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**Development of Ultrafast Indirect Flash Heating Methods
for RDX**

**by Nhan C. Dang, Jennifer L. Gottfried, Stephanie M. Piraino, and
Frank C. De Lucia, Jr.**

ARL-MR-862

February 2014

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Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) February 2014		2. REPORT TYPE Final		3. DATES COVERED (From - To) October 2012–September 2013	
4. TITLE AND SUBTITLE Development of Ultrafast Indirect Flash Heating Methods for RDX			5a. CONTRACT NUMBER W911NF-12-2-0019		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Nhan C. Dang, Jennifer L. Gottfried, Stephanie M. Piraino, and Frank C. De Lucia, Jr.			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-WML-B Aberdeen Proving Ground, MD 21005-5069			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-MR-862		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Ultrafast laser techniques enable the observation of material response and dynamic processes with picosecond time resolution during the initial events occurring in explosive initiation. In this memorandum report, we present our progress in the development of experimental methods for measuring the ultrafast thermal behavior of microscale energetic materials, including cyclotrimethylene trinitramine (RDX), under an indirect femtosecond flash heating laser pulse. The femtosecond laser-generated indirect flash heating was combined with imaging analysis of preheated and postheated RDX crystals to compare the sensitivities of RDX crystals with different morphologies, sizes, and shapes to an ultrafast temperature jump. Additionally, ultrafast transient absorption and vibrational coherent anti-Stokes Raman spectroscopy were demonstrated to offer the potential to measure even more details of the molecular thermal response to flash heating in real time. Experimental data from monitoring the responses of RDX and phenylacetylene behind an ultrafast shock front were used to demonstrate the capability of the spectroscopic methods.					
15. SUBJECT TERMS RDX, ultrafast spectroscopy, flash heating, CARS, transient absorption					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON Nhan C. Dang
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-278-6141

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1. Introduction

The mission of the Multiscale Response of Energetic Materials program is to establish the capability to predict how explosives will react in any given scenario. Prediction of explosive initiation requires a framework that includes mechanisms for mechanical and thermal energy to couple into molecular bonds, which are the initial events and determining steps toward explosive detonation. However, on the molecular level, very little is known about the dynamic response of these materials. How does energy from an impact couple into molecules? What is the temperature that drives the reactions? What is the chain of chemical reactions induced? How fast do they occur? To answer these questions, observation of dynamic flow of mechanical and thermal energy coupling into molecular bonds on its characteristic time and length scales is required. Results gained from these experiments will provide data to validate and verify computational models for energetic materials.

Explosive initiation occurs on picoseconds (ps) to nanosecond timescales. The temperature of importance is that which occurs preceding and during the chemistry it drives. Since electronic excitations can be observed on femtosecond timescales and vibrational excitations can be observed on hundreds of femtosecond to picosecond timescales, ultrafast (femtosecond) single-shot spectroscopies of explosives under laser-driven shock or heat loading are the ideal experimental tools that offer the ability to observe these processes. Few experiments sensitive to these time and length scales have been developed to achieve these goals (*I-11*).

Here we present our fiscal year 2013 (FY13) progress toward the development of experimental methods for measuring the ultrafast thermal behavior of microscale energetic materials, including cyclotrimethylene trinitramine (RDX), under an indirect femtosecond flash heating laser pulse. Two approaches to characterizing the femtosecond flash heating RDX have been employed: (1) imaging analysis of preheating and postheating RDX crystals and (2) ultrafast spectroscopic methods coupled with a flash heating event. For the first approach, the ultimate goal was to compare the sensitivities of RDX crystals with different morphologies, sizes, and shapes to temperature jump in ps timescale. Also, as a result of this study, we learned how to prepare a sample through which the dynamic flow of thermal energy couples effectively. The second approach will allow us to directly monitor the real-time material response under the influence of thermal energy in a picosecond timescale.

