppression in single-beam CARS measurements, enabling high-contrast spectroscopy and imaging.

Chapter 5

Multi-method Selective CARS

This chapter discusses the use of Multiphoton Intrapulse Interference to provide selective excitation of a single Raman mode. Selective excitation has been previously shown as a method to dramatically decrease the non-resonant response, providing large signal to noise levels and high selectivity desirable for applications that require high data acquisition rates. Various phase shaping methods for performing MII are used in conjunction with single-beam CARS spectroscopy.

5.1 Mulitphoton Intrapulse Interference (MII)

Numerous applications of Multiphoton Intrapulse Interference (MII) have been demonstrated for the coherent control of atomic and molecular systems.^{92-95,19,96-98} In MII, the spectral phase of the pulse is used to constructively or destructively interfere pairs of frequencies within the bandwidth of the laser at a singular desired frequency. This interference allows for enhancement or suppression to occur at the desired frequency. In these experiments, various phase shaping approaches were used to perform selective CARS excitation based upon MII.

Several fundamental phase shaping methodologies were evaluated. Each method has been adapted to the single-beam geometry using a liquid crystal spatial light modulator (SLM) based 4f-pulse shaper. The first phase shape is based upon the use of two chirped pulses. This method has been previously reported for use in a multiple-beam geometry for control of molecular wave packets⁹⁹, improved resolution^{100,87,101},

coherent Raman in highly scattering solids¹⁰², and coherent Raman with white-light pulses.¹⁰³ In the adaption of this method for the single-beam geometry, the pulse spectrum is divided into two portions in the frequency domain (at the center pixel of the SLM), and a uniform chirp phase function is applied to each half using the SLM. The relative delay between the two portions is then tuned, resulting in a time-domain waveform that is matched to the frequency of a desired vibrational mode. Continuous scanning of the delay maps out the entire accessible CARS spectrum. This phase function is described by equation 5.1, where $\varphi(\omega)$ is the desired phase function.

$$\varphi(\omega) = \begin{cases} \varphi_A + \frac{1}{2}\varphi^{(2)} \left(\omega - \omega_D + \frac{1}{2}\Omega_R\right)^2 & \text{if } \omega > \omega_D \\ \varphi_B + \frac{1}{2}\varphi^{(2)} \left(\omega - \omega_D - \frac{1}{2}\Omega_R\right)^2 & \text{if } \omega \le \omega_D \end{cases}$$
(5.1)

In this phase function, $\varphi^{(2)}$ is the amount of linear chirp applied (1000 fs²), ω_D is the divider frequency, and Ω_R (1500 cm⁻¹) is the desired Raman frequency to be excited. This is illustrated in Fig.5.2 using a rectangular spectrum with a bandwidth of ~200 nm to simulate the effect of the pulse shaping in the time domain. Panel a) illustrates the pulse spectrum (pump/Stokes and probe) and the applied spectral phase in the wavelength domain; panel b) shows the pulse in the frequency domain along with the applied phase with respect to τ (relative delay between frequencies). Finally, panel c) shows the time domain profiles for both the pump and probe.



Figure 5.1. Simulation of MII using two chirped pulses with a rectangular spectrum. $\varphi^{(2)} = 1000$ fs, the divider is pixel 319, and $\Omega_R = 1500$ cm⁻¹ a) Pulse spectrum (red, solid), probe spectrum (blue, solid), and pulse shaping (blue, dashed) used in the wavelength domain b) frequency domain pulse spectrum (red, solid) and relative phase delay (blue, dashed) c) temporal profiles of the pump/Stokes (red) and probe (blue).

The second approach makes use of sinusoidal phase modulation to perform MII.

The utility of this type of phase modulation has been demonstrated in numerous

applications relating to coherent Raman.^{52,104} When this function is used for mode

selective excitation, a train of pulses with a time interval determined by the sinusoidal

phase period is generated. This period, or integer multiples of the period, coincides with

the period of molecular vibrations that are excited. The sinusoidal phase can be defined

as follows:

$$\varphi(\omega) = \alpha \cdot \cos\left(2\pi \frac{\omega - \omega_c}{\Omega_R} - \delta\right) \tag{5.2}$$

Here α , ω_{c} , $\Omega_{R, and} \delta$ are the amplitude (2 π), central frequency (770 nm), desired Raman transition (1500 cm⁻¹), and relative shift in period (1) respectively. The values of each are fixed with the exception of the desired Raman transition. The time domain profile for this pulse shape is shown in Fig. 5.2.



Figure 5.2. Simulation of MII sinusoidal phase modulation, with a rectangular spectrum. $\alpha=2\pi$, $\omega_c=770$ nm, $\Omega_R=1500$ cm⁻¹ and $\delta=1$ a) Pulse spectrum (red, solid), probe

spectrum (blue, solid), and pulse shaping (blue, dashed) used in the wavelength domain b) frequency domain pulse spectrum (red, solid) and relative phase delay (blue, dashed) c) temporal profiles of the pump/Stokes (red) and probe (blue).

