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Spectroscopy with shaped femtosecond pulses: styles for the 1990s

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ABSTRACT

Timed sequences of femtosecond pulses produced by pulse-shaping techniques have been used to achieve improved optical control over molecular motion in crystalline solids. Selected lattice vibrational modes in an organic molecular crystal have been driven repetitively by appropriately timed pulse sequences in a manner analogous to that in which a child on a swing is pushed repetitively with timed mechanical forces. Repetitive driving with a pulse sequence results in larger lattice vibrational amplitudes and improved mode-selectivity compared to driving with a single pulse. Numerous applications of pulse-shaping techniques in femtosecond spectroscopy are anticipated.

1. INTRODUCTION

Ongoing advances in ultrafast laser technology¹⁻⁴ have led to the generation and spectroscopic utilization of pulses whose duration is shorter than the time required for most nuclear motions, e.g. molecular translations or rotations, lattice or molecular vibrations, etc. In principle, these elementary motions -- and the chemical and structural rearrangements involving them -- can now be observed in real time. In practice, such observations require not only short pulses but mechanisms through which the pulses can initiate and monitor the motion of interest. The possibility of exercising optical control over molecular motion has stimulated an intense theoretical^{5,6} and experimental⁷⁻¹² effort. New spectroscopic techniques have been explored and new ways of crafting ("shaping") the laser pulses themselves^{13,14} have been invented. In this letter we report the first application of specially shaped femtosecond pulse trains to achieve improved control over elementary molecular motions.

2. IMPULSIVE STIMULATED SCATTERING AND THE LIMITATIONS OF SINGLE-PULSE EXCITATION

Our experiments utilize impulsive stimulated Raman scattering (ISRS), a spectroscopic technique in which an ultrashort pulse exerts a sudden ("impulse") driving

force on Raman-active vibrational modes to initiate coherent vibrational motion. For ISRS excitation to occur, the pulse duration must be short compared to the vibrational oscillation cycle. The uncertainty-limited spectral bandwidth of the pulse then exceeds the vibrational frequency, and stimulated Raman scattering can occur through mixing among frequency components contained within the bandwidth. ISRS provides a mechanism through which femtosecond pulses can be utilized to influence and observe lattice and molecular motion in ground electronic states^{7,8}.

Although impulsive stimulated scattering has proved useful for examination of vibrational motions in a variety of liquids and solids, the extent of control over molecular motion is nevertheless limited. First, the coherent vibrational response driven by ISRS is usually small, e.g. on the order of 10^{-4} Å for molecular stretching modes or translational optic phonons in crystalline solids. Substantially larger amplitudes would allow spectroscopic characterization of well defined, far-from-equilibrium lattice and molecular structures, and could even make possible the use of coherent vibrations to assist chemical reactions^{15,16}. Second, the degree of mode selectivity in ISRS is limited. Many Raman-active modes may respond simultaneously to the impulse force exerted by a sufficiently short pulse.

3. FEMTOSECOND PULSE-SHAPING

Terahertz-rate pulse trains are generated by using a Fourier transform pulse shaping technique¹⁴. Briefly, the constituent optical frequency components of an incident femtosecond pulse are spatially dispersed by a grating and collimated by a lens which directs them into a spatially varying phase and/or amplitude mask. The altered frequency components are then recombined by a second lens and grating to produce a correspondingly altered temporal profile. The pulse shape which results is the Fourier transform of the pattern transferred by the mask onto the spectrum. By using this technique, complex temporal profiles have been produced and encoding and decoding of femtosecond pulses have been demonstrated¹⁷. In the present work we generate trains of femtosecond pulses at THz repetition rates by using phase-only masks, which are patterned with periodic repetitions of a suitable, pseudorandom binary phase code^{14,18}. As described previously^{14,17}, the phase masks are fabricated on fused silica substrates, which are patterned by standard microlithographic techniques and etched by reactive ion etching. The cross-correlation of a typical pulse sequence generated in this manner with a single 75 fsec pulse is shown in Figure 1. Approximately 25 distinct phase patterns fit onto a 1/2-inch diameter substrate. For the current experiment, we designed the masks so that each pattern corresponds to a different pulse repetition rate. A desired repetition rate can be selected simply by translating the corresponding phase pattern into the beam path.

