The goal of this project is the development of a fundamental understanding of nanocomposite energetic materials and fast mechanical processes at a molecular level. We are attacking these difficult problems using three parallel approaches. (1) Laser flash-heating of nanoenergetic materials combined with optical diagnostic techniques; (2) Ultrafast laser shock compression of solids combined with vibrational spectroscopy; (3) Multidimensional vibrational spectroscopy of liquids to study the flow of vibrational energy.
1. Cover sheet for Final Technical Report to AFOSR

PI Name: Dlott, Dana D.

Institution: University of Illinois

PI address: Box 01-6 CLSL, 600 S. Mathews Ave., Urbana, IL 61801

Email: dlott@scs.uiuc.edu

Contract/Grant No. F49620-03-1-0032

Title of project: Ultrafast vibrational spectroscopy of inhomogeneous energetic materials and energetic interfaces

Reporting period: 1 Jan 2003 -- 31 Dec 2005

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2-3. Status of Effort (Objectives have not changed)

The goal of this project remains the development of a fundamental understanding of nanocomposite energetic materials and fast mechanical processes at a molecular level. We are attacking these difficult problems using three parallel approaches. (1) Laser flash-heating of nanoenergetic materials combined with optical diagnostic techniques; (2) Ultrafast laser shock compression of solids combined with vibrational spectroscopy; (3) Multidimensional vibrational spectroscopy of liquids to study the flow of vibrational energy.

In the first part of the project, we have developed a method of studying the distance dependence of chemical reaction propagation from metal nanoparticles embedded in oxidizing matrices, that are flash heated by ultrashort laser pulses. A very interesting effect has been seen by using size-selected Al nanoparticles with different thickness oxide passivation layers. With short time scale heating, such as might be realized in a detonation, the thicker oxide layer keeps the reactive Al fuel confined for a longer time. When the Al breaks out, it explodes more violently and the reaction travels a longer distance. This observation is strongly in contrast to the usual view of oxide passivation layers as deadweight. In conversations with researchers at Penn State—Rich Yetter and Steve Son, who study nanoparticle rocket propellants, we are thinking this type of mechanism might explain some anomalies observed in flame propagation of burning nanocomposites.

We have been developing some new instrumentation to overcome some problems we have encountered in these studies. Optical emission from the flash-heated samples is a real-time probe of energy release and short-distance reaction propagation; however the detector we were using was too slow (~4 ns). We have now installed a streak camera which obtains time and wavelength information on a single shot with a time resolution of 25 ps, which is much better. We have been probing chemistry inside the samples using coherent Raman spectroscopy, which is not very sensitive to transient species. We built a transient IR system using up-conversion detection. However the detection scheme was not very stable. We have now switched to a new detection scheme using a multichannel IR detector and have improved the sensitivity by 2 orders of magnitude. These two developments will enable a new generation of nanoenergetic measurements.

In the second part of the project, we have successfully studied 5-10 GPa ultrafast shock compression of self-assembled monolayers (SAM) of long-chain alkane molecules on metal substrates. This difficult project has three implications. First it is a major advance in the time resolution of molecular shock compression science and it is the first molecular shock compression experiment that provides information on the space and time ranges accessible to simulation. Second SAMs can be used to replace the oxide deadweight passivation layers on nanoenergetic materials, so it is important to understand the shock response of SAMs on metal surfaces. Third, SAMs on metal surfaces have been used as model systems to understand lubrication. Previous lubrication studies have looked at the small-amplitude, long time response of the alkane chains. With our experiment we look at large-amplitude fast motions, which are relevant to high-speed processes at moving metal surfaces, such as high-speed turbine engines.
Using vibrational sum-frequency generation, we can measure in real time the orientation of the methyl head groups of the SAM as it undergoes shock compression. In combination with simulations, the twisting of the head group can be used to infer what the rest of the chain is doing. We found that odd-carbon chains (15-carbons) are simply bent over with shock compression but even-carbon chains (18-carbons) undergo mechanical failure by forming gauche defects at the first two carbon-carbon bonds. We have recently upgraded the laser system and continued this work by looking at these SAMs and other molecular structures with variable pressure and duration shocks.

