Reports

Femtosecond Pulse Sequences Used for Optical Manipulation of Molecular Motion

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Optical control over elementary molecular motion is enhanced with timed sequences of femtosecond (10^{-15} second) pulses produced by pulse-shaping techniques. Appropriately timed pulse sequences are used to repetitively drive selected vibrations of a crystal lattice, in a manner analogous to repetitively pushing a child on a swing with appropriate timing to build up a large oscillation amplitude. This process corresponds to repetitively "pushing" molecules along selected paths in the lattice. Amplification of selected vibrational modes and discrimination against other modes are demonstrated. Prospects for more extensive manipulation of molecular and collective behavior and structure are clearly indicated.

THE DEVELOPMENT AND EVOLUTION of femtosecond laser technology (*1–4*) during the 1980s have revolutionized molecular and condensed-matter spectroscopy. It is now routine in many laboratories to carry out direct time-resolved observations of elementary microscopic motions, such as collective vibrations of crystal lattices, molecular vibrations and rotations, and so forth, as well as chemical and physical transformations involving these motions (*5–8*). Increasing attention is now being turned toward not only observation of, but also control over, molecular and collective motion (*8, 9*), often with the goal of reaching unusual nonequilibrium states and facilitating chemical or structural changes that may not occur under ordinary conditions. New ways of "shaping" laser pulses to produce specified pulse sequences have been invented (*10–12*) that offer great promise for exercising such control. One can anticipate that evolution and applications of pulse-shaping technology will propel the femtosecond spectroscopic revolution well into the 1990s.

We report the application of specially shaped femtosecond pulse trains to achieve improved control over elementary molecular motions. Timed sequences of femtosecond pulses have been used to repetitively "push" molecules in an organic crystal along selected lattice vibrational coordinates, in a manner closely analogous to the way a child on a swing may be pushed repetitively to reach an increased amplitude of oscillatory motion. Optical control over molecular motion inside the crystal is enhanced in two ways by using a pulse sequence instead of a single pulse: (i) the amplitude of molecular motion along the selected lattice vibrational coordinate is increased; and (ii) other molecular motions corresponding to lattice vibrational modes with different frequencies are discriminated against.

The experiments exploit the sudden (impulse) driving force that a sufficiently short pulse exerts on a Raman-active vibrational mode through a mechanism called impulsive stimulated Raman scattering (ISRS) (*5, 6*). For an impulse force to be exerted, the ISRS excitation pulse duration must be short compared to the vibrational oscillation period. The force initiates coherent vibrational oscillations that may be monitored by variably delayed probe pulses. ISRS provides a mechanism through which femtosecond pulses can be used to influence and observe lattice and molecular motion.

The extent of control over nuclear motion is limited, however. First, the coherent vibrational response driven by ISRS is usually small, for example, on the order of 10^{-4} Å for molecular displacements in translational optic phonon modes of crystalline solids. Far larger coherent vibrational amplitudes, that is in the angstrom range, could be driven by readily available femtosecond pulses were it not for sample damage which would occur at the high peak intensities required. 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 (*8*). 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.

We have achieved improved control over molecular motion by using terahertz–repetition rate trains (1 THz = 10^{12} Hz) of femtosecond pulses for repetitive ISRS excitation of selected optic phonons in the organic molecular crystal, α-perylene. This crystal is of special interest in connection with an excited state dimerization (actually excimer formation) reaction that may be phonon-assisted (*13*). 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 that is believed to coincide to a substantial degree with a 104-cm^{-1} translational optic phonon mode (*6, 14*). The motion