A third method using MII for selective CARS excitation with binary phase shaping is also explored. This method was described in greater detail in chapter 4. Briefly, in binary phase shaping, two identical N-bit identical sequences (N=13) are separated by a desired Raman frequency and have phase values limited to zero or π . These sequences are applied to the pump-Stokes frequencies. Alternating zero and π values are written onto all other pixels to prevent excitation at non-desired frequencies. The sequences are chosen based upon minimum autocorrelations at all Raman frequencies except the desired resonance. Scanning of the frequency separation between the two

sequences allows mapping of the Raman excitation at different vibrational frequencies.



Figure 5.3. Simulation of MII sinusoidal phase modulation, with a rectangular spectrum. N=13. a) Pulse spectrum (red, solid), probe spectrum, (blue, solid) and pulse shaping (blue, dashed) used in the wavelength domain b) frequency domain pulse spectrum (red, solid) and relative phase delay (blue, dashed) c) temporal profiles of the pump/Stokes (red) and probe (blue).

5.2 Modeling MII

MII was also used to model the experimental conditions used for the mode-

selective CARS measurements. For these models, the three phase shapes, chirp,

sinusoidal, and binary, were all used. Rather than an idealized rectangular spectrum,

the actually spectrum used for the experiments and the actual phase shapes used for

collection of the experimental CARS data are presented. Two chirp pulses are presented in Fig 5.4 in the same format as the MII simulations. The experimental parameters for these values were selected based upon the experimental limits presented by the pulse shaper resolution and the measurements of various autocorrelations (Chapter 5.4). For the double chirp phase function $\varphi^{(2)}$ = 2000 fs, the divider is pixel 319 and Ω_R =1500 cm⁻¹.



Figure 5.4. Simulation of MII using two chirped pulses and an experimental spectrum. $\varphi^{(2)}$ = 2000 fs, the divider is pixel 319 and Ω_R =1500 cm⁻¹ a) Pulse spectrum (red, solid),

probe spectrum (blue, solid), and pulse shaping (blue, dashed) used in the wavelength domain b) frequency domain pulse spectrum (red, solid) and relative phase delay (blue, dashed) c) temporal profiles of the pump/Stokes (red) and probe (blue).

The same method was also used to examine the Sinusoidal and BPS phase functions for a typical experimental spectrum. Fig. 5.5 shows the results for a sinusoidal function where α =2.25, Ω_R =1500 cm⁻¹, ω_0 =770nm, and δ =0.



Figure 5.5. Simulation of MII sinusoidal phase modulation, using an experimental spectrum. α =2.25 π , ω_c =770 nm, Ω_R =1500 cm⁻¹ and δ =1 a) Pulse spectrum (red, solid), probe spectrum (blue, solid), and pulse shaping (blue, dashed) used in the wavelength domain b) frequency domain pulse spectrum (red, solid) and relative phase delay (blue, dashed) c) temporal profiles of the pump/Stokes (red) and probe (blue).



Figure 5.6 shows the results the MII simulation using BPS functions, where N=37.

Figure 5.6. Simulation of MII using binary phase modulation, and an experimental spectrum. N=37 a) Pulse spectrum (red, solid), probe spectrum (blue, solid), and pulse shaping (blue, dashed) used in the wavelength domain b) frequency domain pulse spectrum (red, solid) and relative phase delay (blue, dashed) c) temporal profiles of the pump/Stokes (red) and probe (blue).

The comparisons between the temporal profiles of the two different excitation spectra

provide very useful information regarding the relative intensities and duration of the

pulse trains produced by the various phase modulations. For the rectangular spectrum,

the pulse train (bottom panel) is always symmetric around time zero, with equal intensity distribution throughout the time duration. The experimental spectrum is asymmetric, with unequal intensity distributions. Furthermore, the phase modulation methods can be compared to one another. For double chirp and BPS, there is nearly the same relative intensity of the pulse train; however, sinsuodial modulation has a much higher relative intensity. The intensity distribution and pulse train duration also differ greatly amongst the pulse shapes.

5.3 Modeling the Excitation Efficiency

Considering the non-interferometric, intensity autocorrelation (Eqn. 5.3) of the excitation pulse with a specific selective excitation phase provides information about the pulse in the time domain.

$$A(\tau) = \int_{-\infty}^{\infty} I(t) I^*(t+\tau) dt$$
(5.3)

This time domain information will contain a repetitive oscillation, or beating frequency, corresponding to a vibrational time period (33.3 fs = 1000 cm⁻¹). This function can then be Fourier transformed to extract the frequency data. According to the Convolution Theorem (Eqn. 5.4), the power spectrum of the intensity of the pulse $I(\Omega)$ is the Fourier transform of the autocorrelation function:

$$F[A(\tau)] = |I(\Omega)|^2 \tag{5.4}$$

Stimulated Raman scattering (SRS) measured is proportional to the product of this spectral intensity (property of the Pump-Stokes light) and cross-section of the Raman transition (property of the molecules).

