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The Responses of Energetic Materials under Indirect Ultrafast Heating: Polarization Dependence of Heat Transfer in Materials

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14. ABSTRACT The primary motivation for this work is the desire to understand the behavior and role of temperature induced by picosecond heat pulses generated from interactions of femtosecond laser pulses on gold (Au) films. Using the indirect ultrafast laser heating technique coupled with transient visible absorption spectroscopy, we investigate how thermal energy generated from the heat pulses interacts with energetic materials. Previously, using this technique we have successfully shown that the thermal energy couples into explosive molecules by changing electronic configurations of the molecules in the excited state, and the changes are temperature dependent. In addition, we found that thermal energy coupling to the energetic molecules was dependent on physical properties of the samples such as thermal conductivity and electron-phonon coupling. In this work, we further show that the method of polarization-resolved transient absorption spectroscopy coupled with the ultrafast indirect heating technique can detect the orientations of liquid dipolar nitromethane molecules that are oriented and aligned due to the thermal gradient generated by heat flow from Au into the liquid sample in the picosecond time scale. Also reported here is the investigation of the dependence of thermal energy coupling into molecules on the orientation of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) using the ultrafast indirect heating technique coupled with polarization-resolved transient absorption spectroscopy. The results of this investigation show that the coupling of thermal energy into RDX molecules was dependent on the orientations of the sample.					
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1. Introduction

Understanding the dynamic of thermal energy flow (generated from different stimuli, such as shock wave, heat pulse, etc.) and the coupling of the thermal energy into molecular bonds on its characteristic time and length scales is necessary to constitute mechanisms for explosive initiation. Of interest here is investigating responses of materials under picosecond heat pulses generated by interactions of ultrafast laser pulses on gold (Au) films.¹⁻⁵ In addition, role(s) and behaviors of the thermal energy generated from picosecond heat pulse in energetic materials are determined. As discussed in previous work,³⁻⁵ we have successfully set up an experimental apparatus that can produce picosecond heat pulses resulting in T-jumps at an extremely high rate, a process which is analogous to that occurring in shock-induced initiation. To generate the T-jump in the indirect ultrafast heating experiments, 35-fs laser pulses with an energy density of 20 mJ/cm² have been used to heat Au films with a thickness of approximately 100 nm. As a result, during early laser-metal interaction in the Au films, a nonequilibrium thermal state and significant hot electron blast waves are generated in the metal films. These lead to extremely high rates of heat pulses due to the hot electron temperature (T_e) in which T_e can jump up to approximately 800 K with the raised time of approximately 1.5 ps and the pulse width at maximum of approximately 3.5 ps. We want to emphasize that this heating process can produce nondestructive T-jumps with extremely high rates of approximately 10¹⁴ K/s, which is 9 orders of magnitude higher than the reported heating rate of 10⁵ K/s in the current research.⁶ Also in this event, up to 4 GPa of initial compressive stresses are generated and pronounced after 60 ps of heating in the Au film.⁷ Therefore, investigations of material responses under the ultrafast indirect laser heating in the first 50 ps enable us to determine what role the T-jump plays during the early stages of initiation.

High-explosive single-crystal shock initiations have been shown to be strongly anisotropic.⁸⁻¹⁰ From these findings, a question in connection with T-jump has been raised whether coupling of thermal energy generated from T-jump into energetic molecules is orientation dependent. Therefore, investigation of the coupling of thermal energy into energetic molecules is necessary.

The molecular responses of energetic materials under ultrafast heat pulses have been observed using picosecond time-resolved visible transient absorption (VIS-TA) spectroscopy. Previously, we have shown that the thermal energy from the heat pulses couples into explosive molecules by changing electronic configurations of the molecules in the excited state.³⁻⁵ It was also found that the thermal energy from T-jump coupling into 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), pentaerythritol tetranitrate (PETN), and octahydro-1,3,5,7-tetranitro-1,3,5,7-

tetrazocine (HMX) is dependent on the physical properties of the materials, such as thermal conductivity and electron–phonon coupling.³ In this work, we expand the previous studies to further investigate how thermal energy affects polar liquid nitromethane (NM) and study the polarization dependence of thermal energy transfer into polycrystalline RDX using the indirect ultrafast laser heating technique coupled with polarization-resolved VIS-TA.