4. EXPERIMENTAL

Our experiment is arranged in a transient grating geometry, shown schematically in the inset to Fig. 2. A colliding-pulse-modelocked (CPM) ring dye laser² and copper vapor laser pumped dye amplifier system³ provides 75-fsec pulses at a 0.62- μ m wavelength with a 5- μ J pulse energy and an 8.6-KHz repetition rate. A small portion of the amplified output is split off to serve as the probe beam; the remaining portion is converted into a suitable THz-rate pulse sequence by the pulse shaping apparatus (described above) and

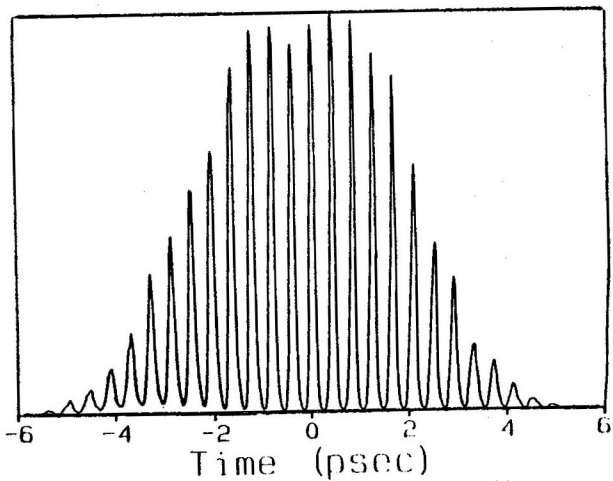


Figure 1. A sequence of femtosecond pulses (repetition rate of 2.39 THz or 419 fsec spacing) produced through pulse-shaping techniques. A single femtosecond pulse was passed through two gratings, two lenses, and a spatially varying phase mask to produce the output shown. The output can be used to exert repetitive "impulsive" driving forces on selected vibrational modes to achieve larger vibrational amplitudes than can be driven with a single pulse.

