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6. AUTHOR(S)
Dana D. Dlott

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
University of Illinois
Box 37- 1, Noyes Lab
505 S. Mathews Ave.
Urbana, IL 61801

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13. ABSTRACT *(Maximum 200 words)*

The problem is to develop experimental methods for studying the first events in initiation of an energetic material by a shock wave, to develop a detailed understanding of how initiation occurs. Using advanced laser systems in our laboratory, we have developed techniques to reproducibly generate microshock waves in energetic materials. We have developed new techniques to probe the behavior of materials and molecules during the shock process. In order to obtain the desired high time resolution of picoseconds, it is necessary in addition to having a laser which reproduces a picosecond pulse, to engineer extremely small, sub-optical wavelength energetic material structures. We have succeeded in doing this and have obtained data on technologically significant energetic materials TATB, RDX, PETN and NTO. The data obtained in our laser shock experiments has time resolution several orders of magnitude faster than the present state of the art, which is needed to understand the initial steps in initiation. In a parallel development, we have used picosecond mid-infrared pulses to investigate molecular energy transfer in nitromethane. These experiments provide insight into the transfer and dissipation of excess energy, such as that produced by the passage of a shock wave, in high explosives.

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energetic material, shock waves, shock initiation, molecular energy transfer, vibrational spectroscopy, ultrafast spectroscopy

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Final progress report

"Response of energetic solids to heat and shock pulses"

30719-CH, DAAH04-93-G-0016

Author: Dana D. Dlott

Statement of the problem and progress to date:

The problem is to develop experimental methods for studying the very first events in the initiation of an energetic material by a shock wave, in order to develop a detailed understanding of how initiation occurs. Understanding initiation could be expected to lead to safer energetic materials which are insensitive to accidents, and to the design of safer and better materials using a bottom-up engineering approach. Furthermore, the tools developed to research energetic material initiation can be extended to a variety of other practical problems involving materials under extreme conditions and shock waves. A specific secondary application where our ARO funded work has resulted in successful technology transfer to US industry is the problem of using lasers to produce high resolution color images with ultra high speed.

There are tremendous obstacles to these experimental measurements. Shock initiation combines some of the most difficult problems in mechanical engineering with some extremely complicated chemistry. The very first events in initiation occur on a very short time scale, at the level of individual molecules, or small groups of molecules. Until our work, no experimental methods existed which could make such measurements.

Using advanced laser systems constructed in our laboratory, we have developed methods to reproducibly generate microshock waves in energetic materials. The intensity of these shocks are of the typical order needed to initiate, namely a few tens of kilobars. In contrast to conventional techniques which require large guns or explosives and hazardous conditions, and which can be repeated infrequently (typically every few days), with our microshock technique we can generate several hundred shock waves per second, in volumes containing just a few ng of explosive. This technique of high repetition-rate microshock generation is the basis for the high resolution imaging methods mentioned above.

In addition to generating the shock waves, we have developed new methods to probe the behavior of materials and molecules during the shock process. Our lasers deliver optical pulses which last for picoseconds or femtoseconds, but until our work, nobody had succeeded in using similar lasers to obtain time-resolution better than even several nanoseconds. This is because shock waves in materials travel at velocities of a few μm/ns, so even the shortest optical pulses will not resolve shock-induced effects in materials unless a method can be found to obtain high spatial resolution. Spatial resolution of perhaps 1/10 of a μm is desired to study processes occurring in a few tens of ps. This resolution is quite a bit less than the wavelengths of lasers used in this research, so new ideas were needed. The important new idea which solves these problems is to engineer into our samples molecular structures which were smaller than a wavelength of light. These take the form of very fine particles, or very thin layers. We have succeeded in obtaining time and space resolution several orders of magnitude better than any prior measurements using this technique. Preliminary experiments using this method were performed on technologically significant energetic materials TATB, RDX, PETN and NTO.

