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Vibrational dynamics of excited states probed by fs/ps CARS: simulations and applications to ultrafast charge transfer dynamics

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Vibrational dynamics of excited states probed by fs/ps CARS: simulations and applications to ultrafast charge transfer dynamics

by

Beth Marie Prince

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Physical Chemistry

Program of Study Committee:
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Iowa State University
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2008

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CHAPTER 1: GENERAL INTRODUCTION

The development of femtosecond lasers and their application to coherent anti-Stokes Raman spectroscopy (CARS) has opened new avenues of research to examine the vibrational characteristics of molecules in both ground and excited electronic states\textsuperscript{1-6}. Though standard tr-CARS experiments can be cumbersome and can shed little direct information about the Raman active vibrations of a molecule\textsuperscript{7}, many efforts have been undertaken to remove some of the complexity and simplify the outputted tr-CARS signal\textsuperscript{8-11}. One such development is the application of a hybrid fs/ps CARS probe which combines the time resolution of femtosecond pulses with the frequency resolution of picosecond pulses\textsuperscript{7,12}. The further development of the technique into fs/ps CARS enables direct monitoring of the vibrational fingerprint via Raman active modes of liquid and gas samples at different ranges of the spectrum. Not only can the ground state spectrum be obtained but the excited state spectrum can be gained at different excitation delays after application of a femtosecond “pump” pulse. This “pump”-fs/ps CARS can then be utilized to probe ultrafast dynamics of the excited state for a particular molecule or system.

Twisted intramolecular charge transfer (TICT) is a type of system that has interested the scientific community for decades.\textsuperscript{13} The prototypical molecule for this process is 4-dimethylaminobenzonitrile (DMABN), which has been shown to undergo twisting about the C-N of the dimethylamino group upon electronic excitation. Even though this is a small and relatively simple molecule, there is still debate as to the nature of this twisting and its relevance to a true TICT state (90° twisting)\textsuperscript{14-16}. Another area that has interested many over the past twenty years is a class of molecules known as push-pull stilbenes.\textsuperscript{17-20} Push-pull stilbenes are donor – acceptor molecules with conjugated stilbene linkers. By varying the
donor or acceptor or the length between them the systems slowly evolve into molecular wire prototypes. Molecular wires are of interest due to desire for smaller and smaller electronics based on nanotechnology but currently involve complicated bridged systems to reduce deformations common during charge transfer. These deformations are sometimes the result of twisting about some bond in the molecular wire that decouples the pi clouds and destroys efficient charge transfer across the system. Examining simpler push-pull systems than molecular wire polymers can elucidate some of the conditions and locations of the deformations and potentially provide insight into the excited state conformational changes observed in these molecules.

An example push-pull stilbene that has seen considerable experimental interest is 4-dimethylamino-4'-nitrostilbene. Of particular interest is the complex relaxation schemes developed to explain the behavior of this molecule in solvents of differing polarity. This molecule is constructed of the electron accepting nitro group and the electron donating dimethylamino group linked by a conjugated stilbene system. This molecule has been discussed as undergoing TICT upon excitation in polar solvents, undergoing twisting about the inner single bonds in slightly polar solvents, and isomerization and fluorescence from the vertically excited state in non-polar solvents. In this thesis, the case of polar solvents will be addressed in chapter 2.

The experimental use of fs/ps CARS in our research group has been complemented by theoretical simulations based on four-wave mixing theory. Of particular interest is the relationship between time-resolved CARS and the hybrid fs/ps CARS in terms of simulated results obtained from experimental data. Previously unexamined phenomena such as the linewidth dependence of the outputted signal at different $\tau_{23}$ delays for a $(\text{sinc})^2$ pulse
(experimentally used) is also detailed and is included chapter 3. Additionally, the theoretical
framework for devising a fitting algorithm that returns molecularly relevant information
about the population, natural linewidth and central frequency of a given Raman active mode
is presented.

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CHAPTER 2: SUBPICOSECOND VIBRATIONAL EVOLUTION OF 4-DIMETHYLEAMINO-4′-NITROSTILBENE DURING INTRAMOLECULAR CHARGE TRANSFER

A paper to be submitted to Journal of Raman Spectroscopy

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2.1 Abstract

The subpicosecond time evolution of a push-pull stilbene, 4-dimethylamino-4′-nitrostilbene (DANS) following 400 nm excitation in acetonitrile is observed with vibrational resolution using the recently-developed fs/ps CARS probe technique. Raman-active modes in the fingerprint region of the vibrational spectrum are observed to evolve, both in intensity and in frequency, on subpicosecond timescales. In particular, the evolution of the DANS vibrational spectrum in the NO₂ symmetric stretch region is probed, exhibiting a frequency upshift on a 300 fs timescale. These findings agree well with timescales observed in transient absorption/gain experiments and support the formation of an intramolecular charge transfer (ICT) state on a subpicosecond timescale in acetonitrile that precedes the fast (~12 ps) internal conversion timescale observed in prior studies.
2.2 Introduction

Molecules containing both electron donor and acceptor groups often experience an intramolecular charge transfer (ICT) upon photoexcitation in polar solvent environments. The charge separation and concurrent increase in dipole of the molecule in a charge transfer state can be stabilized by conformational changes that result in the decoupling of donor and acceptor moieties within the molecule. One well-known example of such a conformational change that decouples donor and acceptor groups is a 90° twist about single bonds connecting them, generating a so-called twisted ICT (TICT) state.\textsuperscript{1-16} The dynamics of TICT state formation following the initial photoexcitation to the locally excited (LE) state have been studied in prototypical TICT molecules such as dimethylaminobenzonitrile (DMABN) for more than 3 decades. Even in this prototypical case, however, the true nature of the charge transfer state accessed in polar solvents is still in question, and several refinements of the initially proposed twisted state have been proposed.\textsuperscript{4,14,16}

The analogous twisting processes following electronic excitation in the donor-acceptor (\textit{i.e.}, push-pull) stilbene \textit{trans}-4-dimethylamino-4′-nitrostilbene (DANS) are even more complex, given the extended nature of the conjugated chain and the possibility for twisting about several of the single bonds shown in Fig. 2.1a). In addition to the \textit{trans-cis} isomerization pathway present in excited-state stilbenoid systems,\textsuperscript{17} multiple fluorescent and non-radiative pathways have been observed for DANS in solvents of various polarity. Based on a wide range of experiments involving sitewise substitution in DANS and a closely-related analogue, 4,4′-dimethylaminocyanostilbene (DCS),\textsuperscript{18-20} a complex set of solvent dependent reaction pathways have been suggested for DANS following initial excitation.\textsuperscript{20-22}
In particular, a large Stokes shift and strong quenching of both fluorescence and \textit{trans-cis} isomerization are observed in DANS in polar solvents (including acetonitrile); these results have been attributed to fast transition from an initially accessed planar ICT state (E$^*$), to the so-called \(A_5^*\) TICT state (the numerical subscript denotes the numbered bond, shown in Fig. 2.1, about which the proposed twisting is presumed to occur).\textsuperscript{20-22} Additionally, it has been shown that a ring-bridged DANS derivative in which the twisting of the nitrophenyl group (about bond 4, Fig. 2.1) is hindered exhibits small changes in fluorescence quantum yield compared to unbridged DANS.\textsuperscript{20} Similar studies of ring-bridged DANS with hindered dimethylamino group rotation (about bond 1) exhibited an increased fluorescence yield in non-polar solvents but effectively no change for polar solvents as compared to unhindered DANS.\textsuperscript{23} Rullière and coworkers conducted picosecond time-resolved coherent anti-Stokes Raman scattering (CARS) experiments and, after excitation into the second absorption band and subsequent relaxation, observed a 37 cm\(^{-1}\) downshift in NO\(_2\) symmetric stretch vibrational frequency associated with ICT formation in polar solvents. This change was in stark contrast to the negligible NO\(_2\) symmetric stretch frequency shift they observed in the weakly polar solvent, toluene, and is consistent with the formation of an \(A_5^*\) TICT state in polar solvents that decays on a \(~12\text{ ps}\) timescale in acetonitrile.\textsuperscript{21} In these time-resolved CARS experiments, however, they did not directly observe the initially populated E$^*$ state following photoexcitation or any dynamical changes connected with solvent rearrangement.