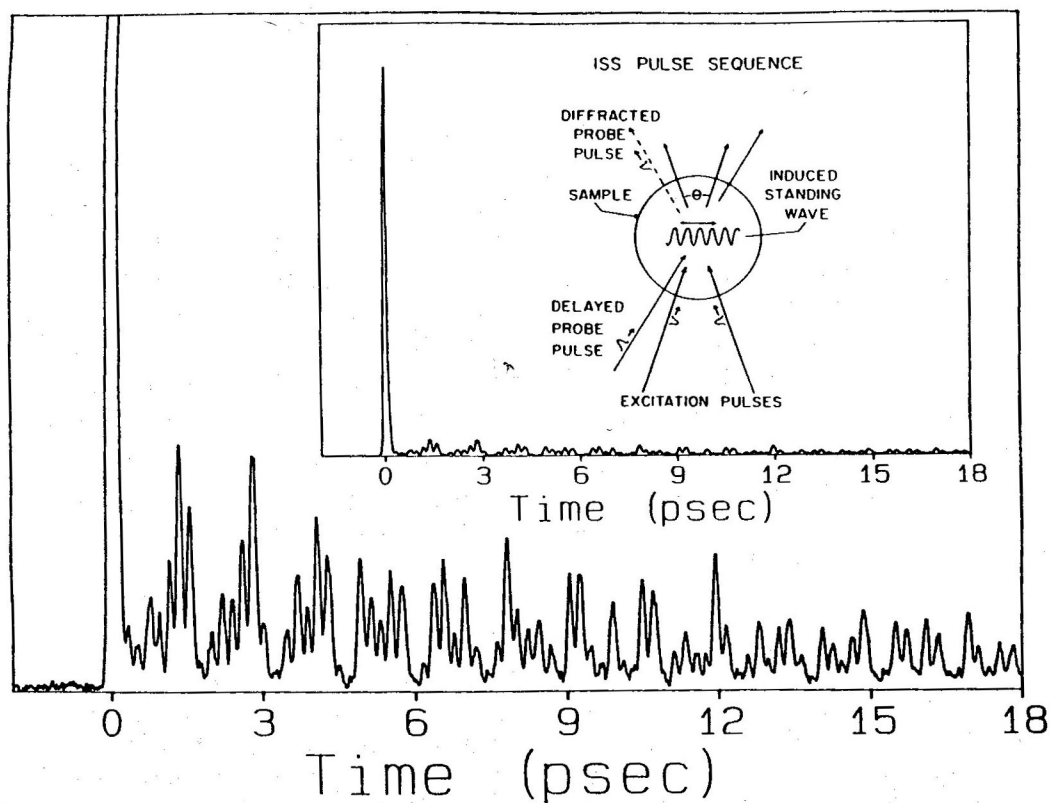


Figure 2. ISRS data from the α -perylene organic molecular crystal for light polarizations parallel to the crystallographic axis b . Several phonon modes are excited by the femtosecond excitation pulses. This gives rise to the characteristic "beating" pattern which contains sum and difference frequencies. The beating pattern changes somewhat over time because the modes have different dephasing rates. The "spike" at $t = 0$ is a purely electronic response of the crystal to the excitation pulses. Since the electronic response is essentially instantaneous, this feature of the data only appears while all three pulses are inside the sample. It provides a measure of the excitation pulse duration. The inset shows the relative signal intensities of the electronic "spike" and the vibrational response.

split to yield two pump beams. All three beams are focused to a common spot in the sample. The diameters of the focused pump and probe beams are about 90 μ . The beams cross in a noncoplanar, phase-matched geometry, with a full angle of about 50° between the beams. The relative delay between the pump beams is set to zero, so that they produce a "grating" pattern of coherent vibrational excitation through ISRS. The vibrational response is monitored by measuring the coherent scattering ("diffraction") intensity of the variably delayed probe pulse. For data acquisition, the probe beam is chopped, the diffraction intensity is measured with a power meter and lock-in amplifier, and the probe delay is scanned under computer control by using a stepper-motor-driven translation stage.

The sample was a 1-mm thick single crystal of α -perylene. Perylene was purified by recrystallization and extensive zone-refining, and single crystals were grown from the melt by the Bridgman method. The sample was mounted on a cold finger and cooled to approximately 5 K. In the experiments, each beam was linearly polarized with all the polarizations parallel to each other and to either the a or b crystallographic axis.

5. MULTIPLE-PULSE ISRS RESULTS

We have achieved improved control over molecular motion by using terahertz-repetition-rate trains of femtosecond pulses for repetitive impulsive excitation in ISRS experiments. In particular, by matching the pulse repetition rate to the vibrational frequency, we have demonstrated selective amplification of individual phonon modes in α -perylene molecular crystal. This crystal is of special interest in connection with excited-state dimerization (actually excimer formation) which may be phonon-assisted^{19,20}. In the ground state the planar perylene molecules align in "sandwich" pairs; upon optical absorption two molecules in a pair move closer together along a path which is believed to coincide to a substantial degree with a 104-cm⁻¹ translational optic phonon mode²¹. Single pulse ISRS experiments on α -perylene crystals were reported previously²², and simultaneous excitation of the 104 cm⁻¹ mode together with low frequency librational modes at 33, 56, and 80 cm⁻¹ was observed. As we shall see, multiple-pulse ISRS makes possible a degree of mode selectivity not available with single-pulse ISRS and opens the way for increased vibrational amplitudes.

As a control we recorded ISRS data from α -perylene excited by a single pair of (unshaped) excitation pulses. The data, shown in Fig. 2 for pulses polarized parallel to the b axis, are similar to those published previously²². The signal consists of a sharp peak at $t=0$, due to the essentially instantaneous nonlinearity associated with distortion of the electronic wave functions, followed by a signal due to optic phonons excited through ISRS. Two points are of note. First, the intensity of the ISRS signal is only about 4% of that due to the electronic scattering peak, which provides an internal intensity calibration. Second, the ISRS diffraction intensity presents an irregular pattern caused by beating between several simultaneously excited phonon modes. Fourier analysis of the scattering data indicates excitation of the known α -perylene modes at 33, 56, 80, and 104 cm⁻¹. Similar data are observed with the polarizations parallel to the a crystallographic axis, although the details of the oscillatory ISRS signal are altered because the various modes are excited with different relative amplitudes.

