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Optical and transport properties of single crystal rubrene: A theoretical study

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ABSTRACT

Optical and charge transport properties of single crystal rubrene are investigated using the multi-mode Brownian oscillator (MBO) model, the charge hopping model with quantum nuclear tunneling, and the Munn–Silbey approach. The MBO model is adopted to calculate absorption and photoluminescence spectra, yielding results in excellent agreement with measurements. In addition, temperature dependence of zero phonon lines (ZPL) and phonon sidebands (PSBs) of absorption spectra is also examined using the MBO model, revealing a nearly linear dependence of line widths of the ZPL and the PSBs on temperature. Model parameters obtained from MBO fitting and TD-DFT computation are then utilized for hole mobility calculations. It is found that temperature dependence of the calculated mobility is in general agreement with measurements, exhibiting "band-like" transport behavior.

1. Introduction

Organic semiconductors based on π-conjugated polymers and small molecule materials have attracted increasing attention in recent years owing to their mechanical flexibility and inexpensive mass production among a variety of promising properties. Decades of efforts have been dedicated to the research of organic semiconducting materials, leading to significant progress in the design and fabrication of devices, such as high performance organic light emitting diodes (OLEDs) [1,2], organic field effect transistors (OFETs) [3,4], and organic photovoltaics (OPVs) [5]. However, commercialization of organic materials is largely limited by its relatively lower charge carrier mobility (typically 1–10 cm^2/Vs or even lower). Recent successful synthesis of single crystalline rubrene provides attractive application potentials thanks to its high hole mobility, which, in the range of 10–40 cm^2/Vs [6–8], is among the highest of acenes, comparable to that of amorphous silicon. Rubrene has also been considered as an important yellow fluorescent dye in the field of OLED with improved electroluminescent efficiency and enhanced device stability and lifetime [9–12].

Despite the high hole mobility and electroluminescence yield of single crystal rubrene, a comprehensive understanding of their underlying mechanisms remains elusive. Absorption spectra of rubrene in amorphous thin films and solutions have been analyzed using the independent mode displaced harmonic oscillator model (IMDHO), and results are supported by the time-dependent (TD) density functional theory (DFT) calculations [13]. Two forms of rubrene isomers were considered, i.e., planner and twisted, and it is found that the thin film spectrum of rubrene is dominated by the twisted isomer. Using a combination of the DFT-GGA level calculations, the GW-Bether-Salpeter equation and quantum Monte Carlo calculations, optical and electronic properties of crystalline rubrene have been investigated taking into account many body effects [14]. Results show that observed yellow-green photoluminescence (PL) in rubrene can be attributed to the formation of intermolecular charge transfer singlet excitons, and the exchange energy plays a decisive role in raising the energy of intra-molecular excitons above the intermolecular ones. A detailed study has been performed on dissolved rubrene molecules by analyzing their optical spectra (absorption and emission) [15]. In this study, normal coordinate analysis and frequency calculations using DFT in conjugation with linear response TD-DFT have been applied to unveil the physical origin of the excited state difference between rubrene and tetracene, and it is found that the difference is mainly caused by the inductive effect of the phenyl group that leads to the HOMO destabilization. The optical response of rubrene crystals has also been studied by providing the full UV–vis dielectric tensor of rubrene crystals [16], and results show that the emission belongs to a series with different origins with respect to transitions, and the intermolecular interactions are weak for the lowest optical transitions. Temperature-dependent absorption and photoluminescence spectroscopy of rubrene multichromophores has been examined by combining the time-dependent long-range-corrected

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DFT with the exciton model [17]. Spectra of rubrene multichromophores up to heptamers are calculated, and the effects of exciton–phonon coupling and temperature on photophysical properties of both H- and J-aggregated oligomers are addressed. It is found that the spectral behavior of rubrene aggregates is very much dependent on aggregation details. PL spectroscopy has been applied to study mechanisms of conductance in rubrene crystals [18,19], revealing that oxygen-related impurities are responsible for the increase of conductivity. As a result of defects and impurities in the crystalline phase, the detailed theoretical analysis of the rubrene PL spectra is nontrivial [20]. Kloc and coworkers compared observed Raman spectra of single rubrene crystals with calculated spectra of isolated molecules [21]. It is found that unlike many other oligoacenes, rubrene has very weak intermolecular coupling and no observable intermolecular Raman vibrational modes. It follows that intermolecular forces in rubrene are too small to be measurable by Raman spectroscopy, a conclusion that is consistent with those in Ref. [16].

Coordinate-dependent electronic structures underlie charge transport in organic crystals. A computational protocol incorporating numerical evaluations of electronic and electron–phonon coupling was obtained by a combination of molecular dynamics (MD) simulation and semi-empirical calculation at the INDO/S level to predict charge carrier mobility of rubrene [22], in which time-dependent fluctuations of transfer integrals based on MD trajectories are utilized to compute the off-diagonal carrier-phonon coupling strength. Girlando and coworkers [23] calculated the diagonal and off-diagonal carrier-phonon coupling of orthorhombic rubrene from derivatives of the site energy and transfer integral with respect to the normal mode coordinate [24,25], respectively. Li et al. calculated the electronic structure of rubrene crystals [26] and investigated the influence of off-diagonal carrier-phonon coupling on infrared optical properties and charge transport of the rubrene crystal [27].

