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COHERENT STUDIES OF MOLECULES FROM THE WEAK TO THE STRONG FIELD LIMIT

by

Matthew Comstock

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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Abstract

COHERENT STUDIES OF MOLECULES FROM THE WEAK TO THE STRONG FIELD LIMIT

by

Matthew Comstock

This work involves a series of experiments using the coherent properties of ultrafast lasers. First, vibrational and rotational spectroscopy of the N_2O_4 molecule is examined. The non-resonant four wave mixing rotational coherence spectroscopy method, both homodyne and heterodyne detected, is used to investigate both short time ground state vibrational dynamics and long time scale rotational dynamics. Accurate rotational constants, vibrational frequencies and anharmonicities are measured for the N_2O_4 molecule.

Rotational coherence spectroscopy is also used to investigate the effect of high intensity laser pulses on sample molecules. Both alignment and deformation are observed, in fields from 10^{10} W/cm² to 10^{13} W/cm². These effects are verified by time of flight mass spectrometry. Resonant four wave mixing spectroscopy is used to measure the decoherence cross sections for the coherence between the X($^{1}\Sigma_{g^{+}}$) and B($^{3}\Pi_{0u^{+}}$) states of I₂ in a series of buffer gas molecules. Lennard-Jones parameters are extracted for He, Ar, C₃H₈, N₂, and O₂. Finally, Multiphoton intrapulse interference is examined in an effort to simplify the search space typically investigated by pulse shapers. The concept of Binary Phase Shaping for two photon excitation is investigated as a coherent control method.

In honor of my father

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1. Coherence and Spectroscopy

1.1 Introduction

Since the 1960's, the concept of using lasers to drive chemical reactions to particular outcomes has been a dream of physical chemistry. Processes such as Intramolecular Vibrational Redistribution (IVR) prevented any significant success, however until the late 1980's when theoretical methods that circumvent IVR were developed.^{1,2} At the same time, laser technology progressed to the point of generating pulses on the order of, and even faster than, the IVR timescale.³⁻⁶ This allowed a great expansion in the techniques available to the laser control community. The late 1990's saw

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M. Comstock, V. Senekerimyan, and M. Dantus, "Ultrafast Laser Induced Molecular Alignment and Deformation: Experimental evidence from neutral molecules and from fragment ions", J. Phys. Chem 107, (2003), 8271-8281.

a divergence of techniques, based on the three main properties of the ultrafast laser; time, intensity, and phase.

Early on, phase was used to cause interference on excited state potential energy surfaces.² After the invention of pulse shapers,⁷ genetic algorithms were introduced to produce optimal pulse shapes.⁸⁻¹⁰ Similarly, the short timescales available from modern pulsed lasers allowed another coherent control scheme. Known as pump-dump coherent control, the idea is to interact with the molecule faster than it can relax, avoiding IVR by preempting it.^{1,11-13}

The short timescales and coherent properties of ultrashort laser pulses allowed more complicated nonlinear spectroscopies to be developed and used for coherent control purposes.¹⁴⁻¹⁷ Similarly, the short timescales of ultrashort laser pulses produce extremely high intensities, and these high fields can be used to control the orientation and motion of molecules as well. Molecular alignment and deformation,¹⁸⁻²³ tunneling ionization,²⁴⁻²⁶ Coulomb explosion,²⁷⁻²⁹ and the molecular centrifuge³⁰ are all examples of unique laser molecule interactions which occur at the high peak intensities produced by ultrashort laser pulses.

1.2 Outline of the thesis

In my dissertation I will cover several different types of experiment based on understanding the fundamental light-matter interactions used to control chemical processes. All of these processes involve the coherence of laser pulses, and use this coherence to either investigate or control some aspect of the sample molecule. First, I will discuss a type of ultrafast Four Wave Mixing (FWM) spectroscopy, called Rotational Coherence Spectroscopy (RCS).^{31,32} This is based on observing the refractive index of a medium as a function of time after a strong non-resonant pulse passes through a sample. The signals can be Fourier-Transformed to produce classic microwave rotational spectra, though RCS requires no intrinsic dipole moment in the sample molecules. Resolutions of 10⁻⁶ cm⁻¹ are routinely obtained, and symmetry properties of the molecules can be examined in detail.

Secondly, using the high structural resolution of RCS, I investigate changes to the molecular structure caused by the presence of high electric fields. By applying a femtosecond laser pulse to a sample, peak intensities of 10^{16} W/cm² are achieved routinely. The corresponding electric fields are of the same order of magnitude as the electric field between the nucleus and the electron. This strong coupling of the laser pulse with the molecule can produce alignment,^{18,20,22} deformation²³ and/or ionization.^{24,27,33} These effects change the signal produced by the RCS method, and a full analysis is given.

The third topic I will discuss is electronic decoherence, as studied in our lab by the photon echo method. This is a type of resonant FWM spectroscopy that allows us to measure the rate of homogeneous decoherence in a sample. Iodine was the target molecule, and electronic coherence dephasing cross sections were measured to be roughly 10 times greater than those expected for a number of buffer gas samples.

Finally I will address the relatively new field of pulse shaping technology, specifically a new technique using only two phase values across 128 pixels to control two-photon excitation. This binary phase shaping (BPS) greatly reduces the search space for learning algorithms, leading to better convergence in shorter times. Using the symmetry of the problem, we can design binary phase masks which will produce the desired results, even without resorting to computer algorithms.

1.3 experimental setup (laser systems)

Three laser systems were used for the work covered by this dissertation. The first was a Colliding Pulse Mode-locked dye laser (CPM) operating at 620nm. The Rhodamine 590 Chloride gain jet was pumped by the output of a Spectra Physics Millenia Nd:YLF laser. The saturable absorber dye jet 3,3' diethyloxadicarbocyanine iodide (DODCI) produces 47fs pulses at 87MHz. The pulses are then amplified at 30Hz by a four stage dye cell amplifier, pumped by a Spectra Physics Quanta-Ray Nd:YAG laser. After amplification the pulses are compressed to 60fs using a dual prism arrangement. The CPM system could produce up to 30mW output power.

The second laser system used in this work is a regeneratively amplified femtosecond titanium-sapphire laser system (Figure 2). The output from a continuous wave Nd:YVO₄ laser (Millennia – Spectra Physics Laser) pumps a femtosecond titanium-sapphire oscillator (KM Labs), capable of producing <15 fs pulses at 80 MHz. This output is amplified by a regenerative amplifier (Spitfire – Spectra Physics Lasers) pumped by 1 kHz Nd:YLF laser (Evolution-X – Spectra Physics Lasers). Amplified pulses centered at 805 nm are nearly transform limited and have a maximum energy of 0.8 mJ/pulse and time duration of 50 fs. Characterization of the pulses was performed both with a non-collinear autocorrelator and by frequency resolved optical gating (FROG).³⁴

The third system I used was a Titanium Sapphire oscillator (Kapteyn-Murnane labs) system pumped by a Spectra-Physics Millenia Nd:YLF laser, capable of producing 10fs pulses tunable from 840nm to 780 nm at 87MHz repetition rate. In each chapter, the laser system or systems used will be identified in the experimental section.

2. RCS spectroscopy of N₂O₄

2.1 Introduction

Nitrogen oxides (NO_x) have been the subject of numerous studies primarily for their role in both stratospheric and tropospheric chemistry and in particular, their links to the ozone photochemical cycles and smog formation. These relatively small molecules are especially interesting due to their complex spectroscopy as evidenced by theoretical and experimental studies of their ground and excited states.³⁵⁻⁴⁶ All except NO have multidimensional potential energy surfaces, and numerous curve crossings that result in vibronic chaos making these molecules very interesting to dynamicists.



Figure 2.1. Sketch of the N_2O_4 molecule. Distances and angles are from electron diffraction experiments.⁴⁷

The nitrogen dioxide/dinitrogen tetroxide monomer/dimer pair has received particular attention. At one atmosphere and room temperature their equilibrium concentration is about 3:17 for NO₂:N₂O₄, respectively.^{41,48} The dimer is favored at higher pressures and lower temperatures. Dinitrogen tetroxide is particularly intriguing

because of its unusually long N-N bond (1.75 and 1.78 Å, solid and gas phase, respectively)^{49,50} and the fact that the ONO bond length and angle are identical to those of the monomer (see figure 2.1). Because of its (D_{2h}) symmetry N₂O₄ does not have a permanent electric dipole moment. The dissociation energy of the N-N bond is 0.59 eV and its first electronic resonance is at 340 nm.³⁵ It has been proposed⁴¹ that the use of off-resonance excitation should make it possible to probe the dimer directly at room temperature. Most of the vibrational frequencies for these molecules are established and assigned,^{37,38,41,51} but there is still some disagreement between experiment and theory on several modes. The photodissociation dynamics of NO₂ were studied recently using ultrafast methods.^{52,53} Here we exploit the ability to detect low frequency Raman modes of short-lived species and to measure high accuracy rotational constants of femtosecond time-resolved four wave mixing (FWM) to study of the ground state dynamics of N₂O₄/NO₂.

2.2 Experimental

The amplified Titanium Sapphire laser output was split into three beams using dielectric beam splitters and recombined in the forward-box geometry (see figure 2.1a). The beams occupy three corners of a 25 mm square and were determined to be parallel over one meter by using a template of the appropriate geometry. A 50 mm diameter 0.5 m focal length lens focused the beams into the sample cell, the beams crossing at an angle of 2.9°. This crossing angle produces a transient grating with a 16 μ m spacing. In all experiments the output beam was attenuated to ~60 μ J per pulse measured before splitting. Two beams were overlapped in time and space to form a transient grating in the sample while the third one was time delayed with a computer controlled actuator. This

configuration allows homodyne transient grating (TG) and reverse transient grating (RTG) experiments, where the signal beam emerges with wave vector $k_r = k_a - k_b + k_c$. When the initial two pulses are not overlapped in time, other types of FWM experiments (photon echo and virtual echo) are possible.⁵⁴ The main advantage of the homodyne signal is that it is spatially distinct from the other laser beams, and is therefore background free. Another option for FWM experiments is to use only two laser beams (see figure 2.2b) overlapped with a shallow angle to maximize the interaction area. In this case, one beam is chopped and a lock-in amplifier is used to observe changes in the refractive index of the sample caused by the first beam. This heterodyne signal has the advantage that it reveals the phase of the signal, information that is lost in the homodyne configuration.



Figure 2.2. Beam geometry used for the femtosecond four-wave mixing experiments. Homodyne detection (a) produces a background free signal, while heterodyne detection (b) preserves the phase of the signal.

For the homodyne configuration, the event when all three pulses overlap in time is referred to as time-zero. The three 10 mm diameter beams were focused onto a 6 inches long custom-designed quartz cell containing the gaseous sample by a two-inch diameter lens with focal length of 50 cm. Heating the entire cell with heating tape controlled the temperature of the cell. The FWM signal beam was spatially filtered by a set of irises, collimated and sent into a spectrometer (Triax 320, JobinYvon). Before reaching the entrance slit of the spectrometer, the signal was attenuated by a neutral density filter of OD=1-2. The signal was then dispersed by the spectrometer's grating, and was registered by a 2000 x 800 pixel liquid nitrogen cooled CCD. The entrance slit of the spectrometer was 100 micrometers (0.8 nm resolution). The wavelength range on the CCD in this setup (grating dictated) was about 60 nm. In order to preserve disk space, every 20 pixels were binned together. For the shorter scans (~1-2 ps duration) the frequency-dispersed signal was registered for each time delay with an integration time of 100 ms. Each data set is the average of several such scans.

For the heterodyne case one beam, the pump, was mechanically chopped at a frequency of 318Hz, and the other beam, the probe, was delayed in time with respect to the pump using a computer controlled actuator. Heating the entire cell with heating tape, or submerging the cell in an ice bath controlled the temperature of the cell to within 3 degrees centigrade. The event when the two pulses overlap in time is referred to as time-zero. After the sample, the probe beam is spatially filtered and frequency doubled using a 150µm KDP SHG crystal. This allows background free detection with a photodiode, while maintaining signal linearity. This can be seen if one considers that the probe electric field is the sum of the laser and the heterodyne FWM signal. After frequency doubling, the electric field of the probe beam is:

$$E^{2}(t) = (E_{probe}(t) + E_{FWM}(t))^{2} = (E_{probe}(t))^{2} + 2E_{probe}(t)E_{FWM}(t) + (E_{FWM}(t))^{2}$$
(2.1)

So long as the FWM signal is small with respect to the probe field, the $(E_{FWM}(t))^2$ term is negligible. The $(E_{probe}(t))^2$ term is likewise unimportant as it only contributes to the signal at time zero. This leaves the linear term, showing amplification of the FWM signal by the probe beam. The FWM signal intensity was found to be 300 times smaller than the probe beam, therefore the linear signal approximation is very good.

The sample (99.1% N_2O_4) was obtained from Sigma-Aldrich and used without further purification. The sample cell was evacuated to 10^{-5} Torr on the vacuum line and filled directly from the lecture bottle. There was no experimental evidence of contamination. Experiments were performed at different sample pressures. All the data presented here was obtained with a cell that was loaded to an initial pressure of 400 Torr at room temperature.

2.2 Theory

Simulations of TG data presented here follow the quantum mechanical expression for the time dependent susceptibility,⁵⁵⁻⁵⁷ (see appendix for derivation)

$$P_2(t) \propto N \beta \Sigma_{\nu} \Sigma_{J} q_{\nu} \rho_{J} [\cos(2\pi c (F_{J+2} - F_{J})t) + \cos(2\pi c (F_{J} - F_{J-2})t)], \qquad (2.2)$$

where $F_J = B_v J (J+1) - D J^2 (J+1)^2$ for the molecule, B_v is the vibrationally dependent rotational constant, D is the centrifugal distortion constant, β is the anisotropic polarizability, N is the number density, ρ_J is the normalized rotational distribution including spin statistics (g_J) for all natural isotopes, $\rho_J = g_J (2J+1) exp(-2\pi chF_J/kT)$, and q_v is the normalized thermal vibrational distribution for all ground state vibrational modes. Due to the off-resonance nature of the process, $\Delta J=0,\pm 2$, rotational recurrences are seen every $\tau_{rec}=1/(4Bc)$. The homodyned TG signal is given by $(dP_2/dt)^2$, while the heterodyned TG signal is given by (dP_2/dt) . See Appendix 1 for a derivation of these formulae. For samples containing molecules with different rotational constants, the homodyned signal is given by $|(dP_a/dt + dP_b/dt)|^2$, leading to interference terms between the two populations.⁵⁸

2.3 Results

In the gaseous state the N₂O₄ and NO₂ molecules are in thermodynamic equilibrium (at room temperature K = 8.8 atm⁻¹).⁵⁹ We controlled the temperature of the sample cell from 294 K (80% N₂O₄) to 363 K (94% NO₂). A change in optical density of the sample at 800 nm from 0.045 (294 K) to 0.071 (363 K) was observed and was not considered substantial to qualitatively affect the measurements. Some experiments were carried out with a cell filled to 760 Torr. The overall signal level was somewhat smaller due to the increased OD leading to absorption of the excitation photons. The transients yielded qualitatively identical results, but required a higher temperature to obtain good NO₂ signal (383 K), probably due to a change in the equilibrium conditions and some reabsorption of the signal. It is necessary to note that it is impossible to have 100 % pure gaseous N₂O₄ in the cell because of the aforementioned equilibrium.



