Polymorphism and decomposition of HE single crystals: Insight from static and shock compression experiments

Z A Dreger
Institute for Shock Physics, Washington State University, Pullman, WA 99164, USA
E-mail: dreger@wsu.edu

Abstract. Understanding the reactive behaviour of high explosive (HE) crystals at thermo-mechanical conditions generated by shock-waves is an important step toward understanding shock-wave initiation of these crystals. Despite the significant differences in time scales and loading rates, static high pressure and high temperature (HP-HT) experiments can provide key results regarding structural and chemical processes in HE crystals at pressures and temperatures relevant to shock initiation. Here, we present selected examples for utilizing optical spectroscopy to understand molecular processes in HE crystals at static HP-HT conditions to gain insight into their shock initiation mechanisms. The relevant results obtained from static studies up to 15 GPa and 700 K on polymorphism and decomposition are presented for cyclotrimethylene trinitramine (RDX) and pentaerythritol tetranitrate (PETN). This work demonstrates that the static HP-HT results in conjunction with shock-wave experiments provide an important approach to elucidate processes related to the initiation of shocked HE crystals, including polymorphic transitions, conformational changes, identification of crystal phases at decomposition, and mechanisms governing shock induced decomposition.

1. Introduction
Shock wave initiation of high explosives, HE, crystals is a complex process and the fundamental molecular processes that take place during decomposition are not easily identified in shock experiments. Therefore, complementary work under static high pressure and high temperature (HP-HT) is required to aid the insight into processes under shock compression. Here, we present selected examples to demonstrate a recent progress in understanding the response of HE crystals of cyclotrimethylene trinitramine (RDX) and pentaerythritol tetranitrate (PETN) to high pressures and high temperatures using primarily optical spectroscopy [1-5]. Both, RDX and PETN are extensively used in explosives and monopropellants formulations, thus their behaviours at thermo-mechanical conditions generated by shock-waves are of particular interests. Specifically, here we discuss the static high pressure data that were instrumental in assisting the shock results regarding the polymorphic and conformational transitions, determination of crystal phase at the decomposition and in understanding the role of pressure and temperature in accelerating shock induced decomposition.

Extensive spectroscopic and x-ray diffraction studies have shown that, depending on the external conditions, RDX can exist in several polymorphic phases: $\alpha$, $\beta$, $\gamma$, $\delta$, and $\varepsilon$, e.g. see [4] and references therein. Three of these phases ($\alpha$, $\gamma$, and $\varepsilon$) can exist at HP-HT conditions, and can, therefore, contribute to decomposition. However, it was not clear if these phases can also exist under shock conditions. Furthermore, early reports conjectured that the $\varepsilon$-phase (incorrectly identified as $\beta$-phase
initially) [6, 7] can play an important role in shock-induced decomposition. Thus, here we address these issues by comparing the results under static and dynamic compressions.

PETN has attracted considerable scientific attention due to its anisotropic sensitivity to shock-wave initiation [8, 9]. In particular, a model was developed that linked the observed anisotropic sensitivity to differences in molecular changes occurring in crystals shocked along different orientations [10]. Specifically, the large sensitivity observed for shocks along the [110] orientation was attributed to shear deformation-induced conformational changes in PETN molecules. Afterwards, real-time, high spectral resolution Raman measurements on shocked PETN revealed new features in the spectra of crystal shocked along the [110] orientation (sensitive) [11]. They were temporarily attributed to conformational changes based on some similarities to static compression spectra [12]. As we present here, the recent work on statically compressed PETN indicated the importance of nonhydrostatic stresses for inducing the conformational changes [5].

2. Experimental Approach
All experiments were performed with single crystals. Large oriented crystals of RDX and PETN used in shock experiments were provided by Dr. D. E. Hooks from Los Alamos National Laboratory. Small crystals for static experiments were grown in house from acetone solution. Static high pressure experiments were performed in a heated diamond anvil cell (DAC). Cryogenically loaded argon was mostly used as a pressure transmitting medium. However, some experiments were performed with glycerol to examine the effects of nonhydrostaticity. Ruby fluorescence was used to monitor pressure. Temperature of the DAC was controlled using a resistive heater wrapped around the cell. The sample temperature was monitored with iron-constantan thermocouples. A micro-Raman system (T64000, JY-Horiba) equipped with a microscope (Olympus BX-40), utilizing a 532 line from a cw diode-pumped solid-state laser, was used for Raman spectra measurements. Experimental details for static compression measurements can be found elsewhere [2, 4].