2. Experimental

2.1 Experimental Setups

2.1.1 Indirect Ultrafast Laser Heating Setup

The indirect femtosecond laser heating technique used to generate the T-jump has been detailed elsewhere^{1–5} and can be summarized in Fig. 1. Briefly, laser pulses centered at 800 nm with a repetition rate of 1 kHz and a duration of approximately 35 fs were used. To heat the samples, laser pulses with an energy density of approximately 20 mJ/cm² were focused through a sapphire plate onto the sapphire–Au interface. This laser energy density was chosen to be low enough to prevent ablation of the Au layer (110 nm) or the formation of a laser-induced plasma on the Au surface. The sample response under the influence of the heat transferred from the heated Au layer through the sample was monitored using time-resolved VIS-TA in reflective configurations.

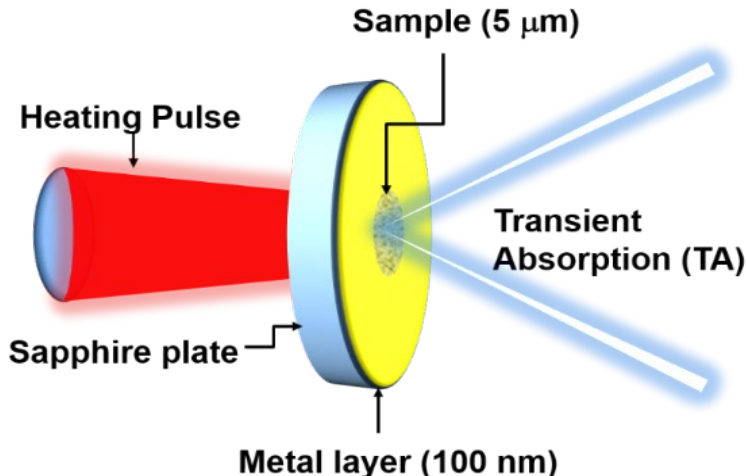


Fig. 1 Schematic diagram of the indirect ultrafast laser heating coupled with visible transient absorption (VIS-TA) spectroscopy

2.1.2 Polarization-Resolved Study

The indirect ultrafast laser heating setup described in Section 2.1.1. was modified to investigate the dependence of heat coupling into explosive molecules on the orientation of samples as summarized in Fig. 2. In this figure, the probing white light was linearly polarized in the P direction with a polarizer. The P-polarized white light was then manually rotated to desired angles with a $\lambda/2$ wave plate and focused onto the sample. The response of materials under the influence of the T-jump in the Au layer transferring into the sample was probed with the polarized white light at different polarization directions using time-resolved VIS-TA spectroscopy in reflective configurations.

