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Exploring Ultrafast Structural Dynamics for Energetic Enhancement or Disruption

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14. ABSTRACT

A better understanding of the very early times during a detonation event has been difficult to obtain due to the rapid physical and chemical changes that are occurring under nonequilibrium conditions. Direct measurements of events leading up to a detonation are a challenge due to the extreme timescale (<100 ps) and highly dynamic environment. A more precise understanding of the excited states, energy flow processes, and chemical reactions at these time scales will lead to better predictive models and a more accurate theoretical treatment of energetic initiation. To explore this time scale we need to use ultrafast pump probe techniques to resolve the early time events of a detonation. We used 2 pump techniques, indirect laser heating and on-resonant optical pumping, to excite/perturb the energetic material to observe changes in the electronic and molecular structure with transient absorption and Raman probes, respectively. These techniques allowed us to monitor the temporal and molecular dynamics at time scales necessary to monitor early times of energetic events.

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1. Introduction/Objective

During the very earliest times of a detonation, energetic materials undergo rapid physical and chemical changes under nonequilibrium conditions. The fundamental challenges involve understanding the energy flow processes at ultrafast time scales that follow dynamical stimuli, energy localization and delocalization, changes in lattice structure, decomposition, and the fundamental chemical reactions involving excited states. Determining the decomposition pathways of an energetic material is difficult due to their dependence on temperature, pressure, initiation method, and atmosphere. An understanding of the behavior of a material at the relevant time scales can lead to better predictive detonation models and more-accurate theoretical treatment of energetic initiation. How do we examine and understand the pathways starting from dynamic stimuli, lattice molecular vibrational and electronic responses, excited-state chemical dynamics, and chemical decomposition and initiation? Direct real-time measurement of the interaction between excited states, defect structures, and chemical reactions that are occurring at these time scales (picoseconds) requires the use of ultrafast (femtosecond [fs]) pump-probe methods to resolve the mechanisms involved in the earliest moments of a detonation.

Although most scientists agree that excited electronic and vibrational states may play a role in the initiation process of energetic materials, direct insight into the roles of short-time dynamics is not well understood. Previously, studies of excited-state dynamics in energetic materials have been performed theoretically through atomistic-level modeling of the system or by indirect experimental measurements and postreaction observations such as investigating decomposition products. Theoretical studies of excited states have focused on either the initiation process from a solid-state physics point of view or exploration of the excited-state potential energy surfaces of energetics (i.e., the various excited-state structures). Several theoretical studies have investigated the effects of shock waves on the electronic excitation of crystal structures. Specifically, a model has been suggested that links the electronic structure of the explosive crystal with the decomposition of the material.[1] Decomposition pathways have also been calculated from excited states of various energetic systems.[2,3] In an earlier experiment, X-ray photoelectron spectroscopy and electron paramagnetic resonance were used to study recovered shocked samples of several explosives and compared with the products collected from ultraviolet (UV) and slow thermal decomposition.[4] The decomposition effect in cyclotrimethylenetrinitramine (RDX) explosive due to UV photolysis was similar to that found in the shock decomposition. Since the first step in UV decomposition is an electronic excitation, an electronic excitation was suggested as a step in shock decomposition. Interestingly, this was not observed with trinitrotoluene (TNT) decomposition.[4] Another study combined theoretical modeling of the various electronic states at different points on the potential energy surfaces with experimental monitoring of the decomposition product.[3,5,6] This work has shown that energetic materials rapidly move from upper excited states to lower electronic states through radiationless transitions. The decomposition occurs during an excited-state to ground-state transition. In contrast, a nonenergetic model system (DMNA) decomposed during an excited-state to excited-state transition. These differences may be what determine the effectiveness of an energetic material.[3]

The overall objective is to observe in real-time the extremely short-lived excited-state temporal and structural dynamics that occur during energy release of energetic materials in order to determine the influence these states have on energetic initiation and decomposition.[6,7] Furthermore, we plan to perturb the excited state using external stimuli that could potentially alter the performance of the energetic material, assuming the excited states play a role in the initiation/decomposition processes.