2. Experimental Method

2.1 Samples

Military grade, class 1 (<850 μm) RDX crystal was obtained from colleagues at the U.S. Army Research Laboratory (ARL). To prepare samples, a gold (Au) layer (approximately 50 nm thick) was first deposited onto a 0.5-in-diameter glass substrate using a sputter-coating technique. RDX crystals were then deposited onto the surface of the Au. To ensure the RDX crystals bind properly with, and spread out evenly on, the Au surface, methods such as drop-casting thin film, using a mineral oil thin film interface, and partially dissolving samples directly on the Au surface were investigated. The drop-casted thin film sample was prepared by dropping an RDX in acetonitrile solution (1.0 mg/ml) on the Au surface. The sample was then allowed to dry in open air at room temperature. To prepare a sample using mineral oil thin film interface, an RDX powder was sprinkled on a preapplied thin film of mineral oil on the gold surface. Excess oil was removed by placing a piece of Kimwipes* paper directly in contact with the excess oil around the sample. Loose RDX particles were gently blown away using compressed air. To prepare a sample using the partial dissolution method, a thin layer of a RDX powder was first deposited on the Au surface and then acetonitrile solvent was dropped directly on the RDX layer. The sample was allowed to dry quickly in open air at room temperature; as before, loose RDX particles were gently blown away using compressed air.

2.2 Methods

The lasers used for experiments discussed in this report include a regenerative Ti:sapphire amplifier (Coherent Hydra-25) seeded by a femtosecond-pulsed oscillator (Coherent Vitesse, 800 nm, 100 fs). An Nd:YLF pump laser (Coherent Evolution-15) amplified the output energy of the femtosecond laser to 900 μJ , and an Nd:YAG pump laser (Continuum Powerlite Precision II 8000) further amplified the femtosecond pulse energy up to approximately 20 mJ.

2.2.1 Optical Microscopy

An Olympus MX50 reflected-light optical microscope was used to image the RDX samples before and after flash heating. The objectives used ranged 5X–100X. Pictures were taken with the attached SPOT Insight 12 MP camera (Diagnostic Instruments Inc., Sterling Heights, MI).

The scheme for indirect flash heating of RDX crystals with a femtosecond laser pulse is shown in figure 1. In this scheme, a laser beam of 900 μJ from a 100-fs laser pulse (1-kHz repetition rate) focused through a 125-mm lens was directed onto the glass side of the prepared Au layer. Upon contact, the laser pulse will generate heat on the first surface of the Au layer. The heat then travels through the Au layer and transfers onto the samples. To prevent ablation of the Au layer

* Kimwipes is a registered trademark of Kimberly-Clark, 351 Phelps Dr., Irving TX, 75038.

or the formation of a laser-induced plasma on the Au surface, the laser energy density was attenuated by adjusting the laser beam size (or adjusting the distance between the sample and the lens) so that the maximum laser energy density resulted in no visible damage on the Au surface. Through trial and error, we determined that the optimal laser beam diameter (at 900 μJ) was approximately 2 mm. After flash heating, the images of heated samples were obtained using an optical microscope. Material responses are monitored using optical imaging, transient absorption, or coherent anti-Stokes Raman spectroscopy (CARS) methods. In contrast to the scanning electron microscope images obtained in FY12 (12), where the beam interaction with the RDX particles could adversely affect the morphology of the particles, preheating and postheating images could be obtained with the optical microscope. In addition, a washer was used to mask most of the glass slide and confine the Au layer (and prepared RDX sample) to a small region that was easier to locate during the image analysis.

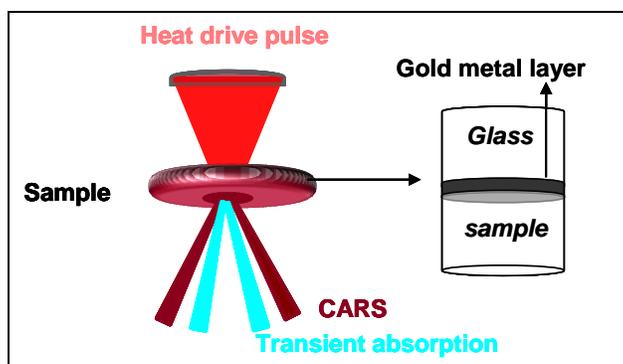


Figure 1. Schematic diagram for flash heating experiment.

