

# EQUATION OF STATE AND STRUCTURAL CHANGES IN DIAMINODINITROETHYLENE FROM EXPERIMENTAL STUDIES AND AB-INITIO QUANTUM CALCULATIONS

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**Abstract.** Structural and molecular changes in 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7) compressed to high pressures were investigated using both anvil cell experiments and ab-initio calculations. The experiments consisted of angle-dispersive x-ray diffraction analysis and Raman spectroscopy with compression. The results indicated higher compression along the b-axis than along the a- or c- axis, and a trend towards the freezing of H-wagging vibrations, possibly due to increased H bonding with compression. In addition, the ambient temperature isothermal equation of state of FOX-7 was generated from this data. Vibrational modes were calculated using GAUSSIAN 98, and experimental spectra were mode matched using the calculated normal modes. Equations of state were generated using CRYSTAL 98, first with the rigid-body approximation, and then with molecular geometry optimization at each volume. Comparison of results from experiments and quantum calculations are discussed.

## INTRODUCTION

Detonations of energetic materials occur in the high pressure (10-50 GPa) and high temperature (600-4000°C) regime. Modeling of the detonation properties of any explosive requires high-pressure equations of state and other pressure- and temperature-dependent thermodynamic parameters. Investigations of detonative chemical reactions, initiation, kinetics, and reaction

mechanisms of detonating explosives, require information about the structure and molecular composition of the energetic material at the high pressures and temperatures approaching detonation. Therefore, we study the effect of high pressure and temperature on the structure of energetic materials. This particular work is on the effect of high pressure on a newly developed energetic material 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7) whose utility is being currently investigated. It was

originally produced in Sweden, and therefore best known as FOX-7, the designation given it by the Swedish Defense Research Agency (FOA).

FOX-7 is an energetic material with high performance, but low sensitivity comparable to TATB. [1] The crystal structure of FOX-7 has been determined to be monoclinic with space group P2(1)/n and four molecules per unit cell. [2] Under ambient conditions, the structure of FOX-7 is similar to the structure of TATB, with strongly hydrogen-bonded neighboring molecules within each zigzagging layer, with weak Van der Waal bonds connecting the zigzagging layers.

We report here the results of x-ray diffraction studies and Raman spectroscopy of FOX-7 at room temperature. Our x-ray studies to 7.1 GPa show anisotropic compression above 1.1 GPa and no phase changes to 4.2 GPa. Above 4.5 GPa, under non-hydrostatic conditions, a lattice transformation occurs to an almost amorphous phase, which could also be the result of slow pressure-induced decomposition of the material. Our Raman spectroscopy studies corroborate the discontinuity in the compression seen by x-ray at 1.1 GPa, and also show vibrational mode softening to 8.2 GPa, the highest pressure accessed in this study.

Ab-initio quantum-mechanical calculations of the Raman spectra for the isolated FOX-7 molecule were compared to the experimentally determined spectra for the crystalline material and a reasonably good correspondence was established. The calculated vibrational modes were used to assign symmetries to the experimentally observed Raman modes

We also report here the results of ab-initio equation of state calculations of the zero-degree isotherm for crystalline FOX-7. Optimizing the bond lengths of the molecule for each compressed volume of the crystal gave improved agreement with the experimental data compared with the fixed molecular-geometry approximation. Calculations involving complete optimization of the internal molecular geometry are underway and will be reported in a forthcoming publication.

## PROCEDURE

### EXPERIMENTAL METHOD

The FOX-7 samples used in this study were obtained from Richard Gilardi at NRL. Samples for angle-dispersive x-ray diffraction were loaded into Merrill-Bassett cells with diamond anvils that had 0.6-1mm culets. [3] Stainless steel gaskets 0.1mm thick, drilled with 0.3-0.6 mm holes, were used to contain the sample. A 5:1 mixture of finely ground FOX-7:NaCl was used. Pressures were determined from the measured compression of NaCl with diffraction collected simultaneously with FOX-7. The pressure reported is the average of the values obtained from the modified Decker equation of state [4] and the Spetzler[5]-Fritz[6] EOS as analyzed by Birch. [7]

Angle-dispersive x-ray diffraction experiments were carried out at the B2 line of the Cornell High Energy Synchrotron Source (CHESS). Diffracted x-rays were collected on an x-ray-sensitive image plate for 10-30 minutes at each pressure. The image plate was then scanned and analyzed using SIMPA software. [8] The d spacing associated with each diffraction peak was estimated by fitting a Gaussian to the peak. The 5-15 peaks observed up to 4.2 GPa were indexed using the monoclinic P2(1)/n space group.

