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THE EFFECT OF A SIMULATED VOLUMETRIC EXPANSION: CALCULATED VIBRATIONAL PROPERTIES AND ELASTIC CONSTANTS OF PENTAERYTHRITOL

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Abstract. Current ab-initio calculations do not include the van der Waals interactions. These long range forces are important in the binding of many molecular crystals. Using current theory one may include empirical van der Waals forces to describe the binding of a molecular solid. The results of ab-initio calculations are at 0K. But, experiments measuring material properties are often at ambient conditions. The exclusion of thermal effects produces an inherent disparity between measurements and first-principles calculations of physical properties. In this work, the vibrational spectra and second-order elastic constants (SOECs) of pentaerythritol (PE) are found using density functional theory (DFT) with the B3LYP-D* functional. B3LYP-D* is the B3LYP functional with an empirical description of the van der Waals dispersion force. PE is chosen because it has a small, highly symmetric, unit cell and exhibits anisotropic binding. Also, recent experimental and theoretical vibrational studies show an interesting behavior of the OH-stretch mode for PE. Using DFT, the SOECs and vibrational spectra of PE are calculated at 0K. The volumetric expansion to ambient temperature is simulated by fixing the unit cell to an experimental volume, optimizing the structure, and recalculating properties. Results of elastic and vibrational properties for 0K, simulated ambient temperature, and experiment are compared.

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Keywords: DFT, dispersion correction, elastic constant, vibrational spectra, pentaerythritol

INTRODUCTION

Recently a density-functional theory (DFT) potential has been proposed which accounts for the van der Waals (vdW) dispersion interaction in crystalline systems [1]. This potential has been modified for use with the CRYSTAL09 [2] program and tested on molecular crystals [3], and is referred to as the B3LYP-D* potential. The purpose of the current work is to address the questions:

- Does the B3LYP-D potential improve agreement with experiment for properties in organic molecular crystals?
- Can better agreement with experiment be

achieved by calculating properties using the volume at finite temperature, effectively simulating volumetric expansion?

The crystalline binding in organic molecular crystals (OMCs) is dominated by intermolecular forces such as hydrogen bonding and van der Waals interactions. Covalent intramolecular interactions in OMCs are accurately modeled by current first-principles calculations (Hartree-Fock, B3LYP DFT, etc.). However, B3LYP DFT methods have shown poor performance in modeling OMCs with significant vdW interactions. A semi-empirical dispersion correction to DFT of the type r^6 has been proposed by S. Grimme [1]. In this work B3LYP is the standard Becke 3-

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parameter exchange with the Lee-Yang-Parr correlation. B3LYP-D and B3LYP-D* refer to B3LYP with the Grimme empirical dispersion corrections fitted for molecular and crystalline systems, respectively. All calculations were done using the CRYSTAL09 software.

The present work is motivated by the fact that most experimental data on OMCs is under ambient conditions whereas first-principles methods model OMCs at 0K, hindering quantitative comparison. The correction proposed by Grimme has been implemented in CRYSTAL09 and detailed testing on an OMC can provide a benchmark for other dispersion corrections. Pentaerythritol, $C(CH_2OH)_3$, (PE) was chosen as the test case for a vdW OMC because of the 21 atom highly symmetric unit cell and the anisotropy in crystal binding and is similar to PETN. The system is body centered tetragonal, with space group I-4, molecular S_4 point group, and 2 molecules per unit cell. The intramolecular binding is covalent, the intermolecular is hydrogen bonding in the (100) plane forming parallel (001) planes. The planes are held together by vdW interactions in the c-direction, as illustrated in Fig. 1.

B3LYP-D* calculations to date indicate that the dispersion interaction must be included to accurately model structural properties of vdW OMCs. This suggests improvement in the second-order elastic constant determination between B3LYP and B3LYP-D* [4].

IR spectroscopy finds the OH stretch mode of PE to decrease with increasing hydrostatic pressure. This behavior is confirmed qualitatively up to 4GPa [5] using HF and B3LYP theories. B3LYP-D* is applied in this work with pressures up to 2GPa.

