

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 12 Jan 2005		3. REPORT TYPE AND DATES COVERED Final Technical Report, 01 Apr 2000 to 31 Dec 2004
4. TITLE AND SUBTITLE Ultrafast spectroscopy of energetic materials: Toward a molecular understanding of impact sensitivity			5. FUNDING NUMBERS DAAD19-00-1-0036	
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 40444.26-CH	
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 Approved for public release; distribution unlimited			12 b. DISTRIBUTION CODE	
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			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	

1. LIST OF MANUSCRIPTS

a. Manuscripts submitted but not published

1. “Dynamical Effects of the Oxide Layer in Aluminum Nanoenergetic Materials”, Shufeng Wang, Hyunung Yu, Yanqiang Yang and Dana D. Dlott, *Propellants, Explosives and Pyrotechnics* (in press).
2. “Near-infrared and Visible Absorption Spectroscopy of Nanoenergetic Materials Containing Aluminum and Boron”, Yanqiang Yang, Shufeng Wang, Zhaoyong Sun and Dana D. Dlott, *Propellants, Explosives and Pyrotechnics* (in press).
3. “Ultrafast Dynamics of Self-Assembled Monolayers Under Shock Compression: Effects of molecular and substrate structure”, Alexei Lagoutchev, James E. Patterson, Wentao Huang and Dana D. Dlott, *J. Phys. Chem. B* (in press).
4. “Ultrafast shock compression of self-assembled monolayers: a molecular picture”, James E. Patterson and Dana D. Dlott, *J. Phys. Chem. B* (in press).
5. “Quantitative vibrational sum-frequency generation spectroscopy of thin layer electrochemistry: CO on a Pt electrode”, G. Q. Lu, A. S. Lagutchev, D. D. Dlott and A. Wieckowski, *Surf. Sci.* (submitted 12/04).

b. Papers published in peer-reviewed journals

1. (*invited*) “Vibrational energy redistribution in polyatomic liquids: 3D infrared-Raman spectroscopy”, Dana D. Dlott, *Chem. Phys.* (Special issue on multidimensional spectroscopies) **266**, pp. 149-166 (2001).
2. (*invited, special issue on laser ablation*) “Ultrafast microscopy of laser ablation of refractory materials: ultra low threshold stress-induced ablation”, Serguei G. Koulikov and Dana D. Dlott, *J. Photochem. Photobiol. A: Chemistry* **145**(3) (2001), pp. 183-194.
3. “Real time ultrafast spectroscopy of shock wave nanopore collapse”, Selezion A. Hambir, Hackjin Kim, Dana D. Dlott and Robert B. Frey, *J. Appl. Phys.* **90**, 5139-5146 (2001).
4. “Ultrafast vibrational spectroscopy imaging of nanoshock planar propagation”, Yanqiang Yang, Selezion A. Hambir and Dana D. Dlott, *Shock Waves* **12**, pp. 129-136 (2002).
5. “Ultrafast high repetition rate absorption spectroscopy of polymer shock compression”, Hackjin Kim, Selezion A. Hambir and Dana D. Dlott, *Shock Waves* **12**, pp. 79-86 (2002).
6. (*invited*) “Ultra low threshold laser ablation investigated by time-resolved microscopy”, Dana D. Dlott, *Appl. Surf. Sci.* **197**, pp. 3-10 (2002).
7. “Plume and jetting regimes in a laser based forward transfer process as observed by time-resolved optical microscopy”, D. Young, R. C. Y. Auyeung, A. Piqué, D. B. Chrissey and Dana D. Dlott, *Appl. Surf. Sci.* **197**, pp. 181-187 (2002).
8. “Watching Vibrational Energy Transfer in Liquids with Atomic Spatial Resolution”, Zhaohui Wang, Andrei Pakoulev and Dana D. Dlott, *Science* **296**, 2201-2203 (2002).

