

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 15 Apr 1999	3. REPORT TYPE AND DATES COVERED final progress report, 1 Apr 1996 to 31 Mar 1999	
4. TITLE AND SUBTITLE Initiation of energetic solids: the first nanosecond			5. FUNDING NUMBERS DAAH04-96-1-0038	
6. AUTHOR(S) Dana D. Dlott				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Illinois at Urbana Champaign			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER <i>ARO 34924.20-CH</i>	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by the documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT <i>Approved for public release; distribution unlimited.</i>			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The goal is to understand what occurs at the molecular level during shock initiation of energetic materials. We have developed the nanoshock technique, which lets us shock any solid material and study its molecules using ultrafast vibrational spectroscopy with 25 ps time resolution. Test experiments were conducted with anthracene to verify the performance of this technique, which was subsequently extended to energetic materials including RDX and NTO. A related theoretical effort looked at orientation effects in initiation. A related project is understanding the role of molecular vibrational energy transfer processes in initiation. Since we know little about energy transfer, we are concentrating on simple model systems under non shock conditions. We have used a new experimental apparatus which uses a infrared-Raman technique with 1 ps resolution to study nitromethane and other simpler liquids. A minor effort relates to technology transfer from our ARO-funded shock wave program to industry. In particular we have used ultrafast microscopy and shock wave generation techniques to improve laser photothermal imaging processes used in graphic arts by incorporating energetic materials into the imaging media.				
14. SUBJECT TERMS Energetic materials, shock wave initiation, molecular energy transfer			15. NUMBER OF PAGES 9	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. Z39-18
298-102

19990702 105

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

1. LIST OF MANUSCRIPTS

1. "Ultrafast time resolved studies of computer-to-plate imaging", David E. Hare, Stuart T. Rhea, Dana D. Dlott, Richard J. D'Amato, and Thomas E. Lewis, Proceedings of IS&T International Conference on Digital Printing Technologies, A. Melnyk, Ed. (Society for Imaging Science and Technology, Springfield, VA, 1996) pp. 273-276.
2. "Fundamental mechanisms of lithographic printing plate imaging by near-infrared lasers", David E. Hare, Stuart T. Rhea, Dana D. Dlott, Richard J. D'Amato, Thomas E. Lewis, J. Imag. Sci. Tech. 41, pp. 292-301 (1997).
3. "Ultrahigh time resolution vibrational spectroscopy of shocked molecular solids", Selezion A. Hambir, Jens Franken, David E. Hare, Eric L. Chronister, Bruce J. Baer and Dana D. Dlott, J. Appl. Phys. 81, pp. 2157-2166 (1997).
4. "Pulse duration dependence for laser photothermal imaging media", David E. Hare, Dana D. Dlott, Richard J. D'Amato and Thomas E. Lewis, in Proceedings of the 50th Annual Meeting of the Society for Imaging Science and Technology (Society for Imaging Science and Technology, Springfield, VA, 1997), pp. 290-295.
5. "Shock waves in molecular solids: ultrafast vibrational spectroscopy of the first nanosecond" Jens Franken, Selezion Hambir, David E. Hare and Dana D. Dlott, Shock Waves 7, pp. 135-145 (1997).
6. "New method for exposure threshold measurement of laser thermal imaging materials", David E. Hare, Stuart T. Rhea and Dana D. Dlott, J. Imag. Soc. Tech. 41, pp. 588-593 (1997).
7. "Pulse duration dependence of lithographic printing plate imaging by near-infrared lasers", David E. Hare, Stuart T. Rhea, Dana D. Dlott, Richard J. D'Amato and Thomas E. Lewis, J. Imag. Soc. Tech. 42, pp. 90-97 (1998).
8. "Ultrafast Raman spectroscopy of shock fronts in molecular solids", Guray Tas, Jens Franken, Selezion A. Hambir and Dana D. Dlott, Phys. Rev. Lett. 78, pp. 4585-4588 (1997).
9. "Coherent Raman spectroscopy of nanoshocks", Guray Tas, Selezion A. Hambir, Jens Franken, David E. Hare and Dana D. Dlott, J. Appl. Phys. 82, pp. 1080-1087 (1997).
10. "High power picosecond mid-infrared optical parametric amplifier for infrared-Raman spectroscopy", John C. Deak, Lawrence K. Iwaki and Dana D. Dlott, Opt. Lett 22, pp. 1796-1798 (1997).
11. "Ultrafast vibrational spectroscopy of shocks in molecular materials: the first 100 ps", Selezion A. Hambir, Jens Franken, Jeffrey R. Hill and Dana D. Dlott, in *Shock Compression of Condensed Matter--1997*, S. C. Schmidt, D. P. Dandekar, and J. W. Forbes, eds. (American Institute of Physics, New York, 1998) AIP conference proceedings, vol. 429 (1998), pp. 823-826.
12. "Picosecond vibrational spectroscopy of shocked energetic materials", Jens Franken, Selezion A. Hambir and Dana D. Dlott, in *Shock Compression of Condensed Matter--1997*, S. C. Schmidt, D. P. Dandekar, and J. W. Forbes, eds. (American Institute of Physics, New York, 1998) AIP conference proceedings, vol. 429 (1998), pp. 819-822.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

