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Dana D. Dlott

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University of Illinois - Urbana
1901 S. First Street, Suite A
Champaign, IL 61820 -7406

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14. ABSTRACT
Instrumentation was acquired that allowed for acquisition of emission spectra with high time and wavelength resolution. The acquired instruments were fabricated into a time-resolved spectroscopy system. This system will be used to study the emission from small particles of reactive nanomaterials that are initiated by impact with a flyer plate. The emission spectra so obtained will be used to develop a fundamental understanding of how these materials are initiated by shock waves.

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Report Title

Final Report: Instrumentation for spectroscopy of impact initiation of reactive materials

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TOTAL:

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Patents Submitted

Patents Awarded

Awards

Dana Dlott ACS Physical Chemistry Division Award in Experimental Physical Chemistry, 2013
Dana Dlott Lippincott Award in Vibrational Spectroscopy from the Optical Society of America, 2015
James Christensen National Defense Science and Engineering Graduate (NDSEG) Fellowship, 2014

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
William Shaw	0.00	
William Bassett	0.00	
James Christensen	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Weilong Liu	0.00
Jue Wang	0.00
FTE Equivalent:	**0.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Dana D Dlott	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Gino Gianetti	0.00	Physics
FTE Equivalent:	**0.00**	
Total Number:	**1**	

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Inventions (DD882)

Scientific Progress

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Technology Transfer

none

1. Foreword

Reactive nanomaterials,[1-5] for example nanothermites,[6-10] are emerging types of energetic materials that are of great interest to the Army, in part due to their high energy content, often 2-3 times TNT, and their potential for multifunctionality.[4] They can be incorporated into conventional explosives to add more punch at controllable rates, and they can serve as structural elements in weapons systems. This project is focused on understanding the fundamental mechanisms of shock initiation of reactive nanomaterials. There have been extensive prior mechanistic investigations of how reactive nanomaterials are initiated by gradual heating, but mechanisms of shock initiation must be entirely different, and have not been studied at any significant level of detail.

A few examples of reactive nanomaterials are

$2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$[11]

$Al + 3Ni \rightarrow Ni_3Al$[5,12-16]

and $Al + Teflon \rightarrow AlF_3 + C$.[17-25]

The shock reaction mechanisms are quite different from what is seen in ordinary energetic materials chemistry. For instance in the first reaction, the mechanism has to involve the migration of O-atoms among and within adjacent metal and ceramic nanoparticles.

Here is an important practical application associated with our experiments. It is envisioned to use reactive nanomaterials to replace inert metal bomb casings. When the bomb explodes, the casing will fragment into small high-speed particles. When the particles impact a target, they produce an energetic secondary explosion on target. This impact process looks like a short-duration shock passing through the fragment. Our experiments do an excellent job of mimicking this scenario.

Our approach to understanding these shock mechanisms is to perform experiments where laser-launched flyer plates impact reactive nanomaterial samples at km/s velocities, while the emission burst resulting from initiation is collected and analyzed. These emissions are studied as a function of material composition and material structure. For example, to understand how O-atoms migrate across interfaces and into nanoparticles, we use vacuum-deposited multilayer composites where the number of interfaces can be controlled. A sample consisting of one 100 nm layer of Al and one 100 nm layer of CuO (one interface) can be compared to a sample of two sets of alternating 50 nm layers of Al and CuO (three interfaces).

We are expert in fabricating Al/Teflon composites,[25] and we have partnered with three other groups to obtain well-characterized samples of other materials: The Edward Dreizin group at New Jersey Institute of Technology (NJIT) has provided the Al/CuO_2 nanothermites.[26] The Jon-Paul Maria group at North Carolina State University has provided the multilayer samples. The Michael Zachariah group at the University of Maryland has provided composites with nanothermites uniformly dispersed within reactive polymers.

