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Toward Strong Field Mode-Selective Chemistry

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We demonstrate a new method for coherent control of bond excitation in the strong field regime. We can selectively excite one or more Raman-active modes in a molecular liquid without the need for externally generated coherent sources separated by the Stokes frequency. The method employs excitation with an intense phase-shaped pulse in a learning control loop.

1. Introduction

Mode-selective photochemistry has been a longstanding impetus for coherent control.[1] Along the way, the dream of exciting a specific bond has dimmed for various reasons.[2] Fast relaxation, complicated mode structure, imperfect knowledge of the inter-nuclear potentials along arbitrary coordinates, and the distorting influence of the strong external light field have all been challenging obstacles. However, recent theoretical[3−6] and experimental advances have achieved successful control of molecular ionization and dissociation,[7,8] atomic and molecular fluorescence,[9−11] the shape of electronic wave packets,[12,13] and semiconductor currents.[14,15] Strongly coupled systems, such as molecular liquids, are so complicated that it is difficult and often impossible to calculate optimal control fields, and so recent efforts have used feedback.[4,8,9] Experiments in this area were pioneered by Kent Wilson, who first used learning control techniques to change the fluorescence of a dye molecule in solution.[9]

We consider a multimode molecular liquid excited by an intense laser pulse whose bandwidth is narrow compared to the intramolecular vibrational structure. Normal modes in the molecule may be excited by Raman scattering. Efficient excitation to a specific mode may occur via *stimulated* Raman scattering (SRS), but the Stokes light must build up from noise. SRS could be controlled through seeding the Stokes light with a weak field from an external source, but here we propose a more general method based on *strong-field* coupling between electronic and rovibrational degrees of freedom. Strong field *self-phase modulation* (SPM) can provide a controllable coherent continuum to seed any linear combination of modes via SRS. Thus, the strong-field molecular polarizability can be used as a pathway to controlling the vibration of the molecule with the light pulse.[16] Since the connection between incident pulse shape and final mode selection is far from obvious, this problem lends itself well to learning control algorithms, where the SRS spectrum can be used as feedback.

We have constructed an automated learning apparatus to explore nonlinear vibrational control mechanisms in molecular liquids. By focusing intense, shaped ultrafast laser pulses into our liquid sample and using signatures of SRS and SPM in the forward scattered light as feedback, we were able to reshape the laser pulses to achieve desired forward scattered spectra. The measured spectra were used as input for an evolutionary learning procedure based on a genetic algorithm (GA). This algorithm ran on a computer, which controlled an acousto-optic modulator (AOM) pulse shaper.[18] The algorithm generated new pulse shapes based on the success of previous ones in achieving predetermined goals.

2. Experimental Section

The shaped pulses originated from a Kerr lens mode-locked (KLM) titanium sapphire laser, which produced 100 fs pulses with about 5 nJ of energy at a central wavelength of 790 nm. The pulses were temporally dispersed to 150 ps in a single grating expander and amplified to 2 mJ in a regenerative amplifier at 10 Hz. The output of the amplifier was split to form two beams. One beam was sent to the pulse shaper, and the other was used as an unshaped reference for spectral interferometry[20] measurements of the shaped pulses. The pulse shaper consists of a zero dispersion stretcher with an AOM in the Fourier plane, where different colors in the light pulse map to different positions on the modulator. The AOM carries a shaped acoustic travelling wave, which diffracts different colors with different phases and amplitudes. These colors are reassembled at the output of the pulse shaper, yielding a temporally shaped laser pulse. To compensate for the low efficiency of the pulse shaper (10−15%) we reamplified the shaped pulses in a low gain multipass amplifier and then sent them into a single grating compressor to produce shaped pulses with a minimum pulse width of under 150 fs and an energy of about 1 mJ. For the feedback experiment, the spectral intensity remained constant, and the spectral phase of the shaped pulses was controlled by the GA. The overall intensity fluctuations due to laser noise were about 10%.

The GA started with a collection (population) of random pulse shapes (individuals). The genetic code of each individual was the spectral phase sampled at thirty different wavelengths. Each individual was evaluated by measuring its ability (fitness) to generate the spectrum that most resembled a target spectrum. New pulse shapes (next generation) were generated by combining elements of successful pulse shapes from the current generation (mating), and by adding a small amount of random phase (mutation). We used two point crossover and 5% mutation in our implementation of the GA.[21]

As an initial assessment of the capabilities of the apparatus, we studied nonlinear frequency shifts of intense light propagating through 1 cm of liquid CCl_4. One set of goals was established based on the observation of periodic spectral modulations in the measured transmission spectra when a transform limited pulse entered the cell. These modulations are

