Spectroscopic Analysis of Time-Resolved Emission from Detonating Thin Film Explosive Samples

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Abstract. We report a series of time-resolved spectroscopic measurements that aim to characterize the reactions that occur during shock initiation of high explosives. The experiments employ time- and wavelength-resolved emission spectroscopy to analyze light emitted from detonating thin explosive films. This paper presents analysis of optical emission spectra from hexanitrostilbene (HNS) and pentaerythritol tetranitrate (PETN) thin film samples. Both vibrationally-resolved and broad-band emission features are observed in the spectra and area as electronic transitions of intermediate species.

INTRODUCTION

Understanding the mechanisms by which shock waves initiate reactions in explosive materials is critical to achieving a predictive understanding of explosive sensitivity and initiation of detonation. Although shock-induced reactions in explosive materials have been extensively studied both experimentally and computationally [1], the nature of even the first reactions that occur under shock are not definitely known at present. To predictively understand how explosives respond to shock, the detailed sequence of events that occurs – mechanical deformation, energy transfer, bond breakage, and first chemical reactions – must be understood at the quantum-mechanical level.

One approach to understanding chemical reaction mechanisms involves identifying intermediate and product species and their quantum state distributions. The identities and rotational-vibrational-electronic state distributions of reaction products, for example, often reveal details about the potential energy landscapes that govern the reaction process. This approach has a long history of success in chemical physics – for example, in understanding photochemical reactions [2]. The approach has been employed in reactions of energetic materials as well; for example, in experiments by Dick *et al.* [3] and Dreger *et al.* [4] on shock-induced reactions in pentaerythritol tetranitrate (PETN). In those investigations, time-resolved emission spectroscopy was used to observe emission from intermediate species, and from the observed spectra, a mechanism for the initial reaction steps was proposed.

This work follows along the lines of Dick *et al.* [3] and Dreger *et al* [4]. We use time- and wavelength-resolved emission spectroscopy to analyze light from detonating thin film explosive samples. Optical emission from the samples is passed sequentially through a spectrometer and streak camera, producing a two-dimensional spectrogram (wavelength vs. time). The thin film samples are used to aid in observation of reactive intermediate species that could be obscured in larger reacting samples. In these experiments, we observe emission in detonating hexanitrostilbene (HNS) and pentaerythritol tetranitrate (PETN) from multiple intermediate species. Vibrationally-resolved emission from hot CN radicals is observed in detonating HNS samples, and broadband emission from as-yet unidentified intermediate species is observed in experiments on both HNS and PETN. These observations are compared with previous observations on shocked and detonating PETN and HNS samples.

EXPERIMENT

Our experiments employ thin films of hexanitrostilbene (HNS) and pentaerythritol tetranitrate (PETN). All samples are prepared by vapor deposition using the techniques described in [5]. Both HNS and PETN are deposited as 200-300 μm thick linear strips on polycarbonate substrates. The PETN films are initiated directly on one end by a parylene flyer, launched by an exploding foil that is driven by a capacitive discharge unit. The HNS films are initiated by a flyer-initiated PETN pellet, and both the HNS film and PETN pellet are held in place using a fused silica plate. Initiation of the samples at one end produces a detonation wave that propagates toward the opposite end of the film. The detonation front passes under a 1 mm diameter fused silica fiber (Polymicro), which directs the emitted light to the streak spectrometer for analysis. Emission is analyzed by passing the light through a 0.3m spectrometer (Princeton Instruments SP300i) equipped with a 300 lines/mm diffraction grating and then to a streak camera (Hamamatsu C7700-1) set to a 2- or 5-μs sweep time. The spectrometer/streak camera combination provides an overall resolution of ~0.5 nm per pixel. The streak spectrometer is calibrated using a mercury-argon lamp and the DAAAC software package (Voss Scientific). The data is corrected for both nonlinear wavelength dispersion and nonlinear spectral intensity response of the system. A series of 4-5 streak spectra are acquired for both HNS and PETN across the 250 – 650 nm range.

RESULTS AND DISCUSSION

Streak spectra of emission from detonating PETN films are shown in Figure 1. Figure 2(a) shows time-integrated spectra, produced by integrating the spectrum in 100 ns segments. The spectrum peaks at ~380 nm at early time, and becomes broader at later times. Figure 2(b) shows a comparison between the late-time emission and a series of blackbody radiation curves. The emitted light does not fit a blackbody spectral distribution, and thermal radiation with the same peak emission wavelength (~425 nm) would imply a temperature of 6,000 – 7,000 K; much higher than the detonation temperature of PETN (3,900 – 4,400K by thermochemical estimates [6]). The radiation also does not correspond to electronic emission from stable detonation products (N_2, H_2O, CO_2, CO, etc.); the observed spectrum is not consistent with a diatomic molecule, and the excited states of the polyatomic species that could produce radiation at these wavelengths are too high in energy to be thermally excited under these conditions. It therefore appears that the observed emission is due to one or more intermediate species.