For Raman spectroscopy, FOX-7 powder was loaded into Merrill-Bassett cells with sapphire anvils. The gaskets were made from 127 $\mu$ m Inconel 600, with a gasket hole diameter of 200-250  $\mu$ m. A small ruby sphere (10  $\mu$ m in diameter) was added to each sample, and the frequency shift of the ruby R1 line was used as a pressure gauge. [9]

The Raman system consisted of an Ar ion laser operating at 514.5 nm with 150 mW of power, and a SPEX 0.85m double-mate spectrometer employing a CCD detector. Peak positions were determined by fitting a Gaussian function to the observed Raman vibrations.

### THEORETICAL METHOD

Calculations were performed with the GAUSSIAN 98 [10] quantum chemistry program to identify the experimentally determined Raman

modes. The B3-PW91 density functional method was used. This method combines Becke's three-parameter hybrid method [11] with the Perdew-Wang generalized gradient approximation functional [12]. The basis set used was the 6-31+G\*\* basis set of Pople et al. [13] with "d" polarization functions for heavy atoms and "p" polarization functions for hydrogen, supplemented with diffuse functions for heavy elements [14]. The vibrational frequencies computed by the B3-PW91 methods were scaled by a factor of 0.9573 to correct for systematic errors in the calculations. [15] Calculations were also performed at the MP2 level and the results were in reasonable agreement with the B3-PW91 calculations and earlier results published by Sorescu, et al. [16]

The zero-degree isotherm for FOX-7 was calculated with CRYSTAL 98 [17]. It was found that the best agreement between calculated and experimental crystal structures is obtained with standard Hartree-Fock solutions of the many-body Schrodinger equation. The density functional methods available in CRYSTAL predicted a unit cell volume more than ten percent smaller than experimentally observed. A 6-21G basis set with scaling factors of 1.05 for carbon, nitrogen and hydrogen, and 1.00 for oxygen was used. The scaling factors were chosen to minimize the Hartree-Fock energy. [18] Similar scaling factors have been used for other energetic materials. [19]

## RESULTS

### MEASURED RESULTS

X-ray diffraction patterns were obtained for FOX-7 as a function of pressure, to 7.1 GPa. No phase changes were observed up to 4.2 GPa. Analysis of the diffraction patterns shows anisotropic compression starting at about 1.1 GPa. Above 1.1 GPa, the b axis of the unit cell compresses faster than the a or c axis. [20] The b axis lies in the direction perpendicular to the zigzagging layers within the FOX-7 crystal. These layers are bonded by Van der Waal's bonds and separated by 3.31 Å at ambient P and T. Near a

pressure of 1.1 GPa, there is a discontinuity in the compression of the b axis. After further compression above 4.2 GPa, the diffraction loses intensity, and above 4.5 GPa, the material appears almost amorphous, as shown in Figure 1. The single diffraction peak from FOX-7 remaining at 7.1 GPa, at a  $2\theta$  of 14.0 indicates that the layering in the structure of FOX-7 is probably still intact. Samples decompressed back to ambient pressure from a pressure above 4.5 GPa gives a diffraction pattern with a few broad peaks. Hence, the transition at 4.5 GPa appears to be irreversible.