The data in Fig. 2 illustrate the two main limitations of single-pulse ISRS, i.e. small vibrational amplitude and lack of mode-selectivity. Multiple-pulse excitation ("multiple-

pulse ISRS") can be used to help overcome these limitations. We have demonstrated this point by using multiple-pulse ISRS to selectively and individually drive the 80 cm^{-1} librational mode (an in-phase libration of the molecule pairs) and the 104 cm^{-1} translational mode in α -perylene crystal. Data obtained using the pulsetrain shown in Fig. 1, which is timed to match the vibrational period of the 80 cm^{-1} mode, are shown in Fig. 3. Initially, the signal is dominated by the crystal's electronic responses to each of the pulses in the sequence. After about ten pulses, however, ISRS signal due to the amplified 80 cm^{-1} mode becomes apparent. By the end of the input pulse train (at $t > 3 \text{ ps}$), the ISRS signal becomes as intense as the strongest electronic scattering peak. Also, the ISRS oscillations are essentially monochromatic, as confirmed by Fourier analysis of the scattering data. Figure 4 shows the same data on a longer time scale. The coherent oscillations decay with a $1/e$ time of 14.3 ps , indicating a phonon dephasing time of 28.6 ps . Note that the oscillations in signal occur at twice the vibrational frequency and decay at twice the decay rate because the diffraction intensity is proportional to the square of the dielectric response (and therefore to the square of the vibrational displacement) in the medium.

The multiple-pulse ISRS data shown demonstrate substantial amplification of the vibrational response and considerable enhancement of mode selectivity compared to single-pulse ISRS experiments. We have also performed multiple-pulse ISRS experiments with the repetition rate of the input pulse train detuned slightly from the 80 cm^{-1} librational period. As the detuning is increased the strength of the phonon response gradually decreases, but the oscillations are still monochromatic with the same frequency and decay rate. In addition to driving the 80 cm^{-1} mode, we have also used multiple-pulse ISRS to drive the 104 cm^{-1} mode whose motion is essentially a vibration of neighboring perylene molecules in a pair against each other²³. Improved mode-selectivity and vibrational amplitude were again obtained.

We have carried out numerical simulations to model our experimental results. Our modelling is an adaptation of an analysis which was previously developed for single pulse ISRS experiments and which has been described in detail elsewhere²⁴. We begin our analysis of multiple pulse ISRS by describing the intensity profile $I(x,t)$ of the shaped pump pulse train incident on the sample, using the following approximate form:

$$I(x,t) = \sum_{n=0}^{N-1} I_0 \exp \left[\frac{-[t - (n - \frac{N}{2})T]^2}{\tau_p^2} - \frac{(\frac{N}{2} - n)^2}{\tau_{env}^2} \right] \cos^2 kx \quad (1)$$

where N is the number of pulses in the pulse train, T is the spacing between the pulses, τ_p is a measure of the pulse duration of the individual pulses in the sequence, τ_{env} is a measure of the duration of the pulse train itself, and I_0 is the peak intensity. The first term in the exponential gives the temporal profile of the individual pulses (assumed to be gaussian) and the second term describes the temporal profile of the pulse train (also assumed to be gaussian). The $\cos kx$ term describes the spatial interference of the two crossed pump beams. The vibrational response of the sample is characterized by an impulse response function (Green's function) $G(t)$ given by:

$$G(t) = \frac{C e^{-\gamma t} \sin \omega t}{\omega} \quad (2)$$

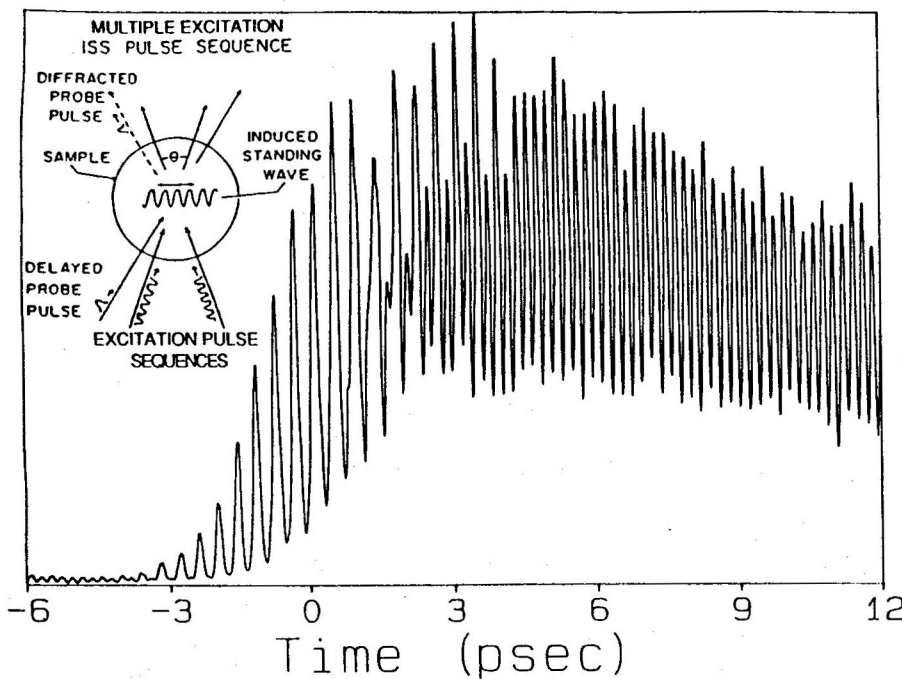


Figure 3. ISRS data from the perylene crystal driven by the pulse sequence shown in Fig. 1, which is tuned to drive the 80 cm^{-1} mode. The diffracted signal from the mode grows stronger with each successive pulse, eventually reaching intensity levels comparable to the strongest electronic response. Selective amplification of the 80-cm^{-1} mode has been demonstrated.

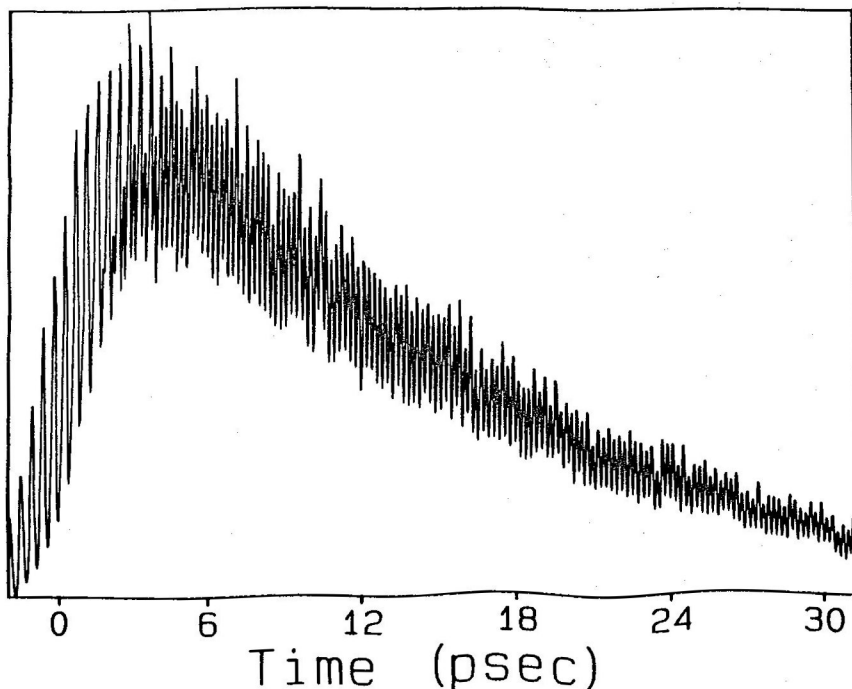


Figure 4. ISRS data from α -perylene collected as in Fig. 3, but extending to longer time scales. The data indicates a phonon dephasing time of 28.6 psec at 5 K.

where γ is the damping rate, ω is the natural vibrational frequency, and C is a constant. The convolution of $I(x,t)$ and $G(t)$ gives the time- and space-dependent vibrational response, $Q(x,t)$, i.e.

$$Q(x,t) = \int_{-\infty}^t dt' I(x,t') G(x,t-t') \quad (3)$$

which is proportional to the variation in dielectric constant, $\delta\epsilon(x,t) \propto Q(x,t)$. The diffraction efficiency is proportional to the square of the dielectric response at the grating peaks, i.e. $|\delta\epsilon|^2(x=0,t)$. The actual ISRS signal is taken to be the convolution of $\delta\epsilon^2(t)$ over the probe pulse intensity profile (assumed to be identical to the profile of the individual pulses in the pump pulse sequence). In Fig. 5 we show the simulated results for resonant excitation of the 80 cm^{-1} mode. The numerical results are in excellent agreement with the data of Fig. 3, even though only the 80 cm^{-1} librational mode of α -perylene is included in the vibrational Green's function $G(t)$. Our omission of the contributions of the other vibrational modes is justified due to the strong mode selectivity of the multiple pulse ISRS technique.