In the third part of the project, we are developing techniques to watch vibrational energy flowing through molecules. We have concentrated on two systems, water and its isotopomers and reverse micelles. Our 3D IR-Raman method allows us to input vibrational energy into a specific part of a molecule and watch where it goes. The water studies are model systems needed to understand the spectroscopy. Water is the most important liquid and arguably the most complicated, so this is a critical test of our understanding of vibrational energy. In the reverse micelles, we can study the transmission of vibrational energy across an interface. A reverse micelle consists of a nanodroplet of confined water, circled by a monolayer of surfactant, suspended in a bulk nonpolar liquid such as CCl₄ or octane. We can pump vibrational energy into the water and watch as it moves through the surfactant layer and into the nonpolar layer. This is a milestone in vibrational spectroscopy and it shows how we will be able to track the flow of vibrational energy molecule-by-molecule.

4. Accomplishments/new findings

- Real time measurements of vibrational energy flow across an interface
- Real time measurements of nanoenergetic material initiation, ignition and propagation with picosecond time resolution and atomic spatial resolution. Effects of oxide layer thickness.
- Shock front detection with 1.5Å spatial resolution
- Mechanism of fast deformation of long-chain molecules at rapidly moving metal interfaces

5. Personnel Supported

<table>
<thead>
<tr>
<th>Number of Contract/Grant Co-Investigators*</th>
</tr>
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<tbody>
<tr>
<td>Faculty 1</td>
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</tbody>
</table>

1. Dana D. Dlott, PI, leads the project.
2. Dr. Zhaohui Wang works on the multidimensional spectroscopy project
3. Mr. Yoonsoo Pang works on multidimensional spectroscopy of energetic materials
4. Dr. Hyunung Yu works on the nanoenergetic materials project
5. Dr. Selezion Hambir works on the nanoenergetic materials project
6. Mr. James Patterson, a graduate student, was the lead on the SFG project until he graduated
7. Dr. Alexei Lagoutchev leads the SFG project
8. Dr. Wentao Huang works on the SFG project
9. Dr. Shufeng Wang worked on fast IR spectroscopy of nanoenergetic materials and took a position as Associate Professor, Department of Physics, Beijing University in May 2004.
6. Publications Related to Aforementioned Contract/Grant

Title of Article: Vibrational relaxation and spectral evolution following ultrafast OH stretch excitation of water
Authors: Andrei Pakoulev, Zhaohui Wang and Dana D. Dlott
Volume 378 Pages 281-288 Month Published: Sept. Year: 2003

Title of Article: Fast molecular processes in energetic materials
Authors: Dana D. Dlott
Volume Pages 125-192 Month Published: Year: 2003

Title of Article: Vibrational energy relaxation pathways of water
Authors: Andrei Pakoulev, Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott
Volume 380 Pages 404-410 Month Published: Year: 2003

Title of Article: Shock compression of proteins: The energy landscape model
Authors: H. Kim and Dana D. Dlott
Volume 706 Pages 1448-1457 Month Published: Aug. Year: 2004

Title of Article: Shock-induced chemical reaction propagation in nanoenergetic materials observed with nanometer spatial resolution
Authors: Shufeng Wang, Yanqiang Yang, Zhaoyong Sun and Dana D. Dlott
Volume 706 Pages 1065-1068 Month Published: Aug. Year: 2004
Title of Article: Shock compression of molecules with 1.5 angstrom resolution
Authors: James E. Patterson, Alexi Lagoutchev and Dana D. Dlott
Volume 706 Pages 1299-1302 Month Published: Aug. Year: 2004

M. M. Martin and J. T. Hynes, eds.
Title of Article: Three-dimensional spectroscopy of vibrational energy relaxation in liquids
Authors: Zhaohui Wang, Andrei Pakoulev, Yoonsoo Pang and Dana D. Dlott
Volume Amsterdam, Elsevier Pages 169-176 Month: Year: 2004

