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Investigation of the Role of Electronic Excitations in Shock-Induced Initiations of Explosives Using an Optical Pump-Probe Technique

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14. ABSTRACT
Electronic excitation has been identified as playing a key role in the explosive initiation process in both experimental and theoretical research. Therefore, to develop a complete mechanism for explosive initiation, understanding the early timescale electronic excitations during a shock-induced initiation is essential for predictive capability. However, energies that drive electronic excitations in the initiation are a convolution of rapidly changing temperature, pressure and strain, etc., generated during the shock loading. It is difficult to extract an accurate mechanism for electronic excitations in the initiation events without a standard mechanism. To build a standard mechanism, electronic excitations of high-energetic materials under an optical pump have been performed at the US Army Combat Capabilities Development Command Army Research Laboratory. Here, we report results from the optical pump-probe experiment developed for these studies. With this setup, we can obtain more reliable data compared to earlier works. Therefore, our results can provide experimental parameters to accurately determine a standard electronic excitation mechanism for Army materials of interest. We further propose and discuss future studies of determining the role(s) of electronic excitations in potentially enhancing the performance of an explosive.

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Weapons Sciences, ultrafast, transient absorption, nitroanilines, energetics, excited states

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Contents

List of Figures

1. Introduction

Electronic excitations are believed to be involved in the shock-induced initiation of explosives. Previous studies demonstrate that electronic structure changes have significant effects in strong shock loadings.[1–10] In general, the theoretical predictions for changes in electronic configuration under shock stress show that chemical bonds are compressed and bent, leading to rapid and short-lived reductions of electronic energy bandgaps. Therefore, the electrons excited by the shock energy are promoted across these short-lived, reduced band gaps, and this chemistry is dissimilar to chemistry under non-shock conditions. Electronic excitations were also observed in several explosives under ultrafast heating with a heat rate of 10^{14} K/s and a pulse width of 3.5 ps.[11–13] The mechanism for the electronic excitations observed under ultrafast heating has been proposed to be similar to that hypothesized for the shocked-induced electronic excitation mechanism.[12] Under the conditions of the ultrafast heating experiments, thermally induced perturbations on the electronic configurations lead to reductions in energy bandgaps, resulting in temporary lowering of the higher-energy excited states to which electrons from ground states can be promoted by the rapid heating energy.

In addition to the observations mentioned above, it has been shown that short-lived excited-state species play a role at this early stage. In the previous studies of decomposition products from shocked 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 2,4,6-trinitrobenzene-1,3,5-triamine (TATB), it was found that the products from the shock decomposition are identical to the products from ultraviolet photolysis decomposition.[14,15] The first step in photolytic decomposition involves an electronic excitation, suggesting shock decomposition could also involve electronic excitations.

Several questions arise for understanding changes in electronic configurations due to shock/thermal/optical excitations. What are the differences and similarities in the pathways of electronic excitations between the optical and shock/thermal-induced excitations? In the event of shock/thermal-induced initiations, does an addition of optical-pumped electronic excitation enhance the sensitivity of explosives? Simultaneous investigations of changes in electronic configurations of explosives under optical pump, shock/heat loadings, and shock/heat loadings with optical pump will provide insight to answer these questions. By comparing the results, we can distinguish changes in the electronic configurations and provide additional information to determine an accurate electronic excitation mechanism in shock-induced initiations.

Although the pump-probe technique has been developed and applied to investigate electronic excitations and/or electron transfers in energy-storage materials for several decades, using the technique to obtain high-quality data is still challenging. Coherent artifacts and background noise from laser fluctuations are common factors inducing additional spectral features or obscuring the spectral resolution, which leads to inaccurate analyses of the data. Typical reported data can be seen in references.[16–18] We have made efforts to obtain improved spectra from a transient absorption pump-probe technique. Here we summarize the results obtained from our experimental setup for several nitroanilines, including the energetic TATB.

