Ultrafast Spectroscopy and Coherent Control of Bulk and Thin Film Materials

Faculty

Keith A. Nelson, Professor of Chemistry

Collaborators

J. Joannopoulos,Physics
E.L. Thomas, DMSE
J.F. Scott, Earth Sciences, Cambridge University
M.M. Murnane, Physics, University of Colorado
H.C. Kapteyn, Physics, University of Colorado
Y. Gupta, Physics, Washington State University
J. Levy, Physics, University of Pittsburgh
K. Webb, EECS, Purdue
R.M. Osgood, Electrical Engineering and Applied Physics, Columbia U.

Research Staff

T. Feurer, Research Associate
M. Yamaguchi, Postdoctoral Associate
T. Hornung, Postdoctoral Fellow
K. Katayama, Postdoctoral Fellow
R. Slayton, Postdoctoral Fellow

Graduate Students

P.R. Poulin, Chemistry
J.D. Beers, Chemistry
D.W. Ward, Chemistry
J. Vaughan, Chemistry
B. Paxton, Chemistry
D. Torchinski, Physics
E. Statz, Chemistry
C. Bolme, Chemistry
K. Stone, Chemistry
K.-L. Yeh, Chemistry

Degree Granted

N. Stoyanov, Ph.D., Physical Chemistry, *Phonon-Polaritons in Bulk and Patterned Materials*, June, 2003.

Research Reports

Optical Characterization and Metrology of Thin Films: Research and Outreach

Personnel: J. Beers, B. Paxton, M. Yamaguchi, D. Torchinski, R. Slayton
Sponsorship: NSF

Thin films play central roles in almost all advanced devices, yet their characterization is often difficult. We use picosecond and femtosecond laser pulses to generate acoustic and thermal responses that propagate in or through the plane of the film, and we monitor the propagation of these waves to determine film thickness, anisotropic elastic moduli and thermal diffusivities, delamination from substrates, cure kinetics, and other properties. Polymer, metal, ceramic, low-k dielectrics, and other film materials used in microelectronics, photographic and recording media, and protective coatings have been examined. The methodology is currently being extended through the use of

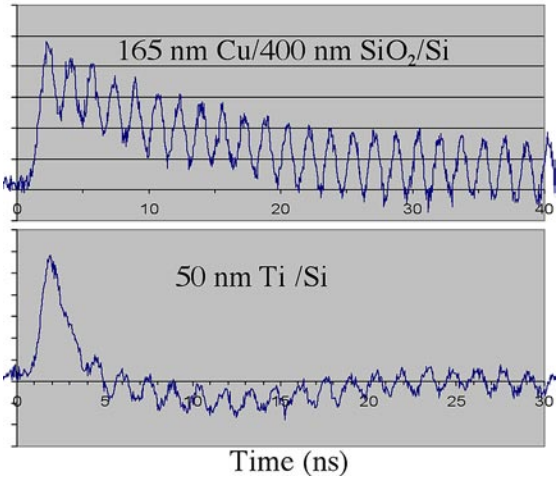

Figure 1: Four-wave mixing "impulsive stimulated thermal scattering" (ISTS) data from metal films on silicon substrates, recorded by high school outreach students. Crossed excitation laser pulses generate coherent acoustic waves that are monitored through time-resolved diffraction of probe laser light. From the measured acoustic frequency, the film thickness and other properties can be determined.

timed sequences of femtosecond pulses to generate narrow-band, ultrahigh-frequency acoustic waves in thin films, both to characterize the films themselves and to use them as transducers for study of adjacent materials.

Methods developed in our lab have been commercialized for noncontact, nondestructive measurement of metal film thickness (±1-3 Å) in the microelectronics industry. These methods have been incorporated into an outreach laboratory associated with the Harrison Spectroscopy Laboratory and with the Materials Research Experiences for Teachers summer program administered through the MIT Center for Materials Science and Engineering. The program, entitled "The Wavelength Project," enables high school and four-year college students and teachers to gain real experience in time-resolved laser spectroscopy and to learn about advanced materials and modern optics. Data collected by students in the program appear in Figure 1.