2.2.2 Ultrafast Spectroscopic Methods

We have set up two ultrafast spectroscopic methods, ultrafast white light transient absorption and CARS, to carry out the approach (2). The white light transient absorption experimental setup, summarized in figure 2, consists of a regeneratively amplified Ti:sapphire laser used to produce a 1- or 10-Hz train of 1-mJ pulses centered at 800 nm with a full width at half maximum (FWHM) of 450 cm^{-1} and a pulse width of 100 fs. An 80:20 beam splitter splits the amplifier output into two beams. The 80% beam is directed onto the back side of the sample through a 125-mm focal lens to produce the heat pump. A small portion of the 20% beam is focused onto a 2-mm CaF_2 or sapphire plate using a 150-mm-focal-length lens to generate a white light continuum. The energy of the input 800-nm laser beam was attenuated just high enough to give nonlinear interactions within the plate. The continuum is then recollimated with an off-axis paraboloid. The beam is further spatially filtered by an iris to obtain the most stable and intense spectrum with a beam size of approximately 0.5 cm in diameter. The continuum is then split into absorption probe and reference beams by a 50:50 beam splitter. The pump and probe beams are spatially and temporally overlapped and focused on the sample. The reflected probe and

reference pulses of 0.5-cm diameter are focused with a lens on the 100- μm slit of an imaging spectrometer (locally built). An electronically gated charge-coupled device detector records the probe and reference intensities simultaneously on each. During the measurements, the probe intensity spectrum was normalized with respect to the reference for the same laser pulse to account for any fluctuations and the errors due to the wavelength-dependent sensitivity of the detection system and wavelength dependence of the spectral density of the probe spectrum.

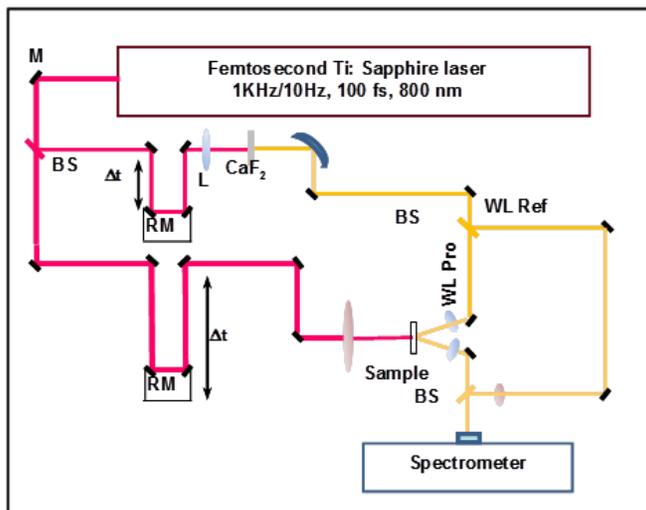


Figure 2. Schematic diagram of the white light transient absorption experiment. Key: M = mirror, BS = beam splitter, L = lens, RM = time delay translational stage, and WL = white light continuum.

The configuration of the CARS experiment is similar to the setup for white light transient absorption shown in figure 2, except that the white light transient absorption probe is replaced with the CARS probe. The CARS probe requires three pulses, as shown in figure 3. The spectrally narrow pump and probe pulses are formed by passing 100-fs pulses through two narrow band filters (Omega optical, 800-nm center, 2-nm FWHM) to achieve 31-cm^{-1} spectral resolution. A beam splitter separates this light into pump and probe pulses. The Stokes (“fs”) pulse is generated by focusing 30 μJ of 800-nm, 100-fs light into a 4-mm-thick CaF_2 plate with a 6-in-focal-length lens and collimating with a 2-in-focal-length lens. The Stokes pulse then traverses an 800-nm-long pass filter to remove the residual pump pulse and short wavelengths that would overlap the CARS. All three pulses are aligned parallel in three corners of a box with 15-mm sides before focusing onto the sample with a 125-mm-focal-length lens. The CARS is collected with a 6-in-focal-length lens, and the signal is spatially isolated with a 3-mm iris. The principle behind the three-pulse CARS setup is that the pulse width determines the spectral resolution, but also determines the delay required between the first two pulses and the probe. This delay removes the electronic contribution to the CARS signal, the nonresonant background, by ensuring that all three pulses are not overlapped in time at the sample. Instead, the first two

