EXPLORING THE HIGH-PRESSURE BEHAVIOR OF PETN: A COMBINED QUANTUM MECHANICAL AND EXPERIMENTAL STUDY

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ABSTRACT

In an effort to increase the efficiency of the developmental cycle for future munitions and propellants, integration of standard atomistic simulation methods into the research and development process is being aggressively pursued. In many cases, this approach is not feasible due to the neglect of important crystalline forces in the formulations of the simulation methods. However, within high-pressure regimes it has been shown the predictions are in much closer agreement with experiment. This paper describes a combined theoretical/experimental study to elucidate the high-pressure behavior of Pentaerythritol Tetranitrate (PETN). The pressure-induced alterations in the Raman frequencies were studied in a compression sequence up to 25 GPa and subsequent decompression to ambient conditions. The observed changes indicated a non-reversible phase transition at ~ 8.0 GPa. High-pressure x-ray diffraction experiments corroborate the Raman results. Quantum mechanical calculations were performed in an attempt to elucidate the structure of this new material.

1. INTRODUCTION

In recent years, there has been increased momentum towards integrating standard atomistic simulation methods in the research and development process of energetic materials (EM). Complete integration of these methods into the developmental cycle of future munitions and propellants will have substantial pecuniary and time savings by eliminating steps that currently rely on formulation/synthesis and subsequent testing of the material. By using models to predict performance properties, sensitivity and environmental hazards of candidate EMs, non-ideal materials can be eliminated from consideration before investing in expensive and often hazardous synthesis and testing. Full exploitation of this computer-based approach requires that the atomistic simulation methods produce accurate values. In many cases, this is not yet feasible; for example, the errors in key performance properties using the popular quantum mechanical method known as density functional theory (DFT) have been shown to be quite large [Byrd et al., 2004].

The accurate prediction of crystalline densities is of critical importance in the model-based design process, since detonation velocities and pressures of energetic materials are proportional to powers in the density. Although most current theoretical density predictions using semi-empirical models parameterized for CHNO explosives are within 2 - 4% of the experimental values, this error is often unacceptable to experimentalists, who desire errors of less than 1% before undertaking a costly and risky synthesis [Byrd et al., 2004]. Further, the existing predictive tools are limited to a small class of explosives that have not yet demonstrated their transferability to more exotic chemical composition (i.e. high nitrogen compounds). Thus, it is desirable that inherently transferable theories, i.e. quantum mechanical theories, be applied to this problem. Unfortunately, part of our group has found that the only computational tractable quantum mechanical method used for crystal density predictions at this time does not adequately predict densities of CHNO molecular crystals at ambient conditions. It has been proposed that these errors arise from a lack of van der Waals forces implemented in the functionals. The lack of van der Waals forces results in crystalline expansion because the attractive forces between the molecules are non-existent or extremely weak. However, within high-pressure regimes, the work discussed here shows that DFT predictions are in much closer agreement with experiment, indicating that within these regimes other intermolecular forces begin to dominate [Byrd et al., 2004].

In the last decade, Pentaerythritol Tetranitrate (PETN), shown in Figure 1, has been the subject of numerous experimental and theoretical reports aimed at understanding a wide variety of chemical and physical properties, such as the molecular structure [Trotter, 1963], thermal expansion [ref], electronic [Kuklja et al.] , vibrational [Park et al., 2004; Lipinska-Kalita et al., 2005 and Gruzdkov et al., 2001] and shock sensitivity [Dick, 1994; Dick et al., 1994; Dick et al., 1991; Yoo et al., 2000]. In spite of these efforts, a more comprehensive understanding of PETN is needed, not only at ambient conditions, but also under high-temperature/high-pressure regimes, before the capabilities of this material can be fully exploited. This paper will focus on the high-

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pressure behavior of PETN from both a computational and experimental view-point.
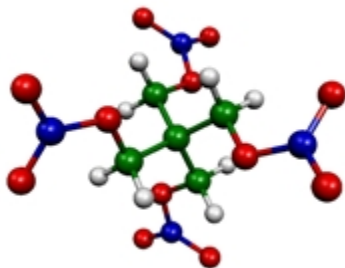

Figure 1. The molecular structure of PETN

Classical atomistic simulation studies of the hydrostatic compression of PETN crystals based on the rigid-molecule approximation agree well with experimental data up to 5 GPa [Sorescu et al., 1999]. Unfortunately, this model fails at higher pressures. Linear and volumetric hydrostatic compressions have been also been estimated within the pressure range of 4.3 GPa and 10.5 GPa, but are inconsistent when extrapolated to higher pressures [Olinger et al., 1975 and Dick et al., 1994]. Under certain experimental conditions, it has been reported that PETN undergoes a phase transition from a low-density (Phase I) to high-density phase (Phase II). This phase transition was first observed using Raman spectroscopy under quasi-hydrostatic conditions at pressures greater than 5 GPa [Gruzdkov et al., 2004] and later confirmed with x-ray diffraction measurements under non-hydrostatic conditions [Lipinska-Kalita et al., 2005]. A comparison of theoretical and experimental vibrational frequencies led to the conclusion that molecules within the crystal undergo conformational changes from the highly symmetric S_4 state to the lower symmetry C_2 state [Gruzdkov, 2004]. The previously reported Raman and diffraction results have indicated the phase transition was reversible. Recently, another Raman study has been performed under quasi-hydrostatic conditions up to 31.3 GPa and no evidence of a phase transition was observed [Lipinska-Kalita et al., 2005]. Since there appears to be conflicts in the various high-pressure experimental measurements, we will use theoretical and experimental methods to explore these high-pressure states.

We have experimentally studied the behavior of PETN using x-ray diffraction in addition to spectroscopic measurements up to pressures of 26 GPa using diamond anvil cells. Spectroscopic measurements performed under quasi-hydrostatic conditions show evidence of the Phase I → Phase II transition within the pressure range studied. We find that upon decompression, the material does not revert to Phase I but instead remains in Phase II. Under non-hydrostatic conditions, the sample detonates at pressures above 6 GPa. This supports the earlier proposal

that non-hydrostatic conditions tend to accelerate the phase transition [Lipinska-Kalita et al., 2005] but contrasts previous data that indicates no phase transition is observed under hydrostatic conditions.