Viscoelastic Properties of Glass-forming Liquids and Polymers

Personnel: J. Beers, B. Paxton, M. Yamaguchi
Sponsorship: NSF

Measurement of acoustic and thermal transport properties of viscoelastic fluids is of great practical interest since both processing and functionality often depend on temperature-dependent mechanical and dynamical behavior and on thermal conductivity. At the same time, such measurements permit fundamental questions concerning the origins of viscoelasticity to be addressed. Viscoelastic materials ranging from biopolymers to ionic melts to organic molecular liquids display remarkable similarities in their temperature-dependent dynamical behavior, with broad structural relaxation spectra that move from high to low frequencies (i.e. complex relaxation dynamics that move from fast to slow time scales) as the liquid is cooled. These striking similarities suggest universal underpinnings, but in contrast to the theoretical framework describing phase transitions and critical phenomena, there is no widely accepted first-principles treatment of complex relaxation dynamics in viscoelastic materials. A successful theory would resolve fundamental questions in condensed matter statistical mechanics, and would offer predictive power of immediate value in polymer processing, biophysics, microfluidics, and other areas. But difficulties in measurement of structural relaxation dynamics over the very wide relevant range of frequency (or time) scales have prevented adequate testing or guidance of the nascent theoretical predictions that have been formulated.

We have used picosecond pulses to generate MHz-frequency acoustic waves and thermal responses that permit direct measurement of density relaxation dynamics in the nanosecond through microsecond ranges. See Figure 2. Very recently, we have generated far higher-frequency (> 100 GHz) acoustic responses to examine picosecond density dynamics, offering a total of seven decades of dynamic range for determination of temperature-dependent relaxation dynamics. Current statistical mechanical theories of underlying dynamic critical behavior in viscoelastic fluids, related to a

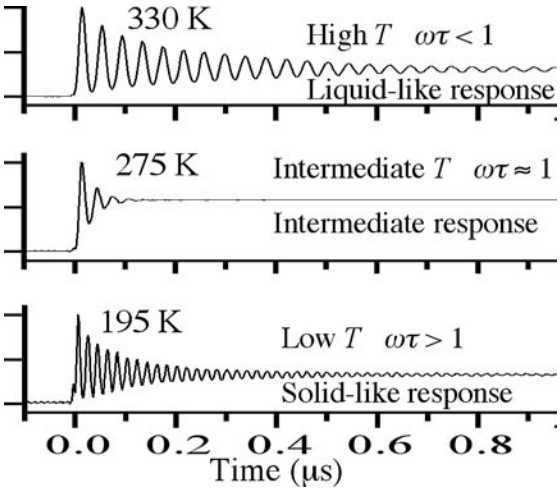

Figure 2: ISTS data from supercooled liquid glycerol at various temperatures. As the temperature is reduced, the sample goes from liquid to solid-like. When the structural relaxation time scale t of the viscous liquid overlaps the acoustic frequency w, i.e. $\omega\tau \approx 1$*, the acoustic damping rate is extremely high and the acoustic velocity is strongly dispersive.*

transition from ergodic to nonergodic liquid as temperature is reduced, are being tested.

Terahertz Polaritonics: Spectroscopy and Coherent Control of Ultrafast Lattice Waves

Personnel: T. Feurer, J. Vaughan, T. Hornung
Sponsorship: NSF

Most high-frequency lattice vibrations (optic phonons) have near-zero group velocity, and therefore do not move through macroscopic regions of the host crystal. An exception occurs for polar vibrations whose symmetry, frequency, and wavevector match those of the corresponding electromagnetic mode. In this case, mixed lattice waves—part vibrational, part electromagnetic—called phonon-polaritons (or hereafter, simply polaritons) are formed. Polaritons, with frequencies typically in the 0.1-10 THz range, propagate at light-like speeds through the host crystal lattice. Our research on polaritons stems from (1) the insights they can provide concerning lattice rearrangements and linear and nonlinear lattice dynamics in some materials, especially ferroelectrics; (2) their applications in linear and nonlinear THz spectroscopy of