pulses excite all the Raman active vibrational coherences that then decay with the coherence time of each particular vibrational mode. CARS signal is the coherence remaining at the time the probe pulse arrives.

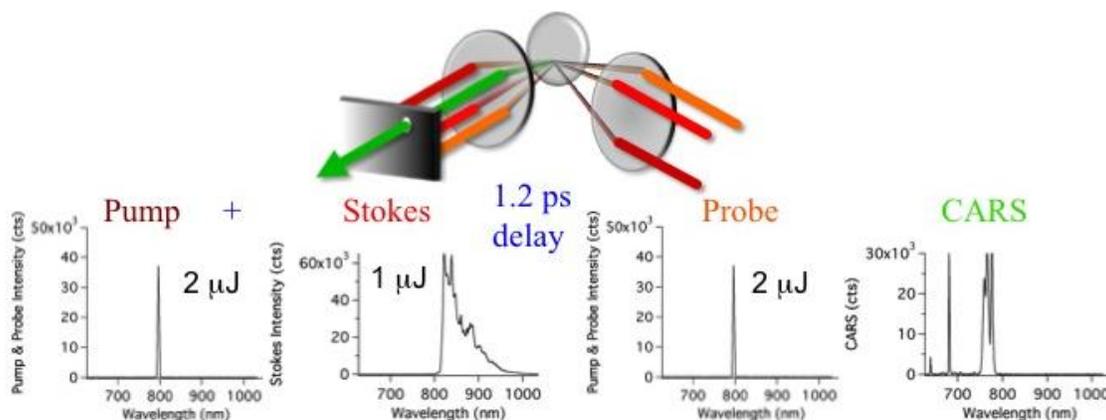


Figure 3. The pump, Stokes, and probe pulses are focused from three corners of a square, with the CARS emission isolated at the fourth corner after the sample. The pump and Stokes pulses are time-coincident, while the probe is delayed by 1.2 ps to make the nonresonant contribution negligible.

3. Preliminary Results and Discussion

3.1 Imaging Analysis

The increase in temperature (T-jump) and response time for a material under direct heating by a femtosecond/ps laser pulse depend on sample morphology and thickness (13, 14). For the indirect flash heating experiment, because of the Au layer and Au-sample interface, additional time delay and lower T-jump are expected. Therefore, to obtain effective heat transfer from the Au layer to the RDX and reproducible data, properly preparing the sample is a crucial step for indirect flash heating study. Several samples prepared in different ways (see section 2.1) were used for this study.

Figure 4 shows the images from preheating and postheating military-grade RDX (class 1), using the drop-casting thin film method. Note that there are different crystal forms in the sample when using this method (figure 4a): thin dendritic crystals and well-defined, bigger crystalline particles/rods. After flash heating, as shown in figure 4b, the thin dendritic crystals were sublimed by the T-jump generated in the sample by the femtosecond laser but the bigger crystalline particles/rods were not. Thicker and bigger crystal samples prepared using mineral oil interface and partial dissolution method were also unaffected by the flash heating laser. Figures 5 and 6 show the preheating and postheating images of class 1 military-grade RDX samples

prepared using a mineral oil interface and partial dissolution methods, respectively. Comparing the preheating and postheating images shown in these figures, no visible change is observed for both samples after heating. The results obtained indicate that there is not enough heat to initiate the RDX samples with thicker, bigger crystal forms. These results again confirm that T-jumps are strongly dependent on the size, shape, and thickness of a material. With our given experimental conditions, thin film samples prepared using drop-casting or inkjet printing method are the best candidates to obtain data with effective heat transfer to the RDX.

