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First principles study of the electronic structure and phonon dispersion of naphthalene under pressure

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ABSTRACT

The structural, electronic and vibrational properties of crystalline naphthalene has been investigated within the framework of density functional theory including van der Waals interactions. The computed lattice parameters and cohesive energy have good agreement with experimental data. We study on the structural and electronic properties of the naphthalene under the hydrostatic pressure of 0–20 GPa. The isothermal equations of state calculated from the results show good agreement with experiment in the pressure intervals studied. The phonon dispersion curves have been computed at ambient and hydrostatic pressure of 10 and 20 GPa. We have also calculated the quasiparticle band structure of naphthalene with the G_0W_0 approximation.

1. Introduction

One of the promising directions for development of organic crystals application is the possibility to create cheap and simple-to-manufacture semiconductor devices [1]. At present, more and more practical applications are found for organic molecular crystals including oligoacenes, and these compounds are thought to be promising materials for many uses. Both experimental and theoretical methods have been used for their investigation. The electronic and optical properties of compounds with two to five aromatic rings, using first principle methods, were studied by Hummer et al. [2]. Flexibility is one of the main advantages of organic semiconductors. For this reason it is interesting to investigate the effects of mechanical deformations on electronic and vibrational properties.

Bridgman described phase transition at 3 GPa [3]. However, further investigations did not confirm this result [4]. In recent years there have been studies of the effects of pressure on the crystalline structure of naphthalene, however, there are no definitive results concerning the presence or absence of phase transition. Due to the experimental investigations, the effect of pressure on unit cell has been thoroughly studied [5–8]. The crystal structure and the phonon spectra of naphthalene at a high pressure have been investigated using the methods of elastic and inelastic neutron scattering and optical Raman spectroscopy [6–13]. Phonon spectrum calculations have been made using potential of atom–atom type, involving interactions of pairs of atoms on neighboring molecules, so-called Buckingham potential (exp − 6) [14]. Phonon dispersion curves calculations at high pressure have not been carried out. The Raman spectra of a crystalline naphthalene have been measured at room temperature in the pressure range up to 20 GPa. The pressure shift and Grüneisen parameters for intermolecular and intramolecular phonons have been determined [13]. Likhacheva et al. using the diffraction experiment and calculations show the initial monoclinic phase of naphthalene with the space group $P\ 2_1/c$ ($P\ 2_1/a$) to be stable up to at least 773 K in the pressure range of 3–15 GPa [7,8]. These authors have calculated the frequency dependence on pressure and compared the results with those obtained by Meletov [13]. Earlier we and other authors studied electronic properties of naphthalene and the effect of hydrostatic pressure on its structure [7,15,16]. In this paper, we have been to study the effect of pressure on the electron density distribution, band structure and phonon dispersion.

The London dispersion energy plays an important role in molecular interactions in molecular clusters, solutions, solids, and biological macromolecules. Despite its small contribution to the total energy (∼1%), the lack of models of this term leads to fundamentally wrong predictions, namely, the impossibility of existence of a molecular crystal. Dispersion interaction is caused by correlation of electrons and many-body effects, which are not taken into account in the existing density functional theory (DFT)

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approximations [17]. Nowadays, several algorithms have been developed, making it possible to include this interaction into standard DFT scheme [18]. Some innovations have been proposed to improve current DFT methods: (*i*) fully ab initio approaches (i.e. non-empirical), (*ii*) the reparameterization of existing functionals and (*iii*) the inclusion of empirical terms. The possibility of including van der Waals (vdW) energies in DFT has been suggested by Kohn and co-workers [19] and the van der Waals density functional (vdW-DF) [20] is the most well-known first principle scheme. The latter type includes the algorithms suggested by Grimme [21,22] as well as DFT-D3 [23], which presents further modification of these schemes. The works in Refs. [24-27] contain more detailed information on different schemes. Tkatchenko et al. [28,29] established that in some cases the inclusion of many-body van der Waals interactions may play a substantial role in the properties of molecular crystals. Taking into consideration these interactions systematically improves the agreement between the calculated and experimental values of sublimation enthalpy of molecular crystals [30].

The most molecular crystals of hydrocarbons have a monoclinic symmetry and, as was shown by Kitaigorodsky [31] with using the atom–atom potential method, this type of molecular packing is the most optimal. The naphthalene unit cell has the symmetry group $P2_1/a$ under normal conditions. The crystal structure of naphthalene was first determined by Robertson [32], and investigated later on [33,34]. The projection of the unit cell on the *ab* plane is shown in Fig. 1. The unit cell contains two equivalent molecules involved in vdW interactions. The "herringbone" molecular stacking, typical for aromatic hydrocarbon crystals, can be observed here. The naphthalene molecule in the crystal, which have C_{2h} symmetry, is presented in Fig. 1. Isolated molecule of naphthalene have D_{2h} symmetry.