The relative energetics of the \(A_5^*\) and other proposed TICT states of DANS in a variety of solvents have also been explored in semiempirical calculations by Ernsting \textit{et al.}.\textsuperscript{24} SAM1 calculations suggest that the most stable S\(_1\) conformation of DANS in strongly polar
solvents (acetonitrile and water) resulted from twisting about the nitrophenyl moiety based on the relative energetics of five different sampled conformations involving $90^\circ$ twisting about each of the numbered bonds in Fig. 2.1. These calculations further concluded that, in polar solvents, nearly every sampled conformation was energetically more stable than the initially accessed Franck-Condon region. Most notably, twisting of the NO$_2$ moiety about the C-NO$_2$ bond is predicted to be energetically favorable relative to the vertically excited state, but is calculated to be $\sim$3000 cm$^{-1}$ less stable than the nitrophenyl-twisted conformation in these polar solvents. Thus, these results corroborate the complexity of unique pathways available for electronic relaxation in the excited state of DANS. However, these authors do not discuss the apparent differences between the theoretical predictions associated with DANS excited state evolution in polar solvent environments and the $A_5^*$ ICT state assignment proposed by Rullière and coworkers.$^{21,22}$

More recent studies by Rullière and coworkers explored transient absorption and gain following excitation into the first absorption band of DANS in a range of solvents; these experiments suggest that dynamics associated with conformational change following vertical excitation to $E^*$ to the $A_5^*$ TICT state occur on timescales $\leq$ 2 ps in acetonitrile. Thus, we have applied a time-resolved vibrational probe recently developed in our laboratory, called fs/ps CARS. Thus, in order to access these early time dynamics and better elucidate the initial conformational changes undergone by DANS in acetonitrile, we have studied vibrational dynamics, after excitation to $S_1$, with sub-ps time resolution. To obtain state-specific Raman active vibrational spectra of DANS following subpicosecond electronic excitation, we used the recently developed fs/ps CARS probe technique.$^{25}$ This probe
technique, which allows multiplexed detection of CARS spectra, combines two broadband pulses ($\omega_1$ and $\omega_2$), which triggers the molecular response, with a narrowband, picosecond duration pulse ($\omega_3$). When combined with a sub-ps excitation pulse, this probe maintains the subpicosecond time-resolution dictated by the initial broadband pulses while providing spectral resolution dictated by the final narrowband pulse.

### 2.3 Experimental

The fs/ps CARS probe setup has been described previously in detail,\textsuperscript{25} and is therefore only briefly outlined here. The signal and idler outputs of an ultrafast optical parametric amplifier (OPA-800CF) are mixed with a ~800 nm output from a Ti:sapphire amplifier to make $\omega_1$ and $\omega_2$ pulses (19400 cm$^{-1}$ and 17900 cm$^{-1}$, respectively). An additional fraction of the 800 nm beams is split to generate a narrowband $\omega_3$ pulse (12600 cm$^{-1}$, $\Delta\omega$~16 cm$^{-1}$, ~2 ps duration), which is generated using a 4f-stretcher/compressor pulse shaping set up\textsuperscript{26} containing a ~200 $\mu$m spatial filter at its Fourier plane. The delay at the sample between the intensity maxima of the time-overlapped broadband pulses and the narrowband final pulse, $\tau_{23}$, is fixed using a computer-controlled translation stage (Physik Instrumente M-505.4DG), and is typically chosen to minimize non-resonant contributions to the observed fs/ps CARS signal, unless otherwise noted.

A final portion of the 800 nm output is focused into a BBO crystal to generate a pulse, $\omega_{ex}$, at 400 nm, used for electronic excitation of the sample. The delay of this excitation pulse relative to the initiating pulses of the fs/ps CARS probe, $\Delta\tau$, is controlled using a second computer-controlled translation stage (Physik Instrumente M-505.4DG) with minimum step of 7 fs. For the fs/ps CARS experiments, the three CARS input beams are
aligned in a folded BOXCARS input configuration. The output, $\omega_{\text{CARS}}$, signal beam direction is dictated by the phase matching conditions ($k_{\text{CARS}} = k_1 - k_2 + k_3$); this beam is then spatially and spectrally (750 nm short pass) filtered and focused into a spectrometer (Ocean Optics USB-2000). The excitation pulse, $\omega_{\text{ex}}$, (400 nm) is positioned along the central axis of the box created by the three CARS input beams. To avoid saturation and to minimize undesirable nonlinear optical processes, the $\omega_1$ and $\omega_2$ pulse energies are filtered to under 300 nJ, while the $\omega_{\text{ex}}$ pulse energy is approximately 2 $\mu$J and the pulse-shaped narrowband probe beam energy is about 5 $\mu$J. In order to precisely define $\Delta \tau = 0$, we obtain optical Kerr effect (OKE) signal from either $\omega_1$ or $\omega_2$ with $\omega_{\text{ex}}$ in 150 $\mu$m glass at the position of the sample. Steps were taken to account for the glass thickness of the sample cell in precisely defining this zero of time.

For transient absorption (TA) experiments, an additional detection scheme is used. The signal beam is focused into a Si photodiode detector (Thorlabs DET210) and is isolated using a lock-in amplifier (Stanford Research Systems SR810) triggered at the 500 Hz frequency associated with a mechanical chopper placed in the $\omega_{\text{ex}}$ beam path, which generates spectrally integrated data. Changes in $\omega_1$, $\omega_2$, or $\omega_3$ (probe) intensities are monitored as a function of delay following pump beam ($\omega_{\text{ex}}$) excitation. The TA signals associated with the broadband $\omega_1$ and $\omega_2$ frequencies can be measured concurrently with the spectrally resolved pump-fs/ps CARS probe data. Transient absorption scans involving the $\omega_3$ frequency are taken in a modified detection setup, in which the spatial filter at the Fourier plane of the pulse shaper is removed to allow the full spectral range of the broadband 800 nm pulse to be used in TA experiments. In the discussion below, positive transient optical densities correspond to transient absorption by the excited-state species, whereas negative
optical densities correspond to transient gain (stimulated emission) from these species. The polarizations of the pump and all probe beams are parallel in all experiments.

Samples of trans-4-dimethylamino-4'-nitrostilbene (DANS) (Aldrich, 97%) were dissolved in acetonitrile (Fisher Scientific, >99.4%) to a concentration of 1 mM. The DANS samples were placed in a 0.2 mm gap between two fused silica windows of a motorized rotating cell that allows complete sample refreshment in the laser interaction volume after each pulse. No deterioration of these samples has been observed after several hours of exposure to 400 nm laser radiation.

2.4 Results

The fs/ps CARS spectrum of ground state DANS in acetonitrile is shown in Fig. 2.2, along with an excited-state spectrum observed at \( \Delta \tau = 730 \) fs following electronic excitation. The ground state spectrum (Fig. 2.2b) very closely resembles the resonance Raman spectrum of DANS measured using 457.9 nm excitation wavelength by Moran et al.\textsuperscript{27} and Okamoto et al.\textsuperscript{28} Several of the ground state peaks have been assigned previously to the C-NO\(_2\) stretch at 1105 cm\(^{-1}\), the NO\(_2\) symmetric stretch at 1338 cm\(^{-1}\), the nitro ring “quinoidal” stretch (8a) mode at \( \sim 1582 \) cm\(^{-1}\), and the ethylenic C=C stretch at 1631 cm\(^{-1}\).\textsuperscript{27,28} In the excited-state spectrum (Fig. 2.2a), the ground state contribution has been removed by subtraction of the observed ground state spectrum. The slightly negative-going peak results from a small degree of bleaching of the ground state population upon excitation. Several excited state peaks are shifted relative the ground state peaks, suggesting notable changes in geometry upon excitation and subsequent excited-state evolution. Many of these observed peaks agree well with the observations from the ps CARS study\textsuperscript{21} as well as transient peaks observed in
earlier resonance Raman and transient IR studies.\textsuperscript{28,29} Most notably, these previous studies suggest that the peak at 1300 cm\textsuperscript{-1} corresponds to a down-shifted NO\textsubscript{2} symmetric stretch frequency relative to that observed in the ground state.

### 2.4.1 Long Time Dynamics

Transient absorption/gain scans using three broadband probe wavelengths (515 nm, 559 nm, and 800 nm) have been taken following excitation at 400 nm for DANS in acetonitrile. Two of these are depicted in Fig. 2.3 along with the observed temporal dependence of two selected fs/ps CARS peaks over the full temporal range of the ICT state lifetime. The 515 nm and 559 nm transient absorption scans exhibit similar behavior, and only the 515 nm data is depicted here. The long time transient absorption of 515 nm (Fig. 2.3B) shows a double exponential decay with decay times of \( \tau_{1,515\text{nm}} = 560 \pm 20 \) fs and \( \tau_{2,515\text{nm}} = 8.7 \pm 0.2 \) ps. These timescales are similar to those observed for the 510 nm absorption band in previous subpicosecond transient absorption studies of DANS in acetonitrile (\( \tau_1 = 1.0 \pm 0.2 \) ps and \( \tau_2 = 13 \pm 1 \) ps).\textsuperscript{22} Additionally, a transient gain is observed at 800 nm (Fig. 2.3A); this transient gain also exhibits double exponential decay behavior with decay times of \( \tau_{1,800\text{nm}} = 750 \pm 30 \) fs and \( \tau_{2,800\text{nm}} = 14.2 \pm 0.4 \) ps. The long time component is reasonably similar to the long timescale observed for the absorption at 515 nm. Similar long-time (~12 ps) decay behavior was observed for picosecond time-resolved transient gain at 850 nm;\textsuperscript{21} however, this same long time decay was not observed in the 750 nm gain band in subsequent subpicosecond transient gain experiments.\textsuperscript{22}

Several fs/ps CARS spectra were taken over the range of \( \Delta \tau = 0 \) to \( \Delta \tau = 16 \) ps. After fitting the resulting signal to Lorentzian lineshapes, the integrated intensity growth and subsequent
decay of the NO$_2$ symmetric stretch peak (~1300 cm$^{-1}$), and a representative of the other observed peaks, the phenyl CH rocks at ~1200 cm$^{-1}$, are shown in Figs. 2.3C and 2.3D, respectively. Due to the fact that the nonlinear susceptibility, $\chi^{(3)}$, observed in these fs/ps CARS experiments is proportional to the square of the number density of chromophores (i.e., $\chi^{(3)} \propto N^2$), the ordinates in Figs. 2.3C and 2.3D correspond to the square roots of the observed Lorentzian peak integrated intensities. The long time decays observed for these two peaks are nearly identical with timescales of ~13 ps; these long-time decay timescales are comparable to the long-time components of the observed transient absorption at 515 nm and the transient gain at 800 nm. Again, these long-time results appear consistent with those of Oberlé et al.$^{21,22}$ Note, however, that the NO$_2$ symmetric stretch peak undergoes a slower rise compared to the rise of the CH rocks peak.