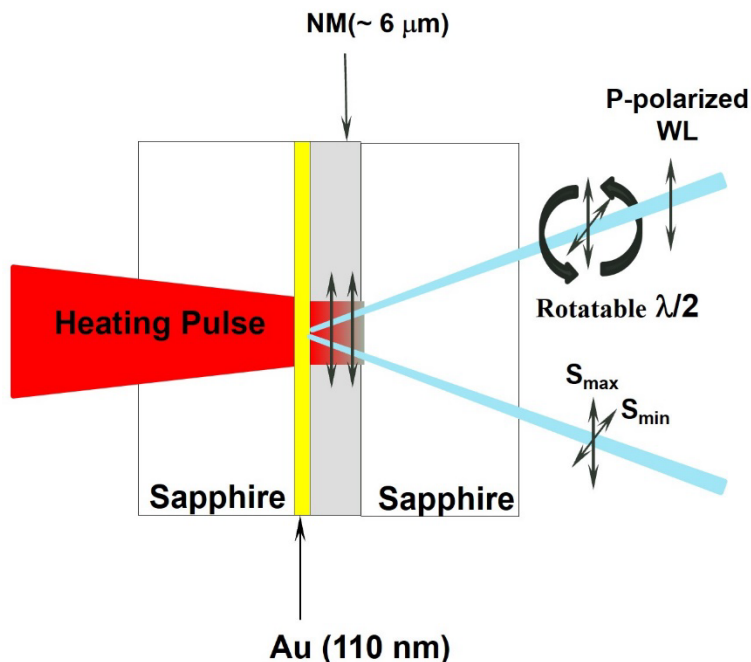


Fig. 2 Schematic diagram of the indirect ultrafast laser heating coupled with polarization-resolved VIS-TA spectroscopy. WL = white light; $\lambda/2$ = half wave plate; $S_{\max}$ = maximum signal intensity; $S_{\min}$ = minimum signal intensity.

2.2 Sample Preparations

Liquid samples of NM (Sigma-Aldrich ACS reagent, $\geq 95\%$) were configured in multiple layers (Fig. 2). Starting from the heat pump laser entry side of the sample, the layers are 500 μm of sapphire substrate (Esco, not oriented), 110 nm of Au film (physical vapor deposited on the back of the sapphire substrate), approximately 50–100 μL of liquid NM pressed inside of a 6- μm -thick mylar spacer (Harrick Scientific), and 500 μm of sapphire window (Esco, not oriented).

The solid RDX crystalline sample was prepared by the following steps. First, military-grade, class 1 powder was dissolved in acetonitrile. A thin film of RDX

was prepared by dropping approximately 30 μL of the solution onto the 100-nm-thick Au surface, which had been deposited onto a 0.5-mm-thick sapphire substrate using the thermal vapor deposition technique. The drop-cast solution was spread out using a spin coater set at 1000 rotations/min for 90 s. During spinning, evaporation of acetonitrile occurred and left a film of approximately 5- μm -thick RDX crystal on the Au surface. Note that RDX crystal would have different orientations at different locations on the Au surface; polarization-resolved data reported in this work were obtained at identical locations.

3. Results and Discussions

In general, depending on the orientation of excited molecules of a crystal sample or an orderly orientated sample with large dipole moments, one should expect to observe an absorption intensity change if the polarized probing light rotates to a different direction, and a maximum absorption intensity is observed when excited molecules are parallel to the polarized probe. Conversely, a minimum absorption intensity is observed when the excited molecules are perpendicular to the polarized probe. In this work, the polarization-resolved study was used to investigate (1) the orientations of NM molecules in a liquid state under ultrafast heating, and (2) the dependence of the energy coupling into RDX molecules in the solid state on the RDX.

3.1 Polarization-Resolved Study of Liquid NM

The polarization induced in polar liquids by a temperature gradient has been widely studied as described in Bresme et al.¹¹ and references therein. It has been found that the temperature gradient can result in large electric fields whose strength scales linearly with the temperature gradient. Therefore, in the polarization-resolved study of NM liquid (see Fig. 2 for the experimental configuration), under heating, two events would be expected to occur simultaneously at the Au–NM interface: (1) NM molecules are oriented in a certain direction due to the thermal gradient, and (2) the TA intensity of the Au surface reflected through the NM film is changed due to the change in orientation of the NM molecules in the film. Note that no VIS-TA signal was observed for NM at these experimental conditions; therefore, in this sample configuration, the NM film acts as a transient thermal polarizer in front of the Au surface and would attenuate the intensity of the probing light if the polarization direction of the probing light is different from the direction of the NM orientation.

