



**AFRL-OSR-VA-TR-2014-0027**

**ULTRAFAST DYNAMICS OF ENERGETIC MATERIALS**

**DANA DLOTT**

**UNIVERSITY OF ILLINOIS**

**01/23/2014**

**Final Report**

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**AIR FORCE RESEARCH LABORATORY  
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# REPORT DOCUMENTATION PAGE

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<b>14. ABSTRACT</b> The objective of this project was to develop a fundamental understanding of the fast dynamical processes involved in energetic material (EM) initiation, ignition and detonation, using state-of-the-art experimental techniques based on time-resolved laser spectroscopy, developed in the Dlott laboratory. The motivation for our project was to look at some of the most fundamental processes occurring on short length and time scales, say picoseconds and nanometers. Current understanding of these processes comes mainly from theories and atomistic simulations, and there is a lack of data needed to understand whether these theories and simulations give an accurate picture. To this end, workers in the Dlott group devised a number of experiments that look at EM when large amounts of vibrational energy are suddenly input, at the earliest (picosecond) stages of shock compression when the molecules are just beginning to feel the shock, when ultrafast flash-heating suddenly inputs large amounts of heat, and at the second (nanosecond) stages of shock compression when materials experience large strain deformation and molecules have had time to react exothermically. Development of advanced lasers in the Dlott group also led to a spin-off project to study electrocatalytic conversion of CO <sub>2</sub> to CO, needed for economic production of synfuels.					
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## Final report

Award FA9550-09-1-0163

PI and author of report: Dana D. Dlott

Title of project: Ultrafast dynamics of energetic materials

Report period 01 Mar 2009 to 30 Nov 2013

### 1. Objectives:

The objective of this five year project was to develop a fundamental understanding of the fast dynamical processes involved in energetic material (EM) initiation, ignition and detonation, using state-of-the-art experimental techniques based on time-resolved laser spectroscopy, developed in the Dlott laboratory. We focused on two kinds of EM, conventional homogeneous EM that were molecular materials, and heterogeneous EM composed of nanometric fuel and oxidizer components. The latter are sometimes called nanoenergetic materials or reactive materials (RM).

Energetic material initiation, ignition, combustion/deflagration and detonation all involve materials under extreme conditions with high temperatures, pressures, mechanical strains and lots of vibrational energy. The motivation for our project was to look at some of the most fundamental processes occurring on short length and time scales, say picoseconds and nanometers. Our current understanding of these processes comes mainly from theories and atomistic simulations, and we do not need good data to understand whether these theories and simulations are giving us an accurate picture. To this end we have devised a number of experiments that look at EM when large amounts of vibrational energy are suddenly input, at the earliest (picosecond) stages of shock compression when the molecules are just beginning to feel the shock, when ultrafast flash-heating suddenly inputs large amounts of heat, and at the second (nanosecond) stages of shock compression when materials experience large strain deformation and molecules have had time to react exothermically.

Our progress can be summarized with respect to five subprojects. Four of these were focused on the topics above related to EM and RM. The fifth, our spectroelectrochemistry project, was a synergistic effort that arose unexpectedly as a spin off from laser technologies developed for the EM and RM studies.

**A. Vibrational energy.** EM and RM dynamics always involve the generation and decay of highly vibrationally excited molecules and solids. We lack a firm understanding of how vibrational energy is transferred and redistributed in condensed-phase materials. In this subproject we developed a technique termed three-dimensional IR-Raman spectroscopy that allowed us to use a specialized femtosecond laser apparatus to create vibrational excitations in a selected state of a chosen molecular species, and then probe the dynamics of the initial vibrational excitations and the vibrational excitations generated by the decay of the initial excitations.

**B. Ultrafast shock compression and large-amplitude temperature jump.** In these experiments, we used another specialized femtosecond laser apparatus to produce large

temperature jumps (T-jump) and shock waves with GPa pressures in molecular monolayers. Using monolayers allowed us to monitor these processes with uniquely high time and space resolution and have precise control over the molecular structures we studied.

**C. Flash-heating of nanoenergetic materials.** In these experiments we studied RM comprised of nanometric Al fuel particles and Teflon binder. This combination produces a multifunctional EM with extremely high energy potential (about 3 times TNT). The dynamics of these materials were studied using a picosecond laser apparatus to flash-heat the Al nanoparticles, causing the materials to ignite.

**D. Laser flyer plates and impact initiation of energetic materials.** After the flash-heating project was complete, we developed a new method to initiate EM and RM. This method is based on the use of a laser to launch a metal flyer plate into the EM samples, producing powerful shock waves. This unique apparatus was used to study shock compression in different materials and shock initiation in RM.

**E. Spectroelectrochemistry of fuel cells, batteries and synfuel synthesis.** During discussions with chemistry and chemical engineering colleagues and AFRL and AFOSR personnel, we realized that the laser instrumentation developed for the monolayer flash-heating and shock experiments could play an important role in understanding the fundamental mechanisms of electrocatalysis in many applications, and following discussions with our AFOSR program officer Berman, a portion of our effort was devoted to collaborative efforts in these areas.

## 2. Status of effort

A competitive renewal proposal was submitted to AFOSR in Feb 2013, and we have just been notified of intent to fund. The vibrational energy experiments have been completed and published. We intend to combine the ultrafast shock compression and T-jump methods, in order to understand the earliest stages of EM initiation with a high degree of time and space resolution. The flash-heating of RM project was completed and published, and it has been replaced by shock initiation studies, which are ongoing. The electrocatalysis project is now entirely focused on synfuel synthesis, and it has been transitioned to another AFOSR fund stream. This project is being performed with collaborators at Dioxide Solutions, Inc., and it is funded by a subcontract from their AFOSR SBIR Phase II grant.

## 3. Personnel supported

Dana D. Dlott, principal investigator

*Former group members*

Alexei Lagutchev postdoc. Presently Staff Scientist, Purdue University, Birck Nanotechnology Center

Hiroki Fujiwara postdoc, currently staff scientist University of Bristol  
Zhaohui Wang, postdoc, currently Professor of Chemistry Xiamen University  
Nak Seong, postdoc, currently staff scientist, Yonsei University  
Jeff Carter, Ph. D. 2011, currently postdoc, Lawrence Livermore Laboratory  
Kathryn Brown, Ph. D. 2012, currently postdoc, Los Alamos National Laboratory  
Rusty Conner, Ph.D. 2011, Currently Intel Corp., Portland, OR

*Current group members*

Christopher Berg grad student.  
Yuanxi Fu, graduate student  
Brandt Pein graduate student. Ph.D. expected Feb. 2014 and postdoc MIT (Keith Nelson)  
Yuxiao Sun, graduate student  
Bruno Giuliano Nicolau, graduate student  
William L. Shaw, graduate student  
Alexandr Banishev, postdoc  
Mingwei Chen, postdoc

**4. Publications acknowledging support from this AFOSR grant (grouped by topic)**

**Vibrational energy**

1. B. C. Pein, N.-H. Seong, and D. D. Dlott, Vibrational Energy Relaxation of Liquid Aryl-Halides  $X-C_6H_5$  ( $X = F, Cl, Br, I$ ), *J. Phys. Chem. A* **114**, pp. 10500-10507 (2010).
2. Ph.D. Thesis of Ying Fang, 2011, "The distribution of local enhancement factors in surface enhanced Raman-active substrates and the vibrational dynamics in the liquid phase".
3. (invited) "Vibrational energy and molecular thermometers in liquids: Ultrafast IR-Raman spectroscopy", Brandt C. Pein and Dana D. Dlott, To appear in "Ultrafast Infrared Spectroscopy", M. D. Fayer, editor (Taylor and Francis, New York, 2012).
4. "Unidirectional vibrational energy flow in nitrobenzene", Brandt C. Pein, Yuxiao Sun and Dana D. Dlott, *J. Phys. Chem. A* **117**, pp. 6066-6072 (2013).
5. "Three-dimensional spectroscopy of vibrational energy in liquids: nitromethane and acetonitrile", Yuxiao Sun, Brandt C. Pein and Dana D. Dlott, *J. Phys. Chem. B* (in press 2013).
6. "Controlling vibrational energy flow in liquid alkylbenzenes", Brandt C. Pein, Yuxiao Sun and Dana D. Dlott, *J. Phys. Chem. B* **117**, pp. 10898-10904 (2013).
7. "Modifying Vibrational Energy Flow in Aromatic Molecules: Effects of Ortho Substitution", Brandt C. Pein and Dana D. Dlott, *J. Phys. Chem. A* (in press).

