

REPORT DOCUMENTATION PAGE

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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Michael R. Berman <i>/NA</i> 875 N. Randolph St. Suite 325, Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR/NA	
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13. 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.					
14. ABSTRACT This report documents progress made by the Dlott group at the University of Illinois during the 32 month period of this AFOSR award.					
15. SUBJECT TERMS Vibrational energy, nanoparticles, nanoenergetic materials, energetic materials					
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1. Cover sheet

To: <http://afosr.finalreport.sgizmo.com>
Subject: Final Progress Report (Dr. Michael Berman)

Contract/Grant Title: Vibrational energy in molecules and nanoparticles:
applications to energetic materials

Contract/Grant #:FA9550-06-1-0235
Reporting Period: 15 Mar 2006 to 30 Nov 2008

2. Objectives:

Our objectives, which have not changed, involve developing a fundamental understanding of the vibrational and chemical reaction dynamics of condensed-phase molecules and nanostructures under extreme conditions relevant to energetic material performance. We will conduct experimental studies of vibrational dynamics and chemical dynamics of condensed phase molecules and nanostructures using novel laser techniques developed in our laboratory. These techniques combine time resolution of femtoseconds with high spatial definition. The proposed work is divided into three parts. Part 1: Vibrational energy is input to molecules and molecular nanostructures using resonant vibrational infrared (IR) pulses. Part 2: Vibrational energy is input to molecules using femtosecond laser-driven shock waves. Part 3: Molecular nanostructures that form the basis of a new generation of nanoenergetic materials are studied using either laser flash heating or laser-driven shock compression to initiate chemical reactions.

3. Status of effort:

We have continued to develop the IR-Raman method to study vibrational energy redistribution and we have published the most detailed and accurate study of vibrational energy in a polyatomic molecule, nitromethane. Work on water and amino acids partially supported by AFOSR are developmental in nature, helping us refine the technology. We have developed ultrafast shock wave and heat shock techniques and used them to study vibrational energy with high time and space resolution. These measurements use a nonlinear coherent IR spectroscopy technique "vibrational sum-frequency generation" or SFG. Using SFG we have developed the technology to watch vibrational energy flow from one end of a molecule to another in real time, and also the ability to watch molecules rearrange on surfaces. This technique can be used to study vibrational energy in nitrated alkane and aromatic molecules. We have characterized the surface vibrations of HMX explosive and their interaction with polymer binders. We have introduced a major improvement in SFG technology, a pulse sequence that eliminates the nonresonant background. We have studied the energetic reactions of Al nanoparticles with Teflon oxidizer using time-resolved IR spectroscopy, which lets us find the detailed mechanisms. We have developed new methods to study surface-enhanced Raman scattering in order to enable us to use time-resolved vibrational spectroscopy to study heat flow in molecular monolayers.

4. Accomplishments/new findings

- A. Vibrational energy transport along molecular chains
- B. Elimination of nonresonant background in SFG
- C. Surface vibrations of HMX
- D. Vibrational energy in nitromethane and benzene

- E. Time resolved spectroscopy of chemistry in flash-heated nanoenergetic materials
- F. Complete measurement of Raman enhancement factors in SERS

5. Experimental methods

We have improved our IR-Raman vibrational energy transfer apparatus which now has greater sensitivity and the ability to study small amounts of precious or toxic materials. These improvements are described in paper #14. We have developed an ultrafast flash-heating thermal conductance apparatus as described in paper #18. We have developed a compact and improved SFG apparatus as described in paper #17. This apparatus features the ability to deeply suppress nonresonant backgrounds. We have developed a method to measure the distribution of site enhancements in surface-enhanced Raman spectroscopy, as described in paper 21.