By autocorrelating each shaped pulse with itself and Fourier transforming the autocorrelation, the SRS excitation can be generated for that particular pulse shape. By evaluating a matrix of phase values, a 2D plot can be generated and can be used to highlight the efficiency at a particular frequency as a function of the excitation phase. This is illustrated in Fig. 5.7. The diagonal feature illustrates the correspondence between the expected excitation frequency (Ω_R) as a function of phase shaping and the measured excitation efficiency.



Figure 5.7. Simulation of autocorrelation data for a) two chirped pulses, b) sinusoidal modulation, and c) binary phase shaping.

From these simulations the following conclusions can be made. First, we expect the chirp and sinusoidal phase functions to have the highest intensity, particularly in the lower wavenumber region. Both of these phase functions use the entire bandwidth of the excitation pulse, unlike BPS which only uses a portion. It is possible to modify the BPS function to use the entire bandwidth; however, this would result in the production of additional higher frequency contributions such as those seen with sinusoidal modulations near 2000 cm⁻¹. Secondly, the BPS is most effective in the middle of the scan region (1300-1600 cm⁻¹), as this is where the binary phase function uses the largest portion of the excitation spectrum.

5.4 Experimental Set-up

The experimental set-up used in this study has been described in great detail previously in this dissertation. Briefly, the output from a regenerative amplifier (Legend, Coherent) was focused into a narrow (300 μ m I.D.) capillary filled with Ar gas at 1.5 atm. The 2500 cm⁻¹ continuum output is then collimated and directed into a reflective 4-*f* pulse shaper with a 640 pixel liquid crystal spatial light modulator (640D, CRi) capable of phase and polarization or phase and amplitude modulation. This allows for the necessary phase modulation for implementing the various pulse shaping strategies as well as correction of phase distortions.

The phase distortion correction is performed using mulitphoton intrapulse interference phase scanning (MIIPS). MIIPS allows the spectra phase distortions to be directly measured, then implements the opposite function of the measured distortion, which cancels it. This allows for high accuracy pulse shaping at the target. The beam is then steered from the pulse shaper and direction into a symmetric, home built autocorrelator, which is used for the collection of autocorrelation data. The CARS data is collected using a thin (200 μ m) cuvette for liquid samples or a home built pressure

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cell for gas phase samples. The output signals are recolimated and focused on to an optical fiber which is coupled into a compact spectrometer (Ocean Optics QE65000).

5.5 Measurement of Excitation Efficiency

The intensity autocorrelation was collected for a matrix of phases with different excitation scan parameters. Each autocorrelation was then Fourier transformed, generating a two-dimensional plot indicating the SRS excitation frequency as a function of a particular scan parameter. These plots should mirror the plot generated by the modeling of the excitation efficiency. Experimental data for chirp, sinusoidal, and binary phase shaping methods in the 1000 and 2000 cm⁻¹ region is shown in Fig.5.8. This experimental data shows very good agreement with the modeled data. This data is then used to ensure proper excitation frequencies and to optimize experimental parameters for collecting CARS from various samples.



Figure 5.8. Experimental autocorrelation data for a) two chirped pulses, b) sinusoidal phase modulation, and c) binary phase modulation.

5.6 Mutli-method CARS in liquid and gas phase

Using the parameters determined from the autocorrelation data, CARS data for neat toluene in a 200 μ m path length cuvette was collected for chirp, sinusoidal, and binary phase functions. For the chirp function, the phase was split at the center pixel of the SLM, and 2000 fs² of chirp was used. The CARS spectrum was measured from 600-2000 cm⁻¹, and Ω_R scanned from 600-1800 cm⁻¹. The resulting 2D plot is shown in Fig. 5.9



Figure 5.9. 2D plot for two chirped pulses. The measured CARS spectrum for toluene is along the y-axis, and the scan parameter for the selective excitation is along the x-axis.

For the sinusoidal phase function, the CARS signal was observed in the same region, while scanning through the same range. The parameters for this function were as follows: α =2.25 π , δ =1, and Ω_R =600-1800 cm⁻¹. Fig. 5.10 displays the 2D plot for this phase function.



Figure 5.10. 2D plot for sinusoidal phase modulation. The measured CARS spectrum for toluene is along the y-axis, and the scan parameter for the selective excitation is along the x-axis.