Figure 3 depicts 2D time-resolved VIS-TA spectra of Au film in which the polarization dependence of the signal intensity on the orientation of NM molecules due to the thermal gradient is shown. In this figure, the maximum (upper panel) and

the minimum (lower panel) absorption intensities of Au were obtained with S- and P-polarized probing light, respectively. Time-resolved TA intensities at 525 nm of Au obtained with S- and P-polarized probes are compared in Fig. 4. In these figures, one can clearly see that NM molecules orientate and align parallel and perpendicular to the direction of S- and P-polarization, respectively. The findings confirm that NM molecules orientate and align due to the thermal gradient. Most importantly, we are able to observe the transient orientation of polar molecules due to the thermal gradient using ultrafast heating.

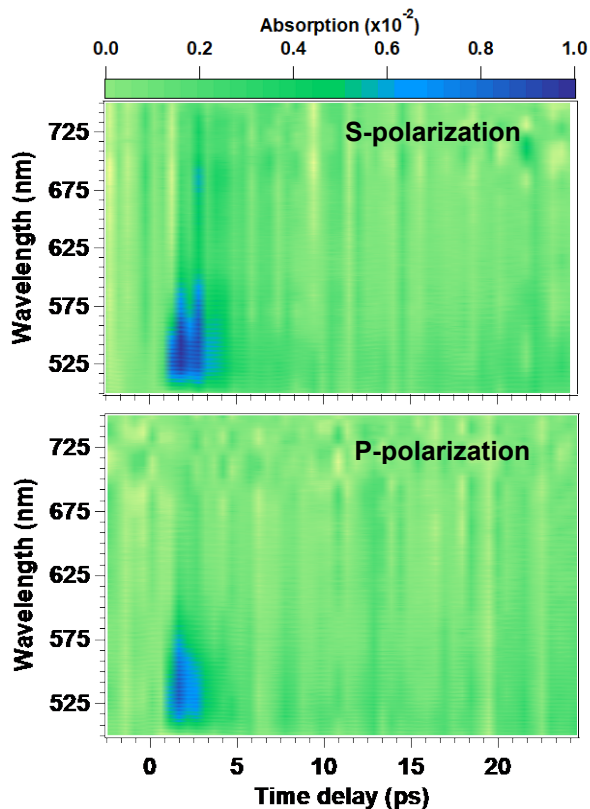


Fig. 3 Time-resolved VIS-TA spectra of an Au–NM film obtained with S- and P-polarized probes

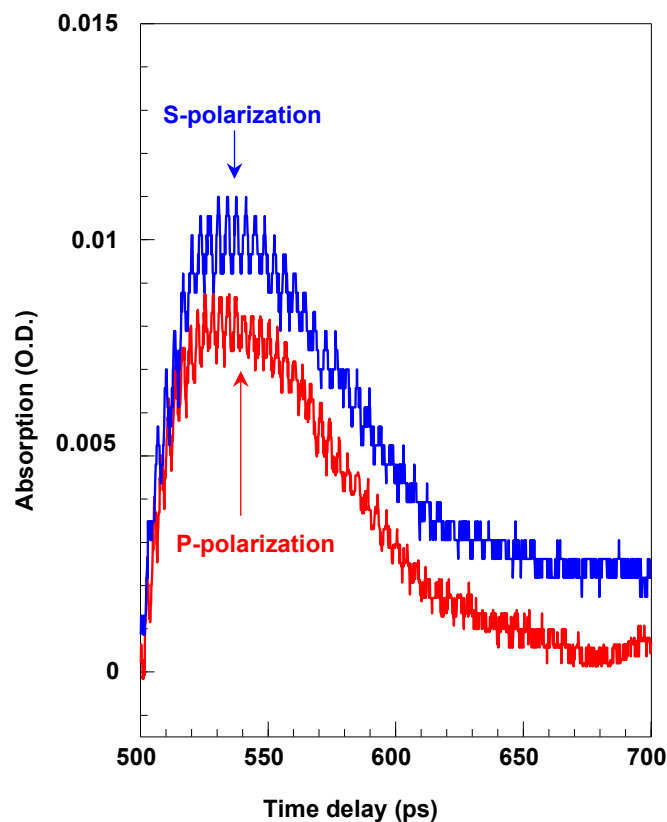


Fig. 4 VIS-TA intensities at 525 nm from an Au–NM film obtained with S- and P-polarized probes