6. Personnel supported

- A. Dana Dlott, Principal Investigator
- B. H. Yu, former postdoc now with Korean Research Institute of Standards and Science
- C. Yoonsoo Pang, former graduate student, now postdoctoral associate at Berkeley
- D. Alexei Lagutchev, postdoctoral associate
- E. Rusty Conner, graduate student
- F. Nak-Hyun Seong, postdoctoral associate
- G. Shinsuke Shigeto, former postdoctoral associate now Assistant Professor, Department of Applied Chemistry, National Chiao Tung University, Taiwan
- H. S. Eric Surber, former postdoctoral associate now Program Manager, ATK Corp.
- I. Jeffrey A. Carter, graduate student

7. Publications

1. (*invited*) "Thinking big (and small) about energetic materials", Dana D. Dlott, *Materials Science and Technology* 22, pp. 463-473 (2006).
2. "Surface and interface spectroscopy of energetic materials: HMX and Estane", Hackjin Kim Alexei Lagutchev and Dana D. Dlott, *Propellants, Explosives, Pyrotechnics* 31, pp. 116-123 (2006).
3. (*invited*) "Ultrafast dynamics of nanotechnology energetic materials", Hyunung Yu, Selezion A. Hambir and Dana D. Dlott, in *Multifunctional Energetic Materials*, MRS Symp. Proc.; Vol. 896, edited by R. W. Armstrong, N. N. Thadhani, W. H. Wilson, A. Gash, and Z. Munir (2006), Article H03, 9 pages.
4. (*feature cover article*) "Time-resolved microscopy analysis of laser photothermal imaging media", Hyunung Yu, Dana D. Dlott, F. Richard Kearney, *J. Imag. Sci. Tech.* 50, pp. 401-410 (2006).

5. (*invited*) "Nanotechnology energetic material dynamics studied with nanometer spatial resolution and picosecond temporal resolution", Dana D. Dlott, Selezion A. Hambir, Hyunung Yu, in *Advancements in Energetic Materials and Chemical Propulsion*, K. K. Kuo and J. DeD. Rivera, eds. (Redding Ct: Begell House, Inc.), pp. 22-38.
6. (*invited*) "Shock compression spectroscopy with high time and space resolution", Wentao Huang, James E. Patterson, Alexei Lagutchev and Dana D. Dlott, *AIP Confer. Proc.* 845, pp. 1265-1270 (2006).
7. "Vibrational Sum Frequency Generation Studies of the $(2 \times 2) \rightarrow (\sqrt{19} \times \sqrt{19})$ Phase Transition of CO on Pt(111) Electrodes", A. Lagutchev, G. Q. Lu, T. Takeshita, Dana D. Dlott and A. Wieckowski, *J. Chem. Phys.* 125, 154705 (10 pages) (2006).
8. "Long-lived interfacial vibrations of water", Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott, *J. Phys. Chem. B* 110, pp. 201150-20117 (2006).
9. (*invited*) "Vibrational energy with high time and space resolution", Yoonsoo Pang, John C. Deak, Wentao Huang, Alexei Lagutchev, Andrei Pakoulev, James E. Patterson, Timothy D. Sechler, Zhaohui Wang and Dana D. Dlott. *Int. Rev. Phys. Chem.* 26, pp. 223-248 (2007).
10. "Surface vibrational spectroscopy of energetic materials: HMX", Eric Surber, Aaron Lozano, Alexei Lagutchev, Hackjin Kim and Dana D. Dlott, *J. Phys. Chem. C* 111, pp. 2235-2241 (2007).
11. (*invited feature article + cover photo*) "Hydrogen-bond disruption by vibrational excitations in water", Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott. *J. Phys. Chem. A.* 117, pp. 3196-3208 (2007).
12. "Ultrafast Chemistry of Nanoenergetic Materials Studied by Time-resolved IR Spectroscopy: Aluminum Nanoparticles in Teflon", Mikhail A. Zamkov, Rusty W. Conner and Dana D. Dlott, *J. Phys. Chem. C* 111, 10278-10284 (2007).
13. "Ultrafast Flash Thermal Conductance of Molecular Chains, Zhaohui Wang, Jeffrey A. Carter, Alexei Lagutchev, Yee Kan Koh, Nak-Hyun Seong, David G. Cahill and Dana D. Dlott, *Science.* 317, pp. 787-790.
14. "Vibrational relaxation of normal and deuterated liquid nitromethane, Shinsuke Shigato, Yoonsoo Pang, Ying Fang and Dana D. Dlott, *J. Phys. Chem. A,* **112**, pp. 232-241(2007).
15. "Vibrational energy dynamics of glycine in aqueous solution", Shinsuke Shigeto and Dana D. Dlott, *Chem. Phys. Lett.* 447, pp. 134-139 (2007).
16. "Ultrafast shock wave coherent dissociation and spectroscopy of materials", Jeffrey A. Carter, Zhaohui Wang, Alexei Lagutchev, Ying Fang, Nak-Hyun Seong, David G. Cahill and Dana D. Dlott, *AIP Conf. Proc.* 955, pp. 1221-1224.
17. "Nonresonant Background Suppression in Broadband Vibrational Sum-Frequency Generation Spectroscopy", Alexei Lagutchev, Selezion A. Hambir and Dana D. Dlott, *J. Phys. Chem. C.*; (Letter); **111**, pp. 13645-13647 (2007). DOI: 10.1021/jp075391j.
18. "Ultrafast dynamics of heat flow across molecules", Zhaohui Wang, David G. Cahill, Jeffrey A. Carter, Yee Kan Koh, Alexei Lagutchev, Nak-Hyun Seong and Dana D. Dlott, *Chem. Phys.* 350, pp. 31-44 (2008).