**Ultrafast shock compression and large-amplitude T-jump**

8. Carter, J. A., Wang, Z., Fujiwara, H., and Dlott, D. D., Ultrafast excitation of molecular adsorbates on flash-heated gold surfaces, *J. Phys. Chem. A* **113**, pp. 12105-12114 (2009).
9. Brown, K. E. and Dlott, D. D., High pressure Raman spectroscopy of molecular monolayers adsorbed on a metal surface, *J. Phys. Chem. C* **113**, pp. 5751-5757 (2009).

10. Lagutchev, A., Brown, K. E., Carter, J. A., Fu, Y., Fujiwara, H., Wang, Z., and Dlott, D. D., Ultrafast vibrational spectroscopy of shock compression with molecular resolution, *AIP Conf. Proc.* **1195**, pp. 301-304 (2010).
11. Y. Fu, E. A. Friedman, K. E. Brown, and D. D. Dlott, Vibrational spectroscopy of nitroaromatic self-assembled monolayers under extreme conditions, *Chem. Phys. Lett.* **501**, pp. 369-374 (2011).
12. Paranjothy Manikandan, Jeffrey A. Carter, Dana D. Dlott and William L. Hase, “Effect of carbon chain length on the dynamics of heat transfer at a gold/hydrocarbon interface: Comparison of simulation with experiment”. *J. Phys. Chem. C*, **115**, pp. 9622–9628 (2011).
13. PhD. Thesis of Jeffrey A. Carter, 2011, “Dynamics of molecular adsorbates exposed to ultrafast thermal gradients”.
14. “The distributions of enhancement factors in close-packed and non-close-packed surface-enhanced Raman substrates, Ying Fang, Dana D. Dlott, Hongta Yang and Peng Jiang, *J. Raman Spectr.* **43**, pp. 389-395 (2012).
15. “Nitro stretch probing of a single molecular layer to monitor shock compression with picosecond time resolution” C. Berg, A. Lagutchev, Y. Fu and D. D. Dlott, *AIP Confer. Proc.*, **1426**, pp. 1573-1596 (2012).
16. “Probing of molecular adsorbates on Au surfaces with large-amplitude temperature jumps,” Christopher M. Berg, Alexei Lagutchev and Dana D. Dlott, *J. Appl. Phys.* **113**, 183509 (11 pages).
17. “Molecular adsorbates under high pressure: a study using surface-enhanced Raman scattering and vibrational sum-frequency generation spectroscopy”, Yuanxi Fu and Dana D. Dlott, *Journal of Physics: Conference Series* (in press).
18. Temperature-dependent dynamic response to flash heating of molecular monolayers on metal surfaces: vibrational energy exchange, Christopher M. Berg, Yuxiao Sun and Dana D. Dlott, *J. Phys. Chem. B.* (published online Nov. 29, 2013. **DOI:** 10.1021/jp410728j).

### **Flash heating of nanoenergetic materials**

19. Conner, R. W. and Dlott, D. D., Ultrafast condensed-phase emission from aluminized explosives: Nano-aluminum in Teflon, *J. Phys. Chem. A*, **114**, pp. 6731-6741 (2010).
20. Conner, R. W. and Dlott, D. D., Ultrafast emission spectroscopy measurements of ignition of nano-aluminum in Teflon, Proceedings of the 2010 Technical Meeting of the Central States Section of The Combustion Institute (submitted and presented Feb 2010, but apparently never published).
21. Ph.D. Thesis of Rusty W. Conner, 2011, “Initiation and ignition of nano-aluminum in Teflon”.
22. “Ultrafast emission spectroscopy of exploding nanoaluminum in Teflon: observations of aluminum fluoride”, Rusty Conner and Dana D. Dlott, *Chem. Phys. Lett.*, **512**, pp. 211-216 (2011).
23. (*invited*) “Experiments Probing Fundamental Mechanisms of Energetic Material Initiation and Ignition”, Christopher M. Berg, Kathryn E. Brown, Rusty W. Conner, Yuanxi Fu, Hiroki Fujiwara, Alexei Lagutchev, William L. Shaw, Xianxu Zheng and Dana D. Dlott, *MRS Online Proceedings Library* **1405** (2012).

24. (invited feature article + cover art) “Time-resolved spectroscopy of initiation and ignition of flash-heated nanoparticle energetic materials”, Rusty W. Conner and Dana D. Dlott, *J. Phys. Chem. C* **116**, pp. 14737-14747 (2012).
25. “Comparing boron and aluminum nanoparticle combustion in Teflon using ultrafast emission spectroscopy”, Rusty W. Conner and Dana D. Dlott, *J. Phys. Chem. C*, **116**, pp. 2751-2760 (2012).

### **Laser flyer plates and impact initiation of energetic materials**

26. Fujiwara, H., Brown, K. E., and Dlott, D., Laser-driven flyer plates for reactive materials research, *AIP Confer. Proc.* **1195**, pp. 1317-1320 (2010).
27. H. Fujiwara, K. E. Brown, and D. D. Dlott, High-energy flat-top beams for laser launching using a Gaussian mirror, *Appl. Opt.* **49**, pp. 3723–3731 (2010).
28. D. D. Dlott, New Developments in the Physical Chemistry of Shock Compression, *Annu. Rev. Phys. Chem.* **62**, pp. 575-597 (2011).
29. “Microscopic states of shocked polymers”, K. E. Brown, R. Conner, Y. Fu, H. Fujiwara, and D. D. Dlott, *AIP Confer. Proc.*, **1426**, pp. 1593-1596 (2012).
30. “A thin-film Hugoniot measurement using a laser-driven flyer plate”, H. Fujiwara, K. E. Brown and D. D. Dlott, *AIP Confer. Proc.*, **1426**, pp. 382-385, (2012).
31. “Simplified laser-driven flyer plates for shock compression science”, Kathryn E. Brown, William L. Shaw, Xianxu Zheng and Dana D. Dlott, *Rev. Sci. Instrum.* **83**, 103901 (2012).
32. Time-resolved emission of dye probes in a shock-compressed polymer, Kathryn E. Brown, Yuanxi Fu, William L. Shaw and Dana D. Dlott, *J. Appl. Phys.* **112**, 103508 (2012).
33. Ph.D. Thesis of Kathryn E. Brown, 2012, “New technologies for spectroscopy of materials under static and shock compression”.
34. “Shock initiation of nano-Al + Teflon: time-resolved emission studies”, Xianxu Zheng, Alexander D. Curtis, William L. Shaw and Dana D. Dlott, *J. Phys. Chem. C* **117**, pp. 4866-4875 (2013).
35. “Laser-driven flyer plates for shock compression spectroscopy”, William A. Shaw, Alexander D. Curtis, Alexandr A. Banishev and Dana D. Dlott, *Journal of Physics: Conference Series* (in press).
36. “Using laser-driven flyer plates to study the shock initiation of nanoenergetic materials”, William A. Shaw, Rayon A. Williams, Edward L Dreizin and Dana D Dlott, *Journal of Physics: Conference Series* (in press).
37. “Dynamics of shocks in laser-launched flyer plates probed by photon Doppler velocimetry, Alexander D. Curtis, William A. Shaw, Alexandr A. Banishev and Dana D. Dlott, *Journal of Physics: Conference Series* (in press).

### **Spectroelectrochemistry of fuel cells, batteries and synfuel synthesis**

38. Lagutchev, A., Lozano, A., Mukherjee, P., Hambir, S. A., and Dlott, D. D., Compact broadband vibrational sum-frequency generation spectrometer with nonresonant suppression, *Spectrochim. Acta. A* **75**, pp. 1289-1296 (2010).
39. Behrens, R. L., Lagutchev, A., Dlott, D. D., and Wieckowski, A., Broad-band sum frequency generation study of formic acid chemisorption on a Pt(100) electrode, *J. Electroanal. Chem.* **649**, pp. 32-36 (2010).

