

First-principles study of pentaerythritol tetranitrate single crystals under high pressure: vibrational properties

W. F. Perger¹, Jijun Zhao², J. M. Winey, and Y. M. Gupta

*Institute for Shock Physics, Washington State University, Pullman, WA
99164-2816*

Abstract

First-principles theoretical methods were used to investigate the vibrational properties of pentaerythritol tetranitrate (PETN) under hydrostatic compression up to 4 GPa. Bond lengths and bond angles for the PETN molecules and the pressure-volume relation for the crystal under high pressure were calculated and compared with previous calculations and with experimental results. Based on the calculated optimized geometries at ambient conditions and under hydrostatic pressure, the frequencies of the internal vibrational modes of the PETN molecules in the crystal and pressure-induced frequency shifts of these vibrational modes were obtained. The calculated vibrational frequencies are compared with previous single molecule calculations and with experimental data.

Key words: molecular crystals, vibrational frequencies, first-principles

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1 Introduction

The vibrational properties of a molecular solid provide information about the intra- and inter-molecular bonding of the system [1]. Therefore, changes in the vibrational properties are important indicators for understanding physical and

Email address: wfp@mtu.edu (W. F. Perger).

¹ Permanent address: Department of Physics and Department of Electrical Engineering, Michigan Technological University, Houghton, Michigan 49931-1295

² Current address: College of Advanced Science and Technology, Dalian University of Technology, Dalian 116024, China

chemical changes in molecular crystals under high pressure. Such information is particularly useful when considering compression-induced changes in high explosive (HE) organic solids. For this reason, the vibrational properties of several important HE crystals have been investigated experimentally under hydrostatic compression using Raman spectroscopy [2–4].

To achieve a comprehensive understanding of the high-pressure behavior of HE crystals and to associate the measured Raman spectra with changes in structure and chemical bonding, a complementary theoretical investigation of the vibrational properties of HE crystals under high pressure is needed. Historically, first-principles calculations for the vibrational properties of HE materials have been performed for single molecules [5,6], which corresponds to the gas phase. For the solid state, the weak van der Waals intermolecular interaction and the large size of the HE molecules make the theoretical description of HE crystals a challenging problem. Here we report on a first-principles calculation of the vibrational frequencies for HE single crystals. The ability to perform such calculations for the solid state is necessary for examining changes to the vibrational properties under compression.

In this letter, we present first-principles calculations for the molecular structure and frequencies of the internal vibrational modes of pentaerythritol tetranitrate (PETN, $C(CH_2ONO_2)_4$) single crystals at ambient conditions and under hydrostatic pressure up to 4 GPa. Calculations were performed using both a Gaussian basis all-electron code (CRYSTAL03) and a planewave-pseudopotential code (CASTEP). Results from the various calculations are compared with each other and with experimental data. One of the coauthors of this paper (J. Zhao) has also participated in work on frozen nitromethane, a simpler molecule, using plane-wave codes [7].

2 Computational methods

First-principles solid state calculations for PETN single crystals were performed using density functional theory (DFT). We used both the generalized gradient approximation (GGA-PW91) [8] and the B3LYP [9] hybrid functional to describe the exchange-correlation interaction of the electrons. The calculations were performed using two software packages. The first one, the CRYSTAL03 code [10,11], is based on the all-electron linear combination of atomic orbitals (LCAO) method. The 6-31G** Gaussian basis set was used in the calculations. We also employed the CASTEP code [12], which implements DFT within the planewave-pseudopotential method. In our CASTEP calculations, the ion-electron interaction was modeled using norm-conserving pseudopotentials [13]. A cutoff of 1200 eV for the plane-wave basis was used in the computations, along with a correction for the finite basis set. Within the

planewave-pseudopotential framework, the stress on the unit cell in a given crystal lattice can be directly calculated using the stress theorem [14]. Therefore, in the CASTEP calculations, the atomic positions and unit cell volume for PETN at ambient conditions or under a given hydrostatic pressure were determined by minimizing the Hellmann-Feynman force on the atoms for a specified stress on the unit cell. In the CRYSTAL03 code, calculation of the stress on the crystal unit cell is not available. Therefore, for a given volume V , the optimal ratio of the lattice constants a and c was determined that provided the lowest total energy. The zero-pressure volume V_0 and the pressure P corresponding to a volume V were obtained from the computed energy-volume (E-V) curve. Both the CRYSTAL and the CASTEP calculations are performed at an effective temperature of 0K. Therefore, the calculated unit cell volumes contain a systematic error, relative to experimental values, due to thermal expansion. Existing data [15] suggest expansions of several percent upon heating PETN crystals from 0K to room temperature.