2. Methods/Approach

Shock, spark, photolysis, and thermal initiation will induce changes in the chemical and electronic structure of the energetic molecule. The decomposition pathway can vary depending on initiation method. Further complicating matters is the need to decouple the effects of rapid temperature and pressure changes on the molecule. Thus our approach is to use different ultrafast pump-probe techniques to isolate the multiple excited-state pathways. For example, we used an on-resonance laser pulse pump to promote the molecule into an excited state without any rapid temperature or pressure change.

In general, an ultrafast pump-probe technique involves an fs laser source. The laser pulse is divided into 2 separate beam arms, the pump and the probe. The pump and the probe are then overlapped spatially and temporally at the sample. A delay line in the probe arm can be used to delay when the probe beam arrives at the sample relative to the pump beam. The pump is used to perturb the sample. The probe beam is used to monitor the change in the sample due to the pump. By changing the delay line, one can observe the changes in the sample at various times after the pump beam perturbs the sample.

For this work, we used 2 different types of pump beams, an optical pulse and a flash heating pulse, and 2 types of probes, transient absorption and transient Raman spectroscopy. A Ti:Sapphire regenerative amplifier generated 800-nm 1-mJ 1-kHz fs laser pulses. Single-shot autocorrelation was used to determine the pulse width. The pulse shape was captured with an oscilloscope and fitted with a Gaussian curve. Using the calibration factor determined from the autocorrelator and the oscilloscope with the Gaussian FWHM (full width at half maximum), the pulse width was determined to be 95.7 ± 1.2 fs.

What follows is a description of one of the optical layouts used for our studies, the ultrafast pump-probe technique transient absorption. Similar setups are used for the flash heating pump. Figure 1 shows the layout. The pulse train from the fs laser is split into a pump beam (90%) and the probe beam (10%). The harmonic generator was installed in the pump arm to provide the second harmonic of the 800-nm source laser for pump wavelengths of 400 nm. A supercontinuum was formed in the white-light generator by focusing the beam into a transparent media.[8] We studied several different materials (quartz, sapphire, water, calcium fluoride [CaF_2], and magnesium fluoride [MgF_2]) for generating a continuum and determined that a water cell was the best material for creating a stable broadband white-light source (350–650 nm). Generating a stable white-light continuum is extremely important to ensure quality spectral data. The probe pulse energy was lowered and the probe pulse diameter was spatially reduced with an iris until a small white disk surrounded by a red ring was formed on the iris after the parabolic mirror shown in Fig. 1, indicating a stable white-light continuum. The iris was added to spatially filter the white-light continuum, allowing only the middle portion of the continuum to pass through the sample. Furthermore, the white light was split into 2 portions by a 50:50 beam splitter. One part of the white light served as the reference beam, and the other part probed the excited state induced by the pump beam.

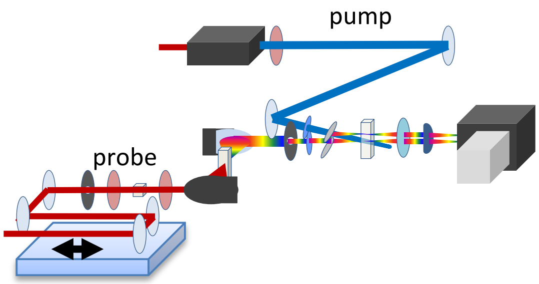

Fig. 1 Transient absorption optical pump-probe experimental setup

The white-light probe and the 400-nm pump beam were overlapped spatially and temporally in the sample to generate transient spectra. A BBO (beta barium borate) crystal that generates the third harmonic was placed where the pump and probe beams overlap. When the delay line is positioned so that the probe beam path is equal in distance to the pump beam path, the 2 pulses are overlapped temporally, indicated by the generation of 266-nm light. After establishing the delay line position that corresponds to zero time, the delay line can be adjusted to collect transient absorption spectra at various times after initial excitation due to the pump beam.