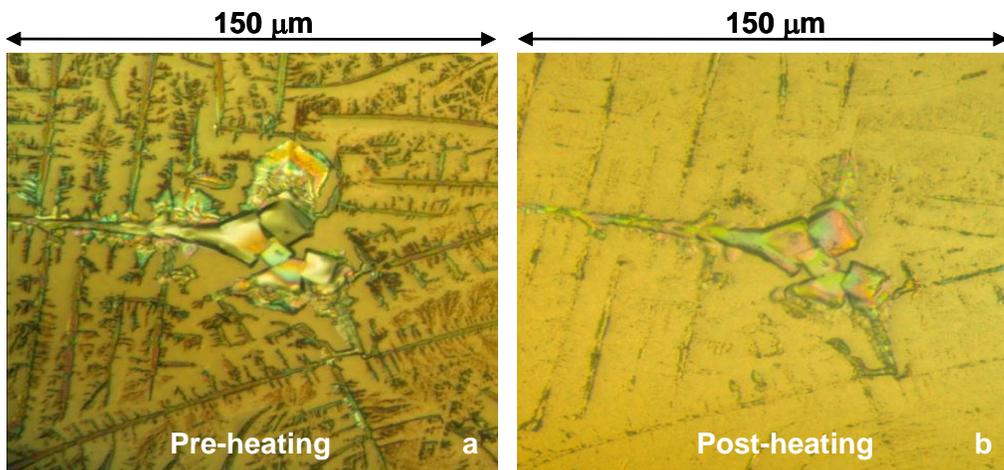


Figure 4. Preheating (a) and postheating (b) images of military-grade RDX (class 1) sample prepared using drop casting thin film method.

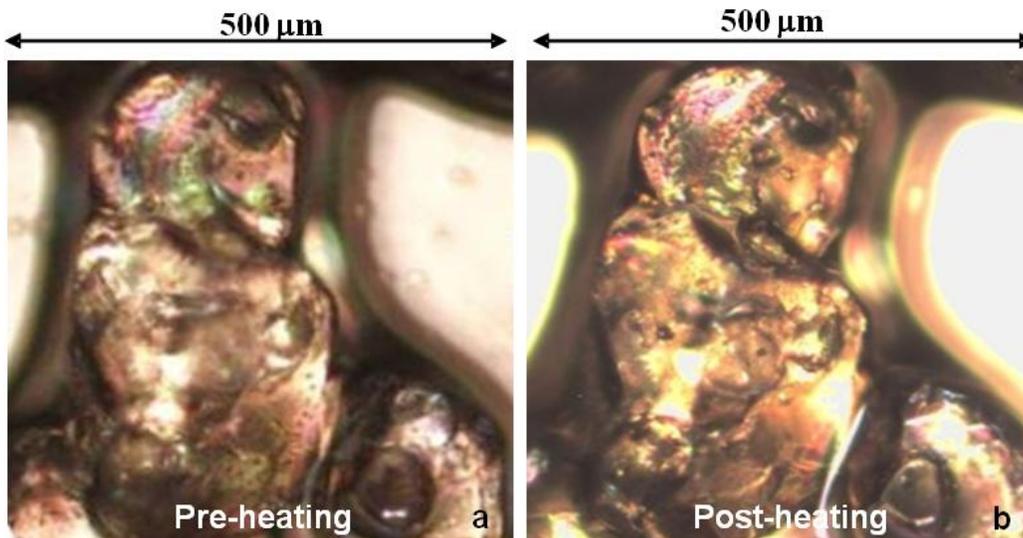


Figure 5. Preheating (a) and postheating (b) images of military-grade RDX (class 1) sample prepared using a mineral oil interface.