### 2.4.2 Short Time Dynamics

The waterfall graph in Fig. 2.4 shows the transient species peaks in DANS at selected time delays from $\Delta \tau = 0$ to $\Delta \tau = 1.3$ ps. By focusing on early pump-probe delays, additional insight into the conformational changes occurring upon charge transfer can be gained. At negative $\Delta \tau$ times there are coherences that enhance the ground state peaks while the excitation pulse (400 nm) is between fs/ps CARS probe pulses. These residual peaks are present at and near $\Delta \tau = 0$ arising from coherent four- and six-wave mixing signal in which the pump beam overlaps the three pulses involved in the fs/ps CARS probe, but by 200 fs it can be clearly seen that the transient peaks are growing in and their frequencies are evolving in time. This will be the focus of upcoming work.
The evolutions of two distinct peaks are shown in Figs. 2.5 and 2.6. The ring CH rocks mode has a relatively constant FWHM with a small upshift in frequency. This upshift in frequency appears to be commonly seen in nearly all modes and will be discussed later. The limiting FWHM observed here is comparable to the spectrometer resolution limit, 16 cm\(^{-1}\). (Fig. 2.5D). Fig. 2.5B shows the intensity growth for this peak and at early delays the residual ground state peak is present as stated above which reflects the non-zero starting point for the intensity growth. To ascertain the fitness of the Lorentzian intensity, the manual peak area (right axis, Fig. 2.5B) was also calculated and was integrated from 1145 cm\(^{-1}\) to 1228 cm\(^{-1}\).

The NO\(_2\) symmetric stretch mode at 1300 cm\(^{-1}\) (see Fig. 2.6) behaves uniquely. The FWHM for this mode is significantly broader near \(\Delta \tau = 0\), which suggests that the molecule is still evolving in its environment before it stabilizes at \(\Delta \tau \sim 300\) fs. A much larger frequency shift of about 20 cm\(^{-1}\) is observed for this peak compared to other peaks showing less than 10 cm\(^{-1}\) shifts. The intensity starts non-zero due to the selected area for integrating (1241 cm\(^{-1}\) to 1324 cm\(^{-1}\)) at early time is infiltrated with the residual ground state peak at centered at 1362 cm\(^{-1}\) as can be seen in Fig. 2.4. By 130 fs, this effect is gone and the intensity of the NO\(_2\) symmetric stretch grows in on \(\sim 300\) fs timescale.

2.4.3 Dependence of fs/ps CARS spectra on \(\tau_{23}\)

In fs/ps CARS experiments the sensitivity to peaks depends on the decay time associated with that peak. This sensitivity is seen in the data via the FWHM of peaks. Based on the fact that the measured linewidths differ amongst the two peaks we have discussed, there is reason to believe that the 1300 cm\(^{-1}\) peak is difficult to observe at the earliest times.
due to its much faster decay. That is why we are looking at the intensity and linewidth differences for these two peaks at different \( \tau_{23} \) values. \( \tau_{23} \) is timing between pulse 2 and pulse 3 (800 nm, probe). Fig. 2.7 demonstrates the difference of having \( \tau_{23} = 0 \) (Fig. 2.7A) or having \( \tau_{23} = 2.36 \) ps which is a node location\(^{25} \) (Fig. 2.7B). When \( \tau_{23} = 0 \) the spectrum is dominated by wide peaks and non-resonant background. However placing the timing to the node (\( \tau_{23} = 2.36 \) ps), the spectrum narrows and the non-resonant background diminishes leaving the excited or ground state spectrum desired. After looking at the \( \tau_{23} = 0 \) data as has been shown for the \( \tau_{23} = 2.36 \) ps data set, the only differences between the two experiments were the broader peaks and added non-resonant signal.

### 2.5 Discussion

The detected transient absorption at 515 nm has as an instantaneous rise, convoluted by an instrument response function of approximately 125 fs, followed by a bi-exponential decay with timescales of \( \tau_{1,515\text{nm}} \sim 0.5 \) ps and \( \tau_{2,515\text{nm}} \sim 10 \) ps. The longer timescale has been previously ascribed to the decay, presumably via internal conversion to the ground state, of an ICT state accessed by DANS in polar solvent environments. As noted above, this ICT state has been attributed to an excited state conformation, \( A^*_5 \), involving twisting about the phenyl-NO\(_2\) bond that effectively separates charge within the molecule.

In contrast to the agreement observed in the 515 nm transient absorption signal, the 800 nm transient gain signal observed in this experiment exhibits a slightly different behavior than the 750 nm gain band obtained by Oberlé et al. In that work, the 750 nm gain band was found to have two exponential decay timescales of 300 fs and 1.2 ps. These fast decays were attributed to relaxation of an initially populated ICT state, \( E^* \), with conformation similar to
that of the ground state. However, a nearly immediate appearance of emission from the vertically excited state at 750 nm following vertical excitation would be surprising since that would imply a nearly instantaneous Stokes shift of ~9,700 cm\(^{-1}\). The transient gain at 800 nm observed here also exhibits a bi-exponential decay; however, in this case, decay times of \(\tau_{1,800\text{nm}} = 750\ \text{fs}\) and \(\tau_{2,800\text{nm}} \sim 14\ \text{ps}\) are observed. It is likely that \(\tau_{1,800\text{nm}}\) corresponds to the two timescales observed by Oberlé \textit{et al.}, whereas a longer decay component, corresponding to \(\tau_{2,800\text{nm}}\), was not observed in the subpicosecond time-resolved gain work. While the experiments described here only allow observation of a narrow (300 cm\(^{-1}\)) range of the entire gain band in this region, we note that \(\tau_{2,800\text{nm}}\) is quite similar both to \(\tau_{2,515\text{nm}}\) and to the observed decay timescale (12 ps) of the 850 nm transient gain observed in picosecond time-resolved experiments. This decay can therefore be reasonably attributed to the timescale for internal conversion from the ICT state, \(A^*_5\). The presence of this strongly quenched weak transient gain shows that some oscillator strength back to ground state is present in this ICT state prior to nonradiative decay. We attribute the faster timescale, \(\tau_{1,800\text{nm}}\), to a strong dynamic Stokes shift of the emission band through the 750 - 850 nm region. Oberlé \textit{et al.} do not specify the integration range used for the 750 nm gain band results; however, it is possible that their integration window only captures the fast timescales of the dynamic Stokes shift associated with this emission band, particularly since the static fluorescence spectrum of DANS in acetonitrile reaches a maximum beyond 825 nm.\(^{22}\) It is worth noting that 300 fs – 1 ps timescales are typical solvation timescales observed for solvent reorganization dynamics in acetonitrile.\(^{31}\) Additional pump-supercontinuum probe or fluorescence upconversion experiments in the 800 nm – 1000 nm range would be useful to elucidate the dynamics associated with this emission band.
The long time dynamics observed in the fs/ps CARS signal also indicate the modes probed decay on this same timescale of approximately 10 ps – 14 ps. From the short time dynamics, the frequencies of the peaks in acetonitrile are evolving on 300–400 fs timescale which appears faster than the fast time components observed for the gain and absorption bands. This timescale again seems to agree with the typical timescale observed from solvation in acetonitrile and suggests the solvents role in stabilizing the generated twisted confirmation. The short time dynamics also illustrate that some peaks are undergoing larger frequency shifts than others. The NO$_2$ symmetric stretch has a $\sim$20 cm$^{-1}$ frequency shift from $\Delta\tau = 0$ to $\sim$300 fs while other modes typically only show $\sim$5 cm$^{-1}$ shifts. Additionally, the FWHM for the NO$_2$ symmetric stretch mode is larger at times close to $\Delta\tau = 0$ and becomes narrower during the first $\sim$300 fs after excitation. The timescale of narrowing of the FWHM is in agreement with the timescale for frequency shift of the NO$_2$ suggesting this part of the molecule is in transition from the initial excited state to its final excited state position in the ICT state. Other modes such as the CH rocks do not exhibit this behavior but have a constant FWHM at all sampled delay times. Given the large FWHM and frequency changes it is clear the NO$_2$ moiety of DANS is playing a large role in the conformational changes DANS is undergoing upon excitation.

