



Phase transition and related electronic and optical properties of crystalline phenanthrene: An ab initio investigation



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ABSTRACT

This investigation discusses a structural phase transition of organic crystalline phenanthrene and the resulting changes of its electronic and optical properties investigated by ab initio calculations based on density functional theory (DFT). The structure of phase I has been optimized then its electronic and optical properties have been calculated. Our computational results on phase I (at ambient pressure) get along well with the available experimental data. Calculating the electronic and optical properties of phase II are proceeded in the same way and the results, particularly Raman spectra, reveal a crystallographic phase transition indicated by abrupt changes in lattice constants which are accompanied by rearrangement of the molecules. This results in modifications of the electronic structure and optical response. For both phases the band dispersion of the valence and conduction bands are anisotropic, whereas the band splitting is strongly noticeable in phase II. By calculating the imaginary part of the dielectric function of phase II, we have found the appearance of new peaks at the lowest z-polarized absorption and about 30 eV in all absorption components. Excitonic effects in the optical properties of phases I and II have been investigated by solving the Bethe–Salpeter equation (BSE) on the basis of the FPLAPW method. Phase II shows four main excitonic structures in the energy range below band gap, whereas phase I shows two. The excitonic structures in the optical spectra of phase II show a red shift in comparison to phase I. The calculated binding energies of spin-singlet excitons in phase II are larger than the ones in phase I.

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1. Introduction

Organic π -conjugated molecules and polymers have attracted considerable interest over last decades [1–3]. The combination of their semiconducting properties with their potential for low cost, the excellent mechanical properties and the possibility to modify their properties with organic chemistry techniques, make them promising candidates for various device applications, such as organic light emitting diodes (OLED), field effect transistors (OFET) and solar cells [4–8]. Although defects in organic solids can be extremely

important for their physical properties [9], pure crystals are particularly interesting for the study of intrinsic material properties and have motivated theoretical and experimental investigation [10–13]. Different studies have demonstrated that the physical properties of molecular solids are strongly influenced by their structure which in turn is governed by the intermolecular interactions. Their relation to electronic and optical properties is essential for designing the devices and efficient applications [11–13]. For instance, intermolecular interactions change the size of the exciton binding energy [14] and influence the excitonic effects which are indeed important in order to correctly account for quantitative as well as qualitative features of optical spectra of organic semiconductors [12,13]. The strength and the nature of these inter-molecular interactions are determined by the

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distances between individual molecules and their orientation relative to each other. One possibility to alter the intermolecular interactions is to apply hydrostatic pressure on crystalline samples. This allows systematic reduction in the intermolecular distances and, additionally, changes in the relative orientation without altering the chemical structure of the molecules. Furthermore, the discovery of superconductivity in aromatic compounds like potassium-doped picene [15] and alkali metal doped phenanthrene [16] opens a new path for superconductivity in organic materials. The mechanism for superconductivity is not clear yet, but the dependence of T_C on external pressure has been found which hints to a non-conventional type of superconductor [17]. The pressure effect of such systems is remarkable as it can be considered that T_C increases to nearly doubled in K_3 picene from 18 to 30 K under 1.2 GPa [18]. This positive pressure effect is also observed in doped phenanthrene under pressure [19,20].

Phenanthrene is an aromatic molecule composed by three benzene rings arranged in an armchair structure. It crystallizes in herringbone-stacked monoclinic structure with the space group $P2_1$ at ambient pressure [21,22]. Experimental data showed that phenanthrene undergoes reversible structural change at 2.3 GPa [23–25]; an additional transition occurs at 5.4 GPa [23]. The available studies and the obtained results on optical properties of phenanthrene are limited to the following experiments. Dielectric tensor components of phenanthrene have been obtained by Venghaus from energy loss experiments at ambient pressure and related dipole transition has been discussed [26]. For studying exciton-phonon interaction, absorption and luminescence spectra of phenanthrene under pressure have been investigated using a diamond anvill cell by Mizuno et al. in 1991 [27]. Fluorescence spectra of crystalline phenanthrene have been measured at different pressures by Jones et al. to investigate the role of excimers in transferring energy [24]. In addition, Huang et al. [23] have measured the Raman spectra of phenanthrene crystal under pressure, and for identifying of structural phases, the authors proposed the space group of $P2_1$ for phase I at 0–2.2 GPa, $P2_1/m$ for phase II at 2.2–5.6 GPa and $P2_1/m+Pmmm$ for phase III at 5.6–11.4 GPa, and they identified the structure above 11.4 GPa with space group of $Pmmm$.