2. Computational details

First-principles total energy calculations were carried out within density-functional theory with a plane-wave pseudopotential approach. The computations were performed with the Quantum ESPRESSO (QE) [35] suite of electronic structure, using the Perdew–Burke–Ernzerhof (PBE) parametrization of the generalized gradient approximations (GGA) [36,37]. The structures were relaxed by using the Broyden, Fletcher, Goldfarb, and Shannon method [38]. The cutoff energy of plane waves was set to 55 Ry. Brillouin zone sampling was performed by using the Monkhorst–Pack scheme [39] with a k-point grid of 3 × 4 × 2 (six **k**-points). The values of the kinetic energy cutoff and the **k**-point grid were determined to ensure the convergence of total energies.

Geometry optimization was considered to be performed when all components of all forces are smaller than 0.1 mRy (a.u.)$^{-1}$. The accuracy of the calculations under the current conditions makes up about 5 meV atom^{-1}. Structural data [34] were used as the initial geometry. Also, the calculations were performed with the CRYSTAL09 [40], using the hybrid functional PBE0 [41,42]. Basis sets H_3-1p1G and C_6-31d1G [43], also studied in ref. [44] were used for calculations. In this case structural parameters, calculated using QE, were used as the input data. Other parameters for the calculations were saved by default.

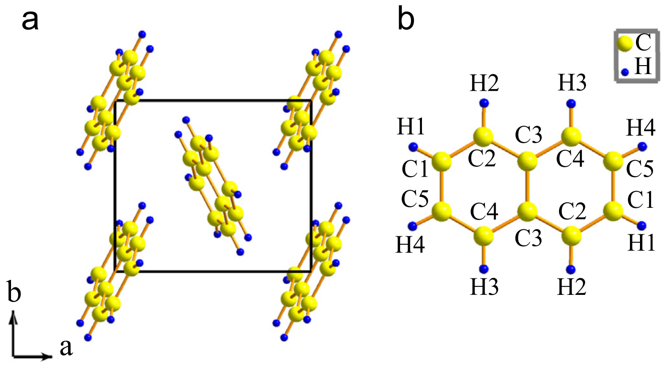

Fig. 1. (a) Crystal structure of naphthalene. (b) The naphthalene molecule in the crystal.

We used in our study a London-type empirical correction for dispersion interactions (DFT-D). The main idea of the algorithm consists in adding the empirical potential to the exchange-correlation potential. The total energy is given by

$$E_{DFT-D} = E_{KS-DFT} + E_{disp} \tag{1}$$

where $E_{KS\text{-}DFT}$ is the usual self-consistent Kohn–Sham energy as obtained from the chosen DF and E_{disp} is an empirical dispersion correction [22].

The DFT-D2 scheme is included in the QE [45]. Also, we carried out computations within the DFT-D3 framework with rational damping function proposed by Becke and Johnson [46–48]. In the following, we will use the term "DFT-D3(BJ)". The dispersion energy is

$$E_{disp} = -\frac{1}{2}\sum_{A\neq B} s_6 \frac{C_6^{AB}}{R_{AB}^6 + [f(R_{AB}^0)]^6} + s_8 \frac{C_8^{AB}}{R_{AB}^8 + [f(R_{AB}^0)]^8}, \tag{2}$$

with

$$f(R_{AB}^0) = a_1 R_{AB}^0 + a_2, \tag{3}$$

$$R_{AB}^0 = \sqrt{\frac{C_8^{AB}}{C_6^{AB}}}. \tag{4}$$

Here, the sum is over all atom pairs in the system, C_n denotes the averaged (isotropic) *n*th-order dispersion coefficient (orders $n = 6,8$) for atom pair AB, and R_{AB} is their internuclear distance.

Global (functional dependent) scaling factors s_n can be used to adjust the correction to the repulsive behavior of the chosen exchange-correlation density functional. The actual parameters are taken from the original [23,46] and the freely available dftd3 code [49].

The cohesive energy is given by

$$E_{coh} = E_{mol} - \frac{1}{n}E_{bulk} \tag{5}$$

where E_{mol} and E_{bulk} are the total energies of the molecule and the bulk crystal, respectively, and *n* denotes the number of molecules per unit cell. With this definition, the lattice energy is positive for any stable crystal.

We have used the implementation of the G_0W_0 approximation [50,51] provided by the code YAMBO [52,53]. Here, we used Troullier-Martins norm-conserving pseudopotentials [54]. The cutoff energy of plane waves was set to 65 Ry. The dielectric function is calculated using the plasmon-pole approximation. The GW dielectric matrix cutoff is 8 Ry. To obtain convergence, we used 400 unoccupied states.

3. Results and discussion

3.1. *Geometry optimization and cohesive energy*

Our optimized lattice parameters *a*, *b*, *c* and *β* for the naphthalene are given in Table 1. Experimental values are also listed. When studying naphthalene, anthracene, coronene, perylene