



Short communication

The molecular structure and inelastic neutron scattering spectra of 2,6-Diamino-3,5-dinitropyrazine

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Abstract

Using solid-state density functional theory (DFT) and inelastic neutron scattering (INS), we have studied the structural and vibrational properties of the energetic material, 2,6-Diamino-3,5-dinitropyrazine (ANPZ). The molecular geometry and vibrational spectra are compared to those obtained from DMol3 calculations using the BLYP and BP functionals with the dnd numerical basis set (BLYP/dnd and BP/dnd). In most cases, good agreement was found between the calculated and experimental molecular geometries and vibrational frequencies. In particular, we find the BLYP/dnd method to be slightly superior to the BP/dnd approach for molecular vibrations.

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1. Introduction

Considerable attention has recently been focused on gaining a detailed understanding of the chemical and physical processes of condensed energetic materials that lead to detonation, because of ongoing questions relating to their safety, sensitivity, and performance. The volatile nature of these materials makes the development of quantum mechanical models that can accurately predict a variety of properties a centralized focus. Structural and vibrational properties are perhaps the most important, as they determine a wide range of macroscopic behavior [1]. Vibrational properties are of particular interest because one of the key mechanisms leading to shock detonation is thought to be an energy transfer from the lattice vibrations to the internal molecular vibrations, a phenomena commonly referred to as ‘vibrational up-pumping’ [2]. As such, there exists a clear need to understand the vibrational spectra of energetic materials. In this paper, we focus on one such material, 2,6-Diamino-3,5-dinitropyrazine (ANPZ), shown in Fig. 1.

The density of ANPZ (1.812 Mgm^{-3}) is very similar to the widely used energetic material RDX (1.816 Mgm^{-3}) [3], implying that ANPZ should have a comparable energy output. ANPZ has a greater insensitivity to external conditions such as temperature, shock, and impact [4] than RDX, making it much safer to use. The insensitivity of ANPZ has been proposed to arise from the extensive hydrogen-bonding network. The hydrogen-bonding network is also attributed to the insensitivity of the energetic material, TATB [5,6].

The interest in the INS vibrational spectra of ANPZ stems in part from our previous work on the INS spectrum of the hydrogen-bonded energetic material, α -ANTA [7]. The results indicated that solid-state DFT methods could be applied to hydrogen-bonded energetic materials to obtain reliable results for molecular structure and vibrational spectra. ANPZ is a somewhat more rigorous test of DFT because of the presence of both intramolecular and intermolecular hydrogen bonds. ANPZ is also of interest because there has been no reported vibrational characterization. In this paper, we report the INS spectra of ANPZ to 1500 cm^{-1} and the results of the periodic DFT calculations on the unit cell. When used together, the INS and DFT studies test the reliability of a theoretical representation. The vibrational intensities of an INS spectrum are directly proportional to the contribution of the hydrogen motion

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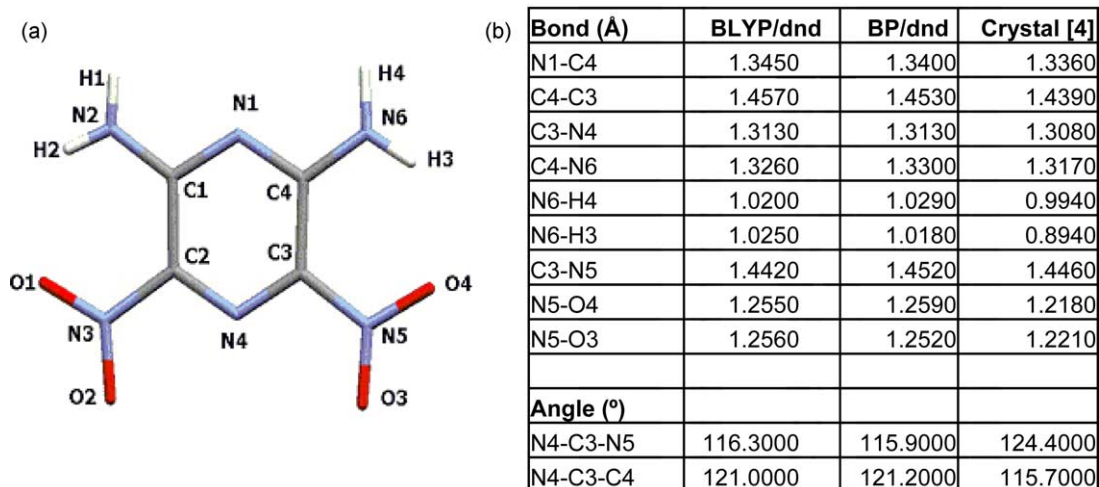


Fig. 1. (a) (left). The molecular structure of the ANPZ molecule, showing the numbering scheme employed at the right. (b) (right). A comparison of the structural parameters obtained using BLYP/dnd, BP/dnd, and the reported crystal structure.