40. B. Braunschweig, P. Mukherjee, D. D. Dlott, and A. Wieckowski, Real-Time Investigations of Pt(111) Surface Transformations in Sulfuric Acid Solutions, *J. Am. Chem. Soc.* **132**, pp. 14036-14038 (2010).
41. B. Braunschweig, P. Mukherjee, R. B. Kutz, A. Wieckowski, and D. D. Dlott, Sum-frequency generation of acetate adsorption on Au and Pt surfaces: Molecular structure effects, *J. Chem. Phys.* **133**, pp. 234702-234708 (2010).
42. R. B. Kutz, B. Braunschweig, P. Mukherjee, R. L. Behrens, D. D. Dlott, and A. Wieckowski, Reaction pathways of ethanol electrooxidation on polycrystalline platinum catalysts in acidic electrolytes, *J. Catalysis* **278**, pp. 181-188 (2011).
43. "Study of Ethanol Electrooxidation in Alkaline Electrolytes with Isotope Labels and Sum-Frequency Generation", Robert B. Kutz, Björn Braunschweig, Prabuddha Mukherjee, Dana D. Dlott, and Andrzej Wieckowski, *J. Phys. Chem. Lett.* **2**, pp. 2236–2240 (2011).
44. "In Situ Probing of Solid-Electrolyte Interfaces with Nonlinear Coherent Vibrational Spectroscopy", Prabuddha Mukherjee, Alexei Lagutchev and Dana D. Dlott, *J. Electrochem. Soc.* **159**, pp. A244-A252 (2012).
45. "In Situ Spectroscopic Examination of a Low Overpotential Pathway for Carbon Dioxide Conversion to Carbon Monoxide", Brian A. Rosen, John L. Haan, Prabuddha Mukherjee, Björn Braunschweig, Wei Zhu, Amin Salehi-Khojin, Dana D. Dlott, Richard I. Masel, *J. Phys. Chem. C* **116**, pp. 15307-15312 (2012). (invited) "Vibrational sum-frequency generation spectroscopy of interfacial dynamics", Christopher M. Berg and Dana D. Dlott, in: *Vibrational Spectroscopy at Electrified Interfaces*, Editors A. Wieckowski, C. Korzeniewski and B. Braunschweig (Wiley, Hoboken N. J., 2013), pp. 85-119.
46. (invited) Spectroscopy of electrified interfaces with broadband sum frequency generation: From electrocatalysis to protein foams, B. Braunschweig, P. Mukherjee, R. B. Kutz, A. Rumpel, K. Engelhardt, W. Peukert, Dana D. Dlott and A. Wieckowski in: *Vibrational Spectroscopy at Electrified Interfaces*, Editors A. Wieckowski, C. Korzeniewski and B. Braunschweig (Wiley, Hoboken N. J., 2013), pp. 120-150.

## 5. Interactions/transitions

### a. Participation at conferences, seminars, etc.

1. (invited) International Conference on Time Resolved Vibrational Spectroscopy (TRVS), New Hampshire, May 2009, "Vibrational dynamics at interfaces probed by vibrational sum-frequency generation spectroscopy".
2. (invited) ACS Colloids and Surface Chemistry Symposium, Columbia University, June 2009, "Vibrational dynamics at interfaces probed by vibrational sum-frequency generation spectroscopy".
3. APS Topical Meeting on Shock Compression in Condensed Matter, Nashville, TN, June 2009, "Ultrafast vibrational spectroscopy of shock compression with molecular resolution: energetic material simulants".
4. (invited) Telluride workshop on Vibrational Dynamics, Telluride, CO, July 2009, "Vibrational energy transport in molecules".

5. (*invited*) Pinhead Institute Town Talk, Telluride Conference Center, Telluride, CO, July 2009, "The science of explosions: Blowing things up for fun, profit, war and medicine".
6. (*invited*) Gordon Conference on Vibrational Dynamics at Surfaces, Proctor Academy, Andover, NH, Aug. 2009, "Dynamics at interfaces probed by time-resolved sum-frequency spectroscopy".
7. (*invited*) 21st Century Needs and Challenges of Compression Science Workshop, Santa Fe, NM, Sept. 2009, "Shock compression of molecules with high time and space resolution".
8. (*invited*) Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) annual meeting, Louisville, KY, Oct. 2009. "Vibrational energy in molecules studied with 2D vibrational sum-frequency generation".
9. (*invited*) North Carolina State University, Jan. 2010, "Vibrational energy in materials with high time and space resolution".
10. (*invited*) Army Research Office Review of Nano-engineered energetic materials, Aberdeen, MD, Mar. 2010, "Ultrafast dynamics of NEEMs".
11. (*invited*) American Chemical Society Annual Meeting, San Francisco, CA Mar. 2010, "Vibrational Energy in Molecules with High Time and Space Resolution".
12. (*invited*) Northwestern University Department of Chemistry, Evanston, IL Mar. 2010, "Vibrational Energy with High Time and Space Resolution".
13. NATO Munitions Safety Information Analysis Center (MSIAC) Workshop on Insensitive Energetic Materials, NATO Headquarters, Brussels, Belgium, May 2010, "Molecular mechanisms of insensitive explosives".
14. (*invited*) Molecular Dynamics Contractors' Meeting, Air Force Office of Scientific Research, Chantilly, VA, May 2010, "Time resolved spectroscopy of molecules at interfaces".
15. (*invited*) Army Research Office Symposium on Insensitive Energetic Materials, Aberdeen, MD, June 2010, "Fundamental Processes and Properties of Insensitive Energetic Materials".
16. (*invited, plenary*), "Vibrational energy in molecules with high time and space resolution", International Conference on Raman Spectroscopy (ICORS X), Boston, MA, Aug. 2010.
17. (*invited*) "The science of explosions: Blowing things up for fun, profit, war and medicine", Countryside Elementary School, Champaign, IL, Oct. 2010.
18. (*invited*) "Ultrafast Dynamics of Impact Chemistry: Initiation to Detonation", Aug. 2010, Joint JSF-IAS Workshop on Interface Physics Singapore August 29-September 5, 2010.
19. (*invited*) "Vibrational energy with high time and space resolution", Dec. 2010, Pacificchem, Honolulu, HI.
20. (*invited*) "Shock compression with atomic resolution", Workshop on Dynamic Phenomena, Jan 2011, Austin, TX.
21. (*invited*) "Molecular transformations and energy transfer at interfaces", USC-DOE conference on "Materials for Energy Applications - Experiment, Modeling and Simulations", Mar. 2011, Los Angeles, CA.
22. (*invited*) "Heat and electrons at interfaces", Workshop on Nonlinear Optics and Interfaces, Apr. 2011, Erlangen, Germany.

23. *(invited)* Air Force Office of Scientific Research Molecular Dynamics Meeting, Pasadena, CA, May 2011, “Nonlinear coherent vibrational spectroscopy in electrochemical surface science and electrocatalysis”.
24. *(invited)* Studium Conference on in situ molecular spectroscopic technique and application, Orleans, France, June 2011, “In situ probing by time-resolved vibrational spectroscopy: shocked materials and energy storage media”.
25. *(invited)* American Chemical Society National Meeting, Denver, CO Aug. 2011, “Interfaces under extreme conditions”.
26. *(invited)*, Federation of analytical chemistry and spectroscopy (FACSS) national meeting, Reno, NV, Oct. 2011, “Three dimensional vibrational spectroscopy of molecular energy”.
27. *(invited)* “Interfaces under extreme conditions”, Oct. 2011, Rice University Department of Chemistry.
28. *(invited)* “Ultrafast shock compression spectroscopy”, Oct. 2011, Carnegie Defense Alliance Annual Review, Argonne National Laboratory.
29. *(invited)* Materials Research Society National Meeting, Boston, MA Nov. 2011, “Experiments Probing Fundamental Mechanisms of Energetic Material Initiation and Ignition”.
30. Materials Research Society National Meeting, Boston, MA Nov. 2011, “Solid Electrolyte Interfaces and Interphases in Lithium Batteries: In Situ Studies Using Nonlinear Optical Probes”.
31. *(invited)* “Interfaces under extreme conditions”, National Chiao Tung University Department of Chemistry, Hsinchu, Republic of China, Feb. 2012.
32. *(invited)* “Nonlinear coherent vibrational spectroscopy of electrochemistry”, Xiamen University Department of Chemistry, Xiamen, P. R. China, Feb. 2012.
33. *(invited)* “Lithium-ion battery SEI formation using nonlinear coherent IR spectroscopy”, The Electrochemical Society National Meeting, Seattle, WA, May, 2012.
34. *(invited)* “Spontaneous energy concentration in energetic molecules, interfaces and composites: response to ultrasound and THz radiation”, Office of Naval Research Program Review, Basic Research - Sciences Addressing Asymmetric Explosive Threats, Arlington, VA May 21, 2012.
35. *(invited)* “Experiments probing initiation and ignition of energetic materials”, International Center for Applied Computational Mechanics (ICACM) symposium New York, NY June 11-13 2012.
36. *(invited)* “Shock physics for dummies!”, Gordon Conference on Energetic Materials, W. Dover, VT, June 2012.
37. *(invited)* “Overview of Shock Wave Energy Dissipation” and “Diagnostics for Shock Wave Energy Dissipation on the nanoscale”, Office of Naval Research, Multiuniversity Research Initiative for Shock Wave Energy Dissipation, Arlington, VA July 30, 2012.
38. *(invited)* “Nonlinear coherent vibrational spectroscopy of electrochemical transformations”, American Chemical Society National Meeting, Philadelphia, PA, Aug. 2012.
39. *(invited)* “Molecular dynamics of explosives” Department of Chemistry, Colorado State University, Ft. Collins, CO, Oct. 2012.

