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THE TERAHERTZ INFRARED SPECTRUM OF CYCLOTRIMETHYLENETRINITRAMINE: TARGETING ANHARMONIC MODES FOR THE FINGERPRINTING AND DETECTION OF RDX

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Abstract. Recent approaches to the modeling of molecular solids have provided for a dramatic improvement in the prediction of zero Kelvin behavior for some properties of interest. Most notably the vibrational spectrum for these systems can now be calculated robustly via *ab initio* methods employing density functional theory. This improvement, however, leads to a quandary: the accurate physical modeling of these systems at zero Kelvin in many cases will not provide values and even physical behavior matching experimental values under ambient conditions. We examine this quandary in detail by considering zero Kelvin calculations using the B3LYP-D* functional of the terahertz infrared spectrum of the energetic material cyclotrimethylenetrinitramine (RDX). Most importantly we show what knowing the deviation from the simple harmonic approximation of a given mode at zero Kelvin says about the anharmonicity of the mode near ambient volumes. Finally, we discuss the practical implications for using *ab initio* calculations to create "finger-prints" for the detection of explosives such as RDX.

Keywords: RDX, CRYSTAL09, terahertz spectroscopy, anharmonic modes, detection, B3LYP-D*, molecular crystal

PACS: 61.66.Hq, 62.50.-p, 61.50.Ah

I. INTRODUCTION

Cyclotrimethylenetrinitramine ($(\text{CH}_2\text{NNO}_2)_3$), also known as 1,3,5-trinitro-1,3,5-triazacyclohexane and commonly as RDX, is an energetic material usable as a propellant and as an explosive.¹ In solid form it is a molecular crystal with individual molecules held together through hydrogen bonding and dispersion forces. The accurate representation of dispersion forces in molecular crystals with density functional theory (DFT) methods has represented a long standing challenge to the modeling of these materials.² Recent approaches using *a posteriori* semi-

empirical terms with density functionals, such as the Grimme B3LYP-D model, have been shown to yield improved descriptions of dispersion forces with little cost in additional computational time.³ This approach, however, should yield properties for molecular crystal systems at a temperature of zero Kelvin. Given the nature of the bonding mechanisms in molecular solids, it is to be expected that accurate calculations on the properties of these systems will yield values for zero Kelvin behavior that will differ noticeably from those under ambient temperature conditions.⁴ For example, the density of molecular solids may be more than 5% higher at zero Kelvin than at

ambient. Since experimental results or the sought after behavior for a molecular solid is often for ambient temperature, the realization exists that the results from increasingly accurate modeling of zero Kelvin behavior must be carefully used when the prediction of behavior under different temperature conditions is intended.

The remainder of this paper is structured as follows. Section II describes the computational modeling of the alpha phase of crystalline RDX (α -RDX). An *a posteriori* semi-empirical DFT chemical model (B3LYP-D*) is used in the Hamiltonian for all calculations. The resulting structure for α -RDX is discussed in section III. Section IV shows the calculated spectrum with comparison to available experimental data. The anharmonic behavior of vibrational modes is discussed and characterized in section V. Section VI summarizes the main findings from this study.

II. COMPUTATIONAL APPROACH

Our calculations on the RDX system were performed using a parallel version of the all-electron CRYSTAL09 modeling program.^{5, 6} CRYSTAL09 employs a periodic extension of linear combinations of localized atomic orbitals, as well as symmetry routines to represent the electronic structure of crystalline solids. A chemical model using a 6-311G** basis set⁷ and a B3LYP density functional with an *a posteriori* semi-empirical term (B3LYP-D*) was employed. The B3LYP-D* approach is a refitting of the Grimme B3LYP-D correction parameterized for use in molecular crystal systems.^{4, 7} The construction of an equation of state and equilibrium crystal structures as used in this study was completed in a fashion similar to that detailed in previous work done by the authors.⁹

The unit cell of α -RDX contains 8 molecules organized in a crystal structure of orthorhombic space group Pbca.¹⁰ The RDX molecules are of C_s point group symmetry with two nitro groups of the molecule in an axial position relative to the puckered C-N ring, and the nitro third group in an equatorial placement (AAE configuration). Crystal structures as a function of density/volume were found by minimizing total unit cell energy and residual forces.

The CRYSTAL09 modeling program calculates

harmonic vibration frequencies at the gamma-point using the FREQCALC routine.^{11, 12} The frequencies, intensities, and normal modes of the α -RDX crystal system were obtained using the default values as set in this routine.⁶

Once the vibration problem for RDX has been solved under the harmonic approximation, a complete set of eigenvectors exists that can then be explored to generate the actual potential for a given mode. The SCANMODE routine⁶ within the CRYSTAL09 program moves a system through a number of equally-spaced steps along the direction specified by the eigenvector for the mode of interest. The total energy of the system, as well as the energy that the system would have under the simple harmonic approximation, is calculated at each step. The difference between these two energy values illustrates the deviation from a simple harmonic potential at each displacement value along the eigenvector of the mode under study.

