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The response of solids composed of large molecules, to the rapid deposition of a large amount of energy was studied experimentally and theoretically. Laser equipment capable of inducing a solid state explosion, and studying, via ultrafast microscopy, and a variety of nonlinear optical techniques, was constructed, and used to investigate the behavior of a variety of solid materials on times ranging from 2 picoseconds (trillionths of a second) to seconds. The theory of statistical mechanics, and the methods of supercomputer simulations was used to analyze the results of the experiments, and to make predictions about planned experiments where laser driven shock waves are used to induce chemical reactions in energetic solids.

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"Ultrafast laser investigation of a 'solid-state explosion'"

Final Report

Dana D. Dlott

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Abstract

The response of solids composed of large molecules, to the rapid deposition of a large amount of energy was studied experimentally and theoretically. Laser equipment capable of inducing a solid state explosion, and studying, via ultrafast microscopy, and a variety of nonlinear optical techniques, was constructed, and used to investigate the behavior of a variety of solid materials on times ranging from 2 picoseconds (trillionths of a second) to seconds. The theory of statistical mechanics, and the method of supercomputer simulations was used to analyze the results of the experiments, and to make predictions about planned experiments where laser driven shock waves are used to induce chemical reactions in energetic solids.

A. Statement of the problem studied

The goal of this research was to develop an understanding of the behavior of molecular solids when a great deal of excess mechanical energy is added to the solid in a very short time, typically in a few picoseconds (1 ps = 10^{-12} s). The resultant behavior was to be analyzed as a microscopic phenomenon (e.g. energy levels, quantum mechanical transition rates, etc.) and as a macroscopic phenomenon (e.g. blast waves, shock waves, heat transfer, melting, etc.)

B. Summary of the most important results

We made substantial progress on five fronts: (1) development of novel ultrafast laser equipment, (2) development of new optical measurement techniques, (3) experimental measurements of the ultrafast microscopic dynamics of mechanical energy transfer in molecular solids, (4) experimental measurements of the ultrafast macroscopic dynamics of ultra hot molecular materials, and (5) theoretical studies of vibrational energy transfer and shock wave induced chemical reactions.

(1) development of novel ultrafast laser equipment. As described in [1], (reference numbers refer to the publications listed in part C) we invented a new Nd:YAG regenerative laser amplifier which utilizes some novel acousto optic and electro optic switching techniques. We also invented a new way of switching high voltages (up to 5,000 V) in one nanosecond. The regenerative amplifier provides an exceedingly stable source of synchronized 100 ps laser pulses at high repetition rates up to 1,000 pulses per second. It was incorporated into a sophisticated laser system which furnishes a variety of synchronized laser pulses whose durations ranged from 100 ps to < 100 femtosecond (1000 fs = 1 ps). This laser system was used to perform many of the experiments described below (e.g. [2,7,8,14]).

(2) development of new optical measurement techniques. We developed several new optical coherence techniques to monitor the flow of vibrational energy within a large organic molecule excited by a ps laser pulse. The most interesting sequence was called "pump-induced CSRS" [6]. This method used one photon from a pump pulse to excite a specific vibration of a solid state molecule at low temperature, and then used three photons from a delayed pulse pair to probe the energy flow out of the initial state and into the ground state. The significance of this result: it is the first technique capable of simultaneous observation of energy flow out of one state and into another state. We also developed the "ultrafast microscope". This is an apparatus which acquires stop action images of solid materials irradiated by intense light pulses with 2 ps resolution in time and one μm resolution in space. This apparatus is the first practical ultrafast imaging system, and it was used to obtain time and space resolved information about solids caused to explode by laser pulses.

(3) experimental measurements of the ultrafast microscopic dynamics of mechanical energy transfer in molecular solids. The idea here is to excite a specific vibrational mode of a large molecule and investigate the loss of excitation due to energy transfer with the surrounding solid matrix (vibrational relaxation) and the appearance of excitation in lower energy states. Experimentally, the excitation loss is far easier to study, but having performed extensive work in this area, we have now turned to studying the latter phenomenon. In [6], we studied the reappearance of the ground state after excitation of about ten different vibrations of the large molecule pentacene. The large body of data obtained was found to be in agreement with the "phonon random walk" model discussed below. The significance of this work is that we have, for the first time, a detailed understanding of how excess vibrational energy is dissipated in a solid. This issue bears strongly on the issue of chemical reaction rates, and mechanical (e.g. shock) stimulation of chemical reactions.