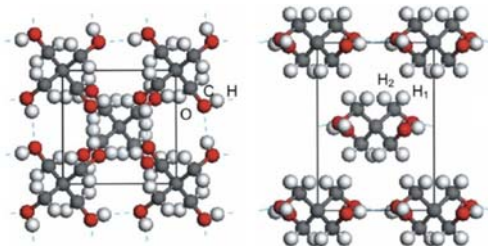


FIGURE 1. Ambient crystal structure of PE. (100) on left, (001) on right

APPROACH

The first step was to perform optimization of atomic positions and cell parameters for a range of Gaussian type functions (GTF) using the linear combination of GTF (LCGTF) method with B3LYP, B3LYP-D, and B3LYP-D* exchange-correlation potentials (EC). The basis sets investigated were 6-21G, 6-21G(d,p), 6-31G, 6-31G(d,p), 6-311G, 6-311G(d,p), 6-311G(2d,2p). Next the 3rd-order Birch-Murnaghan equation of state (EOS) was used for B3LYP-D* 6-311G(d,p) PE system. The EOS was then used to determine cell volumes at various pressures. The atomic positions were re-optimized and the vibrational modes and intensities calculated at each pressure. Volumetric expansion was then simulated by optimizing atomic positions at experimental volume. Finally, the simulated ambient elastic tensor was calculated.

RESULTS

Table 1 shows the calculated lattice constants and volumes for PE using the B3LYP, B3LYP-D and the B3LYP-D* potentials.

As can be seen from that table, the B3LYP-D* potential with a good basis set (6-311G(2d,2p)) underestimates the equilibrium volume, presumably because the calculation was performed at 0K whereas the experiment was performed at room temperature. Also, the results suggest that B3LYP-D* with the 6-311G(d,p) basis set is a sufficient level of theory because little improvement is seen when increasing to 6-311(2d,2p).

TABLE 1. Calculated PE structure and compared with experiment [6].

	a(Å)	c(Å)	Vol (Å ³)
B3LYP 6-311G(d,p)	6.15	9.16	347.13
B3LYP-D 6-31G(d,p)	6.03	7.84	285.57
B3LYP-D* 6-311G(d,p)	6.11	8.20	306.07
B3LYP-D* 6-311G(2d,2p)	6.11	8.23	307.33
Expt [6]	6.07	8.745	323.2

Fig. 2 shows the volume calculated using a variety of basis sets and exchange-correlation potential. As is evident from that figure, the B3LYP-D* value approaches the experiment one with increasing quality of basis set; however, as previously noted, it is not expected to reach it because the calculations are at 0K and the experiment at room temperature.

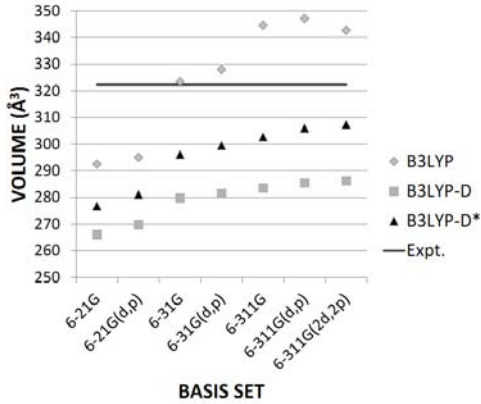


FIGURE 2. Calculated volumes of PE given various basis sets and compared with experiment [6].

Figs. 3 and 4 show the elastic constants c_{11} and c_{33} , respectively, for the same choices of basis sets and exchange correlation potentials as used for the structure. As with the structure results, the values of c_{11} and c_{33} approach the experimental values but because the calculations are at 0K and the experiment at room temperature, exact agreement is not expected. The results for the c_{11} elastic constant suggest that the inclusion of dispersion correction has a modest effect where crystalline binding is hydrogen bonding. Also, the use of a polarized basis set is crucial in modeling hydrogen bonding.