Title of Article: 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
Authors: Andrei Pakoulev, Zhaohui Wang, Yoonsoo Pang, Dana D. Dlott
Volume 385 Pages 332-335 Month Published: Feb. Year: 2004

Title of Article: Propagation of shock-induced chemistry in nanoenergetic materials: the first micrometer
Authors: Yanqiang Yang, Shufeng Wang, Zhaoyong Sun and Dana D. Dlott
Volume 95 Pages 3667-3676 Month Published: Apr Year: 2004

Title of Article: Ultrafast spectroscopy of laser-initiated nanoenergetic materials
Authors: Y. Yang, Z. Sun, S. Wang, S. A. Hambir, H. Yu, and Dana D. Dlott
Volume 800 Pages 151-160 Month Published: Year: 2004

Title of Article: The vibrational Stokes shift of water (HOD in D₂O)
Authors: Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott
Volume 120  Pages  8345-8348  Month Published: May  Year: 2004

12. Name of Book: Advances in Computational & Experimental Engineering & Sciences '04, S. N. Atluri and A. Tadeu, eds.
Title of Article: Nanotechnology energetic material dynamics studied with nanometer spatial resolution and picosecond temporal resolution
Authors: Dana D. Dlott, Hyunung Yu, Shufeng Wang, Yanqiang Yang, Selezion A. Hambir
Volume  Pages  1427-1432  Month Published: July  Year: 2004

Title of Article: Near-infrared laser ablation of poly tetrafluoroethylene (Teflon) sensitized by nanoenergetic materials
Authors: Yanqiang Yang, Shufeng Wang, Zhaoyong Sun and Dana D. Dlott,
Volume 85  Pages  8345-8348  Month Published: Aug.  Year: 2004

Title of Article: Vibrational Substructure in the OH Stretching Transition of Water and HOD
Authors: Zhaohui Wang, Andrei Pakoulev, Yoonsoo Pang and Dana D. Dlott
Volume 108  Pages  9054-9063  Month Published: Oct.  Year: 2004

Title of Article: Vibrational energy dynamics of water studied with ultrafast Stokes and Anti-Stokes Raman spectroscopy
Authors: Zhaohui Wang, Yoonsoo Pang and Dana D. Dlott
Volume 394  Pages  40-45  Month Published: Sept.  Year: 2004

16. Name of Journal: Science
Title of Article: Vibrational energy transfer across a reverse micelle surfactant layer
Authors: John C. Deák, Yoonsoo Pang, Timothy D. Sechler, Zhaohui Wang, and Dana D. Dlott

Volume 306      Pages 473-476     Month Published: Oct.  Year: 2004

17. Name of Book: “Advances in Computational & Experimental Engineering & Sciences '04”,
S. N. Atlurl and A. Tadeu, eds.

Title of Article: Nanotechnology energetic material dynamics studied with nanometer spatial
resolution and picosecond temporal resolution

Authors: Dana D. Dlott, Hyunung Yu, Shufeng Wang, Yanqiang Yang, Selezion A. Hambir

Volume       Pages 1427-1432     Month Published: Year: 2004

18. Name of Journal: Overviews of Recent Research on Energetic Materials, D. Thompson, T.
Brill and R. Shaw, eds.

Title of Article: Multiphonon Up-pumping in Energetic Materials

Authors: Dana D. Dlott

Volume 16      Pages 303-333     Month Published: Year: 2005

19. Name of Journal: Propellants, Explosives and Pyrotechnics

Title of Article: Dynamical Effects of the Oxide Layer in Aluminum Nanoenergetic Materials

Authors: Shufeng Wang, Hyunung Yu, Yanqiang Yang and Dana D. Dlott

Volume 30       Pages 148-155     Month Published: Mar  Year: 2005

20. Name of Journal: Propellants, Explosives and Pyrotechnics

Title of Article: Near-infrared and Visible Absorption Spectroscopy of Nanoenergetic Materials
Containing Aluminum and Boron

Authors: Yanqiang Yang, Shufeng Wang, Zhaoyong Sun and Dana D. Dlott

Volume 30       Pages 171-177     Month Published: May  Year: 2005


Title of Article: Ultrafast dynamics of shock compression of molecular monolayers