Table 1

The INS and DFT molecular vibrational modes for ANPZ vibrational modes obtained using the TOF instrument are found in italics

INS (cm^{-1})	BLYP/dnd	BP/dnd	Symmetry	Normal mode
	17	25	B_1	1
	27	28	A_1	2
<i>44</i>	43	42	B_2	3
<i>54</i>	58	59	A_2	4
<i>68</i>	74	69	B_2	5
<i>100</i>	100	98	B_1	6
<i>108</i>	109	107	A_2	7
<i>141</i>	138	144	B_2	8
<i>147</i>	150	147	B_1	9
<i>165</i>	166	171	B_1	10
<i>206</i>	206	208	B_1	11
<i>307</i>	309	315	B_1	12
<i>333</i>	335	339	A_2	13
<i>355</i>	355	360	B_1	14
<i>371</i>	373	376	A_2	15
<i>379</i>	384	379	B_2	16
<i>413</i>	411	415	B_2	17
<i>428</i>	419	420	B_2	18
<i>483</i>	482	481	A_1	19
<i>557</i>	563	563	A_1	20
<i>597</i>	597	605	A_1	21
<i>621</i>	619	628	B_2	22
<i>645</i>	650	656	A_2	23
<i>686</i>	686	674	B_2	24
<i>726</i>	729	741	A_1	25
<i>758</i>	761	767	A_1	26
<i>819</i>	822	811	A_1	27
<i>840</i>	845	844	A_1	28
<i>899</i>	902	905	A_1	29
<i>964</i>	961	962	A_1	30
<i>980</i>	975	972	A_1	31
<i>1045</i>	1041	1049	B_1	32
<i>1133</i>	1145	1153	B_2	33
<i>1181</i>	1172	1177	A_1	34
<i>1198</i>	1197	1192	A_2	35
<i>1240</i>	1245	1236	A_1	36
<i>1300</i>	1306	1272	B_2	37
<i>1320</i>	1321	1316	B_1	38
<i>1334</i>	1334	1340	A_1	39

Table 1 (continued)

INS (cm^{-1})	BLYP/dnd	BP/dnd	Symmetry	Normal mode
1376	1380	1386	B_1	40
1440	1441	1447	B_1	41
1500	1497	1484	A_1	42
	1599	1619	A_1	43
	1649	1638	A_1	44
	1787	1793	A_2	45
	3317	3323	A_1	46
	3376	3390	A_1	47
	3520	3525	B_2	48

INS frequencies obtained with the TOF instrument are indicated in italics.

for a particular normal mode. In addition, all normal modes of vibration are present in an INS spectrum, making it possible to assign and compare all calculated modes [8].

2. Methods

The INS experiments were performed at the NIST Center for Neutron Research [9] using the Filter Analyzer Neutron Spectrometer (FANS) and the Fermi–Chopper Time-of-flight instrument (TOF). Detailed descriptions of the FANS instrument [10] and the TOF instrument [11] are available. The INS measurements were performed on ~ 1 g of polycrystalline ANPZ held at 25 K. The sample was supplied by Picatinny Arsenal. The experimental spectra were normalized with respect to the background scattering with the DAVE program [12].

Periodic DFT geometry optimizations and normal mode calculations were performed with the BLYP [13] and BP [14] functionals using DMol3 [13] on the SGI Origin Array at the Wright–Patterson Aeronautical Systems Major

Shared Resource. All solid-state results are unscaled. The calculated INS spectra were constructed using the A-Climax program v.5.1.3 and included combination and overtone vibrations to four quanta [15].

3. Results and discussion

The geometric parameters of ANPZ and atom labels are presented in Fig. 1. The BLYP/dnd bond lengths differ from the crystal bond length averages with an rms deviation of 0.0486 Å. This rms deviation decreases slightly to 0.0475 Å using BP/dnd. The large differences between the experimental and calculated N–H bond lengths are understandable as the reported X-ray bond lengths are always shorter than the true crystal bond lengths [16]. Both calculations produce an N4–C3–N5 angle that is substantially smaller than experimentally observed. As a result, the calculated N4–C3–C4 angle is significantly larger than the experimental value. This type of error has also been observed in ab initio calculations of TATB [17]. In calculations on TATB,