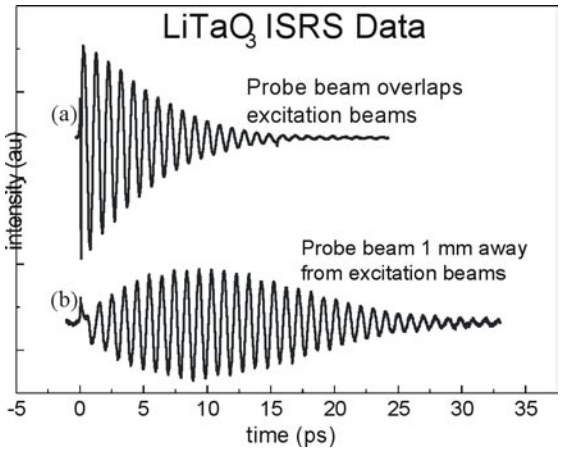

Figure 3: Polariton THz-frequency oscillations in lithium tantalate observed through femtosecond time-resolved four-wave mixing with the probe beam either overlapped with the excitation region or displaced from it by 1 mm. Propagation of the coherent polariton waves out of the excitation region is clearly observed.

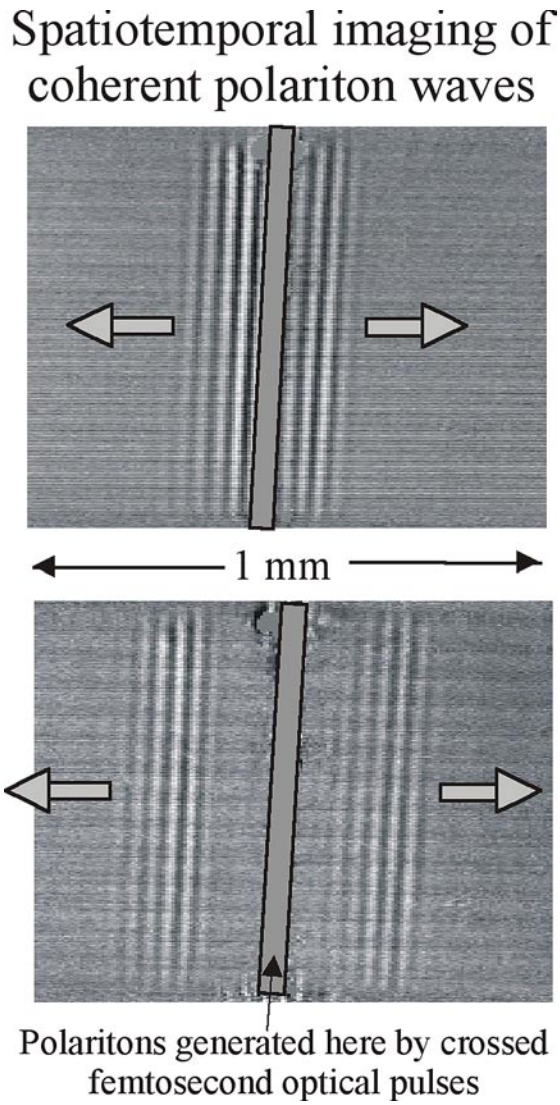

Figure 4: Spatiotemporal images show coherent polariton waves in $LiTaO_3$ crystal 300 (top), and 1300 fs (bottom) after excitation by crossed femtosecond pulses. The propagation speed is c/6.

complex materials; and (3) their potential for novel applications for THz signal generation, control, and processing.

Coherent polariton waves can be generated by femtosecond laser pulses through impulsive stimulated Raman scattering (ISRS). An ultrashort pulse exerts a sudden ("impulse") driving force on Raman-active modes, including polariton modes, through ISRS. Since the polariton response moves

