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CALCULATION OF THE VIBRATIONAL SPECTRA OF α -RDX USING THE GRIMME DFT POTENTIAL

Warren F. Perger*, William Slough*, Loredana Valenzano* and K. M. Flurchick†

*Michigan Tech University

†North Carolina A&T State University

Abstract. The density-functional theory (DFT) potential by Grimme has been proposed for describing long-range dispersion corrections. This potential has been implemented into the CRYSTAL09 program and used to calculate the vibrational spectra in α -RDX at equilibrium. The frequencies and intensities are reported and compared with prior theory and experiment where possible.

Keywords: vibrational spectra, RDX, DFT

PACS: 78.40.-q, 71.15.Mb

INTRODUCTION

Inter-molecular interaction is responsible for mechanical and elastic properties. Therefore, characterization of the inter-molecular potential is valuable for understanding the shock initiation-to-detonation transition in energetic materials. An accurate description of inter-molecular interaction is also necessary for ambient volume/density calculations. The atomistic calculations require quantum mechanics (non-relativistic) and must go beyond Hartree-Fock and address the complexity of exchange-correlation theory. The intermolecular potential, often van der Waals, yields $\sim r^{-6}$ radial dependence. Unfortunately, commonly-used exchange-correlation density-functional theory functionals are not well-suited [1] to describe the van der Waals interaction. Organic molecular crystals (OMC) can have many electrons in the unit cell; e.g. RDX has 912 which makes all-electron calculations expensive. The critical issue in molecular crystal simulation is the proper description of noncovalent interactions between molecules, that is, hydrogen bonding, dispersive interactions (van der Waals), dipolar effects, etc. In this work, the B3LYP-D* DFT potential, which was shown to be successful

for molecular crystal calculations [2] using the CRYSTAL program [3], is used to calculate the IR spectrum of α -RDX. It is important to note that in this work we are primarily interested in calculating the low-frequency (lattice) modes where an accurate description of the intermolecular, van der Waals, potential is critical (as opposed to higher frequency modes which are dominated by intramolecular effects). It is therefore expected that the B3LYP-D* potential will provide a more accurate prediction of the lattice modes reported here.

The B3LYP-D functional of Grimme [4] is given by:

$$E_{B3LYP-D} = E_{B3LYP} - s_6 \sum_{\mathbf{g}} \sum_{ij} f_{dmp}(R_{ij,\mathbf{g}}) \frac{C_6^{ij}}{R_{ij,\mathbf{g}}^6} \quad (1)$$

where s_6 is the scaling factor for the given DFT method, C_6^{ij} is the dispersion coefficient for the ij pair of atoms, and $R_{ij,\mathbf{g}}$ is the interatomic distance between atoms i in the reference cell and j in the neighboring cell with translation vector \mathbf{g} . The damping function, f_{dmp} , and scaling factors were as used in ref.[2]:

$$f_{dmp}(R_{ij,\mathbf{g}}) = \frac{1}{1 + e^{-d(R_{ij,\mathbf{g}}/R_{vdw} - 1)}}, \quad (2)$$

where d is the steepness of the damping function ($d=20$, see ref. [4]). The value of the s_6 scaling factor was 1.00 and the atomic van der Waals radii, R_{vdW} (in Å), used were 1.30 for hydrogen and 1.05 for carbon, nitrogen, and oxygen. With these scaling factors, the potential is hereafter referred to as B3LYP-D*. The atomic C_6 coefficients were taken from ref. [4]. Note that the same scaling factors and radii were used for all calculations reported here.

RESULTS

Table 1 shows the effects of using various basis sets and exchange-correlation potentials for calculating the lattice constants and equilibrium volume for α -RDX. Recognizing that all the theoretical values are at 0K and the experiment was performed at room temperature, the volumetric expansion of Cady [6] was used to correct the theoretical volumes and those values are given in parentheses in the last column. The B3LYP 6-311G* and 6-31G** results illustrate that when the B3LYP potential is used, an overestimation of equilibrium volume is observed for both basis sets, as found in prior work [5]. When the B3LYP-D* potential is used (with the 6-31G** basis set), an underestimation relative to experiment is observed: 1526.9 vs. 1633.86 Å³. However, considering the finite-temperature volumetric expansion, the B3LYP-D* becomes 1639.7 Å³, in much better agreement with the experimental value of 1633.86 Å³. The prior theoretical values for PBE-D [7] and DFT-D [8] are lower than experiment but, when corrected for room temperature, considerably overestimate the experimental value.

Vibrational Frequencies

To determine the vibrational modes, both the cell lattice parameters and atomic positions are optimized. That is, the number of runs, $n_{runs} = 3N(n_{pts} - 1)$, are created, where N is the number of atoms and n_{pts} is the number of points in the numerical 2nd-derivative grid. Note the first derivatives were determined analytically by the CRYSTAL09 program. Finally, a cartesian Hessian matrix is formed from the

TABLE 1. Optimized lattice parameters for α -RDX. The values in the last column for volumes which are in parentheses have been corrected for room temperature using Cady [6].

	a(Å)	b(Å)	c(Å)	Vol (Å ³)
B3LYP 6-311G*	13.53	11.78	11.09	1764.4 (1897.3)
B3LYP 6-31G**	13.53	11.60	10.83	1698.9 (1824.5)
B3LYP-D* 631G**	13.19	11.19	10.35	1526.9 (1639.7)
CASTEP	13.49	11.64	11.11	1744.2 (1872.6)
PBE-D[7]	13.2	11.45	10.71	1618.7 (1737.5)
DFT-D[8]	13.237	11.391	10.770	1623.93 (1743.1)
Expt[9]	13.18	11.57	10.71	1633.86

second-derivative of the total energy:

$$f_{cart,ij} = \frac{\partial^2 E}{\partial Q_i \partial Q_j} \quad (3)$$

Once the Hessian is computed, conversion to a mass-weighted coordinate system is performed, and diagonalizing the resulting matrix produces the eigenvalues as the vibrational frequencies and the eigenvectors give the mode atomic displacements.