19. "Broad-band sum frequency generation studies of surface intermediates invoked in fuel cell electrocatalysis", G. Q. Lu, A. Lagutchev, T. Takeshita, R. L. Behrens, Dana D. Dlott and A. Wieckowski. To appear in, **Fuel Cell Catalysis: a Surface Science Approach**, Marc Koper, ed. (John Wiley and sons).
20. "Spatially resolved vibrational energy transfer in molecular monolayers," Jeffrey A. Carter, Zhaohui Wang and Dana D. Dlott, *J. Phys. Chem. A* 112, pp. 3523-3529 (2008).
21. "Measurement of the distribution of site enhancements in surface-enhanced Raman scattering", Y. Fang, N.-H. Seong, and D. D. Dlott, *Science* 321, pp. 388-391 (2008).
22. "Watching vibrational energy in molecules with high time and space resolution," J. A. Carter, Z. Wang, and D. D. Dlott, in *Proceedings of the XXIst International Conference on Raman Spectroscopy*, edited by R. Withnall and B. Z. Chowdhry (IM Publications LLP, Charlton, Chichester, 2008), pp. 112-113.
23. "Measuring the distribution of Raman enhancements on a nanoparticle lattice," Y. Fang, N.-H. Seong, and D. D. Dlott, in *Proceedings of the XXIst International Conference on Raman Spectroscopy*, edited by R. Withnall and B. Z. Chowdhry (IM Publications LLP, Charlton, Chichester, 2008), pp. 469-470.
24. "Vibrational energy dynamics of glycine, N-methyl acetamide and benzoate anion in aqueous (D₂O) solution", Y. Fang, S. Shigeto, N.-H. Seong, and D. D. Dlott, *J. Phys. Chem. A* 113, pp. 75-84 (2009).
25. "Electrochemically driven reorientation of three ionic states of p-amino benzoic acid on Ag(111)", S. K. Shaw, A. Lagutchev, D. D. Dlott, and A. A. Gewirth, *J. Phys. Chem. C ASAP* pp. (2009).
26. "Sum-Frequency Spectroscopy of Molecular Adsorbates on Low-Index Ag Surfaces: Effects of Azimuthal Rotation", S. K. Shaw, A. Lagutchev, D. D. Dlott, and A. A. Gewirth, *Anal. Chem.* DOI 10.1021/ac802332h, pp. (2008).
27. "Vibrational energy dynamics of normal and deuterated liquid benzene", N.-H. Seong, Y. Fang, and D. D. Dlott, *J. Phys. Chem. A* in press, pp. (2009).

8. Interactions/transitions

a. Participation at conferences, seminars, etc.

Dana Dlott

1. (*invited*) American Physical Society March Meeting, Baltimore, MD (Mar. '06), "Vibrational energy at interfaces: Material transformation dynamics".
2. (*invited*) Auburn University, Auburn, AL (Apr. '06), "Vibrational energy in molecules and molecular nanostructures".