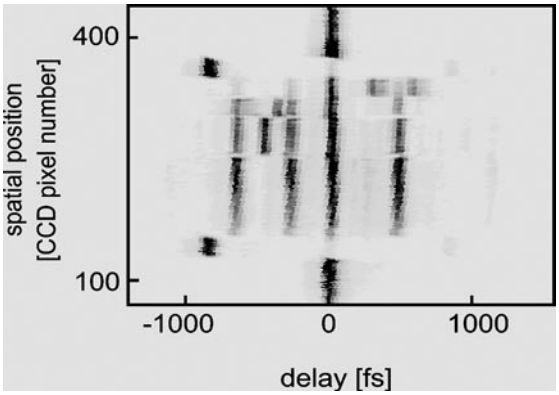

Figure 5: Spatiotemporally shaped femtosecond waveform. The output consists of about 30 spatially distinct beams, each with an independently specified temporal profile. The beams near the top and bottom have one pulse each, while the beams that spell "MIT" have several pulses with separations of a few hundred femtoseconds. Spatiotemporally shaped waveforms are used for polariton coherent control.

rapidly across macroscopic distances, it may be monitored either at the excitation region or elsewhere. Figure 3 shows the polariton response to crossed femtosecond pulses in the ferroelectric crystal lithium tantalite.

The complete spatial and temporal evolution of polaritons may be monitored through spatiotemporal imaging, in which the variably delayed probe pulse passes through the crystal with a large spot size and is projected onto a CCD camera. The real-space images thereby recorded may be displayed in rapid succession, providing "movies" of polariton propagation. Several such movies may be viewed at the website address http://nelson.mit.edu/index.html. Figure 4 shows two frames from one such movie, illustrating propagation of the polariton response to crossed excitation pulses as in Figure 3. Similarly, the response to a cylindrically focused "line" of excitation light consists of counterpropagating, single-cycle polariton "ripples" rather than the multiple-cycle waves shown in the figure.

Extensive control over the polariton response can be exerted through both the spatial and temporal properties of the excitation light field. To permit programmable tailoring of the field, we have developed spatiotemporal femtosecond pulse shaping methods through which a single incident beam with a single pulse is transformed into many spatially separated beams, each with an independently specified temporal profile. An example of a spatiotemporally shaped waveform is shown in Figure 5.

The use of programmably tailored waveforms for spatiotemoral coherent control over polariton responses is illustrated schematically in Figure 6. Spatiotemporal pulse shaping and imaging are integrated into the spatiotemporal coherent control system. Traveling wave amplification and phased array generation of polaritonic signals have been demonstrated with this system.

The lattice vibrational components of phonon-polaritons play central roles in the phase transitions and domain switching transitions of many ferroelectric crystals. The "soft" lattice vibrations in these materials move ions along collective pathways from their positions in one ferroelectric crystalline phase or domain orientation toward their positions in an incipient structure. The lattice dynamics thus reveal the dynamics of collective structural change. The lattice transitions are exploited in devices such as ferroelectric DRAMS, in which an applied electric field is used to induce domain switching. In ongoing work, polariton amplification and focusing are being used to generate large-amplitude vibrations (and the associated high electric fields) that should permit coherent optical control and direct observation of nonlinear lattice

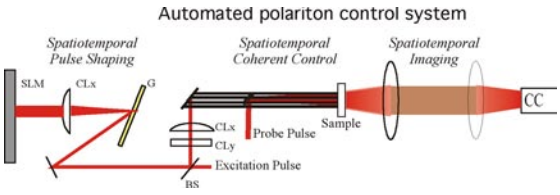

Figure 6: Polaritons can be amplified and controlled through spatiotemporal pulse shaping, which transforms a single laser beam with a single pulse into many spatially separated beams with specified pulse sequences; spatiotemporal coherent control, in which the multiple beams and pulses are used to generate and manipulate polaritons; and spatiotemporal imaging, which permits direct polariton observation and feedback.

