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# $\gamma$ PHASE RDX: INITIAL STUDY OF GEOMETRY, SPECTRUM AND EOS

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**Abstract.** We present a full 3D periodic density functional theory study of the geometry and vibrational spectrum of  $\gamma$  phase nitramine, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The B3LYP-D\* functional as adjusted for molecular solids from Grimme's semi-empirical approach for molecules is used to better describe the van der Waals interactions in this system. Specifically, the low terahertz portion of the spectrum is computed to determine modes that change substantially in behavior with respect to an alpha phase that is near the transition pressure for the system. These key modes provide possible clues into the nature of the  $\alpha - \gamma$  phase transformation.

**Keywords:** Gamma Phase RDX, DFT

**PACS:** 43.35.Ei, 78.60.Mq

## INTRODUCTION

This work focuses on an initial all-electron study of RDX ( $(C_3N_6O_6H_6)$ ) in the  $\gamma$ -phase using a development version of the Crystal09 program[1, 2]. The goal is to determine a description of inter-molecular interactions for ambient volume/density. RDX has 912 electrons (which makes all-electron calculations expensive) plus the  $\gamma$ -phase of RDX has low symmetry which further increases the computation time. Note that the commonly used exchange-correlation density-functional theory is not well suited for crystals with long range electrostatic interactions. That is, the important issue for these systems is the description of the non-covalent interactions between the molecules, such as the hydrogen bonding and dispersive interactions (van der Waals) dipolar effects.

Different approaches are possible for the modeling of energetic solids:

- Hartree-Fock (HF). The exchange energy is correct, however, there is no electron-electron correlation.
- Density Functional Theory (DFT). Using an

approximate exchange-correlation functional for both exchange and correlation interactions. However, dispersive effects are a difficulty as DFT is a local approximation.

- Perturbation theory. Theoretically very solid, but computationally this approach is extremely challenging.

The  $\gamma$ -phase crystal[3] is an orthorhombic structure with space group  $Pca2_1$  with lattice parameters  $a = 12.5650 \text{ \AA}$ ,  $b = 9.4769 \text{ \AA}$ ,  $c = 10.9297 \text{ \AA}$  and an ambient volume of  $1301.283 \text{ \AA}^3$ . There are two conformers of the RDX molecules present in the  $\gamma$ -phase of the RDX crystal labeled axial-axial-axial  $AAA$  and axial-axial-intermediate  $AAI$  molecules. The crystal structure with the two conformers is shown in Figure 1, and the  $AAI$  conformer is shown in Figure 2.

## METHODS

In this study, crystal properties of  $\gamma$ -phase RDX are calculated in the framework of DFT with van der

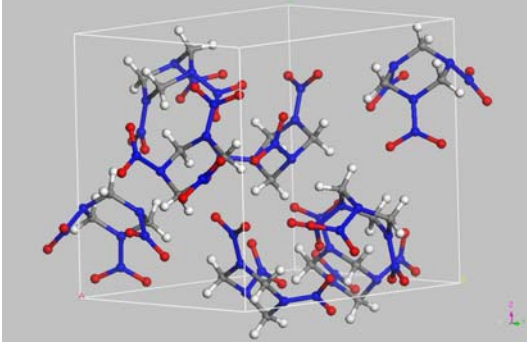


FIGURE 1.  $\gamma$ -phase RDX

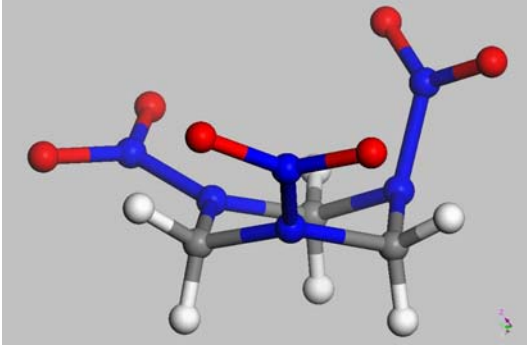


FIGURE 2. RDX AAI Conformer

Waals corrections  $E_{DFT-D}$ [4, 5].

