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Ultrafast spectroscopy of energetic materials: Toward a molecular understanding of impact sensitivity

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6. AUTHOR(S)
Dana D. Dlott

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Illinois at Urbana Champaign

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13. ABSTRACT (Maximum 200 words)
We have progress to report in three areas: (1) fast vibrational spectroscopy of nanoenergetic material ignition; (2) ultrafast surface spectroscopy; (3) 3D spectroscopy of ultrafast vibrational energy transfer. The original goals of this project have not changed, however we have extended our work to include nanotechnology energetic materials. We developed a fast laser-ignition technique for these materials and have successfully probed the time and space dependence of chemistry of Al + oxidizer systems. Using vibrational sum-frequency generation (SFG) we have probed the structure of shock fronts with 1.5Å resolution. With 3D spectroscopy we have studied vibrational energy transfer in water and for the first time we have been able to watch vibrational energy flow across the interface between a molecular nanostructure and its surroundings.

14. SUBJECT TERMS
energetic materials, shock initiation, ultrafast spectroscopy, combustion, nanotechnology

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1. LIST OF MANUSCRIPTS

a. Manuscripts submitted but not published


b. Papers published in peer-reviewed journals


21. “Propagation of shock-induced chemistry in nanoenergetic materials: the first micrometer”, Yanqiang Yang, Shufeng Wang, Zhaoyong Sun and Dana D. Dlott, J. Appl. Phys. 95, pp. 3667-3676 (2004). This paper was selected to appear in both the “Virtual journal of Nanoscale Science & Technology” and the “Virtual journal of ultrafast science”


c. Papers published in non-peer reviewed journals or conference proceedings


d. Papers presented at meetings but not published in conference proceedings


2. (invited, plenary lecture), 2001 International Conference on Time-resolved Vibrational Spectroscopy, Okazaki, Japan (May ’01), “Ultrafast three dimensional vibrational spectroscopy of vibrational energy relaxation in liquids”.


5. (invited) Sixth International Conference on Molecular Reaction Dynamics in Condensed Phases, Laguna Beach, Ca (Feb. ‘01), “Three dimensional vibrational spectroscopy of molecular liquids”.


10. (invited) Gordon Conference on Vibrational Spectroscopy, Newport, RI (July ’02), “Three-dimensional spectroscopy of vibrational energy transfer in liquids”.

11. (invited) Advanced Energetics Technology Exchange, Lawrence Livermore National Laboratory (Sept. ’02), Livermore, CA, “Ultrafast spectroscopy of nanoenergetic materials”.

12. (invited) Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI (Oct. ’02) “Three-dimensional spectroscopy of vibrational energy transfer in liquids”.

13. (invited) Coblentz Award Symposium, Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI (Oct. ’02), “Three-dimensional spectroscopy of vibrational energy transfer in liquids”.

14. (invited) 2003 Symposium on Nano Materials for Aerospace (Jan ’03), Corpus Christi TX, “Ultrafast spectroscopy of nanoenergetic material ignition”.

15. (invited) Argonne National Laboratory, Advanced Photon Source (May ’03), “Vibrational sum-frequency generation spectroscopy at high pressure”.


17. (invited) Molecular Dynamics of Energetic Materials Workshop, International Technology Research Institute, Inc., Laurel, MD (June ’03), “New ideas and limits for energetic materials”.

18. (invited) Femtochemistry VI, Paris, France (July ’03), "Three dimensional spectroscopy of vibrational energy relaxation in liquids".

19. APS Conference on Shock Compression of Condensed Matter, Portland, OR, (July ’03), “Shock compression of molecules with 1.5 angstrom resolution”.


23. Seventh International Conference on Molecular Reaction Dynamics in Condensed Matter, Laguna Beach, CA (Mar. ’04), “Molecular dynamics with ultrahigh time and space resolution with multidimensional vibrational spectroscopy”.

24. (invited) CDAC Workshop, Argonne National Laboratory, Argonne, IL (May ’04), “Interface molecular dynamics at high dynamic and static pressure”.

