Coherent control of multiple vibrational excitations for optimal detection

S D McGrane, R J Scharff, M Greenfield and D S Moore

Los Alamos National Laboratory, Shock and Detonation Physics Group, MS P952, Los Alamos, NM 87545, USA
E-mail: mcgrane@lanl.gov

New Journal of Physics 11 (2009) 105047 (14pp)
Received 10 June 2009
Published 30 October 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/10/105047

Abstract. While the means to selectively excite a single vibrational mode using ultrafast pulse shaping are well established, the subsequent problem of selectively exciting multiple vibrational modes simultaneously has been largely neglected. The coherent control of multiple vibrational excitations has applications in control of chemistry, chemical detection and molecular vibrational quantum information processing. Using simulations and experiments, we demonstrate that multiple vibrational modes can be selectively excited with the concurrent suppression of multiple interfering modes by orders of magnitude. While the mechanism of selectivity is analogous to that of single mode selectivity, the interferences required to select multiple modes require complicated non-intuitive pulse trains. Additionally, we show that selective detection can be achieved by the optimal pulse shape, even when the nature of the interfering species is varied, suggesting that optimized detection should be practical in real world applications. Experimental measurements of the multiplex coherent anti-Stokes Raman spectra (CARS) and CARS decay times of toluene, acetone, cis-stilbene and nitromethane liquids are reported, along with optimizations attempting to selectively excite nitromethane in a mixture of the four solvents. The experimental implementation exhibits a smaller degree of signal to background enhancement than predicted, which is primarily attributed to the single objective optimization methodology and not to fundamental limitations.

1 Author to whom any correspondence should be addressed.
1. Introduction

The ability to selectively excite multiple vibrational modes while suppressing others is critical to several applications. Coherent control of chemical reactions [1]–[11] typically relies on vibrational wavepacket dynamics to achieve the desired objective. Recent efforts at shaped pulse chemical threat detection [12]–[14] could benefit from the ability to excite the molecular spectrum of a threat agent while suppressing interfering spectra; this objective is a primary motivation for the work reported here. The ability to experimentally implement any of a number of theoretical suggestions for achieving molecular vibrational quantum information processing [15]–[20] requires well controlled selective excitation of multiple modes. An improved understanding of how to selectively excite multiple vibrations will have a positive impact on these and other applications.

All of the considerations detailed in this paper are a direct extension of well established methods of using ultrafast pulse shaping to control impulsively stimulated Raman scattering (ISRS) excitation [21]–[29]. ISRS is the excitation of vibrations by difference frequencies that reside within the spectral bandwidth of an ultrafast laser pulse. For a compressed pulse, all Raman active vibrational modes that have a lower frequency than the spectral bandwidth will be excited. The use of Fourier domain ultrafast pulse shaping to create pulse trains that selectively excite a single vibrational mode through ISRS was established long ago, and has been implemented with improvements and adaptation many times since [12]–[14], [21, 22, 26], [30]–[36]. Essentially, each sub-pulse of the pulse train provides a force that is timed with the motion of the vibrational oscillator. Classically, the amplitude of the oscillator increases with each pulse. Quantum mechanically, the probability amplitude of an oscillator at a certain eigenfrequency increases with each pulse [23, 29]. With non-resonant Raman, this process is in the low excitation limit, and the probability of exciting a given oscillator is much less than unity. Pulse shaping allows other vibrations to be suppressed while maintaining most of the excitation
of the desired mode. For resonance Raman, pulse shaping can actually enhance the excitation probability above the transform limit [32, 37].

The problem we address in this paper is the determination of the properties of pulse trains that excite multiple modes while broadly suppressing other spectral content. Experimentally, we wish to select modes corresponding to a single chemical component of a mixture as measured by coherent Raman spectroscopy. As we show below, the solution to this problem is not nearly as simple as the equally spaced pulse train of the single oscillator problem. Since each sub-pulse exerts forces on all oscillators and each oscillator has a different frequency and thus accumulates phase at a different rate, the interference of multiple pulses can be constructive for some frequencies and destructive for others. In this paper, we test how well this simple process can perform when the effects of experimental limitations are included. First, we summarize the theoretical understanding of this problem in the simplest possible form. The theory is coupled to optimization algorithms to determine the extent to which selective multiple vibrational excitations can be achieved, as well as the dominant mechanisms limiting the selectivity. Next, we present experimental tests which demonstrate substantial, though incomplete, selectivity under real conditions. The coupling of theory and experiment leads to a simple understanding of the degree of selectivity that can be achieved and both the fundamental and experimental factors that limit selectivity.