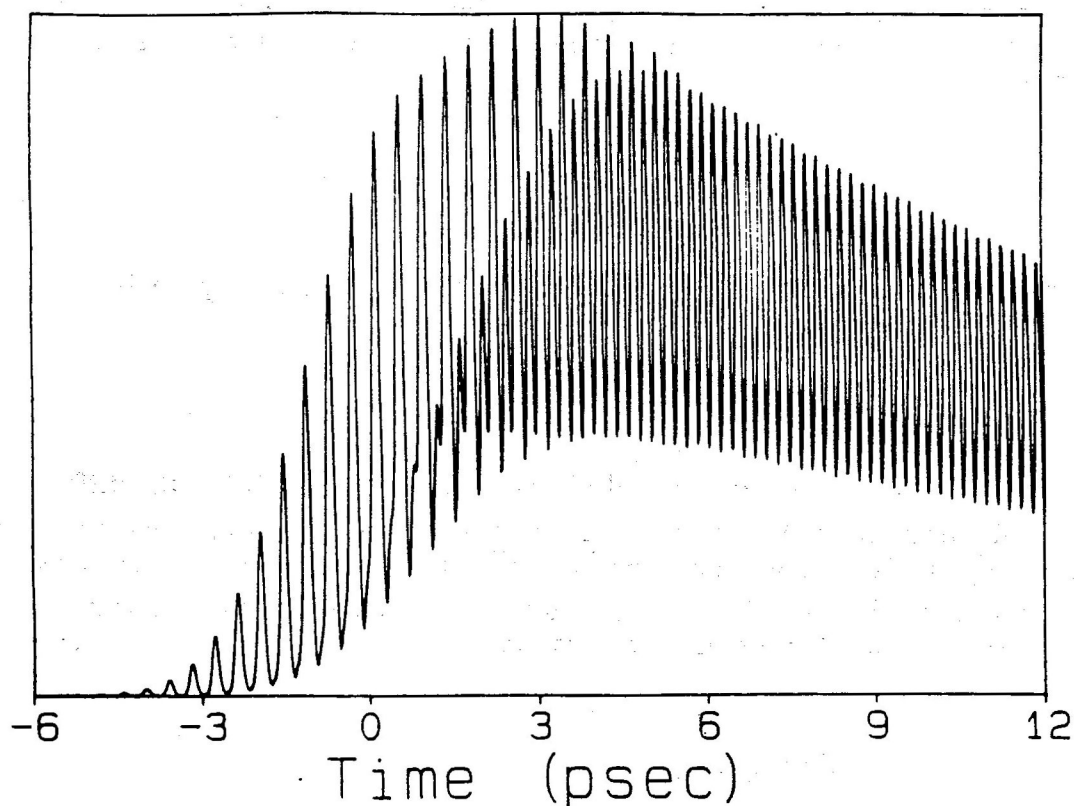


Figure 5. Simulation of the data in Fig. 3, assuming a Gaussian temporal profile for the excitation pulsetrain. The simulation closely resembles the experimental data, illustrating the mode-selectivity of multiple-pulse ISRS excitation. See text.

6. INHOMOGENEOUS BROADENING: IS VIBRATIONAL LINE-NARROWING POSSIBLE WITH MULTIPLE-PULSE ISRS?

Another aspect of "mode selectivity" warrants comment. It is well known that local variations (i.e. inhomogeneity) in condensed-phase structure or composition can lead to shifts of vibrational frequencies. This gives rise to inhomogeneous broadening of vibrational lines in spontaneous Raman spectra^{25,26}. Multiple-pulse ISRS excitation can be used to selectively amplify only those modes which are closest to resonance with the pulse sequence selected, i.e. to amplify one part of a vibrational line. This would appear to make possible a kind of vibrational line-narrowing experiment. For example, one might expect that for vibrational line centered at 100 cm⁻¹, with a 5 cm⁻¹ homogeneous linewidth which is masked by 50 cm⁻¹ of inhomogeneous broadening, multiple-pulse ISRS excitation with the excitation pulsetrain timed to excite modes at 120 cm⁻¹ would result in ISRS signal showing 120-cm⁻¹ oscillations decaying at the homogeneous dephasing rate. In general, one might expect the multiple-pulse ISRS signal to vary in frequency as the timing of the excitation pulse sequence is varied for an inhomogeneously broadened line but not for a homogeneously broadened line. Here we discuss this possibility.

