Static and shock compression of RDX single crystals: Raman spectroscopy

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Abstract. We report an examination of the polymorphic $\alpha$ – $\gamma$ transformation for the energetic crystal RDX under static and shock compression. Raman spectroscopy was utilized as a probe of the molecular level response. We observed splitting of several Raman modes with the occurrence of the phase transition. From the response of the lattice and internal modes to static compression, we propose that the $\gamma$ phase structure is isomorphous with the $D_{2h}$ point group with eight molecules per unit cell occupying $C_1$ symmetry sites. The phase transition was observed to occur under shock wave loading with a transition time of $\sim$100 ns for a peak stress of 5.5 GPa. The occurrence of the phase transition under shock wave loading has important implications for the onset of chemical decomposition in RDX.

1. Introduction
The response of energetic materials to high pressures has important relations to sensitivity, performance and safety. Energetic materials are highly compressible and often undergo polymorphic transformations. Structural changes accompanying these transformations can affect the sensitivity to shock wave initiation. Therefore, it is important to characterize the physical response of energetic materials under both static and dynamic compression.

In this paper, we report on the structural stability and high pressure polymorphism of single crystals of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). Pressure effects were examined under hydrostatic compression to 15 GPa and under shock wave compression to 5.5 GPa. RDX is known to exist in three polymorphic phases, termed $\alpha$, $\beta$, and $\gamma$.[1,2] The ambient $\alpha$ phase structure belongs to the orthorhombic $Pbca$ space group with eight molecules per unit cell. The three nitro ($-\text{NO}_2$) groups are chemically inequivalent, with two in the axial (A) position and one in the equatorial (E) position (the AAE conformer).

The $\beta$ phase exists primarily under conditions of high pressure and high temperature. The molecular symmetry is believed to be $C_{3v}$, with all three nitro groups in the axial position (the AAA conformer). The $\gamma$ phase exists at ambient temperatures above 3.8 GPa. Raman spectroscopy, particularly of the CH stretch modes [2], is sensitive to this phase transition. For this reason, we use Raman spectroscopy to study the structural changes that accompany the $\alpha$ – $\gamma$ phase transition under both hydrostatic [3] and dynamic compression.[4]

2. Experimental Methods
Small, single crystals of RDX were used for hydrostatic compression experiments. Static pressures were generated in a modified Merrill-Bassett type diamond anvil cell (DAC). The sample
compartment was formed from a pre-indentented 0.06 mm thick stainless-steel gasket with a central hole of 0.18 mm diameter. Cryogenically loaded argon was used as hydrostatic pressure transmitting medium. A cw Ar-ion (514.5 nm) laser was employed for Raman excitation. The resolution of Raman spectra was ~0.8 cm$^{-1}$. All experiments were carried out at room temperature.

For shock experiments, single crystals of RDX were prepared with dimensions of 7 x 7 x 0.4 mm$^3$ and confined between two Z-cut quartz windows. Crystals were of the [111], [210] or [100] orientation. Shock waves were generated by impacting the target assembly with a Z-cut quartz crystal launched with a light gas gun. Peak stresses were between 3.0 and 5.5 GPa. High-resolution Raman spectra were measured with a single 20 ns pulse from a Nd:YAG (532 nm) laser. Time-resolved measurements were obtained with a 2 µs pulse from a tunable dye (514.5 nm) laser.

3. Static Compression

3.1. Lattice modes

Raman spectra of the lattice modes provide insight into the structural changes that accompany the $\alpha - \gamma$ phase transition. Figure 1 depicts spectra of the lattice modes at 4.0 and 6.1 GPa. Group theory considerations predict 24 Raman active lattice modes in the $\alpha$ phase. From the experiment, we were able to distinguish 9 lattice modes.

As the pressure is increased, the modes shift to higher frequency, as shown in Figure 2. Above the phase transition, the number of peaks increases from 9 to 12, but remains below 24. Note that the low frequency internal modes exhibit pressure dependent shifts that are very similar to the shift of external modes. The frequency gap between internal and external modes is relatively small compared to values typical for molecular solids. This indicates a small disparity between intermolecular and intramolecular bonding in the RDX crystal.

![Figure 1](image1.png)  
**Figure 1.** Raman spectra of lattice (solid) and low frequency internal modes (dashed) of RDX at (a) 4.0 GPa and (b) 6.1 GPa.