The results for the c_{33} elastic constant suggest that dispersion correction is important in modeling vdW binding but polarization in the basis set is less crucial. Again, the experiment was conducted at 300K so when comparing to calculation it is expected that elastic constants will be overestimated (the crystal is more rigid at 0K).

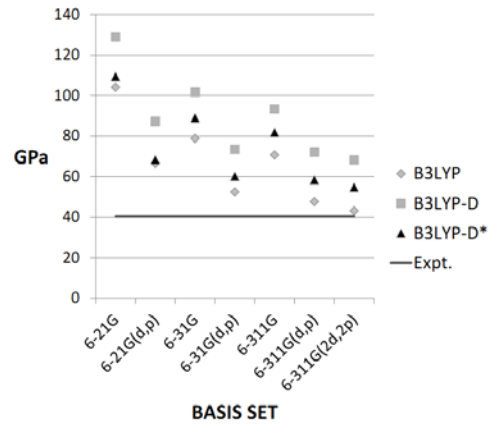


FIGURE 3. Calculated value of c_{11} using various basis sets and compared with experiment [7].

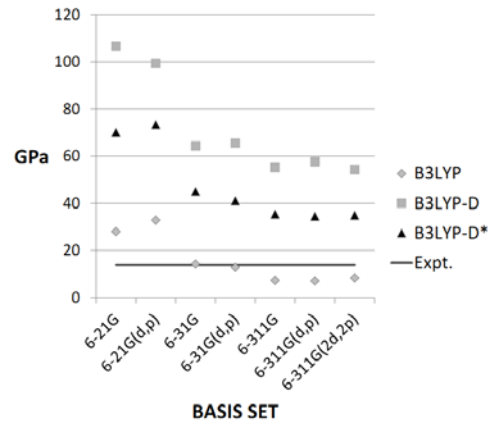


FIGURE 4. Calculated value of c_{33} using various basis sets and compared with experiment [7].

Vibrational Frequencies

The vibrational frequencies for PE as a function of pressure were determined up to 2GPa, as shown in Table 2. As can be seen from that table, the OH-stretch mode (A-symmetry) frequency decreases as a function of increasing pressure, as observed experimentally [5].

TABLE 2. Calculated vibrational frequencies of the OH-stretch mode (A symmetry) as a function of pressure.

Pressure	Frequency (cm^{-1})
0 GPa	3414.7
1 GPa	3382.7
2 GPa	3346.2

Simulating volumetric expansion

The next step is to “simulate” the volumetric expansion due to finite temperature. The procedure was to use the experimental volume at room temperature and re-optimize the internal co-ordinates holding the volume fixed. The results of this approach are shown in Table 3 and, as expected, the trend is to achieve better agreement with experiment in the simulated volumetric expansion case.

TABLE 3. Second-order elastic constants for PE using the B3LYP-D* potential at 0K (2nd column) and simulated volumetric expansion (3rd column).

	B3LYP-D* 6-311G(d,p)	B3LYP-D* 6-311G(d,p) Equil. vol.	Expt [7]
c_{11}	58.3	49.1	40.5
c_{12}	45.4	36.2	26.6
c_{13}	8.84	6.28	10.5
c_{16}	3.07	2.72	3.13
c_{33}	34.5	19.8	13.9
c_{44}	6.59	4.84	2.74
c_{66}	15.2	13.7	2.52

DISCUSSION

From the results presented here, the B3LYP-D* is a significant improvement in modeling vdW binding over B3LYP. Furthermore, simulating the volumetric expansion due to finite temperature substantially improves calculations for properties such as elastic constants. The equilibrium volume asymptotically approaches the experimental value using B3LYP-D* with increasing completeness of basis set. The elastic

constant calculation with B3LYP-D* shows significant improvement over B3LYP. This work will be completed by calculation of vibrational frequencies at a wider range of pressures. Future work will be to repeat these calculations with a different dispersion correction and compare the results.

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