2. MATERIALS AND METHODS

Polycrystalline PETN, obtained from the Naval Surface Warfare Center at Indian Head, Maryland, was carefully ground into a fine powder prior to any experiments. For both the Raman spectroscopic and x-ray diffraction measurements, a rhenium gasket was pre-indented to a pressure of approximately 30 GPa, using a piston-cylinder diamond anvil cell and then drilled via electronic discharge. The resulting sample well was approximately 120 μm in diameter with a depth of 35 μm. The pressure was determined from the shift of the R_1 ruby fluorescence line with pressure, which is precise to ± 0.05 GPa under quasi-hydrostatic conditions [Mao et al., 1986]. All experimental measurements employed a helium pressure medium. High-pressure Raman experiments were performed using the 488.0 nm line of an argon ion laser (Coherent Innova 90) as the excitation source, with output power kept at less than 0.1W. A 460-mm focal length $f/5.3$ imagining spectrograph (ISA HR 460) equipped with an 1800-grooves/mm grating with a resolution of ± 0.5 cm^{-1} was used. The wavelength calibration was performed using a neon light and has an accuracy of ±1 cm^{-1}. Angle dispersive x-ray diffraction measurements using a focused synchrotron beam, HPCAT, Sector 16, Advanced Photon Source, were carried out in-situ at room temperature as a function of pressure. In the present experiments, the x-ray beam with a wavelength of 0.368 Å was collimated to 50 μm. The data were recorded on a MAR charge-coupled device (CCD) calibrated with a CeO$_2$ standard. The pressure was determined from the spectral shift of the R_1 ruby line with pressure.

Calculations of the crystalline geometry and vibrational frequencies for pentaerythritol tetranitrate (PETN) were performed using the Perdew-Wang 91 (PW91) [Perdew, 1991] GGA density functional theory as implemented in the Vienna Ab-Initio Package (VASP) [Kresse et al., 2003] The Vanderbilt ultrasoft pseudopotentials (USP) [Vanderbilt, 1990], a 2x2x2 k-point grid, generated with the Monkhorst-Pack method, and a 545 eV planewave kinetic energy cut-off (E_{cut}) were used for all calculations. Starting from the zero pressure (ambient conditions) experimental crystal structures, all ionic and cell degrees of freedom were allowed to relax concurrently and without enforcing symmetry restrictions at various imposed isotropic pressures. All theoretical equilibrium crystal structures were obtained through analytic gradient techniques implemented in VASP. The electronic energies were converged to 2.0 x 10^{-6} eV, while

the structures were converged once the difference in free energy between gradient steps was less than 2.0×10^{-5} eV. As these molecular crystals are insulators, setting the smearing width to 0.0001 eV in the Methfessel-Paxton method minimized electron smearing [Methfessel et al., 1989]. To accelerate convergence, the RMM-DIIS method was employed, except for certain calculations where it was necessary to use conjugate gradients instead. After obtaining the theoretical geometries at the various isotropic pressures, we proceeded to calculate the vibrational frequencies based on these structures. The exact same kinetic energy-cutoffs, k-point grids, pseudopotentials, and density functional theory (PW91) were employed in all cases. Vibrational frequencies were generated for the 5.6, 7.6, and 10.5 GPa structures.

3. RESULTS AND DISCUSSION

At ambient conditions, PETN has a tetragonal structure with a space group of $P\text{-}42_1c$ and molecular point group of S_4. The lattice parameters for the tetragonal cell are a = 9.302 Å and c = 6.640 Å at 298 K [Trotter, 1963]. We found good agreement with the reported results [Trotter, 1963] with nine characteristic diffraction peaks below 15 ° at 1.0 GPa: (200), (201), (211), (002), (220), (102), (310), (301), (311), (212). In an attempt to understand the high-pressure behavior of PETN, we measured x-ray diffraction on isothermal compression at room temperature. Representative x-ray diffraction patterns of PETN are shown in Figure 2. Upon compression, the tetragonal doublets tend to merge into one peak with two clearly resolvable maxima. At 2.3 GPa, the higher angle peaks begin to broaden and at 9.0 GPa, these peaks are completely merged into the background. The diffraction pattern observed above 7.9

GPa noticeably differs from the diffraction pattern of the starting material. Although the disappearance of the peak splittings can be attributed to pressure gradients (nonhydrostatic environment) at higher pressures, we feel that relatively good hydrostatic conditions were achieved from the reproducibility of the results. In addition, the Raman results shown below give strong support for a transition that is intrinsic to the material.

The pressure dependence of the volume is shown in Figure 3. The results of an earlier x-ray diffraction study of PETN [Olinger et al., 1975], as well as theoretical simulations are also presented. The data obtained under the experimental conditions discussed in this paper compares favorably, at pressures below 5 GPa, with the previous experimental data. Our volumes are slightly smaller than the previous experimental values but this may be due to the more hydrostatic nature of our pressure medium. Although no abrupt discontinuities are observed in the experimental volume, our data shows a decrease in the compression rate between 2.3 GPa and 5.3 GPa. This behavior is typically associated with the onset of a phase transition.

Figure 3. Pressure dependence of the volume for PETN at 298K. The blue diamonds show the data obtained by Olinger et al., [1975], the pink squares indicate theoretical data and the orange triangles are the experimental data obtained in this report.
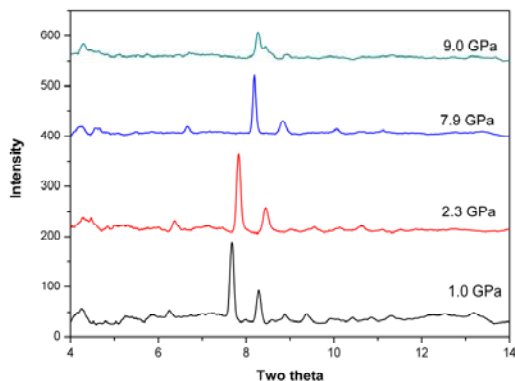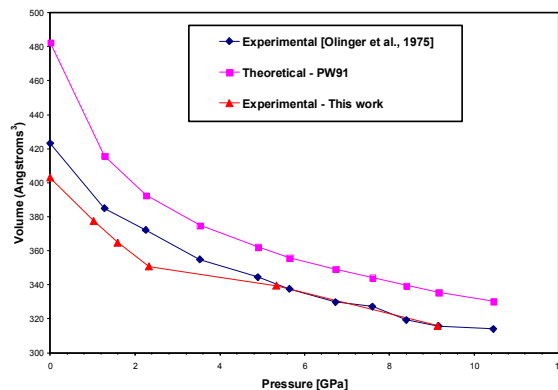

Figure 2. Typical examples of powder x-ray diffraction patterns of PETN recorded under hydrostatic conditions. With increasing pressure, the peaks shift at different rates leading to well-resolved peaks. At 9.0 GPa, the peaks begin to broaden and a phase transition occurs.