3.2 Polarization-Resolved Study of RDX

Figure 5 depicts 2D time-resolved TA spectra of a 100-nm-thick Au monolayer (a) and indirectly heated 5- μm -thick film of RDX on the Au layer probed with polarized light, which is oriented at 40° (b) and 20° (c) with respect to P-polarization. Compared to the TA of the Au monolayer alone (Fig. 5a), additional TA due to the RDX is observed in both Figs. 5b and 5c. Furthermore, we observe stronger TA of the RDX when the sample is probed with the polarized light oriented at 20° with respect to P-polarization compared to the sample probed with polarized light at 40° . The stronger TA of RDX suggests that TA of the RDX crystal excited by ultrafast indirect heat pulses is orientation dependent and therefore efficiency of heat energy coupling into RDX molecules depends on orientation of RDX.

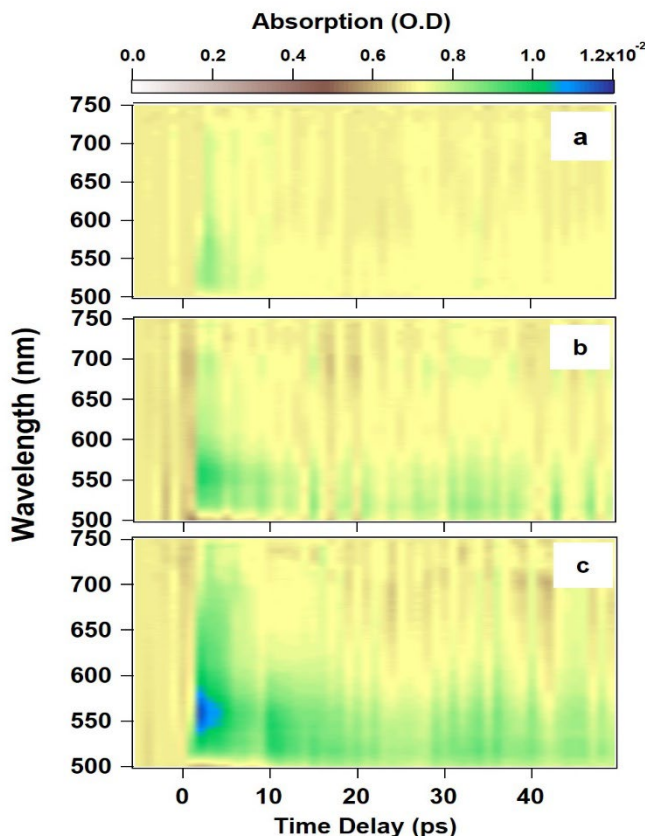


Fig. 5 Time-resolved VIS-TA spectra of (a) 100-nm film of Au, (b) 5- μm film of RDX on the 100-nm Au film obtained with the polarized light, which is oriented at 40° with respect to P-polarization, and (c) 5-mm film of RDX on the 100-nm Au film obtained with the polarized light, which is oriented at 20° with respect to P-polarization

4. Conclusions

Findings herein show that the indirect ultrafast laser heating technique coupled with ultrafast TA spectroscopy developed in our laboratory is a powerful tool to monitor the dynamic thermal energy flow and molecular response under ultrafast heat pulses in the picoscale time scale. The results of polarization-resolved studies of the polar NM and RDX samples show that the coupling of heat energy into molecules depends on the orientation of the samples. Under the thermal gradient generated by the heat pulses, the NM molecules orientate and align in one unique direction, therefore polarization dependence of heat coupling into molecules is observed. For RDX crystal, since the temperature distribution and thermal gradient in the solid do not affect the orientation of the sample, the observed polarization dependence is due to the difference in efficiency of heat coupling into RDX molecules at different orientations of the RDX crystals.

