

Chapter 5. Ultrashort Laser Pulse Interactions With Matter - New Effects and Spectroscopic Applications

Sponsor

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The main thrust of this research has been to understand and exploit the unique ways in which femtosecond laser pulses interact with condensed materials. A femtosecond pulse is shorter in duration than the times required for most elementary atomic and molecular motions, e.g., lattice or molecular vibrations. This leads to several unusual effects which occur unavoidably whenever such a pulse propagates through or reflects off nearly any material. Since the effects are ubiquitous, they can play important roles in any ultrafast device or spectroscopic application.

Through theoretical and experimental work, we have reached an understanding of the ways in which ultrashort pulses can initiate *phase-coherent* motion in crystal lattices, liquids, and isolated molecules. We have shown how these effects can be used to control the motions and configurations of molecules and crystals, and how new spectroscopic information about molecular dynamics and electron-phonon interactions in condensed media can be extracted. Most of the samples examined to date have been organic molecular liquids and crystals. Semiconductors and other important electronic materials and nonlinear optical materials are now under investigation.

5.1 Impulsive Stimulated Raman Scattering of Ultrashort Pulses

We have confirmed experimentally² our theoretical prediction³ that a sufficiently short laser pulse will coherently excite any Raman-

active medium (i.e., nearly any medium) through which it passes. The only requirement is that the laser pulse duration be short compared to a single vibrational oscillation period of the Raman-active mode. The transform-limited spectral bandwidth of the pulse will then exceed the vibrational frequency, and stimulated Raman scattering excitation will occur through mixing among

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² S. Ruhman, A.G. Joly, and K.A. Nelson, "Time-Resolved Observations of Coherent Molecular Vibrational Motion and the General Occurrence of Impulsive Stimulated Scattering," *J. Chem. Phys.* (Communication) 86:6563-6565 (1987); S. Ruhman, A.G. Joly, and K.A. Nelson, "Coherent Molecular Vibrational Motion Observed in the Time Domain Through Impulsive Stimulated Raman Scattering," *IEEE J. Quant. Electron.* (Special Issue on Ultrafast Spectroscopy) 24:470-481 (1988); S. Ruhman, A.G. Joly, B. Kohler, L.R. Williams, and K.A. Nelson, "Intramolecular and Intermolecular Dynamics in Molecular Liquids Through Femtosecond Time-Resolved Impulsive Stimulated Scattering," *Revue de Phys. Appl.* 22:1717-1734 (1987).

³ Y.-X. Yan, E.B. Gamble, Jr., and K.A. Nelson, "Impulsive Stimulated Scattering: General Importance in Femtosecond Laser Pulse Interactions with Matter and Spectroscopic Applications," *J. Chem. Phys.* 83:3591-5399 (1985).

the Fourier components contained within the bandwidth. In such a case, the pulse exerts an "impulse" force on the vibrational mode through what has been coined impulsive stimulated Raman scattering (ISRS).

ISRS, which in most media cannot be avoided with ultrashort pulses, affects both the medium and the pulse. This is, therefore, of widespread importance in ultrafast optics, electro-optics, and spectroscopy.⁴ The medium through which the pulse passes is left undergoing coherent vibrational oscillations which modulate its optical and electronic properties. The pulse itself has its temporal and spectral profiles altered as it passes through the medium. Both of these effects have been verified experimentally.

Current efforts are now directed toward driving large vibrational amplitudes through ISRS. We believe that it should be possible to make ions or molecules in crystals move several tenths of an angstrom relative to each other. This is a substantial fraction of the lattice spacing in most crystals, and is the distance scale over which structural or chemical change within the solid could occur. One of the most intriguing possibilities is that of inducing selected structural or chemical rearrangements through large-amplitude ISRS excitation.⁵

In general, ISRS excitation removes a sample from equilibrium in a well defined way, through distortion along a known vibrational

coordinate. Time-resolved spectroscopy of the vibrationally distorted species is then carried out. Through ISRS, real-time observations of lattice and molecular vibrations are carried out. The technique is now being applied to nonlinear optical crystals and semiconductors to learn about electron-phonon interactions which may influence material and device performance.

5.2 Exciton-Phonon Interactions in Organic Molecular Crystals

In this project, we have examined the dramatic effects of electron-phonon interactions in cases where they lead to localization of excited states and rearrangements of local lattice structure around the localized excitation. These effects are important in mediating energy transfer and relaxation in insulators and semiconductors.