$$E_{DFT-D} = E_{KS-DFT} + E_{DISP} \quad (1)$$

where  $E_{KS-DFT}$  is the standard Kohn-Sham DFT energy and  $E_{DISP}$  is the energy correction due to the van der Waals interactions. In this work, the functional used is the B3LYP-D\*[6].

$$E_{B3LYP-D} = E_{B3LYP} - s_6 \sum_g \sum_{ij}^{N_{at}} f_{dmp}(R_{ij}) \frac{C_6^{ij}}{R_{ij,g}^6} \quad (2)$$

$$f_{dmp} = \frac{1}{1 + e^{-d(R_{ij,g}/R_{vdW}-1)}} \quad (3)$$

where  $N_{at}$  is the number of atoms,  $C_6$  is the dispersion coefficient for atom pair  $i, j$  and  $R_{ij}$  is the distance between atoms  $i, j$ , and the damping function is  $f_{dmp}$ . The term  $R_{vdW}$  is the sum of the van der Waals radii of the two atoms labelled by  $i, j$ . For this work, the coefficients are listed in Table 1.

The basis sets are composed of Bloch orbitals

$$\phi_\mu(k, r) = \sum_g \xi(r - A_\mu - g) e^{ikg} \quad (4)$$

TABLE 1. Dispersion correction values for this work, with  $s_6$  is the scaling factor,  $d$  the steepness, and  $R_{cut}$  the cut-off radius.

$s_6$	$d$	$R_{cut}$
1.00	20.0	25.0 Å

where the atomic orbitals,  $\xi(r - A_\mu - g)$ , composed of a linear combination  $n_G$  Gaussian-type functions (GTF's):

$$\sum_g \xi(r - A_\mu - g) = \sum_{j=1}^{n_G} d_j G(\alpha_j; r - A - g) \quad (5)$$

## RESULTS

### Crystal Geometry

Using the Gaussian basis sets 6-21G, 6-31G, 6-31G\*\* and dzp with the B3LYP-D functional, the lattice parameters were computed. Note the ambient volume from experiment is 1301.283 (Å<sup>3</sup>)[7].

The lattice parameters, ambient volumes and densities are listed in Table 2.

### Vibrational Frequencies

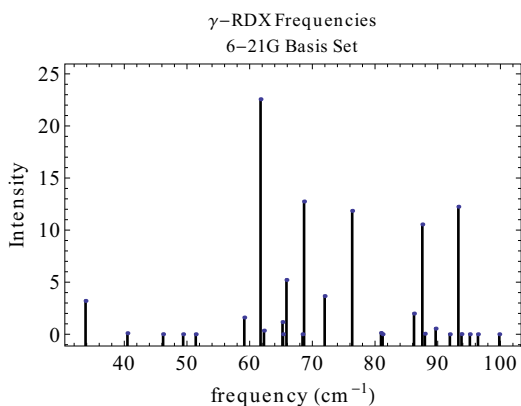
To determine the vibrational modes, begin by optimizing both the cell lattice parameters and atomic positions. That is, a set of computer runs  $n_{runs} = 3N(n_{pts} - 1)$  are performed where  $N$  is the number of atoms and  $n_{pts}$  is the number of points in the numerical 2nd-derivative. Note the first derivatives are determined analytically by the Crystal09 program and are more accurate than the numerically computed second derivatives used to form the Hessian matrix. Finally, create a cartesian Hessian matrix from the second derivative of the total energy:

$$f_{cart,ij} = \frac{\partial^2 E}{\partial Q_i \partial Q_j} \quad (6)$$

Once the Hessian is computed, convert to a mass-weighted coordinate system, diagonalize the resulting matrix and the eigenvalues are the vibrational fre-

**TABLE 2.** Lattice parameters, volume and density computed for different basis sets.

Basis Set	a (Å)	b (Å)	c (Å)	Volume (Å <sup>3</sup> )	Density ( $\frac{g}{cm^3}$ )
6-21G	13.0222	10.2647	10.6571	1424.52	2.071
6-31G	13.2060	10.3884	11.1634	1531.85	1.925
6-311G**	12.6048	9.5513	10.8102	1301.46	2.266
dzp	12.6162	9.5453	10.8067	1301.41	2.266
Expt[7]	12.5650	9.4769	10.9296	1301.238	



**FIGURE 3.** RDX Spectra

quencies. The lowest frequencies ( $< 100 \text{ cm}^{-1}$ ) and intensities are listed in Table 3 and are displayed in Figure 3.