Figure 2.3.¹ Experimental time-resolved FWM signal obtained during the first 2 ps: a) Frequency integrated NO₂ data as a function of time delay, b) Frequency dispersed signal obtained as a function of time delay for NO₂. c) Frequency integrated N₂O₄ data as a function of time delay, d) Frequency dispersed signal as a function of time delay for N₂O₄. For all scans the signal intensity is plotted on a logarithmic scale.

In figure 2.3 we present frequency-dispersed transients obtained as a function of time-delay between the two time-overlapped pulses and the third pulse for NO₂ (2.3a) and N₂O₄ (2.3c). In the two-dimensional contour plots (a and c) the spectrum of the signal in the region from 780 nm to 830 nm is registered versus delay time every 10 fs. The dark current level of the CCD was subtracted from these data. The intensity scale is logarithmic to highlight the weaker features. In the case of NO₂ (figure 2.3a) there is a broad, featureless peak 160 fs after time zero as well as another at 500 fs. Figure 2.3b shows the frequency-integrated (780-830 nm) transient signal. These features (figure 2.3a)

and b) can be assigned to the initial rotational dephasing in the sample and are consistent with results for off-resonance FWM signal.^{57,60} Measurements for N_2O_4 were collected in the same manner as described for NO_2 and are presented in figure 2.3c and 2.3d. These results show in addition to a broad rotational dephasing envelope a series of beats with a period of 133 fs. The beats are detectable up to 3 ps after time zero but with much lower intensity.



Figure 2.4 Heterodyne detected FWM signal from N_2O_4 at 273K. Inset is a MEM-FT of the transient, showing the 79cm⁻¹ and 81cm⁻¹ torsional frequencies, as well as the 255cm⁻¹ and 234cm⁻¹ vibrational frequencies.

Figure 2.4 shows the first 4 ps of the heterodyne detected FWM signal at 273K. The initial rotational dephasing observed during the first picosecond is vibrationally modulated. The 125fs oscillations correspond to the NN stretching motion of the N_2O_4

molecule. Fourier transform of the signal results in a single frequency at 242 cm⁻¹, which is in agreement with the experimentally obtained value for the N-N stretching mode from gas-phase Raman spectroscopy.⁴¹ Applying the Maximum Entrophy Method (MEM) of analysis⁶¹ on the same set of data yielded two frequencies; 255cm⁻¹ and 234cm⁻¹. These two values were consistently obtained following analysis of different data sets (not shown). The wave packet motion involves at least three vibrational levels in the ground state and from the spacing of the two peaks one can obtain an anharmonicity constant for the molecule, $v_e x_e = 21$ cm⁻¹. The 79cm⁻¹ and 81cm⁻¹ frequencies correspond to the torsional motion of the NN bond.^{41,62}



Figure 2.5.ⁱ Experimental time-resolved and frequency integrated Heterodyne FWM signal (a) NO₂ and (b) N_2O_4 taken at 363 K and 294 K, respectively. Note the subtle differences in the shape of the rotational recurrences obtained for both cases. The signal intensity is plotted on a logarithmic scale.

Long time homodyne scans were performed at 363 K (NO₂) or 294 K (N₂O₄). We present data in the time-delay range from 9 to 42 ps in figure 2.5. The transients show the

frequency-integrated intensity recorded in the 785-825 nm range as a function of time delay. Note that the vertical axis (intensity) is logarithmic. The NO₂ data presented in figure 2.5a, show rotational recurrences every 9.945 ps. The transient in figure 2.5b, taken at 294 K, exhibits similar features with the same periodicity. The recurrences observed at 294 K are about four times lower in intensity than those observed for NO₂ at 363 K taking into account the attenuation filter used for the higher temperature transients. The transients for both temperatures were taken under identical laser conditions except for attenuation. This results in slightly different background and noise levels between the two transients. In this range of time delays both data sets exhibit rotational recurrences that can be assigned to NO₂. Under close examination some differences are observed in the shape of the rotational recurrence observed in both transients. The differences are especially clear at the half recurrence observed in both transients near 29.5 ps (see figure 2.5), and are due to centrifugal distortion effects.

Nitrogen dioxide is an asymmetric top molecule, but the similarity of the B and C constants allows us to view it as a symmetric top with $B_{ave}=(B+C)/2$. From the observed rotational recurrences of 19.680 ps (9.840 ps half-recurrences) in the long time delay transient of NO₂ (figure 2.5a) we can calculate the average rotational constant as $B_{ave}=1/4c\tau_{rec}$, were c is the speed of light and τ_{rec} is the time between rotational recurrences.^{57,60} The obtained value is 0.42343 cm⁻¹ ± 0.00007 cm⁻¹. This value can be compared to the experimental (0.42202 cm⁻¹)⁶³ and theoretical (0.423325 cm⁻¹)⁴³ values calculated for B_{ave} , respectively. Simulations based on the semiclassical formalism outlined in Appendix I and the average rotational constant for NO₂ using the literature values are in general agreement with the observed data. The rotational recurrences

obtained at longer time delays ($\tau > 40$ ps) exhibit more complex modulation that cannot be simulated with a symmetric top approximation, even though their positions can be reproduced exactly.

In the case of N_2O_4 the signal obtained at long time delays is more complex. The small features at 9.840 and 19.680 ps (figure 2.5b) could be assigned to rotational recurrences originating from the 16% NO₂ molecules present at room temperature. The positions of these features coincide precisely with the rotational recurrences of NO₂, however, the signal intensity is about one order of magnitude stronger than expected based on the observed intensity at 363 K and because of these measurements' dependence on the square of the number density.^{57,60} Furthermore, there are some subtle differences in the shape of the recurrences (see figure 2.5) leading us to consider assigning a significant contribution of these features to photoproducts that result from excitation by the first two pulses. The N-N bond dissociation energy is only 0.59 eV while the photon energy of each pulse is 1.55 eV. The principal axis of the NO₂ moieties is aligned with the N-N bond of N_2O_4 , therefore, the initial rotational alignment would be preserved in the photodissociation process. The product NO₂ molecules formed by photodissociation would realign and become 'visible' to the third pulse at the same time delays as the thermal NO₂ molecules originally in the sample, but would have a different rotational temperature. There is a possibility that multiphoton excitation yields NO_2 molecules in the ²B₂ excited state, which has slightly different (and still not exactly determined) rotational constants.



Figure 2.6.ⁱ Experimental time-resolved and frequency-integrated signal obtained at 363 K (a) and 294 K (b). The main difference between the two transients after the first two picoseconds occurs at 76.265 ps and is indicated by an arrow. Both intensity axes are plotted on a logarithmic scale. Some fine differences are observed in the modulation of the rotational recurrences but not in their position.

Only one rotational recurrence feature was observed after the first picosecond that can be assigned to N₂O₄. At 76.265 ps (figure 2.6) a small feature is present in the room temperature sample that is clearly absent at higher temperatures. This feature gains in intensity compared to the one at 78.540 ps (NO₂ recurrence) if the temperature of the sample is lowered to 0° C (data not shown). The lower temperature shifts the equilibrium further toward the dimer. If a semiclassical model and available rotational constants^{38,40} are used, it is possible to simulate this recurrence. The experimental data showed no evidence of a half recurrence at 38 ps. Scans taken for time delays of up to 160 ps showed no other feature that could be distinctly assigned to N₂O₄. One possible reason for the absence of N₂O₄ rotational recurrences at long time delays is the rapid thermodynamic exchange $2NO_2 \Rightarrow N_2O_4$ estimated at 300 K to be $\tau \sim 0.1$ ns.



Figure 2.7. Heterodyne detected Transient Grating spectroscopy of N_2O_4 . Raw data at the full and half recurrence time of N_2O_4 at two temperatures (a and b, respectively). Subtraction of the two different temperature signals reveals a clear full recurrence for N_2O_4 (d), but no half recurrence (c).

Heterodyne detected transients around the N₂O₄ recurrence time are shown in figure 2.6. In the Heterodyne case, the phase and linearity of the signal is preserved so signal subtraction is a possibility. In figure 2.6a I show Heterodyne detected Transient grating signals from 0° and 86°C at the time of the first half recurrence of N₂O₄ (38.2ps). figure 2.6b shows the first full recurrence of N₂O₄ at the same two temperatures. There is clearly an additional feature around 76ps in the 0°C trace, but there is no clear feature at the half recurrence time. Figure 2.6c and 2.6d show signal subtraction at the half recurrence and full recurrence, respectively. The gray line corresponds to the expected half recurrence signal from N₂O₄ in the D_{2b} geometry. The small differences at the recurrence time of NO₂ are due to centrifugal distortion effects which are not accounted for in this simulation. Clearly the half recurrence of N₂O₄ is absent, implying that the geometry of N₂O₄ cannot be D_{2h}. From the subtracted data, a more accurate rotational constant of $(B+C)/2=0.10915\pm.00001$ cm⁻¹ can be determined.

2.4 Discussion

The signal observed for both molecules is primarily non-resonant and therefore depicts ground state dynamics. Experiments were carried out at both temperatures; photon echo (PE) and virtual echo (VE) pulse sequences⁶⁴⁻⁶⁶ were performed but yielded no significant feature other than the time zero signal. The PE and VE pulse sequences are produced by electronic coherences, and are isolated spatially from other processes due to the phase matching geometry. The photon echo signal, for example, is produced by the purely homogeneous decay of the electronic coherence, which is typically hundreds of picoseconds long (see chapter 4 for more details). If the experiments shown here did involve a resonant one-photon transition to the ²B₂ state of NO₂, the PE and VE signals would have revealed it.

The absorption cross section of NO₂ at 800 nm is very small.^{67,68} The reported and calculated values of the B and C rotational constants for this state are very dissonant,⁶⁸ and fall in the range from 0.458 to 0.548 cm⁻¹ and 0.38 to 0.449 cm⁻¹, respectively. If this transition were involved additional rotational recurrences corresponding to these values would have been observed in the time-resolved FWM transients. Close examination of the data did not reveal any other features except for the aforementioned recurrences every 19.680 ps. Given that homodyne detected FWM signal depends on the transition dipole moment to the eighth power^{57,60} this process is not likely to be detected by our setup.

In conclusion, the average rotational constant measured from our experiments of 0.42343 cm⁻¹ reflects the average (B+C)/2 rotational constant of NO₂ in the ground state. Similarly, using heterodyne detected transient grating spectroscopy, we were able to measure the rotational constant of the N₂O₄ molecule (B+C)/2=0.10915±.00001 cm⁻¹ to high accuracy. The experiments at room temperature (N₂O₄) allowed us to measure the frequency of the N-N stretch of 242 cm⁻¹ and the anharmonicity of this unusual bond. The weakness and high anharmonicity of this bond is likely due to the changes in the electronic symmetry of the NO₂ required to form the N-N bond, leading to its high barrier to rotation and long bond length. The next electronic state known is the ³B_{3u} is >3 eV⁴⁶ and would require two photon transitions to be reached. There is no evidence in our data of single or multiphoton transitions to a long-lived excited state. However, excitation to a dissociative state would be difficult to rule out. Perhaps the negative time delay shoulder in the N₂O₄ transient in figure 2.3d and not found in the NO₂ transient in figure 2.3b is the evidence of this dissociative pathway.

The transient grating method allows us to measure, with high accuracy, rotational constants for molecules that may be inaccessible by other means due to spectral congestion or lack of appropriate dipole moments. We can also use half recurrences to eliminate certain symmetry properties of molecules with indistinguishable nuclei. In this case, rotational constants for the NO₂ and N₂O₄ molecules were determined to 10^{-5} cm⁻¹ accuracy, and D_{2h} symmetry for the N₂O₄ molecule has been excluded.

3. High Intensity effects

3.1 Introduction

High-intensity off-resonance laser fields from ultrafast laser pulses can cause very large electric-field gradients. Molecules can experience a large torque along the polarization vector of the field due to their anisotropic polarizability. With long laser pulses the torque is enough to cause adiabatic alignment,^{18,20} however, with ultrafast pulses the torque provides an 'instantaneous' kick toward alignment with the electric field polarization.⁶⁹ Pulses with peak intensities of 10¹³ W/cm² generate electric fields of one volt per angstrom, causing significant changes in the electronic energy levels of the molecule. When the electronic states have different geometry, the fast strong field excitation process leads to molecular structure deformation. In this report we study alignment and deformation for a number of molecular species using the time resolved transient-grating (TG) method. For CS₂, we obtain angle resolved ion yields following Coulomb explosion in the molecular beam and find evidence for the molecular deformation.

This chapter bridges these two types of measurements and provides experimental evidence regarding alignment and structural deformation. The results presented here shed new light on the understanding of the behavior of molecules in the presence of intense and ultrashort laser fields.⁷⁰


Figure 3.1^{ii} Plot of the induced rotational trap depth on a highly polarizable molecule like CS₂ (dotted line, left axis) and the electric field strength (solid line, right axis) as function of peak laser intensity. The predominantly observed molecular processes that occur at any given intensity are indicated in the top.

Figure 3.1 illustrates the dependence of the electric field trap depth measured in Kelvin for molecules with relatively large anisotropic polarizability (for example, CS₂). Laser intensities of 10¹¹ W/cm² are enough to align cold (10 K or less) molecules, for example from molecular beams.⁷¹ Also shown in Figure 3.1 is the electric field strength as a function of the peak intensity of the laser. The electric field is calculated using $E = \sqrt{2IZ_0}$, where Z_0 is the resistivity of vacuum (376.7 Ω) and *I* is the peak intensity of the laser pulse. For laser intensities of 10¹² W/cm² the electric field can exert sufficient force on a molecule to cause alignment. Higher peak intensity fields ~10¹³ W/cm², produce an electric field strength that is comparable to that experienced by valence electrons in molecules (~ 1V/Å), and structural deformation takes place. At these electric

field strengths ionization takes place and at higher laser intensities multiple ionization and Coulomb explosion are observed.

The observation of molecular alignment stemming from high intensity nonresonant laser excitation has been theoretically explored by Friedrich and Hershbach.^{18,72} The intense laser field causes an induced dipole in the molecule, which suppresses the rotational motion and leads to aligned pendular states.^{18,72} Friedrich and Herschbach developed the laser-induced alignment theory based on earlier observations of dissociative multiphoton ionization experiments on CO and I₂ with intense infrared lasers conducted by Normand et al.⁷³ and Dietrich et al.³³ respectively. Demonstrations of the laser-induced alignment technique have been conducted by Kim and Felker on large non-polar molecules^{19,20} and by Stapelfeldt and coworkers on smaller molecules.^{74,75} Posthumus et al. have examined the multiphoton dissociative ionization of H₂, N₂ and I₂ with 50 fs pulses and found that only H_2 and N_2 showed alignment characteristics.⁷⁶ Corkum and coworkers have combined intense off-resonance chirped circularly-polarized fields to induce rotational acceleration and thus constructed a molecular centrifuge.³⁰ Alignment with resonant intense laser fields has been examined theoretically by Seideman. When on-resonance fields are used, the intensity does not have to be as strong as in off-resonance experiments to generate alignment.²² She noted that as the mass of the molecule increased (and thus the rotational period increased), longer pulse duration is required to align the molecules. The study by Brown et al; on the resonant excitation of I₂ using 50 fs pulses confirmed the propensity for multiphoton excitation rather than alignment for a relatively heavy molecule.⁷⁷ Non-resonant excitation is advantageous, especially with larger molecules, because there is less propensity for ionization.²²

Ortigoso *et al.* calculated the conditions (laser pulse and rotational constant of the molecule) for which recurrences of alignment can be expected with nonresonant short pulses.⁷⁸

One of the most widely used methods for studying the behavior of molecules under intense laser fields is the Coulomb Explosion (CE) method. In the CE method, the ultrafast intense field causes mulitple ionization of the parent molecule. Mapping the distrubution of the fragment ions gives information about the molecular structure prior to explosion.^{28,29,79-93} While powerful, it is very difficult to determine a sequence of events leading to the observed fragment distribution using the CE method. For example, it is important to determine if structural deformation takes place in the neutral molecules or it arises after ionization. Similarly, it is important to determine the laser intensity that causes alignement and deformation, an aspect that is difficult to determine by the CE method. This specific question is addressed in this study.