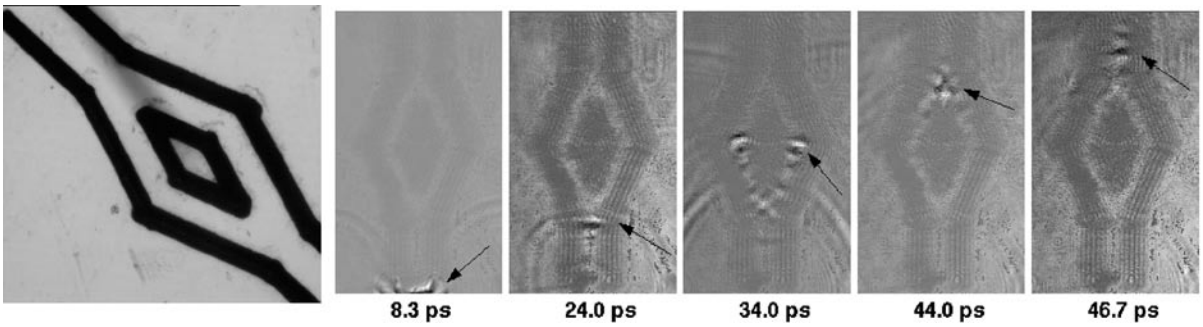

Figure 7: Polaritonic waveguide interferometer fabricated in a lithium niobate crystal through femtosecond laser machining. (a) Optical microscope image of the structure. The waveguide widths are about 200 mm. (b) Spatiotemporal images of polaritonic signals that are focused into the structure, split, and recombined interferometrically. Polaritonic resonators, bandgap materials, and other structures may be fabricated.

responses, and perhaps even domain switching, as ions are collectively driven far from their initial equilibrium locations.

Polariton-based THz spectroscopy and THz signal generation and processing applications are also being pursued actively, as described below.

Polaritonic Bandgap Materials and Patterned Polaritonic Structures

Personnel: D. Ward, E. Statz, T. Feurer, K. Webb, J. Joannopoulos, K. Huang, P. Bienstman
Sponsorship: NSF/MRSEC

Wave propagation in photonic bandgap materials and other patterned structures is of great current interest for a wide range of applications. Phonon-polariton propagation in periodically patterned ferroelectric crystals should show unique properties since even in bulk crystals, phonon-polaritons show unusual dispersion properties, multiple branches, and pronounced bandgaps. The interplay between these intrinsic features and the dispersion and bandgap features that are introduced through patterning is under theoretical and experimental exploration. Some of the unique features of polaritonic bandgap materials include extremely high refractive index contrast between air and the crystalline material ($n \approx 5–10$ in the THz frequency range) and generation and detection of signals in the (THz) bandgap range using light whose (visible) wavelength lies far outside the bandgap, and to which the crystal is transparent. The latter feature permits facile, multiplexed signal generation, manipulation, and detection at any location within the material, and permits ultra-high-bandwidth signal generation and readout.

Ferroelectric materials cannot be processed through conventional etching methods. We have explored the use of femtosecond laser machining for fabrication of patterned structures in these materials. Figure 7 shows a polaritonic waveguide interferometer and the spatiotemporally imaged polaritonic signals propagating within it. These and other results illustrate the potential for a solid-state THz signal processing platform in which multiplexed signal generation, signal propagation, signal manipulation, and signal readout can all be executed with THz bandwidths.

Optical Properties of Nanoscale Arrays

Personnel: D. Ward, E. Statz, T. Feurer, M. Dawber, J. Scott
Sponsorship: Cambridge-MIT Institute (CMI)

In this collaboration with Cambridge University, the effects of polariton waves on nanometer-sized ferroelectric nanotubes fabricated through electron-beam lithography or self-organization methods are examined. Through polariton

amplification and focusing, we hope to generate THz electric field levels in the 1–10 MV/cm range with temporal profiles that can be tailored to drive specified linear or nonlinear responses in ferroelectric nanodomains. This raises the possibility of polariton-induced electrical and optical effects that could be exploited for ultrahigh-bandwidth signal processing applications. The linear and nonlinear responses of ordered ferroelectric nanoscale arrays to polaritons will be explored. More generally, the development of methods for near-field THz spectroscopy of small volume elements is under way.

Semiconductor Polaritonics

Personnel: E. Statz, D. Ward, K. Katayama
Sponsorship: ARO

In polar semiconductors, bulk and surface polariton modes may form and may show strong coupling to electronic excitations, resulting in unusual dispersion and propagation properties in the linear-response regime and unique nonlinear responses including polaritonic modulation of the semiconductor bandgap. In this project, the spatiotemporal imaging, pulse shaping, and coherent control methods developed and demonstrated with ferroelectric crystals are applied semiconductors. Electrical detection of phonon-polaritons in the semiconductor host, coupling of THz radiation generated by femtosecond pulses at semiconductor surfaces into integrated ferroelectric structures, and copropagation of polaritons in ferroelectric-semiconductor hybrid assemblies are among the objectives, which will represent a major step in the development of integrated polaritonic-electronic signal processing systems. Semiconductor quantum well structures with intersubband transitions at THz frequencies are of special interest, since these transitions can be driven resonantly and nonlinearly by shaped polariton fields.