In spite of some ambiguity in the interpretation of intensity dynamics in the first 200 fs the results of this work clearly show the sub picosecond evolution of peak frequencies and FWHM in the first excited state of DANS which has not been observed previously. The NO$_2$ symmetric stretch frequency shows both the largest frequency downshift following excitation as well as the largest frequency upshift during the subpicosecond evolution of these observed excited-state vibrational modes. Note that frequency of NO$_2$ symmetric stretch is 1340 cm$^{-1}$
in the ground state and the first moment it is detected in the final state is about 1280 cm\(^{-1}\) which is a 60 cm\(^{-1}\) red shift. Essentially all other observed excited state vibrational modes are within 10 cm\(^{-1}\) of their position in the ground state. These changes might indicate a significant change in N-O bond lengths as well as charge becoming more localized onto the NO\(_2\). It is unclear if this would be the result of twisting about the A\(_5^*\) state, twisting of the entire nitrophenyl ring, or merely a small perturbation to the end NO\(_2\) group. Comparison to the difference between the symmetric stretch of the neutral NO\(_2\) (1318 cm\(^{-1}\))\(^{32}\) and NO\(_2^-\) (1284 cm\(^{-1}\)) anion\(^{33}\) suggest, it could be reasoned out from merely some sort of charge localization. But despite not quite understanding exactly how the NO\(_2\) symmetric stretch mode is changing, the end frequency is consistent with previous work and there is currently no direct evidence to say that the final excited state that is observed here is not the A\(_5^*\).

Also note that transient absorption and gain exhibit no evidence of an emission or absorption band from a E\(^*\) state or from the initially populate electronic state that is observed in hexanes and in toluene.\(^{22}\) The peak intensity dynamics show no discontinuation or any other manifestation of transition between different electronic states once the CARS signal is observed. Thus it seems unreasonable to conclude that two states are being observed in acetonitrile. The observed delay between time zero and the rise of vibrational peaks could be attributed to the presence of E\(^*\) which has low Raman cross section, extremely large bandwidths due to the very short lived nature of the electronic state or lack of resonances which could result in low intensities of the E\(^*\) fs/ps CARS spectrum. Since the E\(^*\) excited state is a Franck-Condon state one would expect the structure and symmetry very similar to that in the ground state as well as Raman cross sections. There are peaks in the data during the overlap of the pulses that may suggest coming modes coming from the E\(^*\), but the peaks
are not present after the duration of the pulse suggesting that if it was from the E* the life of
the state is less than 125 fs. The transient absorption/gain spectra show no delay between
rise times and time zero. If population transfer from the E* state to the final observed state
occurs, it must happen on very fast timescales (< 100 fs) which would result in broad (>100
cm^-1) vibrational peaks resulting in small absolute intensity of the peaks. Also the delay of
ω₃ relative to ω₁ and ω₂ pulses, which eliminates the nonresonant signal, could also eliminate
any signal which is due to fast dynamics. In order to investigate if the observed absence of
fs/ps CARS signal could be due to the pulse sequence scheme, we positioned the probe pulse
at time zero (overlapping ω₁ and ω₂) and repeated the experiment at the identical conditions
(Fig. 2.7). The resultant peaks had broader linewidths and nonresonant background as
expected but we observed exactly the same shift between time zero and rise time of the
vibrational spectrum.

Resonance Raman studies of DANS by Moran et al. suggest that the largest
conformational change during vertical excitation is associated with the NO₂ sym. stretch
mode. These fs/ps CARS studies have directly confirmed this fact, since, at the very
earliest observed times, the excited state vibrational spectrum exhibits a dramatically
downshifted NO₂ symmetric stretch frequency (from 1338 cm⁻¹ in the ground state to ~1280
cm⁻¹ upon initial observation in the excited state). We note that in these fs/ps CARS studies,
there is no evidence, even at the earliest observable times, of an initially occupied state that
exhibits vibrational character, particularly in the NO₂ symmetric stretch region, similar to the
ground state frequency. This observation contrasts the excited-state.

While it is tempting to conclude from the observed timescales for intensity growth of
the excited state vibrational peaks (approximately 300 fs for both peaks described above), it
is important to note that the third order nonlinear susceptibility, $\chi^{(3)}$, of the solute molecule depends strongly both on the proximity of electronic resonances (which are observed in the transient absorption/gain data shown above to be evolving on these timescales) as well as on the local solvent environment. Still, it is clear that these observed intensity growth timescales are quite similar to the timescales observed for relaxation of the observed vibrational frequencies.

The NO$_2$ symmetric stretch in the excited state exhibits a large frequency upshift (as noted above) on a 300 fs timescale. It would be expected that direct observation of the conformational relaxation from a locally excited state to $A_5^*$ would result in a down-shifting of this frequency on this timescale, based on the bond changes that would occur; therefore, we ascribe the observed frequency shift to vibrational relaxation of a ‘hot’ ICT state and/or to concomitant solvation dynamics associated with the rearrangement of acetonitrile around the evolving dipole of the solute during formation of this ICT state. Further work is underway in polar solvents of differing solvent response times as well as experiments with excitation at lower excess energy to compare the effect of excess vibrational energy.

2.6 Conclusions

In this work, we extend previous vibrationally-resolved studies of DANS in a polar solvent (acetonitrile) to subpicosecond timescales using the fs/ps CARS probe technique. The observed intensity and frequency evolution of transient spectral peaks is consistent with molecule being in ICT $A_5^*$ state observed in previous studies. No direct evidence of a Franck-Condon $E^*$ state was observed in DANS following photoexcitation in this work, however the absence of signal in the vicinity of time zero suggests the possibility of
existence of some other state with small intensities at earlier times. The large 60 cm\(^{-1}\) red shift between ground state NO\(_2\) symmetric stretch and that of the first moment in the excited state and subsequent 20 cm\(^{-1}\) blue shift of NO\(_2\) symmetric stretch due to solvent rearrangement is consistent with large charge localization and twisting in NO\(_2\) part of DANS. The blue shift of all observed modes with about 400 fs time constant is attributed to collective solvent motion about the molecule.

2.7 References


### 2.8 Figures

**Figure 2.1.** The structure of the push-pull chromophore DANS. The electron donor is the dimethylamino group while the nitro group is the electron acceptor. Bond numbers correspond to the bond numbering scheme used to describe potential twisted ICT states.

![DANS](image-url)
Figure 2.2. CARS spectra for DANS in acetonitrile, normalized to the strongest peak in the excited state spectrum. A) Excited state spectrum at $\Delta \tau = 730$ fs (ground state spectrum has been subtracted). B) Ground state spectrum; this spectrum has been normalized to the excited state maximum to depict the typical relative intensities of the ground and excited state peaks. Solvent peak is denoted by an asterisk (*). The excited state spectrum clearly shows the NO$_2$ symmetric stretch peak at 1300 cm$^{-1}$, downshifted from the observed mode (at 1338 cm$^{-1}$) in the ground state.
Figure 2.3. Comparison of transient absorption/gain results with fs/ps CARS intensity results. In all cases, least squares fits to 1 or 2 exponential decays are shown as solid curves. A) Transient gain at 800 nm probe following 400 nm pump (red open circles); best fit decay timescales: \( \tau_{1,800\text{nm}} = 750 \pm 30 \) fs and \( \tau_{2,800\text{nm}} = 14.2 \pm 0.4 \) ps. B) Transient absorption at 515 nm probe following 400nm pump (green); \( \tau_{1,515\text{nm}} = 560 \pm 20 \) fs and \( \tau_{2,515\text{nm}} = 8.73 \pm 0.2 \) ps. C) Square root intensity of the NO\(_2\) symmetric stretch peak (~1300 cm\(^{-1}\)) from fs/ps CARS experiments (blue); \( \tau = 13.4 \pm 1.5 \) ps (fit to single exponential decay). D) Square root intensity of the CH rocks peak, (~1200 cm\(^{-1}\)) from fs/ps CARS experiments(purple); \( \tau = 12.1 \pm 1.2 \) ps (fit to single exponential decay).
Figure 2.4. Waterfall graph of observed fs/ps CARS spectra of excited state DANS in the 1000 cm\(^{-1}\) – 1700 cm\(^{-1}\) range from $\Delta \tau = 0$ to $\Delta \tau = 1.3$ ps. Discussion in the text will focus predominantly on the evolution of two specific peaks: the phenyl C-H rocks mode near 1200 cm\(^{-1}\) and the NO\(_2\) symmetric stretch mode near 1300 cm\(^{-1}\).
Figure 2.5. Subpicosecond dynamics of the CH rocks peak (~1200 cm$^{-1}$). A) Observed fs/ps CARS spectra in this region at denoted pump-fs/ps CARS probe time delays, $\Delta \tau$, time progression is indicated by the arrow. B) Solid curve, right axis: integrated area of the peak at each delay integrated from 1145 cm$^{-1}$ to 1228 cm$^{-1}$. Open circles, left axis: Peak area obtained via fits to Lorentzian lineshapes. C) The frequency of the CH rocks peak over time that is growing in on a 400 ± 30 fs timescale with a final frequency of 1197.1 cm$^{-1}$. D) The FWHM of the fits not changing over the timescale within the uncertainty of the fits.
Figure 2.6. Subpicosecond dynamics of the NO$_2$ symmetric stretch peak (~1300 cm$^{-1}$). A) Observed fs/ps CARS spectra in this region at denoted pump-fs/ps CARS probe time delays, $\Delta \tau$, time progression is indicated by the arrow. B) Solid curve, right axis: integrated area of the peak at each delay integrated from 1241 cm$^{-1}$ to 1324 cm$^{-1}$. Open circles, left axis: Peak area obtained via fits to Lorentzian lineshapes. C) The frequency of the NO$_2$ symmetric stretch peak over time that is growing in on a 310 ± 10 fs timescale with a final frequency of 1303 cm$^{-1}$, with a frequency shift of ~20 cm$^{-1}$. The point at 60 fs has not been included in the fit. D) The FWHM of the fits shows a decrease in the FWHM changing on a 350 ± 25 fs timescale. The point at 60 fs has not been included in the fit. The decrease in the FWHM shows that the molecule is still evolving in the NO$_2$ symmetric stretch area of the molecule.
Figure 2.7. Dependence of fs/ps CARS excited state DANS signal ($\Delta \tau = 715$ fs) on time delay, $\tau_{23}$. A) 800nm probe pulse at $\tau_{23} = 0$. The peaks are broad and the signal has non-resonant background present. B) 800nm pulse at $\tau_{23} = 2.36$ ps, corresponding to overlap of the first node in the $\text{sinc}^2$ temporal profile of the $\omega_3$ pulse with the fs/ps CARS initiation pulses. The spectrum narrows and non-resonant background is diminished.
CHAPTER 3: EXCITED STATE VIBRATIONAL DYNAMICS PROBED WITH
FS/PS CARS: I. THEORY AND SIMULATION