Authors: James E. Patterson, Alexei Lagutchev, Wentao Huang and Dana D. Dlott
Title of Article: Ultrafast Dynamics of Self-Assembled Monolayers Under Shock Compression: Effects of molecular and substrate structure
Authors: Alexei Lagoutchev, James E. Patterson, Wentao Huang and Dana D. Dlott

Title of Article: Ultrafast shock compression of self-assembled monolayers: a molecular picture
Authors: James E. Patterson and Dana D. Dlott

24. Name of Journal: Shock Waves
Title of Article: Time and space resolved studies of shock compression molecular dynamics
Authors: J. E. Patterson, A. S. Lagutchev, S. A. Hambir, W. Huang, H. Yu, and Dana D. Dlott

25. Name of Journal: Materials Science and Technology
Title of Article: Thinking big (and small) about energetic materials
Authors: Dana D. Dlott

Title of Article: Nanotechnology energetic material dynamics studied with nanometer spatial resolution and picosecond temporal resolution
Authors: Dana D. Dlott, Selezione A. Hambir, Hyunung Yu

27. Name of Journal: Propellants, Explosives, Pyrotechnics
Title of Article: Surface and interface spectroscopy of energetic materials: HMX and Estane
Authors: Hackjin Kim Alexei Lagutchev and Dana D. Dlott
Volume in press Pages Month Published: Year: 2006

Title of Article: Time-resolved Microscopy Analysis of Laser Photothermal Imaging Media
Authors: Hyunung Yu, Dana D. Dlott, F. Richard Kearney
Volume in press Pages Month Published: Year: 2006

Title of Article: Shock compression spectroscopy with high time and space resolution
Authors: Wentao Huang, James E. Patterson, Alexei Lagutchev and Dana D. Dlott
Volume in press Pages Month Published: Year: 2006

30. Name of Journal: PhD thesis
Title of Article: Ultrafast molecular dynamics at a shock-compressed metal-liquid interface
Authors: James E. Patterson
Volume Pages Month Published: Dec Year: 2004

7. Interactions/Transitions

a. Conferences attended and presentations made

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

175. (invited) Purdue University (Apr. '03). “Three dimensional spectroscopy of vibrational energy transfer in liquids”.

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

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177. *(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".

178. *(invited)* Molecular Dynamics of Energetic Materials Workshop, International Technology Research Institute, Inc., Laurel, MD (June '03), "New ideas and limits for energetic materials".

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

180. APS Conference on Shock Compression of Condensed Matter, Portland, OR, (July '03), "Shock compression of molecules with 1.5 angstrom resolution".

181. *(invited)* Gordon Conference on Liquids, New Hampshire (Aug. '03), "Three dimensional spectroscopy of vibrational energy relaxation in liquids".

182. *(invited)* Second Advanced Energetics Technology Exchange Workshop (Sept. '03), Army Research Laboratory, Aberdeen Proving Grounds, Aberdeen, MD, "Ultrafast vibrational spectroscopy of Energetic Materials"

183. *(invited)* Department of Theoretical and Applied Mechanics, University of Illinois at Urbana-Champaign (Oct. '03), Ultrafast spectroscopy of nanoenergetic materials".

184. *(invited)* Materials Research Society National Meeting, Boston, MA (Dec. '03), "Ultrafast spectroscopy of laser-initiated nanoenergetic materials".

185. *(invited)* Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, (Feb. '04), "Ultrafast spectroscopy of shock compression of condensed matter".

186. *(invited)* Department of Chemistry, Boston College, Boston, MA, (Feb. '04), "Ultrafast spectroscopy of shock compression of condensed matter".

187. 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".

188. *(invited)* Cyber College Distinguished Lecture Series, University of Arkansas at Little Rock, Little Rock, AR (Mar. '04), "Ultrafast spectroscopy of shock compression of condensed matter".

189. *(invited)* CDAC Workshop, Argonne National Laboratory, Argonne, IL (May '04), "Interface molecular dynamics at high dynamic and static pressure".