40. (*invited*) "Probing molecular dynamics and transformations at metal-organic interfaces", University of Colorado, Boulder, CO, Oct. 2012.
41. (*invited*) "Laser-driven flyer plates for shock compression spectroscopy", International Symposium on Pulsed Power Applications, Kumamoto University, Kumamoto, Japan, Mar. 2013.
42. (*invited*) "Ultrafast spectroscopy of molecules at metal surfaces", University of Florida, Department of Chemical Engineering, Gainesville, FL, Mar. 2013.
43. (*invited*) "Laser-driven flyer plates for shock wave spectroscopy", Los Alamos National Laboratory, May 2013.
44. (*invited*) "Shock wave energy dissipation". ONR MURI Review, Arlington, VA, June, 2013.
45. "Laser-driven flyer plates for shock wave spectroscopy", APS SCCM Meeting, Seattle, WA, July 2013.
46. (*invited*) "Ultrafast diagnostics for particulate composites", DTRA review, Springfield, VA. July 2013.
47. (*invited*) "Ultrafast vibrational spectroscopy of energy flow in molecules", CECAM Workshop on Nanophononics, Bremen, Germany, Aug. 2013.
48. (*invited*) "Vibrational energy transfer on surfaces and in liquids". ACS National Meeting, Indianapolis, IN Sept. 2013.

#### **b. Consultative and advisory functions**

- Jupiter Laser Review Committee, Lawrence Livermore
- External Advisory Board, PULSE center, Stanford Linear Accelerator Center, Stanford University, 2011-12
- Journal of Physical Chemistry Editorial Advisory Board 2009-2011
- Journal of Raman Spectroscopy Editorial Advisory Board 2011-2013
- Chemical Physics Editorial Advisory Board, 2012-
- Army Research Laboratory Technical Assessment Board 2013-J

#### **c. Honors/awards**

Chemical Physics Letters "Most cited paper" 2003-2007 award, 2008

J. Phys. Chem. A, "Most accessed paper", 2007.

William H. and Janet G. Lycan Professor of Chemistry, 2009-

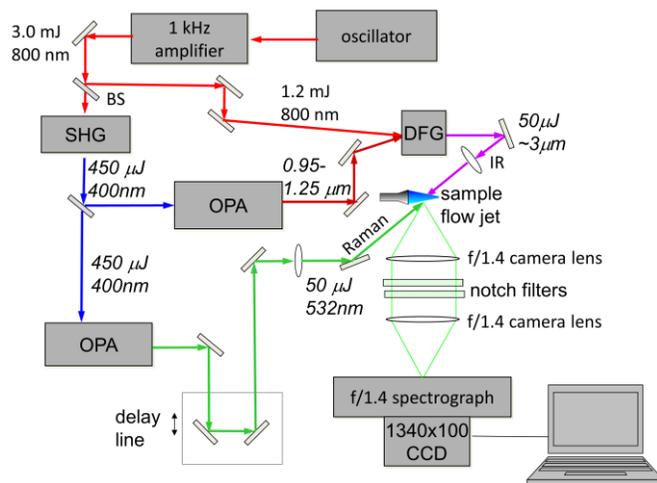
ACS Physical Chemistry Division Award in Experimental Physical Chemistry, 2013.

### **6. Research findings**

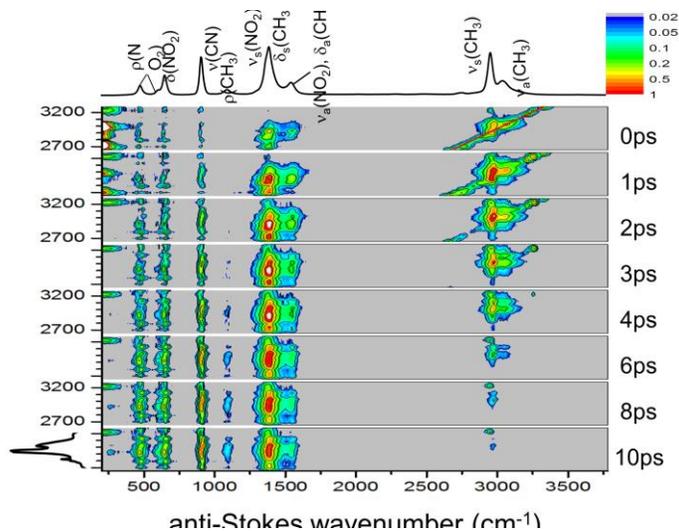
**A. Vibrational energy.** The laser apparatus for 3D IR-Raman vibrational spectroscopy<sup>1</sup> is shown in Fig. 1. The 3 dimensions are IR wavenumber, Raman wavenumber and delay time. The IR wavenumber is scanned, inputting vibrational energy into different states of molecules in liquid phase. At a series of different delays, we detect Stokes and anti-Stokes Raman spectra. These spectral intensities are combined to determine the vibrational populations in many of the molecules states. With this method we can choose where to input the vibrational energy and watch it as it leaves the input state and flows to

other states. Figure 2 shows a 3D spectrum obtained on nitromethane (NM) liquid at ambient temperature.<sup>1</sup> Figure 3 shows our most significant result. In those experiments we looked at nitrobenzene (NB).<sup>2,3</sup> Using quantum chemistry we computed the normal modes and we divided them into three classes: nitro modes, phenyl modes, and global modes with significant amplitudes on both nitro and phenyl.<sup>2-4</sup> From our 3D spectra and those calculations, we selected IR pulses that most selectively input energy into either the nitro group (through a stretching overtone) or into the phenyl group (through a ring stretching mode). Then we watched energy flow through the molecules. In NB, we found that when nitro was excited there was no nitro-to-phenyl transfer (nor nitro-to-global transfer), but significant amounts of phenyl-to-nitro (and phenyl-to-global) transfer.<sup>2</sup> This was a remarkable observation. NB appears to act as a vibrational energy diode supporting only unidirectional energy transfer. As shown in Fig. 3b,c, when ortho substituents were added (either methyl or fluorine), the nitro-to-phenyl channel was opened up.<sup>3</sup>

**B. Ultrafast shock compression and large-amplitude temperature jump.** In these experiments, a molecular monolayer is fabricated on a metal film deposited onto a glass substrate. The vibrational transitions of these molecules is probed by a nonlinear coherent vibrational spectroscopy method termed “sum-frequency generation spectroscopy” or SFG. SFG is a method capable of generating vibrational spectra from a monolayer in 1 picosecond,<sup>5,6</sup> which ordinary vibrational spectroscopies cannot do. We



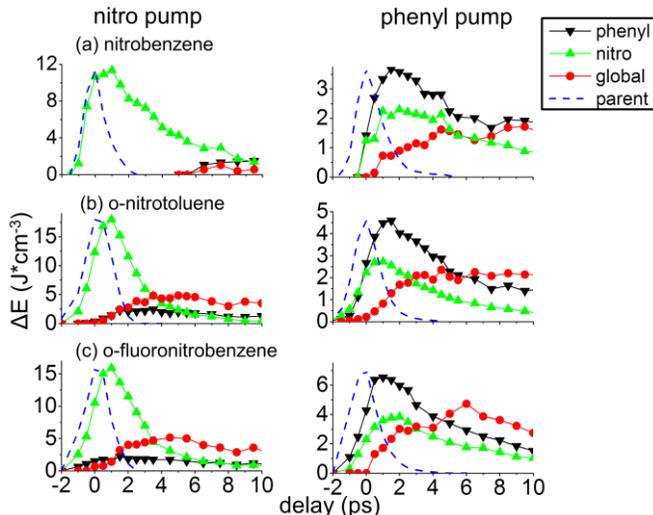
**Fig. 1.** Block diagram of laser apparatus used for three-dimensional IR-Raman vibrational spectroscopy.