The CASTEP and CRYSTAL03 calculations involved one unit cell of the PETN crystal together with periodic boundary conditions, where each of the two molecules in the unit cell possessed an S_4 molecular configuration (Fig. 1). During the geometry optimizations, the internal coordinates of the eight inequivalent atoms were relaxed under the constraint that the $P\bar{4}2_1c$ space group symmetry was maintained. Similar to previous calculations for PETN crystals [16], the Γ point was used to sample the reciprocal space of the unit cell. Our test calculations showed that including more \mathbf{k} points had little influence on the computational results.

Using the optimized crystal structures, vibrational frequencies (at the Γ point in reciprocal space) for the PETN crystal were obtained using the finite displacement method for both CRYSTAL03 and CASTEP computations. To enable these calculations for the CRYSTAL03 code, a supplemental script was developed. Each vibrational mode was identified by examining the symmetry of its eigenvectors and by visualizing the associated atomic motion with the aid of the Molden software [17].

3 Results and discussion

3.1 Structural properties

To determine the theoretical equilibrium structure for PETN, we performed a full optimization of both the lattice constants and the internal atomic coordinates. Results from CRYSTAL03 and CASTEP calculations for the lattice constants and the unit cell volume are compared with experimental data

[18,19] in Table 1. Similar to previous work by Gan *et al.* [16], the all-electron CRYSTAL03 calculations with gradient-corrected exchange-correlation functionals (B3LYP and PW91) reproduce the experimental lattice constants and cell volume fairly well. In contrast, the CASTEP calculations with the PW91 exchange-correlation functional significantly overestimate the cell volume. We obtained similar overestimates from additional planewave-pseudopotential calculations using different first-principles codes, pseudopotentials, and GGA functionals. In addition, increasing the cutoff energy for the planewave basis produced little change in the calculated cell volume. Therefore, although the reason for the difference between the CASTEP calculations and the CRYSTAL03 calculations is not known, our preliminary investigations suggest that the CRYSTAL03 calculations may suffer from an insufficient Gaussian-type basis set that acts to reduce the unit cell volume for a give pressure. Such an effect would be similar to that observed by Byrd, *et al* [20] when an insufficient planewave basis set was used. Further work is in progress to resolve this issue.

Starting from the zero-pressure equilibrium lattice structure, we applied hydrostatic compression to the PETN unit cell by gradually increasing the external pressure (CASTEP) or reducing the cell volume (CRYSTAL03). The experimental Raman data [2,21] show evidence for a conformational change around 5 GPa. However, because the $P\bar{4}2_1c$ space group was maintained during the geometry optimizations, we limited the pressures to 4 GPa in this study. In Fig. 2, we compare the theoretical pressure-volume (P-V) curves from CRYSTAL03 and CASTEP calculations with previous experimental results by Olinger [22,23]. Similar to previous first-principles calculations for the PETN structure [16,24], our CRYSTAL03 calculations show reasonable agreement with the experimental data. Although our CASTEP calculations overestimate both the cell volume and the compressibility at ambient conditions, the calculated unit cell volume is closer to the experimental values at higher pressure (see Fig. 2). The better agreement at higher pressures is presumably related to an increase in the strength of the intermolecular interactions as the molecules are forced closer together.