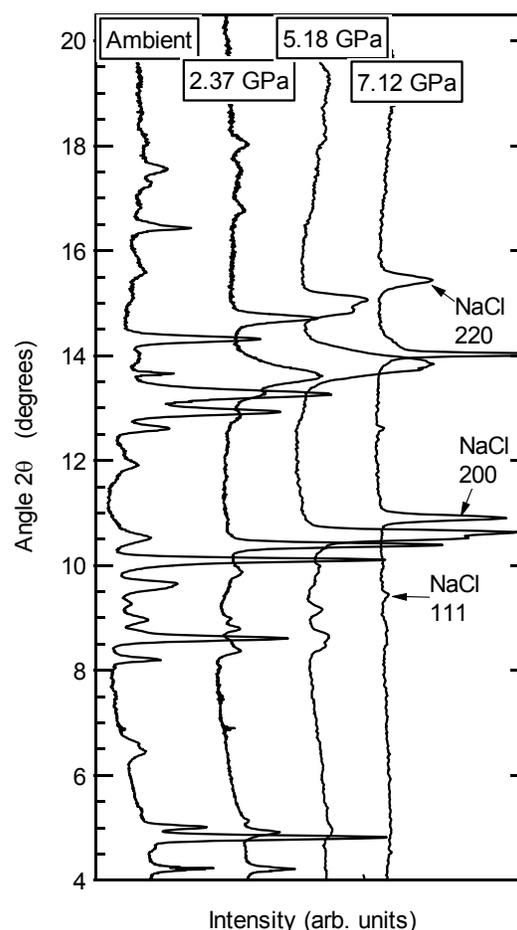


Figure 1. X-ray diffraction patterns of FOX-7 at the various pressures listed. Notice the loss of intensity at 7.1 GPa.

Thermodynamic parameters were calculated by using the Birch-Murnaghan (BM) [7] equation of state formalism to model the P,V, data obtained from x-ray diffraction. The second order BM equation of state yields a zero-pressure isothermal bulk modulus ( $K_0$ ) of  $20.6 \pm 0.5$  GPa, where the pressure derivative of the bulk modulus ( $K_0'$ ) is held constant at a value of four. The third order BM EOS gives a  $K_0$  of  $17.9 \pm 1.4$  GPa, and a  $K_0'$  of  $6.6 \pm 4.9$ . [20] The latter equation of state is then;  $P = 11.93[(V_0/V)^{7/3} - (V_0/V)^{5/3}]\{2.95[(V_0/V)^{2/3} - 1]\}$  where  $V_0 = 515 \text{ \AA}^3$ .

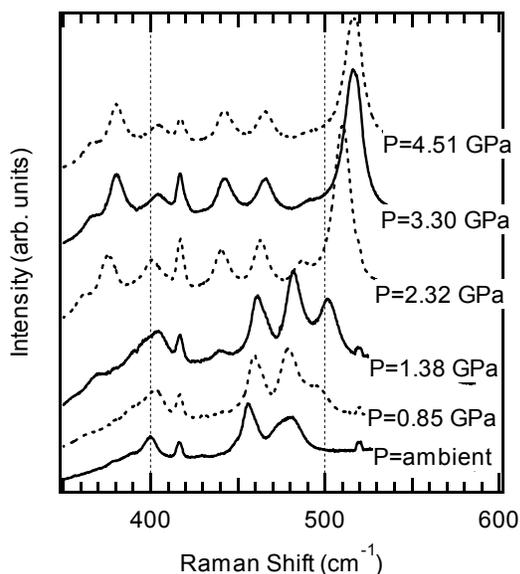


Figure 2. Raman spectra of FOX-7 at the pressures listed. Notice the peaks at 400 and 480  $\text{cm}^{-1}$ , broaden above 0.85 GPa and evolve into a new peak at higher pressure.

Raman spectra taken at various pressures from ambient to 8.2 GPa show most of the modes stiffen or shift to higher frequencies at higher pressure. A couple of peaks deviate from this regular behavior. Above 1.1 GPa peaks with Raman shifts of 400, 480, and 1340  $\text{cm}^{-1}$  start broadening and eventually split into new peaks. This is demonstrated in Figure 2 showing the peaks at 400 and 480  $\text{cm}^{-1}$ , and Figure 3, showing the peak at 1340  $\text{cm}^{-1}$ .

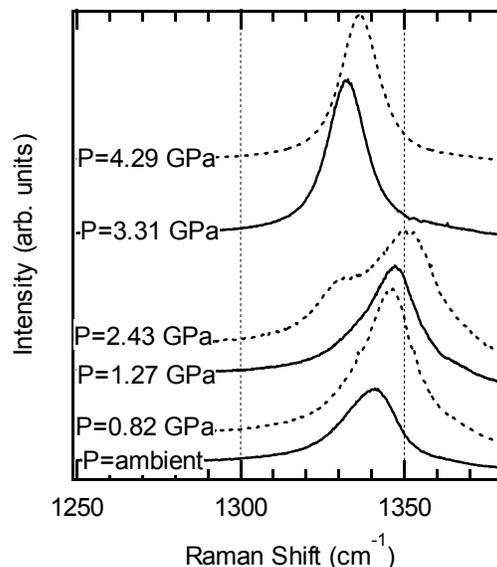


Figure 3. Raman spectra of FOX-7 at the pressures listed. Notice the peak broadening above 1.27 GPa. At higher pressure, a new peak emerges at 1330  $\text{cm}^{-1}$  while the original peak at 1340  $\text{cm}^{-1}$  disappears.