190. *(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”.


192. (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”.


194. (invited) University of Illinois at Urbana-Champaign Department of Chemistry, Urbana, IL (Sept. '04), “Vibrational energy at interfaces”

195. (invited) Argonne National Laboratory Chemistry Division, Argonne, IL (Sept. '04), “Vibrational energy at interfaces”.

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

197. (invited) Los Alamos National Laboratory, Physics Division (Feb. '05), “Ultrafast nonlinear spectroscopy of molecular shock compression”.

198. (invited) 2nd International Symposium on Interdisciplinary Shock Wave Research, Sendai, Japan (Mar. '05), “Shock compression of molecules with picosecond time and 1.5 angstrom spatial resolution”.

199. (invited, plenary talk) Sixth International Symposium on Special Topics in Chemical Propulsion, Santiago, Chile (Mar. '05). “Nanotechnology energetic material dynamics studied with nanometer spatial resolution and picosecond temporal resolution”.

200. (invited) University of Southern California Department of Physics (Apr. '05), “The new wave in shock waves”.

201. (invited) University of Southern California Department of Chemistry (Apr. '05), “Vibrational energy in molecules and molecular nanostructures”.

202. (invited) Air Force Office of Scientific Research Molecular Dynamics Conference (May '05), “Vibrational energy with high time and space resolution”.


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204. (invited) American Physical Society Topical Meeting on Shock Compression of Condensed Matter, Baltimore, MD (July '05), “Shock compression spectroscopy with high time and space resolution”.

205. (invited) Army Research Office MURI Kick-off meeting, Caltech, Pasadena, CA (July '05), “Insensitive energetic materials”.

206. (invited) Telluride workshop on vibrational dynamics, Telluride, CO (Aug. '05), “Vibrational energy in molecules and molecular nanostructures”.


209. (invited) University of Maryland Department of Chemistry (Oct. '05), “Vibrational energy in molecules and molecular nanostructures”.

210. (invited) University of Pennsylvania Department of Chemistry (Oct. '05), “Vibrational energy in molecules and molecular nanostructures”.

211. (invited) Michigan State University Department of Chemistry (Nov. '05), “Vibrational energy in molecules and molecular nanostructures”.

212. (invited) University of Michigan Department of Chemistry (Nov. '05), “Vibrational energy in molecules and molecular nanostructures”.

213. (invited) DARPA workshop on Standoff Detection of Improvised Explosive Devices, Chantilly, VA (Nov. '05), “IED detection by nonlinear coherent vibrational spectroscopy” (With Dr. W. G. Clark).

214. (invited) US Army Program Review of Nanotechnology Energetic Materials Efforts (MURI review), Aberdeen, MD (Nov. '05), “Fundamental dynamic mechanisms”.


216. (invited) Materials Research Society Fall Meeting, Boston, MA (Nov. '05), “Vibrational energy transfer in reverse micelles”.

b. Consultative and advisory functions

b.1. Consultant, Presstek, Inc.

b.2. Consultant, Optodot, Inc.
b.3. Consultant, MeadWestvaco, Corp.
b.4. APS International Conference on Shock Compression, 2004, Graduate fellowship committee
b.5. External Review Panel, Interdisciplinary Shock Wave Research Center, Sendai, Japan, 2005

c. Transitions

c.1. MURI: “Nanotechnology Engineered Energetic Materials” with USC and Penn State U.
c.2. MURI: “Insensitive Energetic Materials”, with USC and Caltech
c.3. We have discussed using our nonlinear coherent laser methods for detecting high explosives on the surfaces (see article 15) of distant objects with ARO and DARPA.

d. New discoveries, inventions or patent disclosures

9. Honors and Awards


Invited, plenary talk at the Sixth International Symposium on Special Topics in Chemical Propulsion, Santiago, Chile (Mar. ’05). “Nanotechnology energetic material dynamics studied with nanometer spatial resolution and picosecond temporal resolution”.

Elected Fellow of the American Association for the Advancement of Science 2005.