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SHOCK INITIATION OF PENTAERYTHRITOL TETRANITRATE CRYSTALS: OPTICAL ABSORPTION AND EMISSION STUDIES

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Absorption and emission spectra of initiating crystals are obtained at two times during initiation, and a time-resolved record of integrated light is obtained during plane-wave shock initiation of single crystals of PETN at 4 GPa. Time-resolved photodiode records clearly show an induction time during which the crystal becomes absorbing, a region of increasing emission with increasing shock travel time, and termination of emission by the returning rarefaction. Evidence exists for emergence of a superdetonation wave at least 1.5-mm behind the shock front. Resolved spectroscopic records identify the absorbing region as shocked PETN, and suggest evolution of NO_2 and NO as part of the early chemistry in the initation.

1. INTRODUCTION

Shock initiation sensitivity of single crystals of pentaerythritol tetranitrate (PETN) has been extensively studied.[1,2,3] It has been shown that PETN sensitivity depends on the orientation of crystal axes relative to the direction of shock propagation, with the <110> orientation proving most sensitive.[2] An anomalously high sensitivity of the <110> orientation around 4 GPa corresponds with light emission, as determined in photographic (framing camera) records, suggesting the utility of spectroscopic experiments in determining the mechanism of initiation.

Behavior at 4 GPa has been studied in detail using optical absorption and emission spectroscopy as part of a thorough study.[4]

2. EXPERIMENTAL

PETN crystals were shocked with plane waves generated in a single stage light gas gun at pressures between 3.45 and 4.37 GPa. Absorption spectra were measured during shock traversal of the crystal using a projectile with an internal mirror to direct illumination from a 1000W arc lamp through the crystal. A field lens and a mirror direct the transmitted light to detection optics. Emission spectra were measured similarly, without the illumination mirror. The spectrum was dispersed with a 1 m monochrometer and acquired at two times with two optical multichannel analyzers with image intensifiers.

3. RESULTS AND DISCUSSION

Time-resolved records were obtained from photodiode output voltages. Photodiode records for several experiments are shown in Figure 1. Absorption experiments are characterized by non zero initial intensity, as the arc lamp shines through the unshocked crystal. Transmission is extinguished 0.2 to 0.3 μsec after the shock wave enters the material, and is replaced by emission of linearly increasing intensity which overtakes the intensity of the arc lamp signal. The emission spectrum confirms that this light has its origin within the shocked crystal. Absorption and emission records are considered to be indistinguishable after the first 0.2 to 0.3 μsec, since the opacity of the shocked crystal terminates light from the arc lamp. Two records show an inflection on the rise and a single peak. The other records show a double peak structure, followed by a decay. This decay is initially exponential, and may or may not continue to zero light level.

Analysis of the data is facilitated by comparison of the record with the x t diagram, as shown in Figure 2.

The induction time for emission is consistent with a zone of highly absorbing shocked PETN existing

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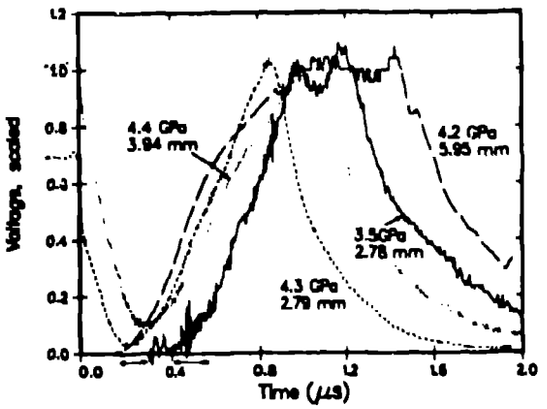

FIGURE 1.
Photodiode records from several absorption and emission experiments.

Immediately behind the shock wave, with a thickness of 1.2 mm for <001> and 0.6 mm for <110>. This early absorbance is most likely attributable to the increased absorption observed across the entire visible spectrum for shocked PETN,[4] possibly due to scattering from inhomogeneities generated during inelastic deformation in the shock. This phenomenon is consistent with other observations[4] of an 0.2 μsec induction time for reaction observed in other experiments.