Lastly, the CARS response from toluene was measured using BPS. For this

phase, the sequence used was N=37; the phase was alternated between 0 and π for all

pixels not in the N-bit sequence. The resulting 2D plot is shown in Fig. 5.11. The

resonant Raman peaks for toluene at 800 and 1000 cm⁻¹ are easily distinguishable

along the diagonal feature. The intensity of the CARS response near 800 and 1000 cm

¹ for all three phase functions is shown in Table 1.



Figure 5.11. 2D plot for binary phase (BPS) modulation. The measured CARS spectrum for toluene is along the y-axis, and the scan parameter for the selective excitation is along the x-axis.

Table 1. CARS intensity of the Raman transitions of Toluene for each type of phase modulation

Phase Function	CARS Intensity at 800 cm ⁻¹	CARS Intensity at 1000 cm ⁻¹
Chirp	200 a.u.	400 a.u.
Sine	900 a.u.	1000 a.u.
BPS	200 a.u.	300 a.u.

In addition to these functions, several other functions were evaluated based upon modifications of the previous functions. Of the phases examined, only one was comparable to the previously used phase functions. This is an asymmetric chirp function in which the low frequency phase is fixed and only the high frequency portion of the phase is scanned. This is in contrast to the symmetric chirp in which both the high and low frequency components are scanned. This phase function can be described as follows:

$$\varphi(\omega) = \begin{cases} \varphi_A + \frac{1}{2}\varphi^{(2)}(\omega - \omega_D - \Omega_R)^2 & \text{if } \omega > \omega_D \\ \varphi_B + \frac{1}{2}\varphi^{(2)}(\omega - \omega_D)^2 & \text{if } \omega \le \omega_D \end{cases} \end{cases}$$
(4)

The resulting 2D plot for the asymmetric chirp phase functions is shown below for the neat toluene sample.



Figure 5.12. 2D plot for two asymmetric chirp pulses. The measured CARS spectrum for toluene is along the y-axis, and the scan parameter for the selective excitation is along the x-axis.

The CARS signal from the asymmetric chirp function is slightly larger than that from the

chirp function with less background signal than is observed with the other pulse shaping

methods.

These same four phase functions were also applied to carbon dioxide in a 125

mm path length pressure cell to examine the resonances at 1280 and 1388 cm⁻¹. The

data for CO_2 is illustrated in Fig. 5.13.



Figure 5.13. Two-dimensional plots showing the scan parameter (Ω_R) vs. the measured CARS response for a) asymmetric chirp b) chirp (c) sinusoidal and (d) BPS phase modulation methods in carbon dioxide.

5.7 Results and Discussion

In evaluation of the data for the different phase modulations, three different

factors are apparent. The first of these is the signal intensities. The second factor is the

off diagonal signal corresponding to non-resonant and off-resonant contributions (in the case of the sine function). Third is the region of highest excitation efficiency for each phase function. From the autocorrelation data, it can be seen that sinusoidal has the highest efficiency in the 800-1000 cm⁻¹ region, versus BPS which has the highest efficiently near 1400 cm⁻¹. In addition to the 2D data sets, integrated plots are generated for each phase function.

For the integrated plots, one band along the scan parameter axis (light yellow in Fig. 5.14a) and a region of the CARS spectrum bound by the parameter axis and spectra resolution (dark yellow in Fig.5.14a) are integrated. The ratio of the two areas can be plotted as a function of the scan parameter. This allows for closer examination of the diagonal feature corresponding to the scanned excitation and resonant Raman transitions. Performing this analysis for each data set allows for direct comparison of the different pulse shaping methods as shown for toluene in Fig. 5.14 a-b.



Figure 5.14. a) Two-dimensional plot for two chirped pulses with the integration scheme highlighted, b) integrated spectra for the various phase functions as a function of the scan parameter.

Examining the data in this manner allows for more direct discussion of the observations made for the 2D data sets. First, sinusoidal and chirp functions have much more intensity than the BPS function; this is evident in the simulation, autocorrelation, and CARS data. The signal strength for the sine function and the chirp functions are nearly equivalent and much higher than the BPS methods. In this situation, the phase function is applied over the entire spectral bandwidth using all frequencies to contribute to the signal, whereas with the BPS only the frequencies from the two active regions contribute, which results in lower signal intensities. Another consideration for the differences in signal intensities between chirp/sinusoidal modulation and BPS is that the BPS method is typically reliant on a rectangular shaped spectrum. In this work, the spectrum is far from this shape, thus reducing the overall effectiveness of the BPS method. While the sine functions produce more off diagonal signal this is to be expected as the sine functions are periodic. This results in higher noise levels and less defined peak structure.

5.8 Conclusions

By comparing the various methods available for mode selective CARS excitation it can be concluded that no single method is more desirable than another. Each method has its own advantages and disadvantages. Sinusoidal modulation has very high signal intensities, but much higher background. The double chirped phase has very low background, but lowers signal intensities. BPS also has low background, suffers from decreased excitation efficiency. The ideal phase is dependent on the desired transition to be measured.