In general, the volume predicted by the theoretical calculations is larger than the experimental values over the entire pressure range. At ambient conditions, the volume is substantially overestimated, due to deficiencies in current formulations of density functional theory, as discussed earlier. However, at pressures above 2.3 GPa, the theoretical volumes approach those of experiment, due to a decrease in the dominance of the van der Waals forces in the crystal at ambient conditions and an increase in other crystalline forces, which are more adequately described by DFT.

3

Several representative Raman spectra of polycrystalline PETN obtained during the compression sequence from 0.4 GPa to 10.8 GPa at room temperature are presented in Figure 4, within the vibrational range of 150 – 3400 cm^{-1}. The instrumental configuration used for these experiments restricts the obtained data to below 150 cm^{-1}. In addition, the strong first order scattering arising from the diamond anvils masks the Raman shifts between 1300 cm^{-1} and 1375 cm^{-1}.
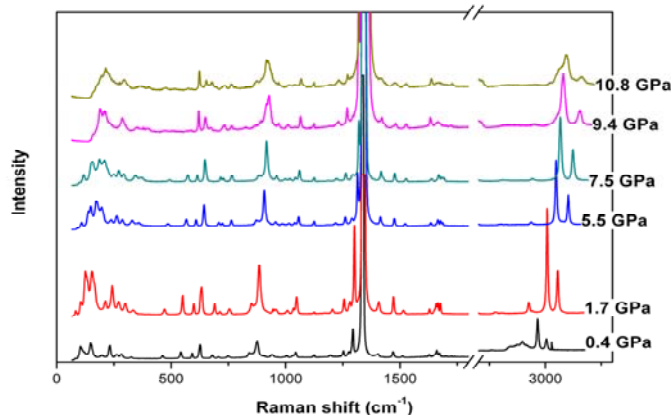

Figure 4. Selected Raman spectra of PETN as a function of compression. Each spectrum is appropriately marked by a pressure value. The first order diamond scattering vibration (~1300 cm^{-1}) is truncated to allow for clarity of the lower intensity vibrational modes of PETN.

The Raman spectra of PETN up to 7.5 GPa agree well with previous studies of this spectral region [Lipinska-Kalita et al., 2005]. We observed over 35 Raman scattering features in PETN within this spectral range at 0 GPa. These features are caused by skeletal deformations, N-O, C-C, and C-H stretching and bending motions, as well as some translational-type motions of larger units, such as vibrations of the PETN molecule within its molecular cage. Although the low molecular and crystal symmetries leads to many 'impure' modes, which arise from motions of several functional groups rather than one distinct group, normal mode analysis has been performed at ambient conditions [Gruzdkov et al., 2001]. While distinct band assignments have not been made of PETN under high pressure, some insights into the likely assignments can be derived from the pressure shifts. On compression, all bands shift to higher frequency. Up to pressures of 7.5 GPa, we observe significant and gradual changes in intensity of a few bands, with the increase in amplitude being most noticeable for the C-H stretching modes in the spectral range of 2700 – 3200 cm^{-1}. The changes in the vibrational pattern of the Raman spectrum of PETN at 9.4

GPa are consistent with a phase transition. The most noticeable changes are the appearance of a single vibrational maxima for the O-N-O stretch at ~ 882 cm^{-1} and the new intensity pattern of the triplet of skeletal motions centered at ~ 540 cm^{-1}, 589 cm^{-1}, and 620 cm^{-1} (0 GPa). On decompression, the vibrational characteristics of Phase II are retained.

There have been several conflicting reports regarding the existence of the high-pressure phase transition in PETN. The phase transition was first observed using a glycerol pressure medium and was reversible [Gruzdkov et al., 2004]. More recently, a Raman experiment using a nitrogen pressure medium observed no phase transition up to 31 GPa [Lipinska-Kalita et al., 2005]. Our results are in contrast to both experiments in that a non-reversible phase transition was observed. Since the pressure media used in all experiments should be fairly hydrostatic at least to 10 GPa, clearly, other experimental conditions play an important role in determining the high-pressure behavior. While there is no simple explanation for the behavior of the material above 8 GPa, it has been suggested that non-hydrostatic compression accelerates the transition. Non-hydrostatic compression could be associated with the development of significant preferred orientation within the sample, which has been shown to be rather prevalent in PETN. To test this hypothesis, PETN was placed in the diamond anvil cell without a pressure medium and compressed. In all trials, detonation occurred at pressures above 6 GPa. Particle size may be a dominating factor in this transition. Smaller particles within the diamond anvil cell may be less subject to grain boundary effects, provided there is adequate pressure media in the cell, while larger ones may meet at the grain boundaries as the pressure is increased. Experiments are currently underway in our laboratory to test this hypothesis.

One of the primary motivations for the current Raman measurements was to determine the molecular structure of the high-pressure phase through the comparison of the experimental and calculated vibrational frequencies. We found relatively good agreement between the experimental and calculated frequencies at 5.5 GPa and 7.6 GPa, with RMS values of 38.22 cm^{-1} and 40.25 cm^{-1}. As previously mentioned, it has been suggested that Phase II has a $P2_12_12$ structure, rather than the $P-42_1c$ structure of Phase I. However, the RMS values of the highest pressure spectrum are comparable to those at lower pressures (40.44 cm^{-1}). It may be possible to discern the structure of Phase II using this approach from the phonon frequencies and we are currently exploring that experiment.