(4) experimental measurements of the ultrafast macroscopic dynamics of ultra hot molecular materials. The thermal explosion resulting when a solid (e.g. a polymer) is irradiated by an intense picosecond light pulse was studied by ultrafast microscopy [2-4,7-8,14]. We have performed quantitative measurements of the mechanism of initiation, the blast wave, the solid state shock wave, thermally stimulated solid state acoustic waves, and the motion of melt fronts. This work is the first to study these phenomena on the ultrafast time scale. We invested considerable in developing experimental methodologies to acquire and

interpret ultrafast images, and developing new experimental probes of these complex phenomena. The most significant result was the observation of a 20 ps delay between the time the polymer was heated, and the time it exploded. The delay is induced by the redistribution of mechanical energy within the molecules. The significance of this delay is that it should be possible to study chemical and physical properties of ultra hot matter, simply by conducting the entire investigation in the 20 ps prior to the explosion.

(5) theoretical studies of vibrational energy transfer and shock wave induced chemical reactions. There has been a lot of previous work on vibrational relaxation. We set out to understand the entire process of vibrational cooling, which consists of many sequential and parallel vibrational relaxation steps. We developed the phonon random walk model, which describes how an excitation steps through many different states before it reaches the ground state. It is in excellent agreement with the data obtained in [6]. Then we began to realize that shock wave induced multiphonon up pumping is the same process, but in reverse. We developed a new model to describe the chemical reactions induced in molecules pumped by a shock wave, and developed a new explanation for the formation of "hot spots" which are produced in shocked energetic solids. We are extending this work, using supercomputer simulations, in order to understand how chemical reactions induced by a shock wave can propagate their influence to nearby regions of the lattice. This theoretical work will shortly be joined to experiments involving ultrafast imaging studies of laser generated solid state shock waves.

C. Publications acknowledging support by this grant

1. "Picosecond YAG Laser Amplifier and Electrooptic VFET Pulse Switch for High Power, High Repetition Rate Operation", J. C. Postlewaite, J. Miers, C. Reiner, and Dana D. Dlott, IEEE J. Quantum. Electron. QE-24, pp. 411-417 (1988).

2. "Ultrafast Imaging Study of Optical Damage Dynamics and Laser-produced Wave Propagation in Polymethyl Methacrylate", H. Kim, J. C. Postlewaite, T. Zyung, and Dana D. Dlott, J. Appl. Physics 64, pp. 2955 (1988).

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5. "Application of a Two-color Free-Electron Laser to Condensed Matter Molecular Dynamics", Dana D. Dlott and Michael D. Fayer, J. Opt. Soc. Am. B, 6, pp. 977-994 (1989).

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7. "Ultrafast Imaging of 0.532 μm Laser Ablation of Polymers: Time Evolution of Surface Damage and Blast Wave Generation", T. Zyung, H. Kim, J. C. Postlewaite, and Dana D. Dlott. J. Appl. Phys. 65, pp. 4548-4563 (1989).

8. "Time Dependent Self-Focusing and a 20 Picosecond Delay in Laser Ablation of Polymers". H. Kim, T. Zyung, J. C. Postlewaite, and Dana D. Dlott. Appl. Phys. Lett., 54, 2274-2276 (1989).

9. "Ultrafast Vibrational Energy Transfer in the Real World: Laser Ablation, Energetic Solids, and Hemeproteins, Dana D. Dlott, J. Opt. Soc. Am. B. (in press).

10. "Biast and Shock Wave Dynamics in Complex Molecular Solids", Hackjin Kim and Dana D. Dlott, Shock Waves in Condensed Matter, 1989 (in press).

11. "Vibrational Cooling (and Heating) of Large Molecules in Solids", Dana D. Dlott, J. Lumin. (in press).

12. "Shocked Molecular Solids: Vibrational Up Pumping, Defect Hot Spot Formation, and the Onset of Chemistry", Michael D. Fayer and Dana D. Dlott, J. Chem. Phys. (in press).

13. "Theory of Ultrahot Molecular Solids: Vibrational Cooling and Shock Induced Multiphonon Up Pumping" Hackjin Kim and Dana D. Dlott, J. Chem. Phys. (submitted).

14. "Ultrafast Microscopy of Solids Irradiated by Giant Picosecond Pulses", Hackjin Kim and Dana D. Dlott, in Optics, Electrooptics & Laser Applications in Science & Engineering, Ed. J. I. Steinfeld (SPIE Proc. Vol. xx, 1990) (in press).

D. List of all participating scientific personnel

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