Chapter 6

Group Velocity Measurements of Combustion Gases

This chapter details the measurement of Group Velocity Dispersion (GVD) for gases related to the combustion processes. These measurements are very valuable in that they provide insight into the amount of temporal broadening that will occur as a short pulse propagates in combustion environments. This understanding allows for more accurate models and simulations of experimental conditions. The following chapter is reproduced with permission from P. Wrzesinski, D. Pestov, V. V. Lozovoy, J. R. Gord, M. Dantus, and S. Roy, "Group-velocity-dispersion measurements of atmospheric and combustion-related gases using an ultrabroadband-laser source", *Optics Express* **2011**, 19, 5163-5170. Copyright 2011. Optical Society of America

6.1 Group Velocity Dispersion

Developments in the optical diagnostics of combustion and reacting-flow environments have been closely linked to advances in ultrafast-laser technology. Historically, this field of study has been dominated by the use of nanosecond (10⁻⁹ sec) and picosecond (10⁻¹² sec) sources. However,femtosecond (10⁻¹⁵ sec)-laser sources have recently been successfully applied for gas thermometry¹⁰⁵⁻¹⁰⁷, pressure studies¹⁰⁸, and imaging of turbulent gas flows.¹⁰⁹ While these experiments reinforce the numerous advantages of broadband-laser sources and optical diagnostics on the femtosecond time scale, they also bring attention to an inherent nuance of ultrashort (spectrally broadband)-pulse propagation--femtosecond pulses are much more

susceptible to temporal broadening due to group-velocity dispersion (GVD) than picosecond and nanosecond pulses.

The GVD of many solids $^{110\text{-}112}$ and liquids 113,114 have been measured with several experimental methods. However, GVD information for gas phase molecules is not as prevalent. In this study we focus on the dispersion properties of common atmospheric and combustion gases at room temperature and explored their scalability with gas pressure. We relied on the Multiphoton Intrapulse Interference Phase Scan (MIIPS) technique¹⁰ to obtain the chromatic dispersion of these gases over the 700-900 nm range, limited by the spectral bandwidth of our laser. MIIPS directly measures the second derivative of the pulse spectral phase, $\varphi(\omega)$, at the target. This is accomplished by scanning a well calibrated reference phase $f(\omega)$ and observing changes in the second harmonic spectrum. When the curvature of this function, $f''(\omega)$ corrects for the local phase distortion, $\phi''(\omega)$, a local maximum appears in the second harmonic signal, thus allowing $\phi''(\omega)$ to be mapped for the entire spectrum. From the integration of $\varphi''(\omega)$ the phase distortion can then be corrected. However for this work, the $\varphi''(\omega)$ information is sufficient as GVD is defined as

$$GVD(\omega) \equiv \frac{d}{d\omega} \left(\frac{1}{V_g(\omega)} \right) = \frac{d^2 k(\omega)}{d\omega^2} \equiv k''(\omega), \tag{6.1}$$

where $V_g(\omega)$ is the group velocity, $k(\omega) = (\omega/c)n(\omega)$ the wavenumber, and $n(\omega)$ the refractive index of the media, GVD can be obtained from differential MIIPS measurements performed with and without gas in a pressure cell. For a homogenous

gas distribution, the phase difference is proportional to the path length in the cell, $\Delta \phi(\omega) = \Delta k(\omega)L$, and the GVD

$$GVD = \frac{\Delta(\varphi''(\omega))}{L} = \frac{\varphi''_{gas}(\omega) - \varphi''_{vac}(\omega)}{L},$$
(6.2)

where *L* is the interaction length with the dispersive media. A similar approach was previously demonstrated to provide GVD in solutions with high precision and accuracy.¹¹⁵ Note that the MIIPS measurement yields GVD as a function of frequency, ω , i.e., it contains information concerning several leading orders of dispersion in the Taylor-series expansion near the carrier frequency ω_0

$$GVD(\omega) \equiv k''(\omega) = k''(\omega_0) + k'''(\omega_0) \cdot (\omega - \omega_0) + K$$
(6.3)

6.2 Experimental

The dispersion measurements were performed using an ultrabroadband femtosecond oscillator (Venteon; Pulse 1), operating at 75 MHz with 40 mW of average power. The spectral bandwidth covers over 400 nanometers, extending from 620 to 1050 nm (see Fig. 6.1). Such a broad spectrum allowed the measurement of dispersion across the entire 700–900 nm range without wavelength tuning. The output beam passed through a spatial filter and was then directed into a 4f reflective pulse shaper^{16,74} (BioPhotonics Solutions Inc.; MIIPS Box 640) using a 640-pixel, dual-mask, liquid-crystal spatial-light modulator (SLM). Upon exiting the pulse shaper, the beam passed through one of two different pressure cells. One cell, with a path length of 0.90

m, was used for measurements in the low-pressure regime (1–4 bar) and was double passed, increasing the interaction length. The other cell had a path length of 0.20 m and was used for measurement in the high-pressure regime (10–50 bar). After exiting the pressure cell, the beam was focused onto a thin 10-µm KDP crystal for generation of the second harmonic. The second-harmonic-generation (SHG) signal was separated from the fundamental spectrum and focused into a spectrometer (Ocean Optics; QE65000).