25. (invited) International workshop on "Materials under extreme conditions: experimental validation of atomistic modeling, European Centre for Atomic and Molecular Computations Lyon, France, (May ’04), “Shock compression of molecules with picosecond time resolution and angstrom spatial resolution”.


27. (invited, Keynote address), International Conference on Computational & Experimental Engineering and Sciences, Madeira, Portugal, (July ’04). “Nanotechnology energetic material dynamics studied with nanometer spatial resolution and picosecond temporal resolution”.


29. (invited) Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Providence, RI (Oct. ’04) “Ultrafast three-dimensional IR-Raman spectroscopy”

2. SCIENTIFIC PERSONNEL
Dana D. Dlott: principal investigator
Yanqiang Yang: postdoctoral associate
James Patterson: graduate research assistant
Zhaoyong Sun: postdoctoral associate
Selezion A. Hambir: postdoctoral associate
Hyunung Yu: postdoctoral associate

Honors/Awards/Degrees:

Our paper, “Propagation of shock-induced chemistry in nanoenergetic materials: the first micrometer”, was selected to appear in both the “Virtual journal of Nanoscale Science & Technology” and the “Virtual journal of ultrafast science”
James Patterson received his PhD degree in 2004.

Fellow of the Optical Society of America, 1999
Associate, Center for Advanced Study, 1999
2001 Charles E. Ives Award from the Society for Imaging Science and Technology, 2001
Panel on International Assessment of Molecular Dynamics Simulations of Energetic Materials, 2002
Cyber College Distinguished Lecture Series, University of Arkansas at Little Rock

3. REPORT OF INVENTIONS

Provisional application 60/327,733, “Jetting behavior in the laser forward transfer of rheological systems”.

4. SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

We have progress to report in three areas: (1) fast vibrational spectroscopy of nanoenergetic material ignition; (2) ultrafast surface spectroscopy; (3) 3D spectroscopy of ultrafast vibrational energy transfer. We have completed an extensive review of fast processes in energetic materials.

1. Fast vibrational spectroscopy of nanoenergetic material ignition. We are developing methods to study the ignition of nanoenergetic materials with high time and space resolution. In these experiments, we suspend metal nanoparticles in an oxidizing matrix and flash-heat them with a short 100 ps duration laser pulse. So far we have published work on model systems where the oxidizer is a continuous polymer, either nitrocellulose (NC) or Teflon, but we have also begun investigating materials where the oxidizer is a nanoparticle such as MoO3 and CuO. Using time-resolved vibrational spectroscopy to monitor oxidizer consumption via O=O or CF stretching transitions, we found that chemistry occurred in two stages. In the first stage, the hot Al particle reacted with nearby oxidizer. In the second stage, the hot spot formed as a result of laser plus chemical heating, caused reactions to spread through the surrounding oxidizer between the nanoparticles, creating a roughly spherical reaction volume. The rate of these processes depends on a number of factors, but roughly the first stage is about 300 ps and the second stage is a few ns. When the concentration of nanoparticles was high enough, these reaction volumes merged, which could be seen under a microscope. Using size-selected nanoparticles and varying concentrations, we were able to measure the distance of reaction propagation over distance ranges of 100 nm to 2 µm. By analyzing the dependence of the propagation distance on laser power, we were able to determine the second stage of reaction was caused by shock-induced dissociation of NC or Teflon polymer. Curiously, Teflon is more susceptible to this shock dissociation than NC, which is often regarded as more reactive.

2. Surface and interface spectroscopy. We have made the first detailed experimental measurements of shock compression in molecules with time and space resolution good enough for a direct comparison to MD simulations. In shock compression spectroscopy, the time resolution is usually limited by the shock transit time across the sample layer. Over the past several years we have developed a laser shock spectroscopy apparatus that can detect molecular monolayers. We can put down a wide variety of molecular structures into self-assembled monolayers (SAMs). Using vibrational sum-frequency generation, we can selectively detect the vibrational transitions of the atomic groups at the top of this monolayer. For instance in a monolayer consisting of 18-carbon chains, we can probe only the surface CH3 groups, giving us spatial resolution of 1.5Å. After launching a shock into this monolayer, we observe a shock induced phase transition to a disordered state. The monolayer spontaneously reorders in 10-30 ps. Chains with an odd number (15) of carbons reorder faster than chains with an even number (18), which we can explain by molecular mechanics calculations of the potential surface. This work provides useful fundamental information about shock compression of lubricants and
biological membranes. It will serve as a benchmark to validate or refute the accuracy of shock molecular dynamics simulations. This technology will serve as an enabling platform for subsequent studies of a wide variety of molecular groups and interfaces.