Using an organic solvent, cyclohexane, we collected transient absorption spectra around the zero time delay setting. In the spectra there is minimal absorption but there is a large inverted peak at 450 nm due to stimulated Raman emission from the C-H stretch in cyclohexane at approximately 2,800 cm^{-1}. The Raman shift is calculated using the following equation:

$$\Delta\omega(cm^{-1}) = \left(\frac{1}{\lambda_{o}} - \frac{1}{\lambda}\right)(10^{7}). \tag{1}$$

While stimulated Raman emission is generally not desirable in transient absorption spectra, we were able to use it to find the instrument response function and determine the time resolution of the instrument.[9] In this case the time resolution was calculated to be around 200 fs after fitting the shifting Raman peaks at early time delays (<1 ps) to a Gaussian.

3. Results

3.1 Optical Pump

To determine the appropriate optical pump wavelength for energetic materials, ground-state UV-visible absorption spectra were collected of 3 energetic materials: 2-Methyl-1,3,5-trinitrobenzene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), shown in Fig. 2. The RDX and TNT were dissolved in acetonitrile. TATB was dissolved in DMSO (dimethyl sulfoxide). Based on the absorbance spectra, the second harmonic (400 nm) can be used to promote the TATB into the upper excited state. The TATB solution was diluted so the absorbance range at 400 nm (the pump wavelength) is 0.5–2.0. The third harmonic (266 nm) must be used to excite either the TNT or RDX.

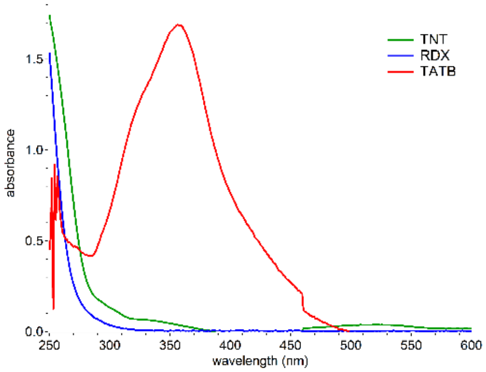

Fig. 2 UV-visible absorption spectra of RDX, TATB, and TNT

Before probing the energetic materials, we collected transient absorption spectra of salicylidene aniline (SA). The fast early-time dynamics of this photochromic material have been investigated previously.[10] We wanted to collect transient absorption from a previously studied sample to compare literature results with results from our transient absorption experimental setup. The SA was dissolved in cyclohexane to a concentration of 5.7×10^{-3} mol/L. Thousands of spectra were collected and averaged at several delay times. The difference absorbance spectra were then calculated at each delay time using the following equation:

$$\Delta A = -log\left[\left(\frac{T_{pump+probe}}{T_{ref2}}\right)\left(\frac{T_{ref1}}{T_{probe}}\right)\right], \qquad (2)$$

where $T_{pump+probe}$ is the transmission spectrum collected with the probe and pump beam on, T_{ref2} is the transmission spectrum collected from the reference beam simultaneously with $T_{pump+probe}$, T_{probe} is the transmission spectrum collected with only the probe beam, and T_{ref1} is the transmission spectrum collected from the reference beam simultaneously with T_{probe}. In Fig. 3 we show some representative transient absorption spectra from the SA. At zero time delay, the inverted peak at approximately 450 nm is due to the stimulated Raman emission used to calculate the instrument response function described in Section 2.

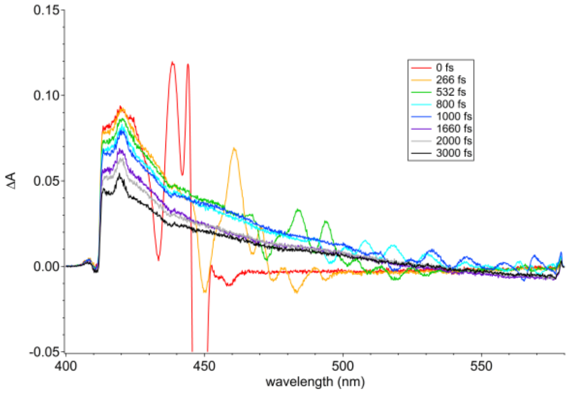

Fig. 3 Transient absorption spectra of SA at several delay times

Using an on-resonance pump pulse at 400 nm, we optically pumped the TATB into an excited state. The photophysics and photodecomposition of TATB are complicated and still not entirely understood.[11–13] The white-light continuum was used to probe the sample at various delay times from 0 to 10 ps. Difference absorbance spectra were calculated at each delay time. The spectra are shown in Fig. 4. The transient absorption spectra allow us to directly monitor the time dynamics of the TATB excited state. At the earliest times (1 ps) there are still distortions due to coherent artifacts (the oscillations observed at >500 nm). We observe a broad structure with a maximum at 430 nm that is gone by 10 ps. These spectra provide new information about TATB excited states formed due to optical pumping.