Figure. 6.1. a) Broadband spectrum produced by the Venteon oscillator; b) Diagram of experimental setup.

Prior to dispersion measurements, the cell was evacuated, and the intrinsic phase distortions to the system were measured and corrected using MIIPS. The sample gas was then introduced at the desired pressure, and MIIPS was again employed to measure the phase distortions produced by addition of the gas. For each gas measurement a pressure point was randomly selected, and the dispersion was measured in triplicate. All dispersion measurements were performed at room temperature (295 K).

6.3 GVD Measurements

The results of low-pressure measurement of dispersion for seven cylinder gases are summarized in Fig 6.2. For five of those gases, the dependence of dispersion on pressure was measured in a high-pressure regime as well [see Fig. 6.3].



Figure 6.2 Measured GVD at 800 nm as a function of pressure in low (1–4 bar) pressure regimes for several atmospheric and combustion-related gases.



Figure 6.3. Measured GVD at 800 nm as a function of pressure in high (1–50 bar) pressure regimes for several atmospheric and combustion-related gases.

We found that for all gases, the dispersion changed linearly with pressure in the low-pressure regime, as expected due to direct pressure/density relationship (ideal gas behavior) in this limit. However, two of the measured gases--carbon dioxide and ethylene--exhibited a nonlinear dependence of GVD on gas pressure in the high-pressure regime.

The GVD of materials scales linearly with density. To illustrate this dependence for gases we obtain the density using the first approximation of the virial equation of state¹¹⁶
$$P = \rho RT [1 + \beta \rho] \tag{6.4}$$

with the first virial coefficient (β), and plot dispersion as a function of gas density in Fig. 6.4. As expected we see the linear dependence on density.



Figure 6.4 Measured GVD at 800 nm as a function of gas density for nitrogen, oxygen, carbon dioxide, and ethylene along with linear fitting of the data.

For extracting the dispersion values of each gas or gas mixture, the rise of the second derivative of the phase with pressure within 1–4 bar (with 1-bar step) and for some gases within 10–50 bar (with 5-bar step) is fitted by a linear function at every spectrometer wavelength. The measured dispersion is then normalized on the beam path length in the pressure cell and used to determine the second- and third-order

dispersion coefficients by linear fitting of the data in the frequency domain, as shown in Fig. 6.5 and 6.6 for nitrogen.



Figure 6.5 Measured dispersion for nitrogen (raw data) over the entire pressure range (data for some pressure values have been eliminated for clarity of presentation)



Figure 6.6 Dispersion of nitrogen normalized on path length and pressure, along with the linear fit. The intercept value provides the second-order coefficient, while the slope provides the third-order dispersion. The carrier frequency, ω_0 , is set to 2.3526 rad/fs ($\lambda_0 = 800.65$ nm).

This analysis was performed for all measured gases. The experimental GVD curves and their linear fits are shown in Fig. 6.7. The retrieved second-and third-order dispersion coefficients are reported in Table 1 which contains the GVD coefficients for oxygen, nitrogen, and air that were obtained using the entire pressure range (1-50 bar). For carbon dioxide and ethylene, only the low-pressure (1–4 bar) data were used

because of the nonlinearity at high pressures. The GVD of acetylene and propane was measured in the low-pressure (1–4 bar) regime only.



Figure 6.7. Dispersion normalized on the path length and pressure for all the gases, along with the linear fit. For oxygen, nitrogen, and air, dispersion data from both pressure ranges are used; for all other gases only the low-pressure data, exhibiting linear pressure dependence, are used.

Table 2. Second- and third-order dispersion values at 800 nm for each gas at a pressure of 1 bar, along with the standard error in fitting and the statistics of the linear fit.