Bond lengths and bond angles from our optimized structures are in general agreement with previous calculations [16,24] and with experimental data. The agreement for the CASTEP results is particularly noteworthy given the overestimation of the unit cell volume (Table 1). Under compression both the CRYSTAL03 and CASTEP results agree qualitatively with the Gan *et al.* results [16] in predicting the O-N bond length (ester linkage) to reduce the most under hydrostatic compression. This finding contradicts the results of Brand [24], which predict the C-C bond to be most compressible. Our calculations also agree with previous studies [16,24] in predicting bond angle changes to be relatively small ($< 1^\circ$) under hydrostatic loading to 4 GPa.

3.2 Vibrational modes at ambient conditions

For the optimized structure of the PETN crystal at ambient conditions, we computed the vibrational frequencies using both the CASTEP and CRYSTAL03 codes. For the S_4 molecular point group of the PETN molecule, the irreducible representations for the 81 internal vibrational degrees of freedom are: $20A + 21B + 20E$ [5]. For the PETN crystal, with 2 molecules in the unit cell, the number of internal modes doubles to 162. However, because the crystal field is weak, the additional modes from the second molecule are for practical purposes degenerate with those from the first molecule. Therefore, for a given vibrational mode, the calculated frequencies of a given mode from each molecule in the unit cell are averaged to compare with the experimental values. In the work presented here, we do not consider the lattice modes of PETN. Calculation of the lattice modes requires a more accurate description of the intermolecular van der Waals forces, which is not within the reach of current computational capabilities for large systems like PETN.

In Table 2, we compare our calculated results for the PETN crystal with previous experimental data [5] as well as previous single molecule calculations using the Gaussian98 program [5]. The irreducible representation and assignment for each vibrational mode are also displayed. The assignments obtained from the analysis of our CRYSTAL03 and CASTEP results are in general agreement with those obtained from the previous molecular calculations [5]. Furthermore, the vibrational frequencies predicted by the CRYSTAL03 calculations agree quite well with the single molecule calculations. Therefore, since our CRYSTAL03 calculations used the same exchange-correlation functional (B3LYP) and basis set (6-31G**) as in the previous Gaussian98 calculations [5], the good agreement between the two calculations indicates that the weak intermolecular interactions in the uncompressed crystal do not significantly alter the internal vibrational frequencies of the PETN molecule compared to the gas phase.

A careful comparison between the theoretical results and the experimental IR/Raman spectra shows reasonable overall agreement. Over the entire frequency range studied, the average deviation of the calculated vibrational frequencies using the CASTEP code compared with the experimental values is about 5.1%. The CRYSTAL03 results are better, with an average deviation from the experimental values of 2.4% for the B3LYP functional and 3.0% for the PW91 functional. For the higher-energy vibrational modes (greater than 1100 cm^{-1}), the CASTEP calculations with the PW91 functional agree with the experimental data better than the CRYSTAL03-B3LYP results. The average deviation of the CASTEP PW91 results from the experimental values for the higher frequency modes is 1.9%, which is smaller than the 3.4% deviation of the CRYSTAL03-B3LYP results for the same frequency range. On

the other hand, the average deviation of the CASTEP PW91 results from the experimental values increases to 8.2% for frequencies lower than 1100 cm^{-1} , while the deviation is only 1.3% for the CRYSTAL03-B3LYP calculations. Using the PW91 functional with CRYSTAL03 results in an average deviation from experiment of 2.3% for frequencies higher than 1100 cm^{-1} and 3.8% for the lower-energy modes. Overall, the CRYSTAL03-B3LYP calculations tend to overestimate the higher vibrational frequencies, while the CASTEP-PW91 calculations tend to underestimate the lower vibrational frequencies. The CRYSTAL03-PW91 results appear to be intermediate between the other two cases. The better description of vibrational frequencies by the CRYSTAL03-B3LYP calculations in the range from 300 to 1100 cm^{-1} correlates with the fact that the CRYSTAL03-B3LYP calculations predict bond lengths that are closer to the experimental values than CASTEP-PW91.