9. (*invited*) “Focus fluctuations in laser materials interactions”, Dana D. Dlott, *Optics and Photonics News*, **13**, pp. 34-37 (2002).
10. “Fast spectroscopy of energy release in nanometric explosives”, Shufeng Wang, Yanqiang Yang, Zhaoyong Sun and Dana D. Dlott, *Chem. Phys. Lett.* **368**, pp. 189-194 (2003).
11. “Fast spectroscopy of laser-initiated nanoenergetic materials”, Yanqiang Yang, Zhaoyong Sun, Shufeng Wang and Dana D. Dlott, *J. Phys. Chem. B* **107**, pp. 4485-4493 (2003).
12. “Vibrational relaxation and spectral evolution following ultrafast OH stretch excitation of water”, Andrei Pakoulev, Zhaohui Wang and Dana D. Dlott, *Chem. Phys. Lett.* **371**, pp. 594-600 (2003).
13. (*invited*) “Fast molecular processes in energetic materials”, in *Energetic materials: Initiation, Decomposition and Combustion*, (part 2), P. Politzer and J. S. Murray, eds. (New York, Elsevier, 2003), pp. 125-192.
14. “Vibrational substructure in the OH stretching band of water”, Zhaohui Wang, Andrei Pakoulev, Yoonsoo Pang and Dana D. Dlott, *Chem. Phys. Lett.* **378**, pp. 281-288 (2003).
15. “Vibrational energy relaxation pathways of water”, Andrei Pakoulev, Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott, *Chem. Phys. Lett.* **380**, pp. 404-410 (2003).
16. “Shock-induced chemical reaction propagation in nanoenergetic materials observed with nanometer spatial resolution”, Shufeng Wang, Yanqiang Yang, Zhaoyong Sun and Dana D. Dlott, *AIP Confer. Proc.* **706**, pp. 1065-1068 (2004).
17. “Shock compression of molecules with 1.5 angstrom resolution”, James E. Patterson, Alexi Lagoutchev and Dana D. Dlott, *AIP Confer. Proc.* **706**, pp. 1299-1302, (2004).
18. “Three-dimensional spectroscopy of vibrational energy relaxation in liquids”, Zhaohui Wang, Andrei Pakoulev, Yoonsoo Pang and Dana D. Dlott, in “Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science”, M. M. Martin and J. T. Hynes, eds. (Amsterdam, Elsevier, 2004), pp. 169-176.
19. “Reply to: *Comment on: Vibrational relaxation and spectral diffusion following ultrafast OH stretch excitation of water*, by H. J. Bakker, A. J. Lock, D. Madsen”, Andrei Pakoulev, Zhaohui Wang, Yoonsoo Pang, Dana D. Dlott, *Chem. Phys. Lett.* **385**, pp. 332-335 (2004).
20. “Multiphonon Up-pumping in Energetic Materials”, Dana D. Dlott, in *Overviews of Recent Research on Energetic Materials*, D. Thompson, T. Brill and R. Shaw, eds. In press.
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”
22. “Ultrafast spectroscopy of laser-initiated nanoenergetic materials”, Y. Yang, Z. Sun, S. Wang, S. A. Hambir, H. Yu, and Dana D. Dlott, in *Synthesis, Characterization and Properties of Energetic/Reactive Nanomaterials*, MRS Symp. Proc.; Vol. 800, edited by R. W. Armstrong, N. N. Thadhani, W. H. Wilson, J. J. Gilman, Z. Munir, and R. L. Simpson, pp. 151-160, (2004).

23. Yanqiang Yang, Shufeng Wang, Zhaoyong Sun and Dana D. Dlott, "Near-infrared laser ablation of poly tetrafluoroethylene (Teflon) sensitized by nanoenergetic materials", Appl. Phys. Lett. 85, pp. 1493-1495 (2004).
24. Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott, "The vibrational Stokes shift of water (HOD in D₂O)", J. Chem. Phys. 120, pp. 8345-8348 (2004).
25. Zhaohui Wang, Andrei Pakoulev, Yoonsoo Pang and Dana D. Dlott, "Vibrational Substructure in the OH Stretching Transition of Water and HOD", J. Phys. Chem. **108**, 9054 (2004).
28. "Vibrational energy dynamics of water studied with ultrafast Stokes and Anti-Stokes Raman spectroscopy", Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott, Chem. Phys. Lett. **397**, 40 (2004)
29. Protein printing via a capillary-free fluid jetting mechanism, J. A. Barron, D. Young, D. B. Krizman, D. D. Dlott, and B. R. Bringeisen, Nature Biotech., submitted, 2004.
30. "Vibrational energy dynamics of water studied with ultrafast Stokes and Anti-Stokes Raman spectroscopy", Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott, Chem. Phys. Lett. 394, pp. 40-45 (2004).
31. "Nanotechnology energetic material dynamics studied with nanometer spatial resolution and picosecond temporal resolution", Dana D. Dlott, Hyunung Yu, Shufeng Wang, Yanqiang Yang, Selezion A. Hambir, in "Advances in Computational & Experimental Engineering & Sciences '04", S. N. Atlurl and A. Tadeu, eds., pp. 1427-1432.
32. "Ultrafast dynamics of shock compression of molecular monolayers", James E. Patterson, Alexei Lagutchev, Wentao Huang and Dana D. Dlott, Phys. Rev. Lett. 94, 015501 (2005).
33. "Ultrafast molecular dynamics at a shock-compressed metal-liquid interface", James E. Patterson, Ph.D. thesis, University of Illinois at Urbana-Champaign, 2004.