13. "Ultrafast Spectroscopy of Laser-driven Shock Waves in Molecular Materials", Jens Franken, Selezion A. Hambir and Dana D. Dlott, *Mol. Cryst. Liq. Cryst.* 314, pp. 25-36 (1998).
14. "Ultrafast Spectroscopy of Laser-driven Nanoshocks in Molecular Crystals", Selezion A. Hambir, Jens Franken and Dana D. Dlott, *Rev. High Pressure Sci. Technol.* vol. 7, (1998), pp. 891-896.
15. "The new wave in shock waves", Dana D. Dlott, Selezion Hambir and Jens Franken, *J. Phys. Chem. B* **102**, pp. 2121-2130 (1998).
16. "Orientation dependence of shock-induced heating in anharmonic molecular crystals", V. K. Jindal and Dana D. Dlott, *J. Appl. Phys.* 83, pp. 5203-5211 (1998).
17. "When Vibrations Interact: Ultrafast Energy Relaxation of Vibrational Pairs in Polyatomic Liquids", John C. Deak, Lawrence K. Iwaki and Dana D. Dlott, *Chem. Phys. Lett.* 293, pp. 405-411 (1998).
18. "Vibrational Energy Relaxation of Polyatomic Molecules in Liquids: Acetonitrile", John C. Deak, Lawrence K. Iwaki and Dana D. Dlott, *J. Phys. Chem. A* 102, pp. 8193-8201 (1998).
19. "Time-resolved three-dimensional microscopy of laser photothermal imaging processes", Serguei G. Koulikov and Dana D. Dlott, in *Advances in Non-Impact Printing Technologies 14* (Society for Imaging Science and Technology, Springfield, VA, 1998) pp. 172-175.
20. "Vibrational energy transfer in condensed phases", Lawrence K. Iwaki and Dana D. Dlott, in *Encyclopedia of Chemical Physics and Physical Chemistry*, J. H. Moore and N. D. Spencer, eds., (Institute of Physics, Philadelphia, PA, 1998), (in press).
21. "Ultrafast shock-induced orientation of polycrystalline films: applications to high explosives", Jens Franken, Selezion A. Hambir and Dana D. Dlott, *J. Appl. Phys.* (in press, 1998).
22. "Vibrational Energy Redistribution in Polyatomic Liquids: Ultrafast IR-Raman Spectroscopy of Nitromethane" John C. Deak, Lawrence K. Iwaki and Dana D. Dlott, *J. Phys. Chem. A* 103, pp. 971-979 (1999).
23. "Vibrational energy redistribution in liquid benzene", Lawrence K. Iwaki, John C. Deak, Stuart T. Rhea and Dana D. Dlott, *Chem. Phys. Lett.* (in press).
24. "Vibrational energy redistribution in liquid benzene", Lawrence K. Iwaki, John C. Deak, Stuart T. Rhea and Dana D. Dlott, *Chem. Phys. Lett.* (in press).
25. "Ultrafast spectroscopy of shock waves in molecular materials", Dana D. Dlott, *Annu. Rev. Phys. Chem.* (submitted Jan. 1999).
26. "Effects of energetic polymers on laser photothermal imaging materials", Serguei G. Koulikov and Dana D. Dlott, *J. Appl. Phys.* (submitted Feb. 1999).
27. "Picosecond vibrational spectroscopy of shocked solids", Ph.D. thesis of Jens Franken, 1998, University of Illinois.