2. Setup

The femtosecond pump-probe transient absorption experimental layout is shown in Fig. 1 and has been described previously.[19] A femtosecond laser system (Coherent Astrella Integrated titanium-sapphire [Ti:S] Amplifier) produces a pulse train of 6-mJ, 800-nm, 35-fs pulses at a 1-kHz repetition rate. The pulse train is then split into pump and probe pathways. The pump pulse is converted to 400 nm via Type I second harmonic generation. A lens (50-cm focal length) was used to focus the pump beam onto the sample. Concurrently, the probe pulse is focused into a calcium fluoride plate (Newport, 10CF20)/water cell to generate white light. Rotating the calcium fluoride plate or stirring the water in the water cell is necessary to prevent damage on the plate or to eliminate bubbles generated by the laser heating in water. The white light is collimated by a lens (10-cm focal length) and passes through a broadband plate beam splitter (Thorlabs, BSW26R) splitting into a reference pulse and a probe pulse. The reference pulse is directed into the spectrometer while the probe pulse is focused into the sample. The pump pulse and the probe pulse are overlapped spatially and temporally in the sample cell (Starna Scientific, 5-mm path length). A micro stirrer is used to perturb the sample to avoid the formation of a bubble due to laser–sample interaction with the solution. After exiting the sample, the white light is directed into the spectrometer.

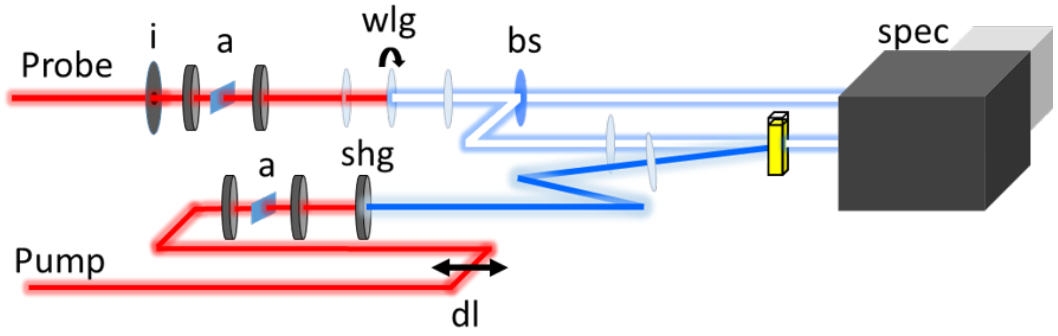

Fig. 1 Transient absorption experimental setup (i) iris, (a) attenuator, (wlg) white light generator, (bs) beam splitter, (dl) delay line, (shg) second harmonic generator, and (spec) spectrometer and camera

The full pump-probe transient absorption experiment is described in detail previously.[19] The pump and probe pulses arrive at the sample relative in time to one another, determined by the delay line. At various delay times, the transient transmission is determined by the following equation:

$$T = \left[\frac{T_{pump\ on}}{Reference} - \frac{T_{pump\ off}}{Reference}\right] / \frac{T_{pump\ off}}{Reference} \quad (1)$$

where $T_{pump\ on}$ and $T_{pump\ off}$ are the transmitted probe pulse spectrum with the pump pulse on and off, respectively. The transient absorption for a particular delay time is then calculated using Eq. 2:

$$A = -log\ (T + 1) \quad (2)$$

This process is repeated many times to obtain a good signal-to-noise ratio. Experiments are repeated multiple times on different days under identical conditions to test repeatability and improve the signal-to-noise ratio. In general, we collect a total of a few thousand transient absorption spectra at each time delay over several days.