Emission intensity is approximately linear with shock run distance, suggesting linear buildup of light with linear increase in thickness of emitting species. That the shape of the rise does not reflect the existence of the absorbing region, except at its start and finish, indicates that the absorbing region behind the shock maintains a constant thickness. The slight inflection in photodiode records for shots at 4.2 and 4.4 GPa results from arrival of a rarefaction wave at the PETN anvil interface, at the back of the shocked region in the PETN. That this has an immediate effect on the intensity indicates that a nontrivial fraction of the emitted light has its source deep in the shocked region, in this case, at least 2.1 to 2.5 mm behind the shock front. Other evidence for emission from a broad zone behind the shock front includes the exponential decay of detected light intensity on arrival of the rarefaction.

Comparison of photodiode records and x-t diagrams for the shock experiments producing them shows that the maximum in emission intensity occurs about 0.15 μsec after the arrival of the shock at the free boundary of the crystal and the start of the rarefaction.

This time interval is exactly half the time required for onset of emission in any particular experiment. This behavior is consistent with an absorbing zone occupying 0.75 to 1.5 mm (0.20 to 0.40 μsec) behind the shock. The returning rarefaction first passes through this absorbing region, then, at a penetration depth of 0.6 to 0.8 mm, begins to quench the emission, travelling back through the emitting material. A smooth decay is observed as the returning rarefaction progresses, which confirms that the reaction is evolving at a rate sufficient to reach a steady state intensity before arrival of the rarefaction. Figure 2 shows correlation of the x-t diagram with the photodiode record for the 3.5 GPa experiment. Other photodiode records show longer decay periods before arrival of the superdetonation wave. The record at 4.2 GPa shows a flat region that corresponds to the development of the intermediate-velocity shock.

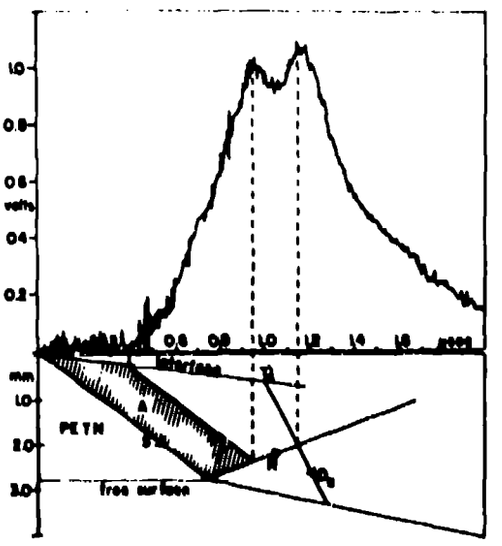

FIGURE 2.
Correlation of photodiode record with x-t diagram for experiment.

A second peak is visible in shots G753 and G784, shown in Figure 1, but not in shots G781 and G782. This second peak can be correlated with the expected intersection of the superdetonation and the rarefaction. The emergence of the superdetonation as a peak in the intensity supports the idea of continuing reaction of the material behind the shock, which is developing into the superdetonation. In G782 and G781, where the superdetonation does not develop in time to be observed, the light level returns to zero as the rarefaction completes its return through the PETN crystal.

Absence of the superdetonation in shots G781 and G782 may further suggest the importance of continuing reaction in the shocked material in promoting development of the superdetonation. In both shots, the returning rarefaction from the fused silica anvil reduces the pressure at 0.75 and 0.60 μsec behind the shock wave, respectively, 0.25 to 0.4 μsec before the anticipated onset of superdetonation, if the superdetonation wave is imagined to originate at the back surface of the crystal, at the earliest possible time. The drop in pressure deep within the shocked region apparently inhibits emergence of the superdetonation on the usual timescale.

Consideration of the data in terms of a more sophisticated model for emergence of the superdetonation in homogeneous initiation leads to even more satisfactory correlation between the x-t diagrams and the data. Gradual increase in velocity of the reactive wave explains why the onset of the second emission peak occurs after the anticipated start of a linear superdetonation.

From the Beer-Lambert Law, the exponential decay of the emission intensity is consistent with light from a source of constant intensity passing through a region of linearly increasing depth with extinction coefficient $\epsilon = 1.33 \times 10^{-20}$ cm^2. For comparison, 6.64×10^{-22} cm^2 is the upper bound for ϵ in the spectral region above λ 433 nm in unshocked material.[5] This factor of 20 between extinction coefficients is consistent with the value of about 40 obtained from comparison of absorbance of PETN shocked in a ringup experiment with absorbance of unshocked material.

