

Exciton effects on optical absorption spectra of electroluminescent polymer poly(*para*-phenylenevinylene)

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ABSTRACT

Component of photoexcited states with large spatial extent is investigated for optical absorption spectra of the electroluminescent polymer poly(*para*-phenylenevinylene) (PPV) by using the intermediate exciton theory. We find that there is a peak due to long-range excitons at the higher energy side of the lowest main feature of the optical spectra. The energy position is nearly the same as the Hartree-Fock (HF) energy gap. The oscillator strengths of long-range excitons are larger when the electric field of light is perpendicular to the chain axis. The fact, that the onset of the long-range excitons is located near the HF gap, might be related with the mechanisms of large photocurrents measured in such the energy region. Next, we calculate the ratio of oscillator strengths due to long-range excitons with respect to sum of all the oscillator strengths of the absorption as a function of the PPV monomer number. The ratio depends on the system size largely when the monomer number is a few, but the magnitude of the ratio becomes almost constant when the monomer number is more than 10 and near 20.

1. INTRODUCTION

The observation of remarkable electroluminescent properties of poly(*para*-phenylenevinylene) (PPV)¹ has attracted physical and chemical research activities. The polymer structure is shown in Fig. 1. The onset of the photocurrents locates at the excitation energy between 3.0eV and 4.0eV,^{2,3,4} and this energy is significantly larger than both of the optical absorption edge at about 2.0eV and the lowest peak energy at 2.4eV. This fact has been interpreted theoretically by excitonic effects which have been taken into account by the single excitation configuration interaction (single-CI) method^{5,6} and also by the density matrix renormalization group method.⁷ The binding energy of excitons is about 0.9eV, as have been estimated by the single-CI theory.⁵

The spatial extent of excitons, in other words, the distance between electrons and holes might depend on their photoexcitation energies. If an exciton is strongly bound, its extent can be smaller than the region of the PPV monomer unit and thus the exciton becomes Frenkel-like as observed in molecular crystals. If the binding is weaker, the photoexcited electron-hole pair tends to distribute over several monomer units, like the charge-transfer exciton in molecular systems. The main purpose of this paper is to characterize the extent of photoexcited states of the PPV by using the single-CI theory recently developed in Ref. 6. The polymer backbone structure is modeled by a tight binding model Hamiltonian with electron-phonon interactions, and attractions between electrons and holes are taken into account by long-range Coulomb interactions. When the distance between an electron and a hole is shorter than the spatial extent of the monomer, we call the exciton as a “short-range” exciton. When the exciton width is larger than the extent of the monomer, we call the exciton as a “long-range” exciton. We shall characterize each photoexcited state as “short-range” or “long-range” by calculating the probability that the photoexcited electron and hole exist on different PPV monomer units. The similar characterization method has been used in the recent investigations of charge-transfer excitons in C₆₀ cluster systems,^{8,9,10} too.

2. MODEL

We consider the following model with electron-phonon and electron-electron interactions. The same Hamiltonian has been used in the previous work by Shimoi et al.⁶

$$H = H_{\text{pol}} + H_{\text{int}}, \quad (1)$$

$$H_{\text{pol}} = - \sum_{\langle i,j \rangle, \sigma} (t - \alpha y_{i,j}) (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{H.c.}) + \frac{K}{2} \sum_{\langle i,j \rangle} y_{i,j}^2, \quad (2)$$

$$H_{\text{int}} = U \sum_i (c_{i,\uparrow}^\dagger c_{i,\uparrow} - \frac{n_{\text{el}}}{2}) (c_{i,\downarrow}^\dagger c_{i,\downarrow} - \frac{n_{\text{el}}}{2}) + \sum_{i,j} W(r_{i,j}) (\sum_{\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - n_{\text{el}}) (\sum_{\tau} c_{j,\tau}^\dagger c_{j,\tau} - n_{\text{el}}). \quad (3)$$