3. Results

We collected transient absorption spectra of ortho-nitroaniline (oNA) and para-nitroaniline (pNA) using a 400-nm pump wavelength shown in Fig. 2. We also observe significant differences in the transient absorption spectra even though the two molecules have identical chemical formulas ($C_6H_6N_2O_2$) and similar structures (shown in the figure) but different relative positions of the functional groups. The spectral features of these spectra are comparable/more detailed than those collected in previous studies.[16,17] With these higher-quality spectra, we are able to more accurately determine lifetimes and wavelengths of the excited states of these molecules.

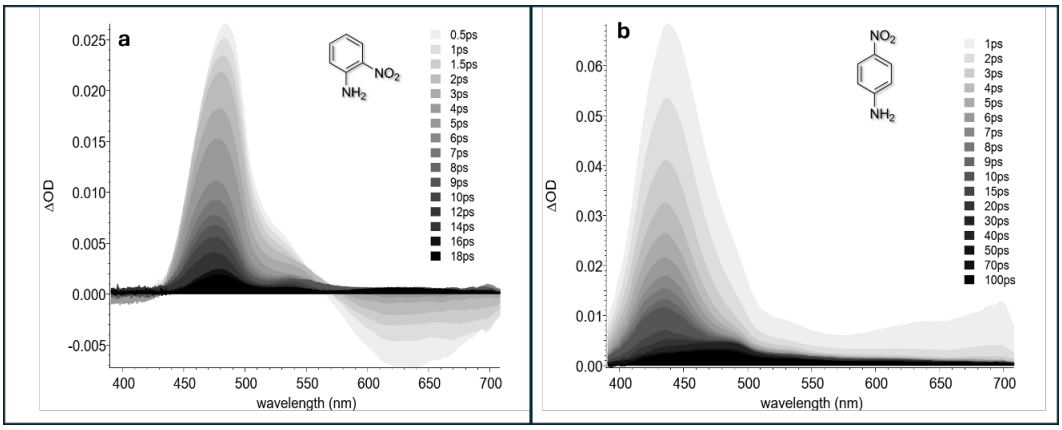

Fig. 2 Transient absorption spectra of a) ortho-nitroaniline and b) para-nitroaniline at various time delays

Comparing the spectra shown in Fig. 3a to those shown in 3b, the overall change in optical density (ΔOD) is larger for pNA compared to oNA. The largest ΔOD in oNA and pNA occurs at 484 and 438 nm, respectively. In addition, oNA has a negative transient feature at 640 nm not observed in pNA. A negative feature has been assigned to stimulated emission, and the large red shift from the 400-nm excitation is probably due to a charge transfer occurring at very early times (<0.5 ps).[20] We used a double exponential global fit from 390 to 490 nm to determine the time dynamics of the pNA excited states. There is a short component that has a lifetime of 1.8 ps and a longer component with a lifetime of 5.6 ps. By contrast, only a single exponential global fit from 430 to 530 nm is necessary to determine that the lifetime of the oNA excited state was 6.6 ps. The simple difference in positioning of the nitro group relative to the amine group has implications in the electronic structure and time dynamics of the excited states of these nitro-amines.

In Fig. 3, we show the transient absorption spectra of the nitroaniline energetic, TATB in dimethyl sulfoxide (DMSO). The spectra obtained over a range of time delays show detailed spectral features from the electronic excitations in TATB excited with 400-nm laser light. As discussed in the previous work by De Lucia et al., using global lifetime analysis, TATB was shown to have two prominent excited state components.[19] A short-lived component with a lifetime of 0.72 ps has two absorption features at 477 and 650 nm, while a long-lived component with a lifetime of 4.4 ps has one absorption feature at 420 nm.