We also used DFT calculations to explore the hypothesized compression-induced polymorphic phase transition [Gruzdkov 2004]. The initial crystal in these

calculations had the $P2_12_12$ space group symmetry and C_2 molecular structure, as recommended by Grudzkov *et al.* [2004]. The cell parameters, and orientation and placement of this conformer within the $P2_12_12$ unit cell was determined using *ab initio* crystal prediction methods [Holden et al., 1993] and a generalized CHNO interaction potential energy function [Sorescu et al., 1997]. The initial crystallographic parameters of the $P2_12_12$ unit cell, as determined by ab initio crystal prediction were *a, b* and *c* (9.952, 9.389 and 6.538 Å). These values are similar to those of the ambient structure ($P-42_1c$) (*a=b*=9.303 Å, *c*=6.640 Å). Several attempts were made to obtain an optimized unit cell with $P2_12_12$ symmetry but the cell consistently optimized to the $P-42_1c$ structure. Further experimental work is being done using specialized diamond anvil cells that will allow for resolution of more diffraction peaks, and using single crystals, which will allow for refinement of molecular positions.

4. CONCLUSIONS

The high-pressure study of the PETN up to 10.5 GPa at room temperature revealed the formation of a high-pressure phase which is distinctly different from that of the starting material. This high-pressure phase first appears near 9.5 GPa and is associated with several changes in the vibrational pattern, such as intensity increases and mode splitting. In contrast to other reports, we found this phase transition to be irreversible. While no simple explanation exists for the contrasting behavior of the material above 8 GPa, it has been suggested that non-hydrostatic compression accelerates the transition and we have confirmed this through uniaxial compression experiments, where detonation occurred upon compression above 6 GPa. We suggest that particle size may play an important role in the high-pressure dynamics of this material, as smaller particles may be less subject to grain boundary effects than larger particles.

In an effort to elucidate the structure of Phase II, a combined theoretical/experimental approach was used. Several attempts were made to obtain an optimized unit cell with $P2_12_12$ symmetry but the cell consistently optimized to the $P-42_1c$ structure. In future work, we will attempt to discern more information from the lattice frequencies.

X-ray diffraction measurements of PETN corroborate the phase transition observed in the Raman spectra. The pressure dependence of our volume measurements is slightly smaller than the previous experimental measurements, which may be due to the differing pressure media. The calculated V/V_0 ratios closely parallel our experimental values, but are severely underestimated due to lack of adequate dispersion forces in the calculation. At pressures above 2.3 GPa, the theoretical volumes

approach those of experiment, due to a decrease in the dominance of the van der Waals forces. Although no abrupt discontinuities are observed in the experimental volume, our data shows a decrease in the compression rate between 2.3 GPa and 5.3 GPa. This behavior is typically associated with the onset of a phase transition and unfortunately the simulations are unable to model this transition. Future work will employ specialized diamond anvil cells that permit the resolution of more diffraction peaks and ultimately the molecular positions.

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Exploring the High-Pressure behavior of PETN: A combined Quantum Mechanical and Experimental Study
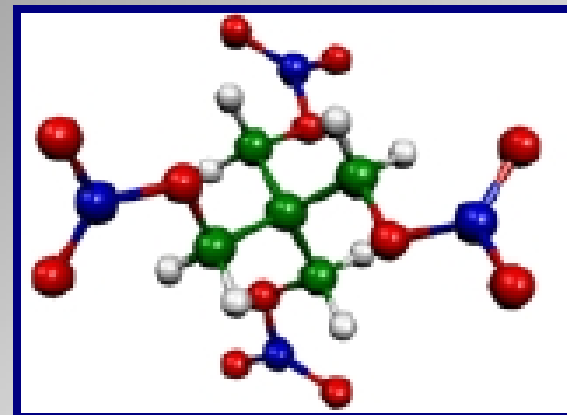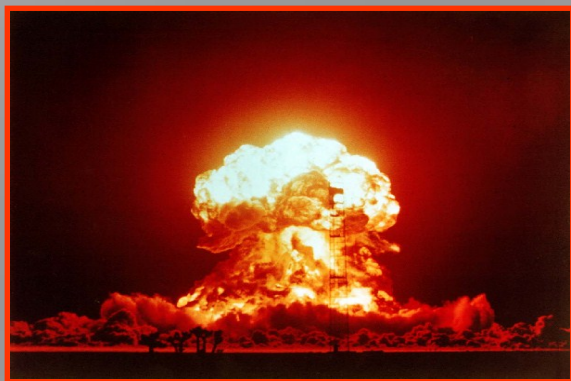
Weapons and Materials Research

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November 28, 2006

This talk presents a combined experimental and theoretical study on the high-pressure behavior of PETN
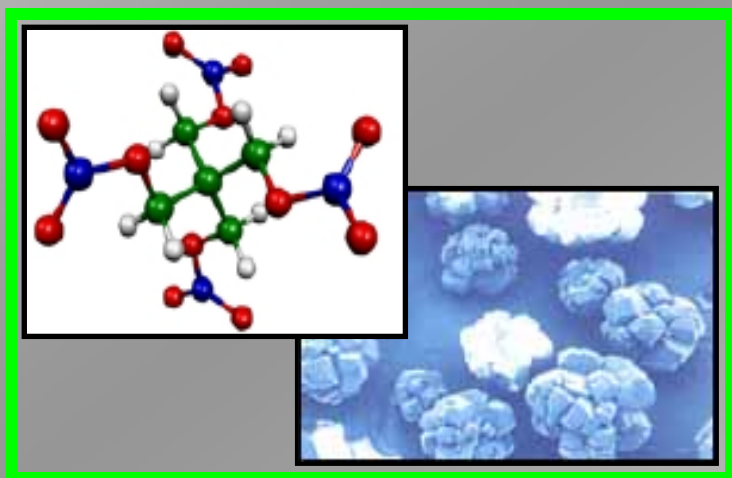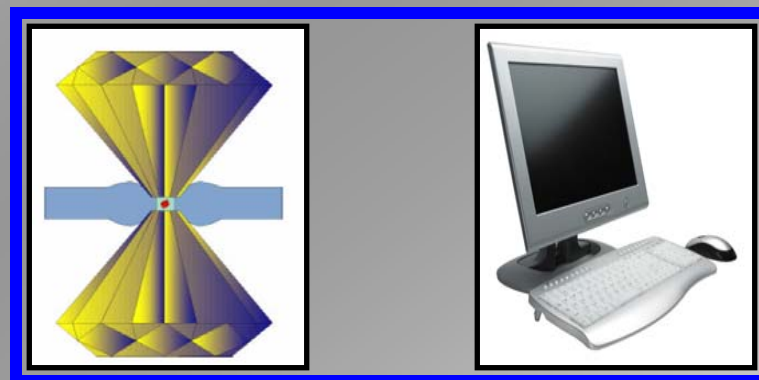
Why are we interested?