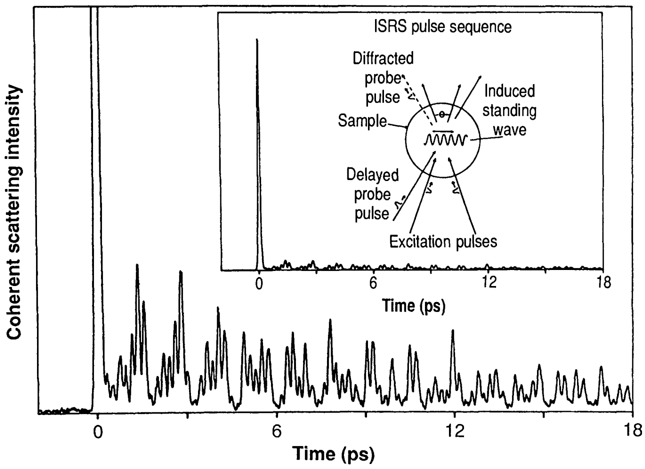

Fig. 1. ISRS data from the α-perylene organic molecular crystal. The femtosecond excitation pulses drive several phonon modes whose combined response yields a characteristic beating pattern. The pattern changes somewhat over time because the modes have different dephasing rates. The "spike" at *t* = 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 as well as an internal calibration for the ISRS response. The inset shows the relative signal intensities of the electronic "spike" and the vibrational response. The data were collected with all pulses linearly polarized parallel to the *b* crystallographic axis.

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of this mode is essentially a vibration of neighboring molecules in a pair against each other.

The experiment is arranged in a transient grating geometry, shown schematically in the inset to Fig. 1. A colliding pulse mode-locked (CPM) ring dye laser (*2*) and copper vapor laser-pumped dye amplifier system (*3*) provide 75-fs, 620-nm, 5-μJ pulses at 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 terahertz–rate pulse sequence by the pulse-shaping apparatus (described below) and split to yield the two excitation beams that overlap temporally and spatially inside the sample. The vibrational response is monitored by measuring the time-dependent diffraction intensity of the probe pulse, whose arrival time at the sample is varied with a stepping motor-controlled delay line. The sample was a 1-mm-thick crystal of α-perylene at 5 K, cleaved in the *ab* crystallographic plane.

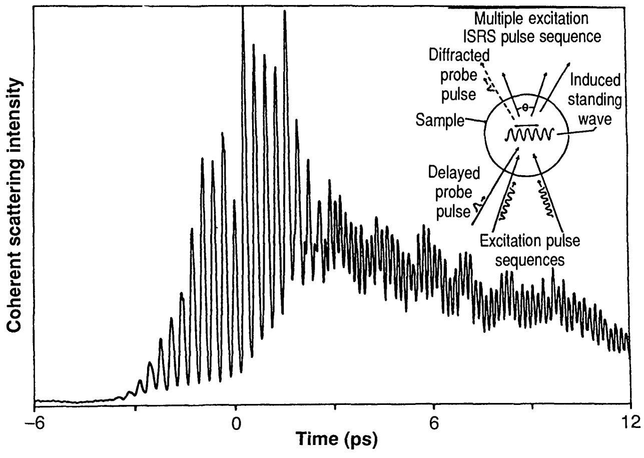

Fig. 3. ISRS data from α-perylene driven by a sequence of (*a*-polarized) pulses spaced at 319 fs to match the vibrational period of the 104 cm^{-1} mode. Selective amplification is again demonstrated.