3.3 Pressure-induced shift of vibrational frequencies

We investigated the vibrational properties of PETN crystals under hydrostatic compression up to 4 GPa using CRYSTAL03 with the B3LYP functional and CASTEP with the PW91 functional. Here we present our initial results; additional details will be described in a future publication. Pressure-induced vibrational frequency changes for several representative modes are shown in Fig. 3, along with experimental results from Raman measurements on PETN crystals in a diamond anvil cell [2,21]. We include the antisymmetric CH_2 stretch mode (E symmetry, 3025 cm^{-1}), the ON stretch + CC stretch mode (A symmetry, 873 cm^{-1}), and the CC bend + ONO_2 rock mode (A symmetry, 589 cm^{-1}).

From Fig. 3, we see that the CRYSTAL-B3LYP calculations reproduce the slopes of the measured pressure-induced changes in the vibrational frequencies rather well. For example, the fitted coefficients for the measured pressure-induced changes are 14.8 $\text{cm}^{-1}/\text{GPa}$ for the CH_2 stretch mode, 5.9 $\text{cm}^{-1}/\text{GPa}$ for the ON stretch + CC stretch mode, and 3.5 $\text{cm}^{-1}/\text{GPa}$ for the CC bend + ONO_2 rock mode, while the corresponding coefficients from the CRYSTAL03-B3LYP calculations are 15.0, 8.6, and 3.9 $\text{cm}^{-1}/\text{GPa}$, respectively. The CASTEP-PW91 calculations show reasonable agreement with the experimental results for the CH_2 stretch and the ON stretch + CC stretch modes, producing fitted pressure coefficients of 11.9 and 7.0 $\text{cm}^{-1}/\text{GPa}$, respectively. However, the results for the low frequency CC bend + ONO_2 rock mode are not as good, with the calculated frequency for the zero pressure vibration being strongly underestimated relative to the experimental value. In spite of this discrepancy, it is of interest that the calculated vibrational frequency is closer to the experimental value at higher pressure in a manner similar to that observed with the unit cell volume in Fig. 2.

These results indicate that first-principles calculations are able to provide information on the pressure dependence of vibrational frequencies for PETN, which in turn provides information about changes in the chemical bonding of PETN under compression. The response of energetic materials to shock compression is of particular interest. Therefore, calculations for the vibrational properties of PETN under uniaxial strain loading conditions are currently underway.

4 Summary and Conclusions

First-principles density functional theory calculations were performed for PETN crystals at various pressures (0-4 GPa) using the CRYSTAL03 and CASTEP programs. The CRYSTAL03 calculations reproduced the experimental structural properties quite well, while the CASTEP calculations significantly overestimated the unit cell volume and compressibility of the uncompressed PETN crystal. Both the CRYSTAL03 and CASTEP calculations yielded molecular bond lengths and bond angles in good agreement with experimental data and predicted the O-N bonds (ester linkage) to be most compressible under high pressure. Calculated vibrational frequencies for the PETN crystal at ambient conditions compared reasonably well with measured values, with the CRYSTAL03-B3LYP calculations performing better for the lower frequencies and the CASTEP-PW91 calculations performing better for the high frequencies. Comparison of the results from our solid state calculations with previous single molecule calculations indicates that the crystal field has little effect on the frequencies of the internal vibrational modes of the molecule for the uncompressed crystal. We also calculated the change in the vibrational frequencies as a function of hydrostatic pressure. Our calculations were able to predict the pressure-induced change in frequency for different vibrational modes, which showed reasonable agreement with experimental values. Thus, our results indicate that first-principles calculations, despite their current inability to correctly describe the intermolecular van der Waals forces, can be an important and useful tool for providing insight to changes in the structure and bonding of energetic molecular crystals under compression.

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Table 1

Theoretical and experimental lattice parameters $a(\text{\AA})$, $c(\text{\AA})$ and unit cell volumes $V(\text{\AA}^3)$ for the PETN crystal.

	Experiment		Theory				
	Ref.[18]	Ref.[19]	Ref.[16]	Ref.[24]	CRYSTAL03		CASTEP
					B3LYP	PW91	PW91
$a(\text{\AA})$	9.383	9.378	9.425	9.2546	9.439	9.431	9.868
$c(\text{\AA})$	6.711	6.708	6.758	6.6636	6.762	6.746	6.925
$V(\text{\AA}^3)$	590.8	589.9	600.3	593.7	602.4	599.0	674.3

Table 2: Selected vibrational frequencies for the PETN crystal from current and previous theoretical calculations compared with experimental data. IrrRep refers to the irreducible representation; CA, B3, PW, and G98 refer to the CASTEP, CRYSTAL03-B3LYP, CRYSTAL03-PW91, and Gaussian 98 calculations, respectively; IR and Raman refer to the infrared and Raman spectroscopy results [5]; (a) = antisymmetric and (s) = symmetric.