For shock experiments, oriented, single crystals of RDX were prepared with dimensions of 7 x 7 x 0.4 mm³ and confined between two optical windows. Shock waves were generated by impacting the target assembly with quartz or sapphire crystals launched by a single stage light-gas gun. Because of the impedance mismatch between the optical windows and HE crystals, the sample was compressed under stepwise loading. Three experimental techniques were used to obtain the Raman and emission spectra. High spectral resolution Raman measurements were performed with a single 20 ns pulse from a Nd:YAG (532 nm) laser. Time-resolved Raman measurements were obtained with a 2 µs pulse from a tunable dye (514.5 nm) laser. In the emission experiments, light produced by the shocked crystal was detected by the spectroscopic system to provide time-resolved emission spectra. Details of shock experiments and detection techniques can be found elsewhere [13-15].

3. Results and Discussion
3.1. RDX
Our previous work on RDX demonstrated that static compression results are useful for elucidating processes under shock compression. In particular, changes in the Raman spectra under static compression were used to understand the phase changes in shocked RDX crystals. The $\alpha-\gamma$ phase transition, well established under static compression and recognized by characteristic changes in the Raman spectra around 4 GPa, was shown to occur on nanosecond time scales under shock compression [14, 16].

Here, we show that the results obtained from statically-compressed RDX can aid in understanding the initiation processes in shocked RDX. To properly account for shock-induced decomposition of RDX, we need to know the crystal phase at the onset of decomposition. In figure 1, we present the result of shock experiment to peak stress of 10 GPa [15]. The figure includes the CCD image of Raman signal in the CH₃ stretching modes region, stress profile in the crystal during the shock
reverberation between two optical windows, and Raman spectra at the selected times. As can be seen from the CCD image, there is discontinuity in Raman peaks shift at the shock entry and then evolution of modes with time and reverberating stress. At 200 ns crystal is already in gamma-phase, as indicated by characteristic features in the spectrum. However, at later times there is gradual increase of light emission, which finally dominates the spectrum. Because, the emitted light was shown to be associated with the chemical decomposition, the presence of Raman and emission signal at the same time can be used for identifying the phase of crystal which decomposes under shock compression.

Previous reports speculated that the ε-RDX can be responsible for RDX reactivity under shock conditions [6, 7]. We examined this conjecture by comparing the Raman spectra obtained from a shocked, decomposing crystal with the spectra of statically compressed ε- and γ-RDX. The three spectra, measured at comparable pressures, are shown in figure 2.

Figure 1. CCD image and selected time-resolved Raman spectra of the CH$_3$ stretching modes of [111] oriented RDX crystal shocked in a stepwise loading to the peak stress of 10 GPa. Shock enters crystal at 0 ns. At ~ 200 ns crystal transforms to γ-phase and 95% of peak stress is reached at about 400 ns. At ~ 450 ns a broadband emission starts and after ~ 600 ns Raman peaks can no longer be resolved from the emission.
When comparing these spectra, one should keep in mind that the shocked crystal spectrum was obtained as a time-resolved (~ ns resolution) spectrum, with a single-pulse laser excitation on a sample undergoing decomposition. Thus, this spectrum has a lower signal-to-background ratio than the two other spectra, and the interpretation of the low intensity peaks requires care. Furthermore, peaks in the shocked spectrum are broad due to both thermal broadening and lower spectral resolution of the detection system than that used in static experiments. Despite of these limitations, it is clear from figure 2 that the spectrum quality of the shocked crystal is sufficient to make useful comparisons.

Examination of the three spectra reveals several features that can be used to infer similarities between the shocked spectrum and the other two spectra. Below 1100 cm\(^{-1}\), there are two peaks between 300-400 cm\(^{-1}\) and peaks around 1080 cm\(^{-1}\) that are present in both, the shocked crystal and \(\gamma\)-phase spectra, but not in the \(\varepsilon\)-phase spectrum. Furthermore, the shape of the CH stretching modes, in particular around 3000 cm\(^{-1}\), in the shocked crystal spectrum resembles the \(\gamma\)-phase rather than the \(\varepsilon\)-phase. Overall, the Raman features provide good evidence that shock-induced decomposition in RDX takes place from the \(\gamma\)-phase but not \(\varepsilon\) or other phases. This conclusion is consistent with the P-T diagram shown in figure 2 (panel c). Because shock induced-decomposition in RDX crystals is observed at stresses above ~ 5-6 GPa, the phase diagram in this figure makes a good case that decomposition starts from the \(\gamma\)-phase. This finding addresses a long lasting question: What is the RDX phase at decomposition? Resolution of this issue is central for modeling the shock-induced decomposition of RDX.