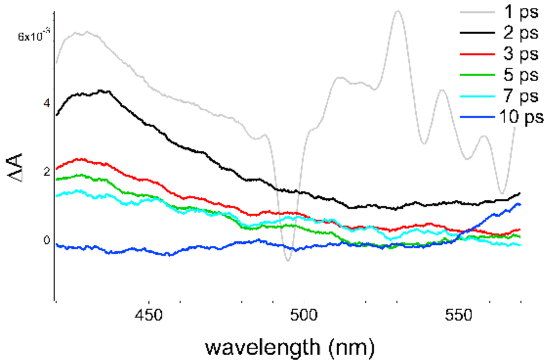

Fig. 4 Transient absorption spectra of TATB at several delay times

3.2 Thermal Pump

The indirect flash heating technique[14] allows us to observe the effect of thermal energy on energetic materials and thus determine the role temperature plays in the initial detonation events. It can tell us how thermal energy couples into a molecule and at what rate. In this case we used an 800-nm fs laser pulse to heat the back of a thin gold substrate. On the side opposite of the laser impact is a thin layer of RDX crystals. We used 2 probes to analyze the thin layer of RDX crystals, a white-light continuum and a Raman probe. Both probes interrogate the RDX crystals at an angle, pass through the sample, reflect off the gold substrate, and then are used to determine the transient absorption and the Raman spectrum of the RDX at several delay times after the indirect heating pulse as shown in Fig. 5. The excitation of RDX was completely reversible (i.e., the transient absorption signal was reproducible over thousands of laser shots at the same position). The change in the transient absorption spectra of RDX following ultrafast indirect flash heating indicates that thermal energy couples into the RDX molecules via electronic excitation. This excitation starts approximately 50 ps after the laser pulse, with peak excitation occurring around 300 ps. During this time scale we also observed the thermal energy couple into the molecular structure by monitoring the change in the Raman peak intensities of the symmetric ring stretch at 875 cm^{-1} and the N-NO$_2$ torsion at 188 cm^{-1}. These 2 probes allowed us to measure thermally excited RDX for the first time.

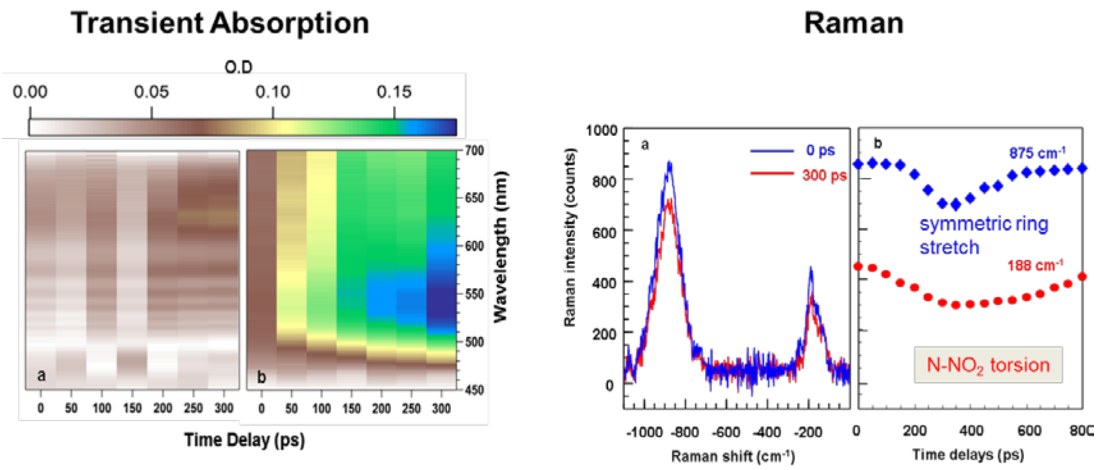

Fig. 5 Transient absorption spectra of RDX after flash heating (left) Raman spectra of RDX after flash heating (right)