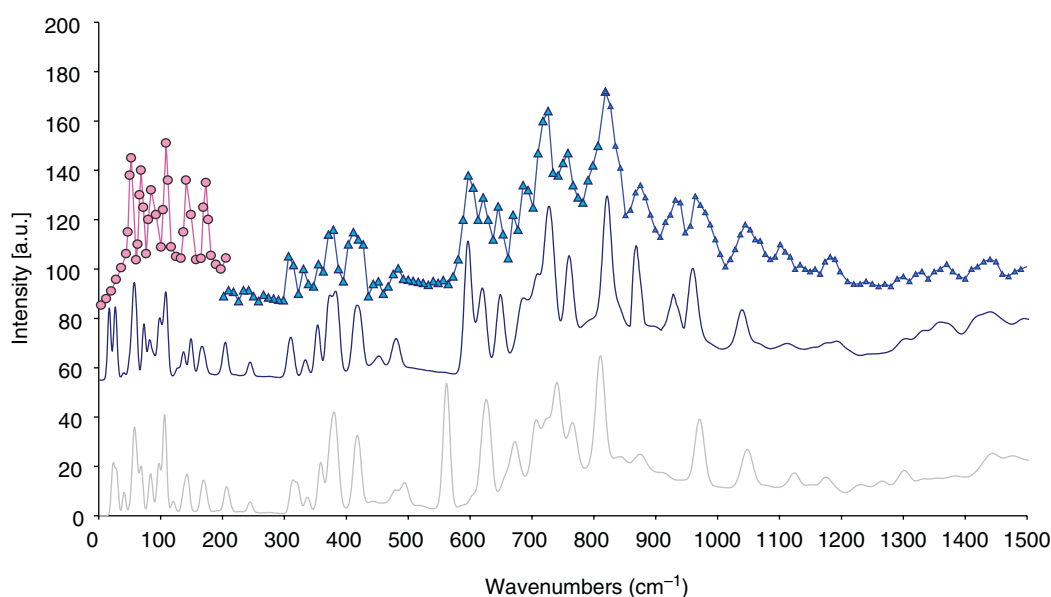


Fig. 2. The experimental and calculated INS vibrational spectra. The TOF data is shown (top circle) along with the FANS data (top triangle). The BLYP/dnd calculated spectrum is shown in the middle (black) and the BP/dnd calculated spectrum is shown at the bottom (gray).

Table 2

The combination and overtone band assignments of ANPZ in the 100–1500 cm^{-1} spectral region

INS (cm^{-1})	BLYP/dnd	BP/dnd	Assignment
125	128	122	v7+v1
182	186	190	v8+v3
234	245	247	v10+v5
267	261	263	v10+v6
451	454	444	v12+v9
540	544	544	v11+v13
710	708	708	2×v14
799	793	792	v15+v18
875	874	876	v4+v27
932	930	917	v11+v25
1069	1068	1080	v16+v24
1101	1110	1125	v17+v24

The INS frequencies obtained using the TOF instrument are indicated in italics.

the electronegativity difference between the nitrogen atoms of the amino groups and the nitrogen atoms of the nitro groups was found to result in an increase of the angles of the nitro groups and a corresponding decrease in the angles of the amino groups. This effect was enhanced by π -donation from the amino groups to the nitro groups [18]. Our results indicate the same error is present in DFT calculations of ANPZ.

The 48 internal vibrational modes of ANPZ belong to the following irreducible representation of the C_{2v} point group: $\Gamma = 19A_1 + 7A_2 + 11B_1 + 11B_2$

In Table 1, we present the vibrational frequencies determined from the BLYP/dnd and BP/dnd calculations, the corresponding INS frequencies, and symmetry assignments. Overall, the BLYP/dnd frequencies compare more favorably to the experimental frequencies than do the calculated BP/dnd frequencies. The rms frequency deviations are 4.21 cm^{-1} using BLYP/dnd and 8.86 cm^{-1} using BP/dnd. The simulated vibrational spectra obtained from the BLYP/dnd and BP/dnd calculations are compared to the experimental INS vibrational spectra in Fig. 2. As can be seen in Fig. 2, both methods of calculation reproduce the intensities and frequencies of the experimental INS spectra remarkably well. The BP/dnd calculation fails to reproduce the intense INS vibration ca. 597 cm^{-1} and instead predicts a high intensity for the 557 cm^{-1} INS vibrational band. This error could be due to mixing of the intensities of the two calculated vibrations since both are A_1 symmetry.

The overtone and combination bands can be identified based on the INS/DFT normal mode assignments. Table 2 lists the combinations and overtone vibrations. One rather intense combination band appears in the experimental spectrum at 875 cm^{-1} . The intensity

difference observed between the experimental and calculated spectra of this vibration presumably reflects some anharmonicity. The anharmonicity has little to no effect on other vibrations and for the most part the A-Climax program used with BLYP/dnd calculations reproduce the INS spectrum very well.

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