Deviations from true exponential decay indicate bright emission at late times, as the rarefaction samples material at increasing depth in once-shocked material. Where a superdetonation can form, these deviations from exponential decay become large, indicating that the rarefaction does not completely quench the superdetonation. Nonlinear distribution of light intensity behind the shock, increasing to the level of a superdetonation, is consistent with more sophisticated models describing the gradual increase in amplitude of the reactive wave.

2.1. Spectra

Spectrally resolved emission records suggest the identity of the emitting species. Since decomposition is underway in the process of shock initiation of detonation, the radiance is probably due to chemiluminescence from species generated by PETN decomposition. The shock-induced temperature rise in the bulk is only about 100 °C.

The spectral records shown in Figure 3 are treated as absorption and emission spectra superimposed, with cutoff of light at 320 nm attributed to self-absorption by shocked PETN in the dark zone preceding emission, as well as to the unshocked PETN, according to the absorption profile determined in the ringup experiment. Where both this dark zone and unshocked

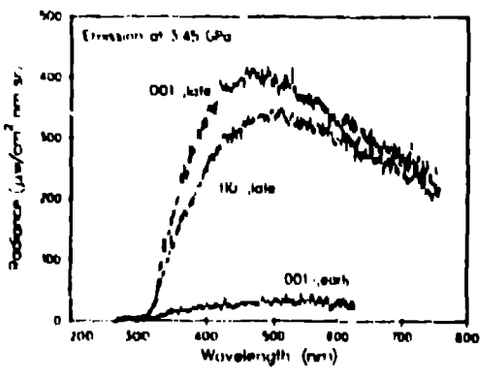

FIGURE 3.
Spectrally resolved emission from PETN shocked to 3.45 GPa.

material are eliminated in the ringup experiment, the cutoff is shifted accordingly to 270 nm, and the total intensity is increased.

In records from experiments G782 and G781, the cutoff appears to shift as the absorption edge is saturated by increasingly bright emission. Emission profiles suggest the NO_2 $A(^2B_2)$ state as the emitting species, as the NO_2 $A(^2B_2) - X(^2A_1)$ transition is most often observed and exhibits a broad profile like that evident in emission from photodissociation of nitromethane,[6] in which spectra of NO_2 A-X emission are observed. These spectra have a band maximum of about 600 nm, whereas 470 nm is the maximum observed in this experiment and in the spectrum of NO_2 arising from a detonating hexanitrostilbene free surface.[7] Very high local temperatures in the PETN crystal may account for this shift, or shock induced profile broadening resulting from changes in the molecular potentials under shock conditions[8] may contribute, if they are exceptionally large in this case. A more striking discrepancy between the data and the spectrum expected for the NO_2 $A(^2B_2)$ - $X(^2A_1)$ transition is the emission in the region below 390 nm, which should be terminated by predissociation of the NO_2 A state. Possibly, a second emitting species gives light below 390 nm. Emission for the NO $B(^2\Pi_{3/2})$ - $X(^2\Pi_{1/2})$ transition has been observed between 240 nm and 520 nm, peaking at 390 nm,[9] and could account for light observed between 390 nm and 270 nm. The short timescale on which the NO must emerge makes NO unlikely to be a secondary product. The formation of both NO_2 and NO is consistent with molecular mechanics expected in deformation of the crystal along slip planes.[4] No other evidence for formation of NO is available. The relatively short 0.2 μsec lifetime of the NO B state may permit NO to exhibit emission intensity higher than that of NO_2, out of proportion to its relative abundance.

Since the shock energy, about 1287 cm^{-1}, is insufficient to directly excite NO_2 above the first few vibrational states, production of electronically excited NO_2 must depend on a specific reaction mechanism for the decomposition of the shocked PETN, for example, a mechanism by which the molecular mechanical processes localize the shock energy in particular reactive modes. Molecular distortion along glide planes in the crystal, besides being correlated with the shock initiation sensitivities of the orientations, may be governing the geometry of the decomposition mechanism at the molecular level.

4. SUMMARY

In the initiation of PETN crystals at about 4 GPa, integrated light levels correlated with the shock state of the material indicate that light emission occurs behind the shock wave, increases as superdetonation occurs, and decreases when rarefactions reduce pressure. The source of the light may be related to the chemical origin of the initiation process. Resolved spectra of the emission indicate that it is due to excited NO_2 and possibly NO. Appearance of these species is consistent with molecular interactions expected for motion along glide planes in the <110> and <001> orientations.

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