Physics Letters A 379 (2015) 482–486

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Polarization and dissociation of a high energy photon-excited state in conjugated polymers

Xiao-xue Li

School of Physics and Technology, University of Jinan, Jinan 250022, China

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form 24 November 2014
Accepted 28 November 2014
Available online 3 December 2014
Communicated by R. Wu

Keywords:
Conjugated polymer
Reverse polarization
Organic semiconductor
Electron–electron interaction

ABSTRACT

We use the tight-binding Su–Schrieffer–Heeger model for the one-dimensional conjugated polymers to explore the static polarization behavior of a high energy photon-excited state under the electric field. An obvious reverse polarization is obtained although the electric field is weak. With the increase of field strength, the degree of polarization increases first and then decreases. When the electric field is strong enough, the excited state is dissociated into the polaron pair. In addition, the effects of electron–electron interaction and interchain coupling are also discussed. The results indicate that the electron–electron interaction could weaken the reverse polarization of the high energy photon-excited state, which tends to be dissociated into a high-energy exciton and a pair of solitons with the including of interchain coupling.

1. Introduction

As the promising organic semiconductor materials, π-conjugated polymers possess quasi-one-dimensional structure and abundant electrical, optical and magnetic properties. During the past decades, polymers have been widely used to fabricate various photoelectric devices, such as polymer light emitting diodes [1–3] and polymer solar cells [4–6]. Compared with the inorganic materials, polymers have strong electron–lattice interaction. The extra electron and hole produced by the charge injection or photoexcitation could induce the distortion of the lattice structure, and then the formation of the self-trapped elementary excitation, such as soliton [7–9], polaron and exciton [10]. In-depth exploration of these elementary excitations is of great importance for the better application of the polymer's optical–electrical characteristic.

In 2004, An et al. theoretically investigated the single-photon excitation process of polymers [11]. To facilitate the description, they denoted ε_m^v to be the mth energy level counted from the top of the valence band, and ε_n^c the nth from the bottom of the conduction band $(m, n = 1, 2, 3, \ldots)$, as is shown schematically in Fig. 1. By a simple calculation of the dipole moment between them, it is found that the most possible dipole-allowed transitions are those from ε_i^v to ε_i^c $(i = 1, 2, \ldots)$. Among these photon-excited states, the one formed by the single-photon band-edge transition from ε_1^v to ε_1^c is defined as the exciton, and the one formed by the single-photon non-band-edge transition from ε_2^v to ε_2^c is defined as the high-energy exciton. Subsequently, by using the femtosecond pulsed electric field to simulate the photoexcitation, Gao et al. further explored the band-edge and non-band-edge transition processes of electron in polymers [12]. The calculated results show that with the increase of photoexcitation energy, three peak values of transition probability appear, which correspond to $\varepsilon_1^v \to \varepsilon_1^c$ at $\hbar\omega_1 = 2.7$ eV, $\varepsilon_2^v \to \varepsilon_2^c$ at $\hbar\omega_2 = 3.0$ eV and $\varepsilon_3^v \to \varepsilon_3^c$ at $\hbar\omega_3 = 3.4$ eV. So we get that when the photoexcitation energy is increased from band gap energy by above 10%, a new high energy photon-excited state could be formed. However, their results

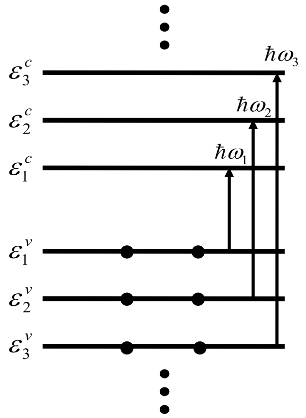

Fig. 1. Schematic diagram of energy levels for polymer molecule in the ground state. The filled circles indicate electrons with the spin omitted.

E-mail address: sps_lixx@ujn.edu.cn.

http://dx.doi.org/10.1016/j.physleta.2014.11.054

also show that for a higher energy photoexcitation corresponding to $\varepsilon_i^v \to \varepsilon_i^c$ ($i > 4$), it is not easy to be obtained.

In a word, since the photon energy applied in photoexcitation experiment is usually larger than the band gap of polymer, both exciton (corresponding to the single-photon transition $\varepsilon_1^v \to \varepsilon_1^c$) and high-energy exciton (corresponding to the single-photon transition $\varepsilon_2^v \to \varepsilon_2^c$) are formed. Besides this, due to the fact that the energy difference between ε_i^v and ε_i^c is comparable for $i = 1, 2$ and 3, a higher energy photon-excited state (corresponding to the single-photon transition $\varepsilon_3^v \to \varepsilon_3^c$) could also be formed when the photoexcitation energy is a little (10%–30%) higher than the energy needed for the excitation of exciton or high-energy exciton.

It is worth noting that in previous works, the polarization behaviors of both exciton and high-energy exciton have been discussed in detail [13–15]. It is reported that after applying an electric field, the exciton is normally polarized while the high-energy exciton is reversely polarized. For reverse polarization, the direction of the induced dipole moment is opposite to the electric field. This is a very interesting physical phenomenon. The system with negative polarizability would exhibit novel electrical property, and be of great value for both fundamental research and technique application. Then we can't help to ask if the high energy photon-excited state formed by transition $\varepsilon_3^v \to \varepsilon_3^c$ could also be reversely polarized by the electric field. In addition, Virgili et al. have experimentally explored the photoexcitation of polymers and presented that the free carriers were generated from the dissociation of the photon-excited state with higher energy rather than the lowest excited state [16]. Since the higher-lying excited states play an important role in charge dissociation, it is necessary to further explore the dissociate process of the high energy photon-excited state.

