

# Optical excitations in PPV aggregates

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## Abstract

Linear optical responses of large PPV (poly(p-phenylenevinylene)) aggregates have been investigated numerically using the linear-scaling (LDM) method. The semiempirical CNDO/S (Complete Neglect of Differential Overlap in Spectroscopy) Hamiltonian is adopted in the calculation. Distinct intermolecular excitations have been identified, and their characteristics have been determined by examining real-space electron–hole pair distribution. Relevance of our results to the experimental observation is discussed. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Poly(p-phenylenevinylene); Localized-density-matrix; Optical excitations; Complete neglect of differential overlap in spectroscopy Hamiltonian

## 1. Introduction

Conjugated polymers have been of great research interests. Important progress is being made towards the commercialization of LED display. However, many aspects of the photoexcitation mechanism remain controversial. One of major debate has been the characteristics of photoexcitations: whether the excitations are intra-chain or inter-chain [1–14]. Poly(p-phenylenevinylene) (PPV) is the most widely studied luminescent polymer. Its thin film has been used in the fabrication of the LED [15,16]. We chose it to investigate the nature of photoexcitations.

Because of the size and complexity of PPV and its derivatives, most theoretical works have been limited to one or two polymer chains. The recently proposed LDM method has achieved the linear-scaling computation [17] for both ground and excited states of the  $\pi$ -electron system including the electron–electron Coulomb interaction [18–23]. We further implemented the method in the segment molecular orbital (SMO) representation, where a SMO is a molecular orbital (MO) spanned over a segment of a molecule.

This led to a higher computational efficiency [24]. The Complete Neglect of Differential Overlap in Spectroscopy (CNDO/S) Hamiltonian [25,26] is employed. Thus the LDM method with the SMO representation (LDM/SMO) allows us to explore the excited states of a large and complex system. In this work, we examine the optical response of the PPV aggregate by using LDM/SMO. The CNDO/S Hamiltonian has been employed to have a quali-

tative understanding of the inter- and intra-chain excitations between PPV chains [24].

## 2. Model

We use the CNDO/S Hamiltonian to describe the behavior of valence electrons. In the presence of an external electric field  $\varepsilon(t)$ , the total Hamiltonian is given by the following expression

$$H = H_{\text{CNDO/S}} + H_{\text{ext}} \quad (1)$$

The dipole matrix elements  $\mu_{ij}$  in  $H_{\text{ext}}$  are evaluated using the zero differential overlap approximation and the Nishimoto–Mataga formula [27] is employed for the two-electron integrals.  $H_{\text{ext}}$  describes the interaction between the electrons and the external electric field  $\varepsilon(t)$ . Within the TDHF approximation [28], a closed non-linear self-consistent equation of motion is yielded for the reduced single-electron density matrix  $\rho(t)$  [29,30]

$$i\hbar\dot{\rho}(t) = [h(t) + f(t), \rho(t)] \quad (2)$$

Here  $h(t)$  is the Fock matrix

$$h_{n,m}(t) = t_{n,m} + 2\delta_{n,m} \sum_l v_{n,l} \rho_{l,l}(t) - v_{n,m} \rho_{n,m}(t) \quad (3)$$

where  $t_{n,m}$  is the hopping matrix element between orbital  $m$  and  $n$ , and  $v_{n,m}$  is the Coulomb repulsion between two electrons at  $m$  and  $n$ , respectively.  $f(t)$  describes the interaction between an electron and the external field  $E(t)$  and  $f_{i,j}(t) = e\mu_{ij}\varepsilon(t)$ . The LDM/SMO method is employed to solve Eq. (2), and its detail is described in another paper [24].

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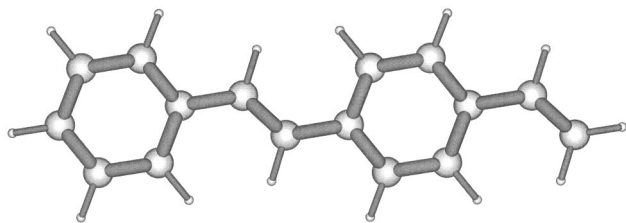


Fig. 1. 1-chain PPV used in our calculation.

We use the same bond lengths and angles of a PPV oligomer given in Ref. [4]. Each chain in our calculation is the 2-unit PPV chain as shown in Fig. 1. To investigate the interchain excitations we construct several PPV aggregates. Two of aggregates are shown in Fig. 2a,b where each chain is aligned to the  $x$ -axis and there are  $-3.28$  Å and  $-1.64$  Å displacements along  $x$ -direction between chains, respectively. The two PPV chains (A and B) are either parallel (Fig. 2a) or tilted to each other with an angle  $76^\circ$  (Fig. 2b). The axis of B is displaced by  $4.00$  and  $3.13$  Å in  $y$ - $z$  plane from that of A in Fig. 2a, and  $-0.31$  and  $4.53$  Å in Fig. 2b. More chains are added with the same displacement vectors and angles between adjacent chains, see Fig. 3. The geometries are fixed in the calculation.