The atomic Born charge tensors are key quantity for calculation of IR intensities, LO modes, and static dielectric tensor and defined by [10]:

$$Z_{\alpha,ij} = \frac{\partial}{\partial u_{\alpha j}} \left(\frac{\partial U}{\partial E_i} \right) \equiv \frac{\partial}{\partial u_{\alpha j}} u_j \quad (4)$$

where U is the total energy, E_i is a component of the electric field, μ_i is the i^{th} component of the cell dipole moment and u_j is the displacement relative to equilibrium. In crystalline systems, the dipole moment is not a bulk property (as it depends on arbitrary choice of cell). The intensity of the k^{th} mode is given by:

$$I_k = d_k \left| \frac{\partial \vec{\mu}}{\partial Q_k} \right|^2 \quad (5)$$

which is proportional to the square of the first-derivative of the dipole moment with respect to the

normal mode coordinate Q_k times the d_k degeneracy of the k^{th} mode. The dipole moment derivative is evaluated numerically by using the unit cell well-localized Wannier functions.

Fig. 1 shows the lowest IR active modes of α -RDX using B3LYP-D* and the 6-31G** basis set. Table 2 presents the 24 lattice modes calculated with the CRYSTAL09 program, the B3LYP-D* potential, and the 6-31G** basis set, and compares them with prior calculations and experiment. Comparing the present results with experiment, it should be noted that the experiment was performed at room temperature whereas the present results calculated at 0K. The trend is that the present theoretical results overestimate the vibrational frequencies and we would expect that if we could perform a room temperature calculation, we would see a softening (decrease in the vibrational frequency), likely bringing the theoretical results in closer agreement with experiment. As can be seen from that table, the present values are generally closer to experiment than prior theory (T1 and T2 columns), as shown clearly in Table 3 where the standard deviation and average deviation are calculated for the 3 theoretical calculations each relative to experiment and are much lower for the present calculation.

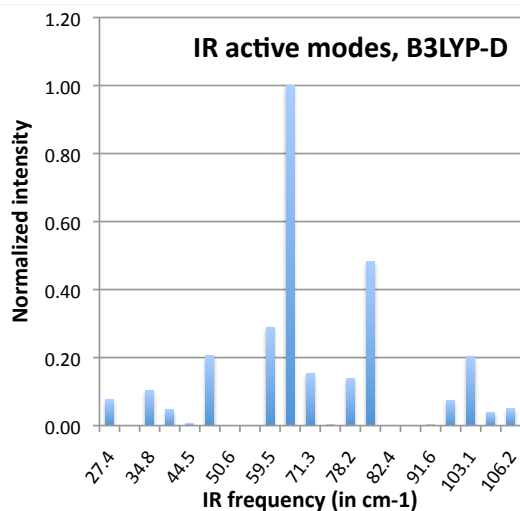


FIGURE 1. The lowest IR active modes of α -RDX using B3LYP-D*.

TABLE 2. Lattice modes for α -RDX with columns showing the mode, symmetry, two prior theoretical results (T1 and T2), experiment (Exp), and present work (Pres), respectively. All values are in cm^{-1} .

Mode	Sym	T1[7]	T2[11]	Exp[12]	Pres
L_6	A_g	92.8	98	70	70.0
	B_{1g}	89.1	91	70	78.0
	B_{2g}	82.3	98	74	76.7
L_5	B_{3g}	85.3	100	70	79.0
	A_g	84.5	88	59	60.8
	B_{1g}	74.1	80	59	67.6
L_4	B_{2g}	74.3	85	60	70.1
	B_{3g}	79.7	77	59	66.2
	A_g	72.0	73	51	49.6
L_3	B_{1g}	69.3	68	52	59.4
	B_{2g}	67.8	74	49	57.2
	B_{3g}	71.5	66	49	61.8
L_2	A_g	63.4	60	51	49.6
	B_{1g}	56.6	56	47	51.0
	B_{2g}	54.6	56		55.4
L_1	B_{3g}	58.3	53	49	51.3
	A_g	43.1	52	33	34.8
	B_{1g}	34.5	48	28	33.4
L_1	B_{2g}	34.6	23	29	48.0
	B_{3g}	45.8	41	37	37.2
	A_g	9.6	32	20	26.5
L_1	B_{1g}	-8.7	-38	20	-9.1
	B_{2g}	-21.9	-30	20	-7.5
	B_{3g}	-23.1	-25	19	-7.2

TABLE 3. Lattice modes statistics, standard deviation and average deviation in columns 2 and 3, respectively, for α -RDX comparing prior theoretical calculations (rows 2 and 3, T1 and T2 as denoted in Table 2) with this work. Values are in cm^{-1} .

	Std dev	Ave Dev
T1[7]	8.2	6.3
T2[11]	8.9	7.1
This work	5.1	4.1

CONCLUSION

The Grimme potential shows promise for van der Waals bonded crystals as shown in this work for α -RDX. The temperature-compensated equilibrium volume for B3LYP-D* is closer to experiment than B3LYP and prior theoretical results. The lattice modes were calculated with B3LYP-D* and were likewise closer to experiment than either the B3LYP

result. The standard deviation of the B3LYP-D* values relative to experiment was significantly smaller than the corresponding standard deviations from prior theoretical work.

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