Research from our group has taken advantage of the experimental measurement of rotational recurrences following the formation of an off-resonance polarization transient grating, a method introduced by Heritage *et al.*⁹⁴ With femtosecond pulses one is able to make much more accurate determinations of rotational constants and hence better determination of molecular structure.⁵⁵⁻⁵⁷ Soon after we recognized that the transient grating method would allow us to measure alignment and molecular deformation induced by the strong off-resonance field provided the third pulse (the probe) was kept at a low and constant intensity while the first two pulses, which coincide in time and form the transient grating, provide the strong field. This setup was used to make our first observations of alignment and structural deformation following intense off-resonance excitation.^{23,60,95}

3.2 Experimental

The data presented here comes from two different laser systems. Most of the data was acquired with the CPM laser system described in the introduction. The pulse energy used for each experiment is indicated in the text. The transient grating experiments were obtained using the forward box geometry. The first two high-intensity laser pulses coincided in time and were followed by a weak probe pulse delayed by a computer controlled actuator. The signal registered corresponds to the diffraction of the probe laser from the transient grating formed by the two intense pulses.⁵⁷ The degree of molecular alignment and deformation are measured from changes in the rotational recurrence intensity and shape observed after field-free evolution of the rotational wave packets. The data for CO₂ was obtained using the regeneratively amplified titanium sapphire laser described in the introduction.



Figure 3.2ⁱⁱ Schematic drawing of the experimental setup for time-resolved transient grating (top) and molecular beam (bottom) experiments. The transient grating signal was detected at phase matching angle as a function of time delay between the first two strong-field pulses and the weak probe. Ion detection, in the molecular beam, was recorded as a function of the angle that the polarization vector of the laser pulse makes with the time-of-flight axis.

For TG experiments (see Figure 3.2 left) the intensity of the first two laser pulses was varied between 10^{10} to 10^{13} W/cm² using a set of matched neutral density filters, all with the same substrate thickness. The intensity of the third pulse, the probe, was maintained at a fixed 10^{10} W/cm². The signal was collected background-free at the phase matching geometry. The samples were introduced in a 10 cm long cylindrical quartz cell. In some cases, for example in CS₂, a cold finger in the cell was kept in ice to reduce the sample density to 100 torr. Sample densities were 400 torr for C₂H₂ and CO₂, 100 torr for CS₂, and 150 torr for C₆H₆.

Ionization data was obtained using a molecular beam apparatus (see Figure 3.2, right). The samples were introduced using He as a carrier gas, which entrained some of the vapor pressure of the sample. The sample and carrier gas (He, 1700 torr) expanded

through the 1 mm diameter aperture in the pulsed valve. A 2 mm diameter skimmer produced the molecular beam, which proceeded to the ionization chamber. The pulses 0.25 mJ in energy were focused onto the molecular beam by an f = 150 mm lens. Diffraction size of the beam in the focal plane is estimated at 20 um and experimentally determined beam size is 26 µm. At the focus, the peak power on the molecular beam then is 4.6×10^{14} W/cm². The voltages on the extractor and repeller plates were kept at 1800 and 2500 V respectively with a distance between them being equal to 1.5 cm. The pressure in the ionization chamber was $\sim 8 \times 10^{-8}$ Torr when the valve was closed and $\sim 7 \times 10^{-7}$ when the valve was operated at 30 Hz. The ions were allowed to travel in a drift free zone of 50 cm before being detected by a micro-channel plate. Twenty time-of-flight mass spectra (TOF-MS) were averaged before they were analyzed. The polarization dependence of the ion intensities was obtained taking advantage of a zeroth-order halfwave plate, which was rotated manually from 0 to 180 degrees in 15 degree increments with respect to the time of flight axis. A calcite polarizer was used to ensure very high polarization purity (greater than 1:10000) of the beam.

3.3 Results

3.3.1. Evidence of Alignment and structural deformation from Transient Grating Measurements

Three-pulse transient grating experiments were carried out to explore the occurence of alignment and structural deformation. The first two pulses, overlapping in time, provided the strong electric field, while the third pulse with much lower intensity, probed the molecules at their rotational recurrence. The full rotational recurrence of CS₂

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is expected at 76.5 ps.^{57,94} When the laser pulses are weak, this feature can be observed and accurate rotational constants can be determined.^{57,60,96-99} Fig. 3.3a, shows experimental data for the case when all laser pulses are weak. The simulation of the data with no adjustable parameters fits well the experimental results (see Fig. 3.3a). When the laser intensity of the first two pulses is increased by an order of magnitude, the full rotational recurrence observed increases in intensity. The data obtained at this intensity can still be fitted by a room temperature distribution of linear CS₂ molecules (see Fig. 3.3b). Under these conditions, signal intensity can only increase if there is a larger anisotropic polarization of the sample. This higher polarization results from a greater number of molecules being pulled into alignment by the electric field. Previous work describing the timescales needed for alignment have considered the very low temperature available in molecular beams.^{21,71} At the higher temperatures here, the time scale of molecular rotation is much closer to the pulse duration of the laser. The RMS rotational time of CS_2 at room temperature is 1.8 ps (J_{RMS} =62). This means that during the 60 fs laser pulse, a molecule with the RMS rotational energy can rotate 15 degrees.



Figure 3.3^{ii} First rotational recurrence of CS₂ at three different laser intensities. Probe intensity was held constant throughout at $2x10^{10}$ W/cm². (a) Low intensity data (circles) and simulation (solid line) based on unperturbed molecules. (b) Data (circles) under higher intensity indicating laser induced alignment. The simulation (solid line) assumes unperturbed molecular geometry. (c) High intensity data (circles) showing a change in the observed rotational revival, evidence for structural deformation of the CS₂

molecule. The solid line in (c) is a simulation based on 35% of the sample having a bond angle of 160°.

Simulations of TG data presented here follow the quantum mechanical expression for the time dependent susceptibility given in Chapter 2 (see equation 2.2)

When the intensity of the first two pulses is increased above 10^{12} W/cm², the full rotational recurrence increases in intensity and changes shape (see Fig. 3.3c). Most markedly, the first feature increases in intensity by a factor of two. The features observed at long time delays, >77.5 ps, increase in intensity and new oscillations are observed. Attempts to explain these changes in the rotational recurrence structure by Raman induced changes in the rotational population in the manner of Rosca-Pruna and Vrakking.¹⁰⁰⁻¹⁰² have previously been shown to be inadequate to explain our experimental results.⁹⁵ Simulation of the data for high intensity excitation shown in Fig. 3.3c, requires the introduction of bent molecules. Α static bond angle of 160° (B=0.110536cm⁻¹.C=0.109995cm⁻¹) was used in our simulation to reproduce the experimental data.

3.3.2. Evidence of structural deformation for Coulomb Explosion

In order to corroborate the observed molecular structure changes we studied the effects induced by the strong field in Coulomb explosion experiments. Figure 3.4a shows the TOF-MS resulting from excitation with pulses with 4.6×10^{14} W/cm² peak intensity. In addition to the parent ions (CS₂⁺), (CS₂²⁺) multiple fragments are observed. We can distinguish the singly ionized fragments (C⁺ and S⁺) from the doubly ionized fragments (C²⁺ and S²⁺). Figure 3.4b shows the ionization yield of the parent ion as a function of the polarization vector of the excitation beam. Notice that the yield is isotropic, as expected,

because of the isotropic distribution of CS_2 molecules in the molecular beam. The data in Figure 3.4b serves also to confirm that there is no systematic bias in the probability of ion detection as a function of the polarization vector of the excitation field with respect to the time of flight axis. A similar isotropic distribution was observed for the $CS_2^{2^+}$ ion.



Figure 3.4ⁱⁱ Time of flight mass spectrum obtained for CS_2 molecules (a) when the laser polarization vector is aligned with the TOF axis. The zoomed inset shows splitting of the sulfur fragment ion peaks caused by their Coulomb explosion toward and away from the detector. (b) Angle dependent distribution of CS_2^+ ions, showing an isotropic distribution.

The angle dependent ionization yield for S^+ and for C^+ was measured, and the results are presented in Figure 3.5 in Cartesian and polar coordinates. The experimental data obtained for three separate runs are depicted as circles, squares and triangles. The lines are best fitted by cosine or sine functions to the fourth power. Notice that the yield

for S^+ follows a cosinusoidal distribution, with maxima at zero and 180 degrees (see Figure 3.5a). The yield for C^+ ions follows a sinusoidal distribution with maxima at 90 and 270 degrees (see Figure 3.5b).



Figure 3.5ⁱⁱ Angle dependent detection of singly charged fragment ions following Coulomb explosion. Anisotropic distributions are observed for C⁺ (a) and S⁺ (b) ions in polar and Cartesian plots. Data for three independent experiments (squares, circles, triangles) are accompanied by a guide to the eye (solid line) in the form of a $\cos^4(\theta)$ function. S⁺ shows a maximum ion yield at 0° and 180°, while C⁺ shows a maximum at 90° and 270°. The anisotropy for the C⁺ ions is less pronounced.

The angle dependent ionization yield for S^{2+} and for C^{2+} was measured, and the results are presented in Figure 3.6 in Cartesian and polar coordinates. The experimental data obtained for three separate runs are depicted as circles, squares and triangles. The lines are best fitted by cosine or sine functions to the fourth power. Notice that the yield

for S^{2^+} follows a cosinusoidal distribution, with maxima at zero and 180 degrees (see Figure 3.6a). The yield for C^{2^+} ions follows a sinusoidal distribution with maxima at 90 and 270 degrees (see Figure 3.6b). Notice that the results for the doubly ionized fragments show greater sensitivity toward the angle of the polarization vector of the excitation pulse compared to the singly ionized fragments in Figure 3.5. This indicates the doubly charged particles are ejected from a multiply charged parent with more significant bending than the singly charged ions.



Figure 3.6ⁱⁱ Angle dependent detection of doubly charged fragment ions following Coulomb explosion. Anisotropic distributions are observed for C^{2+} (a) and S^{2+} (b) ions in polar and Cartesian plots. Data for three independent experiments (squares, circles, triangles) are accompanied by a guide to the eye (solid line) in the form of a cos⁴(θ) function. S²⁺ shows a maximum ion yield at 0° and 180°, while C²⁺ shows a maximum at 90° and 270°.

The ionization data shown in Figure 3.5 and 3.6 is consistent with the angular distribution of the fragment ions obtained with a titanium sapphire laser centered at 800 nm.^{87,88} Similarly we are able to interpret our data in terms of a molecular structure deformation that is consistent with bending. The angular dependence observed in the molecular beam is consistent with the molecular structure deformations measured by the TG method on the neutral molecules.

3.3.3. Alignment and Deformation of polyatomic molecules

Figure 3.7 demonstrates the behavior of CO₂ molecules under strong field excitation. These experiments were carried out with a titanium sapphire laser centered at 800 nm. For low intensities (Figure 3.7a) the rotational recurrence can be fit by a simulation of CO₂ molecules at room temperature with overall signal intensity as the only adjustable parameter. As the laser intensity is increased (Figures 3.7 b-d), the rotational revival gains in intensity and changes overall shape. Increases in intensity can be related directly to laser-induced alignment, while changes in the shape of the revival are linked directly to changes in the molecular structure. Based on our simulation the angle of the deformed CO₂ molecules is 161 ± 0.5 degrees. For stronger fields (Figures 3.7e-g) a background signal is observed and the shape of the revival changes substantially. The background is due to ionization and plasma formation. The rotational recurrences are deformed by interference between the plasma emission and the TG signal. This aspect will be discussed below.



Figure 3.7ⁱⁱ Time resolved TG experimental data centered on the first rotational recurrence of CO₂, with the probe intensity held constant at $2x10^{10}$ W/cm². At low intensities ((a) and (b)), the data (circles) matches well the simulation (solid line) based on an unperturbed linear molecules. Near 10^{12} W/cm² ((c)and(d)) the data shows evidence of bending. Solid lines in (c) and (d) are simulations assuming 35% of the sample has a bond angle of 160°. At higher intensity ((e), (f) and (g)), the signal appears above a constant background signal. The simulation assumes that molecules in the intense field have been destroyed and the signal arises from unperturbed linear molecules heterodyned by a constant background.

Figure 3.8 analyzes the effect of strong field excitation at 620 nm on acetylene. As the laser intensity is increased the intensity of the rotational revivals increases. Again, this increase is directly linked to laser induced alignment. For the higher intensity data (Figure 3.8c), the intensity has increased by a factor of almost 480 and some deformation is observed. Interestingly, the main deformation is a broadening of the first feature of the rotational revival.



Figure 3.8^{ii} Time resolved TG experimental data centered on the first rotational recurrence of acetylene, probe intensity held constant at $2x10^{10}$ W/cm². At low intensity (a), the data (circles) matches well the simulation (solid line) based on unperturbed molecules. As the laser intensity is increased (b and c), the first peak of the recurrence broadens, beginning to overlap with the second peak. The factor of 40 in intensity from (a) to (c) can be explained by an enhanced alignment of the acetylene molecules in the laser field.

Finally, Figure 3.9 demonstrates the structural deformation of benzene as a function of 620 nm laser intensity. The data obtained for low intensities (Figure 3.9a) can be fit with the spectroscopic parameters of room temperature benzene. For higher intensity excitation, there is not a large change in the amplitude of the features, indicating that the alignment observed is not as substantial as that observed for the linear molecules. Already for intermediate intensities (Figure 3.9b) the first feature in the rotational revival is broadened towards early times, a feature that was observed for acetylene. For higher excitation energies, the signal level increases by a factor of two and there is substantial molecular deformation.



Figure 3.9ⁱⁱ Time resolved TG experimental data centered on the first rotational recurrence of benzene, probe intensity held constant at $2x10^{10}$ W/cm². When the grating intensity is low (a) the data (circles) is in good agreement with the simulation (solid line) assuming unperturbed molecules. At $3x10^{11}$ W/cm² (b), the first peak of the recurrence broadens, and by $7x10^{12}$ W/cm² there is evidence for significant deformation of the benzene molecule. Simulation in (c) assumes a symmetric top with a c₃ symmetry axis (ring puckering mode).