For the liquid sample, the focus here is of polar liquid NM; however, for nonpolar liquid, a recent theoretical study¹² showed that a temperature gradient to a fluid consisting of nonpolar tangent spheres, which is representative of a molecular fluid consisting of diatomic molecules, induces the alignment of the molecular axis along the temperature gradient. Therefore, our experimental technique is not limited to polar liquids but can be used to investigate the dependence of heat coupling into nonpolar molecular liquids. From the findings obtained for the RDX sample, which is an ensemble average of multiple crystals of different orientations, the dependence of heat coupling into molecules and their orientation in solid samples should raise concerns in the field of design or modification of explosives, especially if the sensitivity of the explosive is due to how heat couples to the molecule. We propose that investigations of the dependence of heat coupling into molecules in solid single crystals will give results that can determine the influence of heat-specific orientations.

5. References

1. Carter JA, Wang ZH, Fujiwara H, Dlott DD. Ultrafast excitation of molecular adsorbates on flash-heated gold surfaces. *J Phys Chem A*. 2009;113:12105.
2. Berg CM, Lagutchev A, Dlott DD. Probing of molecular adsorbates on Au surfaces with large-amplitude temperature jumps. *J Appl Phys*. 2013;113:183509.
3. De Lucia FC Jr, Gottfried JL, Sausa RC, Dang NC, Dean SW. Ultrafast nonequilibrium chemical control. Army Research Laboratory (US); 2016 Feb. Report No.: ARL-SR-0352.
4. Dang NC, Gottfried JL, De Lucia FC Jr. Energetic material response to ultrafast indirect laser heating. *Appl Opt*. 2017;56(3):B85–B91.
5. Dang NC, Gottfried JL, De Lucia FC Jr. The initial response of energetic materials in the first 50 picoseconds. *Proceedings for the Sixteenth International Detonation Symposium*; 2018.
6. Zhou L, Piekiet N, Chowdhury S, Zachariah MR. T-Jump/time-of-flight mass spectrometry for time-resolved analysis of energetic materials. *Rapid Commun Mass Spectrom*. 2009;23(1):194–202.
7. Gan Y, Chen JK. Thermomechanical wave propagation in gold films induced by ultrashort laser pulses. *Mechanics of Materials*. 2010;42:491–501.
8. Dick JJ. Anomalous shock initiation of detonation in pentaerythritol tetranitrate crystals. *J Appl Phys*. 1997;81:601.
9. Yoo CS, Holmes NC, Souers PC, Wu CJ, Ree FH, Dick JJ. Anisotropic shock sensitivity and detonation temperature of pentaerythritol tetranitrate single crystal. *J Appl Phys*. 2000;88:70.
10. Dang NC, Dreger ZA, Gupta YM, Hooks DE. Time-resolved spectroscopic measurements of shock-wave induced decomposition in cyclotrimethylene trinitramine (RDX) crystals: anisotropic response. *J Phys Chem A*. 2010;114:11560–11566.
11. Bresme F, Lervik A, Bedeaux D, Kjeslstrup S. Water polarization under thermal gradients. *Phys Rev Lett*. 2008;101:020602.
12. Romer F, Fernando Bresme F, Muscatello J, Bedeaux D, Rubi JM. Thermomolecular orientation of nonpolar fluids. *PRL*. 2012;108:105901.

List of Symbols, Abbreviations, and Acronyms

2D	two dimensional
Au	gold
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
NM	nitromethane
PETN	pentaerythritol tetranitrate
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
T _e	temperature
VIS-TA	visible transient absorption

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