3. **Vibrational energy transfer.** Our IR-Raman apparatus has been used to study condensed phase vibrational energy transfer. Vibrational energy transfer is important in the dynamics of energetic materials, but the fundamental mechanisms are still poorly understood. We have developed the first experiment capable of directly measuring the flow of vibrational energy with high time and space resolution. We have studied the vibrational dynamics of water, which remains a mysterious and complicated problem. In addition we have been able to study vibrational energy flow across interfaces between nanostructures and their surroundings.

5. **TECHNOLOGY TRANSFER**

**Naval Research Laboratory.** Our ultrafast microscopy apparatus has been used by visitors from the NRL (Doug Chrisey’s group) to study laser-induced material transfer in materials that can be used to fabricate electronic and biological components. Some of these are viscous or rheological liquids. We found that under the right conditions a very thin focused jet of liquid could be transferred to a substrate, resulting in spatial resolution that was quite a bit finer than the diameter of the laser beam. A patent has been applied for. Don’t start spending any of the money any time soon, however. This high resolution has been exploited by other groups at NRL to develop methods of fabricating biochips by printing viscous protein and nucleic acid solutions with high speed and high resolution.

**Presstek, Inc.** We have continued our longstanding collaboration with Presstek, Inc., in studying the laser ablation imaging of thin films used for computer to press imaging. Ultrafast microscopy is used to look at the explosive removal and transfer of material initiated by short laser pulses.

**Optodot, Inc.** Dlott’s studies on fast laser heating with near-IR dyes have in part formed the basis for a new generation of fast laser switching technologies in the optical internet region of 1.3 to 1.8 µm. The fast transient techniques developed in our lab have been used to evaluate samples sent to us by a start-up company, Optodot, Inc. of Cambridge MA. Dr. Stephen Carlson who worked with us in the early near-IR project started the company last year. The idea is to use fast absorption and photothermal effects in new near-IR dyes to turn on and off signals in optical fibers.

**Optics and Photonics News.** In the past few years, in conversations with engineers in industries that use laser ablation for various manufacturing and imaging processes, we found that a significant practical problem involved keeping one or more lasers focused on a target mounted on a production machine that was moving and vibrating. We developed a theory of this “misfocus” problem and derived conditions to maximize tolerance. We determined how to make laser imaging materials that tolerated more misfocus. A popular account of this work was written and published in this magazine, which is the monthly news magazine of the Optical Society of America.

**MeadWestvaco.** We have collaborated with researchers from Mead Westvaco Corp. on laser photothermal imaging processes and the use of energetic nanoparticles in imaging science.
**REPORT OF INVENTIONS AND SUBCONTRACTS**

(Pursuant to "Patent Rights" Contract Clause) (See Instructions on back)

The 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 comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Services and Communications Directorate (9000-0095). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

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### SECTION I - SUBJECT INVENTIONS

1. **NAME OF CONTRACTOR/SUBCONTRACTOR**
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   - b. FINAL

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   - b. TO 200412

5. **NAME(S) OF INVENTOR(S)**
   - a. Dlott, Dana D.
   - b. Young, H. D.
   - c. Ringeisen, B. R.

6. **ADDRESS (Include ZIP Code)**
   - a. C/O Grants and Contracts, 109 Coble Hall, 801 S. Wright St., Champaign, IL 61820
   - b. Naval Research Laboratory
   - c. Naval Research Laboratory

7. **SUBCONTRACTOR(S)**
   - a. Naval Research Laboratory
   - b. Naval Research Laboratory

8. **ADDRESS (Include ZIP Code)**
   - a. Washington, D.C. 20375
   - b. Washington, D.C. 20375

9. **DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)**
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### SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)

6. **NAME OF SUBCONTRACTOR(S)**
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