III. α -RDX STRUCTURE

Table 1. Comparison of calculated and measured lattice structure parameters for α -RDX.

$\text{\AA} / \text{K}$	Calculated 0K	Exp (90K) ¹³	Exp (220K) ¹⁴	Exp (295K) ¹⁰	Calculated (295K)
a	13.20	13.14	13.17	13.18	13.37
b	11.21	11.42	11.54	11.57	11.41
c	10.47	10.59	10.67	10.71	10.71
$V/\text{\AA}^3$	1549.3	1589.1	1620.6	1633.2	1633.8
$\rho/\text{g cm}^{-3}$	1.905	1.858	1.821	1.806	1.805

Our 6-311G**/B3LYP-D* chemical model produces a zero Kelvin structure for α -RDX that is 5.1% smaller than is measured at ambient temperature (see Table 1). In order to computationally simulate α -RDX at ambient temperature, a full optimization was done with the single constraint of imposing a constant volume of near 1633 to 1634 \AA^3 . The resulting structure was able to fairly accurately reproduce the known lattice parameters. This is especially true for the c-lattice parameter which is along the direction in

which adjacent RDX molecules are held together primarily through dispersion forces.

Figure 1 shows that the density of α -RDX follows a quadratic function of temperature for the range from zero to 300 Kelvin. The fit uses our calculated density at zero Kelvin and available experimental data.^{10, 13, 14}

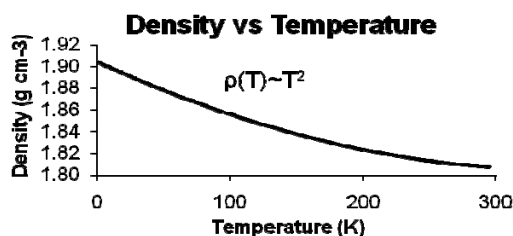


Figure 1. Density versus temperature for α -RDX.

Fitting the results of a series of calculated total energy versus volume data to a Murnaghan equation of state produces the volume versus pressure relationship shown in Figure 2.

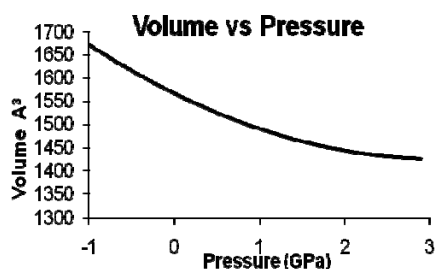


Figure 2. Volume versus pressure for α -RDX for a Murnaghan equation of state from computational simulation.

Of special note is that the pressure versus volume relationship shown in Figure 2 is for a temperature of zero Kelvin. Also of interest is that the ambient pressure structure at 295 K as measured by experiment has a volume of 1633 \AA^3 . Our calculations show that at zero Kelvin the ambient pressure structure has a volume of 1549 \AA^3 . In this region of thermodynamic space, a change in volume caused by a change in temperature of 300 K roughly corresponds to a change in volume caused by a pressure change of 0.6 GPa.

IV. LOW TERAHERTZ IR SPECTRUM

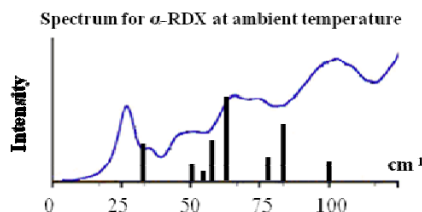


Figure 3. IR spectrum for α -RDX at ambient temperature.

The significant difference in structure between calculations executed at zero Kelvin and the measured physics at ambient temperature suggests that the vibrational spectrum in the low terahertz region will also show similar disparities. This is indeed the case. Figure 3 shows the calculated infrared (IR) line spectrum for this region at the ambient temperature volume. The continuous curve in figure 3 is derived from the experimental results of Allis, et al.¹⁶ When compared to the line spectrum calculated at zero Kelvin (Figure 4) there is a significant shift in the frequency and intensity of the modes. The continuous curve in Figure 4 was experimentally obtained at 7 K.¹⁶

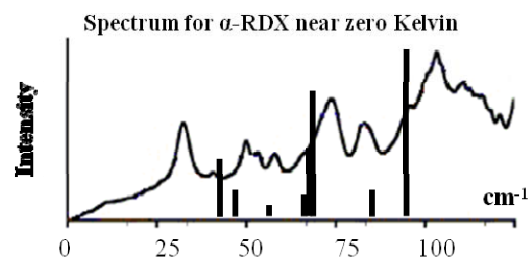


Figure 4. IR spectrum for α -RDX near zero Kelvin.