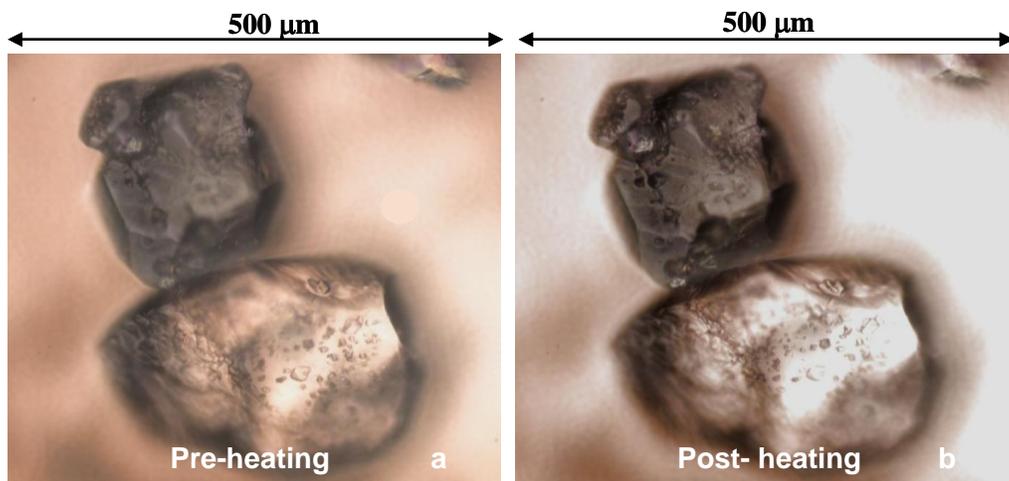


Figure 6. Preheating (a) and postheating (b) images of military-grade RDX (class 1) sample prepared using the partial dissolution method.

3.2 Work in Progress With Ultrafast Spectroscopic Methods

Ultrafast spectroscopic methods are challenging diagnostics that have been used to observe the dynamic changes in matter at the molecular level in real time. Currently, we are developing and testing experimental setups for white light transient absorption and CARS. Here we present some related results obtained by Nhan Dang in previous work at Los Alamos National Laboratory to show the capability of the current setups under development at ARL.

Figure 7 shows transient absorption spectra that were recorded as a function of time delay for a single crystal of RDX (001) (7a) and RDX sample prepared using thin film drop-casting method (7b) under ultrafast laser shock loading up to approximately 23 GPa. As seen in figure 7a, a broad absorption builds in during the shock. During the shock transit, the absorption builds to over 20%. This absorption continues to build up to the latest time observed, 466 ps after shock arrival. The RDX drop-cast thin film samples exhibit strong transient absorption on even faster timescales, as can be seen in figure 7b.

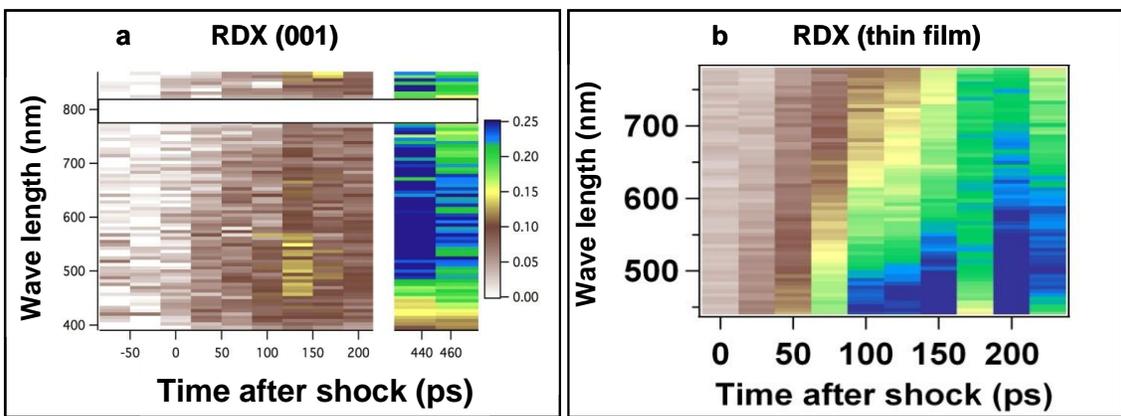


Figure 7. Transient absorption of RDX crystals shocked to approximately 23 GPa.