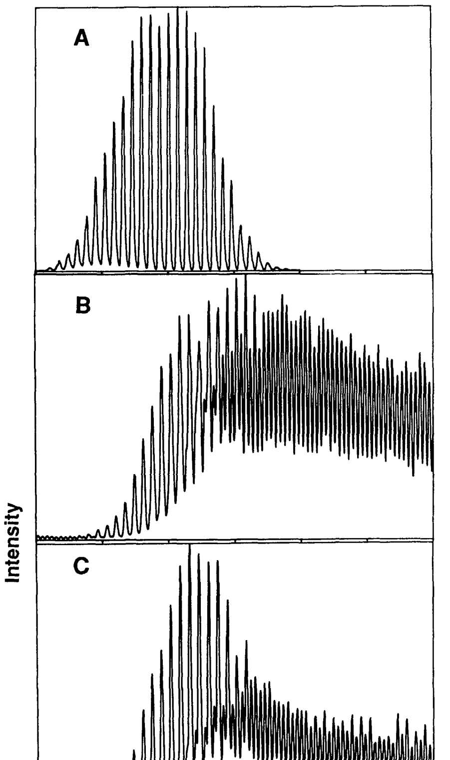

Fig. 2. (**A**) Cross-correlation measurement of a sequence of femtosecond pulses with a repetition rate of 2.39 THz (419 fs between pulses) produced through pulse-shaping techniques. The pulses can repetitively drive a selected vibrational mode to increase the vibrational amplitude. (**B**) ISRS data from the α-perylene organic molecular crystal driven by a sequence of (*b*-polarized) pulses spaced at 419 fs to match the vibrational period of 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 is demonstrated. (**C**) ISRS data from α-perylene driven by a sequence of (*b*-polarized) pulses spaced at 429 fs, slightly off resonance for the 80-cm^{-1} mode. The signal intensity is reduced relative to that in (A), but the vibrational oscillation period is still 419 fs. (**D**) Simulation of data in (B), assuming a Gaussian temporal profile for the excitation pulse train. In (A) through (D), the zero of time is defined as the center of the input pulse train.

The terahertz–rate trains of femtosecond pulses are generated by passing a single femtosecond pulse through an optical network consisting of only two gratings, two lenses, and a spatially varying mask (*11, 15, 16*). The first grating and lens spatially separate and collimate the different optical frequency components of the incident pulse. The mask then alters the relative phases of the dispersed frequency components. [In general both phases and amplitudes can be modulated (*11, 17*), but for the current work only phase modulation was required.] The second lens and grating recombine the phase-altered frequency components to produce a "shaped" pulse whose temporal profile is given by the Fourier transform of the pattern transferred by the mask onto the spectrum. For the current experiment, different phase patterns were designed to produce pulse sequences with different pulse repetition rates and different numbers of pulses. Approximately 25 masks can be fabricated on a ½-inch-diameter fused silica substrate by using standard microlithography and reactive ion etching techniques (*11, 15, 16*). The desired pulse sequence is selected by translating the appropriate pattern into the beam path.

As a control, ISRS data were recorded from α-perylene excited by a single pair of (unshaped) excitation pulses. The results (Fig. 1) are similar to those published previously (*6*). The data consist of a sharp peak at time $t = 0$, due to the essentially instantaneous electronic response of the sample, followed by quasi-periodic signal due to the coherent oscillations of optic phonons excited through ISRS. Two points are of note. First, the intensity of the ISRS signal due to lattice vibrations is about 4% of that due to the electronic response (which serves as an internal calibration of the ISRS signal). Second, the signal presents an irregular temporal pattern caused by beating between several phonon modes simultaneously excited through ISRS. Fourier analysis of the scattering data indicates excitation of known α-perylene modes (*14*) at 33, 56, 80, and 104 cm^{-1}. These results illustrate the two limitations of single-excitation ISRS discussed above.

Multiple-pulse ISRS excitation was used to selectively drive the 80-cm^{-1} and 104-cm^{-1} modes in the α-perylene crystal. Figure 2A shows the intensity profile of a 2.39-THz (79.6-cm^{-1}) excitation pulse train, timed to match the vibrational period of the 80-cm^{-1} mode [an in-phase libration of the molecule pairs (*14*)]. Figure 2B shows the resulting ISRS data from α-perylene. Initially, the signal is dominated by the crystal's electronic responses to each of the pulses in the sequence. After several pulses, however, ISRS signal due to the amplified 80-cm^{-1} mode becomes apparent. By the end of the input pulse train ($t = 3$ ps), the ISRS signal is about as intense as the strongest electronic scattering peak. Furthermore, the ISRS signal after the pulse train has ended appears oscillatory at a single frequency [twice the vibrational frequency (*5, 6*)], and this observation is confirmed by Fourier analysis of the data. The data clearly demonstrate mode-selective vibrational amplification. The decay of coherent oscillations, measured on an extended time scale, yields a phonon dephasing time of 28.6 ps (*18*). Figure 2C shows ISRS data obtained with the input repetition rate detuned to 2.33 THz (77.8 cm^{-1}). Although the strength of the phonon scattering is reduced, the oscillations are still monochromatic with the same frequency and dephasing rate. Figure 2D shows simulated ISRS data from the repetitively driven 80-cm^{-1} mode, assuming a Gaussian temporal profile for the train of excitation pulses. The numerical results are in good agreement with the data in Fig. 2B.