V. MODE ANHARMONICITY

An example of the simple harmonic approximation and the actual energy for a displacement of the α -RDX system along an eigenvector is shown in Figure 5 for the lowest active IR mode at zero Kelvin. In order to quantitatively characterize the anharmonic behavior of a mode, a quartic polynomial is fit to the difference in energy between the actual energy of the system and the harmonic approximation for each displacement along the eigenvector. As shown in Figure 6, the anharmonic nature of the

mode is a strong function of the temperature over the range of zero to 295 K.

After fitting the difference between the actual energy of the system and the harmonic approximation energy the modes can be rank ordered by strength of anharmonic behavior.

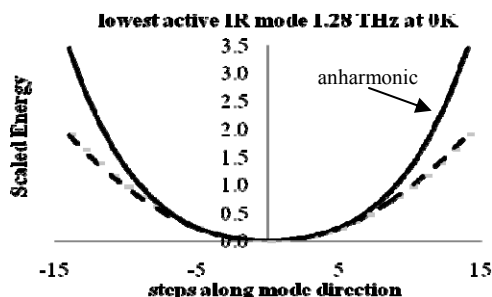


Figure 5. Anharmonic and harmonic behavior for lowest active IR mode at zero Kelvin. Harmonic behavior is dotted-line curve. Anharmonic is solid curve. Units of Scaled Energy are $\times 10^{-1}$ millihartree.

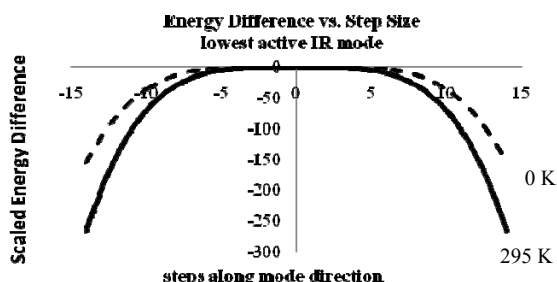


Figure 6. Difference between anharmonic and harmonic energies for the lowest active IR mode. Units of Scaled Energy Difference are $\times 10^1$ millihartree.

VI. SUMMARY

An accurate ab initio model describes the physical behavior of a molecular crystal such as RDX at zero Kelvin. The physical behavior of a molecular crystal system may be expected to differ substantially from its behavior at ambient conditions. A proper “translation” is then required for comparing ab initio results with experiments conducted under different conditions. Low terahertz IR modes in alpha-RDX can be identified and ranked according to the significance of their anharmonicity. The characterization of the anharmonicity of these modes may be employed to add another layer of information in creating a more

richly detailed “fingerprint” for the manipulation and detection of RDX.

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REFERENCES

1. Cooper, P., *Explosives Engineering*, Wiley-VCH (1996).
2. Byrd, F., Scuseria, G., Chabalowski, C., *J. Phys. Chem. B*, 108, 13100 (2004).
3. Schwabe, T., Grimme, S., *Phys. Chem. Chem. Phys.*, 8, 4398 (2006).
4. Slough, W., Perger, W., *Chem. Phys. Lett.*, 498, 97 (2010).
5. Dovesi, R., Orlando, R., Civalleri, B., Roetti, C., Saunders, V., Zicovich-Wilson, C., *Z. Kristallogr.*, 220, 571 (2005).
6. Dovesi, R., Saunders, V., Roetti, C., Orlando, R., Zicovich-Wilson, C., Pascale, F., Civalleri, B., Doll, K., Harrison, N., Bush, I., D’Arco P., Llunell, M., *CRYSTAL09 User’s Manual* (University of Torino, Torino, 2009).
7. www.emsl.pnl.gov/forms/basisform.html
8. Civalleri, B., Zicovich-Wilson, C., Valenzano, L., Ugliengo, P., *CrystEngComm*, 10, 405 (2008).
9. Slough, W., Perger, W., *AIP Conf. Proc.* 955, 417 (2007).
10. Choi, C., Prince, E., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 28, 2857 (1972).
11. Pascale, F., Zicovich-Wilson, C., Lopez, F., Civalleri, B., Orlando, R., Dovesi, R., *J. Comput. Chem.* 25, 888 (2004).
12. Zicovich-Wilson, C., Pascale, F., Roetti, C., Saunders, V., Orlando, R., Dovesi, R., *J. Comput. Chem.* 25, 1873 (2004).
13. Hakey, P., Oullette, W., Zubieta, J., Korter, T., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 64, o1428 (2008).
14. Millar, D., Oswald I., Barry, C., Francis, D., Marshall, W., Pulham, C., Cumming, A., *Chem. Commun.*, 46, 5662 (2010).
15. Murnaghan, F. D. *Proc. Natl. Acad. Sci. USA* 30, 244 (1944).
16. Allis, G., Zeitler, J., Taday, P., Korter, T., *Chem. Phys. Lett.*, 463, 84 (2008).