3. (*invited*) Workshop on synergy of 21st century high pressure science and technology, Argonne National Laboratory (May '06), "Surfaces and interfaces at high pressure via nonlinear optics".
4. (*invited*) Carnegie Institute of Washington Geophysical Laboratory, Washington, D. C. (May '06), "Vibrational spectroscopy with high time and space resolution".
5. (*invited*) Stockholm Discussion Meeting, Local Structure and Molecular Scale Properties of Liquid Water, Stockholm, Sweden (June '06), "Ultrafast IR-Raman measurements of water vibrations".
6. (*invited*) Gordon conference on Vibrational Spectroscopy, University of New England, Biddeford, ME (July '06), "Vibrational Dynamics With High Time and Space Resolution"
7. (*invited*) Telluride summer school on vibrational dynamics, Telluride, CO (July '06), "Vibrational energy relaxation in condensed phases".
8. (*invited*) Telluride summer school on vibrational dynamics, Telluride, CO (July '06), "Vibrational energy in liquids".
9. (*invited*) Telluride summer school on vibrational dynamics, Telluride, CO (July '06), "Vibrational energy in water".
10. (*invited*) International Workshop on Time-Resolved Spectroscopy, RIKEN, Wako-shi, Japan (Aug. '06), "Vibrational Dynamics With High Time and Space Resolution"
11. (*invited*) International Conference on Raman Spectroscopy, Yokohama, Japan, (Aug. '06), "Vibrational Dynamics With High Time and Space Resolution"
12. (*invited*) Joint Army-Navy-NASA-Air Force Interagency Propulsion Committee Workshop on R&D Required to Implement New Energetic Ingredients in Munitions, Aberdeen, MD (Aug. '06), "Energetic materials: landscapes, surfaces and interfaces".
13. (*invited*) American Chemical Society National Meeting, San Francisco, CA (Sep. '06), "Ultrafast dynamics of molecules at interfaces under extreme conditions".
14. (*invited*) Bowling Green State University, Bowling Green, OH (Oct. '06), "Vibrational Dynamics With High Time and Space Resolution".

15. (*invited*) University of Southern California, Viterbi College of Engineering, Los Angeles, CA (Oct. '06) "Vibrational Dynamics With High Time and Space Resolution".
16. (*invited*) Army Research Office review of "Nanotechnology Engineered Energetic Materials", (Nov. '06) Army Research Laboratory, Aberdeen, MD, "Fundamental dynamic mechanisms of nanoenergetic material initiation and ignition".
17. 2007 Stewardship Science Academic Alliances Program, (Feb. '07), Carnegie Institute of Washington, Washington, D. C., "Surfaces and interfaces of high explosives probed by nonlinear coherent vibrational spectroscopy".
18. (*invited*) MIT Seminar on Modern Optics and Spectroscopy, George R. Harrison Spectroscopy Laboratory, (Feb. '07) "Vibrational energy in molecules with high time and space resolution".
19. (*invited*) American Chemical Society National Meeting, Chicago, IL (Mar. '07), "Infrared-Raman studies of vibrational energy transfer".
20. (*invited*) Argonne National Laboratory Users' Week, Workshop on *In Situ* Studies of Interfacial Reactivity, Argonne, IL (May '07), "Vibrational Sum-Frequency Generation Studies of Reactivity and Dynamics at Interfaces".
21. (*invited*) Department of Energy Materials under Extreme Environments Workshop, Bethesda, MD (June '07).
22. (*invited*) American Physical Society Topical Meeting on Shock Compression of Condensed Matter, Hawaii (June '07), "Ultrafast shock wave coherent dissociation and spectroscopy of materials".
23. (*plenary*). "Town hall meeting: Future directions in dynamic high pressure research", W. J. Nellis and D. D. Klott.
24. (*invited*) International Conference on Femtochemistry, "Femto8", Oxford, England (July '07), "Energy transfer at interfaces".
25. (*invited*) Telluride Vibrational Workshop, Aug. 6-10, 2007, Telluride, CO. "Vibrational energy in molecules and interfaces".
26. Army Research Office MURI Insensitive program review, Sept. 25-26, 2007, Aberdeen, MD. "Spectroscopic observation of structures and molecular response at surfaces of energetic materials".