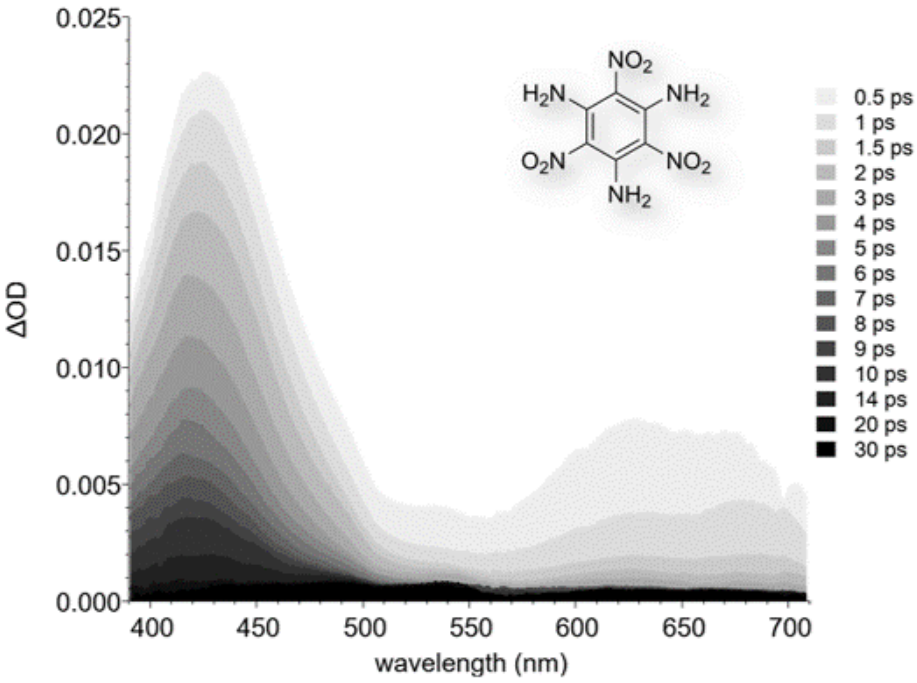

Fig. 3 Transient absorption spectra of TATB at various time delays

We want to emphasize that the improved signal-to-noise allows us to more accurately resolve the excited states and calculate the time dynamics for these nitroaniline compounds. Comparing the transient absorption spectra of the three samples, there are several differences in the transient absorption spectra of TATB compared to those of both pNA and oNA. There is a major absorption feature at 440 nm and another absorption feature at 650 nm. The 650-nm feature is a short-lived excited state (0.72 ps). The lifetime of the 440-nm feature, 4.43 ps, is more comparable to the oNA and pNA features at 484 and 438 nm, respectively. This feature has been assigned to a "hot" ground state or relaxed structure observed in other nitro compounds.[20,21] The differences in the electronic structure of the three nitroamines could have implications for how a material behaves as an energetic, and future studies will look to uncover trends and properties of the excited state dynamics of explosives compared with similarly structured compounds that are nonexplosive.

The excited states of TATB in DMSO via ultrafast heat pulses were also examined, and the results compared to that obtained using the optical pump-probe techniques.[22] The studies revealed that under heating, electronic excitation of TATB molecules occurred at lower energy levels compared to those of the optical pump alone. The findings further validated our hypothesis that ultrafast thermally induced perturbations on the electronic structure of an explosive cause reductions in band gap energies in the explosive. From the study, it shows that the optical

pump-probe technique is a necessary tool to obtain fundamental knowledge in order to develop accurate mechanisms for electronic excitations in the initiation of explosives.

4. Conclusion and Future Studies

The essential key factor during the earliest events of a shock-induced initiation—electronic excitations—has not been the subject of any systematic investigations. This work represents part of our experimental plan to look for similarities and differences among the excitations occurring under optical pump, ultrafast heating, and shock loadings. We have established the capabilities to systematically explore energetic and nonenergetic systems under these different conditions with the intent to deconvolve the complicated chemistry occurring at early times of shock initiations. As reported in this work, we demonstrated that using the optical pump-probe technique can produce reliable data that allow us to fully and accurately obtain important experimental parameters describing the excited states of several nitroanilines. These parameters are essential in validating or enhancing the accuracy of theoretical predictions of explosive performance where electronic excitations occur in the early initial steps.