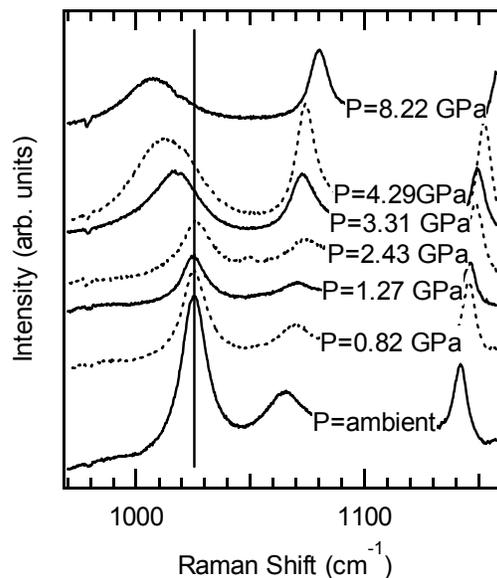


Figure 4. Raman spectra of FOX-7 showing mode softening. The vertical line is placed to assist the eye.

In addition, the Raman mode at  $1025\text{ cm}^{-1}$  shows anomalous mode softening and shifts to lower Raman frequencies above 1.1 GPa. This is shown in Figure 4. Further, a plot of the Raman shifts with pressure of the modes up to  $200\text{ cm}^{-1}$  is shown in Figure 5. While most of the peaks appear to shift linearly with pressure within this pressure range, three of the modes shown here cannot be fitted to a linear pressure shift. These three modes show a discontinuity in the shifts at 1.1 GPa.

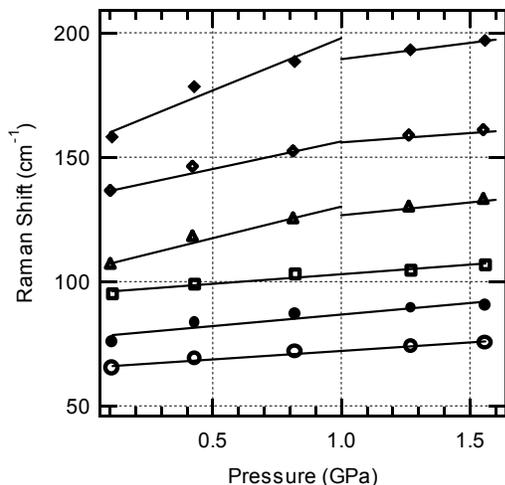


Figure 5. Plot of Raman shifts within  $200\text{ cm}^{-1}$ , versus pressure. Notice the discontinuity in the slopes of some of the fitted lines between 0.85 GPa and 1.27 GPa.

## CALCULATED RESULTS

The calculated vibrational frequencies and intensities were used to construct a calculated spectrum by assigning to each line a full width at half maximum (FWHM) of  $6\text{ cm}^{-1}$ . The spectrum was given a Gaussian distribution profile to match the peak shape and FWHM of the experimental data. The calculated data are plotted in Figure 6, together with a Raman spectrum obtained experimentally at ambient pressure and temperature. The visual correspondence between the calculated and experimental spectra was used to associate the experimental peaks with specific vibrational modes.

The hydrostatic compression of FOX-7 was simulated by scaling the lattice parameters with a factor  $\lambda$  representing a linear expansion with respect to the experimentally determined lattice parameters. Calculations were done with a rigid molecule approximation in which the internal molecular coordinates were fixed while the lattice parameters were varied. Further calculations in which the internal molecular bond lengths were relaxed were also performed.