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

1. (*invited*) "Experimental tests and challenges for molecular dynamics of energetic materials", Charles A. Wight and Dana D. Dlott, in *Molecular dynamics simulations of detonation phenomena*, B. Holian ed. (McLean, VA, Itri, Inc., 2004), pp. 97-128.
2. (*invited*) "New ideas and limits for energetic material performance", Dana D. Dlott, in *Molecular dynamics simulations of detonation phenomena*, B. Holian ed. (McLean, VA, ITRI, Inc., 2004), pp. 129-144.

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

1. (*invited*) American Physical Society March Meeting, Seattle, WA (Mar. '01), "Three dimensional vibrational spectroscopy of molecular liquids".
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".
3. (*invited*) DARPA High Energy Density Materials and Nanotechnology Workshop, Washington, DC (Aug. '01), "Engineered nanometric energetic materials".

4. *(invited)*, International Conference on Laser Ablation 2001, Tsukuba, Japan (Oct. '01), "Laser photothermal ablation studied by ultrafast microscopy: fundamental mechanisms of ultra low threshold ablation"
5. *(invited)* Sixth International Conference on Molecular Reaction Dynamics in Condensed Phases, Laguna Beach, Ca (Feb. '01), "Three dimensional vibrational spectroscopy of molecular liquids".
6. *(invited)*, International Conference on Laser Ablation 2001, Tsukuba, Japan (Oct. '01), "Laser photothermal ablation studied by ultrafast microscopy: fundamental mechanisms of ultra low threshold ablation"
7. *(invited)* American Chemical Society National Meeting, (Mar. 2002), Ultrafast vibrational sum frequency generation spectroscopy of lubricants at moving metal interfaces.
8. *(invited)* Air Force Workshop on High Energy Density Matter, Waltham, MA (May. '02), "Fast vibrational spectroscopy of shock compression and combustion".
9. *(invited)* Gordon Conference on Energetic Materials, Tilton, NH (June '02), "Ultrafast laser spectroscopy of nanoenergetic materials".
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".
16. *(invited)* Molecular Dynamics of Energetic Materials Workshop, International Technology Research Institute, Inc., Laurel, MD (June '03), "Experimental tests and challenges for molecular dynamics of energetic materials".
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".
20. (*invited*) Gordon Conference on Liquids, New Hampshire (Aug. '03), "Three dimensional spectroscopy of vibrational energy relaxation in liquids".
21. (*invited*) Second Advanced Energetics Technology Exchange Workshop (Sept. '03), Army Research Laboratory, Aberdeen Proving Grounds, Aberdeen, MD., "Ultrafast vibrational spectroscopy of Energetic Materials"
22. (*invited*) Materials Research Society National Meeting, Boston, MA (Dec. '03), "Ultrafast spectroscopy of laser-initiated nanoenergetic materials".
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".
26. (*invited*) Gordon Conference on Energetic Materials, Tilton, NH (June '04), "Time and space resolved ultrafast spectroscopy of nanoenergetic materials".
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".
28. (*invited*) American Chemical Society National Meeting, Philadelphia, PA (Aug. '04), "Vibrational energy at interfaces".
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 MoO_3 and CuO . Using time-resolved vibrational spectroscopy to monitor oxidizer consumption via ONO_2 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 CH_3 groups, giving us spatial resolution of 1.5 Å. 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.