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3.1 Introduction

Recently, our group has developed an optical probe technique, based on time-resolved coherent anti-Stokes Raman spectroscopy (tr-CARS), that allows multiplexed detection (i.e., no scanning of the time delay between the penultimate and final pulses is necessary) of the Raman active states accessed via two-photon excitation by broadband pulses. This pulse sequence is called fs/ps CARS, by virtue of the fact that it involves the use of broadband, femtosecond (fs) duration pulses as the first two initiation pulses of the CARS sequence as well as the use of a narrowband, picosecond (ps) duration final pulse within the three pulse CARS sequence. In addition to the multiplex advantage over tr-CARS associated with this newer probe technique, fs/ps CARS also provides the additional advantage that Raman-active vibrational frequencies are directly recovered; they do not need to be deduced from coherent beat frequencies observed in the spectrally-resolved CARS output beam as is the case in tr-CARS. In fact, the significant reduction in signal acquisition and analysis time afforded by the fs/ps CARS technique has led us to use the more euphonious pronunciation, “fast-pass CARS,” (rather than the more laborious “femtosecond-picosecond CARS”) when discussing this probe technique. We note that all of the advantages typically ascribed to femtosecond tr-CARS are retained in fs/ps CARS. In particular, the strong contribution from so-called non-resonant CARS (often described as electronic contributions) that has often found to complicate frequency-domain and
picosecond time-resolved CARS probes\textsuperscript{6} can be discriminated against in both femtosecond tr-CARS and fs/ps CARS by virtue of the fact that the sequential timing of the three interacting CARS pulses can be varied to essentially remove these electronic contributions. Since this initial description of the fs/ps CARS probe technique, others have applied a nearly identical scheme, referred to as hybrid CARS, toward the vibrationally-resolved detection and characterization of a model species that resembles marker molecules in bacterial endospores,\textsuperscript{7} further demonstrating the sensitivity of such a probe.\textsuperscript{8}

The reduced acquisition time via this multiplexing associated with the removal of a scanned time delay also affords the efficient use of the fs/ps CARS technique as a three-pulse probe subsequent to excitation via an initial ultrafast pulse. Thus, fs/ps CARS can be used to probe the evolution of nonequilibrium excited states in much the same way as time-resolved CARS and the related time-resolved degenerate four wave mixing (DFWM) has been used in these applications (often referred to as pump-CARS and pump-DFWM, respectively).\textsuperscript{9-19} However, just as fs/ps CARS exhibits additional advantages over tr-CARS, most notably via direct recovery of actual vibrational frequencies rather than beat frequencies, the use of fs/ps CARS as a probe following ultrafast electronic excitation affords these same advantages. For example, our group has used this probe technique to observe the excited-state evolution of coumarin 153 (C153) and coumarin 102 (C102) with vibrational resolution to directly probe the timescales for hydrogen-bond cleavage and reformation in protic solvents.\textsuperscript{20,21} Similarly, the excited state vibrational evolution of a push-pull stilbene, \textit{trans}-4-dimethylamino-4´-nitrostilbene (DANS), to form a twisted intramolecular charge transfer state has been observed with subpicosecond time-resolution; these results have been presented elsewhere in this thesis.
As noted above, our group has previously described the fs/ps CARS technique via experimental comparison between fs/ps CARS and traditional tr-CARS. Additionally, some computational simulations of tr-CARS were used in this study to emphasize the similarities and differences between these two related optical techniques.\textsuperscript{1,2} However, a thorough treatment of the theoretical aspects of the fs/ps CARS probe, emphasizing its advantages as a simultaneously vibrationally-resolved and time-resolved probe, has not yet been presented. Thus, we present here a theoretical description of the fs/ps CARS probe technique, accompanied by several simulations of expected lineshapes and intensities, in order to explore the advantages and limitations of this recently-developed probe technique. We begin with a brief theoretical description of the time- and frequency-domain signals expected in tr-CARS and fs/ps CARS experiments that provide a basis for the computational simulations provided herein. We then explore several limiting cases, each of which can in practice be attained experimentally, to provide a predictive description of the lineshapes and frequencies observed using the fs/ps CARS technique, both in the presence and absence of overlapping resonant and non-resonant signal. From a practical point of view, we then derive expressions that can be used to directly extract relevant frequency, lifetime, and relative hyperpolarizability information from experimentally observed fs/ps CARS signal.

3.2 Theoretical Considerations

We begin by exploring the CARS signal associated with interaction of a molecular species with three input (optical) electric fields. Currently, practical experimental limitations (predominantly due to non-degenerate input frequencies generally used in CARS schemes) result in observation of the CARS signal that is detected at the intensity level (homodyne
detection scheme), rather than at a field level, as would be the case in a heterodyne detection scheme. Therefore, we will focus here only on the homodyne-detected CARS signal, $S_{\text{CARS}}$, associated with the complex third order polarization ($P^{(3)}$), which, in the frequency domain, is described as a function of signal frequency, $\omega_s$, and pulse delays, $\tau_{12}$ and $\tau_{23}$, by:

$$S_{\text{CARS}}(\omega_s, \tau_{12}, \tau_{23}) \propto \left| P_{\text{CARS}}^{(3)}(\omega_s, \tau_{12}, \tau_{23}) \right|^2$$

(3.1)

in which

$$P_{\text{CARS}}^{(3)}(t, \tau_{12}, \tau_{23}) = \left( \frac{i}{\hbar} \right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \left[ R_4(t_3, t_2, t_1) E_3(t-t_3) E_2^*(t+\tau_{23} -t_3 -t_2) \right.$$

$$\times E_1(t+\tau_{23} + \tau_{12} -t_3 -t_2 -t_1) e^{i(\omega_1 - \omega_2 + \omega_3) t_3} e^{i(\omega_2 - \omega_3) t_2} e^{i\omega_1 t_1} \left) \right]$$

(3.2)

is the Fourier transform of the frequency domain polarization, $P^{(3)}(\omega_s, \tau_{12}, \tau_{23})$, and $E_1$, $E_2$, and $E_3$ are the electric field envelopes of pulses 1 (traditionally called ‘pump’), 2 (‘Stokes’), and 3 (‘probe’) respectively, temporally separated by delays $\tau_{12}$ and $\tau_{23}$ (we follow the standard convention that $t_{mn} > 0$ when pulse $n$ follows pulse $m$). In these expressions, $\omega_1$, $\omega_2$, and $\omega_3$ represent the carrier frequencies associated with these respective pulses, whereas $R_4$ is the relevant molecular response function that survives the rotating wave approximation (RWA), and the carrier CARS frequency, $\omega_{\text{CARS}} = \omega_3 - \omega_2 + \omega_1$, associated with this detected polarization in the time domain, $t$, has been suppressed. In this expression, the integration variables $t_1$, $t_2$, and $t_3$ reflect coherence timescales separating field interactions (as depicted in Fig. 3.1). Assuming the electronic dephasing timescales are fast compared to the
pulse durations, the variations of pulses 1 and 2 during the first electronic coherence time, \(t_1\), as well as the variations of pulse 3 and the output CARS pulse during the final electronic coherence time, \(t_3\), can be neglected, giving

\[
P_{\text{CARS}}^{(3)}(t, \tau_{12}, \tau_{23}) = \left( \frac{i}{\hbar} \right)^3 E_3(t) \int_0^\infty dt_2 \cdot \left\{ R_4(0,t_2,0) \cdot E_2^*(t + \tau_{23} - t_2) \times E_1\left(t + \tau_{23} + \tau_{12} - t_2\right) e^{i(\omega_1 - \omega_2) t_2} \right\}
\]

\[\text{(3.3)}\]