Pretty recently we have studied electronic and optical properties of phenanthrene crystal structure in phase I [28]. In the frame of many-body perturbation theory (MBPT) [29], excitonic effects in the optical properties of crystalline phenanthrene have been studied and compared to those of its isomer, anthracene. The coupling of electron and hole left by the electron transition has been found to be important in the optical responses of phenanthrene. Due to the weak van der Waals (vdW) interaction between molecules in molecular crystals like phenanthrene, it can be expected that this class of materials under hydrostatic pressure exhibits interesting and amazing characteristic optical behaviors. This has been confirmed by the studies concerning the effect of pressure on the dielectric tensor of some organic crystals such as anthracene [30] and the smallest oligomers of poly(para-phenylene) and polythiophene [31]. Whereas the use of organic semiconductors for electronic and opto-electronic application is strongly dependent on the behavior of excitons, i.e., the collective low energy excitation involving the creation of

bound electron-hole (e-h) pairs, and their role in the optical response [32], the high pressure structural and optical properties of phenanthrene are still absent in the literature of organic materials and call for further investigations. Therefore, the more knowledge about the effect of intermolecular interactions on the optical properties and exciton binding energies in phenanthrene we get it will be more beneficial for the organic device applications in the future.

In this work, the existence of different phases of phenanthrene and the phase transition effect on their structural and electronic properties are investigated by ab initio calculations based on corrected density functional theory (DFT+vdW) by adding inter-atomic vdW interaction [33]. The density functional theory (DFT) is presently the most successful and also the most promising approach to compute the electronic structure of matter. DFT calculations have been found to match well with experimental result. The accuracy of DFT+vdW for inter-molecular interaction is remarkable (8% error for energies and 0.1 Å for equilibrium distances) [34]. However, it is well known that excitons present in the excitation spectra are not obtained within DFT and random phase approximation (RPA). Instead within the framework of MBPT, the linear response to an optical perturbation, expressed in terms of the equation of motion for the e-h two-particle Green's function that called Bethe-Salpeter equation (BSE) presents a systematic first-principle approach for the calculation of optical absorption spectra including excitonic effects [35]. Therefore in this study in addition to RPA, the solving of BSE on the basis of the full potential linearized augmented plane wave (FP-LAPW) methods have been used to calculate and interpret optical properties of phenanthrene crystal structure, including the imaginary parts of dielectric function and loss function components in the low energy region.

For the first time we have calculated the structural and optical properties of phase II in details and compared them with our computational results on phase I which are in good agreement with experimental ones. For phase II no experimental results have been reported on electronic and optical properties yet. Our calculated results could serve as a reference for future experimental work. The rest of the paper is organized as follows. In Section 2, we outline the theoretical framework within which the calculations have been performed. In Section 3, we present and discuss the results of the studies concerning the structural, electronic and optical properties of phenanthrene. Finally, in Section 4 we summarize our conclusions.

2. Calculation method

At ambient pressure, phenanthrene ($C_{14}H_{10}$) crystallizes in the monoclinic space group $P2_1$ which is characterized by the lattice parameters $a=8.472$ Å, $b=6.166$ Å, $c=9.467$ Å and $\beta=98.01^\circ$ [18]. Within one unit cell, the molecules form a double-layered structure with their long molecular axis being parallel to the long unit cell axis c . Within one layer, the two transitionally nonequivalent molecules are arranged in the herringbone pattern which is common for many organic molecular crystals. The angle between the planes of two molecules is herringbone angle χ (Fig. 1). The bonding in molecular crystals comprises of two force regimes: strong

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