The organic molecular crystals, pyrene and perylene, have been studied.⁶ These are interesting cases in their own right, and are simple preliminaries to more complicated organic and inorganic semiconductors. In both crystals, photoexcitation produces a delocalized band state. Strong electron-phonon interactions lead to self-trapping and very rapid localization of the excitation on a single lattice site in which the molecular positions become highly distorted. The

⁴ Y.-X. Yan, L.-T. Cheng, and K.A. Nelson, "Impulsive Stimulated Light Scattering," In *Advances in Nonlinear Spectroscopy*, Advances in Spectroscopy Series, Vol. 16, eds. R.J.H. Clark and R.E. Hester, 299-355. New York: Wiley, 1988; K.A. Nelson and E.P. Ippen, "Femtosecond Coherent Spectroscopy," *Adv. Chem. Phys.* 75, in press (1989); K.A. Nelson, "Impulsive Stimulated Raman Scattering." In *Vibrational Spectra and Structure*, Vol. 17, ed. J.R. Durig. New York: Elsevier, in press (1989).

⁵ Y.-X. Yan, E.B. Gamble, Jr., and K.A. Nelson, "Impulsive Stimulated Scattering: General Importance in Femtosecond Laser Pulse Interactions with Matter and Spectroscopic Applications," *J. Chem. Phys.* 83:3591-5399 (1985); K.A. Nelson and E.P. Ippen, "Femtosecond Coherent Spectroscopy," *Adv. Chem. Phys.* 75, in press (1989).

⁶ S. DeSilvestri, J.G. Fujimoto, E.P. Ippen, E.B. Gamble, Jr., L.R. Williams, and K.A. Nelson, "Femtosecond Time-Resolved Measurements of Optic Phonon Dephasing by Impulsive Stimulated Raman Scattering in A-Perylene Crystal from 20- 300K," *Chem. Phys. Lett.* 116:146-152 (1985); L.R. Williams, E.B. Gamble, Jr., K.A. Nelson, S. De Silvestri, A.M. Weiner, and E.P. Ippen, "Femtosecond Time-Resolved Measurements of Electronic Excited-State Relaxation in Pyrene Excimer-Forming Crystals," *Chem. Phys. Lett.* 139:244-249 (1987); L.R. Williams and K.A. Nelson, "Excimer Formation in Pyrene Molecular Crystal: Femtosecond Dynamics of an Oriented Bimolecular Reaction," *J. Chem. Phys.* (Communication) 87:7346-7347 (1987); L.R. Williams and K.A. Nelson, "Subpicosecond Excimer-Formation Dynamics in Organic Molecular Crystals," In *Advances in Laser Science - III*, eds. A.C. Tam, J.L. Gole, and W.C. Stwalley, 599-601. IAP Conference Proceedings 172, New York, 1988.

molecular distortions actually correspond to a simple chemical reaction and so these samples are interesting from both lattice dynamics and chemical points of view. We have carried out experiments to measure the localization dynamics in these crystals. The initial work on this project was carried out in collaboration with Professors J.G. Fujimoto and E.P. Ippen.⁷ We have determined the localization time (about 200 fs in each crystal) by transient absorption spectroscopy. We have also made preliminary measurements of the electron-phonon coupling strengths. These were achieved through ISRS excitation of the phonons followed by optical absorption measurements of the electronic energy levels, which are shifted by lattice distortions along the phonon coordinates.

5.3 Phonon and Polariton Dynamics in Nonlinear Optical Crystals

In this recently begun effort, ISRS experiments on noncentrosymmetric crystals are carried out to elucidate the dispersive phonon-polariton dynamics. Large-amplitude phonon distortions are excited to evaluate the nonlinear optical performance of the crystal at various configurations. The results could indicate which microscopic factors are most important for nonlinear optical performance and could guide efforts at crystal fabrication.

Experiments on lithium niobate have shown highly dispersive vibrational modes in the

