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ORCID IDs: Nhan C Dang, 0009-0000-5752-8330; Jennifer L Gottfried, 0000-0002-1282-1928; Frank C De Lucia, 0000-0002-1282-1928

14. ABSTRACT

The primary motivation for this work is the desire to observe and understand the heat-pumped mechanism that drives electronic excitations of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) under ultrafast heating. In this work, using the indirect flash heating technique coupled with transient visible absorption spectroscopy, we investigate the electronic excitations in excited states of TATB in dimethyl sulfoxide solution that are excited by heat pulses with a pulse width of 3.5 ps and a temperature rise time of 1.5 ps. In an effort to distinguish the heat-driven mechanism for electronic excitation of TATB from the optically pumped mechanism, the obtained transient absorption (TA) data are then compared with the TA data obtained using the ultrafast optical pump probe technique. Prominent features attributed to thermally induced perturbations on the electronic structure of TATB molecules being promoted to the excited state were observed. Comparisons of the TA spectrum of the sample to that obtained by optical excitation reveal that under heating, electronic excitation of TATB molecules occur at lower energies. A hypothesis for the heat-driven mechanism of the electronic excitation is discussed to support the observations.

15. SUBJECT TERMS
Weapons Sciences, indirect ultrafast laser heating, transient absorption, electronic excitation, ultrafast transient absorption, heat pumped electronic excitation, optical pumped electronic excitation

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Nhan C Dang	(410) 306-0884

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1. Introduction

Electronic excitation has been described as a key role in the explosive initiation process in both experimental and theoretical research.[1–10] Specifically, initiation sensitivity was found to correlate with details of the electronic structure.[9,10] Therefore, in developing a mechanism for explosive initiation, understanding the early timescale electronic excitation mechanism during initiation is essential for predictive capability. However, most of these studies have focused on electronic excitation primarily excited or "pumped" by a shock wave, thus the energy is a convolution of rapidly changing temperature, pressure and strain, and so on, generated during the shock loading. There are no current studies with direct comparisons of electronic excitations excited by optical pump, heat, or shock loading. Therefore, it is necessary to perform isolated studies of electronic excitations under each of the individual stimuli. Comparisons of the results of these studies would shed light on the role of each of these stimuli on the electronic excitations and sensitivity of electronic excitation to these stimuli.

Experiments sensitive to the time- and length-scales necessary to observe the changes in the electronic configurations under optical pump, heat, or shock loading have been developed in our lab to address the problems mentioned. Previously, we observed changes in the electronic configurations of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and pentaerythritol tetranitrate (PETN) under heat loading with transient absorption.[11–13] In these experiments, a 35-fs laser pulse was used to interact with a gold (Au) film to generate a heat pulse (i.e., thermal wave). The ultrafast laser-metal interaction in the Au film created a nonequilibrium thermal state and a significant hot electron blast wave in the film leading to extremely high rates of temperature change (T-jump) and an initial compressive stress within the metal.[14–15] The severe thermal stress on the samples led to thermally induced perturbations on the electronic structure that could reduce the band gap energy—a similar process has been proposed for the mechanism of electronic excitation following a shock impact front through an RDX material containing dislocations.[10]

In this report, we focus on the changes in the electronic configurations of molecules in an excited state pumped by ultrafast heating. The changes of electronic configurations in the excited state are monitored using the same ultrafast transient absorption (TA) spectroscopy coupled with the indirect ultrafast heating technique reported in the earlier work.[11–13] The obtained results will be compared to the TA data obtained using the ultrafast optical pump probe technique reported in De Lucia et. al.[16] While ultrafast optical pump probe experiments allow us to use a singular external stimulus, an optical laser pulse, to observe the electronic transition of a sample in an excited state, the ultrafast indirect laser heating technique allows us to observe the electronic transition of a sample under ultrafast heating pulses. For our initial study, 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) in dimethyl sulfoxide (DMSO) solution was chosen. The use of liquids should eliminate the complications in which molecular crystals can be influenced by many factors such as anisotropy, microstructure, or phase changes, simplifying the model.