2. Theory

A unified treatment of Raman excitation that spans the range from impulsive stimulation to narrow band excitation has been developed for the analysis of data under varying degrees of time and spectral resolution [38, 39]. Essentially, a Raman coherence $Q(t)$ is excited by the simultaneous interaction of a pump and Stokes field according to equations (1) and (2).

$$Q(t) = \int_{-\infty}^{\infty} E_{\text{Pump}}(t') E_{\text{Stokes}}^*(t') \chi(t - t') \, dt'.$$

(1)

The Raman response function $\chi(t)$ is phenomenologically modeled as a sum of $n$ damped oscillators of frequencies $\omega_i$, dephasing times $T_{2i}$, and Raman cross sections given by the amplitude coefficients $A_i$, given in equation (2), where $\theta(t)$ is the Heaviside function.

$$\chi(t) = -i \sum_{j=1}^{n} A_i \exp(-i\omega t) \exp(-it/T_{2j}) \theta(t).$$

(2)

In the simulations and experiments below, we use equivalent shaped fields for the pump and the Stokes, $E_{\text{pump}} = E_{\text{Stokes}}$. This is done to avoid solutions that utilize spectral filtering; it is well known that chirping the pump pulse relative to the Stokes pulse allows the relative time delay to translate into narrow frequency excitation [40]–[43]. By not allowing relative delay between pump and Stokes pulses, we limit the search space to mechanisms that maintain the entire pulse energy to drive the Raman process. Similarly, we do not consider amplitude shaping of the excitation spectrum. Only spectral phase will be used to modulate the excitation, and we demonstrate below that it is sufficient.

The addition of spectral phase can also be considered as a nonlinear frequency filter [29, 44, 45] according to equation (3).

$$E_2(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E_{\text{Pump}}(t) E_{\text{Stokes}}^*(t) \exp(i\omega t) \, dt.$$

(3)
Essentially, the goal is to optimize the nonlinear excitation of multiple frequencies while simultaneously minimizing all other frequencies. This is an optimization problem, the solution to which depends upon the time window that can be accessed by the pulse shaper (there is a maximum delay that depends on the spectral width and number of pixels as well as various artifacts due to gaps between pixels) [46, 47, 54], and on the shortest duration of the sub-pulses as determined by the spectral bandwidth of the excitation. Another limitation is the effect of dephasing on the oscillators, which is simplest to envision in the time domain. Consider two sub-pulses of equal amplitude applied exactly out of phase with an oscillator: this will start and stop the oscillator if dephasing is negligible, but if dephasing is complete between pulses the second pulse will increase the coherent amplitude. For multiple oscillators, each of the vibrations will be dephased to different degrees at the end of the pulse train. The composition and total temporal extent of the optimal pulse train may be affected by the variation in dephasing times of multiple oscillators. To explicitly include all of these experimental limitations, the simulations are performed in the time domain using equations (1) and (2), coupled to the same optimization algorithms used for the experiments.

In the experiments, spectral and temporal resolution is limited as dictated by the probe pulse. We measure coherent anti-Stokes Raman spectra (CARS), which is related to the Raman coherence of equations (1) and (2) as given by equations (4) and (5) [38]. The delay time between the simultaneous pump/Stokes pulses and the probe pulse is $\tau$.

$$E_{\text{CARS}}(t, \tau) = E_{\text{probe}}(t - \tau) Q(t).$$  \hfill (4)

The CARS field is homodyne (intensity) detected through a spectrometer as given by equation (5)

$$S_{\text{CARS}}(\omega) = \frac{1}{2\pi} \left| \int_{-\infty}^{\infty} E_{\text{CARS}}(t, \tau) \exp(-i\omega t) \, dt \right|^2. \hfill (5)$$

In the experiments reported here, the probe field is spectrally filtered to 33 cm$^{-1}$, which limits the time resolution to $\sim 600$ fs. The advantage of not including the probe in the simulations is that the vibrational excitation is optimized independent of the method of subsequent probing.