Our unique laser-launched flyer facility[27,28] allows us to conduct 100 shock experiments in a single day. We have characterized and essentially perfected this apparatus, which uses a high-speed photon Doppler velocimeter (PDV)[27,29] to measure the impact dynamics and a microscope objective to collect the sample emission, as diagrammed in Fig. 1. The flyer plates are thin, 25-100 μm thick, so they produce shock durations in the range of 8-30 ns.[27]

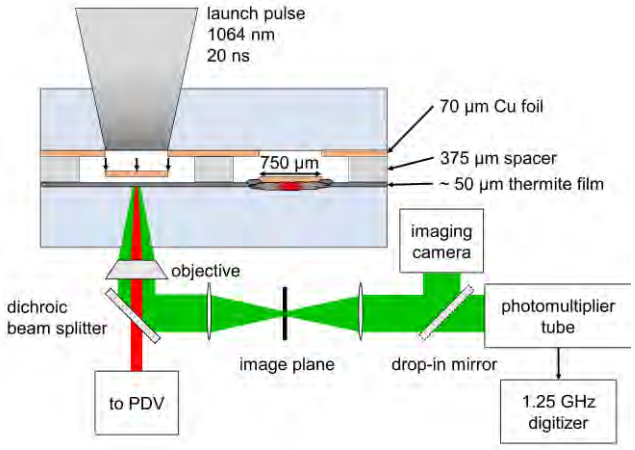

Fig. 1. *Schematic of apparatus to study emission from shocked reactive nanomaterials. PDV is a high-speed optical interferometer that measures the velocity history of the flyer plate. The secondary image in the image plane can be masked with a variable aperture to eliminate parasitic emission sources other than the sample. The imaging camera is used for alignment.*

One of the problems associated with detection of the emission from shocked reactive nanomaterials is the vast range of time scales. The shock lasts nanoseconds. The ensuing reactions include processes occurring during the shock (nanoseconds), post shock (microseconds and even milliseconds) and possibly after burn of the reaction products with the ambient atmosphere (milliseconds to seconds). Thus it would be useful to be able to acquire emission data every nanosecond for seconds. That is billions of points per shot. In addition we wish to spectrally resolve the emission in the range where glass is transparent and PMT photocathodes have reasonably good quantum efficiencies, 360-870 nm, which means we need many channels of billions of points. The emission is expected to involve combinations of triboluminescence, chemiluminescence, blackbody emission and line spectra from gas-phase products such as AlO. Thus we need spectroscopic resolution and high sensitivity. To solve this problem, we used DURIP funds to create a unique instrument consisting of a high-throughput prism spectrograph, a 1 x 32 fiberoptic array to transmit light to the detectors, 32 high-speed (<1 ns) photomultipliers (PMT) and 32 digitizers that could acquire streams of infinite record length at 1.5 GHz.

2. Equipment items acquired

The original proposal budget called for a PMT that had 32 individual anodes, a 32-channel GHz digitizer, and an upgrade to the diffractive optic to smooth the laser beam that launches the flyer plates. After we tested the PMT (Hamamatsu H7260-20), we found it did not work for us. It was supposed to deliver 32 individual channels with low cross-talk, 1 ns time resolution, and high output current pulses. We found that it could do only two out of three of these things. If we tried to pull out fast, high current pulses, the cross-talk was enormous. The manufacturer's tests only looked at cross-talk with small, slow signals, where cross-talk was small. The manufacturer's high-current fast-pulse measurements were always made on a single channel. So the manufacturer's tests did not reveal this fundamental problem. We decided to instead use 32 individual fast PMT modules from Hamamatsu. The delays associated with the PMT characterization and subsequent delivery of new PMTs necessitated a no-cost extension to