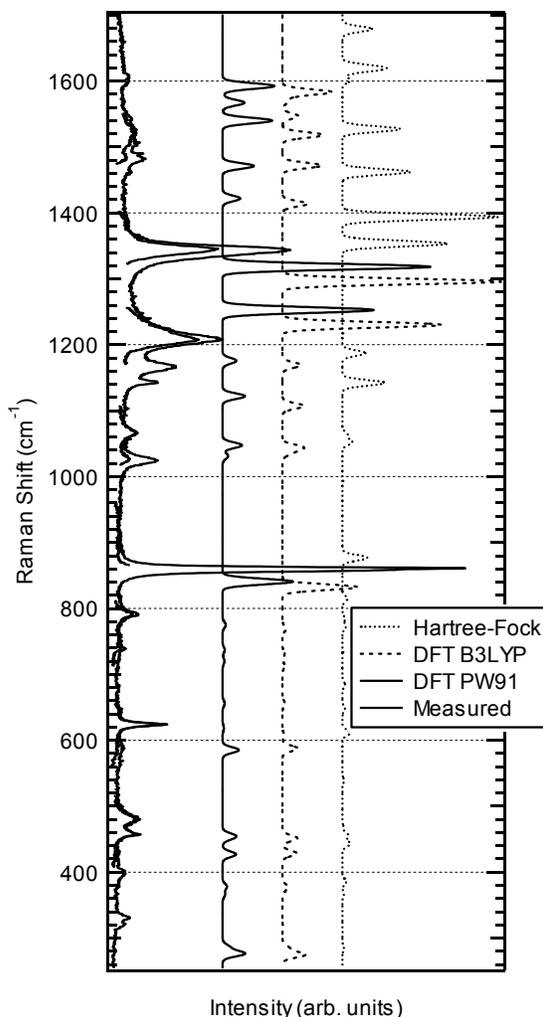


Figure 6. Plot of an experimentally obtained Raman spectrum at ambient pressure, and spectra generated using calculated vibrational modes and intensities.

The calculated energy per unit cell is plotted in Figure 7 vs. the expansion parameter. The rigid molecule approximation is shown by the square symbols, while the optimized bond length calculations are depicted by the solid circles. In both cases, the minimum occurs at 0.99 expansion and agrees well with the experimental result.

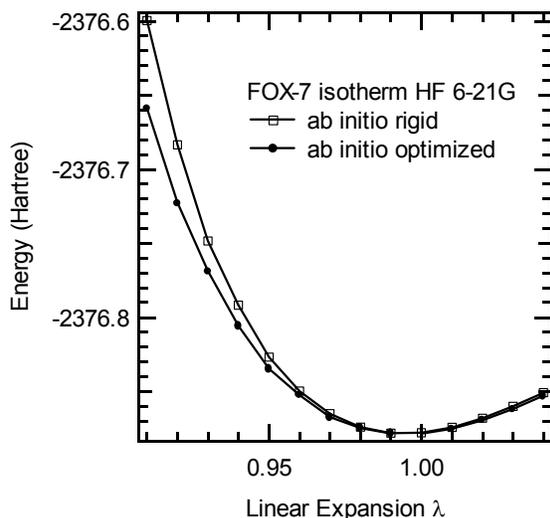


Figure 7. Plot of calculated energy per unit cell versus the expansion parameter.

The pressure vs. volume, determined from the relation  $p = -dE/dV$ , is shown in Figure 8, together with the experimental data. At low compressions, both the rigid molecule approximation and the optimized bond length calculations agree well with the experimental data. At higher compressions, both methods predict a stiffer crystal than shown by experiment, but the optimized bond length calculation is in much better agreement. Complete optimization of the internal molecular coordinates together with inclusion of electron correlation energy should result in even better agreement with experiment.

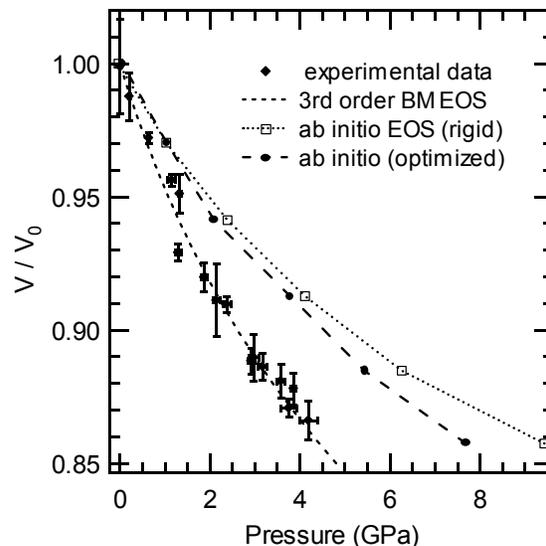


Figure 8. Plot of the calculated pressure versus volume, together with the experimental data.