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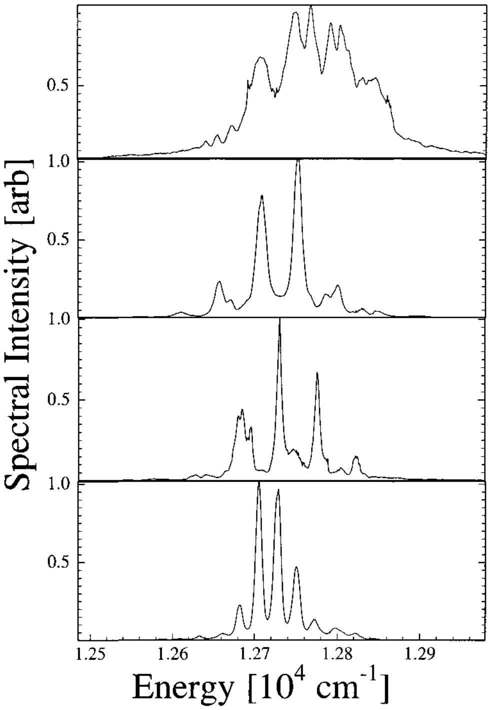

Figure 1. SPM spectra in CCl_4. Top part shows the spectrum for a transform limited pulse incident on the sample. Following parts show spectra for shaped pulses incident after the GA has converged to three separate targets.

typical spectral features for pulses that have undergone SPM under the influence of an intensity dependent index of refraction.[22] We used the genetic algorithm to enhance these modulations. We were able to control their frequency and phase by altering the shape of the driving pulse. Figure 1 shows the spectra of four different pulses after having propagated through the CCl_4 sample.

The optimal shapes for generating these spectra were measured using spectral interferometry. A propagation calculation assuming SPM to be the dominant mechanism responsible for the modulations[23] reproduced their phase and frequency dependence.

Once we had evidence that we were able to control intensity modulations in the spectrum by changing the phase of the shaped pulse through SPM, we attempted to control the interaction between the shaped laser pulse and the vibrational modes of a multi-mode molecule. The idea was that electronic mechanisms such as SPM would allow the driving laser pulse to selectively excite one of possibly many vibrational modes. The forward scattered radiation could once again serve as a diagnostic and as feedback for the GA. One would not expect to see any backward scattered Stokes radiation because of the short duration of the shaped pump pulse (1 ps).[24]

With an unshaped pulse focused into a 10 cm long sample of methanol, the spectrum shown in Figure 2a was obtained. The two peaks in the spectrum correspond to Stokes light with $\delta\nu = 1$ for the symmetric and asymmetric C−H stretch modes. Using samples less than 1 cm in length, and without focusing, we were not able to see any evidence of SRS. The sample length and lens focal length we used for all the data shown are 10 and 40 cm, respectively. The first feedback goal was to maximize the contrast between the two Stokes peaks and the background light resulting from SPM. This goal resulted in the spectrum shown in Figure 2b. The next goal was to generate spectra with each peak separately. These spectra, shown in Figure 2c, correspond to exciting one or another of the two modes alone.

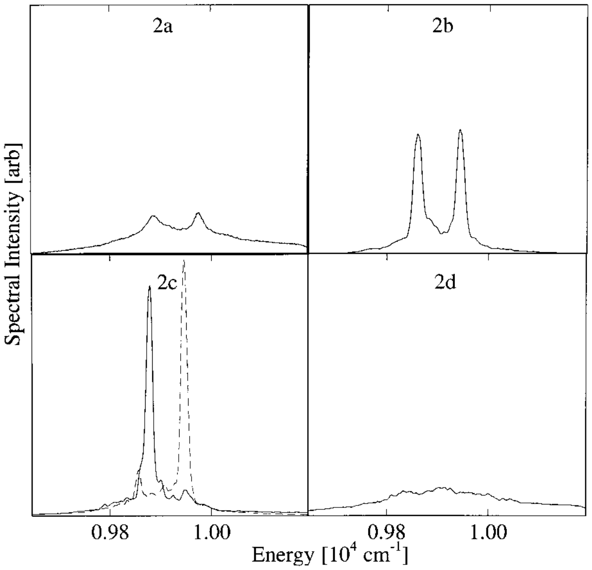

Figure 2. SRS and SPM spectra of the C−H stretch modes of CH_3-OH excited by intense shaped ultrafast radiation. The pulse shape was derived through a GA designed to optimize various targets: (a) spectrum for a transform-limited 150*fs* pulse; (b) optimized for simultaneous excitation of the symmetric and antisymmetric stretch; (c) optimized for only the asymmetric (solid) or symmetric (dashed) mode; (d) optimized to suppress SRS in this region.