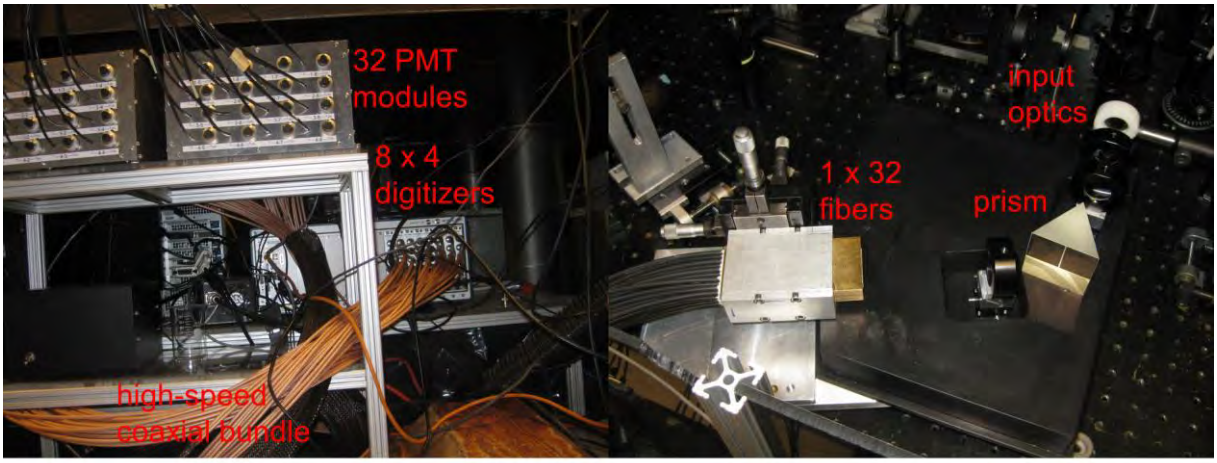

Fig. 2. *Photos of the new instrument, consisting of a prism optical spectrograph, a 1 x 32 fiberoptic array, a chassis containing 32 photomultiplier (PMT) modules with individual gain trim controls, a bundle of high-bandwidth coaxial cables and 32 channels of 1.5 GHz digitizers.*

the DURIP grant. We have confidence in the individual PMT from Hamamatsu because we have used it extensively and it works great. It delivers high-quality fast large-current pulses with 0.6 ns time resolution. Using 32 separate ones will solve the cross-talk problem. Unfortunately these 32 PMTs blew the budget, since they cost $25K whereas the individual 32 channel PMT was only $6K. After talking to program officer Dr. Ralph Anthenien, we rebudgeted for the digitizer and 32 PMTs, and we did not buy the diffractive optic upgrade.

The equipment we purchased consisted of:

1. Digitizer consisting of National Instruments PXIE controller and chassis, and 8x four-channel 1.5 GHz digitizers, model PXIE 5162. The digitizers were not quite what was in the original budget (model PXI 5154). We bought a newer models with more features at a similar cost, that was introduced after the proposal was submitted.

2. PMT modules consisting of 32x Hamamatsu H19720-20 units

3. Fibertech Optica custom 1 x 32 fiberoptic array used to transmit light from the spectrograph to the 32 PMT modules.

We have recently completed the assembly of this instrument and have begun preliminary testing. We had to fabricate the prism spectrograph and a chassis for the 32 PMT modules with 32 independent gain controls, and integrate the other equipment. Photos of the instrument are shown in Fig. 2. The prism spectrograph provides much higher throughput than a conventional grating spectrograph, but the dispersion and spot size varies considerably at the exit plane when the wavelength spans the 360-870 nm range. To partially compensate for this, we designed a 1 x 32 fiberoptic array for the exit plane where the fibers had different sizes, that was custom-built for us. In the red where the spot sizes were bigger and the resolution was worse, the fibers were bigger. The 32 fibers each go to one of the PMT modules in the chassis. The PMT output is sent through 32 high-bandwidth coaxial cables to the digitizer module. Software we wrote takes the data and bins it into log(time) as explained below.

At the present time we are finishing the software and working on calibration. Each PMT channel will have a different gain and spectral sensitivity. Using a calibrated blackbody source, we will determine these parameters, trim the gain controls, and incorporate the calibration information into our computer codes.