27. University of Toronto, Department of Chemistry, Oct. 9, 2007. "Vibrational energy in molecules and molecular nanostructures".
28. (*invited*) Federation of Analytical Chemistry and Spectroscopy Societies, Oct. 14-18, 2007. "Ultrafast heat flow at interfaces: time, wavelength, distance, temperature".
29. University of Rochester, Department of Chemistry, Nov. 14, 2007, "Vibrational energy in molecules and molecular nanostructures".
30. Army Research Office MURI NEEM review, Sept. 25-26, 2007, Aberdeen, MD. "Ultrafast dynamics of nanoengineered energetic materials".
31. (*invited*) Advanced Energetics Technology Exchange, Jan 21-25, 2008, Ft. Belvoir, VA, "Ultrafast diagnostics of energetic materials".
32. (*invited*) American Physical Society National Meeting, Mar. 10-14, 2008, New Orleans, LA. "Vibrational energy on surfaces: Ultrafast flash-thermal conductance of molecular monolayers".
33. (*invited*) Army Chemistry Coordinating Committee, Mar. 25, 2008, Aberdeen, MD. "STAR Army Science Objectives 2008".
34. (*invited*) Robert Shaw Festschrift, Mar. 26, 2008, Aberdeen, MD. "Robert Shaw".
35. (*invited*) University of California Davis, Department of Chemistry, Apr. 15, 2008, "Vibrational energy in molecules and nanostructures".
36. (*invited*) Air Force Research Laboratory Nanotechnology Initiative, Fairborn, OH, May 2008, "Vibrational Energy in Molecules and Nanoparticles: Applications to Energetic Materials".
37. (*invited*) Air Force Office of Scientific Research, Molecular Dynamics Contractor's Meeting, Vienna, VA, May 2008, "Vibrational energy with high time and space resolution."
38. (*invited*) Transmission of Information and Energy in Nonlinear and Complex Systems 2008, June, 2008, National University of Singapore, "Heat flow from surfaces to molecular adsorbates probed with high time and space resolution".
39. (*invited*) Gordon conference on energetic materials, June 2008, Tilton, NH, "Advanced diagnostics of energetic material dynamics".

40. (*invited*) Telluride workshop on nonlinear optics at surfaces and interfaces, June 2008, "Vibrational energy at interfaces".
41. (*invited*) American Chemical Society National Meeting, Aug. 2008, Philadelphia, PA, "Vibrational energy with high time and space resolution".
42. (*invited*) International Conference on Raman Spectroscopy XXI, Aug. 2008, London, England, "Watching vibrational energy with high time and space resolution".
43. (*invited*) International Conference on Raman Spectroscopy XXI, Aug. 2008, London, England, "Measuring the distribution of nanoparticle enhancements on a nanoparticle lattice".
44. (*invited*) Columbia University Department of Chemistry, Oct. 2008, "Vibrational energy with high time and space resolution".

b. Consultative and advisory functions

- Research discussed extensively with collaborators at DOE labs LANL, LLNL and Argonne
- Discussed simulations of nanoparticle combustion with Vashishta at USC and Goddard at Caltech
- Discussed simulations of self-assembled monolayers with Vashishta at USC
- Discussed mechanisms of reaction propagation in nanoparticles with Dr. Michelle Pantoya of Texas Tech U.
- Discussed spectroscopy of fluorocarbon-coated nanoparticles with Jason Jouet of NSWC
- Jupiter Laser Review Committee, Livermore Labs, 2008.
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c. Transitions

None to report

9. New discoveries

Ballistic heat conductance of alkane chains, distribution of site enhancements in surface-enhanced Raman scattering.

9. Honors/awards

Alfred P. Sloan Fellow 1984-85

Fellow of the American Physical Society, 1996

Fellow of the Optical Society of America, 1999

2001 Charles E. Ives Award from the Society for Imaging Science and Technology, 2001

Fellow of the American Association for the Advancement of Science, 2005
Vice-Chair APS Topical Group on Shock Compression of Condensed Matter,
2006
Chair-Elect APS Topical Group on Shock Compression of Condensed Matter,
2007
Chair APS Topical Group on Shock Compression of Condensed Matter, 2008
Past-Chair APS Topical Group on Shock Compression of Condensed Matter,
2008
Editorial Advisory Board, J. Phys. Chem. 2009-10
William H. and Janet G. Lycan Professor of Chemistry, 2009-