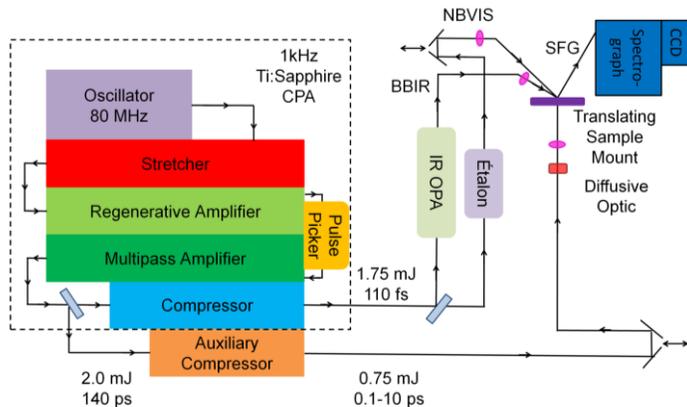
**Fig. 2.** A 3D IR-Raman spectrum of nitromethane. At each delay time the y-axis represents the wavenumber of the vibration pumped by IR and the x-axis represents the populations of the nitromethane vibrations.

then either use a laser to ablate part of the metal film to launch a shock into the monolayer,<sup>7</sup> or we use the same laser at lower intensity to flash heat the metal film, which heats the monolayer by thermal conduction.<sup>6</sup> The reason we are focused on monolayers is to monitor shock and heat with high spatial and temporal resolution. If the sample were a multilayer instead of a monolayer, then we would not know which layer was being shocked or heated. Also it would take longer for the shock and heat to excite the many layers. So with a monolayer we know precisely where the heat or shock front is and we get high time resolution. The drawback of the monolayer is the low signals associated with the small number of molecules. It is the nonlinear coherent nature of the SFG probe technique implemented by our specialized laser system that overcomes this problem. A block diagram of the laser system is shown in Fig. 4.

Figure 5 shows the concept for shock experiments.<sup>8</sup> A sample is fabricated on a 50 x 50 mm<sup>2</sup> substrate. Each shock is 200  $\mu\text{m}$  in diameter, and a single shock destroys the shocked material, but we can make tens of thousands of shocks on the same sample. As shown in Fig. 5, the original sample used a monolayer of nitrobenzoic acid (NBA). Also there is a few micrometer thick polymer tamping layer. The NBA molecule is an EM simulant with a nitro group. We are focused on the nitro groups due to their importance in EM. The acid group anchors the molecules to Al. We developed a method to smooth and homogenize our laser drive beam as shown in Fig. 5d. We have

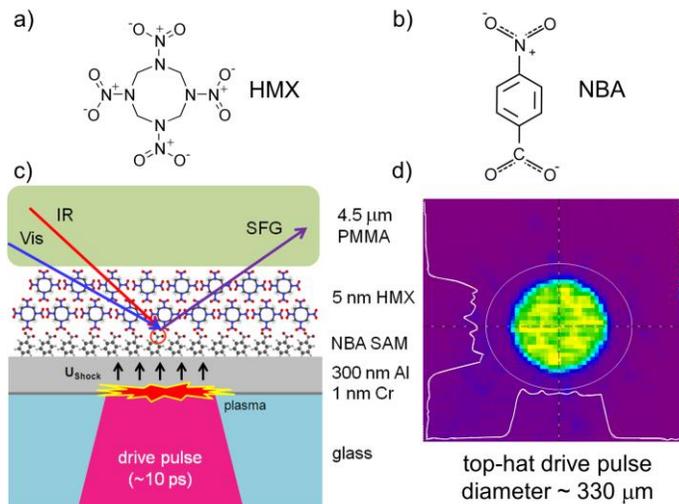


**Fig. 3.** IR-Raman data on nitrobenzenes. In the left column, IR pulses were used that pumped energy into the nitro groups. In the right column the phenyl groups were pumped by pulses with about the same frequency. In nitrobenzene, almost no energy flows from nitro to phenyl but some energy flows from phenyl to nitro. An ortho substituent such as methyl or fluorine turns on the nitro-to-phenyl channel.

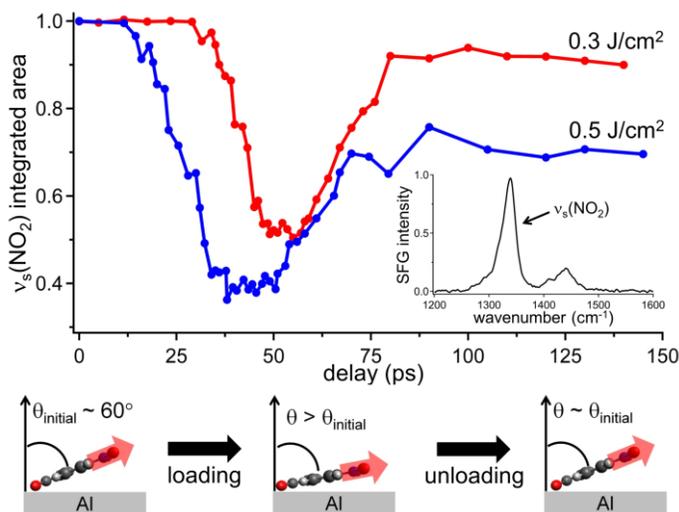


**Fig. 4.** Block diagram of laser apparatus used for ultrafast T-jump or shock compression. The flash-heated or shocked molecular monolayers are probed using nonlinear coherent vibrational spectroscopy.

also learned how to grow a thin layer of  $\delta$ -HMX on top of the monolayer. We lose a little bit of spatial and temporal resolution but in this type of sample we are really looking at a sensitive explosive material. Some results are shown in Fig. 6. We are probing the NBA symmetric nitro stretch at  $\sim 1340\text{ cm}^{-1}$  with SFG following shocks generated by two different laser energies. The nitro signal decreases when the shock arrives and then it partially recovers. The shock risetime is about 8 picoseconds. In the two traces at the top of Fig. 5, the higher shock energy data loses its intensity first. This is because it is a higher-pressure shock and it reaches the monolayer faster. At the bottom of Fig. 5 is a schematic of the SFG intensity loss mechanism. The shock drives the NBA molecules toward the Al layer. This tilts the nitro groups into an orientation that is unfavorable for the SFG probe process. Then the nitro groups reorient back toward their original orientation. But when the shock is stronger, the monolayer structure is disrupted and the nitro groups cannot get back to their original state.



**Fig. 5.** Sample construction for ultrafast shock vibrational spectroscopy. A monolayer of NBA is deposited onto a metal film. The nitro groups are probed by nonlinear coherent vibrational spectroscopy. A layer of  $\delta$ -HMX a few molecules thick can be grown on top of the NBA. A diffusive optic is used to produce a spatially-uniform drive beam.

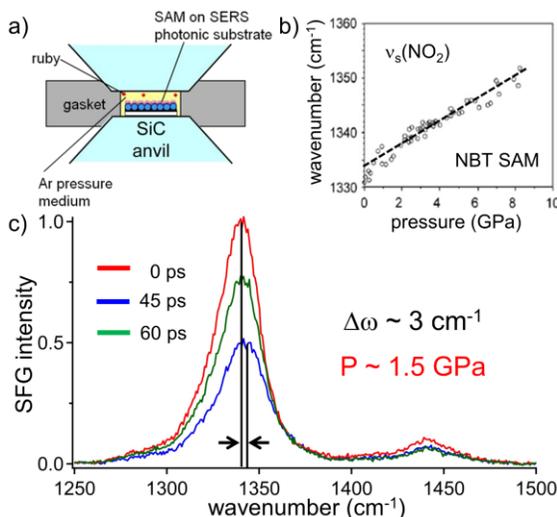


**Fig. 6.** Ultrafast shock vibrational spectroscopy of nitrobenzoic acid monolayer with shocks in the 1 GPa range. The shock causes the molecules to tilt, which reduces the nitro group signal. The effect started sooner when the laser fluence was  $0.5\text{ J/cm}^2$  because the shock traveled faster.