2. Experimental

The details of the optical setup were described elsewhere.[12] Here we briefly describe the technical steps and specifications of the laser and materials used in the experiments, which are summarized in Fig. 1. The solution of TATB in DMSO (VWR, ACS grade) used in this work were prepared identically to a previous work[16] with a concentration of approximately 4×10^{-4} M. The sample was contained in a multiple layer configuration shown in Fig. 1. 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 the solution pressed inside of a 25-mm-thick mylar spacer (Harrick Scientific), and 500 µm of sapphire window (Esco, not oriented). The heat pump laser pulses centered at 800 nm with a repetition rate of 1 kHz and a duration of approximately 35 fs with an energy density of approximately 20 mJ/cm^2, which was low enough to prevent ablation or the formation of a laser-induced plasma on the Au surface, were focused through a sapphire substrate onto the sapphire–Au interface. Due to laser–Au interaction, heat pulses were generated with a T-jump of approximately 800 K and a pulse width at half maximum of 3.5 ps and transferred into the sample. The TA of the sample was monitored with a time resolution of 0.5 ps using time-resolved visible (VIS)-TA in reflective configurations as shown in Fig.1. All final spectra reported here were obtained after averaging 150 laser shots (spectra) in the spectral region from 430 to 650 nm. Before obtaining the TA of the TATB in DMSO solution, TA spectra of the heated Au surface and DMSO liquid of the same sample holder were recorded and used as TA backgrounds for the TATB in DMSO sample.

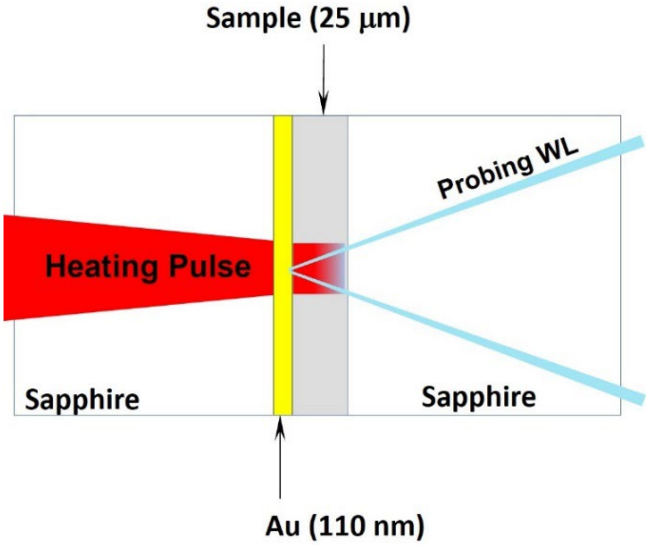

Fig. 1 Schematic diagram of the indirect ultrafast laser heating coupled with VIS-TA spectroscopy used for observing electronic excitations in excited states of DMSO and TATB in DMSO

3. Results and Discussion

Figure 2 shows time-resolved TA spectra of Au (panel a), 25-µm film of DMSO (panel b), and 25-µm film of TATB in DMSO (panel c) in the spectral range from 500 to 650 nm. Our goal is to observe changes in the TA of TATB due to ultrafast heating. The TA spectra of Au and DMSO serve as the backgrounds for the TA spectra of TATB. Due to the presence of the Au surface in the samples, the TA spectra of DMSO and TATB in DMSO obtained and reported in this work are the convolutions of the TA spectra of the Au surface and the samples.

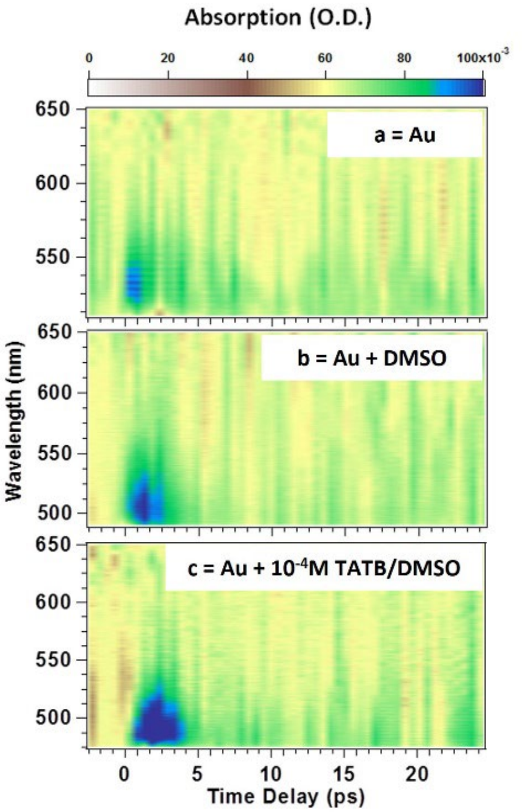

Fig. 2 2D time-resolved transient absorption spectra of ultrafast heated thin films: a) 110-nm-thick Au film, b) 25-μm-thick DMSO film on the Au surface, and c) 25-μm-thick film of 10^{-4} M solution of TATB in DMSO