Gas	Second- Order Dispersion (<i>k″-</i> fs ² /m)	Third- Order Dispersion (<i>k‴-</i> fs ³ /m)	Coefficient of Determination (R ²)	Standard Deviation from the Linear Fit (fs ² /m)	
Oxygen	24 76+0 04	12 5+0 2	0 957	0.66	
(O ₂)	24.70±0.04	12.0±0.2	0.007	0.00	
Nitrogen	18.70±0.04	11.8±0.2	0.950	0.67	
(N ₂)		11 0 . 0 1	0.000	0.90	
Alf Carbon	20.05±0.06	11.8±0.4	0.906	0.89	
Dioxide	30.90±0.05	21.5±0.3	0.977	0.81	
(CO ₂)*					
Acetylene	79 20 0 07	12 7 0 1	0.090	1 1 2	
(C ₂ H ₂)*	70.20±0.07	43.7±0.4	0.969	1.12	
Ethylene	102 18+0 08	57 0+0 5	0 992	1 28	
(C ₂ H ₄)*	102.10±0.00	07.0±0.0	0.002	1.20	
Propane	111.21±0.08	52.8±0.5	0.990	1.30	
(C ₃ H ₈)*		02102010	0.000		

*Values extracted from low-pressure data only.

To the authors' knowledge, most of these values have not been reported previously. The second-and third-order dispersion values of air, measured in Ref.^{117,118,69,119}, are in good agreement with our values (from ref. 83: 20.14 \pm 0.14 fs²/m and 18 \pm 15 fs³/m, respectively). Additional dispersion measurements have been made on several noble gases as well as nitrogen using interferometry; our measured values for nitrogen are also in agreement with these values (18.04 \pm 0.15 fs²/m and

 $10\pm10 \text{ fs}^3/\text{m in}^{117}$). Fitting of refractive index measurements with the Sellmeier¹¹⁷ equation gives GVD values of 19.49 fs²/m for nitrogen and 19.87 fs²/m for air.

To highlight the role of dispersion in experiments where femtosecond pulses are used, we have examined the effect of dispersion on pulse-time duration by simulating the effect of various gas pressures in a 0.15-m-path-length pressure cell. The simulations were performed using the femtoPulse Master software (BioPhotonic Solutions Inc.), assuming Gaussian pulses with transform-limited (TL) time durations of 5, 10, and 50 fs. The software uses the input-pulse spectrum along with the secondand third-order dispersion values from Table 2 to calculate pulse durations at various pressures. Table 3: Simulated pulse durations (fs) due to changes in dispersion as a function of pressure for a 0.15-m path

Gas Pressure (bar)	Oxygen (O ₂)	Nitrogen (N ₂)	Air	Carbon Dioxide (CO ₂)	Ethylene (C ₂ H ₄)	Acetylene (C ₂ H ₂)	Propane (C ₃ H ₈)
0	5	5	5	5	5	5	5
	10	10	10	10	10	10	10
	50	50	50	50	50	50	50
1	5.4	5.2	5.3	5.7	9.8	8.1	10.4
	11.4	11.4	11.4	11.5	11.7	11.6	11.8
	50	50	50	50	50	50	50
2	6.4	5.9	6	7.1	17.5	13.8	19
	11.5	11.5	11.5	11.5	12.9	12.2	13.2
	50	50	50	50	50	50	50
3	7.9	6.8	7	9.1	25.6	19.9	27.9
	11.6	11.5	11.5	11.7	15	13.4	15.7
	50	50	50	50	50	50	50
4	9.6	7.9	8.3	11.2	33.8	27.8	36.9
	11.7	11.6	11.6	11.9	18.1	15.1	19.4
	50	50	50	50	50.1	50	50.1
5	20.9	16.1	17.2	25.6	83.7	64.1	91.6
	13.6	12.6	12.8	15	41.5	32.0	45.3
	50.1	50	50	50.1	50.7	50.4	50.8
10	40.9	30.9	33.3	50.3	167.6	128.3	182.9
	21.2	17	17.9	25.8	82.7	63.4	90.2
	50.2	50	50.1	50.3	52.8	51.7	53.3
20	61.2	46	49.6	75.3	251	192.1	274.4
	30.6	23.7	25.2	37.8	124	94.9	135
	50.4	50.2	50.2	50.6	56.1	53.7	57.2
30	81.6	61	66	100.1	334.5	265	365.6
	40.5	30.8	33	49.9	165.3	126.4	180.2
	50.7	50.2	50.4	50.9	60.5	56.4	62.2
40	101.8	76.4	82.4	125.6	418	320.3	457.1
	50.2	38.1	40.9	62.4	206.6	158.3	225.4
	51	50.6	50.7	51.6	65.6	59.7	68.1

The simulation results indicate a significant temporal broadening of ultrashort pulses at high gas pressures--even for a 0.15-m path. From the values obtained it is obvious that the dispersion due to the gas component of an experimental setup is highly influential for short pulses at pressures typically used for combustion studies and must be taken into account--even at normal pressure conditions for distances of 0.5 m or longer. While the data in Table 2 may discourage one from using shorter laser pulses because of their greater propensity for dispersion, this can also be viewed as an advantage in the case of nonlinear spectroscopic applications, as discussed below.