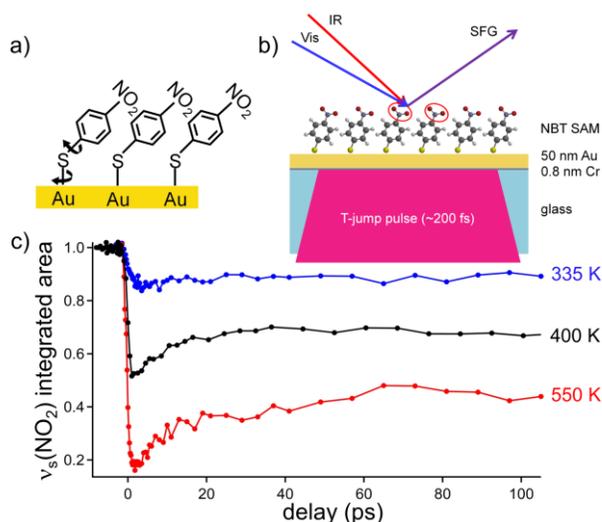
We can estimate the pressure of these ultrafast shock fronts by comparing the nitro vibrational blueshift to data from a static high pressure diamond-anvil cell (DAC),<sup>9</sup> as in Fig. 7. At the peak of the shock compression process, about 45 ps after the laser pulse was delivered, we see a blueshift of  $3\text{ cm}^{-1}$  (Fig. 7c) In the DAC we have to get spectra from a monolayer, which had never previously been done. We accomplished that

using a tiny photonic chip that we fabricated, inside the diamond anvil (Fig. 7a) to amplify the Raman spectrum by a factor of about one million.<sup>10</sup> The frequency shift data we obtained is shown in Fig. 7b.

Figure 8 shows some results using the ultrafast T-jump, with the monolayer on an Au surface.<sup>11</sup> In related work, we have developed an optical thermometer for the Au layer based on femtosecond white-light reflectivity so we know the Au surface temperature with good accuracy. Figure 8a and 8b show the schematic for these experiments. Figure 8c shows some data where the nitro stretch is monitored by SFG after T-jump. During the first 10 ps there are some nonequilibrium effects but then after that time, the system settles down into a state of thermal equilibrium. We can routinely heat the Au surface and the adsorbed monolayers by 250K. Besides the interest in understanding nanoscale thermal conduction for molecular electronics and molecular machinery, we can use this technique to study shock initiation of energetic materials. We plan to preheat the EM before the shock arrives, in order to speed up the chemical reactivity as observed when EM hot spots are created, and to study off-Hugoniot states where the temperature is greater than what is achieved behind a shock front is a homogeneous medium.



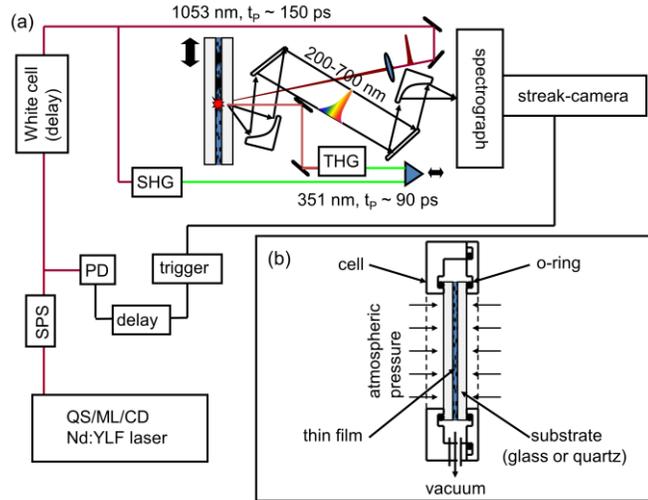
**Fig. 7.** Peak blueshift of the nitro stretch of a nitrobenzoic acid monolayer during a shock was  $3 \text{ cm}^{-1}$ . We compared the shock blueshift to shifts seen in a diamond-anvil cell. A photonic chip in the cell was used to amplify the monolayer Raman spectrum by  $10^6$ . Based on the static pressure blueshift, the pressure of the ultrafast shock compression process was 1.5 GPa.



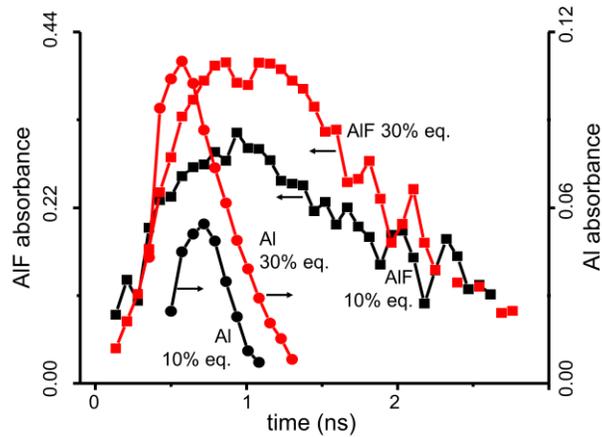
**Fig. 8.** Ultrafast flash-heating of nitrobenzenethiol monolayer probed by nonlinear coherent spectroscopy of the nitro group. A femtosecond white light pulse is used to monitor the temperature of the gold substrate. After  $\sim 10 \text{ ps}$ , the gold and the monolayer are in equilibrium and the T-jump can be as large as 250K.

### C. Flash-heating of nanoenergetic materials.

In this subproject, a picosecond laser was used to flash heat the metallic fuel components of a RM and the subsequent ignition process was studied with time-resolved emission spectroscopy.<sup>12</sup> We studied nanoparticles of Al and B in Teflon oxidizer and in some inert matrices.<sup>13</sup> The reaction starts when the fuel particles are depassivated. The fuel particles are protected by a refractory native oxide layer. In flash-heating, depassivation occurs when the laser heats the metallic interiors of the nanoparticles, which vaporize and blow open the oxide layer. The focus was on the very fast chemistry that occurs in the condensed phases, as opposed to slower processes that happen in the expanding gas clouds, which can be studied by conventional nanosecond laser techniques. The laser apparatus used for these studies is diagrammed in Fig. 9. An interesting result is shown in Fig. 10, where we show the absorption spectra of Al and AIF after flash heating. At the times studied here,  $< 2$  ns, the exploding RM has little time to expand, so chemical processes can occur only in a core region that has nearly condensed phase density. This core is very hot and it emits 30,000K blackbody radiation. Atomic and molecular species in the cooler region immediately outside this core can be observed via their absorption bands, seen as intensity dips in the core emission spectrum. As seen in Fig. 10, the AIF absorption, which is the initial molecular product in the combustion of Al with Teflon (Teflon =  $(-CF_2)_n$ ), has a two-part rise with the faster part from AIF



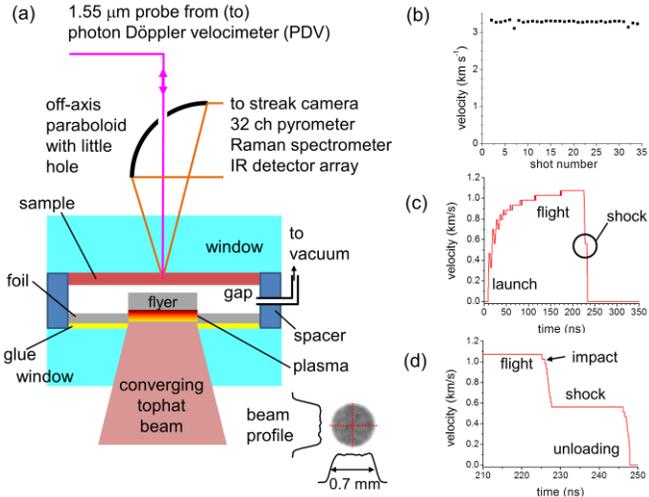
**Fig. 9.** Schematic of picosecond laser apparatus to study the time-resolved optical emission and absorption from Al/Teflon reactive materials.



**Fig. 10.** Time resolved absorption intensities for Al and AIF in flash-heated Al/Teflon. The AIF absorption has a two-part rise with the faster part from AIF created in the condensed phase and the slower part from AIF created in an expanding gas cloud.

created in the condensed phase core and the slower part from AIF created in an expanding gas cloud.<sup>14</sup>

When we compared B/Teflon to Al/Teflon,<sup>13</sup> we found that depassivation of the boron particles occurred when the oxide shell boiled off and the metal core was melted. Depassivation of aluminum occurred when the oxide shell melts and the metal core was almost vaporized. The lifetimes for exothermic chemistries in the RM, which corresponds to the time constant for energy-releasing processes, could be determined from their effects on the plasma lifetime. The rate of energy release from vapor Al + Teflon reactions has a  $\sim 100$  ps lifetime, while energy release from liquid B + Teflon was observed to occur with a  $\sim 200$  ps lifetime.