Compared to the TA spectra of Au, stronger TA signals for DMSO and TATB in DMSO on Au are observed, and the strongest TA is observed for the TATB solution on Au in the region of 450–540 nm. The stronger observed TA signals indicate that changes in the electronic configurations of DMSO and TATB in DMSO occur under ultrafast heating. The TA spectral changes for DMSO and TATB solution can be seen more clearly in Fig. 3. Figure 3A shows comparisons of the time-delay integrated TA spectra of the three samples in the spectral region of 430 to 650 nm. Each spectrum is an integration of 50 spectra obtained in a delay interval of 25 ps with the time resolution of 0.5 ps. Figure 3B shows the differences in TA between Au and DMSO on Au (curve b – a), and Au and TATB in DMSO on Au (curve c – a), which reflect the overall spectral features of DMSO and TATB in DMSO. From Figs. 3A and 3B, one can see that two absorption bands are observed in both samples. A strong TA band (band I) is observed in the spectral regions of 430 nm to 530 nm, and a weaker TA band (band II) appears from 530 nm to beyond 650 nm. In the TA spectrum of the TATB solution, bands I and II are redshifted compared to the TA spectrum of DMSO. In addition, a stronger band I and weaker band II are observed in the TATB solution absorption spectrum compared to those observed in the DMSO absorption spectrum. Note that due to the redshifts of spectral bands I and II and the intensity reduction of band II in the TA spectrum of TATB solution, the subtraction of the TATB solution spectrum from the DMSO spectrum would generate artifacts in the resulting spectrum of TATB. These artifacts can lead to misinterpretation of the resulting spectrum. Therefore, in this report only the Au TA spectrum is used as the baseline for the TA spectrum of TATB solution, while the TA spectrum of DMSO served as a reference spectrum.

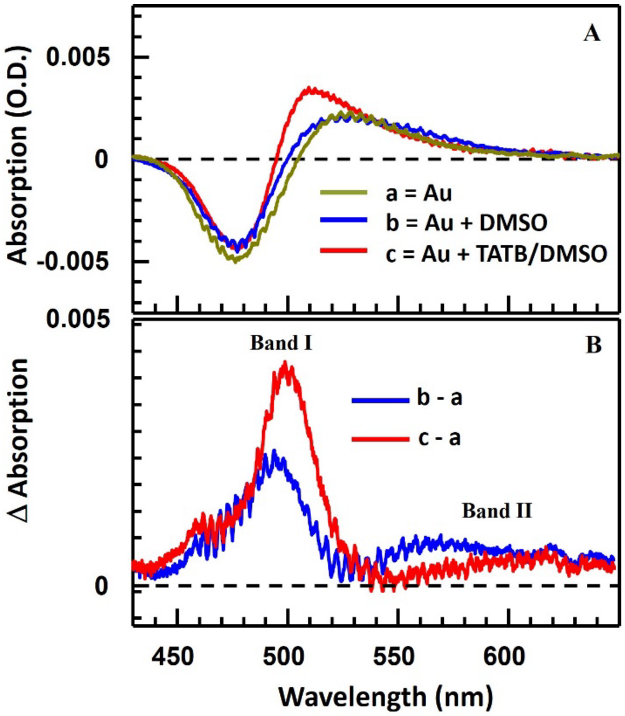

Fig. 3 Panel A shows time-delay integrated transient absorption spectra in the time interval from 1 to 25 ps. Curves a, b, and c are of 110-nm-thick Au film, 25-mm-thick DMSO film on the Au surface, and 25-mm-thick film of 10^{-4} M solution of TATB in DMSO, respectively. Panel B shows differences in TA between Au and DMSO on Au (curve b – a), and Au and TATB in DMSO on Au (curve c – a).