2. SCIENTIFIC PERSONNEL

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Guray Tas: postdoctoral associate. Left 1/1/97 to take a position at Brown University

Jens Franken: graduate research assistant

Joseph J. Cavaleri: postdoctoral associate, Ph.D. 1997 from U. Kansas

Alexi Lagoutchev: postdoctoral associate, Institute of General Physics, Moscow, 1992

Lawrence K. Iwaki: graduate research assistant

Dana D. Dlott: principal investigator

Honors/Awards/Degrees:

Dlott: Elected Fellow of American Physical Society, received NIRIM (National Institute for Research on Inorganic Materials) fellowship from Japanese Government to support Japan visit. One of 8 internationally known shock wave researchers to lecture at the summer school on shock waves at Lake Biwa, sponsored by the Japanese government. Elected Fellow of Optical Society of America.

Franken: Received fellowship from APS to attend 1997 APS conference on Shock Compression of Condensed Matter. Received fellowship from GRC to present invited paper at Gordon Research Conference on Energetic Materials. Received his Ph.D. degree and is presently doing postdoctoral research at the Institute for Atomic and Molecular Sciences, Taipei, Taiwan. Thesis: Picosecond vibrational spectroscopy of shocked solids.

3. REPORT OF INVENTIONS

none

4. SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

We have made progress in three areas: (1) ultrafast shock wave spectroscopy; (2) ultrafast energy transfer; (3) improving laser photothermal imaging

Shock wave spectroscopy. Until recently, most of our work was aimed toward making the apparatus work well and measuring the shock waves we generate. Many experiments were performed with anthracene, to verify the performance of the technique. It was found we could obtain vibrational spectra with 25 ps time resolution and could determine the pressure and temperature of our samples. Most recently we have worked mainly on applications to energetic materials and other materials such as polymers. Unfortunately it turns out the biggest shock we can generate, 4-5 GPa, is not big enough to reliably initiate energetic materials. I suppose this is because initiation tends to scale like P^2t , and since t is short (our shocks last for 1 ns), pressure P must be larger than anticipated. The more powerful YLF laser we installed makes everything work better and more reliably, and it improves the CARS detection part of the apparatus, but it does not generate bigger shocks. Investigating why this is so might lead us to understand how to make bigger shocks.

We have studied two energetic systems in detail and have obtained interesting results. These are NTO, a high performance insensitive energetic material, and cyuranic azide (C_3N_{12}), a model system which is an extremely sensitive material with relatively simple chemistry.

In NTO, we see a big shock go through the NTO, but no chemistry. However there is something interesting and totally unexpected. After the 1 ns shock passes through, the polycrystalline NTO layer becomes partially oriented by the shock (see Fig. 1). Thinking about it, the shock-induced orientation is not a surprise, but was totally unexpected and I have never seen anything about it previously. The implication stems from the

fact that shock initiation of single crystals can be orientation dependent. People don't usually think too much about this because most energetic materials are composites of polycrystals. However if the shock passing through the composite orients the polycrystals in either sensitive or insensitive directions, a substantial effect on sensitivity might result.

The cyranic azide experiment was intended to be the first real time observation of ultrafast shock induced chemistry using molecular-specific vibrational spectroscopy (as opposed, say, to seeing a flash of white light). We expect the shock to knock N_3 (azide) off the molecules. We have actually seen this and it is interesting. We see the N_3 symmetric stretch intensity decline and a broad feature grow in about where condensed phase N_2 should be (see Fig. 2). The lesson for us molecular spectroscopists is this new feature is incredibly broad. That is because it isn't just N_2 in a crystal lattice, it is in a crystal lattice being massively destroyed. Our problem is we don't reproducibly initiate the azide. As we scan through the shock sample, some spots of the azide initiate and others do not. We are trying to fix this. One way is to make a bigger shock.

Ultrafast energy transfer. The energy transfer experiments are going very well. However they are very difficult and it takes a lot of time to get the data and interpret it, so progress is a bit slower than I would like. Our biggest completed accomplishment is a detailed study of nitromethane with unprecedented time resolution and sensitivity. We have done everything we can with nitromethane. One thing this work is teaching me is that essentially everything people have said about vibrational energy transfer in condensed phases is wrong. Things are more complicated and interesting than expected. Our major finding with nitromethane is the model of the "vibrational cascade" which everybody has been using for years does not apply. Our early experiments were just good enough to make us think we were seeing a vibrational cascade, but we were wrong. We are making a lot of progress on other systems. We are trying to move our effort along by studying simple and supposedly understandable model systems like water and methanol, and mixing in some interesting complex and hard to understand systems such as explosives, polymers, etc.