(a)   (b)
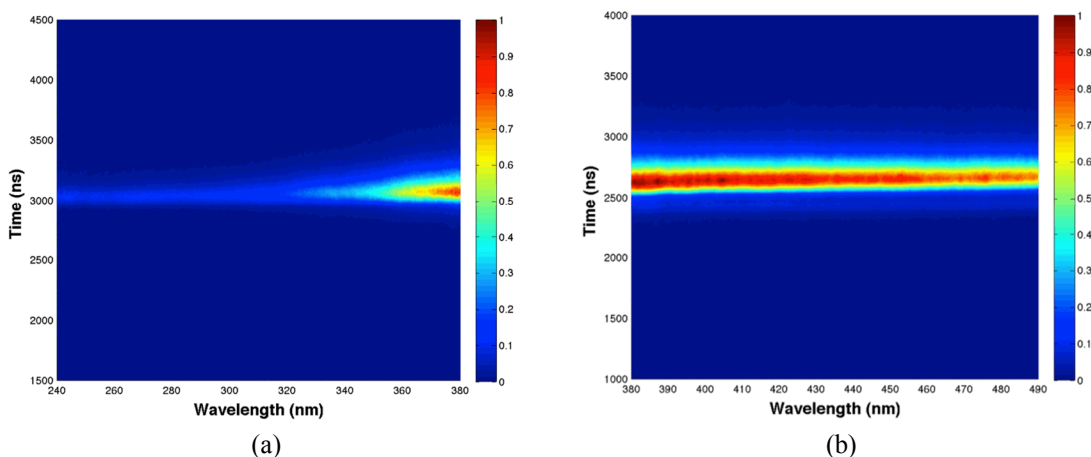
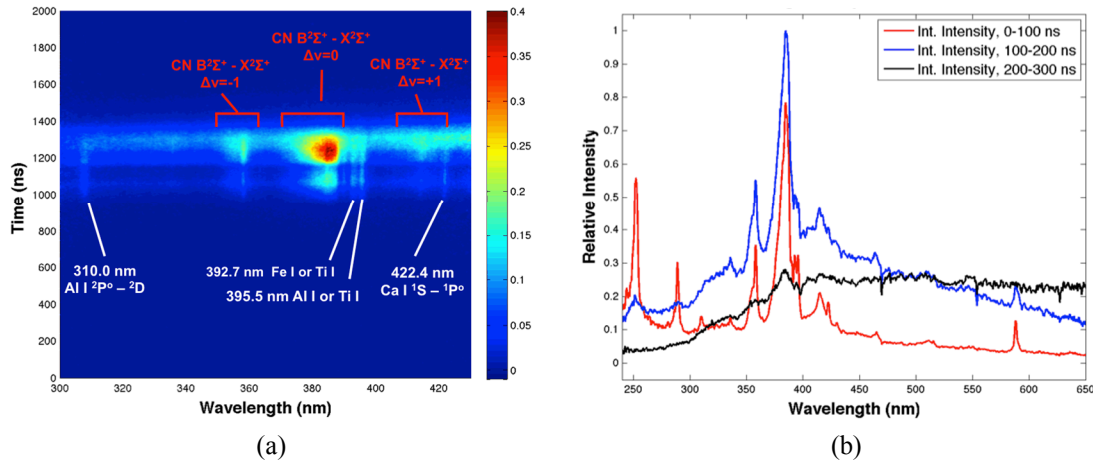**FIGURE 1.** Streak spectra of detonating PETN films. (a) 240-380 nm, (b) 380-490 nm.

One intermediate species that could partially explain the observed spectrum is NO_2. The $\tilde{A}^2B_2$ - X^2A_1 emission spectrum of NO_2 [7] is quasicontinuous, appearing as a broad band with weaker superimposed structure. The emission spectrum begins at 390 nm and peaks between 500-700 nm. NO_2, however, does not emit at wavelengths below 390 nm due to the onset of dissociation to NO + O. The emission we observe may therefore be partially explained by NO_2, but the fact that we observe emission below 390 nm indicates that other species are required to fully explain the observed emission spectrum.

(a)

(b)
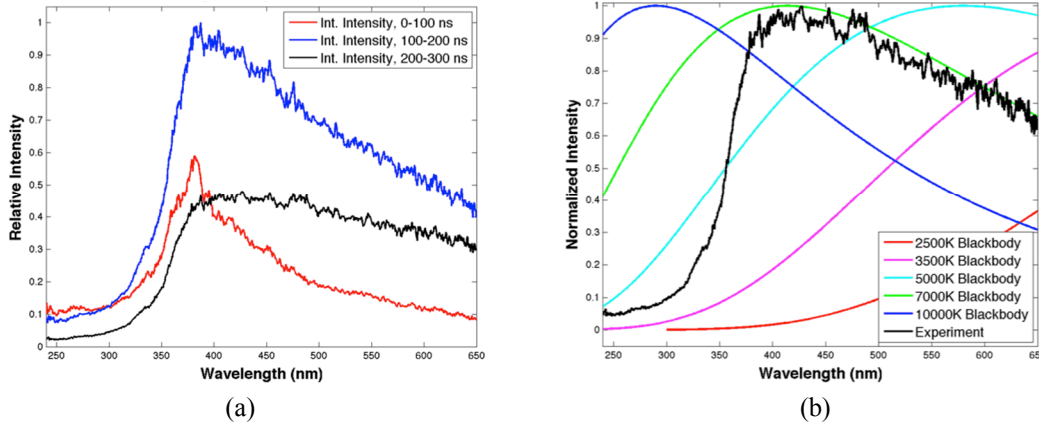
FIGURE 2. Time-integrated intensity of emission from detonating PETN. (a) Integrated intensity from 0-100 ns (red), 100-200 ns (blue), and 200-300 ns (black). (b) Late-time emission compared with blackbody emission curves.