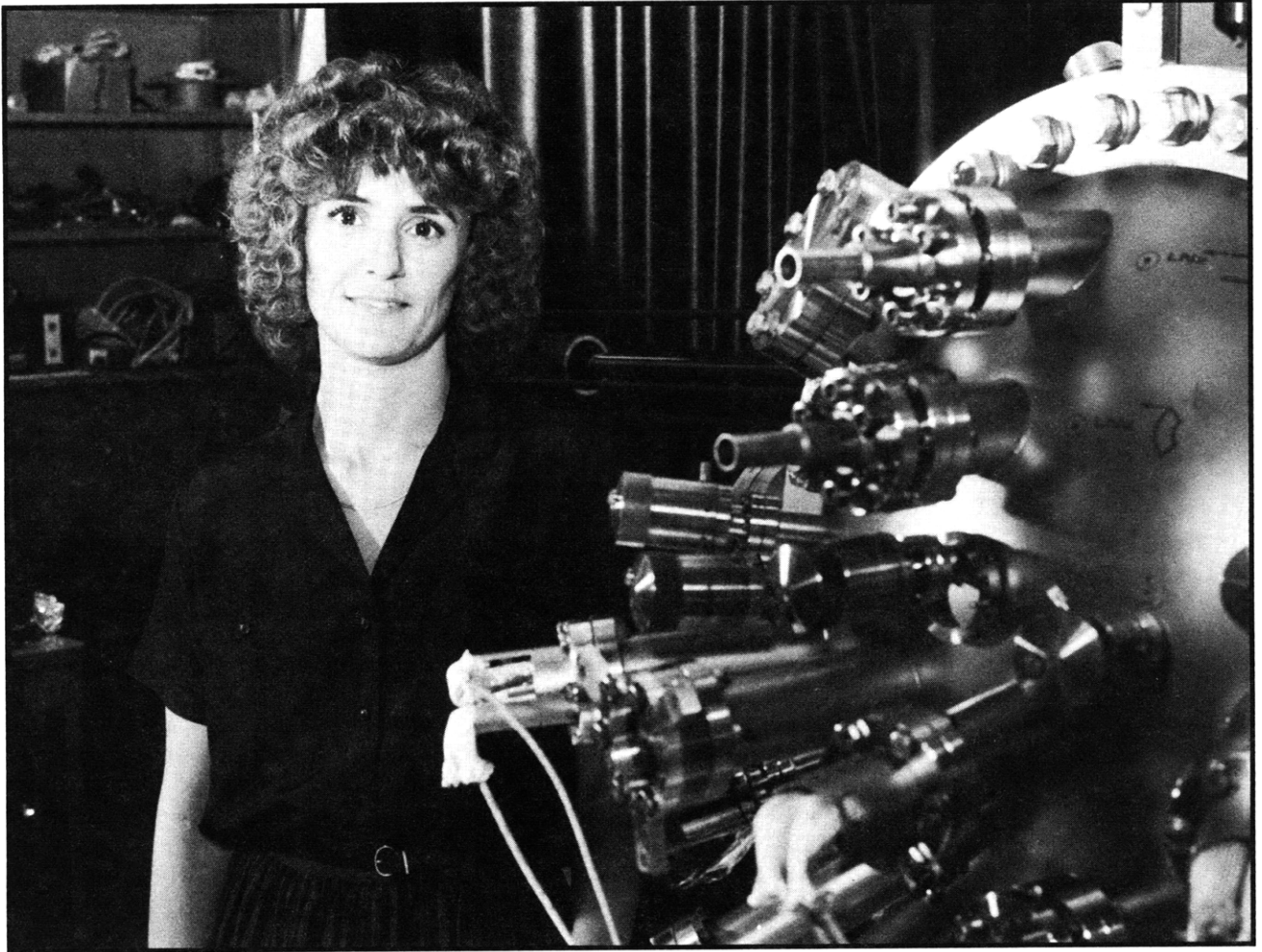
2-4 Terahertz region due to phonon-polariton excitation. Measurements of second harmonic generation efficiency as a function of lattice distortion along the vibrational coordinate are under way.

5.4 Coherent Excitation Through Optical Absorption of Ultrashort Pulses

We first pointed out that optical absorption of ultrashort pulses would result in coherent vibrational motion in excited electronic states, similar to ISRS initiation of coherent vibrational motion in ground electronic states. We have since provided a general description of the coherent effects of ultrashort laser pulses on condensed matter (or isolated atoms and molecules).⁸ Taken together, the absorption or ISRS mechanisms lead to coherent excitation in almost all absorbing or transparent materials which are irradiated by sufficiently short pulses. We have described some of the effects of coherent excitation on the light pulse and on the material, and how these effects may be detected in common spectroscopy experiments. We have indicated the magnitudes of the effects and shown that they provide means for substantial optical control over lattice and molecular motion and configuration. The possibility of using ultrashort pulses to drive structural and chemical changes which do not ordinarily occur has been discussed and is under experimental investigation.

⁷ S. DeSilvestri, J.G. Fujimoto, E.P. Ippen, E.B. Gamble, Jr., L.R. Williams, and K.A. Nelson, "Femtosecond Time-Resolved Measurements of Optic Phonon Dephasing by Impulsive Stimulated Raman Scattering in A-Perylene Crystal from 20- 300K," *Chem. Phys. Lett.* 116:146-152 (1985); L.R. Williams, E.B. Gamble, Jr., K.A. Nelson, S. De Silvestri, A.M. Weiner, and E.P. Ippen, "Femtosecond Time-Resolved Measurements of Electronic Excited-State Relaxation in Pyrene Excimer-Forming Crystals," *Chem. Phys. Lett.* 139:244-249 (1987).

⁸ K.A. Nelson and E.P. Ippen, "Femtosecond Coherent Spectroscopy," *Adv. Chem. Phys.* 75, in press (1989).



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