The reduced-dimensionality third order response function, \(R_4\), is assumed to take the form

\[
R_4(0,t_2,0) = \sum_{a,c} \kappa_{ca} P(a) \Theta(t_2) e^{-i\omega_{ca} t_2 - \Gamma_{ca} t_2}
\]

\[\text{(3.4)}\]

where the summation is carried out over initial states \(|a\rangle\) and accessible Raman active states \(|c\rangle\), \(\kappa_{ca}\) is a constant containing transition dipole moment products associated with the nonresonant electronic transitions, \(P(a)\) is the population of initial state \(|a\rangle\), \(\Theta(t)\) is a Heaviside step function reflecting the causality requirement, and \(\omega_{ca}\) and \(\Gamma_{ca}\) are, respectively, the Bohr frequency and the dephasing rate associated with the \(|c\rangle \leftrightarrow |a\rangle\) transition.\(^{22}\) Upon transforming into the frequency domain, the third order polarization then takes the form

\[
P_{\text{CARS}}^{(3)}(\Delta, \tau_{12}, \tau_{23}) = \frac{1}{\sqrt{2\pi}} \left( \frac{i}{\hbar} \right)^3 \int_{-\infty}^{\infty} dt \cdot E_3(t) e^{i\Delta t} \int_{-\infty}^{\infty} dt_2 \cdot \left\{ R_4(0,t_2,0) \cdot E_2^*(t + \tau_{23} - t_2) \times E_1\left(t + \tau_{23} + \tau_{12} - t_2\right) e^{i(\omega_1 - \omega_2) t_2} \right\}
\]

\[\text{(3.5)}\]
where $\Delta = (\omega_S - \omega_{\text{CARS}})$ represents the detuning relative to the carrier CARS frequency, $\omega_{\text{CARS}}$.

Equation 3.5 can, of course, be readily numerically integrated for arbitrary forms of time-domain electric fields associated with pulses 1, 2, and 3, and the simulated data shown below directly use this expression in combination with Eq. 3.1. However, to derive analytical expressions that emphasize the expected signal in two limiting cases—that of a short, well separated probe pulse, as is utilized in traditional tr-CARS experiments, and that of a narrowband probe—it is instructive to consider additional simplifications of this expression. Furthermore, in the fs/ps CARS experiments that have been carried out to date, the delay between pulses 1 and 2 (i.e., $\tau_{12}$), is held to zero; therefore, we suppress this quantity in further discussion. Assuming that the pulse 1 and 2 intensity envelopes ($I_1(t) \propto |E_1(t)|^2$ and $I_2(t) \propto |E_2(t)|^2$) are impulsive compared to the timescales associated with the molecular response during $t_2$ (i.e., $E_1(t), E_2^*(t) \approx \delta(t)$), Eqs. 3.4 and 3.5 can be combined to give

$$P_{\text{CARS}}^{(3)}(\Delta, \tau_{12} = 0, \tau_{23}) = \frac{1}{\sqrt{2\pi}} \left( \frac{i}{\hbar} \right)^3 e^{i(\omega_1 - \omega_2)\tau_{23}} \times$$

$$\int_{-\tau_{23}}^{\infty} dt \cdot E_3(t) e^{i(\omega_1 - \omega_2 + \Delta)} \sum_{a,c} \kappa_{ca} P(a) e^{-i\omega_{ca}(t + \tau_{23}) - \Gamma_{ca}(t + \tau_{23})}$$

(3.6).
3.2.1 Short Pulse 3 (femtosecond tr-CARS limit)

If the pulse 3 electric field envelope is additionally assumed to have a short
(FWHM = $2\sqrt{\ln 2}\tau_G$, where $\tau_G$ is a width parameter), Gaussian temporal profile, then for
delays between pulses 2 and 3 (i.e., $\tau_{23}$) that are longer than the pulse 3 duration, the lower
integration limit in Eq. 3.6 can be set to $-\infty$. In this limit, the frequency domain third order
polarization is

$$
\begin{align*}
P^{(3)}_{\text{CARS}}(\Delta, \tau_{12} = 0, \tau_{23}) &= \left( \frac{i}{\hbar} \right)^3 e^{i(\omega_1 - \omega_2)\tau_{23}} \times \\
&\sum_{a,c} \kappa_{ca} P(a) e^{-i\omega_{ca}\tau_{23}} - \Gamma_{ca}\tau_{23} \cdot \tilde{E}_3(\omega_{ca} - \Delta - \omega_1 + \omega_2) \cdot e^{\left(\Gamma_{ca}\tau_{23}/4\right)} \cdot e^{i\left(\Gamma_{ca}(\omega_{ca} - \Delta)\tau_{23}^2/2\right)}
\end{align*}
$$

(3.7),

where $\tilde{E}_3(\omega)$ is the Gaussian frequency domain pulse 3 electric field envelope, centered at
$\omega = 0$, defined by

$$
\tilde{E}_3(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E_3(t)e^{i\omega t} dt
$$

(3.8).

Combining Eq. 3.7 with Eq. 3.1 gives rise to the time dependent CARS signal in this limit:

$$
S^{(3)}_{\text{CARS}}(\omega_s, \tau_{12} = 0, \tau_{23}) \propto \\
\sum_{a,c} \kappa_{ca} P(a) e^{-i\omega_{ca}\tau_{23}} - \Gamma_{ca}\tau_{23} \cdot \tilde{E}_3(\omega_s - \omega_{ca} + \omega_2) \cdot e^{\left(\Gamma_{ca}\tau_{23}/4\right)} \cdot e^{i\left(\Gamma_{ca}(\omega_{ca} - \Delta)\tau_{23}^2/2\right)}
$$

(3.9).
From Eq. 3.9, it is clear that the tr-CARS signal is expected to exhibit a series of essentially Gaussian profiles that are centered at \( \omega_s = \omega_{ca} + \omega_3 \) and weighted by factors that depend on transition dipoles associated with the four-pulse pathways depicted in Fig. 3.1 (via \( \kappa_{ca} \)) and the dephasing rates (via \( \Gamma_{ca} \)). Moreover, in cases where multiple vibrational states, \( |c\rangle \), lie within the bandwidth of pulse 3, these Gaussian profiles will overlap and give rise to interferences that exhibit oscillations as a function of the scanned timescale, \( \tau_{23} \). The oscillation frequencies, \( \omega_{c'c} = \omega_{ca}' - \omega_{ca} \), decay with rates, \( \Gamma_{c'c} = \Gamma_{ca}' + \Gamma_{ca} \), that are greater than the dephasing rates associated with each of the individual vibrational state dephasing rates. Thus, while Eq. 3.9 demonstrates that the output signal of femtosecond tr-CARS in principle contains all vibrational information (including relative cross-sections, frequencies, and dephasing rates) associated with a spontaneous Raman spectrum of the molecular species,\(^{3-5}\) two of the major deficiencies of femtosecond tr-CARS, noted in a previous publication,\(^1\) are also emphasized: 1) absolute vibrational frequencies are not directly measured; only beat frequencies, spectrally centered at the average frequency associated with the two contributing vibrational frequencies \( \left( \frac{1}{2} \left( \omega_{ca} + \omega_{ca}' \right) \right) \), are observed in the oscillating intensities of the broadband CARS output spectrum (note that this is not an issue in the specific case of DFWM, where beats can be directly observed between vibrational states of interest and the vibrationless transition), and 2) the observed dephasing rate associated with these beat frequencies is equal to the sum of the dephasing rates of the component vibrations in the beat,\(^{23}\) resulting in reduced resolution in a frequency-domain analysis of the observed beat frequencies.
3.2.2 Long Pulse 3 (fs/ps CARS with $\tau_{23} = 0$ limit)

In contrast, for the case in which pulse 3 has a narrowband spectral profile (as is the case in fs/ps CARS), the limiting case of a monochromatic (cw) field 3 can be explored. As will be noted below, the optimal fs/ps CARS detection scheme does not use a pulse timing scheme that gives identical results; however, it is still instructive to explore this extreme prior to discussing more specifically the timing scheme used in the fs/ps CARS experiments. In this case, by assuming $E_3(t) = 1$, Eq. 3.6 reduces to

$$P_{CARS}^{(3)}(\Delta, \tau_{12} = 0, \tau_{23}) = \frac{1}{\sqrt{2\pi}} \left(\frac{1}{\hbar}\right)^3 e^{-i\Delta \tau_{23}} \sum_{a,c} \kappa_{ca} P(a) \frac{1}{(\Delta + \omega_1 - \omega_2 - \omega_{ca}) + i\Gamma_{ca}}$$

and the detected CARS signal is as follows:

$$S_{CARS}(\omega_s, \tau_{12} = 0, \tau_{23}) \propto \left| \sum_{a,c} \kappa_{ca} P(a) \frac{1}{(\omega_s - (\omega_{ca} + \omega_3)) + i\Gamma_{ca}} \right|^2$$