3.4 Discussion

There are usually two views of off-resonance laser induced alignment. The first one involves adiabatic alignment induced by a slowly increasing electric field (long laser pulse) that creates a directional force that traps the molecules in pendular states.⁷¹ As the electric field strength is reduced to zero, the rotational distribution in the sample is restored unaffected, hence the adiabatic terminology is used. This picture is consistent with experiments involving a nanosecond laser pulse as the source of the strong field. The second view involves an instantaneous 'kick' toward alignment, a view that is consistent with the interaction of an ultrashort pulse with supersonically cooled molecules.²¹ The experiments presented using the TG method at room temperature are in an intermediate regime. Molecules with low angular momentum feel a kick towards alignment, essentially not moving while the field is on. Molecules with high angular momentum are able to rotate on the timescale of the laser pulse and therefore their alignment is more consistent with the adiabatic picture. The data shown in the results section is consistent with alignment induced by strong off-resonance electromagnetic fields. As shown in Figure 3.1, the trap depth as a function of peak intensity reaches hundreds of K for lasers with peak intensity ~ 10^{12} W/cm² and the resulting alignment of the room temperature molecules becomes possible.

In addition to alignment, the data presented here is consistent with large molecular structure deformations. In the case of linear molecules, bending can be understood in terms of electronic state mixing. For CS₂ and CO₂ singlet and triplet excited states are bent. In Figure 3.10 we show a schematic representation, from a 'dressed state' point of view,^{103,104} leading to molecular deformation. Potential energy curves in the absence of external fields are available in the literature.¹⁰⁵⁻¹⁰⁷ In Figure 3.10 we show the electronic ground state¹⁰⁸ as dressed by two 620nm photons and overlapping the bent ¹B₂ electronic state. The ground state wavepacket, originally at the equilibrium geometry evolves within the pulse duration, ~ 60 fs, away from linear geometry. Once the field is turned off, the molecules are left with high amplitude vibrational excitation. Therefore, the rotational recurrence indicates a deviation from the linear geometry.



Figure 3.10^{ii} Schematic representation of laser induced molecular deformation process of CS₂ molecules based on a dressed state picture. The laser dresses the ground state and brings it close to the excited states having a bent geometry. The wavepacket has a short time to evolve in the dressed state potential during the laser pulse. The system returns to the ground state with substantial bending vibrational energy, leading to a deviation from linear geometry, and producing a higher rotational constant.

One of the advantages of the TG method to assess molecular deformation following strong field excitation is that the molecular geometry can be measured long after the field has been turned off. The molecules rotate field free and their rotational revival reveals the average bent angle (the deviation from linear geometry). In the case of CS₂, the data is consistent with 35 % of the population achieving an average bend angle of 20 \pm 0.5 degrees. This value is very close to the measurement from Iwasaki,⁸⁶ who determined the average bent angle following strong field excitation of CS₂ by angular dependent ionization to be 18±3 degrees for CS₂³⁺. The angle we have determined (160°) is between the equilibrium angle of the ¹B₂(¹ Δ_u) and ¹A₂(¹ Δ_u) states of CS₂.¹⁰⁹ The angle and percentage of the population that is deformed was determined by a series of simulations shown in Figure 3.11. Figure 3.11a shows that as the bend angle increases the rotational revival shifts towards earlier times (the rotational constant B increases). Because only a portion of the population is bent, (the 35% value arises from the fact that 72% of the intensity of a Gaussian pulse is contained in the central part of the beam), the rotational revival from all the molecules in the sample needs to be added and then squared to obtain the observed heterodyne detected signal.^{57,60} When we add 35% of bent molecules we see changes in the resulting signal as shown in Figures 3.11b-f. The simulation in Figure 3.11e fits our data closely, while the simulation in Figures 3.11d and 3.11f do not. Because the TG method is much more sensitive to neutral molecules than ions, because of their greater polarizability, we can also establish that the molecular deformation takes place in the absence of ionization. We have carried out ab initio calculations¹⁰⁸ to explore molecular structure changes induced by strong (0.5V/Å)electric fields. We have found that when the field is perpendicular to the molecular axis, a bent molecular structure is preferred. The potential minimum of the polarized molecule no longer corresponds to linear geometry but to a bent geometry. We have confirmed this by ab initio calculations for CS₂ in the presence of a strong 0.5V/Å field. The overall change in the potential energy surface, however, is not large enough to explain the experimental observations.



Figure 3.11^{ii} Simulation showing the effects of molecular deformation on the rotational recurrences of a generic molecule. The time axis is in units of the full-width half maximum of the peaks of the recurrence, with zero being the recurrence time in the linear molecule. Plot (a) shows recurrences from the bent species, showing the increase in rotational constant as a function of bond angle. Plots (b) through (f) show the recurrences of a sample comprised of 35% bent molecules and 65% linear molecules for bond angles from 5°(b) to 25° (f). The simulation in panel (e) is in good agreement with our experimental findings shown in Figure 3.3c.

The bending angle found in the TG data is consistent with the Coulomb explosion data taken in our laboratory with the same laser system. If the molecules remained linear, a case depicted in Figure 3.12, the signal from the S^+ ions would show a marked anisotropy. The anisotropy would result from two situations. When the electric field vector is aligned with the TOF axis the S^+ ions are ejected towards and away from the detector. Because of the repeller plate, the fragments that are ejected away from the detector are deflected back towards the detector. This leads to a well known splitting in the ion signal, evident in the zoomed insert of the mass spectrum in Figure 3.4 for S^{2+} ions, and used in photofragment spectroscopy analysis.¹¹⁰ Note that molecules perpendicular to the field are not affected by the field and yield no ions. When the field is perpendicular to the TOF axis the S⁺ ions are ejected at a high velocity in a direction that is perpendicular to the detector. Despite the acceleration voltage, the Coulomb repulsion is significant and in the time it takes those ions to reach the detector plane ($\sim 4 \mu s$) they are already several centimeters apart and are not detected. For this reason the S^+ ions show a distribution that can be simulated by a cosinusoidal function. For linear molecules, the detection of C^{\dagger} ions is not affected by the angle of the polarization vector of the electric field. The predicted detection is therefore isotropic, a fact that is not supported by the data shown in the experimental data in Figures 3.5 and 3.6.



Figure 3.12^{ii} Conceptual drawing of the Coulomb explosion of linear CS₂ molecules when the electric field polarization is parallel or perpendicular to the time-of-flight axis. The detection of S⁺ fragment ions is expected to show a marked anisotropy. However, the C⁺ fragment ion detection is expected to be isotropic.

Figure 3.13 considers the angle dependent detection of fragment ions resulting from bent CS_2 molecules. Unless the bending angle is very large, there is almost no change in the anisotropic dependence of the S⁺ ions discussed above for linear molecules, see Figure 3.13 top. However, for bent molecules the C⁺ signal becomes anisotropic. The anisotropy results from the following observations, based on the assumption that the bending angle is small and that the polarizability of the molecule remains along the two S atoms. When the electric field vector is aligned parallel to the TOF axis the bent CS_2 molecules can have the two S atoms along the field or perpendicular to the field. If the molecules are oriented along the field, then the C⁺ ions are ejected in a direction that is perpendicular to the detector and miss it. When the electric field vector is aligned perpendicular to the TOF axis the bent CS_2 molecules oriented along the field eject C^+ ions toward the detector and register maximum signal. When the molecules are oriented perpendicular to the field, signal is minimal because the perpendicular component of the polarizability is very small for small bend angles. From this analysis so far, it is clear that C^+ ions are predicted to show anisotropic detection that is perpendicular to that observed for S⁺ ions if the CS₂ molecules are bent. The predicted anisotropic ion signal from the Coulomb explosion from bent CS₂ molecules is shown in Figure 3.13. It is difficult to make an accurate determination of the angle from this data without coincidence imaging. A simple simulation of the parallel and perpendicular components of the polarizability as a function of bend angle leads us to estimate the bend angles from the singly and doubly ionized data sets to be 170 and 155 degrees respectively. The agreement between the findings of Iwasaki et al using mass - resolved momentum imaging (MRMI) and 800nm excitation⁸⁶ wavelength and our angle determination is good. We attempted to measure the behavior of CS₂ molecules under intense 800nm radiation using the TG method in a static cell. Unfortunately we found that for laser intensities of 10¹² W/cm² and higher a chemical reaction occurred in the cell and all the sample in the cell decomposed. After a number of attempts we abandoned this experiment.



Figure 3.13^{ii} Conceptual drawing of the Coulomb explosion of bent CS_2 molecules when the electric field polarization is parallel or perpendicular to the time-of-flight axis. The detection of S⁺ fragment ions are expected to show a marked anisotropy similar to that observed for the linear molecules. However, the C⁺ fragment ion detection is expected to be anisotropic and perpendicular to that observed for the S⁺ fragment ions.

The transient grating method is ideal to measure the signal from neutral species with high anisotropic polarizability. For CO₂ molecules the bond angle of the bent species reaches 161 degrees; this value should be compared to the 140 degrees determined by Hishikawa *et al.*⁸² As the electric field is increased and ionization takes

place the TG signal decreases and gives way to a background signal caused by the plasma. In Figures 3.7e-g, we showed CO₂ molecules in the presence of an increasingly strong electric field. Notice that the background increases and that the rotational revivals change shape. Under these conditions, the plasma emits a spectrally shifted light pulse (a spark) that provides a local field to heterodyne the TG signal.^{54,111} Under these conditions, the TG signal changes from being homodyne detected to heterodyne detected.^{55,56} The weak heterodyne signal corresponds to linear CO₂ molecules that are practically unaffected by the electric field. It is very possible that this signal arises from molecules outside the main focus of the laser field. Banerjee *et al.* have explored differences observed in ionization and Coulomb explosion as a function of the electric field intensity profile at the focus of the laser.⁸⁵ Their observation of single ionization in the wings of the focus and highly charged species at the center is consistent with these findings, that is, ionization and plasma formation in the focus with weak signal from unperturbed molecules from the wings.

Molecular deformation in larger molecules is evident in the experimental data presented here. In the case of acetylene, the electronically excited state responsible for its absorption in the ultraviolet region is known to have a staggered (trans) geometry.⁶³ Based on this knowledge we can determine the deviation angle from linearity by fitting of the experimental data. This data is consistent with bending of 60 ± 10 degrees as shown in Figure 3.14a. Because hydrogen atoms are very light we are unable to make a more accurate determination of the angle. A similar analysis was used for benzene in the presence of strong laser fields. The data clearly shows a distortion, however, the rotational constant does not change significantly. This implies that the molecule is not

stretched in the plane; it is bent outside the plane. Based on this observation we assume that the molecule assumes a puckered geometry that maintains the molecular symmetry and achieves an angle of 15 ± 3 degrees out of planarity, see Figure 3.14b. This observation is consistent with the experiments of Shimizu who studied the molecular deformations of benzene under strong field excitation by Coulomb explosion.¹¹²



Figure 3.14ⁱⁱ Molecular models depicting the average bent angle observed for acetylene (a) and benzene (b) consistent wit the experimental TG data obtained in the presence of strong laser fields.

3.5 Conclusions

In this chapter I have presented a study about the behavior of polyatomic molecules in the presence of strong off-resonance ultrashort laser fields. The experimental data are consistent with alignment of the molecules. This alignment results from a 'kick' induced by the electric field acting on the polarizability of the molecule. Our data provides clear evidence of significant molecular structure deformation resulting from the interaction with the strong field. These observations are consistent with Coulomb Explosion measurements from our group and from other groups.^{60,82,112}

Recent experiments on laser control of photodissociation reactions using shaped pulses require a careful evaluation of the effect of strong off-resonance laser fields on the electronic potentials of molecules.^{9,10} In particular, it is important to determine to what extent these fields align and deform the neutral species. It would be especially important to determine if the observed chemistry takes place in the ground or electronic excited states of neutral molecules or if the chemistry takes place after ionization. The study presented here, especially the TG measurements on the neutral molecules indicates that the electric field can have a major influence on the molecular structure without causing ionization. This study, and that of Banarjee et al. highlight differences caused by the gradient in the electric field intensity of Gaussian Pulses, an aspect that has not been addressed in strong field laser control. The temporal envelope of the excitation pulse has not received sufficient attention in studies of molecular deformation. In our case the pulse duration (60 fs) is similar to the bending period of ground state CS₂. Therefore during the laser pulse the nuclei have time to move away from linear geometry. Once the field is gone, the ground state potential is restored and the molecule is left vibrationally excited. It would be interesting to explore the effects of pulse duration and excitation with different temporal envelopes. This research could yield methodology to figure out the design of the field to carry out a specific chemical reaction such as isomerization.

In conclusion, the time resolved TG method is ideal to measure molecular alignment and molecular structure deformation induced by strong laser fields. The method provides a high degree of accuracy, and has been used to determine structural deformation in CS_2 , CO_2 , acetylene, and benzene. It is important to point out that the TG measurement is made by the time-delayed probe pulse, which has minimal influence on the molecular system and arrives a long time after the strong field has been turned off. This is in contrast to other ionization-based experiments, where the strong field affects the molecule and releases the charged particles. The TG measurements here are consistent with alignment and bending dynamics that take place in neutral molecules, in the absence of ionization.

4. Femtosecond photon echo measurements of electronic coherence relaxation between the $X(^{1}\Sigma_{g^{+}})$ and $B(^{3}\Pi_{0u^{+}})$ states of I₂ in the presence of He, Ar, N₂, O₂, C₃H₈

4.1 Introduction

There is considerable theoretical and experimental interest in controlling the amplitude and phase of quantum mechanical states in atoms and molecules.^{11,60,113} The motivation behind these efforts comes from evidence that intramolecular dynamics and chemical reactivity can be controlled using phase and amplitude shaped pulses.^{2,9} A second motivation is the future construction of a computer that will operate through the coherent manipulation of individual quantum states.¹¹⁴⁻¹¹⁶ For both of these applications, coherent interactions between the laser field and the atom or molecule are required. Here we will explore the loss of electronic coherence in gas phase iodine molecules, a model system that has been explored for the coherent manipulation of information,^{117,118} as a function of number density and the addition of different buffer gases. The rate of decoherence determines how long information can be manipulated without loss of fidelity. The loss of coherence and the nature of the long-range interactions between ultracold atoms and Bose-Einstein condensates has become a subject of recent interest.^{119,120} These measurements may help to shed light on that subject as well.

This chapter is a continuation of work from the Dantus laboratory, where we have used femtosecond three-pulse four-wave mixing (FWM) methods, involving different pulse sequences, to measure many of the processes that contribute to coherence relaxation in ground and excited state iodine.^{58,64,66,121} We make the distinction between different measurements, such as electronic coherence decay (involving two electronic states), from vibrational or rotational coherence decay (involving vibrations or rotational motion in a given electronic state), and spatial coherence decay (involving the motion of atoms or molecules in space). The focus of this chapter is on the nature of interactions (long-range collisions) that lead to a loss of electronic coherence (decoherence). For these measurements, we can ignore the lifetime of the upper electronic state, T_1 , because it is on the microsecond time scale. These measurements involve pure iodine as well as iodine in the presence of buffer gases that range from He atoms to propane molecules.

The signal measured from coherent spectroscopic methods, such as FWM, depends on phase coherence among all molecules emitting the field. As the phase coherence is lost the strength of the signal diminishes. Measuring the rate of decoherence and understanding the nature of the interactions that cause it in gas phase environments are the goals of this work. In the gas phase, decoherence typically results from long-range interactions, which cause a phase change in the polarization of the single molecule. Figure 4.1 shows an iodine molecule in an electronic coherence between the B(${}^{3}\Pi_{0u}^{-1}$) and the X(${}^{1}\Sigma_{g}^{+}$) states, showing the potential energy curves for the relevant electronic states. The molecule, whose polarization oscillates with frequency ω , can be perturbed through long range interactions with buffer gas molecules. This perturbation changes the energy of the B and X states and result in a time dependent frequency change $\Delta \alpha(t)$. The accumulated phase change $\Delta \varphi$ that results from one such long-range interaction leads to

the measured dephasing as the emitted electric field destructively interferes with the emitted fields from other molecules in the sample.