There are three primary experimental limitations: finite pulse duration, finite time window of total excitation, and dephasing. In the absence of these experimental limitations, it is clear that the interference can be complete and arbitrary multiple pulse selectivity could be performed perfectly. We include the first limitation by performing calculations for a 10 fs full-width at half-maximum (FWHM) Gaussian pulse. The second limitation is approximated by a 3.5 ps FWHM Gaussian filter function applied to the time dependent electric field, simulating the theoretical limits of our pulse shaper configuration [54]. The third limitation is considered by using dephasing times that are set at 3 ps unless otherwise noted. Optimizations were performed with 300 pixels of spectral phase equally spaced in frequency. A total time of 10 ps was used to simulate the Raman coherence.

An adaptive genetic algorithm [48]–[51] written for quantum control experiments was employed for optimization. The genetic algorithm was implemented with continuous variables and operators which performed one point, two point, and uniform crossover, mutation, creep, and smoothing. The 300 spectral phase pixels equally spaced between 300 and 450 THz were freely varied parameters. The fitness function used in the optimization was determined empirically. The fitness included a weighted integral over the desired peaks minus a penalty function for changing the spectral intensity ratios of the desired peaks all divided by the integral

New Journal of Physics 11 (2009) 105047 (http://www.njp.org/)
Simulated selective excitation of multiple vibrations. Unshaped spectra are offset above the shaped pulse spectra. The spectrum optimized for the five peaks marked by arrows is shown in (a). The effect of random changes to the coherence time of the interference peaks is shown in (b). The effect of random frequency shifts in the interference peaks is shown in (c). Lower spectra are scaled by 20×.

Figure 2. The optimal spectral phase (lower black) and intensity (upper red) (a), time dependent intensity (b) and two photon excitation spectrum for the shaped (solid) and unshaped (dashed) pulses (c) are presented, corresponding to the optimization shown in figure 1.

Simulations attempting to optimize five weak peaks in the presence of 15 stronger peaks are shown in figure 1. The intensity plotted is the Fourier transform squared of the Raman coherence, $|Q(\omega)|^2$, given by equation (1). The upper plot in each panel of figure 1 is for zero spectral phase, and the lower plot for the optimal pulse detailed in figure 2. Figure 1(a) illustrates the features of typical optimizations. Peaks that are very close in frequency are suppressed to a lesser extent than those further from the target peaks. Suppression of interferences ranged from factors of 190–7000, while the target peaks were suppressed in a range from 4 to 10. On average, the target peaks were suppressed by a factor of 6.6 and the interfering peaks suppressed by a factor of 738, for an improvement in signal to background of a factor of 112.
The question of transferability, i.e. the pulse shape valid for different interferences, was addressed by randomly varying the interfering coherence times and the frequencies. Figure 1(b) is typical for a variation in dephasing times with a random distribution between 0 and 6 ps. The same optimal pulse is used as shown in figure 1(a), and there is no degradation in the suppression of the background. Figure 1(c) illustrates the effect of changing the interference frequencies, which allows very similar suppression to that of figure 1(a), with the exception that some interferences are now very close to the target frequencies and are not suppressed as well. Interferences that overlap the target frequencies cannot be suppressed by this method, which relies on frequency dependent suppression. The two photon excitation spectrum shown in figure 2(c) illustrates the frequency dependent suppression. The two photon excitation is calculated by numerical evaluation of equation (3), applying an inverse Fourier transform after treating the fields in the time domain.

The optimal pulse is described by the spectral phase, figure 2(a), the time dependent intensity, figure 2(b), and the two photon excitation spectrum, figure 2(c). While the phase and pulse trains observed in figure 2 are very highly structured, the effect of this structure is simply to produce the nonlinear frequency filter that governs the ISRS excitation shown by figure 2(c).

4. Experiment

The vibrational excitation was measured experimentally using CARS. A 40 fs, 800 μJ, 800 nm pulse from a 1 kHz Ti:sapphire amplifier was focused with a 2.5 m focal length lens into a 1 m pipe filled with 69 kPa of Ar gas. This broadens the spectrum [52, 53] to allow ISRS of higher frequency modes. The broadened spectrum is passed through a polarizer and an all reflective pulse shaper [54]. The pulse shaper consisted of a 600 g mm\(^{-1}\) grating, 500 mm cylindrical mirror, turning mirror, 640 pixel dual mask spatial light modulator (CRi 640-D-VN SLM) and retroreflecting mirror which slightly displaces the output beam vertically to allow spatial separation. Glan polarizers were inserted at the input and output of the shaper.