It is interesting to note similarities between the spectra described here and spectra of shocked PETN crystals reported by Dreger *et al.* [4], which show similar spectral distribution and temporal evolution. The spectra reported by Dreger *et al.* appear to consist of two emission bands, a "high-energy" band from 300-500 nm that appears at early time, and a "low-energy" band from ~400-700 nm that appears later, which are interpreted as emission from two electronic states of the NO_2^+ ion. While the conditions of those experiments are quite different from the experiments we report here, it is possible that some features are produced by the same species.

A streak spectrum of detonating HNS film is shown in Figure 3a, and time-integrated spectra are shown in Figure 3b. The spectrum shows molecular emission from detonating HNS, as well as atomic lines from impurities in the fused silica sample fixture. A "ghost" image of the emission spectrum appears prior to the main emission spectrum due to transmission of light through the fused silica fixture. The most prominent molecular emission features are from CN; broadband emission from 250-650 nm is also observed.

(a)

(b)

FIGURE 3. Streak spectra of detonating HNS films. (a) Streak spectrum, 300-430 nm. (b) Time-integrated emission intensity, 0-100 ns (red), 100-200 ns (blue), 200-300 ns (black).

Figure 4(a) shows a simulated spectrum of CN $B^2\Sigma^+$ - $X^2\Sigma^+$ emission using the software PGOPHER [8] and molecular constants from [9]. An adequate fit to the experimental data requires rotational and vibrational temperatures of 10,000K. Lower vibrational temperatures fail to account for the intensity of the $\Delta v=\pm 1$ bands, and lower rotational temperatures fail to account for the rotational contours. 10,000K is much higher than the detonation temperature of HNS (3,600 – 3,700K by thermochemical estimates [6]). Although the mechanism by which CN is produced is not known, it is clear that the observed CN is produced with higher rotational and vibrational excitation than expected under equilibrium conditions. Figure 4(b) compares the late-time emission with a series of blackbody

curves. Blackbody radiation fails to account for the observed broadband radiation, which must therefore be produced by one or more intermediate species. As for PETN, emission from NO_2 may account for some of these observations, but additional species are required to account for emission with wavelengths <400 nm. Our observations are consistent with those of Trott and Renlund [10] on detonating HNS pellets, in which emission from CN was also observed, along with broadband emission from ~400–500 nm, attributed to emission from NO_2.
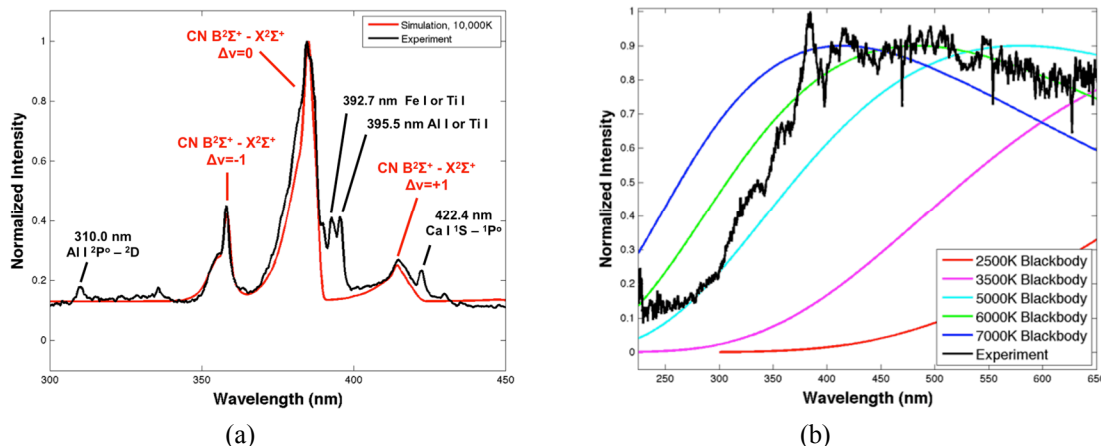
FIGURE 4. Time-integrated spectra of detonating HNS films. (a) Comparison of spectrum with simulated CN spectrum, with rotational and vibrational temepratures set to 10,000K, (b) Comparison of late-time emission with blackbody emission curves.

Future experiments will be performed to determine the identity of the species responsible for the observed broadband emission in both PETN and HNS. Comparison of these results with mass spectrometry experiments of by Fajardo *et al.* [11] are expected to be useful. Impact experiments, in which emission from the film is monitored after controlled impact of a thin flyer, may also help isolate the early stages of reaction.

ACKNOWLEDGMENTS

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