This mode selection was achieved by changing only the phase of the driving pulse. It is interesting to note that the frequency of the asymmetric stretch stokes peak is different when it is excited alone from when it is excited concurrent with the symmetric stretch. However, this has not yet been investigated systematically.

The Stokes shift for these two modes is large compared to the bandwidth of the driving laser pulse. Equivalently, the Raman excitation was nonimpulsive and therefore one would not expect to control mode selectivity through seeding of the stokes radiation with the laser light directly. Our final feedback goal was to eliminate all forward scattered light at either of the two Stokes frequencies and the resulting spectrum is shown in Figure 2d.

3. Discussion

Coupling between molecular polarizability, which gives rise to SPM, and vibration could account for selective excitation of the symmetric or asymmetric stretch modes in methanol. The CCl_4 experiment shows that light generated by SPM is very sensitive to the input pulse shape. Thus the molecular polarizability might effectively control vibrational excitation by providing seed light for SRS into one or more Raman-active modes.

A natural starting point for trying to understand the control mechanism is to examine the fittest driving pulses generated by the feedback learning process. Figure 3 shows spectrograms for the optical pulses that generated the spectra in Figure 2 (with the exception of Figure 2b). These spectrograms $Q(t,\nu)$ were generated by transforming the optical field $E(\nu)$ according to:

$$Q(t,\nu) = \int d\nu' \int dt' S(t',\nu') e^{-(t-t')^2-(\nu-\nu')^2}$$

$$S(t,\nu) = \int E(\nu+\nu') E^*(\nu-\nu') e^{-4\pi i\nu' t} d\nu'$$

The complex field $E(\nu)$ was derived from the phase shifts applied to the A-O modulator, which were calibrated by spectral interferometry with the unshaped reference.[25] The spectrograms of the top five individuals in the generation that produced the

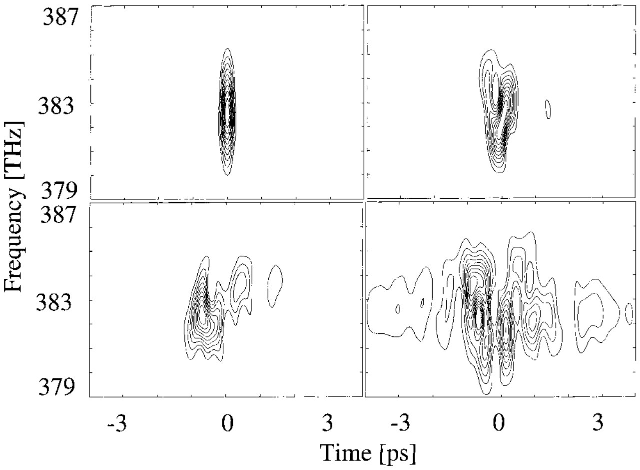

Figure 3. Optical spectrograms for the laser pulse shapes that produce the target SRS spectra in Figure 2. Top left: Nearly Fourier transform-limited incident pulse. Top right: pulse that produced spectrum 2d. Bottom left: pulse that produced spectrum 2c, solid line. Bottom right: pulse that produced spectrum 2c, dashed line.

spectra in Figure 2 were averaged to produce the plots in Figure 3. The physical process responsible for GA optimization is not easy to discern here. We note that while a solution provided by the GA may be sufficient, it may also contain many unnecessary characteristics. The challenging task remains to determine which features in these complicated pulse shapes are necessary for mode-selective excitation. Nonetheless, comparisons between measured pulse shapes and SPM calculations in CCl_4 confirm that the GA pulse shapes contain important information about the control mechanism.

Propagation effects play an important role in our selective mode excitation. This may be seen as a disadvantage in terms of not having a uniform spatial effect on the liquid sample. However, sample cells can easily be constructed that have a separation between a “buildup region” where the light undergoes any frequency modulations that are required to effect control and an “active region” where all the molecules are vibrationally controlled.

The resolution of the measurement was limited by technical systematics to approximately 100 Ghz.

4. Conclusion

The use of Raman scattering in conjunction with other nonlinear but nonresonant processes as a control technique is an attractive approach because of its generality. The technique can be applied to a wide range of molecules with a wide range of light sources since no atomic or molecular resonance is being exploited. Transparent molecular liquids with low group velocity dispersion and nondegenerate vibrations are ideal candidates for this type of control. The requirements on the control laser are that the photon energy be larger than the vibrational energies and that the pulse have sufficient bandwidth and energy to reach the threshold for SRS.

Future goals include looking at vibrational overtones and combining closely spaced modes to activate single bonds in molecules. This might allow for controlling reactions in bimolecular solutions that depend sensitively on bond lengths for activation.

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