6.4 Dispersion and Raman Scattering efficiency

When considering optical spectroscopy or imaging of high-pressure systems, the volume from which the optical signal emerges determines the spatial resolution of the measurement. Typically, three-dimensional sectioning capability in CARS diagnostics at range (i.e., with weakly focused beams) is achieved by crossing of two or more laser beams at a point of interest. Unfortunately, turbulence in the reacting-flow environment renders this cross-beam geometry very problematic. Single-beam spectroscopic imaging methods that have been developed recently^{89,120} are much more immune to the inhomogeneity of the medium; however, another sectioning mechanism must be used to resolve the structure along the beam path. We have found that by implementing adaptive pulse compression to pre-chirp the laser pulses, the pulse can be adjusted to become TL at a specific location and, in turn, can be used to achieve spatial resolution

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along the weakly focused laser beam. Thus, the laser beam can be scanned to obtain an in-plane image, and the input pulse chirp can be tuned to adjust the depth.

This effect is examined in Fig. 6.8 for carbon dioxide at 2.24 mol·L⁻¹ (corresponds to 40 bar at room temperature) by simulating the excitation efficiency of the Raman-active vibrational mode at 1285 cm⁻¹. It is assumed that the pulse energy is sufficiently small that transition saturation effects can be neglected. Pulse durations greater than 20 fs are not considered since they lack the spectral bandwidth to excite impulsively the 1285 cm⁻¹ Raman mode. The input pulse energy is scaled to provide the same excitation efficiency at the zero Raman shift.



Figure 6.8 Simulated Raman scattering efficiency at 1285 cm⁻¹ as a function of propagation distance CO_2 with a density of 2.24 mol·L⁻¹. The inset figure is a schematic example of how this improved spatial resolution can be used to select a region of interest to acquire data in a combustion process.

From the figure one can observe both the large increase in signal and the highly improved spatial resolution that results from the use of shorter pulses. The Raman excitation efficiency is directly related to the signal intensity in single-beam CARS measurements that employ a short pulse to provide the pump and stokes components and a long pulse as a probe. This illustrates the advantage of using very short pulses to perform single-beam CARS measurements. For a 5-fs pulse, one would obtain the full range of Raman shifts, along with a spatial resolution of ~2.5 mm along the *z* axis. The in-plane resolution is determined by the beam focusing and scanning parameters.

6.5 Conclusions

The increasing use of ultrafast laser systems and the greater availability of sub-30-fs laser sources have prompted the evaluation of pulse dispersion and its effects on nonlinear optical spectroscopy. An ultrabroadband laser source was used in this study to measure the spectral dispersion of a number of gases that are of importance to the combustion community. MIIPS was shown to be a straightforward approach for both accurately measuring the dispersion and introducing a pre-chirping phase mask that is capable of recovering TL pulses. It is suggested that dispersion, especially when using ultrabroadband laser sources, can provide a high level of axial resolution for singlebeam spectroscopic methods. Such axial resolution is advantageous for obtaining three-dimensional images of flames.

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Chapter 7

Conclusions

This dissertation has discussed several applications of various pulse shaping methods for single-beam CARS spectroscopy. Phase shaping allows for selective excitation of any Raman active mode of a molecule. Several different methods, binary phase shaping, double chirped pulses, and sinusoidal phase modulation were all used to perform selective excitation. The application of this type of pulse shaping was highlighted as a contrast mechanism that allow for the visualization of a CO₂ jet in ambient air.

A less elaborate pulse shaping method was also used to collect the full CARS spectrum that results from the impulsive excitation from the broadband femtosecond pulse. This full spectrum acquisition was used for the measurement of various gas phase conditions in preliminary work examining the use of single-beam CARS as a method for combustion diagnostics. In addition to these experiments, another set of experiments was conducted that examined the use of the single-beam CARS method for standoff detection. These experiments were conducted at 12m distance and demonstrated the ability to identify solid, liquid, and gas samples as well examine binary mixtures of molecular isomers.

These initial measurements have served to establish single-beam CARS as a viable method for many applications ranging from imaging to remote detection. Currently, efforts are being continued in to our lab in both fields using the advances and methodologies discussed in this dissertation. Future work in the field of combustion diagnostics will involve the use of singlebeam CARS to provide the measurement of the temperature of gas phase molecules in combustion environments along with species information. An ultimate application in this field would be for the use of selective phase shaping to image the combustion environment providing real time information for the monitoring of that particular species as the combustion evolves. This information would provide critical insight to the chemistry and physics of the combustion process on a time scale fast enough to measure transients in the combustion process.

Our lab has also continued to push forward the use of single-beam CARS as a method of standoff detection. Current measurements have been made with a limit of detection below 2.5 μ g/cm², and double chirped pulse have been used to perform selective excitation imaging of thin DNT and PMMA films deposited on to gold substrates at distances great than one meter. As efforts continue to push forward, the distances over which measurements are made should increase and actual field measurements of trace detection of hazardous compounds should become feasible.

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