PETN- Past and present

Overview of the techniques used

Conclusions and Future Direction of work

Introduction

The *a priori* determination of combustion and detonation properties before synthesis could potentially save millions in materials and labor.

However, excessive error in predictive capabilities makes screening techniques ineffective.

We shall illustrate a significant problem with DFT, a common theoretical method, and demonstrate successes of the theory at higher pressures.

• E.F.C. Byrd, G.E. Scuseria, and C.F. Chabalowski. An Ab Initio Study of Solid Nitromethane, HMX, RDX, and CL20: Successes and Failures of DFT. Journal of Physical Chemistry B 108 (2004) 13100-13106.

• E.F.C. Byrd and B.M. Rice. An Ab Initio Study of Compressed HMX, RDX, CL20, PETN, and TATB. (*in preparation*)

The high pressure experiments were performed in diamond anvil cells

Radiation

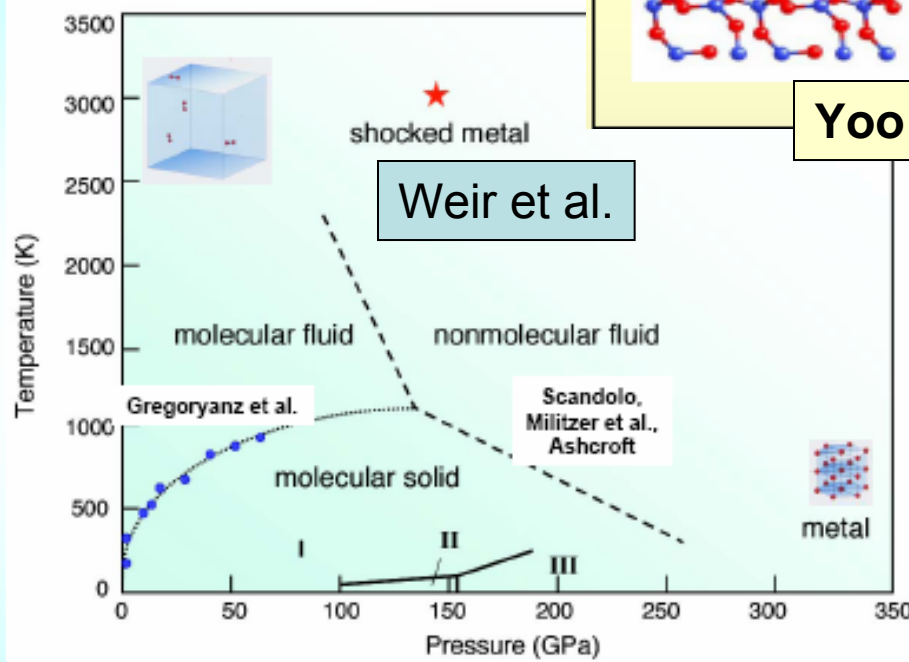Gasket

Sample, pressure medium, Ruby chips

Radiation

- Polymeric materials- N_2, CO_2, O_2
- Phase diagram of H_2- Shocked metal, molecular and non-molecular fluid

POLYMERIC MATERIALS
CO_2

Yoo et al. 1999

Weir et al.

shocked metal

molecular fluid

nonmolecular fluid

Gregoryanz et al.

Scandolo, Militzer et al., Ashcroft

molecular solid

I   II   III

metal
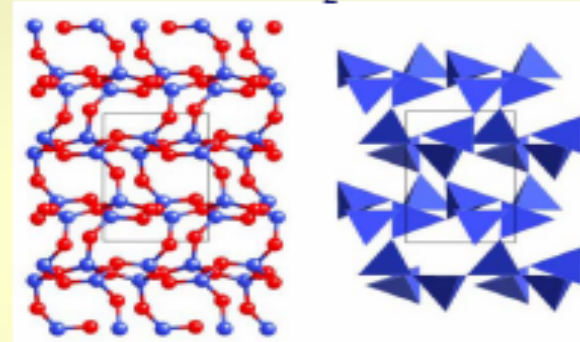
All computations employed the VASP program [1]

- **PW91 DFT functional with Vanderbilt pseudopotentials**
- **Kinetic energy cut-offs (E_{cut}) ranging from 280 to 800 eV**

  – The larger the kinetic energy cut-off (i.e. number of planewaves), the better the "resolution" of the electronic space

 – Tradeoff for accuracy is increased computation time (scales as N^3)

Small E_{cut}

Large E_{cut}
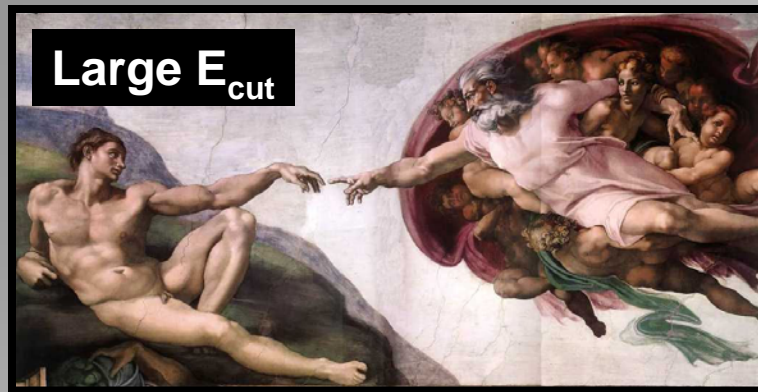
Starting from experimental crystal structures, all ionic and cell degrees of freedom allowed to relax concurrently without enforcing symmetry constraints