### 3. Results

We applied the LDM/SMO to the 8-chain PPV aggregates. For smaller aggregates like 1-, 2- and 4-chain PPV, the full TDHF method is used.

Fig. 2 shows the comparison between 1-chain and 2-chain PPV aggregates absorption spectra with the electric field polarized perpendicular to the plane of the chain A. We use two configurations for the 2-chain PPV aggregates shown in Fig. 2a,b. The absorption spectrum of 2-chain PPV aggregates (solid line) is almost identical to the scaled absorption spectrum of 1-chain PPV oligomer (dashed line) in Fig. 2a. However around the first peak shown in the inset of Fig. 2a we can find a marked difference between the two spectra. New peak appears at  $4.75$  eV and the amplitude of the absorption spectrum around  $6.15$  eV is enhanced for 2-chain PPV. On the other hand, the absorption spectrum of the 2-chain PPV aggregates (solid line) in Fig. 2b is almost the sum of the absorption of the 1-chain PPV oligomers A (dashed line) and B (dotted line) except around  $10$  eV. This difference basically comes from the strength of the coupling between two chains and the feature of each excited mode. Since the chains A and B are parallel in Fig. 2a,  $\pi$  electrons hop more frequently between A and B.

The deviation of the absorption spectra of PPV aggregates from single chain PPV oligomer is more dramatic once more chains are involved. Fig. 3a shows the comparison between the absorption spectra of 2-chain (Fig. 2b) and 8-chain (Fig. 3b) PPV aggregates. The electric field polarized perpendicular to the plane of the chain A or along the  $z$ -

axis. The absorption spectrum of 2-chain aggregate is scaled by a factor of four. The amplitude of the 8-chain absorption spectrum is enhanced, and some of its peaks red shift with respect to those of the 2-chain spectrum. Especially the width of the first peak of the 8-chain is doubled which indicates that it consists two peaks (see the inset of Fig. 3a), and this has been confirmed by the calculation with the dephasing  $\gamma = 0.1$  eV. All these effects come from the interchain excitations, which may be observed from the characteristics of corresponding density matrices. In Fig. 3b, we plot the absorption spectra of 8-chain PPV aggregates with two differently polarized electric fields. Solid line and dashed line show the absorption spectra with the electric field polarized along the  $x$  and  $z$ -axes, respectively. The dashed line is scaled by a factor of two. There is a large absorption peak at  $3.15$  eV when  $\varepsilon$  is polarized along the  $x$ -axis, and this peak is expected to red shift as the lengths of chain increase.

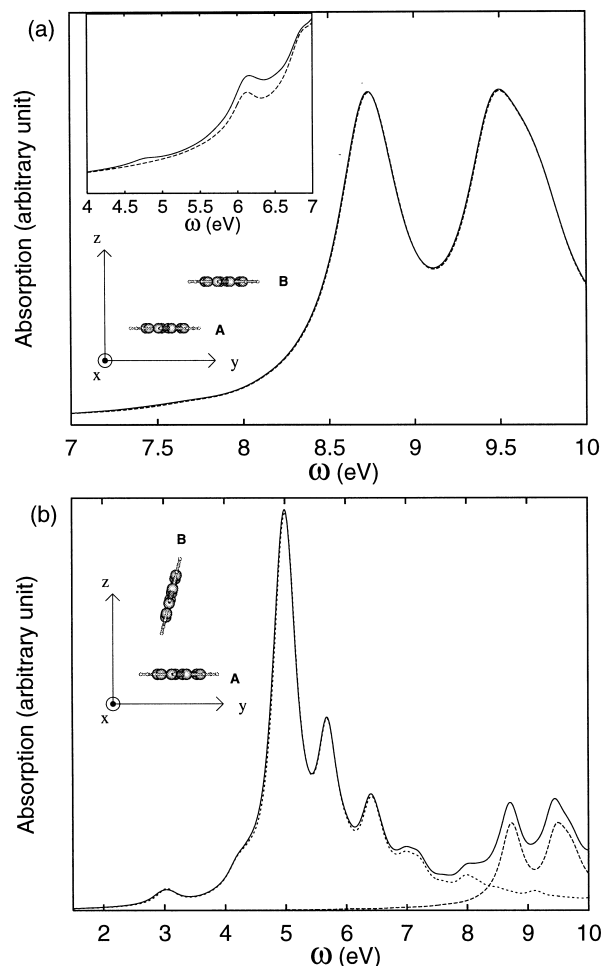


Fig. 2. Absorption spectra for PPV aggregates with the electric field polarized perpendicular to the plane of the chain A, (a) 2-chain PPV aggregates (solid line), 1-chain PPV oligomer A (dashed line). The amplitude of the dashed line is scaled by a factor of two. Inset shows the magnified view of the lower excited states, (b) 2-chain PPV aggregates (solid line), 1-chain PPV oligomer A (dashed line), 1-chain PPV oligomer B (dotted line).