In this paper, by using the tight-binding model we will theoretically investigate the polarization and dissociation of the high energy photon-excited state under the electric field. The effects of both electron–electron interaction and interchain coupling will be discussed. The paper is organized as follows. The model and method are presented in the following section. The result and discussion are given in Section 3 and a brief summary is concluded in Section 4.

2. Model and method

We mainly focus on the representative trans-polyacetylene which possesses the degenerate ground-state structure. In the framework of tight-binding approximation, the extended one-dimensional Su–Schrieffer–Heeger (SSH) model is introduced to describe the isolated polyacetylene chain [7–9],

$$H_{\mathrm{SSH}} = -\sum_{n,s}\left[t_0 - \alpha(u_{n+1} - u_n)\right]\left(C_{n+1,s}^{+}C_{n,s} + C_{n,s}^{+}C_{n+1,s}\right) + \frac{1}{2}K\sum_n (u_{n+1} - u_n)^2 + K'\sum_n (u_{n+1} - u_n). \tag{1}$$

Here, t_0 denotes the hopping integral between two nearest carbon atoms without lattice dimerization. α is the electron–lattice coupling constant and u_n is the displacement of nth carbon atom from its equilibrium position. $C_{n,s}^{+}$ ($C_{n,s}$) denotes the creation (annihilation) operator of electron at site n with spin s. K represents the elastic constant and the linear term K' is introduced to stabilize the open-end chain [17,18].

To investigate the polarization behavior of the high energy photon-excited state, a uniform electric field E is applied along the chain. The interaction between electron and electric field E is described by

$$H_E = |e|E\sum_{n,s}(na + u_n)\left(C_{n,s}^{+}C_{n,s} - 1\right). \tag{2}$$

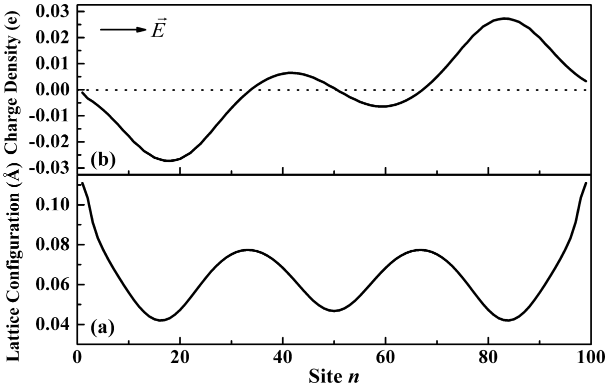

Fig. 2. (a) The lattice configuration and (b) the charge density of the high energy photon-excited state at $E = 1.0$ mV/Å.

Here, a denotes the lattice constant.

The eigenstate $\psi_{\mu,s} = \sum_n Z_{\mu,n,s}|n\rangle$ of electron on μth energy level with spin s and its eigenvalue $\varepsilon_{\mu,s}$ are determined by the static Schrödinger equation

$$\varepsilon_{\mu,s}Z_{\mu,n,s} = -\left[t_0 - \alpha(u_n - u_{n-1})\right]Z_{\mu,n-1,s} - \left[t_0 - \alpha(u_{n+1} - u_n)\right]Z_{\mu,n+1} + |e|E(na + u_n)Z_{\mu,n,s}. \tag{3}$$

By minimizing the total energy of the system, the equilibrium condition of the lattice configuration is given by

$$u_{n+1} - u_n = -\frac{2\alpha}{K}\sum_{\mu,s}^{occ} Z_{\mu,n,s}Z_{\mu,n+1,s} - \frac{K'}{K} + \frac{|e|E}{K}\left(\sum_{m=1}^{n}\sum_{\mu,s}^{occ} Z_{\mu,m,s}^2 - n\right). \tag{4}$$

Obviously, the lattice configuration $u_{n+1} - u_n$ and the eigen wave function $Z_{\mu,n,s}$ depend upon each other, which could be obtained by solving Eq. (3) and Eq. (4) self-consistently.

3. Result and discussion

In our calculation, the parameters are taken as follows for the trans-polyacetylene: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2 and $a = 1.22$ Å [7–9]. For a finite chain composed of N CH groups, $K' = -\frac{2\alpha}{N-1}\sum_{n=1}^{N-1}\sum_{\mu,s}^{occ} Z_{\mu,n,s}Z_{\mu,n+1,s}$ [17,18]. Here, we set $N = 100$ for each isolated chain. To facilitate the description, we introduce the net charge density ρ_n defined as

$$\rho_n = \sum_{\mu,s}^{occ} Z_{\mu,n,s}^2 - 1. \tag{5}$$

Here, the unity is subtracted and then $\rho_n > 0$ denotes the negative charge distribution on site n while $\rho_n < 0$ the positive [19].

Firstly, through exciting one electron from ε_3^v to ε_3^c "by hand" to simulate the single-photon excitation, a stable excited state is formed after a short lattice relaxation process. Since its photoexcitation energy is higher than that needed for both exciton and high-energy exciton, we define this new excited state as the high energy photon-excited state. In Fig. 2, we give its lattice configuration and charge density at $E = 1.0$ mV/Å. As is shown, there are three localized defects in lattice structure. Each of them is confined due to the limitation of chain length.

In Fig. 2(b), the charge density distribution along the chain under the applied electric field is given, where the unit of the ordinate is an electronic charge e. The field strength is weak so as