Based on the fact that the melting temperature of gold is 1,064 °C and the fs laser energy was selected to avoid damaging the gold layer, the change in temperature of the gold (ΔT) has been estimated to be less than 800 K.[15] This temperature corresponds to an energy increase of at most 0.07 eV, which under typical conditions is not sufficient for electronic excitation (the lowest excited state for RDX is calculated to be at 5.1 eV).[3] There are 2 major differences between the current ultrafast flash heating experiment and previous RDX heating experiments: 1) the RDX sample was prepared as a thin film using a spin-coating method with less sample available to dissipate the heat flow and 2) the rate of temperature change under the current experimental conditions is extremely high ($\approx 10^{13}$ K/s). One proposed mechanism for electronic excitation following a shock impact front through the RDX material containing dislocations is a decrease in the energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital[16]; it is possible that a similar reduction in band gap occurs following a thermal "wave". Future theoretical modeling of flash-heated RDX is necessary to try to explain the observed transient absorption and Raman signal. Furthermore, the Raman signal can be used to measure the temperature evolution of the flash-heated RDX experimentally.

4. Conclusions

We have used ultrafast pump-probe techniques to measure the response of energetic materials. These techniques allow us to monitor the temporal and molecular dynamics at the earliest times of detonation. In particular we have used 2 techniques, flash heating and optical pumping, to elucidate the excited-state dynamics that occur due to rapid temperature change and absorption of resonant laser pulse energy, respectively. This also allows us to observe the properties of the excited states in isolation from the complex environment associated with early detonation times—rapid changes in temperature and pressure, chemical reactions, and vibrational and electronic changes all on a picosecond time scale. In other words, we can see how thermal energy couples into the energetic molecule without the rapid pressure change due to a shock wave, thus allowing us to elucidate the role of temperature change in an explosive event. Furthermore, we can determine if the excited-state dynamics observed solely due to an on resonant optical pump are similar to excited-state dynamics observed in the earliest times of a detonation event. By understanding the early time dynamics of energetic materials with ultrafast experimental techniques, we can better develop theoretical and predictive models that could lead to the design of higher performing explosive materials.

In addition to monitoring the complex processes that occur during the early times of initiation and detonation, we would like to explore the possibility of influencing or altering the energy-flow pathways during the excited-state formation and relaxation. A promising idea for accomplishing this complicated task is using an fs pump-push/dump probe technique.[17] The additional push or dump laser pulse allows one to control the evolution of the excited state instead of simply monitoring it. In a pump-push/dump probe experiment, a secondary laser pulse (push/dump) is used after the initial perturbation due to the pump pulse. The laser pulse can either push the excited state further into higher energy electronic states or dump the excited state more quickly into the initial ground state. Pump-push-probe experiments have been used to investigate properties of conjugated polymers.[18] In that work, after the initial excitation generated singlet excitons, a push pulse further excited the excitons into a higher energy state. As a result the charge generation efficiency was increased. The pump-push/dump probe technique is a difficult experiment that requires a highly stable laser source. Ultrafast pump-probe experiments already depend on low noise since one is trying to observe a small change. The push/dump experiments require observing a small change on top of the small change observed in the pump-probe experiments. However, further exploration of this technique is warranted since it could lead to new understandings of the relationships between excited-state pathways and energetic performance and ultimately lead to control of energetic performance.

5. Transitions

The Director's Research Initiative (DRI) project has been transitioned into a mission program entitled "Ultrafast Nonequilibrium Chemical Control". The mission program will continue to investigate the role excited states play in the energetic performance by using a wide range of ultrafast techniques beyond the scope of the DRI. We will also continue to investigate how we can control these excited-state pathways. Ultimately, knowledge elucidated from the early time pathways of initiation could lead to the design of new, better performing energetic materials.

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List of Symbols, Abbreviations, and Acronyms

DRI	Director's Research Initiative
fs	femtosecond
RDX	cyclotrimethylenetrinitramine
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
TNT	trinitrotoluene
UV	ultraviolet

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