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13. ABSTRACT *(Maximum 200 words)*

Despite wide ranging efforts, little is known about the molecular basis of initiation to detonation by shock waves of energetic solid materials. Ultrafast optical spectroscopy was used to study molecular energy transfer and shock wave induced chemistry in energetic materials and related systems. Theoretical models were developed to gain further understanding of these important processes.

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"Response of Energetic Solids to Light, Heat and Shock Pulses"

Final Report

Author: Dana D. Dlott

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A. Statement of the problem studied

Despite wide ranging efforts, little is known about the molecular basis of initiation to detonation of energetic solid materials. The specific systems of interest are useful secondary explosives such as HMX or RDX, which are crystals of relatively large organic molecules. Initiation is ordinarily induced by a shock wave. A shock wave produces a sudden mechanical perturbation of the material leading to temperature and pressure increases. These increases can be much faster than the time required for mechanical or thermal equilibrium, so these processes cannot readily be investigated by static experimental methods such as static high pressure, or slow heating to decomposition.

It is therefore desirable to understand how these molecular materials respond to sudden shock pulses. To assist our fundamental research effort, it is also useful to investigate the response of these materials to sudden heat and light pulses. In order to carry out this research, it is necessary to develop new experimental techniques, use these techniques to make critical measurements, and then develop theoretical models to enhance our understanding of these important processes. The questions we seek to answer are:

- What is the detailed (microscopic) state of molecules just behind a shock front?
- What are the energy transfer dynamics occurring behind the front prior to the attainment of thermal equilibrium?
- How do energetic molecules react when driven by a sudden large amplitude temperature jump?
- What is the microscopic origin of hot spots which often are associated with shock initiation to detonation?
- How do these microscopic level phenomena combine to produce observable macroscopic level phenomena?

B. Summary of most important results

Multiphonon up pumping. Molecular vibrations must be activated in order for chemical reactions to occur. The activation by a shock wave occurs via multiphonon up pumping. In a series of papers, we described this process theoretically, using supercomputer simulations of anharmonic lattice dynamics and molecular dynamics. We also described the influence of up pumping on

initiation to detonation. Finally, using the temperature jump technique described below, we made the first measurements of up pumping in solids and liquids, and we directly determined the rate of up pumping in an energetic material, nitromethane.

Ultrafast temperature jump production. In a detonation, the temperature of the material is increased perhaps 1,000 degrees over the time scale of psec to nsec. The heating rate is therefore on the order of $dT/dt = 10^{12\text{-}15}$ deg/s. Materials subjected to such a large heating rate behave differently from materials heated slowly. In a series of papers, we described how to produce and measure such a large heating rate in a variety of condensed materials. One method we developed involved embedding a near-infrared dye in the material. This dye absorbs light from a psec pulsed laser to heat the material. It also has a visible absorption transition which changes with temperature, so it can be used as a molecular thermometer.

Chemical decomposition reactions at large heating rates. The chemical decomposition of energetic molecules or polymeric binders has been studied extensively using techniques which result in rather slow heating. Using ultrafast temperature jump, we have studied the explosive thermal decomposition of several materials at the large heating rates characteristic of detonations. We find the chemical kinetics to be radically different at large heating rates. Many materials can be rapidly heated to temperatures far beyond those possible with slow heating.

High repetition shock wave generation. There is currently no good way to generate well-characterized solid state shock waves at a high repetition rate (e.g. 10-1000 shocks/sec). High repetition rate is necessary for high precision measurements of shock wave dynamics on the picosecond time scale. A few years ago, I became aware of a laser imaging system developed by Graphics Technology International (GTI) which involved high speed laser ablation transfer (LAT) of a polymer film from a substrate to a receiver. In essence, this system prints by making 10 million solid state shock waves per second. In collaboration with GTI, I began an investigation of the fundamental mechanisms of LAT. This work led to several publications, and to the development of a number of new optical diagnostic techniques for studying laser produced shock waves (ultrafast imaging, optical microscopy), and to the development of novel layered structures for shock wave generation. Using the technology developed at Illinois and at GTI, we have now been able to microfabricate large area shock target arrays which allow us to produce

shock waves in solids at high repetition rates and study their propagation with nanometer spatial resolution.

C. Publications supported by ARO contract

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"Dynamics of Laser Ablation Transfer Imaging Investigated by Ultrafast Microscopy", I. -Yin Sandy Lee, William A. Tolbert, Dana D. Dlott, Mark Doxtader, Dana Arnold, Diane Foley and Ernest R. Ellis, J. Imaging Science and Technology **36**, pp. 180-187 (1992).

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"Applications of Ultrafast Temperature Jump Spectroscopy to Condensed Phase Molecular Dynamics", Sheah Chen, I-Y. Sandy Lee, William Tolbert, Xiaoning Wen and Dana D. Dlott, J. Phys. Chem., **96**, pp. 7178-7186 (1992).

"Chemical Reaction Initiation and Hot Spot Formation in Shocked Energetic Molecular Materials", Andrei Tokmakoff, Michael D. Fayer, and Dana D. Dlott (J. Phys. Chem., in press, 1993). (Reprints not available yet)

"High Speed Color Imaging Using Laser Ablation Transfer Films with a Dynamic Release Layer: Fundamental Mechanisms Investigated by Ultrafast Microscopy and Optical Thermometry", William A. Tolbert, I-Yin Sandy Lee, Dana D. Dlott, Mark M. Doxtader, and Ernest W. Ellis, (submitted to J. Imag. Sci. & Tech.). (Reprints not available yet).

"Ultrafast Dynamics in Complex Molecular Solids", H. Kim, PhD Thesis, 1990 (PhD thesis reprints not available).

"Ultrafast Studies of Diffusion and Electron Transfer", J. Miers, PhD Thesis, 1992 (PhD thesis reprints not available).

(note: "Low Temperature Vibrational Relaxation...." on the ARO list was withdrawn and its contents incorporated into "Applications of Ultrafast Temperature Jump ....").

D. List of participating scientific personnel

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