Pulses were compressed to durations of <20 fs FWHM at the sample, as measured by transient grating frequency resolved optical gating (TG-FROG) [55]. Both the TG-FROG and CARS were performed in box geometry. For multiplex CARS spectral acquisition, a 33 cm\(^{-1}\) FWHM interference filter centered at 785 nm was placed in the probe beam, stretching it temporally to 600 fs. The energies of the pump and Stokes pulses at the sample were attenuated to <1.5 μJ to avoid self-phase modulation in the sample. The probe beam energy of 0.5 μJ was limited by the filter throughput. All pulses were linear parallel polarization. The four wave mixing signal was spatially separated and detected on a 3000 pixel line camera (Thorlabs LC1-USB) through a 0.3 m spectrometer (Princeton Instruments SP-2300i with 300 g mm\(^{-1}\) grating) with 1 nm resolution at 100 μm slit width. The sample was contained in a liquid cell with 150 μm thick sapphire windows. The total path length of the liquid was 1.75 mm. Spectra were collected in single shot mode, with 25–100 shots averaged. Unless otherwise stated, the time delay between the pump/Stokes and probe was 1.25 ps.

All chemicals were used as received: toluene, anhydrous, 99.8% (Acros); Acetone, A.C.S. spectrophotometric grade, 99.5% (Sigma-Aldrich); cis-stilbene, 96% (Sigma-Aldrich) nitromethane, 98% (Alfa-Aesar).
5. Experimental results

5.1. Dephasing times

The dephasing times of each component of the mixture were separately measured by recording the CARS spectra as a function of probe delay, as shown logarithmically in figures 3(a)–(d). These plots illustrate the features commonly seen in multiplex CARS experiments [38, 39, 56]. There is a broad emission from −0.5 to 0.5 ps (600 fs FWHM) which occurs when the probe overlaps the pump/Stokes pulses temporally. After 0.5 ps delay, the CARS spectra have negligible non-resonant contribution. Peaks that are unresolved or partially resolved

Figure 3. CARS spectra versus probe delay on a log scale for toluene (a), acetone (b), cis-stilbene (c) and nitromethane (d). CARS spectra on a log scale at 1.25 ps probe delay for (e) toluene, (f) acetone, (g) cis-stilbene and (h) nitromethane.
Table 1. Mode specific CARS decay times $\tau = T_2/2$, from the data of figure 3. Reference data in parentheses.

| Molecule  | Mode (cm$^{-1}$) | $\tau$ (fs) |
|-----------|-----------------|-------------|
| Toluene   | 227 (217)$^{64}$ | $256 \pm 14$ |
|           | 526 (524)$^{64}$ | $1155 \pm 53$ |
|           | 625 (620)$^{64}$ | $522 \pm 50$  |
|           | 792 (784)$^{64}$ | $1668 \pm 53$ |
|           | 1002 (1002)$^{64}$ | $2918 \pm 47 (2925)^{65}$ |
|           | 1213 (1208)$^{64}$ | $1293 \pm 40$ |
| Acetone   | 784 (783)$^{66}$ | $506 \pm 4 (510 \pm 30)^{66}$ |
| Cis-stilbene | 272 (261)$^{67}$ | $253 \pm 36$  |
|           | 405 (405)$^{67}$ | $370 \pm 14$  |
|           | 560 (561)$^{67}$ | $828 \pm 15$  |
|           | 620 (620)$^{67}$ | $899 \pm 32$  |
|           | 969 (966)$^{67}$ | $783 \pm 35$  |
|           | 1003 (1001)$^{67}$ | $2207 \pm 51$ |
|           | 1613 (1599; 1629)$^{67}$ | $582 \pm 10$ |
| Nitromethane | 475 (480)$^{68}$ | $350 \pm 8$   |
|           | 651 (657)$^{68}$ | $693 \pm 4$   |
|           | 915 (918)$^{69}$ | $1751 \pm 9 (1397)^{69}$ |
|           | 1390 (1377; 1403)$^{69}$ | $716 \pm 38 (590; 758)^{69}$ |