![Figure 2](image.png)

**Figure 2.** Comparison of Raman spectra of statically compressed \(\gamma\)-RDX and \(\varepsilon\)-RDX with spectrum of a shocked RDX crystal in the low frequency range (a) and in the CH\(_3\) stretching modes range (b). The spectra for the \(\varepsilon\)- and \(\gamma\)-RDX were measured at 9.6 and 9.8 GPa, respectively, after quenching to room temperature. The spectrum of shocked RDX was measured at a peak stress of 10 GPa on a [111] oriented crystal. New phase diagram of RDX is shown in panel c [2, 4]. The circle indicates the projected region of shock-induced initiation of RDX.

Under shock compression, separating the role of pressure and temperature on decomposition is difficult because the two are coupled. However, the static HP-HT study on \(\gamma\)-phase decomposition has provided important insight into the role of pressure and temperature in the shock-decomposition of...
RDX. Our previous shock compression studies on RDX showed that the extent of decomposition can be monitored using the light emitted from the decomposing crystal [15]. Subsequently, we found that this light emission increases with the shock stress. Furthermore, the emission rate or the rate of decomposition increases markedly with shock pressure above ~ 10 GPa, as seen in figure 3 (panel a). At first glance, this result could suggest that pressure increase is responsible for the observed increase in decomposition rate. However, under shock compression, increase of pressure is also accompanied by an increase of temperature. We have used the HP-HT studies to separate these effects, as pointed below.

![Figure 3](image_url)

**Figure 3.** Pressure effects on (a) light emission rate from shock-compressed decomposing RDX crystal and (b) decomposition rate of statically compressed γ-RDX at several temperatures.

The static compression results show that at a given temperature the γ-phase decomposition rate decreases with pressure, as shown in figure 3 (panel b). However, the decomposition rates also rapidly increase with increasing temperature, at various constant pressures. Thus, the static compression results reveal that pressure and temperature have opposite effects on the γ-phase decomposition rates: pressure decelerates decomposition while temperature accelerates decomposition. This finding has important implication for understanding the observed acceleration of decomposition under shock compression, figure 3 (panel a), and implies that temperature plays the dominant role in this acceleration.

### 3.2. PETN

The previous work on PETN under static compression provided contradicting results, which depended strongly on experimental conditions, including the quality and state of samples and pressure, e.g. see [5] and references therein. Therefore, to avoid inconsistencies due to random sample morphology, grain interactions, and uncertain compression conditions, the experiments reported here were performed using good quality single crystals and under controlled pressure loading. Under these conditions, we have found that nonhydrostaticity plays important role in driving the phase transitions in PETN crystals [5].
In figure 4, we demonstrate the effect of nonhydrostaticity on the changes in Raman spectra. For this, we have compared spectra obtained in glycerol with those in argon, at transition pressures obtained for each media. It is clear that spectral changes occur at very different pressures in the two media: at 5.3 and 9.2 GPa, respectively, in glycerol and in argon. Despite this large difference in pressure, the spectra shapes are quite similar. Both spectra exhibit comparable patterns of peaks either in the range 600 - 680 cm\(^{-1}\), 5 peaks, or 680 - 800 cm\(^{-1}\), another 5-6 peaks. Also, in the range of CH\(_3\) stretching vibrations there are clear splitting of two modes in both cases. Qualitative agreement of these results suggests that regardless of the large difference in pressures, PETN undergoes the same transformation; PETN-I to PETN-III [5]. Furthermore, as we show in figure 4, the experimental spectra are in good agreement with features in the calculated spectra for the C\(_2\) molecular conformer. The approach for calculating the vibrational spectra of PETN molecular conformers was presented in our earlier paper [12]; we note that the calculations were performed using a single molecule. Despite this simplification, we demonstrated that this approach provided a good approximation to the experimental spectrum at ambient conditions [12]. The close similarity of the experimental spectra to the calculated spectra for C\(_2\) molecular conformer further supports our previous proposal of the molecular symmetry change from S\(_4\) to C\(_2\) under high pressure. However, the pressure onset for this transformation depends on the pressure transmitting media and demonstrates that nonhydrostaticity is an important factor in driving this transition.

![Figure 4](image.png)

**Figure 4.** Selected Raman spectra of PETN obtained in argon and glycerol pressure media and calculated for C\(_2\) symmetry of a single PETN molecule. (a) Spectral region including the CCC deformation modes and (b) spectral region of CH\(_3\) stretching modes.