Multiple-excitation ISRS has also been used to drive the 104-cm^{-1} translational optic phonon mode. The results are shown in Fig. 3. The degree of vibrational amplification achieved for the 104-cm^{-1} mode is comparable to that for the 80-cm^{-1} mode. The intensity of 104-cm^{-1} signal relative to signal from the electronic response is reduced, indicating a smaller differential polarizability for this mode. As with the 80-cm^{-1} mode, slight detuning of the multiple-pulse timing led to a vibrational response with the same frequency and dephasing rate but of weaker amplitude.

We note that femtosecond pulse-shaping technology is still evolving rapidly. Very recently, pulse sequences with square envelopes that would facilitate examination of more heavily damped or inhomogeneously broadened modes have been generated (*16*). Electronically controllable masks based on liquid crystals have been fabricated (*19*) and will allow pulse sequences to be optimized as occasions demand, for example, to drive anharmonic vibrational modes with gradually increased delays between successive pulses. Other electronically controlled pulse-shaping techniques are also moving toward femtosecond time scales (*12*). It is clear that femtosecond pulse shaping will play an important role in optical manipulation of molecular behavior.

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The Framework Topology of ZSM-18, a Novel Zeolite Containing Rings of Three (Si,Al)-O Species

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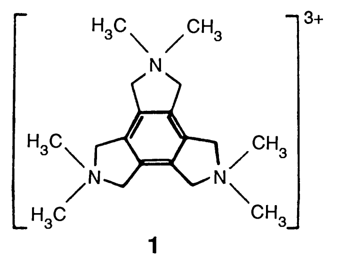
ZSM-18 is the first known aluminosilicate zeolite to contain rings of three (Si,Al)-O species (3-rings). Its framework topology has been determined by hypothetical model building, subsequent constrained distance and angle least-squares refinements of atomic coordinates, and x-ray powder diffraction pattern simulations. Its channel structure is characterized by a linear unidimensional 12-ring channel, with an approximate pore opening of 7.0 angstroms. In addition, the channels are lined with pockets that are capped by 7-rings with dimensions of 2.8 angstroms by 3.5 angstroms. An intraframework packing model of the organic moiety used in the synthesis suggests that a strong templating effect may be responsible for the formation of this unusual zeolite structure.

THE ALUMINOSILICATE ZEOLITE ZSM-18, reported by Ciric in 1976 (*1*), is synthesized in the presence of Na^+ and the triply charged tris-quaternary ammonium cation 2,3,4,5,6,7,8,9-octahydro-2,2,5,5,8,8-hexamethyl-1*H*-benzo[1,2-c:3,4-c′:5,6-c″]tripyrrolium (**1**),



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hereafter referred to as the triquat cation (*2*, *3*). The synthesis was prompted by the hypothesis that large quaternary ammonium cations may serve as effective templates in the crystallization of zeolites from aluminosilicate gels, which, upon calcination, will leave large pores in the zeolite product. Large-pore zeolites have significant application in petroleum refining and petrochemical processing.

ZSM-18 crystallizes with product ratios of SiO_2 to Al_2O_3 ranging from 10 to 30 (*1*). It has high sorptive capacity for large molecules. For the stable H form, sorptions as high as 23.4% (by weight) for H_2O, 15.0% for *n*-hexane, and 14.7% for cyclohexane have been observed (*1*).

Preliminary studies of ZSM-18 indicated that the unit cell is hexagonal with lattice parameters of $a = 13.2$ Å and $c = 15.8$ Å (*1*). The structure was solved when it was recognized that the difference between the *c* parameter of ZSM-18 (15.8 Å) and one-half the *c* parameter of the aluminophosphate MAPSO-46 (AFS) framework (13.45 Å) is 2.35 Å (*4*), which is approximately equal to the O · · · O distance in an $(Si,Al)O_4$ tetrahedron. In considering the AFS framework, it was noted that this particular structure is built entirely out of capped 6-rings. The cap consists of a single T atom (where T is a tetrahedrally coordinated

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