Exhibit beating in the time domain at the difference frequency. There is an inherent tradeoff between the spectral filter width and time resolution in this type of multiplex CARS experiment [38, 56]. We employed multiplex CARS because the application to detection is facilitated by the full spectral acquisition without any scanning. Reference spectra for each component at 1.25 ps probe delay are given in figure 3(e)–(h). Table 1 displays the exponential decay times of the CARS signal for each primary mode of each chemical component. The experimental decays of the 1002 cm$^{-1}$ peak in toluene; the 969 and 1613 cm$^{-1}$ peaks in cis-stilbene; and the 1390 cm$^{-1}$ peak in nitromethane all exhibit observable oscillations. For a single vibrational mode, the time dependent intensity of the CARS signal was fit with equation (6),

$$I(t) = A_0 \exp\left(-t/\tau\right),$$

where $\tau = T_2/2$; $T_2$ is the vibrational dephasing time. For two closely spaced vibrational modes, the time dependent CARS intensity exhibited beating in the decay signal at the difference frequency between the two modes. These decays were fit with equation (7), assuming two independent oscillator decay terms, $\tau_1$ and $\tau_2$ and the cross term modulated by the difference frequency, $\omega$:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) - A_1A_2 \exp(-t(1/\tau_1 + 1/\tau_2)) \cos(\omega t).$$

The oscillation period for the 1002 cm$^{-1}$ peak in toluene was 1.2 ps (28 cm$^{-1}$), consistent with the spontaneous Raman modes of toluene at 1002 and 1028 cm$^{-1}$ [64]. The oscillation
periods for the 969 cm\(^{-1}\) peak in cis-stilbene was 0.97 ps (34 cm\(^{-1}\)), consistent with the spontaneous Raman modes of cis-stilbene at 966 and 1001 cm\(^{-1}\) [67]. The CARS peak at 1613 cm\(^{-1}\) oscillates with a period of 1.2 ps (28 cm\(^{-1}\)) corresponding to spontaneous Raman peaks at 1599 and 1629 cm\(^{-1}\) [67]. Similarly, the 1390 cm\(^{-1}\) CARS peak in nitromethane oscillates with a period of 1.5 ps (23 cm\(^{-1}\)) corresponding to spontaneous Raman peaks at 1377 and 1403 cm\(^{-1}\) [69].

5.2. Optimized spectra

The optimizations were performed in an equal volume mixture of the four chemicals shown in figure 3. The goal of the optimization was to maintain the peaks of nitromethane while suppressing the CARS signal from all the other chemical species present. Figure 4(a) shows the CARS signal of the mixture as a function of probe delay. Figures 4(b) and (c) illustrates the spectrum of the mixture for compressed (unshaped) and optimized pulses at a fixed probe delay of 1.25 ps.

The same genetic algorithm used in the optimizations of the simulations was used in the experiments. The time needed to change the phase mask and evaluate the fitness limited the search speed to approximately two evaluations per second. Initially, the same fitness function as the simulations employed was used, but we observed better performance by evaluating fitness as a weighted sum of desired peaks divided by the sum of all unwanted signals evaluated on a log scale. The use of the log scale helps maintain sensitivity to small peaks; in the equal volume solution shown in figures 4(b) and (c) the nitromethane peaks are more than one order of magnitude smaller than the largest interference peak. The algorithm converged upon the solution shown after evaluating a population of 25 parameter vectors over ~100 generations. The TG-FROG spectrograms of the compressed and optimized excitation pulses are given in figure 5. The degree of success in optimizing the signal to background, the limitations, and the origins of the limitations are discussed below.

Due to the difficulties achieving experimental selectivity of the weak peaks seen in figure 4(c), we also examined a 1 : 1 : 1 volume ratio of nitromethane, toluene and acetone.
Figure 5. TG-FROG measurement of the compressed pulse (a) and the optimized pulse (b) used to generate the CARS spectra in figure 4.

Figure 6. CARS spectra for a 1 : 1 : 1 volumetric mixture of toluene, acetone, and nitromethane on log (a) and linear (b) scales. Arrows mark the desired nitromethane peaks. The black dotted curves are the spectra produced by the compressed pulse, the solid red curves are for the optimized pulse shown in (c).

Without the cis-stilbene, the spectral congestion was considerably less and the nitromethane peaks were more easily isolated. The results of attempts to optimize the nitromethane CARS signal while minimizing the other peaks are shown in figure 6. Figure 6(a) shows the data on log scale, figure 6(b) on a linear scale and figure 6(c) shows the spectrum and phase of the optimal excitation pulse.