[1] Information available at: http://cms.mpi.univie.ac.at/vasp/

The behavior of PETN under extreme conditions is relatively unknown
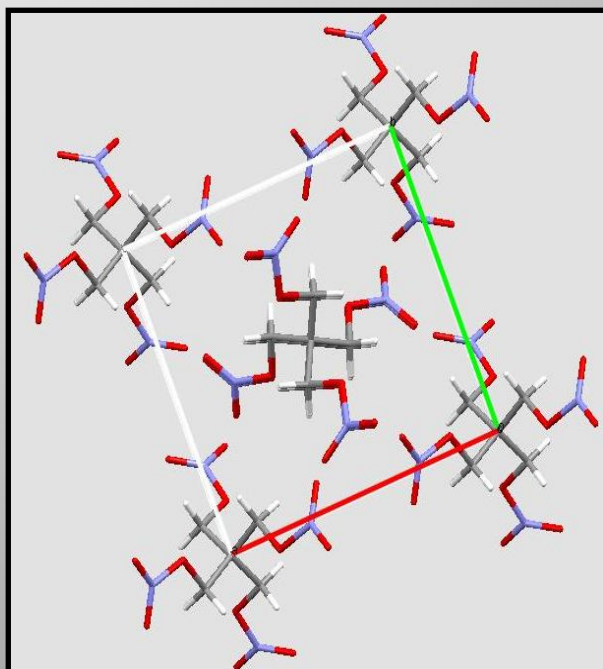
- Shock sensitivity depends strongly on the orientation of the crystal axes relative to the shock propagation direction [1]
  - Suggests the conformation change under shock loading caused by shear deformation may be responsible for the observed anisotropy
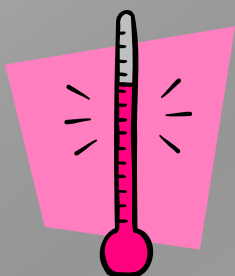
- **High temperature** phase transition

$P\text{-}42_1c \rightarrow Pcnb$

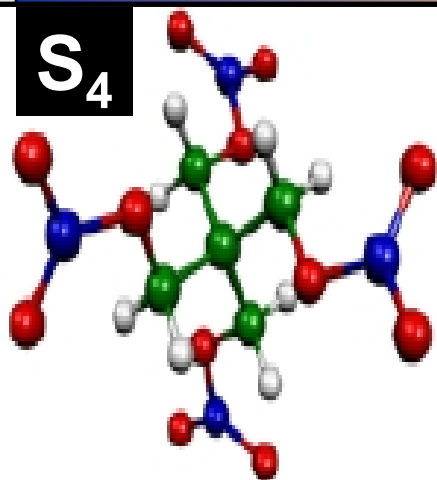 – Results in a slightly different stacking arrangement [2]

[1] J.J. Dick, et al. J. Applied Physics 70 (1991) 3572. [2] H.H. Cady et al. Acta Cryst. B31 (1970) 1864.
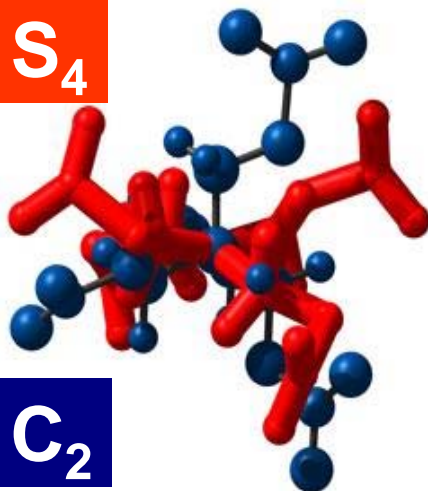
Is there a phase transition at high pressure?

S_4

S_4
C_2

PETN, $C(CH_2-ONO_2)_4$

- Under certain conditions, a transition from a low density to a high density polymorph was noted using Raman spectroscopy
  - A comparison of experimental and calculated vibrational frequencies suggested transformation from $S_4 \rightarrow C_2$ state [1].

This was later confirmed using x-ray diffraction [2].

Most recently, a Raman study reported no phase transition up to 31 GPa [2].

[1] Y.A. Gruzdkov et al. J. Phys. Chem. A 108 (2004) 6216.

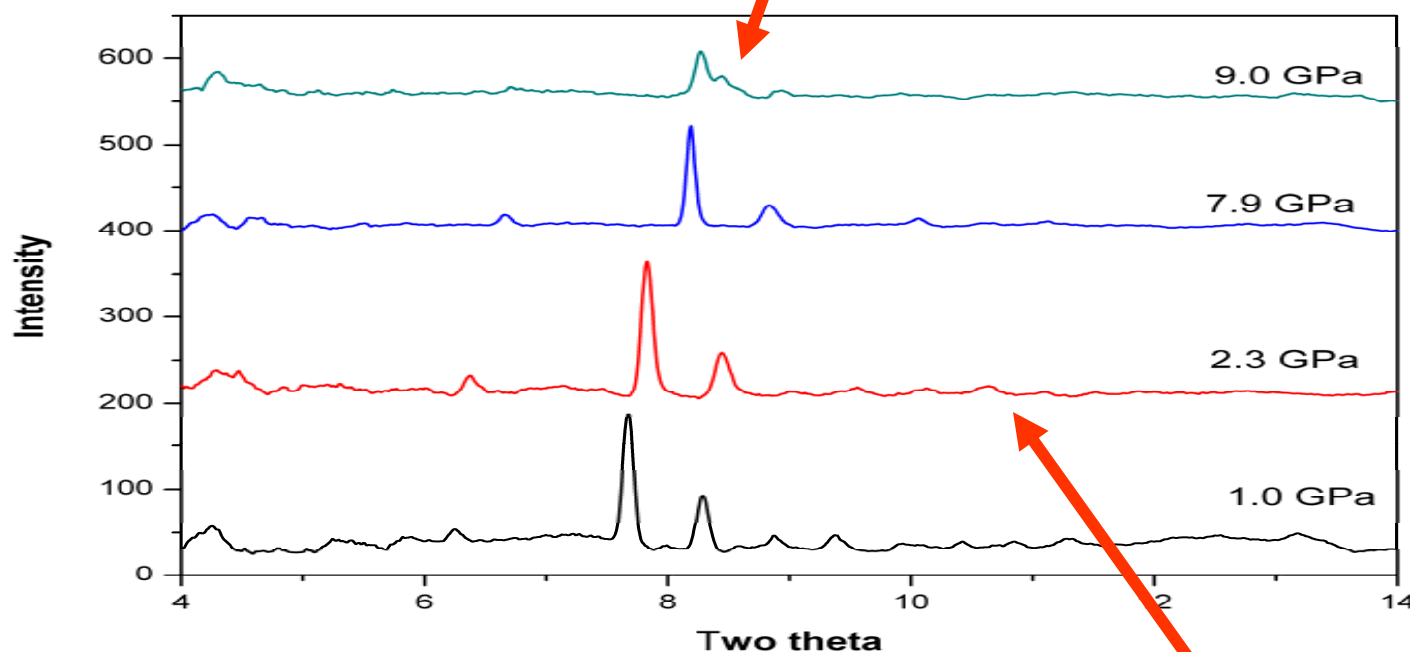[2] K.E. Lipinska-Kalita, J. Phys. Chem. B 109 (2005) 19227.