We also need to obtain information about the molecular-level behavior of energetic materials. The tool we have used is vibrational spectroscopy. Ordinary vibrational spectroscopy, such as IR and Raman cannot provide the necessary time resolution and signal-to-noise, but we have had much success using CARS (Coherent anti-Stokes Raman Spectroscopy). Using CARS we have been able to demonstrate the ability to instantaneously measure the temperature, pressure, and composition of an energetic material subject to an intense shock wave, on the picosecond time scale. We have also used a novel technique termed "Two-dimensional Vibrational Spectroscopy". In this method, we combine a powerful infrared pulse with a Raman probe. The powerful IR pulse deposits energy into a specific vibrational mode of a condensed phase explosive and the Raman probe monitors how the energy flows through the molecules. This experiment provides insight into the molecular energy transfer processes which result when adding excess energy to an energetic material. The intent of these measurements is to better understand the fate of energy deposited by the passage of an initiating shock wave through the explosive. A detailed set of experimental results were obtained on a model homogeneous high explosive, nitromethane. This technique is presently being extended to technologically significant energetic materials.

This three-year research project has had considerable success. The publication list below attests to our productivity--we have published thirty one refereed papers, PhD theses and conference abstracts. More importantly, we have finally succeeded in demonstrating exactly how one goes about investigating the problems of energetic material initiation, using experimental measurements which provide the needed input for a fundamental point of view. It is hoped that continuation of this project will soon lead to a greatly improved understanding of this problem. It was a privilege and an honor to be able to contribute to the Army research mission in this manner. It is also very nice that this work can lead to significant technology transfer from DoD funded programs to US industry to enhance the competitiveness of the US economy.

Publications funded by this grant

1. "Chemical Reaction Initiation and Hot Spot Formation in Shocked Energetic Molecular Materials", Andrei Tokmakoff, Michael D. Fayer, and Dana D. Dlott, J. Phys. Chem., **97**, pp. 1902-1913 (1993).

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3. "High Speed Color Imaging Using Laser Ablation Transfer Films with a Dynamic Release Layer: Fundamental Mechanisms", William A. Tolbert, I-Yin Sandy Lee, Dana D. Dlott, Mark M. Doxtader, and Ernest W. Ellis, J. Imag. Sci. Technol., **37**, pp. 411-421 (1993).

4. "Ultrafast Temperature Jump in Polymers: Phonons and Vibrations Heat Up at Different Rates", Xiaoning Wen, William A. Tolbert and Dana D. Dlott, J. Chem. Phys. **99**, pp. 4140-4151 (1993).

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8. (*invited paper*) "Ultrafast Dynamics of Photothermal Polymer Ablation", William A. Tolbert, I.-Y. Sandy Lee, David E. Hare, Xiaoning Wen and Dana D. Dlott, in *Laser Ablation Mechanisms and Applications-II*, J. C. Miller and D. B. Geohegan, Eds., *AIP Conference Proceedings 288* (New York: AIP, 1994), pp. 559-568.

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30. Sheah Chen, “Vibrational energy transfer in condensed high explosives: nitromethane.” PhD Thesis, 1994, University of Illinois.

31. Sandy Lee, “The study of ultrafast dynamics behind a solid-state shock front using optical nanogauges”, PhD Thesis, 1995, University of Illinois.

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Dana D. Dlott, PhD, principal investigator.
Xiaoyu Hong, PhD, postdoctoral associate. Hong will be leaving in Feb. to take a research staff position at SDL, Inc.
Sheah Chen, research assistant, received his PhD in 1994. He is now a postdoctoral associate at the Institute for Atomic and Molecular Sciences in Taiwan.
Barbara Snider, BA, research assistant, left the group in 1995 to obtain an MS degree.
Edward Wen, received his PhD in 1993. He is now a postdoc at Northwestern.
William A. Tolbert, PhD, left to take a staff position at 3M Corporation.
Sandy Lee received her PhD in 1995 and left to take a postdoctoral position at Caltech JPL.
Larry Iwaki, B.A., is working on energetic materials and molecular energy transfer at UI.