Imaging science. For several years we have been taking some of the techniques developed in our ARO energetic materials effort and applying them to laser photothermal imaging processes. Our new result is exciting. One big constraint in the industry is the expense of laser photons. People are always looking for ways to reduce the laser exposure fluence requirements. Even an improvement of 10% is regarded as significant. For many years researchers at 3M, Polaroid and other places have tried to do this by putting energetic materials in the imaging materials. The idea is to replace some of the expensive optical energy with chemical energy. Nobody has been successful (in fact the energetic materials usually make things worse) until now. By incorporating nitrocellulose into a system used by Presstek, Inc., for computer to plate imaging, we have been able to reduce the exposure threshold by a factor of three, which is a big deal. Energetic materials in a thin film heated by a laser don't explode. They just decompose and make hot gas. In prior designs, this hot gas just leaked into space and didn't do much. We have confined the hot gas from nitrocellulose decomposition under a tough silicone rubber coating 2.5 μm thick. Anybody who works with explosives can tell you the importance of confinement. Time resolved microscopy, a technique developed with ARO support, has shown the confinement is what decreases the need for laser energy. A series of images of exploding nitrocellulose film is shown in Fig. 3.

5. TECHNOLOGY TRANSFER

Presstek, Inc. By studying Presstek laser transfer materials and applying thermal and shock models which were developed in the course of ARO shock wave experiments, we have been able to predict how the materials would respond when subjected to different types of laser pulse conditions. That has helped Presstek in their

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

efforts to develop partnerships with companies which make laser imaging engines, each of which has its own particular laser exposure condition.

Markem Corp. Markem (Keene, NH) uses lasers to transfer marking materials such as epoxy resins to electronic parts. Dlott was consulted to help understand the mechanism, to optimize the process, and to develop new technologies.

Abbott Labs. Representatives from Abbott heard me talk at the ACS annual meeting in San Francisco. They are interested in using laser shock waves to drill into skin, to replace the need for needles. I visited their lab and talked about our work. We might enter in a formal collaboration soon.

ARL. Kevin McNesby of ARL and I have talked a lot about low velocity impact and the sensitivity of energetic materials. He wrote a nice paper which I critiqued. I think there is a lot which is not known about low velocity impact and I am thinking about a new theoretical model based on our conversations.

Figure 1. Ultrafast CARS spectrum of a polycrystalline film of NTO with a 4 GPa shock. After the 1 ns shock, the intensities of some transitions change on the ~5 ns time scale, indicating shock induced orientation of the nanocrystals.