A comparison of the experimental and calculated unit cell volume
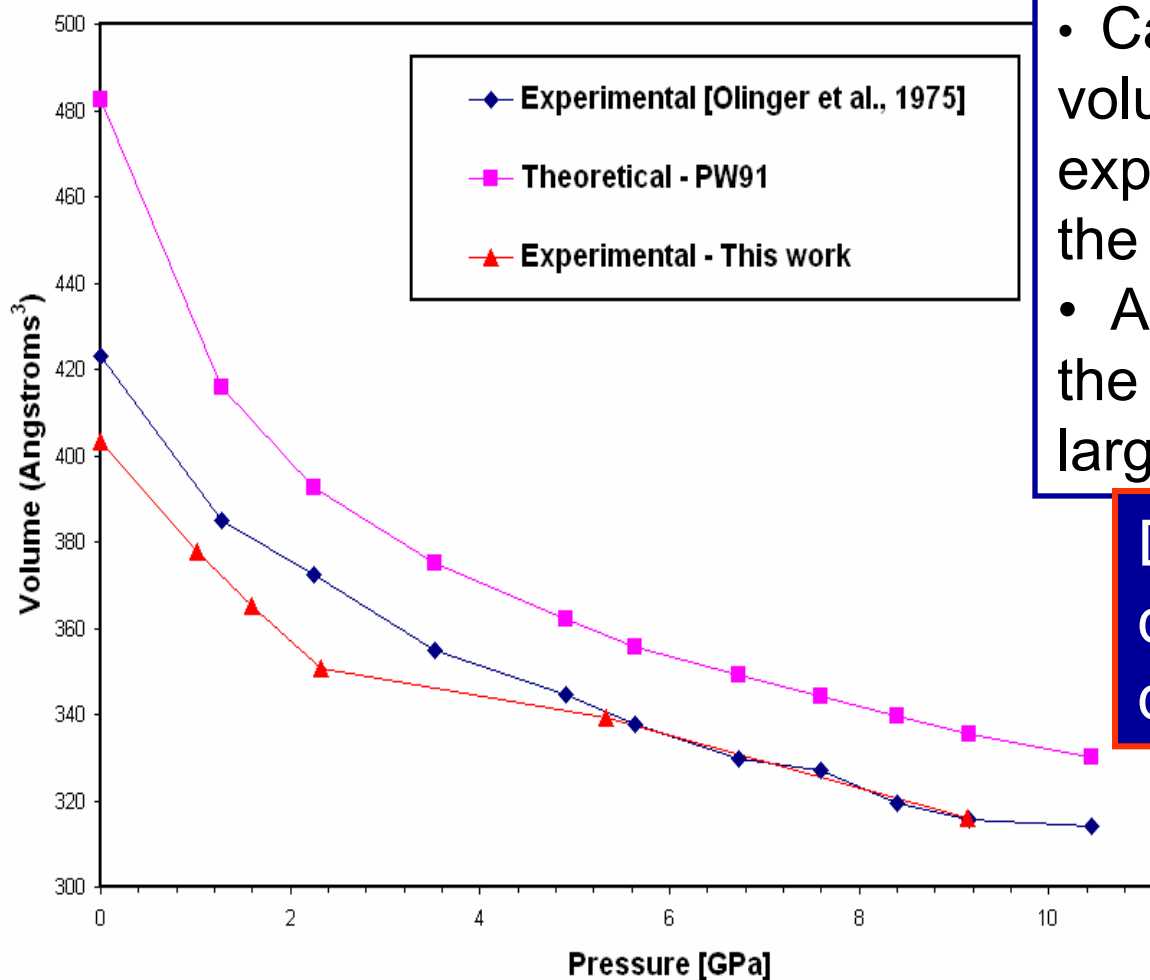
- Calculated unit cell volume is larger than the experimental values over the entire pressure range
- At ambient conditions the difference is quite large!!

Due to lack of dispersion forces in density functionals !

Limits ability to accurately predict the density of candidate energetic materials