To answer the question of whether an addition of optical-pumped electronic excitation in an initiation effects performance/sensitivity of an explosive, we have proposed investigations of changes in electronic configurations of explosives under shock/heat loadings that are simultaneously pumped with 400-nm laser pulse. The proposed experimental setup is summarized in Fig. 4 showing ultrafast transient absorption spectroscopy coupled with ultrafast indirect laser heating and ultrafast laser shock. Briefly, Fig. 4 illustrates the sample configurations used in the experiments. A shock/heat pulse generated from the energy release of a metal layer that absorbs the energy from an 800-nm, 100-fs laser pulse will drive into the back side of the sample. From the front side, the sample is then probed with a white light pulse in a reflective configuration using ultrafast transient absorption spectroscopy. To investigate whether the optical-pumped electronic excitation in a shock- or heat-induced initiation effects the performance/sensitivity of an explosive, the sample was simultaneously excited with an additional 400-nm laser pulse from the front side. The transient absorption spectra obtained with and without the optical pump will be compared to elucidate the effects of optical-pumped electronic excitation in a shock- or heat-induced initiation.

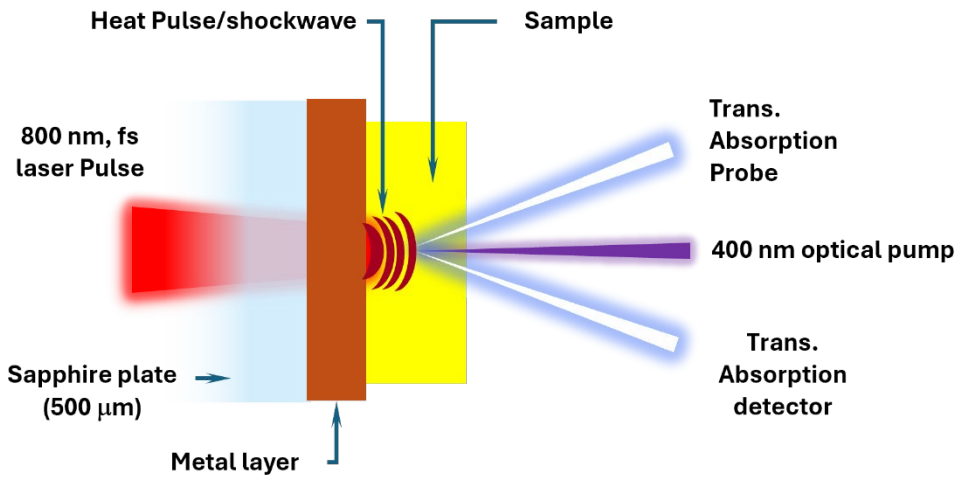

Fig. 4 Experimental scheme for investigating changes in electronic configurations of explosives under shock/heat loadings that are simultaneously pumped with a 400-nm laser pump

5. References

1. Sharma J, Beard BC. Electronic excitations preceding shock initiation in explosives. Mater Res Soc Symp Proc. 1992;296:189.

2. Botcher TR, Landouceur HD, Russel TR. Pressure dependent laser induced decomposition of RDX. In: Schmidt SC, Dandekar DP, Forbes JW, editors. Shock Compression of Condensed Matter-1997: Proceedings of the Conference of the APS Topical Group. 1998;429:989.

3. Aduev BP, Aluker ED, Belokurov GM, Krechetov AG. Kinetics of explosive decomposition of silver azides initiated by a laser pulse. Chem Phys Rep. 1997;16:1479.

4. Owens FJ, Sharma J. X-ray photoelectron spectroscopy and paramagnetic resonance evidence for shock-induced intramolecular bond breaking in some energetic solids. J Appl Phys. 1979;51:1494.

5. Kuklja MM, Aduev BP, Aluker ED, Krasheninin VI, Krechetov AG, Mitrofanov AY. Role of electronic excitations in explosive decomposition of solids. J Appl Phys. 2001;89:4156.