In Eq. (1), the first term H_{pol} is the tight binding model along the PPV polymer backbone (shown in Fig. 1) with electron-phonon interactions which couple electrons with modulation modes of the bond lengths, and the second term H_{int} is the Coulomb interaction potentials among electrons. In Eq. (2), t is the hopping integral between the nearest neighbor carbon atoms in the ideal system without bond alternations; α is the electron-phonon coupling constant that modulates the hopping integral linearly with respect to the bond variable $y_{i,j}$

which measures the magnitude of the bond alternation of the bond $\langle i, j \rangle$; $y_{i,j} > 0$ for longer bonds and $y_{i,j} < 0$ for shorter bonds (the average of $y_{i,j}$ is taken to be zero); K is the harmonic spring constant for $y_{i,j}$; and the sum is taken over the pairs of neighboring atoms. Equation (3) is the Coulomb interactions among electrons. Here, n_{el} is the average number of electrons per site; $r_{i,j}$ is the distance between the i th and j th sites; and $W(r) = 1/\sqrt{(1/U)^2 + (r/aV)^2}$ is the parametrized Ohno potential used in Ref. 6. The quantity $W(0) = U$ is the strength of the onsite interaction; V means the strength of the long-range part ($W(r) \sim aV/r$ in the limit $r \gg a$); and $a = 1.4\text{\AA}$ is the mean bond length. We use the long-range interaction because the excited electron and hole spread over a fairly large region of the system considered. The parameter values used in this paper are $\alpha = 2.59t/\text{\AA}$, $K = 26.6t/\text{\AA}^2$, $U = 2.5t$, and $V = 1.3t$. They are taken from Ref. 6. Most of the quantities in the energy units are shown by the unit of t in this paper.

Excitation wavefunctions of the electron-hole pair are calculated by the Hartree-Fock approximation followed by the single-CI method. This method has been used in the optical spectra of the PPV chain,^{5,6} and C₆₀ (C₇₀) molecules and solids.^{8,9,10,11} The optical absorption spectra become anisotropic with respect to the electric field of light, as expected from the polymer structures. Anisotropy effects are considered by applying electric field in the direction parallel to the chain axis (shown in Fig. 1) as well as in the perpendicular directions.

3. OPTICAL ABSORPTION SPECTRA OF PPV

First, we show the total absorption spectra, and discuss effects of the boundary conditions and anisotropic effects with respect to the directions of electric field of light. Figures 2(a) and (b) show the calculated spectra with periodic and open boundaries, respectively. It seems that the number of the PPV monomer units, $N = 20$, gives the spectral shape, almost independent of the chain length. The optical spectra depend on the system size largely when the number N is less than 10, but they become almost independent of the size when N is near 20. The difference in the spectral shapes of the two boundaries is small also. This is related with the saturated behavior of the spectral shape.

There are four features around, $1.2t$, $2.1t$, $2.4t$, and $3.0t$, in the total absorption spectra in Fig. 2. Anisotropy effects with respect to the electric field are clearly seen: the first and third features are larger when the field is parallel with the polymer axis, while the second and fourth features are larger when the field perpendicular to the axis. We note that the similar fact has been pointed out by Shimoi et al.⁶ The qualitative fact is the same, but there are small quantitative differences between two calculations: there is a small oscillator strength at the lowest feature when the electric field is perpendicular to the chain axis in the calculation by Shimoi et al.,⁶ but the most of its oscillator strength comes from the part where the electric field is parallel to the axis in the present calculation. The oscillator strengths of the fourth features are nearly the same when the electric field is parallel to and perpendicular to the polymer axis in Ref. 6, but the most of the oscillator strengths of the fourth feature comes from the part where the electric field is perpendicular to the axis in the present case. These differences might be due to the different calculation methods.

Next, we look at the origins of the main features in relation to the band structure. Figure 3 shows the band structure by the Hartree-Fock approximation. The branches of the valence (conduction) band are named as VB j (CB j) ($j = 1 - 4$) from the energy gap to band edges. The bands, VB2 and CB2, are almost lack of dispersion. This is due to the fact that the amplitudes at the atoms, A and D, are nearly zero, and the wavefunctions are localized at the atoms, B, C, B', and C'. Therefore, these two bands are nearly flat. This property has been discussed in the previous paper.⁶ In the parallel electric field case, the dominant first and third features are mainly given by the transitions from VB1 to CB1 bands and from VB2 to CB2 bands, respectively. In the perpendicular electric field case, the large second and fourth features come from transitions from VB1 (VB2) to CB2 (CB1) bands and from VB2 (VB3) to CB3 (CB2) bands, respectively.