## DISCUSSION

The experimental observations can be summarized as: A) Asymmetric compression above 1.1 GPa, with the *b* axis compressing faster than the *a* or *c* axis. B) Above 1.1 GPa, new Raman modes appear. C) Above 1.1 GPa, the mode at  $1025\text{ cm}^{-1}$  softens with pressure. D) Above 4.5 GPa, the diffraction pattern (but for a single peak) loses intensity.

Calculated Raman spectra were used to assign vibrational modes to the peaks in the experimentally obtained Raman spectra. The peaks below  $200\text{ cm}^{-1}$  shifts are due to vibrations along the *b* axis. These vibrations change the distance between the layers. The discontinuity shown in Figure 5 of the Raman shifts with pressure, and the discontinuity in the compression of the *b* axis at 1.1 GPa, both indicate discontinuous compression of the *b*-axis at 1.1 GPa. This discontinuity then changes the compression resulting in anisotropic compression of the crystal. However, this change at 1.1 GPa, is not a first-order phase transition since the lattice symmetry is unchanged.

Above 1.1 GPa, new Raman modes appear at 400, 480 and 1340  $\text{cm}^{-1}$ . The vibrations in this region include a mixture of C-C stretching, C-N stretching, and  $\text{NH}_2$  wagging. The C and N atoms are probably moving away from the current symmetry position, to lower symmetry of the molecule further, resulting in new Raman peaks.

Additionally above 1.1 GPa, the Raman mode at 1025  $\text{cm}^{-1}$  starts softening (appearing at lower wave numbers) as pressure is increased. This mode is composed of symmetric and asymmetric H wagging motions. The softening of this mode indicates a slowing of the H motion. H motions would be slowed by increased H-bonding with O atoms from neighboring molecules. There is extensive H bonding between FOX-7 molecules within each layer. Each H atom is within H-bonding distance of two O atoms, each from a different FOX-7 molecule. Unfortunately, we cannot see the H-bonds vibrations themselves with Raman spectroscopy. Therefore, we cannot observe pressure effects on the H-bonding itself, but rather have to speculate on the H-bonding by studying the vibrational motions of N-H or N-O bonds. The slower H-wagging implies that at higher pressure, the H atoms are probably pulled towards multiple neighboring O atoms, loosening the N-H bond, and freezing the motion of H. Also in this study we could not observe the N-H stretching region to use the N-H stretching motions as a guide to the behavior of H.

Above 4.5 GPa, diffraction studies indicate a transition to an almost-amorphous phase. Since this transition is not reversible, it is possible that this transition is actually the decomposition of FOX-7 molecules. At increasing pressures, the backbone of the molecule, the C-C and C-N bonds are compressed. However, increased H-bonding to neighboring molecules are pulling the H away from the C and N atom backbone of each molecule. Eventually, at very high pressures, this atom movement could result in "decomposition" or disorder of the H atoms within the zigzagging layers, yielding the very low diffraction observed. This motion would not affect the layering separated by van der Waals bonding, hence the single peak observed.

This study of FOX-7 only gives us a glimpse to the possible changes occurring within a material as it is shocked to detonation pressures and temperatures. Further investigation of the effect of simultaneously applied high temperature and high pressure on the structure of FOX-7 and studies of kinetic rates etc., are needed to begin elucidating the reaction mechanism of this material during detonation.

## CONCLUSION

Structural and molecular changes in 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7) compressed to high pressures were investigated using both anvil cell experiments and ab-initio calculations. The experiments consisted of angle-dispersive x-ray diffraction analysis and Raman spectroscopy with compression. The results indicate discontinuous compression of the b axis at 1.1 GPa, and anisotropic compression with higher pressure, with the b axis being more compressible than the a or c axis. Above 1.1 GPa, H-wagging vibrations, slow down or appear to freeze, possibly due to increased H bonding within the layers. At pressures above 4.5 GPa the material appears almost amorphous to x-ray, indicating a considerable loss of symmetry or decomposition of FOX-7.

The ambient temperature isothermal equation of state of FOX-7 was calculated from the x-ray data. In addition, equations of state were generated using CRYSTAL 98, first with the rigid-body approximation, and then with a limited molecular geometry optimization for bond lengths at each volume. At higher compressions, both methods predict a stiffer crystal than shown by experiment, but the optimized bond length calculation is in much better agreement.

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