3. Preliminary results

We have a nice preliminary result shown in Fig. 3. This result was obtained using a 70 μm thick Cu flyer at 1.05 km/s impacting an Al + CuO_2 nanothermite particle about 60 μm in diameter, held in a vacuum chamber. We used a Cu flyer because Cu is one of the products of the reaction so the Cu flyer could not participate as a reactant. The measurement uses only a single channel PMT, so the signals represent integration over a wide wavelength band spanning the visible spectrum. It is an important problem how to visualize and interpret data records such as these. In this specific case, the data record consists of a point every 1 ns over a 1 ms period (1 million points). If we simply plotted the points on a linear time axis we would not be able to see the faster processes occurring during the first 20 ns (the first 20 of the 1 million points), and the later processes, where the emission intensity has dwindled, would be very noisy. The solution is to use a compressed log(time) plot. In this type of plot, we divide the time axis into decades (i.e. the 1 ns decade, the 10 ns decade, the 10 μs decade, etc.). We then bin and average the data points to create the same number (ten) of points per decade. In this way the points in the later decades where the overall signal has dwindled, are averaged to a greater degree. For example, in the 1 ns decade, each of the ten displayed points is one acquired data point, but in the 10 μs decade, each of the ten points would be the linear average of 10,000 acquired data points.

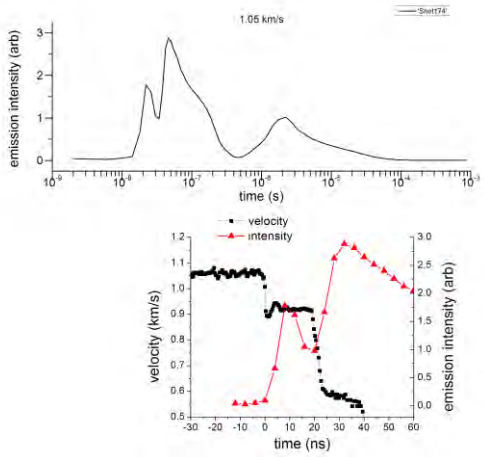

Fig. 3. *Preliminary data using only a single PMT module that detects the wavelength-integrated emission from an Al/CuO nanothermite impacted at 1.09 km/s. Plotting the emission transient versus log(time) (top) shows there were three distinct emission bursts, indicating a 10 ns process, a 100 ns process and a 5 μs process. (bottom) An expanded time plot of the flyer velocity history shows the flyer impacts at t = 0, when its velocity suddenly drops from 1.05 km/s to 0.93 km/s. The shock lasts 16 ns. The coincidence between velocity and emission intensity shows the first emission burst occurs only during the shock..*

The emission transient data is shown in Fig. 3. Not shown are the results of control experiments where the sample was removed so the flyer impacted only a glass window. The emission in that case was far weaker than when thermite was present. There are three distinct emission bursts, denoting three distinct processes, one occurring in the 10 ns decade, one in the 100 ns decade, and one in the 5 μs region. The latter has significantly more integrated intensity than the former two. Also in Fig. 3, we compare the flyer plate velocity profile to the emission intensity at shorter times. At time designated $t = 0$, the flyer plate suddenly slows from 1.05 km/s to 0.93 km/s, as it collides with the nanothermite. At this instant, the emission starts. The

timing of the first burst coincides precisely with the shock caused by flyer impact. Based on this result, our preliminary interpretation of the data assign the first process to triboluminescence, possible due to reactions at interfaces between adjacent nanoparticles, the second process to solid-state chemistries involving O-atom diffusion in the solid, and the third process to gas-phase reactions. In future experiments, we will also flood the reaction chamber with O_2 so we can examine the longest-time reactions in the gas phase with ambient oxygen.

We hope very soon to acquire similar data sets with 32 channels of spectral resolution. The result will be a surface in wavelength-time-intensity space which will show how the spectra vary over vast ranges of time. We believe each individual process will have a distinct spectral signature that we can identify and interpret. Some of these features are likely to represent graybody spectra which will allow us to determine reaction temperatures.

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