Assignment	IrrRep	Theory				Exp.	
		CA	B3	PW	G98	IR	Raman
CH ₂ rock	A	303	324	319	319		319
CCC def. + ON stretch +							
NO ₂ rock	E	375	458	437	453	460	459
C ₅ skeletal + CH ₂ wag +							
ON stretch	B	479	538	502	536		539
CC bend + ONO ₂ rock	A	509	594	568	585		589
C ₅ skeletal + ONO ₂ rock	B	566	627	598	617	618	619
CCC def. + ONO ₂ rock	E	582	632	599	623	624	624
ON stretch + CC stretch +							
NO ₂ scissors	A	592	685	634	673		676
ON stretch + CCC def. +							
NO ₂ rock	E	634	712	666	710	704	704
CCC def. + ON stretch	B	679	750	709	753	746	746
ONO ₂ umbrella	E	776	758	721	756		
ONO ₂ umbrella	A	781	759	721	757		
ONO ₂ umbrella + CCC def.	B	784	760	722	760	755	755
CC stretch	A	750	845	785	842		839
ON stretch	E	795	864	801	855	852	854
ON stretch	B	810	888	820	860	869	869
ON stretch + CC stretch	A	849	903	840	886		873
CCC def. + CH ₂ rock	B	864	928	899	934		900
CH ₂ torsion + CCC def.	E	865	938	902	952	939	939
CH ₂ rock + CO stretch	A	898	1009	972	1023		995

CO stretch + CCC def.	E	946	1019	994	1038	1003	1004
CO stretch + C ₅ skeletal + NO ₂ rock	B	939	1054	1026	1074	1038	1037
CH ₂ torsion + CC bend	A	1058	1059	1030	1071		1044
CH ₂ wag + C ₅ skeletal	B	1161	1188	1152	1194	1159	
CCC def. + CH ₂ wag	E	1175	1202	1164	1212	1193	1195
CH ₂ bend	A	1254	1260	1214	1274		1253
CH ₂ bend + C ₅ skeletal	E	1269	1288	1235	1295	1257	
CH ₂ bend + C ₅ skeletal + ONO ₂ rock	B	1291	1303	1254	1319	1272	1273
NO ₂ stretch + CH bend + C ₅ skeletal	E	1303	1326	1278	1336	1285	1286
NO ₂ stretch + CH ₂ wag	A	1274	1344	1292	1351		1294
CH ₂ wag + C ₅ skeletal + NO ₂ rock	B	1327	1351	1298	1352	1306	
CH ₂ wag + CCC def.	E	1376	1408	1347	1417	1387	
CH ₂ wag + CCC def.	B	1368	1412	1352	1422	1396	1397
CH ₂ wag + CC stretch	A	1398	1428	1367	1435		1406
CH ₂ scissors	A	1497	1519	1475	1535		
CH ₂ scissors	B	1472	1519	1477	1536	1509	1512
CH ₂ scissors	E	1477	1525	1481	1541	1474	1474
NO ₂ stretch (a)	A	1734	1726	1697	1775		1633
NO ₂ stretch (a)	B	1751	1735	1706	1776	1661	1665
NO ₂ stretch (a)	E	1751	1750	1719	1778	1648	1650
CH ₂ stretch (s)	B	2976	3106	3027	3102		
CH ₂ stretch (s)	E	2975	3109	3029	3103		2940
CH ₂ stretch (s)	A	2975	3112	3030	3105	2985	2987
CH ₂ stretch (a)	A	3043	3173	3089	3159		
CH ₂ stretch (a)	E	3042	3175	3091	3161	3023	3025
CH ₂ stretch (a)	B	3033	3178	3094	3163	2916	2918