



First principle calculations of solid nitrobenzene under high pressure



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ABSTRACT

The dispersion corrected density functional theory (DFT-D) calculations were performed to study the structural and vibrational properties of solid nitrobenzene at ambient pressure. Assignments of the calculated vibrational modes were provided. Moreover, using the norm-conserving pseudopotential plus GGA-PBE function, the unit cell parameters, geometries and vibrational frequencies of nitrobenzene were examined under hydrostatic pressure from 0 to 10 GPa. The calculated pressure dependence of lattice parameters and volume were found to be close to the experimental results, but a distinct change in the bond lengths and bond angles was found around 7 GPa. According to the phonon calculations, the pressure-induced changes of the vibrational frequencies were also observed around 7 GPa. These calculated results all suggest a possible structural transformation in the crystalline nitrobenzene.

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1. Introduction

Nitrobenzene (NB) is widely known as a prototype energetic material, it has the simplest structure of aromatic nitro compounds. Over the past few decades, many teams of researchers have studied its physical and chemical properties. In particular, the molecular structure has been widely investigated by microwave [1], gas-phase electron diffraction [2], and X-ray diffraction technique [3,4] as well as some theoretical efforts [5,6]. Moreover, extensive studies of its decomposition mechanisms and processes [7–9] have been proposed. The structural properties of energetic materials are known to be pressure dependence, thus one should expect noticeable differences between the isolated molecules and condensed phase [10–15].

The crystalline structure of NB at zero pressure has been determined by Boese et al. [3] and Trotter [4]. As shown in Fig. 1, the structure of NB crystal is a monoclinic lattice with space group $P2_1/c$, which includes four molecules per unit cell. The dimer was formed through intermolecular hydrogen bonds $C-H1 \cdots O2$ [3,10]. Because of the limited of empirical studies, there was no more studies examined the crystal phase under high-pressure except Koza et al. [16].

The first principles calculation based on density functional theory (DFT) has become one of the most powerful tools to study energetic materials, and some accurate and interesting calculated results have been obtained [17–22]. Compared with the standard DFT, the DFT-D as parameterized by Grimme [23] provides significant improvements for describing intermolecular interactions in molecular crystals [24]. To the best of our knowledge, there are no theoretical reports available on solid NB. Thus, present work may expect to conduct and further get much more valuable information on NB through the DFT calculations.

2. Computational details

DFT calculations were performed with Cambridge Sequential Total Energy Package (CASTEP) code [25,26]. Pseudo atomic calculations were performed for $H1s^1$, $C2s^2 2p^2$, $N2s^2 2p^3$ and $O2s^2 2p^4$. The generalized gradient approximation (GGA) with the PBE parameterization [27] and plane-wave basis set with norm-conserving pseudopotentials [28] and energy cutoff of 830 eV was used. The empirical dispersion correction by Grimme [23] was used to take into account weak interactions. The Broyden, Fletcher, Goldfrab, and Shannon (BFGS) algorithm [29] was utilized to optimize the unit cell parameters and atomic coordinates, while constraining the space group of NB. Structural optimizations were achieved by setting the convergence criteria for maximum total energies of 5×10^{-6} eV/atom, maximum force of 0.01 eV/Å, maximum stress of 0.02 GPa and maximum displacement of

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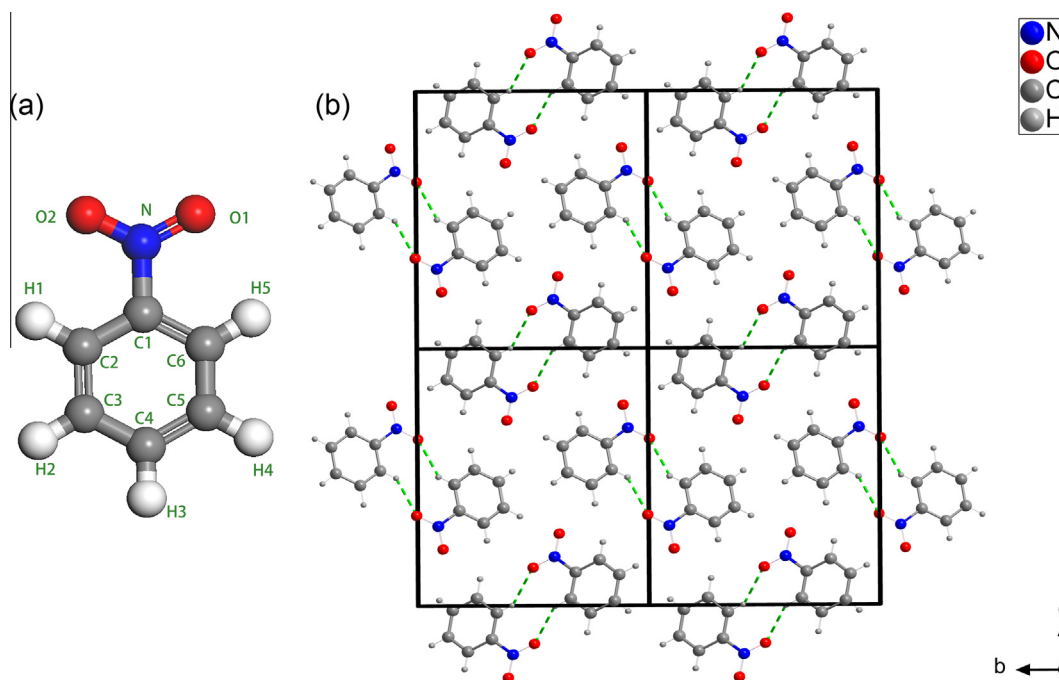


Fig. 1. (a) Molecule with labeled atoms to assist with the bonding designation. (b) Crystal structure of NB; dot lines show hydrogen bonds.