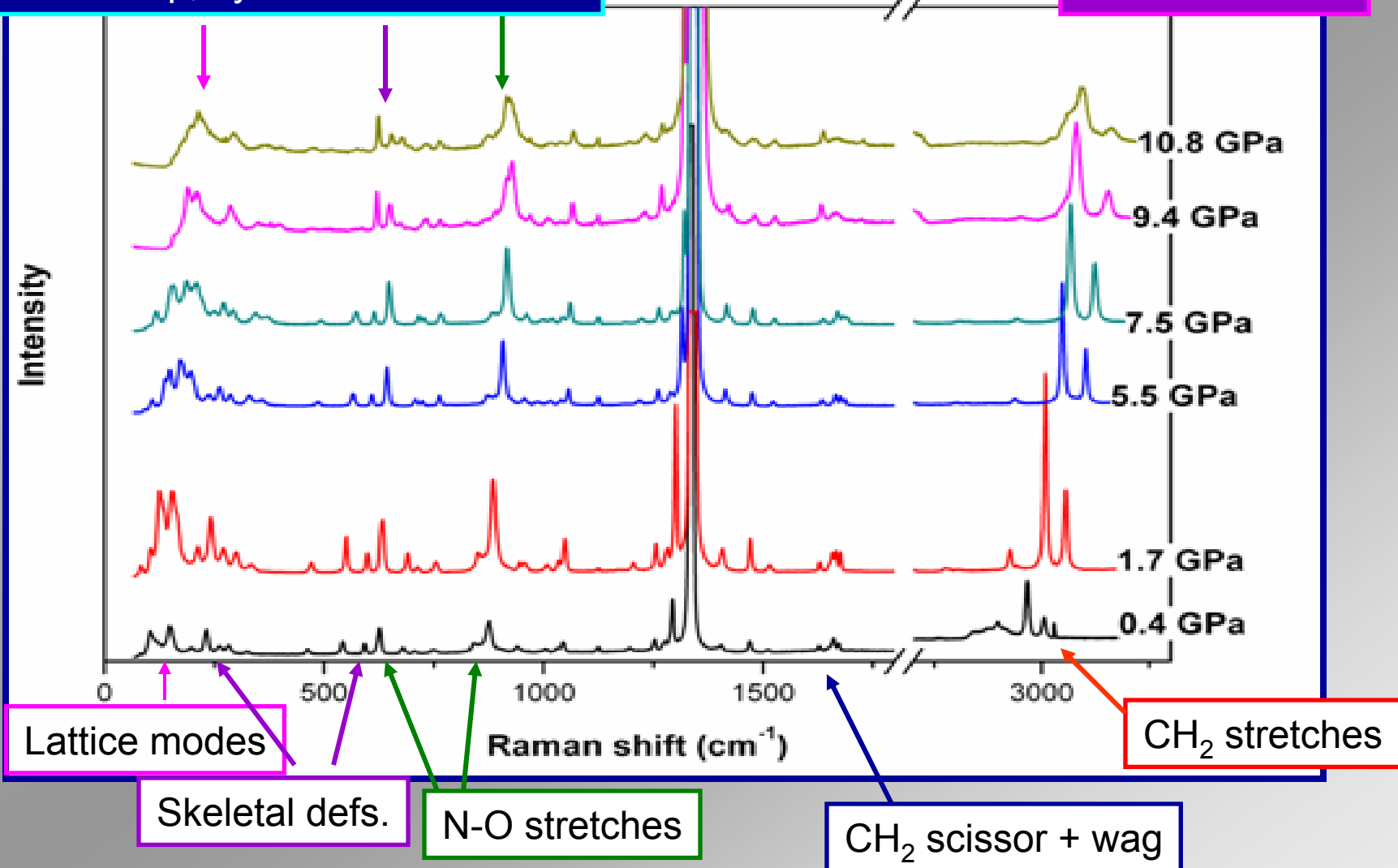**B. Olinger et al. J. Chem. Phys. 62 (1975) 4480.**

The experimental Raman spectra show evidence of a possible phase transition

Room temp, hydrostatic conditions

Not reversible !!

10.8 GPa
9.4 GPa
7.5 GPa
5.5 GPa
1.7 GPa
0.4 GPa

Intensity

Raman shift (cm^{-1})

Lattice modes

Skeletal defs.

N-O stretches

CH_2 scissor + wag

CH_2 stretches

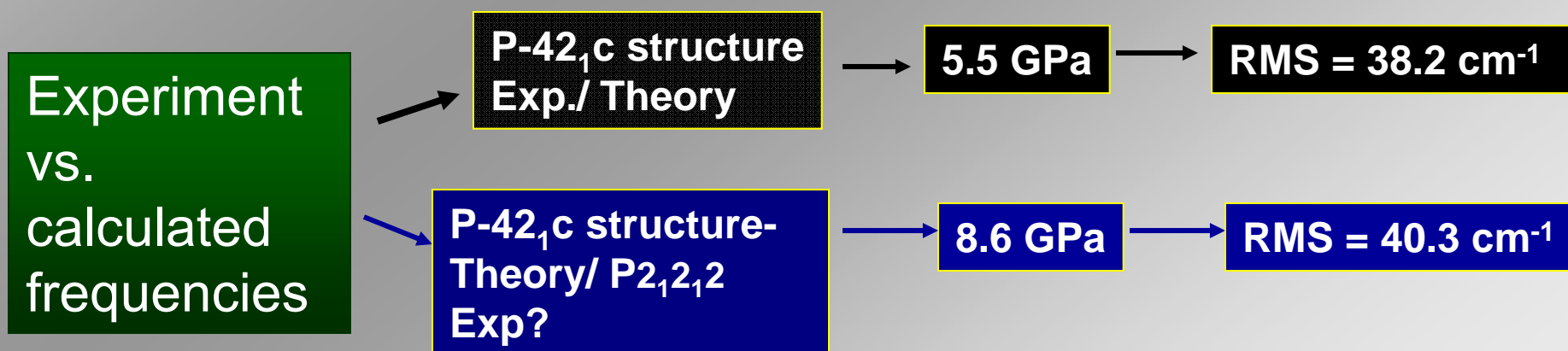# Theoretical calculations were used to explore the high-pressure phase

- The initial crystal had the $P2_12_12$ space group and C_2 molecular symmetry as recommended [1].
  - Initial crystallographic parameters of
    a = 9.95 Å, b = 9.39 Å and c = 6.64 Å

Cell consistently optimized to back to the $P\text{-}42_1c$ space group with S_4 symmetry

Can anything be learned from the vibrational calculations?

Experiment vs. calculated frequencies → $P\text{-}42_1c$ structure Exp./ Theory → 5.5 GPa → RMS = 38.2 cm^{-1}

$P\text{-}42_1c$ structure- Theory/ $P2_12_12$ Exp? → 8.6 GPa → RMS = 40.3 cm^{-1}

[1] **Y.A. Gruzdkov et al. J. Phys. Chem. A 108 (2004) 6216.**

Conclusions and Direction of Future Work

- High pressure phase appears near 9 GPa in both x-ray diffraction and Raman studies
  - Irreversible under hydrostatic conditions, non-hydrostatic samples have detonation near 6 GPa.
  - Role of particle size in phase transition?

- Combined theoretical/experimental studies have shown deficiencies exist in our predictive capabilities
  - Theoretical volumes are severely overestimated relative to experimental volumes
    - Due to lack of proper dispersion forces in the DFT functional
  - We were unable to confirm the symmetry of the high pressure phase using the theoretical calculations.

- Single crystal diffraction
  - Advances in diamond anvil cell technology

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- Argonne National Laboratory

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