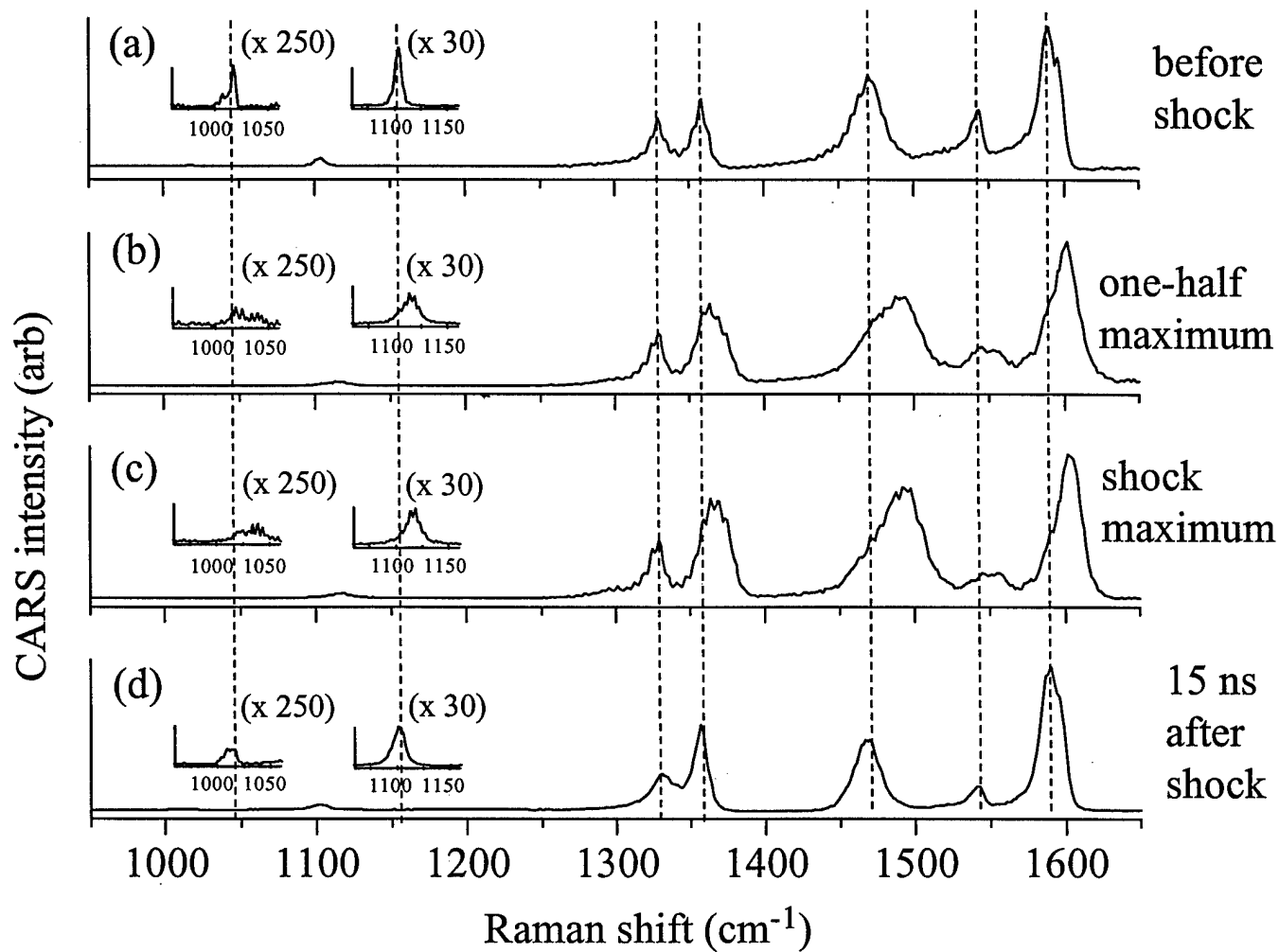
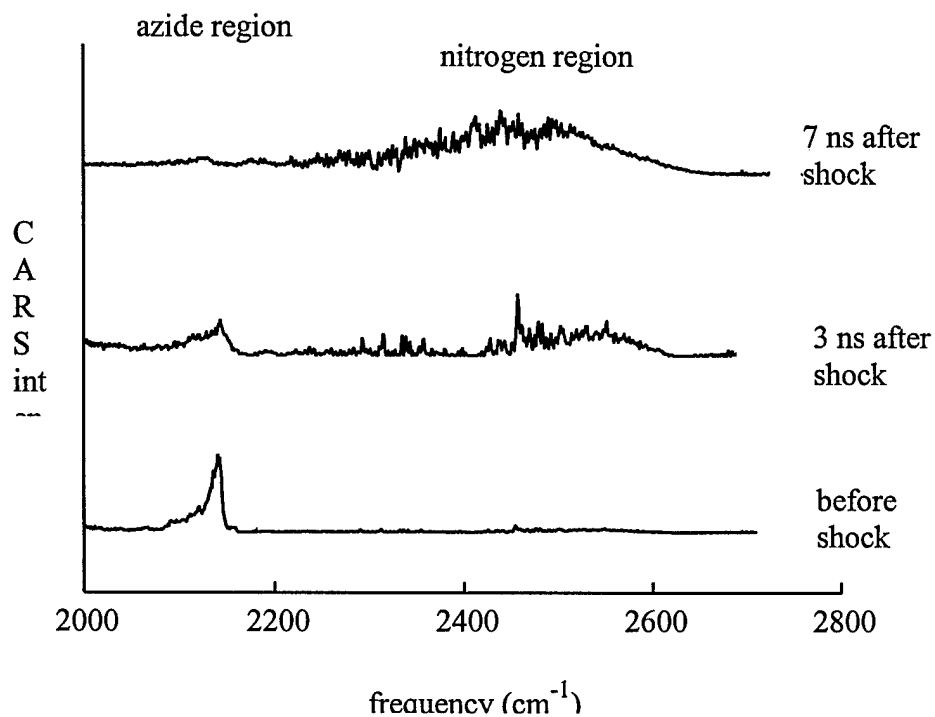


Figure 2. Ultrafast CARS spectrum of a ~ 4 GPa shock going through a thin film of C_3N_{12} . Before shock only the azide symmetric stretch is seen at ~ 2160 cm^{-1} . The broad region which appears is attributed to condensed phase N_2 in a badly damaged crystal lattice.



REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Figure 3. Time resolved microscopic image of the exposure of a single pixel of an image in an imaging material with a silicone coating layer and an energetic nitrocellulose underlayer. The exposure pulse comes in from the right. The imaging material's surface is at left. The laser pulse duration is 100 ns. The diameter of the exposed spot is about 30 micrometers.