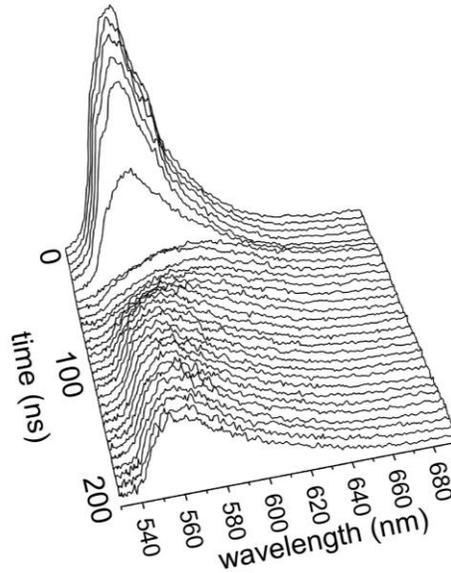
**Fig. 11.** Schematic of laser apparatus for spectroscopy of materials shocked by a laser-launched Al flyer. Notice uniform 0.7 mm laser beam profile generated by a diffractive optic. (a) Sample and light collection. (b) Speeds of 33 flyer launches were remarkably reproducible. (c) Doppler velocimeter history of a flyer launched at 1 km/s. (d) Time-expanded velocity history showing 15 ns duration constant shock in a glass target.

**D. Laser flyer plates and impact initiation of energetic materials.** We have developed a very convenient tabletop source for nanosecond shock compression spectroscopy.<sup>15</sup> In this system, a high-energy Nd:YAG laser (2.5 J in 10 ns) is used to launch a metal foil 700  $\mu\text{m}$  in diameter at a selected target, which can then be studied by spectroscopy instrumentation on the same tabletop. Although these laser-launched flyer plates have been used for several decades now, our instrumentation takes advantage of several recent advances in optics, especially newly-developed diffractive optics that produce laser beams with a homogeneous spatial profile. Figure 11 is a schematic of the apparatus for shock spectroscopy. Note the uniform beam profile. A recently-developed high-speed fiberoptic photonic Doppler velocimetry (PDV) system is used to measure the flyer plate velocity histories.<sup>15,16</sup> This shock system fills an important need compared to large facilities with gas guns or huge multistage lasers found at national labs. It makes well-characterized planar shocks, but the shock duration is much shorter than at a national facility,  $10^3$ 's of nanoseconds compared to microseconds. Such a system is very useful for high-speed measurements. The other important feature is that students can fire 100 or more shocks every day, which allows us accumulate a lot of data. Figure 11b shows the results of an experiment where we launched 33 flyers over the span of an hour, and measured the velocities with PDV. The velocities were reproducible to within 0.6%, and the average velocity in this measurement was  $3.29 \pm 0.02 \text{ km s}^{-1}$ . An important parameter for spectroscopy is the reproducibility of the time of arrival of the flyer at the

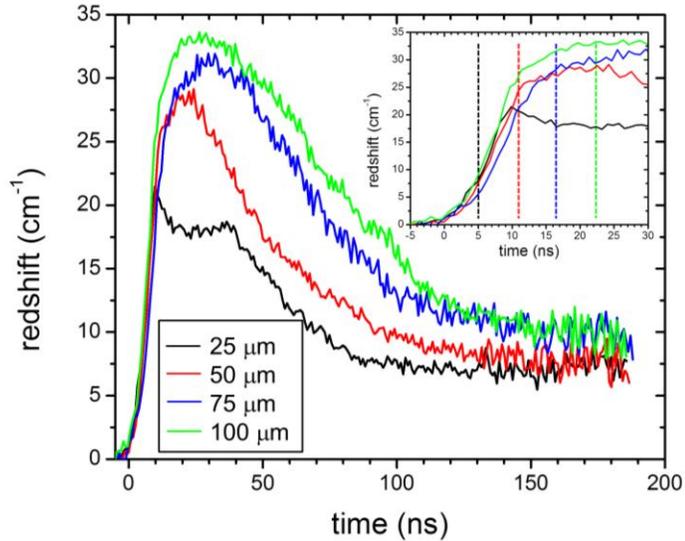
target. Here this flight time was  $168 \pm 1.0$  ns, where the error bounds were one standard deviation. Figures 11c and 11d show some typical flyer PDV velocity histories.<sup>15</sup>

Currently we are using this apparatus for a number of projects. The two most germane involve the development of spectroscopic probes that can determine the local pressure, temperature and composition inside a target material that is subjected to a well-characterized shock, and studies of the shock initiation of reactive materials via time-resolved optical emission. In the next phase of this project we will develop the capability to measure the vibrational spectra of shocked materials using infrared absorption.

Figure 12 show some data where PMMA polymer was doped with an optical emission probe consisting of R6G dye.<sup>17</sup> The dye emission spectrum is normally peaked at 560 nm. As shown in the figure, when a 1 km/s flyer arrives, the dye emission spectrum loses intensity and redshifts. We have determined that the emission loss is due to enhanced intersystem crossing that converts the emissive singlets to darker triplets. The redshift is a measurement of the density in the vicinity of the dye emitter. We have developed computer codes that can take streams of spectra such as these and extract the spectral redshift using the



**Fig. 12.** Time-resolved emission from R6G dye in PMMA polymer during a 1 km/s impact. When the shock front arrives, the dye emission loses intensity and redshifts. A computer extracts the time-dependent redshift.



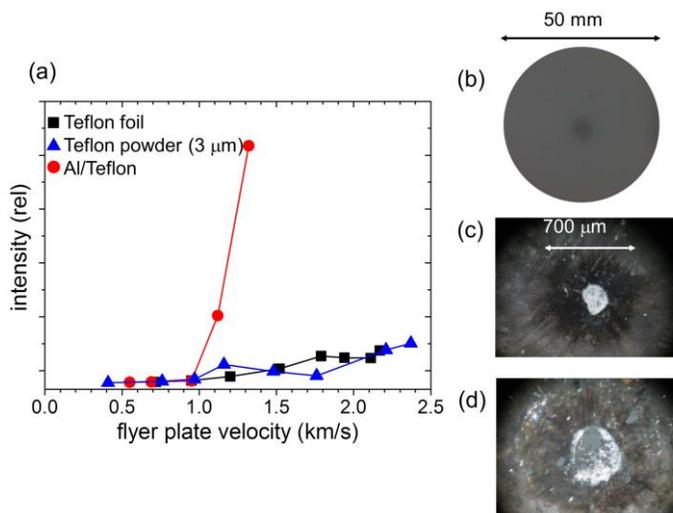
**Fig. 13.** Time-resolved emission redshift from R6G dye in PMMA during 1 km/s shocks from different thickness flyer plates. The mechanical response of the PMMA is highly dependent on the shock duration.

method of moments.<sup>17</sup> Figure 13 shows time-resolved dye emission from PMMA when the PMMA was impacted by flyers traveling at 1 km/s. We varied the thickness of the flyers from 25  $\mu\text{m}$  to 100  $\mu\text{m}$ . This varies the duration of the shock from 5-25 ns. Figure 13 shows the characteristic mechanical response of the polymer is highly dependent on shock duration.

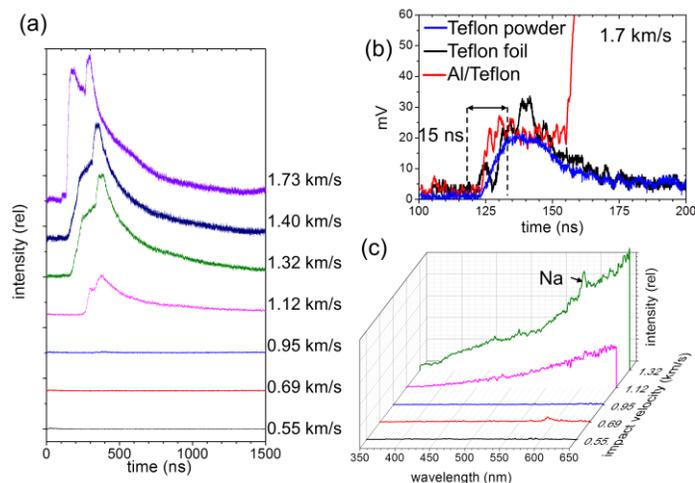
Figure 14 shows data on Al/Teflon shock initiation.<sup>18</sup> The samples consisted of 50 nm Al and 3  $\mu\text{m}$  Teflon plus a small amount of binder (see Figs. 14b-d). As shown in fig. 14a, when Teflon itself was shocked, only a small amount of triboluminescent emission was observed. The same intensity emission was observed from Al/Teflon until the flyer speed was 1 km/s whereupon the Al/Teflon emission increased dramatically, indicating the RM was shock-initiated. Some properties of this shock-induced ignition emission are described in Fig. 15.