For simplicity, we assume that the excitation pulse train consists of N identical pulses of infinitely short duration, separated by time T, the last of which arrives at the sample at t = 0, i.e.

$$I(t) = \sum_{n=0}^{N-1} \delta(t + nT) \quad (4)$$

If several uncoupled modes α are excited, the total dielectric response is given by

$$\delta\epsilon(t) = \sum_{\alpha} \left(\frac{\delta\epsilon}{dQ_{\alpha}} \right) Q_{\alpha}(t) \quad (5)$$

where $Q_{\alpha}(t)$ is the coherent vibrational displacement and $(\delta\epsilon/dQ_{\alpha})$ is the differential polarizability of mode α . In the case of a single inhomogeneously broadened line, the dielectric response is again given by the sum over all vibrational displacements. However, in this case there is a continuous distribution of frequencies $P(\omega_{\alpha})$ spanning the inhomogeneous linewidth, yielding the expression

$$\begin{aligned} \delta\epsilon(t) &= a \int d\omega_{\alpha} P(\omega_{\alpha}) Q_{\alpha}(t) \\ &= a \int d\omega_{\alpha} P(\omega_{\alpha}) \int_{-\infty}^t dt' I(t') G(t - t'; \omega_{\alpha}, \gamma_{\alpha}). \end{aligned} \quad (6)$$

Here we have assumed that $(\delta\epsilon/dQ_{\alpha})$ is the same throughout the inhomogeneously broadened line, and included the term in the constant a. We have also indicated explicitly

the inhomogeneity of ω_α and γ_α in the response function $G(t)$; hereafter we assume that only the frequency varies. In that case Eq. (6) can be written for $t > 0$ as

$$\delta\varepsilon(t) = a \int d\omega_\alpha \left[\frac{P(\omega_\alpha)}{2i\omega_\alpha} \right] \sum_{n=0}^{N-1} \exp[-\gamma(t+nT)] \{ \exp[i\omega_\alpha(t+nT)] - \text{c.c.} \}. \quad (7)$$

This yields, after some work, the result

$$\delta\varepsilon(t) = a \int d\omega_\alpha \left[\frac{P(\omega_\alpha)}{\omega_\alpha} \right] \left[\frac{1 - 2e^{-\gamma NT} \cos \omega_\alpha NT + e^{-2\gamma NT}}{1 - 2e^{-\gamma T} \cos \omega_\alpha T + e^{-2\gamma T}} \right]^{\frac{1}{2}} e^{-\gamma t} \sin(\omega_\alpha t + \phi_\alpha) \quad (8)$$

where the phase ϕ_α is given by

$$\phi_\alpha = \tan^{-1} (B_\alpha/A_\alpha) \quad (9)$$

with

$$A_\alpha = (1 - e^{-\gamma T} \cos \omega_\alpha T) + e^{-\gamma NT} \left[(e^{-\gamma T} - \cos \omega_\alpha T) \cos \omega_\alpha (N-1)T + \sin \omega_\alpha T \sin \omega_\alpha (N-1)T \right] \quad (10)$$

and

$$B_\alpha = e^{-\gamma T} \sin \omega_\alpha T + e^{-\gamma NT} \left[(e^{-\gamma T} - \cos \omega_\alpha T) \sin \omega_\alpha (N-1)T - \sin \omega_\alpha T \cos \omega_\alpha (N-1)T \right] \quad (11)$$

Equation (8) can be simplified considerably by considering the limit of a large number of pulses N . Once the number of pulses exceeds the homogeneous dephasing rate, i.e. $e^{-\gamma NT}$ approaches zero, the system reaches steady-state and additional pulses change nothing. From the point of view of mode-selectivity, one clearly should strive to reach this limit in which the power spectrum of the driving force is narrower than the homogeneous linewidth. Equation (8) can be rewritten in this limit as

$$\delta\varepsilon(t) = a \int d\omega_\alpha \left[\frac{P(\omega_\alpha)}{\omega_\alpha} \right] \left| \frac{e^{-\gamma t} \sin(\omega_\alpha t + \phi_\alpha)}{[1 - 2e^{-\gamma T} \cos \omega_\alpha T + e^{-2\gamma T}]^{\frac{1}{2}}} \right| \quad (12)$$

with

$$\phi_{\alpha} = \tan^{-1} \left[\frac{e^{-\gamma T} \sin \omega_{\alpha} T}{1 - e^{-\gamma T} \cos \omega_{\alpha} T} \right] \quad (13)$$