In this study, two types of pulse sequences are used: photon echo (PE) and reverse transient grating (RTG).¹²² Both methods measure the electronic coherence decay that results from the first order polarization $\rho^{(1)}$ (see Figure 4.2); however, they have a very different dependence on homogeneous and inhomogeneous contributions. In condensed phases, the inhomogeneous contribution to coherence loss is very significant making PE measurements the only viable method to obtain measurements of electronic coherence decay in the condensed phase. In the gas phase, inhomogeneous contributions are much smaller; therefore, both PE and RTG can provide valuable information. In principle, for very low pressures and small molecules it is possible to measure the Doppler free line width of individual spectroscopic transitions to estimate the pure homogeneous broadening. However, for room temperature iodine in the presence of buffer gases, time resolved measurements as performed here are clearly advantageous and provide both homogeneous and inhomogeneous decoherence rates. The theory section, describes the signals from the two methods and recover the isolated molecule and condensed phase limits. The results section shows that, under certain conditions, these measurements involve an intermediate case, between the two limits, that has not received much attention in the literature.



Figure 4.1.ⁱⁱⁱ A graph of the potential energy curves (solid line) involved in the electronic coherence between the B and X states of iodine. Dashed lines represent the perturbation caused by the approaching buffer gas molecule. The overall change in energy is indicated by $\Delta \omega$. The phase shift $\Delta \varphi$ necessary to destroy the coherence during a long range collision is given by the accumulated phase shift taking place during the interaction.

4.2 Theory

The intensity of the PE signal as a function of delay time in the liquid phase has long been known to conform to an exponential decay with time constant $\frac{1}{2}T_2$, where T_2 is the homogeneous relaxation time.¹²³ Similarly, it has been shown that for gas phase samples, the photon echo decays with rate $\frac{1}{2}T_2$.¹²⁴ This section explores the reason for the factor of two difference for these two limits, and develop a means of extracting T_2 even from the intermediate region where neither the gas phase nor the liquid phase limits apply.

To correctly describe the evolution of the system including relaxation and obtain an expression that bridges the gap between the liquid phase and the gas phase limits we will need to use a density matrix approach. The formalism we use to describe PE and RTG is based on this approach, which was published earlier.⁵⁴ Here we apply it to derive simple formulas for the intermediate between liquid and gas phase cases. For PE and RTG, the first pulse arrives at time zero while the second and third coincide in time, following after a delay τ . In the case of PE the emission goes in the phase matching direction $k_{PE}=k_3+k_2-k_1$ (responses R_{11} and R_{111}), while in the case of RTG the emission goes in the phase matching direction $k_{RTG}=k_3-k_2+k_1$ (responses R_1 and R_{11}), ¹²⁵ as depicted in Figure 4.2. There are no differences in amplitude between the Liouville pathways R_1 and R_{11} and R_{111} for a two level system. Notice that the PE signal has a maximum at time 2τ . For RTG the maximum is at zero time (before the second pair of pulses, in the "virtual" non-physical region), as shown in Figure 4.2. The difference between PE and RTG is very important when molecules within the ensemble have different resonance conditions because of inhomogeneities.



Figure 4.2. Pulse sequence and phase matching geometry for PE and RTG measurements. The PE setup (a) with pulse b arrives before pulses a and c undergoes rephasing and has a maximum at time τ after the second two pulses. The RTG (b) with pulse a arriving before pulses b and c, undergoes no rephasing and is thus maximum at the time of the second two pulses.

The inhomogeneous relaxation can be described by the normalized Gaussian spectral distribution $\exp[-(\omega - \omega_0)^2/\Delta^2]$ of each transition frequency with width Δ The signal measured as a function of the delay τ corresponds to the temporal integral of the emission intensity. We can separate the electric field of the PE and RTG signals because they are generated in different directions. It is possible to analytically calculate the relaxation in

the case of an exponential homogeneous decay and a Gaussian inhomogeneous decay. For these cases we obtain

$$S_{\text{PE}}(\tau) \propto \int_{\tau}^{\infty} \exp(-2\gamma t) \exp(-(t-2\tau)^2 \Delta^2/2) dt =$$
$$\exp(2\gamma 2\Delta - 2) [1 - \operatorname{erf}(2^{-0.5}\tau \Delta + 2^{0.5}\gamma \Delta^{-1})](2/\pi)^{0.5}/\Delta \qquad (4.1)$$

$$S_{\rm RTG}(\tau) \propto \int_{\tau}^{\infty} \exp(-2\gamma t) \exp(-t^2 \Delta^2/2) dt =$$

$$\exp(2\gamma 2 \varDelta - 2 - 4\tau \gamma) [1 + \operatorname{erf}(2^{-0.5}\tau \varDelta - 2^{0.5}\gamma \varDelta^{-1})](2/\pi)^{0.5}/\varDelta \qquad (4.2)$$

The first exponent for both cases is the homogeneous decay (2γ is the decay rate which is twice the decay rate of the elements of the density matrix). The second Gaussian function $(\Delta^2/2 - \text{which} \text{ is twice as fast as the Fourier image of the inhomogeneous distribution in}$ the frequency domain) is centered at time 2τ for the PE (echo spike) and at zero time for the RTG (inhomogeneous dephasing).

We define the homogeneous relaxation time in terms of the relaxation rate $T_2'=1/\gamma$ and the inhomogeneous relaxation time in terms of the inhomogeneous spectral width $T_2^*=1/\Delta$. In the limit $\tau T_2' << T_2^{*2}$ there is no difference between the PE and RTG signals. In this case, Equations 4.1 and 4.2 can be simplified to obtain

$$S_{\text{PE}}(\tau) = S_{\text{RTG}}(\tau) \propto \exp(-2\tau\gamma) = \exp(-2\tau/T_2), \qquad (4.3)$$

In the opposite case $\tau T_2^{\prime} >> T_2^{\ast 2}$, the liquid phase limit, there is a difference between the PE and RTG signals. We can replace the integral formula for the PE Gaussian field with

a delta function at time 2τ and get a simple decay with rate 4γ . In this case equations 4.1 and 4.2 can be written as follows. (see appendix II)

$$S_{\text{PE}}(\tau) \propto \exp(-4\tau\gamma) = \exp(-4\tau/T_2), \qquad (4.4)$$

$$S_{\rm RTG}(\tau) \propto \exp(-\frac{1}{2}\Delta^2 \tau^2) = \exp(-\frac{\tau^2}{2T_2^{*2}}),$$
 (4.5)

Note that for short time delays, τ , the product τT_2 is always small. Therefore, for small delays we expect the gas phase limit to be a good approximation. For large τ , the gas phase limit is no longer accurate even for gas phase experiments. Figure 4.3 demonstrates this transition between the two limits. Note that initially the PE has a decay rate of 2γ , then goes through an intermediate region and, finally, at long delay times, has a rate of 4γ . In the case of RTG, the initial exponential decay with rate 2γ transforms to a faster Gaussian decay. For neat iodine at low density we found the PE and RTG signal decays are dramatically different; exponential for PE and Gaussian for RTG.⁶⁴ In the case of high density buffer gas or very short time, homogeneous dephasing is faster than inhomogeneous dephasing, making PE and RTG decay with approximately equal rates (2γ). This condition was accomplished for experiments with relatively high pressure of buffer gas and is different from the previous work from our group, where the homogeneous dephasing much slower.⁶⁴



Figure 4.3. Calculated PE and RTG decays ($\gamma=2\times10^{10}\text{sec}^{-1}$ and $\Delta=2\times10^{10}\text{sec}^{-1}$) showing both gas and liquid phase limits. At short times, both PE and RTG approach the gas phase limit (thin solid line), at longer times, PE follows the liquid phase limit (thin dashed line), and RTG decays non-exponentially.

4.3 Experimental

The experiments were carried out using the CPM laser described in the introduction. For some experiments, requiring longer pulses, the bandwidth of the CPM was purposely narrowed to \sim 1 nm and shifted to 615 nm. The fourth stage of the amplifier was double-passed, producing pulses that were 1.2 ps in duration with average pulse energy of 1 mJ. Pulse durations were determined by autocorrelation in a second harmonic generation crystal.

The laser was split into three beams of equal intensity, which were attenuated to less than 80 μ J per pulse (short pulse mode) or less than 300 μ J per pulse (long pulse mode) and recombined at the sample in the forward box geometry^{126,127} (see Figure 2.2). The beams occupy three corners of a 25 mm square and were determined to be parallel over one
meter by using a template of the appropriate geometry. A 50 mm diameter 0.5 m focal length lens focused the beams into the sample cell, the beams crossing at an angle of 2.9° . This crossing angle produces a transient grating with a 16 μ m spacing at 620nm. At the temperatures used in these measurements, the transient decays by diffusion after 60 ns. This timescale is three orders of magnitude longer than the coherence decay times being determined and is therefore neglected.

A computer-controlled actuator delayed the first beam, and the other two beams were overlapped in time. The pulse sequence defines physical process emission of which we detect in phase matching direction $k_{FWM} = k_a \cdot k_b + k_c$ (see Figure 4.2). By changing the arrangement of the beams at the lens we controlled whether beam b or beam a was first. PE measurements with $k_{PE} = -k_1 + k_2 + k_3$ require beam b to arrive at the sample before beams a and c, while RTG measurements with $k_{RTG} = k_1 - k_2 + k_3$ require beam a to arrive before beams b and c.⁶⁶ Time zero for both beam arrangements occurs when all three beams are overlapped in time. The temporal overlap of the beams was found using a removable 0.1 mm thick quartz plate.

The signal beam was collimated with a 0.5 m focal length lens, identical to the one that initially focuses the beams, and was spatially filtered through a 50 μ m pinhole before being sent to a 0.27 m monochromator for detection (homodyne) by a photomultiplier tube. Data for the short pulse laser was collected at 620 nm, and for the long pulse laser data was collected at 615 nm. Both detection wavelengths represent the center of the laser's Gaussian spectral profile in the particular laser arrangement to which they correspond. Data were collected using a boxcar integrator, averaging 30 laser pulses. The laser pulse intensity was monitored with a photodiode and pulses with energy outside

1.5 standard deviations from the mean energy were discarded. Typical data sets were averaged for at least ten scans of 300 time delays each.

Sample cells consisted of 1 inch quartz cylindrical tubes 4 inches in length, with optical windows. The cells were pumped to 10^{-5} torr while the solid iodine sample (Kodak Chemical) was frozen with dry ice. The sample cells were then thawed, refrozen and pumped out again. Buffer gases (AGA) were added at room temperature and buffer gas pressure was measured with a baratron on a sealed gas line. Optical density measurements were made using a CW intracavity doubled Nd:YVO4 laser (532nm) and a photodiode covered by a 530±10 nm bandpass filter to exclude stray light. The number density of iodine in the neat iodine cell was determined by transmission using established iodine absorption cross-section data.¹²⁸ The Nd:YVO₄ laser was determined to be of sufficient bandwidth to blur any fine structure on the absorption curve. This was confirmed using an absorption spectrometer with resolution set to half the laser bandwidth. A curve of iodine numerical density versus temperature was created. Our measurement of the extinction coefficient, $\varepsilon = 813 \pm 20 \text{ Lmol}^{-1} \text{ cm}^{-1}$ is in excellent agreement with that of previous measurements: $\varepsilon = 810 \pm 24 \text{ Lmol}^{-1} \text{ cm}^{-1}$.¹²⁸ Using $OD = \varepsilon nl$ we calculated the number density, n. These data agreed favorably with measurements from two other sources^{129,130} in the temperature region considered here. Buffer gas sample cells were all heated with a heating tape until the desired iodine number density was reached. For pure iodine measurements, the number density was varied from 1×10^{23} m⁻³ to 8×10^{23} m⁻³ by controlling the temperature of the sample cell. All measurements involving buffer gases were made at a number density of iodine 5×10^{23} m⁻³ and 110°C-120°C.

4.4 Results

4.4.1. Experiments on neat Iodine vapor

Photon echo traces obtained from pure iodine vapor were taken as a function of number density, using 60 fs laser pulses. Figure 4 shows a plot of the homogeneous relaxation rate, γ , as a function of number density. Each point on this plot represents a PE data set at a specific temperature in the pure iodine cell. A typical data set involved the measurement of PE signal intensity as a function of time delay between the first pulse and the other two pulses. Inset is a typical PE data set plotted on a logarithmic scale. The PE decays were measured from $\tau = -10$ ps to as much as $\tau = 800$ ps, with at least 300 data points per scan. The final data sets were the result of from 10 to as many as 100 averages, requiring approximately four hours of acquisition time.



Figure 4.4. Plot of homogeneous relaxation rate, γ , versus number density for neat iodine vapor. Results for 37 measurements are shown. Horizontal error bars indicate uncertainty in the absorption cross section of iodine, vertical error bars indicate uncertainty in the exponential fitting routine. Dotted lines represent the 90% confidence interval based on a linear least squares fit. Inset is a typical PE data trace plotted on a logarithmic scale. This trace corresponds to a number density of 5×10^{23} m⁻³.

Experimental decays were fit to exponential decays of the form $\exp(-2\gamma\tau)$ to obtain γ . It has been verified previously that PE signals from gaseous iodine decay exponentially.^{64,130} We use equation (3) to fit the PE data because the Doppler dephasing time T_2^* for iodine under these conditions is 720 ps, making the condition $\tau T_2^{\prime} << T_2^{*2}$ valid. This was verified experimentally, as the RTG signal decays exponentially with a strong temperature dependence. The solid black line in Figure 4.4 is a linear fit to the data, and the dotted lines represent the 90% confidence interval for that fit. Error bars in each dimension represent two standard deviations of the uncertainty of our measurements. Uncertainty in the decay rate comes directly from noise in the data set. Uncertainty in the number density is due to uncertainty in the absorption cross-section of iodine. The uncertainty in the number density used in Figure 4.4 results from the uncertainty in the absorption cross section reported previously.¹²⁸

From a plot of coherence decay rate versus numerical density, we extract a cross section, σ , for electronic phase relaxation using the equation

$$\gamma = n\sigma \overline{\nu} + \gamma_0, \tag{4.6}$$

where *n* is the number density of the gas sample, \bar{v} is the average relative speed of the colliding molecules $\bar{v} = (8kT)^{1/2} (\pi\mu)^{-1/2}$, and γ_0 is the relaxation rate at zero pressure.

A fit through the experimental data in Figure 4 allows us to determine a cross-section of $1170 \pm 110 \text{ Å}^2$ for neat iodine vapor, and a $1/\gamma_0$ of 58 ± 4 ns. This $1/\gamma_0$ value is in good agreement with our estimation of the diffusional dephasing, 60 ns. The cross section obtained from figure 4 is in good agreement with the measurement obtained earlier in our group, $1150 \pm 150 \text{ Å}^2$.⁶⁴ The electronic coherence decay cross-section for iodine obtained by Zewail et al is $590 \pm 110 \text{ Å}^2$. This value differs from our findings by a factor of 2.¹³¹ It

is unclear how the T_2 values were obtained from the data in this reference. The difference could be explained if they obtained T_2' directly from the observed echo decay time without the factor of 2.

