Ab initio study of the optical properties of crystalline phenanthrene, including the excitonic effects

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Using the ab initio methods for solving the Bethe–Salpeter equation on the basis of the FPLAPW method, optical properties of crystalline phenanthrene were calculated, in a comparison to its isomer, anthracene. It was found that despite the similarity of the structural, electronic, and the overall optical properties in a 40 eV energy range, phenanthrene and anthracene show significant differences in their optical spectra in the energy range below band gaps. Phenanthrene has two spin singlet excitonic features whereas anthracene shows one. The singlet and the lowest triplet binding energies of phenanthrene were found to be larger than anthracene. In this study, in addition, a comparison has been made between the optical spectra in RPA and the existing experimental data.

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1. Introduction

At the head of the 20th century up to the near 50 years later, in solid state physics, because of the drastic applications, metals were highly regarded [1]. Next, the basic researches were inclined towards inorganic semiconductors and also superconductors and their applications in materials science [2–4]. In recent years, many studies have been assigned to another class of materials, i.e. the organic solids, due to their wide variety and their amazing features [5–7]. Semiconducting organic materials which include small π-conjugated molecules, i.e., molecular crystals, recently have attracted intense attention because of a large number of useful properties in many research areas of the electronic and opto-electronic physics as well as in materials science [8–11].

Consisting of benzene rings joined in a linear (zigzag) arrangement, oligoacenes (phenacenes) are a subclass of molecular crystals, with all carbon atoms at the around of the ring system. In their crystalline state, these organic semiconducting materials have received particular attention in the field of electronics and photonics [12–15]. These materials and their derivatives are being increasingly used as active elements in a variety of opto-electronic devices such as organic thin-film field-effect transistors [16,17], light-emitting diodes [18,19], photovoltaic cells [20,21], and liquid crystals [22].

Phenanthrene and anthracene are semiconducting aromatic hydrocarbons with the same molecular formula (C14H10), consisting of three joined benzene rings, former in an armchair-edge scheme but latter in a zigzag-edge. Their structural similarity is an incentive to compare the electronic and optical behavior of phenanthrene crystals with that of anthracene. Recently, studies have been conducted on the physical properties of these two structures especially the anthracene crystal. For example, by a molecular orbital method, it has been shown that dependent on the armchair (phenanthrene) or zigzag (anthracene) type edge structures, the electronic properties of one-dimensional polymers and aromatic hydrocarbons are different. It means that the band gap values in one-dimensional polymers oscillates in phenanthrene-edge type whereas it has a metallic behavior in anthracene-edge one [23,24]. The use of the recent progresses in theoretical methods which lead to the large accordance between the experimental and theoretical optical spectra, has shown that optical absorption spectra of anthracene include a spin singlet exciton in the imaginary part of the dielectric function within energy gap region, due to the strong electron–hole correlations. In addition, the effect of pressure on the imaginary part of the dielectric tensor of anthracene has been calculated [25]. However, there are few studies on structural, electronic, and optical properties of phenanthrene and its derivative crystals, such as energy band gap [26] and superconductivity in potassium and lanthanum metals doped phenanthrene [27–29].

The use of organic semiconductors for electronic and opto-electronic applications 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 [30,31]. There is an electron energy loss