As expected for a cw field 3, these expressions are independent of $\tau_{23}$. Thus, a cw field 3 (or a pulse 3 in which $E_3(t)$ is essentially constant during the timescale of the molecular response) is expected to give rise to CARS signal that consists of the squared magnitude of a sum of complex Lorentzian lineshapes centered at frequencies $(\omega_{ca} + \omega_3)$ with linewidth parameters of $\Gamma_{ca}$. In the case of isolated frequencies (i.e., the vibrations are well separated
relative to their dephasing rates), the observed spectrum will consist of isolated peaks with lineshapes

\[
\left| \frac{1}{(\omega_s - (\omega_{ca} + \omega_3) + i\Gamma_{ca})} \right|^2 = \frac{1}{(\omega_s - (\omega_{ca} + \omega_3))^2 - (\Gamma_{ca})^2}
\]

(3.12),

which are simply Lorentzian lineshapes centered at frequencies, \(\omega_s = (\omega_{ca} + \omega_3)\) (i.e., the anti-Stokes shifted frequency relative to the probe pulse frequency, \(\omega_3\)) with full-width at half maxima (FWHM) of \(2\Gamma_{ca}\). In this well-separated limit, then, a long pulse 3 probe scheme is expected to provide identical spectra to a spontaneous Raman spectrum. This result arises from the fact that the squared magnitude of a complex Lorentzian is proportional to its imaginary component (i.e., \(|L(\omega)|^2 \propto \text{Im}[L(\omega)]\)). In cases where the linewidths of the vibrations are comparable to the vibrational spacing, Eq. 3.11 demonstrates that interferences (or heterodyning) will be observed between overlapping peaks.

### 3.3 Simulations of fs/ps CARS signal

Having established the expected signal in two extreme cases, we now return to simulations of CARS signal using several instructive examples. As noted above, these simulations involve numerical integration of Eq. 3.5 using a variety of parameters associated with the molecular response and the final input pulse field, \(E_3(t)\), while maintaining constant input parameters associated with input pulses 1 and 2 (\(E_1(t)\) and \(E_2(t)\) were assumed to correspond to transform-limited pulses with durations \(\sim 50\) fs centered at arbitrary \(\omega_1\) and \(\omega_2\)
frequencies, constraining only their difference, $\omega_1 - \omega_2$). These simulations were carried out using sufficiently small grid steps (typically 0.5 – 1 fs steps in the time domain, <0.2 cm$^{-1}$ in the frequency) and large enough ranges to ensure negligible numerical errors were introduced into the simulations. All simulations were carried out using code written for a software program (IgorPro) that allows direct graphical viewing of intermediate and final results, and simulations were carried out on Windows-based machines.

### 3.3.1 Simulations of fs/ps CARS, $\tau_{33} = 0$

The molecular response function, $R_d(0,t_2,0)$, is generated from inputted information that includes the central frequencies ($\omega_{ca}$) of interest, gamma ($\Gamma_{ca}$) values, and relative transition dipole product ($\kappa_{ca}$) values. The central frequencies are meant to describe the center of the vibrational modes simulated. Gamma is directly related to the FWHM in the frequency domain and assuming the corresponding lifetime in the time domain (assuming exponential decay via homogeneous broadening). The dipole value is related to the amplitude (intensity) of each individual mode sampled also depends inversely on the gamma value. For the example shown in Fig. 3.2 and 3.3, the frequency is chosen as 1190 cm$^{-1}$, gamma of 10 cm$^{-1}$, and transition dipole defined as 1. Fig. 3.2a) displays the $R_d(0,t_2,0)$ both in the real part of the function (orange) and the magnitude (black). The real part of $R_d(0,t_2,0)$ shows the carrier frequency which corresponds to the central frequency (1190 cm$^{-1}$) of our example system and where the magnitude represents the exponentially decaying lifetime that determines the gamma value after Fourier transform (FT). After FT of the $R_d(0,t_2,0)$, the carrier frequency of the response is converted into the frequency domain where a Lorentzian lineshape centered at the carrier frequency with FWHM determined from the exponential
decay is generated and shown in Fig. 3.2b. Applying a Lorentzian fit to the result in Fig 3.2b returns a mode centered at 1190 cm\(^{-1}\) and FWHM = 20 cm\(^{-1}\) which is \(2\Gamma_{ca}\). \(2\Gamma_{ca}\) is the expected result for an exponentially (time domain) decaying vibrational mode probed with a continuous wave (CW) field.

To move beyond the continuous wave approximation and model the system more in terms of the experimental fs/ps CARS experiments, the electric field of the probe pulse in the frequency domain, \(E_3(\Delta)\), is a narrow square pulse with a FWHM = 6.8 cm\(^{-1}\)(Fig. 3.2d). Taking the inverse Fourier transform (IFT) of the \(E_3(\Delta)\) generates \(E_3(t)\), which is the electric field in the time domain. \(E_3(t)\) has a sinc shape due to having a square \(E_3(\Delta)\). The \(\text{Re}\{\text{sinc}\}\) function can be seen in the inset in Fig 3.2c and demonstrates the general shape of a sinc function with a large central component intensity, nodes at \(\text{Re}\{E_3(t)\} = 0\), and recurrences of intensity. Fig. 3.2c. also shows the \(|E_3(t)|\) over the range in which the \(R_4(0,t_2,0)\) decays. The electric field in time has a curved shape over the range starting at time zero, which is analogous to the fs/ps CARS pulses being overlapped in time at \(\tau_{23} = 0\). Fig. 3.2e shows \(|P^{(3)}(t)|\) assuming the condition of \(E_3(t)\) at time zero from 3.2c above, and the \(\omega_1-\omega_2\) difference of 1300 cm\(^{-1}\). The difference of \(\omega_1-\omega_2\) accounts for the different carrier frequency simulated in Fig. 3.2a vs. Fig. 3.2e. The closer \(\omega_1-\omega_2\) is to the mode of interest the smaller the difference and the smaller the carrier frequency observed. In the case of Fig 3.2e, the frequency oscillations observed are equal to 1300–1190 cm\(^{-1}\) and generate a carrier frequency of 110 cm\(^{-1}\). \(P^{(3)}(t)\) is obtained by taking the response function \(R_4(0,t_2,0)\) (Fig 3.2a) integrated over the electric field (Fig 3.2c) in time. After application of FT to \(P^{(3)}(t)\), \(P^{(3)}(\omega_S)\) is generated. The generated \(P^{(3)}(\omega_S)\) has a central frequency obtained by the difference of \((\omega_1-\omega_2)\) and the observed carrier frequency and the FWHM determined again from the decay
of Fig 3.2e. To generate the signal observed in fs/ps CARS experiments, \( P^{(3)}(\omega_S) \) is magnitude squared to return \( S_{\text{CARS}}(1190, 0, 0) \) which according to equation 3.1 is proportional to \( |P^{(3)}(\omega_S)|^2 \) and shown in 3.2f.

The obtained FHWM in 3.2f is equal to \( \sim 2\Gamma_{ca} \). Given the electric field envelope in 3.2c, the intensity of the electric field is essentially greater than 0.8 over the entire molecular response and can be treated as a quasi-CW beam. Improved spectral resolution is advantageous in the event of close lying peaks common in large molecular systems.

### 3.3.2 Simulations of fs/ps CARS, \( \tau_{23} = \text{node} \)

By careful control of \( \tau_{23} \), fs/ps CARS can improve the spectral resolution observed in the output spectrum over the CW limit. If the probe electric field is positioned in time at a node of the sinc function, the probe pulse appears linear over the time of decay of \( R_d(0,t_2,0) \) (Fig. 3.3c). Assuming the same molecular response generated from the parameters above (reproduced in Fig 3.3a and 3.3b) and using the identical square pulse as Fig 3.2d (reproduced in 3.3d), and instead shifting the resulting \( E_3(t) \) by -4878 fs such that the node time overlaps \( E_1(t) \) and \( E_2(t) \). \( P^{(3)}(t) \) is again obtained via integration of the molecular response \( R_d(0,t_2,0) \) by the now shifted \( E_3(t) \). The resultant \( P^{(3)}(t) \) has a slower rise than \( R_d(0,t_2,0) \) and the decay is longer arising from the fact that the \( E_3(t) \) intensity is growing linearly in intensity over the molecular response. This longer decay in the time domain generates a narrower FHWM in the frequency domain (Fig. 3.3f). In fig 3.3f, the FHWM is found to be 12.68 cm\(^{-1}\) which is the result of placing the electric field at the node in time and thus increasing the spectral resolution from \( 2\Gamma_{ca} \) to \( 2\sqrt{2-1}\Gamma_{ca} \) or \( \sim 1.287 \Gamma_{ca} \).
This improved resolution can aid in the separation of close lying peaks and has been experimentally utilized to separate two different species in fs/ps CARS experiments. Fs/ps CARS experiments on the excited state of coumarin 153 in methanol have unveiled complex hydrogen bonding dynamics at early excitation times. It was found that at excitation times near zero, two species attributed to hydrogen bonded and non-hydrogen bonded complexes coexist. These peaks are shown in Fig. 3.4a along with their simulated fs/ps CARS counterpart (Fig. 3.4b). The two components lie within 12 cm\(^{-1}\) and provide an excellent test case for the advantages of increased spectral resolution. Simulated parameters were obtained from fitting the data in 4a and assuming the \(\tau_{23}\) is positioned at the node. These parameters are then taken and applied to the case of \(\tau_{23} = 0\), and the simulated fs/ps CARS spectra are calculated without contributing non-resonant signal seen in Fig 3.4c. The result at \(\tau_{23} = 0\) is what would be expected using spontaneous Raman or ps-CARS and exemplifies the need for increased spectral resolution in some cases. The asymmetric nature of the peak is due to the centering of \(\omega_1 - \omega_2\) at 1400 cm\(^{-1}\).