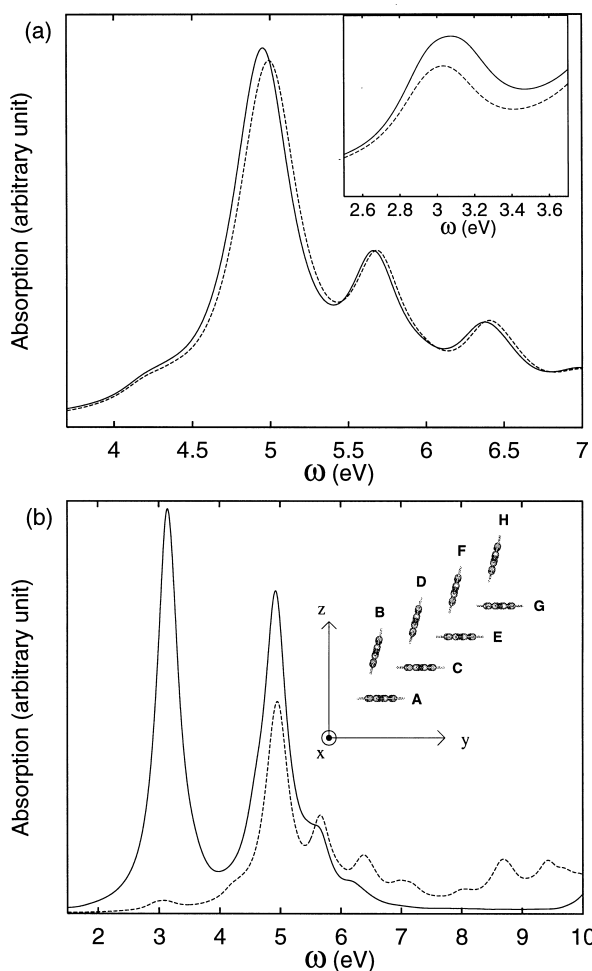


Fig. 3. Absorption spectra for 8-chain PPV aggregates, (a) 8-chain PPV aggregates (solid line), 2-chain PPV aggregates (dashed line). The amplitude of the dashed line is scaled four times. Inset shows the magnified view of the lower excited states. Electric field is polarized perpendicular to the plane of the chain A, (b) absorption spectra for 8-chain PPV aggregates. Electric field is polarized along the chain axis (solid line), and perpendicular to the plane of the chain A (dashed line).

Fig. 4 shows the absorption spectra for 1-chain (dotted line), 2-chain (dashed line), and 8-chain (solid line) PPV aggregates when the electric field  $\epsilon$  is polarized along the chain axis. Blue shift and suppression of the oscillator strength of the first peak are observed as the aggregate grows. This is consistent with the 2-chain calculation with varying interchain distance [14], and may be explained as follows. The electron–hole pairs are highly limited within individual chains when  $\epsilon$  is polarized along the chain axis. Because of the special packing of PPV chains in our model aggregates, the electron–hole pairs in the adjacent chains have the same phase and thus repel each other. This Coulomb repulsion increases the excitation energy and suppresses oscillator strength as well. If there is a different type of displacement along the chain axis between the adjacent chains and the phases of electron–hole pairs in the adjacent chain may happen to differ by  $\pi$ , the excitation

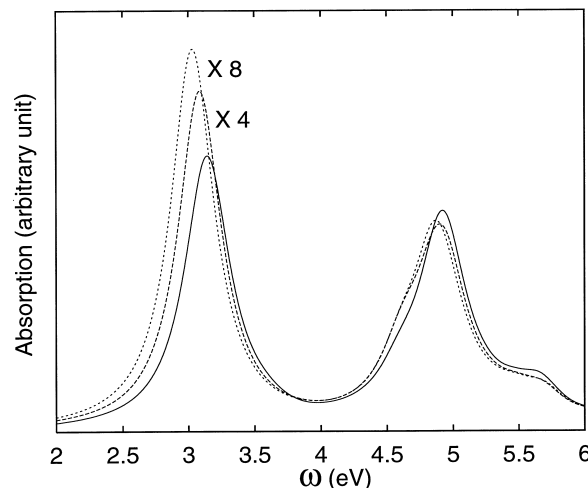


Fig. 4. Absorption spectra for 1-chain (dotted line), 2-chain (dashed line), and 8-chain (solid line) PPV aggregates. Electric field is polarized along the chain axis.

energy is expected to decrease and the oscillation strength increases due to the Coulomb attraction.

#### 4. Discussion

Our calculation shows the existence of inter-chain excitations. More the number of the chains, larger the inter-chain effects. We may expect to have a larger inter-chain effect by taking into account the nuclear motion. As has been shown here and in Refs. [4,14] different configuration of the chains will produce a different results. Thus it will be interesting to vary the arrangement of the chains in the aggregates and investigate the change of photoexcitation dynamics. The relation between the chain length and the inter-chain excitation should also be investigated.

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