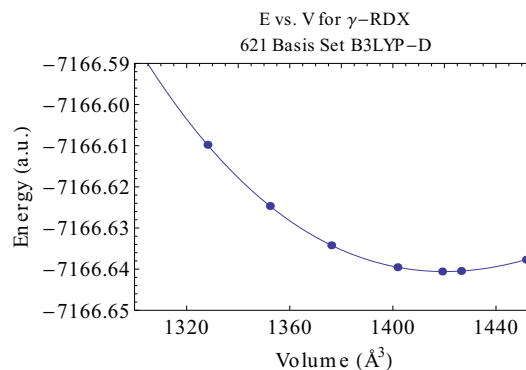
### Equation of State

Using the Gaussian basis set 6-21G, the Equation of State (energy versus volume) is determined. The equation of state (EOS) is fit to the Birch-Murnaghan 3rd-order function.

### DISCUSSION

This is the first computation (to the knowledge of the authors) of the lattice constants, vibrational frequencies, and EOS of the  $\gamma$ -phase of the RDX crystal using the CRYSTAL program.

The  $\gamma$ -phase RDX crystal is computationally difficult to study due to the low symmetry of the crystal. As shown in Table 1, for calculating the lattice pa-



**FIGURE 4.**  $\gamma$ -phase RDX Energy versus Volume Plot

rameters, four basis sets were used: 6-21G, 6-31G, 6-311G\*\* and dzp. From that table, it is evident that the better quality basis sets (6-311G\*\* and dzp) greatly improve upon the agreement with experiment.

The lowest 30 vibrational frequencies for  $\gamma$ -phase RDX in Table 3, using the 6-21G basis set, are presented here for comparison with future calculations using better basis sets and, hopefully, experiment.

Likewise, no prior theoretical study of the EOS for the  $\gamma$ -phase of RDX is known and future calculations and experiments are in order.

### ACKNOWLEDGMENTS

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**TABLE 3.** Vibrational frequencies for  $\gamma$ -phase RDX using the 6-21G basis set.

Frequency ( $cm^{-1}$ )	Intensity	Irreducible Representation	Raman	IR
99.8255	0.001	$B_1$	A	A
96.4215	0.000	$A_2$	I	A
95.1270	0.003	$A_1$	A	A
93.7939	0.015	$B_2$	A	A
93.2951	12.245	$B_1$	A	A
91.9374	0.0	$A_2$	I	A
89.6715	0.543	$B_2$	A	A
87.9492	0.050	$B_2$	A	A
87.5464	10.546	$A_1$	A	A
86.2183	1.9871	$B_1$	A	A
81.2102	0.0	$A_2$	I	A
80.9555	0.121	$A_1$	A	A
76.3564	11.849	$B_1$	A	A
71.9662	3.6640	$B_1$	A	A
68.6800	12.747	$B_1$	A	A
68.4346	0.0	$A_2$	I	A
65.8714	5.2151	$B_2$	A	A
65.3204	0.0	$A_2$	I	A
65.2430	1.1685	$A_1$	A	A
62.2817	0.350	$B_2$	A	A
61.7385	22.565	$A_1$	A	A
59.1444	1.6067	$B_1$	A	A
51.4017	0.0	$A_2$	I	A
49.3906	0.0	$A_2$	I	A
46.1932	0.0049	$A_1$	A	A
40.5022	0.1008	$B_2$	A	A
33.8220	3.2030	$A_1$	A	A

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