Terahertz Spectroscopy of Complex Materials

Personnel: B. Paxton, M. Yamaguchi, T. Feurer, J. Vaughan, T. Hornung
Sponsorship: NSF

The methods we have developed for generation of THz-frequency polariton waves can be used for characterization of more than just the polariton host crystal. When the waves reach the crystal edge, partial transmission of THz radiation occurs. Thus intense THz radiation whose field is completely controllable experimentally, and which can range from single-cycle to a sequence of variably spaced pulses to many-cycle waves at well defined and tunable frequencies, can be generated and used for spectroscopy of samples outside the host crystal. Spectroscopic measurements have been conducted on polar viscoelastic fluids, in which the complex dielectric responses reveal molecular orientational dynamics, and further measurements will be conducted on mixed incipient ferroelectric crystals that are still in the high-temperature, paralectric phase. These materials show large-scale fluctuations of ferroelectric nanodomains, similar in size to those fabricated systematically in the arrays described above, and the time and length scales as well as the magnitudes of these fluctuations vary sharply as the temperature of the ferroelectric phase transition is approached. Nonlinear spectroscopy with THz excitation fields and visible or THz probe fields will reveal nonlinear responses of nanodomains (or of molecular rotations in liquids) and the time-dependent relaxation that follows. At sufficiently high field intensities, it may be possible

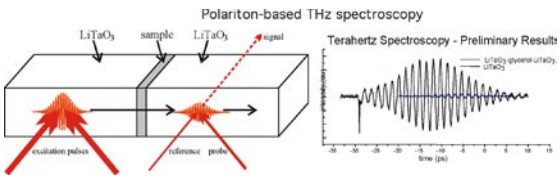

Figure 8: THz spectroscopy based on polaritons generated in one crystal and detected in another. This permits tunable narrowband spectroscopy, or broadband spectroscopy with a single cycle THz pulse. Nonlinear THz spectroscopy with intense THz radiation is a current major objective.

to induce switching in the ferroelectric nanodomains or structural rearrangements (beyond linear response) in polar liquids, in each case permitting direct time-resolved observation of the dynamics of the collective structural change.

Solid-State Chemical Reactivity and Single-Event Femtosecond Spectroscopy

Personnel: P. Poulin, C. Bolme
Sponsorship: ONR

Direct time-resolved observations of solid-state chemical and structural changes on femtosecond time scales are conducted. The objectives are to understand the early stages of chemical reactions in energetic materials, to elucidate the role of the solid-state environment on reaction dynamics, and more generally to determine and understand the dynamics of ultrafast, permanent structural change in condensed matter. A method has been developed for single-event, real-time femtosecond spectroscopy, in which the entire time-dependent response is recorded with just one laser shot. This is important because each laser shot leads to permanent damage or photoproducts which may influence the measurements made with subsequent shots, and flow of fresh material into the irradiated region is not practical. Thus the usual ultrafast spectroscopy approach of a variably delayed probe pulse, in which each laser pulse provides the sample response at just one point on the time axis, is not possible.

Ultrafast changes following intense nonresonant photoexcitation of glasses have been observed recently, and similarly rapid changes have also been seen in energetic organic crystals. Current efforts include resonant photochemical excitation of energetic crystals and intense excitation of phonon-polaritons in ferroelectric crystals, with the objectives of characterization of irreversible chemical and structural rearrangements.