6. Discussion

6.1. Discussion of simulations

The simulation results allowed us to come to a number of conclusions important to achieving selective multiple vibrational excitation. Firstly, the spectral phase necessary to obtain the appropriate constructive and destructive interferences between many different modes had a highly structured and non-intuitive shape. Simple guesses at the phase, such as the summation of sine waves appropriate for selecting each individual peak, were unsuccessful. Secondly, while dephasing is a potential concern for transferability (application of an optimal pulse shape to different interferences), it appeared not to be very important for the case considered. This fact arose from the large number of sub-pulses in the pulse train, which led to an interpulse...
separation that was significantly less than the dephasing time. Generally speaking, the coherence
time limits the useful range of total time accessible to achieve interference. The third main
conclusion that followed from the simulations is that the two photon excitation spectrum
contains the essential information necessary for multiple vibrational excitation selectivity. This
conclusion is valid only because the dephasing, or more importantly the differences in dephasing
amongst different modes, did not play a crucial role.

6.2. Discussion of experiments

While the experimental results demonstrated that the multiple peak selectivity could be
performed under realistic limitations, the primary difficulty was in defining the fitness function.
Essentially, we were trying to perform a multi-objective optimization with a single objective
function. The fitness function produced one number which described how well that pulse
performed. The task then was to evaluate a given CARS spectrum and return a single
number that evaluates how well that phase mask (i) maintained the desired peak intensities,
(ii) minimized the undesired peak intensities and (iii) maintained the relative peak heights of
the desired spectrum. There had to be sufficient fitness pressure to suppress the background,
otherwise a phase mask was found that overlapped some or all of the pump/Stokes pulse
temporally with the probe pulse. Such temporal overlap led to a large non-resonant background
with little spectral information. Alternatively, if the fitness function was too strongly weighted
to suppress the background, the algorithm quickly found solutions that almost completely
annihilated the CARS signal along with the background. Determining a fitness function that
performed reasonably well was a matter of trial and error. The definition of the fitness function
was the primary limitation to the optimization success observed in figure 4(b).

In figures 4(b) and (c), the strongest nitromethane peak at 915 cm\(^{-1}\) has maintained most of
its intensity, and went from being a weak shoulder to the ~1000 cm\(^{-1}\) interfering peaks to being
a fully resolved, dominant spectral feature. The weak nitromethane peaks around 1390 cm\(^{-1}\)
have been suppressed and the peak at 651 cm\(^{-1}\) remains in a background of interfering peaks.
It is clear that the larger peaks dominated the fitness function and were successfully controlled,
while the weaker peaks were sacrificed to some extent by the optimization algorithm. The
pulse shape that achieved this control elucidates some of the mechanisms that the algorithm
is exploiting.

The TG-FROG of the optimized pulse is shown in figure 5. The pulse exhibited significant
time dependent structure, although the total duration of the pulse did not significantly exceed
1 ps. Our choice of 1.25 ps probe delay may have limited this total duration, but longer delays
would have made observation of the vibrations with sub-picosecond dephasing times more
difficult to observe. The limited temporal profile of the optimal pulse shape has a direct impact
on the spectral resolution in the frequency domain, limiting the selectivity that can be achieved.
The choice of spectral filter width and probe time delay must be chosen commensurately with
the dephasing times—short dephasing times dictate less spectral resolution and less total time in
the excitation pulse train. Additionally, the TG-FROG indicated spectral chirp as well as pulse
train formation. This chirp largely selects against high frequency modes, explaining the loss of
the nitromethane peak around 1390 cm\(^{-1}\) as well as the more intense high frequency interference
peak of cis-stilbene at 1620 cm\(^{-1}\). The fitness function drove the algorithm to sacrifice the
1390 cm\(^{-1}\) peak in order to remove the interfering peak at 1613 cm\(^{-1}\), which was achieved
by adding chirp to the pulse, which is a minimally selective mechanism.
In order to demonstrate selective excitation of multiple vibrations with the limitations of our current algorithms, we simplified the problem. Removal of cis-stilbene reduces the number and magnitude of other peaks, making the optimization with the genetic algorithm feasible. Figure 6 shows the resulting reduction of the two largest interfering peaks by more than an order of magnitude, while the desired nitromethane peaks decreased by less than a factor of two.