Figure 8 shows the CARS spectra of phenylacetylene shocked to 18 GPa at times up to 300 ps after shock loading. Phenylacetylene has been observed to chemically react under these conditions, as observed by volume reduction through Hugoniot measurements and by large increases in transient absorption across the visible to near-infrared range (15). The loss of reactants as the shock runs through increasing amounts of the sample is apparent in figure 8, but there are no new peaks attributed to product formation or even due to pressure shifting of the vibrational frequencies. This lack of shocked CARS peaks could originate in the shortened coherence time (much less than 1.2 ps) under the high-temperature/high-pressure reactive shock conditions. Transient absorption of the CARS excitation could also diminish the CARS intensity.

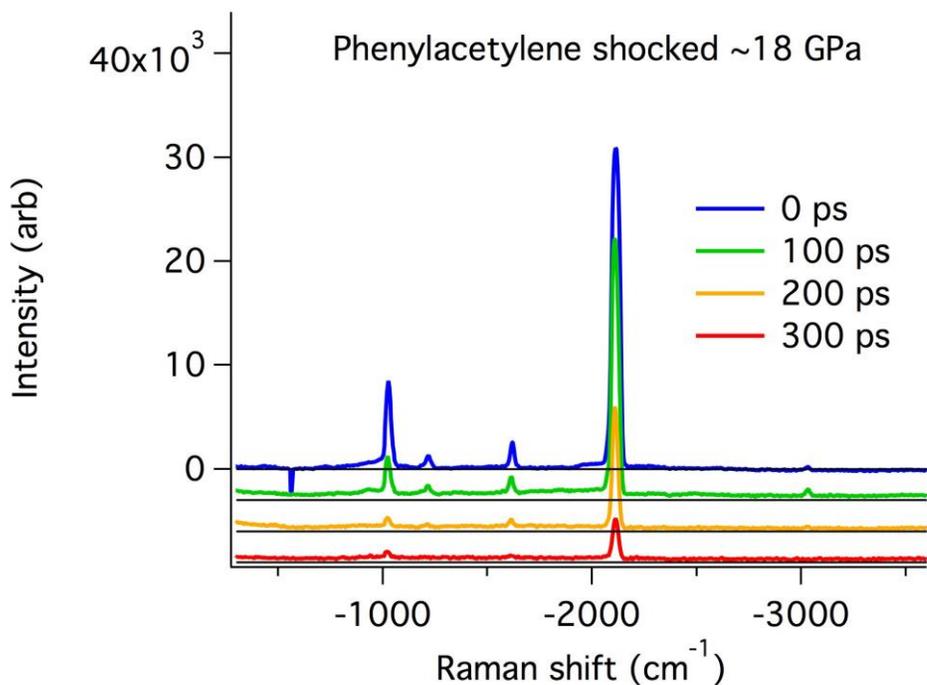


Figure 8. CARS spectra of phenylacetylene liquid shocked to 18 GPa. Phenylacetylene is chemically reactive under these conditions.

These results demonstrate the capability of transient absorption spectroscopy in studying chemical reactions or electronic excitations on a picosecond timescale, which is applicable to our study. Transient CARS spectroscopy also offers the time resolution and chemical specificity necessary to begin to address the details of the thermal-induced chemical dynamics on picosecond timescales.

4. Conclusions

In FY13, we made progress toward the FY14 goal set for this program: real-time observation of the effect of ultrafast flash heating on explosive samples. We now understand how to obtain effective heat transfer in a sample under indirect flash heating with our given experimental conditions. This knowledge is important in order to obtain reproducible and consistent experimental data. We also show the ultrafast spectroscopic methods currently under development will provide the capability to study the role of temperature in initial events occurring in explosive initiation.

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