Ultrafast Coherent Soft X-Ray Spectroscopy of Condensed Matter

Personnel: T. Feurer, M. Murnane, H. Kapteyn, R. Tobey
Sponsorship: DOE

Femtosecond spectroscopy of materials that undergo collective structural change often reveals complex dynamical behavior. For example, the polarization dynamics of crystals near ferroelectric phase transitions and the density dynamics of viscoelastic fluids show highly temperature-dependent responses that may include both oscillatory and relaxational components, the latter often highly nonexponential and extending over many time scales. Even when detailed observation of the collective dynamics is possible, a microscopic understanding of those dynamics often remains elusive because there is no direct experimental association between the dynamics, i.e. the correlation time scale(s), and the corresponding correlation length scale(s). For example, the hierarchy of fast, intermediate, and slow structural relaxation responses observed in polymer liquids is suggestive of the dynamics of chain end groups, small side chains, and larger backbone elements or whole polymer molecules respectively. But small-molecule supercooled liquids also show hierarchical dynamics, even though there is no obvious hierarchy of corresponding structural correlation lengths. Time-resolved optical spectroscopy measurements provide no direct information about the mesoscopic correlation lengths associated with the observed dynamics because those lengths are all shorter than the light wavelengths.

In this collaborative project, femtosecond time-resolved four-wave mixing measurements are conducted with pulses at soft x-ray wavelengths. In this manner, the length scale of the measurement is set directly by the interference fringe spacing formed by crossed soft x-ray excitation pulses. The soft x-ray pulses are produced from visible femtosecond pulses through high harmonic generation and are directed toward the sample through the use of

diffractive optics fabricated for x-ray lithography. Initial measurements are aimed at elucidation of correlation length and time scales in supercooled liquids. These experiments should open new possibilities in x-ray time-resolved nonlinear optical spectroscopy.

Elastic and Thermal Transport Properties of Materials under Static and Dynamic High-Pressure

Personnel: D. Torchinski, J. Beers, C. Bolme, Y. Gupta, Z. Dreger
Sponsorship: ONR

Understanding and modeling of energetic materials under extreme conditions requires experimental input that is often hard to obtain. In the first phase of this project, mechanical, viscoelastic, and thermal transport properties are determined for materials in diamond or sapphire anvil cells. The next and more difficult phase will be extension of the measurement methodology to samples under shock loading which is applied through laser-induced or traditional (projectile) methods. Energetic materials as well as materials of geological interest are under study.

Single-Shot Time-Resolved Spectroscopy of Ballistic Impact Events

Personnel: C. Bolme, T. Feurer, E.L. Thomas, N. Vacchani
Sponsor: ARO (ISN)

In this new project, the responses of advanced materials including polymeric and polymer based nanocomposites to the extreme conditions of shock loading are studied. The first objectives are study of materials subjected to laser-driven shocks, which show similar shock front behavior to conventional shocks. The second state will be to study materials subjected to ballistic impact, including the steady-state high pressure and high temperature conditions that typically are not reached in laser-driven shocks.

Publications

T. Feurer, J.C. Vaughan, and K.A. Nelson, "Spatiotemporal Coherent Control of Lattice Vibrational Waves," *Science* **299**, 374-377 (2003).

K.C. Huang, P. Bienstman, J.D. Joannopoulos, and K.A. Nelson, "Field Expulsion and Reconfiguration in Polaritonic Photonic Crystals," *Phys. Rev. Lett.* **90**(196402):1-4 (2003).

K.C. Huang, P. Bienstman, J.D. Joannopoulos, and K.A. Nelson, "Phonon-Polariton Excitations in Photonic Crystals," *Phys. Rev. B* **68**(075209):1-12 (2003).

J. C. Vaughan, T. Feurer, and K.A. Nelson, "Automated Spatiotemporal Diffraction of Ultrashort Laser Pulses," *Opt. Lett.* **28**, 2408-2410 (2003).

C. Glorieux, K. Van de Rostyne, D. Beers, W. Gao, S. Petillion, N. Van Riet, K. A. Nelson, J. F. Allard, V. E. Gusev, W. Lariks, and J. Thoen, "Acoustic Waves at Interfaces Studied by Laser Ultrasonics," (Invited), *Rev. Scient Instr.* **74**, 1-5 (2003).

R.M. Slayton and K.A. Nelson, "Picosecond Acoustic Transmission Measurements. Part I: Transient Grating Generation and Detection of Acoustic Responses in Thin Metal Films," *J. Chem Phys.* **120**, 3908-3918 (2004).