![Figure 2](image2.png)  
**Figure 2.** Pressure dependent Raman shifts from ambient to 15 GPa for lattice and low frequency internal modes.
3.2. CH stretching modes
Raman spectra of the CH stretching modes for a range of pressures from ambient to 5.5 GPa are depicted in Figure 3a. Note that the Raman modes split above the phase transition. The pressure dependent frequencies of these modes are indicated in Figure 4. Several features are observed above the phase transition: (i) the appearance of a new mode at ~ 3150 cm\(^{-1}\), (ii) the triple splitting of some modes, (iii) changes in the relative intensity of the Raman modes and (iv) discontinuities in the pressure dependent Raman shifts. Other than the continued frequency shifting, no other significant features are observed up to 15 GPa.

![Figure 3. Raman spectra of CH stretch modes of RDX under (a) hydrostatic and (b) shock compression.](image)

![Figure 4. Pressure dependent Raman shifts of CH stretch modes from ambient to 6 GPa for static and shock compression.](image)

3.3. Structure of \(\gamma\) phase
The observed behaviour of the Raman spectra under hydrostatic compression gives us some insight into the structural changes accompanying the \(\alpha - \gamma\) phase transition. In general, for the internal vibrations, the number of Raman modes doubles on average above the \(\alpha - \gamma\) phase transition. The number of lattice modes changes slightly, but remains consistent with four or eight molecules in the unit cell. Therefore, our results indicate that the crystal point group of the \(\gamma\) phase can be isomorphous with the \(D_{2d}[C_{1}(8)], C_{2v}[C_{1}(4)]\) and \(D_{2d}[C_{1}(4)]\) point groups.

Although our Raman data cannot be considered conclusive, we favour the \(\gamma\) phase structure that is isomorphous with the \(D_{2d}[C_{1}(8)]\) group. Furthermore, the splitting of the internal Raman modes is attributed to factor group coupling, which indicates changes in intermolecular interactions. No conformational change of the individual RDX molecules is required for the observed splittings. We conclude that any structural modifications that take place with the phase transition preserve the factor group of the low pressure phase.
4. Shock wave compression

Spectra of shock compressed RDX are shown in Figure 3b for the [111] orientation. Comparison with the static pressure data at similar stresses reveals strong similarity between the two sets of data. Based on these similarities, we state that the $\alpha - \gamma$ phase transition does occur under conditions of shock wave loading. Additional experiments were performed for the other orientations. Those results are shown in Figure 4 with the static pressure results. For all three orientations, similar spectral trends were observed. The peaks split at about 4 GPa and shift to higher stress as the peak stress increases. Similar degrees of shifting were observed for all three orientations, indicating a lack of a measurable dependence on crystal orientation.

To gain insight into the kinetics of the phase transition, time-dependent measurements were performed. The results of these measurements are depicted in Figure 5 together with predicted Raman shifts based on the static pressure results and a simulated stress history of shocked RDX. As the stress increases, the Raman frequency also increases until the phase transition is reached. The predicted frequency decreases slightly in the $\gamma$ phase, and then increases again as the stress is increased further. The results of the shock experiment differ from this prediction, however. The observed frequency increases beyond that predicted by the static pressure results, with a decrease in frequency shift occurring ~100 ns after the stress state is above 4.0 GPa. From this we conclude that a transition time of about 100 ns is required for the phase transition to occur under these loading conditions. Thus the phase transition occurs on time scales of relevance to shock initiation in RDX.

![Figure 5. Simulated stress history for 5.5 GPa shock wave experiment (solid line). Predicted Raman shifts for 2949 cm$^{-1}$ mode under shock indicated by open squares. Observed Raman shifts indicated by closed circles.](image)

5. Conclusion

The results of static [3] and dynamic [4] compression experiments give us some additional insight into the structure of the $\gamma$ phase of RDX. We propose that the space group in the high pressure $\gamma$ phase retains D$_{2h}$ symmetry. We have also observed the occurrence of the $\alpha - \gamma$ phase transition under conditions of shock wave loading, suggesting that this phase transition should be included in complete models of the shock initiation of this material.

Acknowledgments

The authors thank Dr. D.E. Hooks of Los Alamos National Laboratory for providing the RDX single crystals. Dr. N. Hemmi, K. Zimmerman and K. Perkins are thanked for assistance in performing the shock wave experiments. Dr. J.M. Winey is thanked for the stress wave simulations. This work was supported by US DOE and ONR.

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