5×10^{-4} Å. The Brillouin zone sampling was obtained using constant Monkhorst–Pack [30] grid of $4 \times 1 \times 1$ points. As starting input for the calculations, we adopted the experimental crystal structure of solid NB [3], its cell parameters were $a = 3.801$ Å, $b = 11.615$ Å, $c = 12.984$ Å and $V = 571.4$ Å³. Following the full optimization of the lattice parameters at ambient pressure, we simulated the gradual loading of hydrostatic pressure up to 10 GPa. Crystalline vibrations were obtained by computing phonon frequencies at Gamma point using the finite displacement method [31].

3. Results and discussion

3.1. Crystal and molecular structure at ambient pressure

The calculated structural parameters of solid NB compared with the experimental data [3,4] are presented in Table 1. The results show that the optimized atomic coordinates are in good agreement with the experimental data. Also, the calculated equilibrium lattice parameter c is overestimated by 0.79%; a and b are underestimated by 2.9% and 1.1% respectively. Moreover, our simulations predict that the unit cell volume is smaller than experimental results, namely the value of the V is underestimated by 4.6%. It may be a substantial thermal expansion of the crystal lattices [21]. In contrast, the standard GGA calculations overestimate a , b , c and V by 34.3%, 1.8%, 7.8% and 44.9%, respectively; while LDA calculations underestimate by 4.6%, 3.8%, 3.9% and 11.6%, respectively, which confirmed that the DFT-D approach can correctly describe the solid NB at ambient pressure.

The geometric parameters of NB molecule in the crystal at ambient pressure are listed in Table 2. The calculated bond lengths of C1–C2, C2–C3, and C3–C4 are found to be 1.396 Å, 1.389 Å and 1.396 Å respectively. Compared with the corrected experimental results, our calculated mean error is 0.16%. The bond lengths of C–N and N–O are 1.455 Å and 1.261 Å. Both the 6-31G and 6-31G* methods [5] underestimated the C–N bond compared with experimental values [3]. Moreover, the theoretical C–N–O and O–N–O bond angles are in good agreement with the experimental

Table 1

Calculated and experimental unit cell parameters and atomic coordinates of solid NB at ambient pressure.

	LDA CA-PZ	GGA PBE	GGA PBE-D	Experiment ^a	Experiment ^b
a (Å)	3.628	5.106	3.687	3.801	3.86
b (Å)	11.172	11.822	11.486	11.615	11.65
c (Å)	12.478	14.002	12.881	12.984	13.24
V (Å ³)	505.125	828.097	544.92	571.4	592.9
β (deg)	93.05	101.59	92.68	94.98	95.58
	Theory			Experiment ^a	
Fractional coordinates of atoms (x, y, z)					
O1	(0.4795, 0.8896, 0.2184)			(0.4818, 0.8896, 0.2205)	
O2	(0.5574, 1.0093, 0.3503)			(0.5464, 1.0033, 0.3521)	
N	(0.5922, 0.9121, 0.3089)			(0.5887, 0.9101, 0.3102)	
C1	(0.7768, 0.8191, 0.3697)			(0.7768, 0.8188, 0.3702)	
C2	(0.8873, 0.8414, 0.4731)			(0.8862, 0.8401, 0.4730)	
C3	(1.0643, 0.7534, 0.5300)			(1.0645, 0.7537, 0.5291)	
C4	(1.1264, 0.6454, 0.4838)			(1.1285, 0.6489, 0.4828)	
C5	(1.0096, 0.6244, 0.3806)			(1.0125, 0.6292, 0.3801)	
C6	(0.8318, 0.7113, 0.3224)			(0.8340, 0.7145, 0.3224)	
H1	(0.8303, 0.9251, 0.5081)			(0.8380, 0.9085, 0.5019)	
H2	(1.1557, 0.7689, 0.6104)			(1.1594, 0.7679, 0.6048)	
H3	(1.2665, 0.5775, 0.5291)			(1.2555, 0.5907, 0.5224)	
H4	(1.0557, 0.5399, 0.3452)			(1.0469, 0.5579, 0.3473)	
H5	(0.7346, 0.6959, 0.2426)			(0.7533, 0.7001, 0.2539)	

^a Ref. [3] (results obtained at 103 K).

^b Ref. [4] (results obtained at 243 K).

Table 2

Geometric parameters of NB molecule in the crystal at ambient pressure.^a

	Experiment [3]	Corrected values	6-31G [5]	6-31G* [5]	This work
C1–C2	1.389	1.393	1.388	1.386	1.396
C2–C3	1.386	1.389	1.384	1.383	1.389
C3–C4	1.387	1.392	1.385	1.383	1.396
C–N	1.467	1.477	1.448	1.458	1.455
N–O	1.227	1.229	1.226	1.193	1.261
C–N–O	118.4	–	118.2	117.6	118.6
O–N–O	123.2	–	123.4	124.6	122.7

^a Bonds length in Å and angles in degrees.

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