R.M. Slayton and K.A. Nelson, "Picosecond Acoustic Transmission Measurements. Part II: Probing High-Frequency Acoustic Relaxation in Supercooled Glycerol," *J. Chem Phys.* **120**, 3919-3930 (2004).

T. Yagi, J. Kano, T. Watanuki, Y. Tsujimi, and K.A. Nelson, "Femtosecond Time-Resolved Spectroscopic Study of the Slow Dynamics in the Structural Phase Transition," *J. Korean Phys. Soc.* **42**, S1012-S106 Suppl. S. (2003).

J. Kano, Y. Tsujimi, K.A. Nelson, and T. Yagi, "The Extremely Early Stage of the Ferroelectric

B-2 Soft Mode of KDP Studied by the Impulsive Stimulated Raman Scattering," *Ferroelectrics* **285**, 59-66 (2003).

T. Yagi, J. Kano. T. Watanuki, Y. Tsujimi, and K.A. Nelson, "Phase Transition Dynamics Studied by Coherent Phonon Excitation with Ultrashort Laser Pulses," *Ferroelectrics* **284**, 3-13 (2003).

T. Feurer, J.C. Vaughan, N.S. Stoyanov, and K.A. Nelson, "THZ Field Generation and Manipulation by Coherent Control over Phonon-Polaritons," *Proc. 13th Int'l Symp. Space Terahertz Technology*, 215-218 (2003).

T. Feurer, J.C. Vaughan, N.S. Stoyanov, and K.A. Nelson, "Coherent Control over Collective Polariton Excitations: the Dawn of Polaritonics," *Proc. 13th Int'l Conf. Ultrafast Phenomena*, 541-545, M.M. Murnane, N.F. Scherer, R.J.D. Miller, and A.M. Weiner, eds. (Springer-Verlag, Berlin 2003).

N.S. Stoyanov, T. Feurer, D.W. Ward, and K.A. Nelson, "Direct Visualization of the Gouy Phase Shift," *Proc. 13th Int'l Conf. Ultrafast Phenomena*, 401-403, M.M. Murnane, N.F. Scherer, R.J.D. Miller, and A.M. Weiner, eds. (Springer-Verlag, Berlin 2003).

J.C. Vaughan, T. Feurer, and K.A. Nelson, "Automated Two-Dimensional Femtosecond Pulse Shaping and Timed-Array THz Generation," *Proc. 13th Int'l Conf. Ultrafast Phenomena*, 214-216, M.M. Murnane, N.F. Scherer, R.J.D. Miller, and A.M. Weiner, eds. (Springer-Verlag, Berlin 2003).

D.W. Ward, E. Statz, J.D. Beers, N.S. Stoyanov, T. Feurer, R.M. Roth, R.M. Osgood, and K.A. Nelson, "Phonon-Polariton Propagation, Guidance, and Control in Bulk and Patterned Thin Film Ferroelectric Crystals," *Ferroelecric Thin Films XII: MRS Syposium Proceedings* **797**W, 5.9.1-6; A. Kingon, S. Hofmann-Eifert, I.P. Kooutsaroff, H. Funakubo, and V. Joshi eds. (Materials Research Society, Pittsburgh, PA, 2003).

D.W. Ward, E. Statz, N.S. Stoyanov, and K.A. Nelson, "Simulation of Phonon-Polariton Propagation in Ferroelectric $LiNbO_3$," *Engineered Porosity for Microphotonics and Plasmonics: MRS Symposium Proceedings* **762**, C11.60.1-6; R. Wehrspohn, F. Garcial-Vidal, M. Notomi, and A. Scherer, eds. (Materials Research Society, Pittsburgh, PA, 2003).

D.W. Ward and K.A. Nelson, "Finite Difference Time Domain (FDTD) Simulations of Electromagnetic Wave Propagation using a Spreadsheet," submitted to *Amer. J. Phys.* (2004).

K.J. Webb, M. Yang, D.W. Ward, and K.A. Nelson, "Metrics for Negative Refractive Materials," submitted to *Phys. Rev. Lett.* (2004).