Charge transport in organic crystals is often handled by two simplified treatments: the band-like transport model and the hopping-like approach. The former describes coherent charge transport, which is characterized by increased mobility at low temperatures. The latter captures thermally activated charge hopping over energy barriers exhibiting positive temperature dependence of mobility (i.e., the mobility increases with temperature). In pristine organic crystals, however, neither the band-like nor the hopping-type models can correctly predict mobility because charge carrier motion in these systems is between these two limits [28–31]. Following the work of Munn and Silbey, Zhao and coworkers derived temperature-dependent mobility of a molecular crystal incorporating both the diagonal and off-diagonal carrier-phonon coupling [32–36], which is capable to describe the two aforementioned limits. This approach has been successfully applied to study anisotropic transport of holes in two-dimensional perylene single crystals [37]. Vehoff et al. analyzed the relationship among the molecular structure, morphology, percolation network, and charge carrier mobility for rubrene and three other molecules in the framework of the high-temperature non-adiabatic Marcus theory [38]. It was found that close packing and cofacially alignment is preferable to achieve high mobilities. Nan et al. applied a quantum version of charge transfer theory coupled with random-walk simulation to evaluate the temperature dependence of the averaged hole mobility of rubrene and tetracene [39].

In this paper, we present a detailed theoretical study on the optical and charge transport properties of single rubrene crystal. The paper is organized as follows. In Sec. II, we present the methodology including the DFT calculation and the Munn–Silbey method. The former is applied to calculate the electronic structure of rubrene, and the latter, to investigate the charge transport behavior in rubrene crystal. In Sec. III, detailed results on the optical and charge transport properties of rubrene are presented and compared with experimental results. In particular, electronic structures of rubrene monomer and dimer are obtained with the ZINDO and TD-DFT methods, and the multimode Brownian oscillator (MBO) model is utilized to study temperature-dependent optical properties of rubrene. The Munn–Silbey approach is then applied to calculate the mobility in rubrene with parameters obtained from the DFT calculations. Conclusion are drawn in Sec. IV.

2. Methodology

2.1. DFT-based methods

Ground-state electronic structures of molecular systems are often obtained by the DFT calculations with the B3LYP hybrid exchange–correlation functional at the level of 6-31G (d) split valence polarized basis set. The B3LYP functional adopts the VMN functional III and the LYP expression to describe local and non-local correlations, respectively, and has been widely used to model and investigate the electronic properties in polymeric and small molecular materials [29,40]. Molecular excited states, on the other hand, are calculated using the TD-DFT and the semiempirical Zerner Intermediate Neglect of Differential Orbital (ZINDO) method parameterized to fit spectroscopic properties [41,42]. To compare calculated and measured spectra in a solution of toluene, solvent effects are taken into account by applying the self-consistent reaction field approach in the framework of polarizable continuum model (PCM) [43]. Besides the information of the excited states, transfer integrals and reorganization energies are obtained from the DFT calculations which are utilized to study the charge transport properties in rubrene. All quantum chemical calculations in this work are carried out using the Gaussian 09 program [44], and a frequency analysis follows to assure that the optimized structures are the most stable ones.

To gain insight into the measured spectra, the MBO model [45–48] is applied to simulate room-temperature absorption spectrum of rubrene in a toluene solution. The MBO model describes a two level system coupled to some primary oscillators which are, in turn, coupled linearly to a bath of secondary oscillators. This approach has been successfully employed to interpret the spectra of chromophores in liquids [49–51] and conjugated polymers [52]. A detailed description of the MBO method can be found in Appendix A.

Benefiting from the high mobility, rubrene has been applied to fabricate various devices [6–8,53–55] and in this work we also investigate the charge transport in rubrene from a theoretical perspective. To study charge transport properties of organic crystals, we utilize the hopping-like model with the charge transfer (CT) rate between the donor and the acceptor as the most essential parameter [56]. The well-known Marcus expression for semi-classical electron-transfer rates is often used to predict the charge hopping rates in organic semiconductors [56–58]. It is noted that the Marcus theory treats nuclear motion classically and assumes weak electronic coupling between donor and acceptor states. In organic semiconductors, environmental phonons include both intramolecular and intermolecular modes, often with high frequencies. Thus, theory beyond the semiclassical treatment is needed in order to adequately account for the quantum aspects of the charge transfer process. In this paper, we applied a quantum multimode formula to calculate the charge transfer rate using the displaced harmonic oscillator approximation, which can be obtained from the Fermi Golden Rule (FGR) as [59]:

$$k = \frac{J^2}{\hbar^2}\int_{-\infty}^{\infty} dt \times \exp\left\{ i\Delta G^0/\hbar - \sum_j S_j\left[(2n_j+1) - n_j e^{-i\omega_j t} - (n_j+1)e^{i\omega_j t}\right]\right\} \tag{1}$$