Before comparing the TA spectrum of TATB in DMSO in this work to that obtained by the optically pumped method, we first summarize the observations of optically pumped TA data reported in a previous work,[16] which are shown here in Fig. 4. In that work, the TATB in DMSO transient spectrum (curve a) is shown to be a convolution of two prominent absorption bands in the spectral range of 390 to 700 nm. Band I (curve b) centered at 420 nm ranges from below 390 to 540 nm, and a broader and weaker band II (curve c) is centered at 630 nm and ranges from 400 to beyond 700 nm.

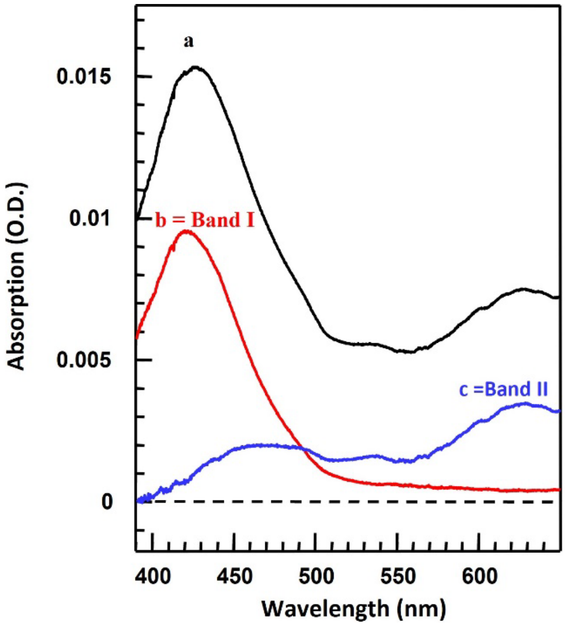

Fig. 4 Transient absorption spectrum of 10^{-4} M solution of TATB in DMSO obtained with optical pump-probe technique (curve a). The TA spectrum consists of two components (curves b and c), which give rise to the two bands in the spectrum at 420 and 630 nm.

The comparison between the TA spectra from Figs. 3 and 4 show two absorption bands that appear in similar spectral regions. However, for the TA spectrum obtained by the indirect ultrafast heating technique, both absorption bands I and II are narrower than those obtained with the optical pump. In addition, it is found that band I is centered at approximately 505 nm, redshifted compared to the band I equivalent obtained with the optical pump. Due to the low signal and high laser fluctuation noise in the spectral region from 600 to 700 nm, the peak value of band II is unable to be accurately determined in this work. Experiments for determining the accurate peak value of band II are currently being performed. The narrowing of the bands suggests that the TATB solution in the heat pumped experiments is structurally more ordered and/or denser compared to that used in the optically pumped experiments, in which polarization-resolved investigation of the solution did not show any indication orientation dependence (unpublished results). A possible reason is that as reported for nitromethane in Dang et al.,[17] under the influence of the transient thermal gradient generated by heat pulses, the TATB and DMSO molecules in the solution orient along the thermal gradient direction, thus the TATB solution becomes more structurally ordered. Consequently, narrower bands are observed. Also, the observation of the band I redshift shows that electronic excitation in the TATB solution under ultrafast heating occurs in an excited state with a lower energy level compared to that observed for the TATB solution under optical pump. This observation further supports our hypothesis that under the conditions in our direct ultrafast heating experiments, thermally induced perturbations on the electronic structure lead to a reduction in band gap energy, resulting in lower energy excited states.

4. Conclusions

The electronic excitations of excited states of TATB in DMSO solution via ultrafast heat pulses were examined in terms of TA spectra in the range from 430 to 650 nm over a time window of 25 ps. Prominent features attributed to thermally induced perturbations on the electronic structure of TATB molecules being promoted to the excited state were observed. Comparisons of the TA spectrum for the sample to that obtained by optical excitation reveal that, under heating, electronic excitation of TATB molecules occurred at lower energy level. The findings further support our hypothesis that ultrafast thermally induced perturbations on the electronic structure of an explosive cause a reduction in band gap energy. Theoretical modeling of rapidly heated TATB is currently being performed to confirm this hypothesis.

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List of Symbols, Abbreviations, and Acronyms

ACS	American Chemical Society
ARL	Army Research Laboratory
Au	gold
DEVCOM	US Army Combat Capabilities Development Command
DMSO	dimethyl sulfoxide
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
PETN	pentaerythritol tetranitrate
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
TA	transient absorption
TATB	2,4,6-triamino-1,3,5-trinitrobenzene
VIS	visible

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