Now, we discuss the long-range component of the optical spectra. The long-range component is defined as below. First, we calculate the probability that the photoexcited electron and hole exist on different PPV monomer units. This probability is $1 - 1/N$ for the system with N monomer units, when the electron and hole distribute uniformly. If it is less than $1 - 1/N$, the electron and hole tend to localize in a single monomer unit, and the excited state is like a Frenkel exciton, which has been typical for molecular crystals. If the probability is larger than $1 - 1/N$, the electron and hole favor to separate in different monomer units, and the excited state has characters like a charge-transfer exciton in molecular crystals. However, the PPV units are connected each other by real bondings in the polymer, so the term charge-transfer exciton might not be practical. Otherwise, we name such the excited state as a "long-range" component. We can separate contribution to the optical spectra from the long-range component by taking sum over such states only. We discuss the properties of the long-range component in the following paragraphs.

Figure 4 shows the calculated optical absorption spectra for the periodic boundary case. The bold lines are the total absorption spectra, and the thin lines are the spectra from the long-range component of excitons.

Figures 4(a) and (b) show the absorption with the parallel and perpendicular electric field cases, respectively. In Fig. 4(a), there is a broad peak around the energy $1.7t$ at the higher energy side of the feature at $1.2t$. At the higher energy side of the $2.4t$ feature, the oscillator strengths of the long-range component are very small, and this is consistent with the origin of the $2.4t$ feature that the bands VB2 and CB2 in Fig. 3 are almost lack of dispersions. The optical excitations of this feature tend to localize on a single PPV monomer. In Fig. 4(b), there are two peaks of the long-range component around the energies, $2.3t$ and $3.6t$, at the higher energy side of the two main features at $2.1t$ and $3.0t$. Figure 4(c) shows the orientationally averaged spectra. The spectral shape of the long-range component is very broad and extends from the energy $1.5t$ to about $2.5t$. The threshold of the long-range component is $1.566t$, and is slightly smaller than the energy of the Hartree-Fock (HF) energy gap $1.581t$. Therefore, it is very interesting if such the long-range excitons play a part in mechanisms of large photoconductions which have been measured in the energy region larger than the HF energy gap $1.581t$. The oscillator strengths of the long-range component are larger when the electric field is perpendicular to the chain axis.

Finally, we calculate the ratio of the sum of oscillator strengths of the long-range excitons with respect to that of the total absorption, in other words, the ratio of the area below the thin line with respect to the area below the bold line in Fig. 4. The quantity is calculated for each case of the electric field direction, and the results are shown as a function of N in Fig. 5. The ratio depends on number of monomer units largely when N is smaller than 10, due to the finite system size. However, the size dependence becomes smaller as N increases. The ratio seems to be almost constant and the value is about 0.08 near $N = 20$. The ratio is anisotropic with respect to the direction of the electric field of light. The numerical data of the parallel and perpendicular electric field cases are shown in Fig. 5, too. We find that the ratio of the perpendicular field case is slightly larger than that of the parallel field case. This is related with the fact that the $2.4t$ feature in Fig. 4(a) has a very small long-range component and the electron and hole around this feature tend to localize on a single PPV monomer.

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FIGURE CAPTIONS

Fig. 1. The structure of the PPV chain. The direction of the polymer chain axis is indicated by the arrow. The eight Carbon sites, inequivalent each other, are shown by the labels, A-F, B', and C'.

Fig. 2. Optical absorption spectra of the PPV for (a) periodic and (b) open boundaries. The number of the PPV units is $N = 20$. The bold line is for the total absorption. The thin (dotted) line indicates the absorption where the electric field is along with (perpendicular to) the polymer axis. The Lorentzian broadening $\gamma = 0.15t$ is used.

Fig. 3. The band structure of the PPV in the Hartree-Fock approximation. There are four branches (named VB_j , $j = 1 - 4$) in the valence band, and there are again four (named CB_j , $j = 1 - 4$) in the conduction band. The wavenumber region, $0 < k < \pi$, is only shown due to the symmetry. The lattice constant of the unit cell is taken as unity.

Fig. 4. Optical absorption spectra of the PPV with periodic boundary. The polymer axis is in the x - y plane. The electric field of light is parallel to the chain and in the direction of the x -axis in (a), and it is perpendicular to the axis and is along with the z -axis in (b). The orientationally averaged spectra are shown in (c). The number of the PPV units is $N = 20$. The bold line is for the total absorption. The thin line indicates the absorption of the long-range component. The Lorentzian broadening $\gamma = 0.15t$ is used.

Fig. 5. Long-range component of the optical absorption spectra as a function of the PPV unit number N for the case with periodic boundary. The squares are for the total absorption. The circles and triangles indicate the data for the cases with the electric field parallel and perpendicular to the polymer axis, respectively.