6. Dang NC, Bolme CA, Moore DS, McGrane SD. Shock induced chemistry in liquids studied with ultrafast dynamic ellipsometry and visible transient absorption spectroscopy. J Phys Chem A. 2012;116:10301.

7. Brown KE, Bolme CA, Moore DS, McGrane SD. Ultrafast chemical reactions in shocked nitromethane probed with dynamic ellipsometry and transient absorption spectroscopy. J Phys Chem A. 2014;118:2559.

8. Brown KE, Bolme CA, Moore DS, McGrane SD. Ultrafast shock-induced chemistry in carbon disulfide probed with dynamic ellipsometry and transient absorption spectroscopy. J Appl Phys. 2015;117:085903.

9. Kuklja MM, Aduev BP, Aluker ED, Krasheninin VI, Krechetov AG, Mitrofanov AY. Role of electronic excitations in explosive decomposition of solids. J Appl Phys. 2001;89:4156.

10. Kunz AB, Kuklja MM, Botcher TR, Russell TP. Initiation of chemistry in molecular solids by processes involving electronic excited states. Thermochim Acta. 2002;384:279.

11. 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.

12. Dang NC, Gottfried JL, De Lucia FC Jr. Energetic material response to ultrafast indirect laser heating. Appl Opt. 2017;56(3):B85–B91.

13. 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.

14. Owens FJ, Sharma J. X-ray photoelectron spectroscopy and paramagnetic resonance evidence for shock-induced intramolecular bond breaking in some energetic solids. J Appl Phys. 1980;51:1494–1497.

15. Sharma J, Owens FJ. XPS study of UV and shock decomposed triamino-trinitrobenzene. Chem Phys Lett. 1979;61(2):280–282.

16. Osawa K, Terazima M, Kimura Y. Electron transfer reaction dynamics of p-nitroaniline in water from liquid to supercritical conditions. J Phys Chem B. 2012;116:11508–11516.

17. Yi J, Xiong Y, Cheng K, Li M, Chu G, Pu X, Xu T. A combination of chemometrics and quantum mechanics methods applied to analysis of femtosecond transient absorption spectrum of ortho-nitroaniline. Sci Rep. 2016;6(19364):1–11.

18. Chu G, Lu F, Xin J, Xi T, Shui M, He W, Gu Y, Xiong Y, Cheng K, Xu T. Excited-state dynamics and electron transfer process of 1,3,5-triamino-2,4,6-trinitrobenzene. RSC Adv. 2016;6(60):55560–55567.

19. De Lucia F and Dang N. Study of excited state relaxation pathways of 2,4,6 trinitrobenzene-1,3,5-triamine using transient absorption spectroscopy. DEVCOM Army Research Laboratory (US); 2023 July. Report No.: ARL-TR-9717.

20. Tang L, Fang C. Nitration of tyrosine channels photoenergy through conical intersection in water. J Phys Chem B. 2019;123:4915–4928.

21. Chu G, Yang Z, Xi T, Xin J, Zhao Y, He W, Shui M, Gu Y, Xiong Y, Xu T. Relaxed structure of typical nitro explosives in the excited state: observation, implication and application. Chem Phys Lett. 2018;698:200–205.

22. Dang NC, Gottfried JL, De Lucia FC Jr. The electronic excitation of 2,4,6-triamino-1,3,5-trinitrobenzene in DMSO solution under indirect ultrafast heating: a comparison to results obtained by optical pumped method. DEVCOM Army Research Laboratory (US); 2023 Sep. Report No.: ARL-TR-9773.

List of Symbols, Abbreviations, and Acronyms

DMSO	dimethyl sulfoxide
oNA	ortho-nitroaniline
pNA	para-nitroaniline
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
TATB	2,4,6-trinitrobenzene-1,3,5-triamine
ΔOD	overall change in optical density

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