4.4.2. Experiments with buffer gases

Electronic coherence relaxation rates were measured as a function of number density for various buffer gases. The number density of iodine in the cell was monitored with a CW laser beam as described in the experimental section. PE transients were obtained for several buffer gas pressures for each of the different buffer gases. Each of the data sets was fit to Equation 4.3 (single exponential decay with lifetime $1/(2\gamma)$, and γ values were extracted. These data are shown in Figure 5 for PE in the presence of He, Ar, O_2 and N_2 . The solid lines are linear fits to the data, from which coherence relaxation cross sections were extracted (see formula 6) and collected in Table 4.1. Error bars represent the 90% confidence limits for each data point based on the uncertainty in the fit. Error in the pressure of the buffer gas is smaller than the data points, about ± 2 torr. For all cases the data points fall within the linear fit taking into account the uncertainty in the measurement. Values for γ were also extracted using Equations 4.1 and 4.2 (to take into account inhomogeneous broadening), with a two-dimensional non-linear least squares fitting method. These γ values agree with the values extracted using Equation 4.3 to within experimental error.



Figure 4.5. Plots of homogeneous relaxation rate γ , of PE signal with 50 fs excitation pulses, versus number density for (a) Helium, (b) Argon, (c) Oxygen, and (d) Nitrogen. Error bars indicate uncertainty in the fit. Error in the number density is smaller than the data points. The point at zero number density in each plot represents the relaxation rate of Iodine at 5×10^{23} m⁻³ number density, uncertainty in this number is smaller than the data point in both dimensions.

Μ	σ, Ų	$R = \sigma^{1/2} / \pi^{1/2}$	v, ms ^{-1 e}	τ _i , ps	α, Å ³	IE , eV	C ₆ , J m ^{6 g}	C_{6cal} , J m ^{6 h}
Не	135±12	6.5 ± 1.5	1435	0.6	0.21 ^a	24.619 ^a	4.9×10 ⁻⁷⁷	0.306×10 ⁻⁷⁷
Ar	500±70	12 ± 3.5	485	3.4	1.63 ^a	15.781 ^a	43.6×10 ⁻⁷⁷	2.061×10 ⁻⁷⁷
N ₂	300±50	10 ± 1.6	567	2.3	1.76 ^b	15.581 ^c	14.2×10 ⁻⁷⁷	2.215×10 ⁻⁷⁷
O ₂	450±40	12 ± 1.1	534	3.0	1.60 ^b	12.0697 ^c	36.9×10 ⁻⁷⁷	1.816×10 ⁻⁷⁷
C ₃ H ₈	500±55	12 ± 1.3	465	3.6	6.31 ^a	10.962 ^a	41.8×10 ⁻⁷⁷	6.861×10 ⁻⁷⁷
I ₂ ^f	1170 ± 110	19 ± 1.4	274	10.1	9 ^d	9.307 ^c	190×10 ⁻⁷⁷	9.046×10 ⁻⁷⁷

Table.4.1 Parameters calculated for the long range interactions responsible for electronic coherence dephasing of I₂ molecules and buffer gases (M).

a. D. A. McQuarrie, J.D.Simon, Physial Chemistry, p.668, University Science Books, Sauslito, California, 1997.

b. D. A. McQuarrie, Statistical Mechanics, p.481, University Science Books, Sausalito California, 1997.

c. W. G. Mallard, *NIST chemistry webbook*, http://webbook.nist.gov/chemistry/ (2001). d. B. Friedrich, Phys Rev A, 2000, 61 025403

e – at 383 K

f - σ =1150±150 Å ¹⁶ 590±110 Å ²⁶

g – calculation with r^{-6} potential and experimental data.

h- calculation with formula for the dispersive force for parameters for Iodine in X state.

4.4.3. Photon Echo and Reverse Transient Grating Measurements

For all the gaseous samples we measured both PE and RTG transients. RTG measurements are helpful in determining the inhomogeneous contribution to the relaxation rate, Δ (see theory section). Figure 4.6 presents data obtained with 5×10^{23} iodine molecules per cubic meter and 2.5×10^{24} propane molecules per cubic meter. Data were taken using 1.2 ps pulses to blur the vibrational dynamics of the coherence. This allowed us to obtain a smooth decay across the entire temporal range. The dots are experimental signal intensities plotted as a function of delay time τ . The solid lines are fits using Equations 4.1 and 4.2, the dashed lines are exponential decays (pure homogeneous dephasing) using the γ determined by the same fit. The difference between

PE and RTG decay times is small and within the experimental error. Similarly, the fits obtained from the theory (Equations 4.1 and 4.2 for the PE and RTG) and the simulations obtained from the single exponential decay (Equation 4.3) are within experimental error.



Figure 4.6. Logarithmic plot of (a) PE and (b) RTG signals with 1200 fs excitation pulses, as a function of time $(5 \times 10^{23} \text{m}^{-3} \text{ Iodine and } 2.5 \times 10^{24} \text{m}^{-3} \text{propane at 400K})$. Experimental data (dots) are fit (solid line) using the theory without approximations, Equations 4.1 and 4.2, presented in the text. The dashed line is a simulation based on a simple exponential decay with a homogeneous decay rate determined by the full fit.

Figure 4.7 shows data points obtained from 37 independent transients for PE and RTG in the presence of propane at various pressures. The values for the decoherence cross section obtained (see formula 6) from these two plots are in agreement to within experimental error. From this we can conclude that inhomogeneous broadening plays a minor role, with an upper limit of 3×10^9 s⁻¹. This observation indicates that under these conditions, $T_2^{*2} >> T_2' \tau$, confirming that the gas phase limit applies for delay times τ less than 1 ns for the I₂-propane case presented.



Figure 4.7. Plot of the coherence relaxation rate γ versus pressure for propane buffer gas. Both Photon Echo data (a) and Reverse Transient Grating data (b) are shown. The plots contain a total of 37 independent measurements. Error bars indicate uncertainty in the fit. Error in the number density is smaller than the data points. The point at zero number density in each plot represents the relaxation rate of Iodine at 5×10^{23} m⁻³ number density, uncertainty in this number is smaller than the data point in both dimensions.

4.5 Discussion

The measurements of electronic coherence relaxation allow us to calculate cross sections. Assuming collisions occur at an average distance, R, determined by $\sigma = \pi R^2$, we can then calculate the average radius of interaction. The decoherence cross-section for iodineiodine collisions was measured to be 1170 Å², giving us an interaction radius of R = 19 Å. Notice that this value for the interaction radius is more than ten Angstroms greater than the Van der Waals radius (see Figure 4.8). Since we are dealing with the relaxation of electronic coherence, no energy needs to be exchanged by this interaction. Here we will use a hard sphere model to describe these interactions, drawing an "interaction region" around the molecules in the coherence. We define this interaction region such that any molecule passing through it will produce at least a π shift in the phase of the electronic wavefunction of the iodine molecule.



Figure 4.8. Depiction of the distances R involved in the long range interactions responsible for electronic coherence dephasing. Molecules are depicted as 98% electron density maps calculated using the Spartan molecular modeling program.

The colliding partner, moving with a velocity in center of mass coordinates \overline{v} , interacts with an impact parameter *b*, the shortest distance between the two molecules during the interaction. The interaction potential $\Delta U(r)$ is a function of the distance between the two molecules, *r*, and it reflects the perturbation in the energy difference between the B and X electronic states of iodine caused by the buffer molecule (see Figure 4.1).

If we picture the interaction region as a sphere around the iodine molecule, using the experimentally determined R (see Table 4.1), we can estimate how long these dephasing interactions take, based on the average speed of the molecules, \bar{v} . The average time of each interaction assuming an average interaction length, $\bar{l} = (4/3)R$, is then given by $\bar{\tau} = \bar{l}/\bar{v}$. The values obtained using our measurements are compiled in Table 1 and range from 0.6 ps to 10 ps for helium and iodine, respectively. The intermolecular distances R, determined in this report, are graphically depicted in Figure 4.8, while the molecules are represented as 98% electron density plots calculated using the Spartan molecular modeling program.¹³² The above analysis of the experimental data shows that the interactions are long range when compared to the Van der Waals radii, and short lived when compared to the lifetime of the electronic coherence.

As a plausible approximation, we assume the interactions to be dispersive and to follow an r^{-6} dependence, as obtained from the second term in the Lennard Jones potential.¹³³ Based on the distance and weakness of the interaction we assume the molecules follow a linear path through the interaction region. The change in phase of the iodine wavefunction is then¹³⁴

$$\left|\Delta\varphi(b)\right| = \left(2/\hbar\right)\int_{0}^{\infty} \Delta U(t)dt = 3\pi C_{6}/\left(8\hbar\overline{v}b^{5}\right)$$
(4.7)

We can then calculate C_6 parameters for the I₂ + M interactions, given in Table 1 using the formula

$$C_{6} = (8/3)\bar{v}\hbar(\sigma/\pi)^{25}$$
(4.8)

The values obtained are summarized in Table 1 and range from 4.9×10^{-77} to 190×10^{-77} J m⁶ for helium and iodine respectively.

In order to learn about the nature of the long range dephasing collisions, we assume the intermolecular interaction is purely due to dispersion forces as a first order approximation. We can calculate the dispersion parameter using and the expression¹³³

$$C_{6cal} = (3/2)\alpha_1 \alpha_2 I_1 I_2 (I_1 + I_2)^{-1}, \qquad (4.9)$$

where α_1 and α_2 are the ground state polarizabilities of the two molecules, and I_1 and I_2 are the ionization energies of the two molecules. The resulting values are summarized in Table 4.1 and are plotted in Figure 4.9. Errors in the experimental numbers in Figure 4.9 represent 2 standard deviations. Comparing the experimental to the calculated C_6 parameters in Figure 4.9, we note that both follow a similar trend. There is about one order of magnitude difference between the two sets of parameters. This difference is primarily caused by the greater polarizability of the B state, a parameter that is not presently known, but is expected to be greater due to the B state's triplet character.



Figure 4.9. Experimental (square points with uncertainties) and calculated (round black points) Lennard Jones C_6 parameters for the buffer molecules in this study. Both data sets follow very similar trends, however experiment and theory values differ by a factor of 15. The round open points correspond to the calculated parameters multiplied by a factor of 15 to compensate for the greater excited state polarizability (see text).

Multiplying the calculated points by 15, using the values obtained from the noble gases as guidelines (see open dots), the simulation reproduces closely the observed trend and close agreement is observed for He, O_2 , Ar, and I_2 . Only the Lennard-Jones parameters for nitrogen and propane are a factor of three smaller. These smaller differences may be related to the absence of non-bonding electrons in these molecules. The factor of 15 increase in the polarizability of the excited state can be justified based on calculations of the polarizability of the ground and excited states of a number of small molecules.¹³⁵ In this study it was determined that the polarizabilities of the excited states of the ground states of those molecules were between 12 and 20 times the polarizabilities of the ground states of those molecules.

For this analysis, a number of processes that take place during collisions have been considered and ruled out. Collision induced predissociation in iodine was studied previously.¹³⁶ The cross-section for Iodine – Argon collision induced predissociation of the B state was measured to be 11.1\AA^2 . This is 1/100 of the cross-section of pure electronic dephasing, measured here, and for pressures less 1 atm can be assumed to be negligible. Collision-induced electronic state mixing for Iodine – Argon collision has also been studied.¹³⁷ The cross section for this process is of the same order of magnitude as the hard sphere (Van der Waals) radius which is two orders of magnitude smaller than the dephasing cross section measured in our paper. Therefore this process is assumed to be negligible. Rotational-vibrational dephasing of iodine was also studied, for example.^{138,139} It was shown that all these relaxations (actually intramolecular dephasing of rotationalvibrational wave packets) take place during the first several picoseconds (less than 15ps for our spectral range of excitation) after excitation of the B state, an order of magnitude shorter time scale than our measurements (up to 200ps). This type of intramolecular pulse relaxation was discussed in our previous work.⁶⁴

The long-range interactions described in this report may involve other effects (quadrupole-induced dipole, quadrupole-quadrupole, etc.). Here we do not speculate beyond the fact that the experimentally derived values can be simulated by a model that only takes into account pure dispersion interaction estimates. Perhaps these measurements will encourage further theoretical analysis about the nature of these long range interactions.

4.6 Conclusion

I have presented a number of photon echo measurements aimed at determining the electronic coherence dephasing time of gas phase iodine vapor, neat and in the presence of buffer gases. We have written the explicit dependence of the dephasing rate on the homogeneous and inhomogeneous contributions. With the full expression, one is able to calculate the dephasing time T_2' without assuming a gas or liquid phase limit. From the experimental decay rates, dephasing cross sections have been extracted, and these are in good agreement with previous measurements in neat iodine.

The gas phase limit applies to the systems studied here, therefore only homogeneous relaxation plays a role and $\tau_{exp} = 1/(2\gamma)$. The Dantus group's earlier work on iodine at lower densities had shown some intermediate behavior where inhomogeneous relaxation was overwhelming and the liquid phase limit applied.⁶⁴ It is interesting to note that the differences between quenching rates for the various buffer gases seem to have no dependence on the number of degrees of freedom available in the molecule, and only depends on the relative polarizabilities of the quenching species. The similarity between (for example argon and propane) could be accounted for by the large distance of interaction and the modest amount of perturbation required to cause electronic dephasing.

In summary, the electronic coherence dephasing rates and cross sections have been determined for iodine molecules in buffer gases that range from low density to the condensed phase limit. These cross sections were determined using a simple hard-sphere model, but seem to describe long range interactions between the iodine and buffer gas molecules.

5. Multiphoton Intrapulse Interference: Binary Phase Shaping

5.1 Introduction

Amplitude and phase shaped laser pulses are often used to control chemical reactions and other physical phenomena. A typical pulse shaper is shown in figure 5.1. The laser pulse is spectrally dispersed and focused through what is known as the 4F geometry. The pulse shaping device, usually an LCD Spatial Light Modulator (SLM),⁷ is placed at the Fourier plane. Voltages applied to the SLM produce a change in the retardance of the individual SLM pixels. In this way different phases can be applied to each frequency component of a laser pulse. As some shapers control both amplitude and phase for at least 128 pixels across the laser spectrum there is a very large space of possible pulse shapes. For a system with *P* different phases and *A* amplitudes across *N* pixels, there will be $(P \times A)^N$ possible pulse shapes. Because the field needed to optimize a given chemical process is not known, the use of evolutionary learning algorithms (ELA) guided by experimental results in a closed feedback loop was proposed⁸. Experimental implementation of this method and successes in control of chemical reactivity have been reported and reviewed.^{9,140,141}



Figure 5.1: A typical 4F pulse shaper. The SLM placed at the Fourier plane applies different phases and amplitudes to different frequency components of the laser pulse.

In the low intensity regime, laser control is dominated by interference of different nonlinear optical pathways connecting the initial and final states.¹⁴² The challenge is finding the proper phase for each frequency within the pulse to achieve constructive interference at the desired pathway and destructive interference elsewhere. Here we consider two-photon excitation of fluorescent probes, as used in two-photon microscopy, as the target for optimization. In particular we envision two chromophores with different two-photon absorption spectra and our goal is to achieve selective excitation by 'focusing' the energy available at a specific region of the two-photon spectrum, as shown in Fig. 5.2.