As we show below, the static results provided further support for the conformational changes proposed to explain the anisotropic response of shocked PETN single crystals [11, 12]. In figure 5, we compare Raman spectra of PETN crystals in the CH\(_3\) stretching region under both static and shock-wave compressions. The static compression spectra represent measurements under hydrostatic and nonhydrostatic compressions at \(\approx 5.3\) GPa, figure 5 (panels a and b). The shock compression data
were obtained for a crystal shocked to a peak stress of 6.5 GPa along the [110] and [100] directions; figure 5 (panels c and d). While comparing the shock and static spectra, we need to point out that the shocked spectra were obtained with a single-pulse laser excitation. Thus, these spectra have lower signal-to-background ratios and lower spectral resolutions than the static spectra.

From the comparison, two aspects are evident: (i) spectrum obtained under shock compression for [100] orientation is similar to spectrum obtained under hydrostatic compression and (ii) spectrum obtained under shock compression for [110] orientation is similar to spectrum obtained under static, nonhydrostatic compression. In the first case, both spectra show no sign of phase transition, implying that shock compression along the [100] direction cannot induce conformational changes. It is consistent with insensitivity of this direction to shock initiation [8]. On the other hand, in the second case, a similar pattern of four peaks is observed, suggesting that the high pressure structures under shock along the [110] direction and static (nonhydrostatic) compressions are likely the same. Since the changes under nonhydrostatic compression, as shown in figure 4, can be attributed to PETN-I to PETN-III transformation and associated with conformational changes, this result provides further support for the proposed conformation change in PETN shocked along the [110] direction [11, 12]. It also emphasizes the importance of plastic deformation on the initiation process in PETN crystal.

4. Final Remarks
We presented selected examples to demonstrate a recent progress in understanding the polymorphic and decomposition processes in RDX and PETN; two important HE crystals. Using Raman spectroscopy under static compression we provided new insight into the factors responsible for reactive behavior of RDX and PETN at the conditions relevant to shock-wave initiation. In

![Figure 5](image_url)
conjunction with spectroscopic shock data we provided evidence that: (i) the $\alpha$-\(\gamma\) phase transition precedes the shock-induced decomposition in RDX, (ii) temperature plays a dominant role in accelerating the decomposition in RDX under shock compression, (iii) nonhydrostaticity is a significant factor in driving the phase change in PETN crystal, and (iv) conformational changes can play important role in initiation and anisotropic sensitivity of PETN under shock-wave compression. This work demonstrates that spectroscopic studies under static compression provide the critical complementary route for elucidating the molecular processes in shocked HE crystals.

Acknowledgments
Prof. Y. M. Gupta is sincerely thanked for many contributions to this work. This work was supported by DOE/NNSA Grant DE-NA0000970 and ONR/MURI Grant N00014-06-1-0459.

References
[1] Dreger Z A and Gupta Y M 2010 J. Phys. Chem. A 114 7038
[2] Dreger Z A and Gupta Y M 2010 J. Phys. Chem. A 114 8099
[3] Dreger Z A and Gupta Y M 2012 J. Phys. Chem. A 116 8713
[4] Dreger Z A, McCluskey M D and Gupta Y M 2012 J. Phys. Chem. A 116 9680
[5] Dreger Z A and Gupta Y M 2013 J. Phys. Chem. A 117 5306
[6] Baer B J, Oxley J, and Nicol M 1990 High Pressure Res. 2 99
[7] Miller P J, Block S and Piermarini G J 1991 Combustion and Flame 83 174
[8] Dick J J 1984 Appl. Phys. Lett. 44 859
[9] Dick J J 1997 J. Appl. Phys. 81 601
[10] Gruzdkov Y A and Gupta Y M 2000 J. Phys. Chem. A 104 11169
[11] Hemmi N, Dreger Z A, Gruzdkov Y A, Winey J M and Gupta Y M 2006 J. Phys. Chem. B 110 20948
[12] Gruzdkov Y A, Dreger Z A and Gupta Y M 2004 J. Phys. Chem. A 108 6216
[13] Hemmi N, Zimmerman K A, Dreger Z A, and Gupta Y M 2011 Rev. Sci. Instrum. 82 083109
[14] Patterson J E, Dreger Z A and Gupta Y M 2007 J. Phys. Chem. B 111 10897
[15] Patterson J E, Dreger Z A, Miao M S and Gupta Y M 2008 J. Phys. Chem. A 112 7374
[16] Dreger Z A and Gupta Y M 2007 J. Phys. Chem. B 111 3893