Another area explored by theoretical simulations is the effect of electric field linewidth on observed FWHM given a specific \(\Gamma_{ca}\) input for \(\tau_{23} = \text{node}\) (Fig 3.5a). To probe the field FWHM dependence on \(\Gamma_{ca}\), two different \(E_3(\Delta)\) fields were generated. These two fields, both square waves, were designed with FWHM values of 13 and 20 cm\(^{-1}\) respectively. For \(\Gamma_{ca}\) values larger than the FWHM of the electric field, the observed CARS FWHM is slightly broader than input \(\Gamma_{ca}\). For values smaller than the electric field FWHM, a non-linear effect was observed where detected CARS linewidths appeared narrower than the electric field FWHM but appeared broader than the inputted \(\Gamma_{ca}\) values.
Because the integrated area of the observed CARS signal at $\tau_{23} = \text{node}$ is a function of the linewidth, $\Gamma_{ca}$, simulations using the same electric fields were undertaken to determine the relative sensitivity of the observed fs/ps CARS signal for a given $\Gamma_{ca}$ input (Fig 3.5b). While both fields result in roughly equal observed integrated area for low $\Gamma_{ca}$ inputs, there exists some measurable differences as $\Gamma_{ca}$ becomes larger. For large values of $\Gamma_{ca}$, the broader electric field generates roughly three times more integrated area than the narrower electric field. Thus, as $\Gamma_{ca}$ increases, the sensitivity of a narrower $E_3(\Delta)$ decreases. These simulations illuminate the advantages of adjustable $E_3(\Delta)$ fields in experimental work.

3.4 Reference


3.5 Figures.

**Figure 3.1.** Level diagram depicting the molecular response function, $R_4(t_1,t_2,t_3)$ that dominates time-resolved CARS signals. Solid arrows represent field interactions with pulses 1, 2, and 3, whereas the wavy arrow represents the emitted CARS field resulting from energy conservation. Time elapsed between successive field interactions are represented by the variables $t_1$, $t_2$, and $t_3$. 

![Diagram of molecular response function](image-url)
Figure 3.2. Simulation of expected signal for a single vibrational resonance observed when $r_{23} = 0$ of sinc function. a) The relevant molecular response function, $R_4$, with respect to ground state vibrational coherence time, $t_2$. The real part of the response function (orange curve) contains the decaying oscillating frequency (1190 cm$^{-1}$) of the simulated mode with a decay constant $\Gamma_{ca} = 10.0$ cm$^{-1}$. The magnitude of $R_4(0,t_2,0)$ is shown as a black curve. b) Fourier transform of (a), giving rise to a Lorentzian lineshape with a central frequency of 1190 cm$^{-1}$ and FWHM of 20.0 cm$^{-1} = 2\cdot\Gamma_{ca}$. c) The time-dependent electric field magnitude, $|E_3(t)|$, resulting from the inverse Fourier transform of the square pulse frequency-domain electric field; the abscissa of this graph represents time, $t$, relative to the peak of this electric field (inset depicts $\text{Re}\{E_3(t)\}$ over a 40000 fs range); note that the magnitude of the electric field over the timescale of the response function is quasi-constant. d) The square frequency-domain electric field magnitude, $|E_3(\Delta)|$, giving rise to $E_3(t)$ in panel (c); the FWHM of this square pulse is 6.8 cm$^{-1}$. e) Simulated third order polarization, $P^{(3)}(t)$ assuming input conditions depicted in panels (a) and (d). Red curve is the real component of $P^{(3)}(t)$, which contains an oscillation corresponding to the vibrational detuning relative to the pulse 1 and 2 difference frequency, $(\omega_1 - \omega_2)$; black curve is the magnitude of $P^{(3)}(t)$. f) The magnitude square of the Fourier transform of (e), $|P^{(3)}(\omega_3)|^2$, FWHM = 21 cm$^{-1}$. 
Figure 3.3. Simulation of expected signal for a single vibrational resonance observed when $\tau_{23} = \text{node of sinc function}$. a) Identical to 2a. b) Identical to 2b. c) The time-dependent electric field magnitude, $|E_3(t)|$, resulting from the inverse Fourier transform of the square pulse frequency-domain electric field; the abscissa of this graph represents time, $t$, relative to the peak of this electric field (inset depicts Re{$E_3(t)$} over a 40000 fs range); thus, placement of the first node for this sinc function occurs at a time of $t = -4880$ fs. Note that the magnitude of the electric field over the timescale of the response function is approximately linear near this node. d) The square frequency-domain electric field magnitude, $|E_3(\Delta)|$, giving rise to $E_3(t)$ in panel (c); identical to 2d. e) Simulated third order polarization, $P^{(3)}(t)$ assuming input conditions depicted in panels (a) and (d). Red curve is the real component of $P^{(3)}(t)$, which contains an oscillation corresponding to the vibrational detuning relative to the pulse 1 and 2 difference frequency, $(\omega_1 - \omega_2)$; black curve is the magnitude of $P^{(3)}(t)$. f) The magnitude square of the Fourier transform of (e), $|P^{(3)}(\omega)|^2$, FWHM = 12.68 cm$^{-1}$. 
Figure 3.4. a) Experimental fs/ps CARS results for C153 in methanol showing two excited state species, a hydrogen bonded (1670 cm$^{-1}$) and free complex (1681 cm$^{-1}$) for four different excitation delays as noted. b) The simulated signal was obtained from fitting the experimental data assuming $\tau_{23} =$ node and $\Delta \omega_3 = 6.8$ cm$^{-1}$. c) Simulated signal using parameters from b and $\tau_{23} = 0$ fs. The spectrum at $\tau_{23} = 0$ shows a single peak and demonstrates the increased spectral resolution seen in b) where two peaks are clearly observed.
Figure 3.5. a) The effect on observed FWHM for two different $E_3(\Delta)$ bandwidths at $\tau_{23} = \text{node}$ for a given input $\Gamma_{ca}$. b) The influence of $\Gamma_{ca}$ on observed integrated area for two $E_3(\Delta)$ as a function of the log(normalized integrated area). As $\Gamma_{ca}$ increases, the outputted integrated area decreases. Blue: 13 cm$^{-1}$ square $E_3(\Delta)$. Black 20 cm$^{-1}$ square $E_3(\Delta)$. 
CHAPTER 4: GENERAL CONCLUSION

The focus of the experimental part of this work was to examine the sub-picosecond dynamics of 4-dimethylamino-4’-nitrostilbene (DANS) in polar solvents. While solvated in polar solvents, DANS is thought to undergo two stage evolution after excitation. First, excitation into a conformationally similar state (compared to the ground state) called E*, followed by twisting about the C-N of the C-NO₂ to end in the state labeled A₅*. Transient absorption/gain experiments, with time resolution of ~120 fs, indicate that once excited DANS remains in one state. Vibrationally DANS undergoes a large 60 cm⁻¹ blue shift in the NO₂ symmetric stretch mode upon initial excitation from the ground state in acetonitrile. After this excitation there is a 20 cm⁻¹ red shift in the frequency of this mode that is not observed to a large degree in other modes. This frequency red-shift occurs on a 300 fs timescale and is also accompanied by a narrowing of the FWHM for this mode. 300 fs is comparable to the known timescale of solvent rearrangement for acetonitrile and suggests DANS is undergoing a conformational change related to twisting about the C-NO₂ region of the molecule. There is no evidence that this occurs by first beginning in an E* state and subsequent relaxation to a separate electronic state. The vibrational signature of the final state is similar to that observed in other experiments and remains consistent with the labeling of the state as A₅*.

Theoretical simulations of fs/ps CARS have examined several experimentally observed phenomena. These observations include the improved spectral resolution gained by positioning the E₃(t) at τ₂₃ = node compared to the decreased resolution observed at τ₂₃ = 0. This increased resolution provides a significant advantage to the examination of close lying
vibrational modes and was demonstrated in experiments on excited state coumarin 153. Additionally, the sensitivity of outputted CARS signal was investigated and the relative integrated area as a function of electric field FWHM and $\Gamma_{ca}$ was shown to result in increased signal sensitivity for broader square wave $E_3(\Delta)$ for larger $\Gamma_{ca}$ values. Finally, the framework for an algorithm that can be applied to experimentally observed data to return molecularly relevant information including the $\Gamma_{ca}$, the $\kappa_{ca}$ and the frequency center $\omega_{ca}$ values under the conditions that $E_3(t)$ is positioned at $\tau_{23} = \text{node}$ and that the $E_3(t)$ is linear over the timescales of the molecular response.
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