Figure 5.2.^{iv} Schematic representation of the problem. The broad bandwidth second harmonic spectrum from transform-limited pulses is represented by a Gaussian (thin line). The objective is to introduce phase modulation to cause the two-photon spectrum to be intense only inside the window defined by frequency $2\omega_c$ and width W, and to minimize the background B outside the window. The contrast ratio C is defined as the integrated intensity inside W divided by the integrated intensity of light outside the window.

Experiments from our group have already shown that selective two-photon excitation is possible when one is able to tune the narrowed non-linear power spectrum to optimize excitation of one chromophore versus another.^{143,144} Here, however, we realize that the phase difference between different frequencies should take only two values, 0 or π , to maximize or minimize a given pathway.

In order to control two-photon excitation, one needs to control the non-linear power spectrum of the laser $E^{(2)}(\omega)$,^{145,146} which can be measured by obtaining the second harmonic spectrum generated using a thin second harmonic generation (SHG) crystal. The experimental and theoretical application of this new paradigm, which we call binary pulse shaping (BPS), is presented herein. The effect of spectral phase modulation on SHG has been studied by a number of groups and can be divided into broad¹⁴⁷⁻¹⁴⁹ and narrow^{150,151} phase matching bandwidth.

Conceptually, the problem depends on the intrapulse interference between pairs of frequencies. If we only consider two phases, zero and π , we can analyze the problem in terms of symmetry. To maximize the SHG intensity at a frequency $2\omega_{C}$ the spectral phase needs to be symmetric or antisymmetric about ω_{C} , such that the frequencies interfere constructively. To minimize the background intensity at all other frequencies, the spectral phase must be asymmetric with respect to all other frequencies away from ω_{C} , so that destructive interference is maximized. Here we propose the use of prime numbers to help us generate the quasi-random phase changes required. The mask to be used to modulate the pulses is shown in Fig. 5.3, and is designed for a 128-pixel SLM.



Figure 5.3.^{iv} Phase mask proposed based on the symmetry requirements of the problem, using the quasi randomness of prime numbers. This mask is reflected about pixel 64, and is designed to obtain a narrow second harmonic signal at the center of the spectrum.

5.2 Experimental section

The experiments are carried out using the titanium-sapphire oscillator laser system described in chapter 1, capable of generating pulses as short as 10 fs after a double pass prism compressor and a pulse shaper.¹⁴³ The spectral phase of the pulse is tailored using a computer-controlled pulse shaper of a design similar to those described by Weiner,⁷ and described elsewhere^{143,144} (see figure 5.1). For the experiments shown here, the pulses were centered near 800 nm. The spectral phase of the laser pulses was corrected using the multi-photon intrapulse interference phase-scan (MIIPS) method, which compensates phase distortions to obtain transform-limited (TL) pulses.^{143,144} The binary phase was introduced as an addition to the compensation phase.

The shaped laser pulses, with an energy of ~ 0.5 nJ per pulse and 87 MHz repetition rate, were focused mildly, to a spot size of ~ 100 microns in diameter, on a 20 micron thin β BBO SHG crystal. The frequency doubled light was collected with an optical fiber and dispersed on a compact spectrometer.

5.3 Results

First, consider spectral amplitude restriction to solve the problem. By narrowing the spectrum of the laser using a slit as shown in Fig. 5.4a, the SHG intensity obtained after amplitude restriction is shown in Fig. 5.4b. For a spectral width of 10% of the available bandwidth, amplitude restriction produces 100 times less second harmonic intensity than transform limited pulses. Although the contrast ratio for this case is favorable, the low intensity obtained at the desired wavelength makes this method experimentally unpractical.



Figure 5.4.^{iv} Effect of spectral amplitude restriction on SHG. (a) Experimental spectrum of the laser before (black) and after filtering with windows of width 40 (red), 20 (blue), and 10 (green) nm. (b) Experimental (points) and simulation (continuous lines) for the second harmonic spectrum of TL and spectrally filtered pulses as indicated in panel (a).

The phase mask shown in Fig. 5.3 was programmed on the SLM and resulted in dramatic narrowing of the SHG spectrum as shown in Fig. 5.5. The contrast ratio as defined in Figure 5.1 for this mask is 2.5 when the SHG peak is centered. By shifting the position of the mask on the SLM, hence tuning the center of symmetry, one can tune the SHG spectrum across approximately 35nm in the SHG spectrum. Sinusoidal phase

modulation,^{143-146,148} can not produce contrast ratios greater than 0.5 in theory, and as the window is tuned away from the central frequency the contrast ratio drops below 0.1.



Figure 5.5.^{IV} Experimental results with binary phase shaping. (a) The spectrum of the laser (dashed lines) and the binary phase mask $(0 \text{ or } \pi)$ are shown as a function of wavelength. (b) The second harmonic spectrum of the TL pulses (dashed line) and second harmonic spectrum of the shaped pulses according to panel (a).

The gray line in Fig. 5.5 corresponds to theoretical calculations. The absolute value of the spectral amplitude of the electric field was calculated from the experimental power spectrum of the fundamental pulse $I(\omega)$ using $|E(\omega)| = I(\omega)^{0.5}$. To simulate the experimental results a double Fourier transform method was used. The electric field in the time domain E(t) was calculated as the Fourier image of the complex spectral amplitude in the frequency domain, with the formula

$$E(t) = \int |E(\omega)| \exp[i\phi(\omega)] \exp(-i\omega t) d\omega, \qquad (5.1)$$

where the spectral phase $\phi(a)$ is the function that is introduced by the SLM. The power spectrum of the SHG was calculated using

$$I_{\rm SHG}(\omega) = |\int E(t)^2 \exp(i\omega t) dt|^2.$$
(5.2)

The SHG amplitude was normalized using the maximum of the SHG intensity calculated for TL pulses, $\phi(\omega) = 0$.

The agreement between experiment and theory in Fig. 5.5 is satisfactory given that there are no adjustable parameters. Differences between experiment and theory are due to the resolution of the pulse shaper at the Fourier plane and errors in the applied phase mask due to cross-talk between adjacent pixels. These resolution and calibration issues cause the experimental SHG spectrum to be slightly broader than expected, though the contrast ratio remains 2.1, comparable to the theoretical contrast ratio of 2.7.

To determine if a better solution exists, one can then use an evolutionary learning algorithm (ELA), assuming a Gaussian electric field corresponding to a 10 fs pulse centered at 800 nm. The SHG intensity was calculated according to

$$I_{\rm SHG}(2\omega_{\rm t}) = |[E(\omega_{\rm t}-\omega)E(\omega_{\rm t}+\omega)d\omega]^2$$
(5.3)

normalized to the maximum SHG amplitude for TL pulses.

BPS simplifies the calculations, especially if we assume the amplitude of the electric field to be a constant, that is, the spectral power is equal to 1 in the allowed spectral region. Each spectral component of the electric field, linearly dispersed in the frequency domain, can be represented as a binary value (\pm 1) determined by $b_k = \exp(i\phi_k)$, for $\phi_k = 0$ or π , respectively. The intensity of the SHG signal measured at frequency $2\omega_k$ can be calculated with the formula

$$\mathbf{S}_{\mathbf{k}} = |\Sigma_{\mathbf{j}} \mathbf{b}_{\mathbf{k}} \cdot \mathbf{j} \mathbf{b}_{\mathbf{k}} \cdot \mathbf{j}|^2 \tag{5.4}$$

where the integral in Eq. (5.3) is now replaced by a discrete sum. The problem of spectral selectivity can now be formulated as finding a vector b_k such that $S_k = 1$ for $\omega_k = \omega_c$ and S_k is minimized at all other frequencies.



Figure 5.6.^{iv} Comparison of a prime number inspired phase mask (black) with a mask that was optimized using a computer based learning algorithm (gray). The insets on the left depict the phase masks for each case. The inset on the right shows the improvement in the contrast ratio, as defined in Fig. 1, as the learning algorithm finds the best solution starting from the prime number phase mask.

Figure 5.6 compares theoretical results from the phase described in Fig. 5.2 (black) and the result of the ELA (gray), which was initiated with the proposed phase. The ELA used 100 individuals and one parent through 30 generations using single double and triple symmetric bit flips. The result from the learning algorithm shows ~2.5 greater contrast.

Experimentally contrast ratios greater than 5 are difficult to obtain when the spectrum is not linearly dispersed over the SLM pixels. Using an SLM with more pixels,¹⁵² and grouping those pixels such that each group covers the same frequency range, would improve the implementation and result in greater contrast, an observation based on these calculations.

5.4 Discussion

The goal of narrowing the SHG spectrum was motivated by the possibility of selective two-photon microscopy. To achieve this goal two conditions had to be satisfied, maximizing the nonlinear power spectrum at $2\omega_{\rm t}$, and minimizing it elsewhere. Maximization has been investigated previously by Silberberg and coworkers, who identified the condition $\phi(\omega_{\rm t}-\omega)=-\phi(\omega_{\rm t}+\omega)$ for continuous functions.^{153,154} Zheng and Weiner explored the narrow phase matching bandwidth SHG output at a single frequency, a problem that is analogous to two-photon excitation of an atom, using binary encoded pulses as used in communications.^{150,151} Zheng and Weiner found that limiting the phase to values of zero and π led to the condition $\phi(\omega_{\rm t}-\omega)=\phi(\omega_{\rm t}+\omega)$. Under both shaping conditions the maximum signal approached that obtained with TL pulses.

The problem of spectral narrowing by pulse shaping under broad phase matching SHG conditions, or selective excitation of large organic dyes and chromophores requires minimization of the nonlinear power spectrum away from $2\omega_c$. Upon study of the problem, as expressed in Eq 5.4, there is an analogy with convolution. In this case, some binary functions have the property of giving a sharp 'delta function' signal in one location and very low background elsewhere.

In principle, the solutions found in this study are members of the set of solutions obtained by arbitrary phase and amplitude pulse shaping. For a pulse shaper with N pixels, one can generate $(P^*A)^N$ shaped pulses, where P and A are the number of different phases and amplitudes a pixel can take. If we assume 100 pixels, each taking 10 different amplitude values and 100 different phase values, the number of different pulses is of order of magnitude 10^{300} . This number is extremely large, therefore, while in principle, the solution exists to achieve the desired photonic transformation or excitation, finding it is very time consuming except for a convex problem with a clear maximum.

Experimentalists have reduced the search space of an ELA by reducing the number of active pixels by grouping, the type of phase functions that are allowed, modulating phase and not amplitude, and introducing phase functions with a reduced numbers of parameters.¹⁵⁵⁻¹⁵⁷ We tried these approaches with limited success.

For one pulse experiments, the periodic nature of electromagnetic waves results in a great deal of redundancy in pulse shaping because nonlinear optical processes do not depend on the absolute phase or a linear variation of the spectral phase. This equivalence can be expressed by $\phi(\omega) \Leftrightarrow \phi(\omega) + a + b\omega$, where a and b are constants. Programming an ELA that acts on the second derivative of the phase can filter out this redundancy. The actual phase is obtained by integrating setting a=b=0. We used such an ELA to optimize smooth phase functions for spectral narrowing, but could not obtain a contrast ratio greater than unity.

The advantage of BPS is that it eliminates most redundancies. For BPS and 128 active pixels the search space is reduced to 2^{128} . If the problem has two-fold symmetry, for example two-photon excitation, then the search space is reduced to 10^{19} , a number

that is at least 281 orders of magnitude smaller than would be considered for arbitrary phase and amplitude pulse shaping as discussed above. An ELA can quickly converge in this small search space without resorting to grouping pixels.

BPS may have significant technological advantages. A retardation equivalent to π is easy and fast to obtain and calibrate. Permanently etched masks can be made in advance and used for specific applications such as selective two-photon microscopy. Scanning the mask's position can yield two-photon excitation spectra.

In summary, the use of BPS for selective two-photon excitation has been demonstrated. The contrast ratio using BPS was 6 times greater than that obtained using sinusoidal phase masks. The amplitude of the signal is 100 times greater than would have been obtained by amplitude modulation. BPS makes it simple to analyze a laser control problem and to propose rational solutions, as demonstrated here with a phase mask inspired by the quasi-random gaps between prime numbers. An ELA can be used to improve on the proposed solution efficiently because of the greatly reduced search space.

6. Appendix I

This appendix shows the derivation of the rotational component of the non-resonant homodyne and heterodyne FWM signal (see figure 2.2). Both signals involve the same physics in the sample, where an initial field sets up a polarization in a sample, which is then interrogated by another laser field. The difference is only in the signal detection, which is described in the experimental section of chapter 2. Initially, the sample consists of rotators with the uncorrelated wavefunction

$$\Psi^{(0)}(\theta,t) = \sum_{J} b_{j} e^{i\phi_{j}} (2J+1) |J\rangle e^{-i\varepsilon_{J}t/h}$$
(6.1)

where the phase ϕ_j is random, and θ is the angle between the moment of inertia (1) and the electric field polarization of the laser. J is the angular momentum, and $|J\rangle$ are ortho-normalized eigen-functions with energy levels $\varepsilon_J = F_J ch$, where $F_J = BJ(J+I)$ - $DJ^2(J+1)^2$, $B=h/(8\pi^2 cI)$, and D is the centrifugal distortion. The initial amplitudes of defined the bv the Boltzmann distribution states are $b_j = \sqrt{n_j} = \sqrt{(2J+1)\exp(-\varepsilon_j/kT)}$. After the first two pulses, applying the Raman selection rule $\Delta J = 0, \pm 2$ we have a wave packet in the sample where each rotational state has produced a wave packet consisting of three states with amplitudes $a_J^{\Delta J}$. This wavepacket will evolve until the third pulse arrives.

$$\Psi^{(2)}(\theta,t) = \sum_{J} b_{j} e^{i\phi_{j}} (a_{J}^{+2} \exp(-i\varepsilon_{J+2}t/\hbar) | J+2 \rangle + a_{J}^{0} \exp(-i\varepsilon_{J-2}t/\hbar) | J \rangle$$
$$+a_{J}^{-2} \exp(-i\varepsilon_{J-2}t/\hbar) | J-2 \rangle)$$
(6.2)

From this point there are two ways we can proceed. Mukamel tells us that the Homodyne FWM signal is proportional to the square of the absolute value of the imaginary part of the third order time dependent susceptibility of the sample $|\chi^{(3)''}(t)|^2$, which is proportional to the time derivative of the full operator

(fluctuation dissipation theorem)
$$\left|\chi^{(3)''}(t)\right|^2 \propto \left|\frac{-1}{kT}\frac{d}{dt}\chi^{(3)}(t)\right|^2$$
.¹²⁵ For a more

intuitive description, we can instead think of the anisotropic polarization produced by the laser passing through the sample. The polarization is proportional to the average transient alignment of the molecules in the sample $P_2(\cos\theta) \propto \cos^2\theta - 1/3$ after interacting with the laser. This polarization will affect the refractive index of the medium, and temporal changes in the refractive index of the medium give us the Heterodyne FWM signal. In this way we can write

$$S_{\frac{FWM}{\text{Heterodyne}}}(t) \propto \chi^{(3)''}(t) \propto \frac{-1}{kT} \frac{d}{dt} \chi^{(3)}(t) \propto \frac{d}{dt} \left\langle \Psi^{(2)}(\theta, t) \middle| \hat{P}_{2}(\cos\theta) \middle| \Psi^{(2)}(\theta, t) \right\rangle$$
(6.3)

and

$$S_{\frac{FWM}{\text{Homodyne}}}(t) \propto \left|\chi^{(3)''}(t)\right|^2 \propto \left|\frac{-1}{kT}\frac{d}{dt}\chi^{(3)}(t)\right|^2 \propto \left|\frac{d}{dt}\left\langle\Psi^{(2)}(\theta,t)\right|\hat{P}_2(\cos\theta)\left|\Psi^{(2)}(\theta,t)\right\rangle\right|^2 \quad (6.4)$$

Since $\langle \Psi^{(2)}(\theta,t) | P_2(\cos\theta) | \Psi^{(2)}(\theta,t) \rangle$ is an oscillating function that depends on J, and wavepackets produced from different J are uncorrelated, we can write

$$\left\langle \Psi^{(2)}(\theta,t) \middle| P_2(\cos\theta) \middle| \Psi^{(2)}(\theta,t) \right\rangle = \sum_J n_J \left\langle a_J^0 \middle| \left\langle a_J^{+2} \right\rangle^2 \cos(\Omega_J^{+2}t) + \left| a_J^{-2} \right|^2 \cos(\Omega_J^{-2}t)) \right\rangle$$
(6.5)

where $\Omega_J^{+2} = 2\pi c (F_{J+2} - F_J)$, and $\Omega_J^{-2} = 2\pi c (F_J - F_{J-2})$.

