Optical properties of phenanthrene: A DFT study for comparison between linear and nonlinear regimes

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ABSTRACT

The present study tries to determine the optical characteristics as well as the electronic structure of phenanthrene as an important nonlinear organic crystal. We have performed our calculations within the framework of DFT. Also, we have used bootstrap exchange-correlation kernel (within the framework of TDDFT) to estimate the excitonic effects. According to the results of our study, the investigated crystal has a band structure with low dispersions which is a sign of low intermolecular interactions. In addition to the high values of linear and nonlinear susceptibilities, the crystal in question has a wide range of transparency as well as sufficient anisotropy which make it promising crystal for nonlinear optical applications. Our TDDFT calculations show that the influence of excitonic effects on optical properties can be very dramatic, particularly near the band edge. In addition, the crystal in question shows extremely small wavelengths of plasmon peaks. Furthermore, this study also covers the $2\omega/\omega$ intra- and inter-band contributions to the dominant nonlinear susceptibilities. Findings indicate that these contributions have opposite signs at higher energies and nullify each other. Our calculations show that $\chi_{xxz}$ and $\chi_{xz}$ have largest values of nonlinear response but $\chi_{xxz}$ is the dominant component at IR-VIS region. Moreover, the current study shows significant similarities between linear and nonlinear spectra, when we draw linear one as a function of both $\omega$ and $2\omega$. Finally, our simulation reproduces the experimental results very well.

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1. Introduction

Organic materials have been the subject of extensive theoretical and experimental investigations in the past two decades. Their applicability in innovative optoelectronic devices such as organic thin-film transistors [1,2] is due to their ability to form well-defined molecular crystals. In particular, nonlinear organic materials have shown great promise, due to their useful physical and optical properties. For optimizing the nonlinear properties of organic molecules, in addition to strong $\pi$-electron delocalization, the non-centrosymmetric crystallization is also an important factor. Generally, in organic crystals, the high valence bands and the lowest conduction bands, mainly come from $\pi$-electrons. This means that, in contrast to $\sigma$ bonds, the electron density of $\pi$ bonds is much more mobile than that of the $\sigma$ bonds. During excitation, the electron transitions from higher valence bands to the lower conduction bands can redistribute the charge density and change the dipole moment, considerably. This electron distribution can also be skewed by substituents (for example, donor–acceptor crystals); the extent of redistribution is measured by the dipole moment, and the ease of redistribution in response to an externally applied electric field is measured by the (hyper) polarizability. The quadratic nonlinearity will happen, when the perturbation to the molecular electronic distribution caused by an intense optical field is asymmetric. Briefly, organic molecules with extensive $\pi$-delocalization have been the focus of the most intense activity because of their ultrafast NLO responses, good processability as thin-film devices, and enhanced non-resonant NLO responses [3–8]. The polarizability of a crystal is generally composed of contribution from, first, the lattice components (atoms, molecules) and, second, the interaction between these components. Whereas the second effect is dominant in inorganic materials with their weakly polarizable atoms and complexes, the first contribution (i.e. the intra-molecular excitations) is dominant in organic materials because of the weak intermolecular bonding (hydrogen bonds, Van der Waals and dipole–dipole interactions). More precisely, due to the low intermolecular interactions, the band structure of organic crystals generally show low dispersions, and the main contributions to the optical response come from the intra-molecular transitions from high valence bands to the lowest conduction bands. In spite of the promising aspects of nonlinear organic materials, still extensive research is required on the...