### E. Spectroelectrochemistry of fuel cells, batteries and synfuel synthesis.

This subproject arose as a result of our development of advanced SFG laser spectroscopy methods. In usual electrochemistry experiments, elements of the chemistries are deduced by monitoring current-voltage relations via cyclic voltammetry (CV). Understanding the fundamental mechanisms is greatly assisted if vibrational spectroscopy can be used to determine the identities of molecules at the electrode surface. However this is a great challenge because molecules on electrode surfaces are overwhelmingly outnumbered by molecules in the electrolyte above the electrode. But



**Fig. 14.** (a) Emission intensity from Al (50 nm)/Teflon (3  $\mu\text{m}$ ) RM impacted at different velocities. There is an initiation threshold at about 1 km/s. (b) Photo of Al/Teflon uniform film on optical window. (c) Photo after impact by 700  $\mu\text{m}$  Al flyer, of Teflon only. (d) Photo after impact of reactive Al/Teflon showing vaporized region.

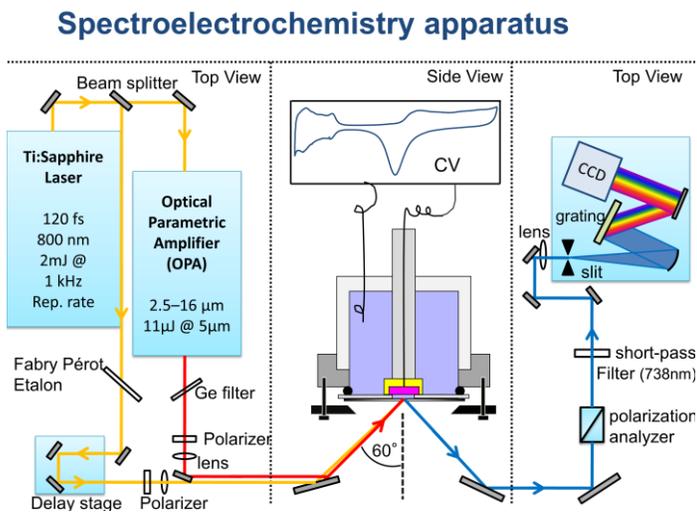


**Fig. 15.** (a) Emission intensity transients from Al/Teflon impacted by Al flyer plates at different speeds. (b) Al/Teflon emission with 1.7 km/s impact looks like Teflon alone until after the shock unloads, when it increases dramatically, indicating initiation. (c) Emission spectra near impact velocity threshold.

the electrolyte is a centrosymmetric environment, so molecules in the electrolyte are invisible to SFG. SFG selectively probes molecules on the electrode surface. In addition, due to the nonlinear coherent nature of SFG, even though the absolute number of molecules on electrodes is small, strong signals can be produced. We have developed a versatile and compact system for SFG electrochemistry that is diagrammed in Fig. 16.<sup>19</sup>

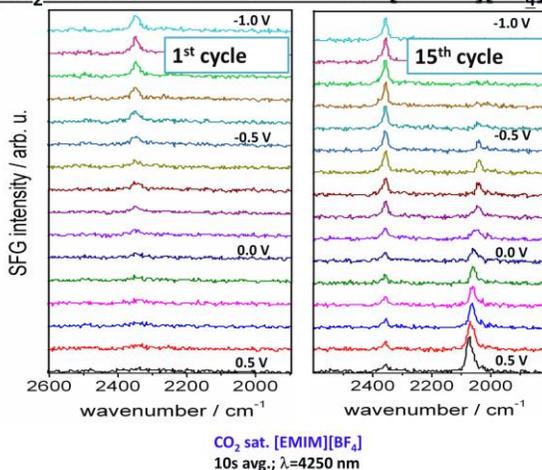
We designed an electrochemical cell with optical access. As CV measurements are made in the usual way, pulses from this laser obtain vibrational spectra at different values of the potential. We have partnered with a number of collaborators who have electrochemical expertise and we have published a number of nice papers in areas highly relevant to the AFOSR mission.

In collaboration with Prof. Richard Masel, formerly of the University of Illinois Department of Chemical Engineering, and now CEO of Dioxide Solutions, Inc., we are studying the fundamental mechanisms of electrochemical reduction of CO<sub>2</sub> to CO. The practical goal of such research is to develop an efficient system that would produce syngas (CO + H<sub>2</sub>) using air and water, powered by wind or solar cells, that would then be able to produce jet fuel. The idealization of this concept would be a portable station that would make enough jet fuel for a squadron using air, water and



**Fig. 16.** Block diagram of laser apparatus for spectroelectrochemistry. The nonlinear coherent vibrational spectroscopy method termed “vibrational sum-frequency generation” (SFG) selectively detects molecules at the electrode-electrolyte interface, ignoring species in the bulk electrolyte.

### CO<sub>2</sub> Electro-Reduction on Pt in [EMIM][BF<sub>4</sub>]



**Fig. 17.** CO<sub>2</sub> reduction to CO with low overpotential is a critical step in economic production of syngas CO + H<sub>2</sub>. An ionic liquid electrolyte EMIM-BF<sub>4</sub> substantially lowers the barrier to CO<sub>2</sub> reduction by stabilizing the intermediate CO<sub>2</sub><sup>-</sup>. These SFG spectra show CO<sub>2</sub> adsorbed on a Pt electrode disappear while CO builds up, in a spectroelectrochemical cell.

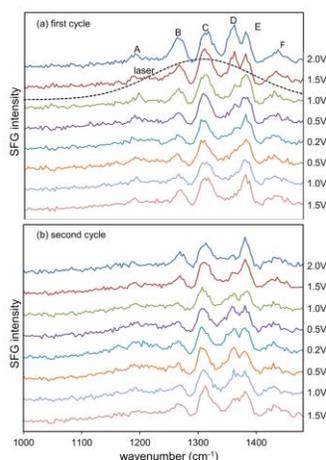
sunlight. Although this might seem fanciful, the actual realization, as a result of Masel's work, seems likely in the next few years. We should mention that reducing water to H<sub>2</sub> and producing jet fuel from syngas are already well-developed technologies. It's reducing the CO<sub>2</sub> that is the critical step. Masel has obtained a Phase II SBIR grant from AFOSR to develop this concept, and part of the effort involves work at UIUC on laser spectroscopy.

The basic concept is to reduce the overpotential for CO<sub>2</sub> reduction using co-catalysts, consisting of a metal electrode and a molecule in the electrolyte that forms a catalytic complex with CO<sub>2</sub> adsorbed on the metal surface. Masel has found that various imidazoliums such as the ionic liquid EMIM-BF<sub>4</sub> have this property.<sup>20</sup> They stabilize the reaction intermediate CO<sub>2</sub><sup>-</sup> on metallic surfaces and greatly lower the barrier to reduction. In our study, we used SFG to observe CO<sub>2</sub> disappearing and CO forming on a metal surface in real time, and in addition we identified a complex formed between CO<sub>2</sub> and ionic liquid, as shown in Fig. 17.<sup>21</sup>

As a final project, we were asked by workers at Argonne Lab to study the mechanisms of surface chemistry in lithium-ion batteries. We studied processes occurring on the anode, where solid-electrolyte interphases (SEI) are formed.<sup>22</sup> These SEI layers are critical to the function of lithium-ion batteries, but their formation *in situ* has never been studied with the power of vibrational spectroscopy. Although it is possible to crack open a battery and study SEI *ex situ*, such studies leave unanswered many crucial questions. Some representative results are shown in Fig. 18.

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**Fig. 18.** SFG studies of the formation of a solid-electrolyte interphase (SEI) layer on an anode during lithium-ion battery chemistry during two successive cycles of charging and discharging.

First two  
charge/discharge cycles  
Electrode SEI interface

Not reversible

Peaks A and D are THF  
Peaks C, E and F are  
lithium ethylene  
dicarbonyl  
Peak B is ? Possibly  
ethylene

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