So long as the temperature is high and the molecule is heavy ($J_{AVG} >>1$), the transition probabilities (a_j) are near equal. The macroscopic polarization will depend linearly on the number density (N) of the sample, and anisotropic polarizability $\beta = |\alpha_{\parallel} - \alpha_{\perp}|$ of the molecules that make up the sample. Additionally, the rotational constant of the molecule, B, depends on the vibrational energy of the molecule, So we get a final expression for the time dependent polarizability of the sample caused by rotational Raman excitation,

$$P_2(t) \propto N \beta \Sigma_v \Sigma_J q_v \rho_J \cos(2\pi c (F_{J+2} - F_J)t) + \cos(2\pi c (F_J - F_{J-2})t)$$
(6.6)

where $F_J = B_v J(J+1) - DJ^2 (J+1)^2$ for the molecule¹⁵⁸, B_v is the vibrationally dependent rotational constant, ρ_J is the normalized rotational distribution including spin statistics (g_J) for all natural isotopes,¹⁵⁹ $\rho_J = g_J (2J+1) exp(-2\pi chF_J/kT)$, and q_v is the normalized thermal vibrational distribution for all ground state vibrational modes. The FWM signals can then be written as

$$S_{\frac{FWM}{Heterodyne}} \propto \frac{dP_2}{dt}$$
(6.7)

and

$$S_{\frac{FWM}{\text{Homodyne}}} \propto \left| \frac{dP_2}{dt} \right|^2$$
(6.8)

For samples containing multiple molecules with different rotational constants, the homodyned signal is given by $|(dP_a/dt + dP_b/dt)|^2$, leading to interference terms between the two populations.⁵⁸

7. Appendix II

This appendix describes the FWM signal decay for the photon echo (PE) and the reverse transient grating (RTG) pulse sequences. The intermediate case is derived, and both the liquid phase (inhomogeneous) and gas phase (homogeneous) limits are applied.

To correctly describe the evolution of the system including relaxation we have to use the density matrix (DM) presentation. In this case the ensemble of molecules can be described by the *n*th order density matrix. Because we use a non-collinear three pulse Four Wave Mixing (FWM) experiment and detect the 3^{rd} order nonlinear polarization that depends on all three pulses, each interaction increases the order of the DM by one. The pulses are weak and the rotating wave approximation is valid, and the system has two electronic states, ground (g) and excited (e). Non-trivial DM elements of the nth order after interaction with the *n*th pulse can be calculated though the recurrence relation:⁵⁴

$$\rho^{(n)}_{eg}(\mathbf{x}, \mathbf{t}_{n+1}) = iexp[(-i\omega_{eg}-\gamma)(\mathbf{t}_{n+1}-\mathbf{t}_n)] \Sigma_{m}[V^{[n]}_{em}(\mathbf{x})\rho^{(n-1)}_{mg}(\mathbf{x}, \mathbf{t}_n)-\rho^{(n-1)}_{em}(\mathbf{x}, \mathbf{t}_n)V^{[n]}_{mg}(\mathbf{x})], \quad (7.1)$$

where t_n is the center of the *n*th very short pulse (the time duration of the pulse is very small compared to the delay times and relaxation times). In the case of homogeneous relaxation the time dependence of the pulses is described by the Green function $exp[(-i\omega <math>\gamma)(t_{n+1}-t_n)]$, where $\omega = \omega_{eg}$ is the electronic resonance frequency and γ is the relaxation rate. The time integrated interaction operators with the *n*th pulse are

$$V^{[n]}_{eg}(\mathbf{x}) = i(2\mu/\hbar)A(\omega)\exp[i\mathbf{k}_n\mathbf{x}], \qquad (7.2)$$

where μ is the dipole moment of the transition, k_n is the wave vector of the *m*th pulse, and x is the special coordinate of the molecule. If all pulses are equivalent (DFWM), for the interaction elements where $A(\omega)$ is the spectral amplitude for the *n*th transform limited pulse at the electronic transition we can write

$$A^{[n]}(\omega) = \int_{-\infty}^{\infty} E_0^{[n]}(t) \exp\left[i\left(\omega - \omega_0\right)t\right] dt$$
(7.3)

where ω_0 is the central frequency of the degenerate pulses with amplitude $E_0(t)$.

The third order density matrix given by the master solution has four components (Liouville pathways)

$$\rho^{(3)}_{eg}(\mathbf{x},t) = \rho^{(3)I}_{eg}(\mathbf{x},t) + \rho^{(3)II}_{eg}(\mathbf{x},t) + \rho^{(3)III}_{eg}(\mathbf{x},t) + \rho^{(3)IV}_{eg}(\mathbf{x},t)$$
(7.4)

In the case of Photon Echo (PE) and Reverse Transient Grating (RTG), the first pulse arrives at time $t_1=0$ and the second and third follow after a delay τ and coincide in time $t_2=t_3=\tau$. The common spatial phase determines the emission directions. In the case of PE the emission goes in the direction $\mathbf{k}_{PE}=\mathbf{k}_3+\mathbf{k}_2-\mathbf{k}_1$ (\mathbf{R}_{II} and \mathbf{R}_{III}), while in the case of RTG the emission goes in the direction $\mathbf{k}_{RTG}=\mathbf{k}_3-\mathbf{k}_2+\mathbf{k}_1$ (\mathbf{R}_I and \mathbf{R}_{IV}). There are no differences in amplitudes between the Liouville pathways \mathbf{R}_1 and \mathbf{R}_4 and between \mathbf{R}_{II} and \mathbf{R}_{III} for a two level system. If only the ground state is populated initially, only the term $\rho^{(0)}_{gg}$ is not zero and using equation (7.1) we can write

$$\rho^{(3)\text{PE}}_{eg}(\mathbf{x},t) \propto \exp[i(\mathbf{k}_{\text{PE}}\mathbf{x} \cdot \boldsymbol{\omega}(t-2\tau))]\exp(-\gamma t)A^{[1]*}(\boldsymbol{\omega})A^{[2]}(\boldsymbol{\omega})A^{[3]}(\boldsymbol{\omega})$$
(7.5)

$$\rho^{(3)\text{RTG}}_{eg}(\mathbf{x},t) \propto \exp[i(\mathbf{k}_{\text{RTG}}\mathbf{x}\cdot\omega t)]\exp(-\gamma t)A^{[1]}(\omega)A^{[2]*}(\omega)A^{[3]}(\omega)$$
(7.6)

The PE DM has zero phase at 2τ , but RTG is maximum at t_3 - t_2 =0 (before the last pulse in the "virtual" unphysical region).

The third order dipole polarization $P^{(3)}$ of the medium is proportional to $Tr(\hat{\mu}\hat{\rho}^{(3)})$. We can easily show that

$$P^{(3)}(\mathbf{x},t) = \mu[\rho^{(3)}_{eg}(\mathbf{x},t) + \rho^{(3)*}_{eg}(\mathbf{x},t)]$$
(7.7)

In the gas phase, the electric field generated is proportional to the third order polarization, and has two components: PE and RTG.

$$E_{PE}(\mathbf{x},t) \propto \exp[i(\mathbf{k}_{PE}\mathbf{x} \cdot \omega(t-2\tau) + \mathbf{\phi}_{PE})] \exp(-\gamma t) \mathbf{A}^{2}(\omega) \mathbf{A}^{*}(\omega) + c.c.$$
(7.8)

$$E_{RTG}(\mathbf{x},t) \propto \exp[i(\mathbf{k}_{RTG}\mathbf{x}-\omega t+\phi_{RTG})]\exp(-\gamma t)A^{2}(\omega)A^{*}(\omega) + c.c.$$
(7.9)

Where we introduce additional phase shits of the pulse's fields $\phi^{[n]}(A^{[n]}(\omega) = exp(i\phi_n)A^{[n]}(\omega)$ and $\phi_{PE} = \phi^{[3]} + \phi^{[2]} - \phi^{[1]}$ and $\phi_{RTG} = \phi^{[3]} - \phi^{[2]} + \phi^{[1]}$

The difference between PE and RTG is very important in the case of an ensemble of molecules with (for example) different resonance conditions. The inhomogeneous relaxation described by the normalized spectral distribution of each transition around some frequency ω_0 with width Δ is given by

$$\mathbf{n}(\omega,\omega_0) = \exp[-(\omega-\omega_0)^2/\Delta^2]/(\pi^{1/2}\Delta). \tag{7.10}$$

The full field is a sum (integral) over all inhomogeneous components. Term $A^{3}(\omega)$ defines the full intensity of the signal, and we set it to unity, because we suppose the spectral width of the pulse is more than the inhomogeneous broadening (any relaxation time is bigger than the pulse duration).

$$E_{PE}(\mathbf{x},t) \propto \exp[i(\mathbf{\phi}_{PE}+\mathbf{k}_{PE})\mathbf{x}]\exp(-\gamma t)\int_{0}^{\infty} \exp\left[-i\omega(t-2\tau)-(\omega-\omega_{0})^{2}/\Delta^{2}\right]d\omega + c.c. \quad (7.11)$$

$$E_{\rm RTG}(\mathbf{x},t) \propto \exp[i(\mathbf{\phi}_{\rm RTG} + \mathbf{k}_{\rm RTG})\mathbf{x}] \exp[-\gamma t) \int_{0}^{\infty} \exp\left[-i\omega t - (\omega - \omega_{0})^{2} / \Delta^{2}\right] d\omega + c.c.$$
(7.12)

After simple integration over the spectrum

$$E_{PE}(\mathbf{x},t) \propto \exp[-i(\omega_0(t-2\tau)-\mathbf{k}_{PE}\mathbf{x}-\mathbf{\phi}_{PE})]\exp[-\gamma t-(t-2\tau)^2\Delta^2/4] + c.c.$$
(7.13)

$$E_{\text{RTG}}(\mathbf{x},t) \propto \exp[-i(\omega_0 t - \mathbf{k}_{\text{PE}} \mathbf{x} - \mathbf{\phi}_{\text{PE}})] \exp[-\gamma t - t^2 \Delta^2 / 4] + \text{c.c.}$$
(7.14)

We can write the time integrated homodyne signal

$$S(\tau) \propto \int_{\tau}^{\infty} \left| E^{[4]}(\mathbf{x}, t) \right|^2 dt$$
(7.15)

Note that S is scalar, as the detector integrates the signal over both space and time.

We can separate the electric field of the PE and RTG signals because they are generated in different directions and for the time integrated signal the common phases $[\omega_0(t-2\tau)-k_{PE}x-\phi_{PE}]$ (PE) or $[\omega_0t-k_{RTG}x-\phi_{RTG}]$ (RTG) disappear.

It's possible to analytically calculate the relaxation in the case of an exponential homogeneous decay and a Gaussian inhomogeneous decay

$$S_{PE}(\tau) \propto \int_{\tau}^{\infty} \exp(-2\gamma\tau) dt \left| \int_{0}^{\infty} \exp\left(-i\omega(t-2\tau) - \left(\omega - \omega_{0}\right)^{2} / \Delta^{2} \right) \right|^{2} dt \qquad (7.16)$$

$$S_{\rm RTG}(\tau) \propto \int_{\tau}^{\infty} \exp(-2\gamma\tau) dt \left| \int_{0}^{\infty} \exp\left(-i\omega t - \left(\omega - \omega_0\right)^2 / \Delta^2\right) \right|^2 dt \, dt \qquad (7.17)$$

The spectral integrals are simple and gave us signal in integral or analytical forms

$$S_{PE}(\tau) \propto \int_{\tau}^{\infty} \exp\left(-2\gamma t - (t - 2\tau)^2 \Delta^2 / 2\right) dt = \exp(2\gamma^2 \Delta^{-2}) [1 - \operatorname{erf}(2^{-0.5}\tau \Delta + 2^{0.5}\gamma \Delta^{-1})](2/\pi)^{0.5} / \Delta$$
(7.18)

$$S_{RTG}(\tau) \propto \int_{\tau}^{\infty} \exp\left(-2\gamma t - t^2 \Delta^2/2\right) dt =$$

$$\exp(2\gamma^2 \Delta^{-2} - 4\tau \gamma) [1 + \operatorname{erf}(2^{0.5}\tau \Delta - 2^{0.5}\gamma \Delta^{-1})] (2/\pi)^{0.5} / \Delta \qquad (7.19)$$

We define the homogeneous relaxation time in terms of the relaxation rate $T_h = 1/\gamma$ and the inhomogeneous relaxation time in terms of the inhomogeneous spectral width $T_i = 1/\Delta$. In the limit $\tau T_h << T_i^2$ there is no difference between the PE and RTG signals. In this case, equations 7.18 and 7.19 can be simplified to obtain

$$S_{PE}(\tau) = S_{RTG}(\tau) \propto \exp(-2\tau\gamma) = \exp(-2\tau/T_h), \qquad (7.20)$$

In the opposite case $\tau T_h >> T_i^2$, the condensed phase limit, there is a difference between the PE and RTG signals. We can replace the integral formula for the PE Gaussian field with a delta function at time 2τ and get a simple decay with rate 4γ . In this case equations 7.18 and 7.19 can be written as follows.

$$S_{PE}(\tau) \propto \exp(-4\tau\gamma) = \exp(-4\tau/T_h), \qquad (7.21)$$

$$S_{RTG}(\tau) \propto \exp(-\frac{1}{2}\Delta^2 \tau^2) = \exp(-\tau^2/2T_i^2),$$
 (7.22)

Note that even for this approximation, for small time delays, τ , the product τT_h is still small. Therefore, for small delays we might expect the "gas phase" limit to apply. For long τ the "liquid phase" limit gives an accurate description. Figure 1 demonstrates this observation. Note that initially the PE has a decay rate of 2γ , then goes through an intermediate region and at long delay times has a rate of 4γ . In the case of RTG, the initial experimental decay with rate 2γ transform to a faster Gaussian decay.

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