6.3. Suggested improvements for achieving selective multiple vibrational excitations

The simulations suggested that the two photon excitation spectrum contains the essential information necessary for multiple vibrational excitation selectivity. This conclusion was valid only because the dephasing did not play a crucial role; the interpulse separation time was shorter than the dephasing time. This result suggests the possibility for avoiding the optimization search and directly optimizing the two photon excitation spectrum by employing the Gerchberg–Saxton algorithm and direct Fourier techniques [57]. Knowledge of the experimental excitation spectrum and the desired CARS spectrum would be sufficient input parameters. This treatment would neglect the effects of the probe pulse, probe pulse delay, and detailed time accounting of the dephasing, but the phase mask determined may be adequate or would minimally be a better starting point for further adaptive optimization.

Another possible improvement is to pursue multi-objective optimization. There have been recent efforts [58]–[63] to use multi-objective optimizations for quantum control problems. Future experiments will test these multi-objective algorithms for ability to converge with a reasonable number of evaluations for our difficult set of simultaneous objectives. Additionally, multi-objective algorithms offer the potential to map the space of competition between different objectives.

7. Conclusions

Simulations coupled to an optimization algorithm found a highly structured and non-intuitive spectral phase capable of selectively exciting multiple vibrational modes while suppressing broad regions of undesired spectral components by orders of magnitude. The spectral phase that achieved this selectivity was robust to changes in the nature of the undesired/suppressed spectra, as verified by changing the dephasing times and the frequencies of interfering peaks. This suggested that the technique of spectral phase shaped CARS will be useful in selectively detecting one component in a mixture. Experimentally attempts to selectively excite one component of a mixture, as monitored by CARS, were achieved with limited success. Multiple peaks could be maintained with enhanced background suppression, but both the maintenance of the desired spectrum and the suppression of the background spectra were incomplete. The limitations in experimental selectivity were attributed not to fundamental physical or measurement origins, but to the complications of implementing a single objective feedback function with multiple goals. Essentially, it was difficult to find a single equation that simultaneously optimized the desired peaks, maintained the peak intensity ratios, and suppressed broad spectral backgrounds.
Acknowledgments

We gratefully acknowledge the support of the US Department of Homeland Security and the Department of Energy through the LANL/LDRD Program for this work. Los Alamos National Laboratory, an affirmative action equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the US Department of Energy under contract DE-AC52-06NA25396.

References

[1] Nuernberger P et al 2007 Phys. Chem. Chem. Phys. 9 2470
[2] Prokhorenko V I et al 2006 Science 313 1257
[3] Carroll E C et al 2006 J. Chem. Phys. 124 114506
[4] Buckup T et al 2006 J. Photochem. Photobiol. B 180 314
[5] Dantus M and Lozovoy V V 2004 Chem. Rev. 104 1813
[6] Brixner T and Gerber G 2003 ChemPhysChem 4 418
[7] Levis R J and Rabitz H A 2002 J. Phys. Chem. A 106 6427
[8] Levis R J, Menkir G M and Rabitz H 2001 Science 292 709
[9] Weinacht T C, Ahn J and Bucksbaum P H 1999 Nature 397 233
[10] Judson R S and Rabitz H 1992 Phys. Rev. Lett. 68 1500
[11] Brumer P and Shapiro M 1986 Chem. Phys. Lett. 126 541
[12] Katz O et al 2008 Appl. Phys. Lett. 92 171116
[13] Li H et al 2008 Opt. Express 16 5499
[14] Li H et al 2009 Appl. Opt. 48 B17
[15] Bigwood R M and Gruebele M 2002 J. Mol. Struct. 589 447
[16] de Vivie-Riedle R and Troppmann U 2007 Chem. Rev. 107 5082
[17] Gollub C, Troppmann U and de Vivie-Riedle R 2006 New J. Phys. 8 48
[18] Goswami D 2002 Phys. Rev. Lett. 8927 9901
[19] Gruebele M 2004 J. Phys.: Condens. Matter. 16 R1057
[20] Troppmann U and de Vivie-Riedle R 2005 J. Chem. Phys. 122 154105
[21] Dhar L, Rogers J A and Nelson K A 1994 Chem. Rev. 94 157
[22] Kawashima H, Wefers M M and Nelson K A 1995 Annu. Rev. Phys. Chem. 46 627
[23] Mukamel S and Yi Jing Y 1991 J. Phys. Chem. 95 1015
[24] Ruhman S, Joly A G and Nelson K A 1987 J. Chem. Phys. 86 6563
[25] Ruhman S, Joly A G and Nelson K A 1988 IEEE J. Quantum Electron. 24 460
[26] Weiner A M et al 1991 J. Opt. Soc. Am. B 8 1264
[27] Yong-Xin Y et al 1985 J. Chem. Phys. 83 5391
[28] Yong-xin Y and Nelson K A 1987 J. Chem. Phys. 87 6240
[29] Yan Y J and Mukamel S 1991 J. Chem. Phys. 94 997
[30] Dudovich N, Oron D and Silberberg Y 2002 Nature 418 512
[31] Oron D et al 2002 Phys. Rev. A 65 043408
[32] Motzkus M et al 2006 Chem. Phys. Lett. 421 523
[33] Oron D, Dudovich N and Silberberg Y 2003 Phys. Rev. Lett. 90 213902
[34] Von Vacano B, Buckup T and Motzkus M 2006 Opt. Lett. 31 2495
[35] Von Vacano B and Motzkus M 2007 J. Chem. Phys. 127 144514
[36] Coello Y et al 2008 J. Opt. Soc. Am. B 25 A140
[37] Hauer J, Buckup T and Motzkus M 2008 Chem. Phys. 350 220
[38] Urbanek D C and Berg M A 2007 J. Chem. Phys. 127 044306
[39] Nath S et al 2006 Phys. Rev. Lett. 97 267401