Equation (12) shows that multiple-pulse excitation of an inhomogeneously broadened vibrational line does result in selective excitation of those oscillators with frequencies near the driving frequency $\omega_0 = 2\pi/T$. The amplitude profile of oscillators is given from Eq. (12) by

$$|Q_{\alpha}| \propto \left[1 - 2e^{-\gamma T} \cos \omega_{\alpha} T + e^{-2\gamma T} \right]^{-\frac{1}{2}} \\ \approx \Pi \left[(\omega_{\alpha} - \omega_0)^2 - \gamma^2 \right]^{-\frac{1}{2}} \quad (14)$$

The last result applies for $\omega_{\alpha} \approx \omega_0$, and shows that the energy spectrum of inhomogeneous oscillators peaks at the driving frequency and falls off with a Lorentzian profile whose width is given by the homogeneous dephasing rate. Excitation of a selected part of the inhomogeneously broadened line with a series of ultrashort pulses is therefore possible.

What happens to ISRS signal from an inhomogeneously broadened line as the number of excitation pulses is increased? If just one excitation pulse is used, the entire line is excited uniformly and time-dependent ISRS signal shows oscillations at the central frequency which decay rapidly due to inhomogeneous dephasing of the different frequency components throughout the line. The signal decay time is given by the spectral linewidth, and no information is provided about homogeneous versus inhomogeneous dephasing. Multiple-pulse excitation with increasing numbers of pulses in a sequence excites an increasingly narrow distribution of oscillators within the line, approaching in the limit of large N a Lorentzian distribution with the homogeneous linewidth. However, consideration of both the amplitude *and phase* distributions of excited oscillators shows that *the total coherence given by Eq. (8) or (12) does not change as the number of excitation pulses is increased from 1 to large N* . Although the amplitude profile becomes narrow at large N , the differing phases of the oscillators yield rapid destructive interference and decay of ISRS signal. Numerical simulations of ISRS signal from inhomogeneously broadened lines showed no significant dependence on the number of excitation pulses used.

It has long been appreciated that conventional time-resolved coherent anti-Stokes Raman scattering (CARS) measurements cannot yield information about homogeneous dephasing²⁷. The excitation source, usually a pair of picosecond pulses whose frequency difference equals ω_0 , produces the same vibrational excitation profile as a series of many femtosecond pulses. If the excitation spectral bandwidth is less than the homogeneous linewidth γ , then the excitation (and usually probe) pulse duration exceeds the homogeneous dephasing rate γ^{-1} and so the rate cannot be resolved. Excitation with a femtosecond pulse sequence in the large- N limit (i.e. with a pulse sequence whose power spectrum is narrower than γ and whose duration exceeds γ^{-1}) and probing with a single femtosecond pulse is analogous to excitation with a pair of picosecond pulses that have abrupt (femtosecond duration), synchronized cutoffs and probing with a femtosecond

probe pulse which could be synchronized with femtosecond precision to the excitation cutoffs. If such pulses were produced, they could be used for time-resolved observation of individual vibrational oscillation cycles as in ISRS. Our present results show that time-resolved CARS measurement of homogeneous vibrational linewidths would still be impossible in general. Although vibrational lifetimes can be measured with various pump-probe techniques, line-narrowing experiments similar to echo or hole-burning techniques used to probe spin or electronic degrees of freedom depend on exciting the system under study beyond its linear-response limit. Large-amplitude ISRS vibrational excitation remains an important goal for us, but has not yet been demonstrated.

5. CONCLUDING REMARKS

In summary, the use of specially shaped femtosecond pulse sequences has been shown to improve the extent to which molecular motion can be controlled through ISRS. Amplification of vibrational amplitudes and enhancement of mode selectivity have been demonstrated. It should be emphasized that this is an initial demonstration and that the pulse-shaping technology is itself still evolving. Very recently, "square" pulse envelopes which will facilitate examination of more heavily damped modes and study of vibrational inhomogeneity have been generated¹⁸. In addition, electronically controllable pulse shaping on femtosecond time scales has been demonstrated^{13,28,29}. These developments could facilitate compensation for vibrational anharmonicity at large amplitudes, for example, by allowing the time between successive pulses in a sequence to be varied as necessary. It is clear that pulse-shaping will play an important role in femtosecond optical manipulation of molecular behavior.

6. ACKNOWLEDGMENTS

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