New Journal of Physics 11 (2009) 105047 (http://www.njp.org/)
[40] Knutsen K P et al 2006 J. Phys. Chem. B 110 5854
[41] Naumov A N and Zheltikov A M 2001 J. Raman Spectrosc. 32 960
[42] Zheltikov A M and Naumov A N 2000 Quantum Electron. 30 606
[43] Konradi J et al 2007 J. Raman Spectrosc. 38 1006
[44] Lozovoy V V and Dantus M 2005 ChemPhysChem 6 1970
[45] Lozovoy V V et al 2005 Opt. Express 13 10882
[46] Vaughan J C et al 2006 Opt. Express 14 1314
[47] Wefers M M and Nelson K A 1995 J. Opt. Soc. Am. B 12 1343
[48] Davis L 1991 Handbook of Genetic Algorithms (New York: Van Nostrand Reinhold)
[49] Goldberg D E 1989 Genetic Algorithms in Search, Optimization, and Machine Learning (Reading, MA: Addison-Wesley)
[50] Weinacht T C and Bucksbaum P H 2002 J. Opt. B 4 R35
[51] Pearson B J et al 2001 Phys. Rev. A 63 063412
[52] Gallmann L et al 2007 Appl. Phys. B 86 561
[53] Hauri C P et al 2005 Opt. Express 13 7541
[54] Weiner A M 2000 Rev. Sci. Instrum. 71 1929
[55] Trebino R et al 1997 Rev. Sci. Instrum. 68 3277
[56] Prince B D et al 2006 J. Chem. Phys. 125 44502
[57] Rundquist A, Efimov A and Reitze D H 2002 J. Opt. Soc. Am. B 19 2468
[58] Beltrani V, Ghosh P and Rabitz H 2009 J. Chem. Phys. 130 164112
[59] Bonacina L et al 2007 Phys. Rev. A 76 023408
[60] Chakrabarti R, Wu R and Rabitz H 2008 Phys. Rev. A 78
[61] Gollub C and de Vivie-Riedle R 2009 New J. Phys. 11 013019
[62] Lindinger A et al 2005 Phys. Rev. A 71 13419
[63] Weber S M et al 2008 J. Mod. Opt. 54 2659
[64] Hitchcock A P and Laposa J D 1975 J. Mol. Spectrosc. 54 223
[65] Hubble H W, Lai T S and Berg M A 2001 J. Chem. Phys. 114 3663
[66] Zinth W, Leonhardt R, Holzapfel W and Kaiser W 1988 IEEE J. Quantum Electron. 24 455
[67] Bree A and Zwarich R 1981 J. Mol. Struct. 75 213
[68] Deák J C, Iwaki L K and Dlott D D 1999 J. Phys. Chem. A 113 971
[69] Shkurinov A, Jonusauskas G and Rullière C 1994 J. Raman Spectrosc. 25 359

New Journal of Physics 11 (2009) 105047 (http://www.njp.org/)