Dynamics of Photogenerated Polarons in Conjugated Polymers

Z. An,[1,2] C. Q. Wu,[1,*] and X. Sun[1]
[1]Research Center for Theoretical Physics, Fudan University, Shanghai 200433, China
[2]College of Physics, Hebei Normal University, Shijiazhuang 050016, China

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Within a tight-binding electron-phonon interacting model, we investigate the dynamics of photoexcitations to address the generation mechanism of charged polarons in conjugated polymers by using a nonadiabatic evolution method. Besides the neutral polaron exciton which is well known, we identify a novel product of lattice dynamic relaxation from the photoexcited states in a few hundreds of femtoseconds, which is a mixed state composed of both charged polarons and neutral excitons. Our results show that the charged polarons are generated directly with a yield of about 25%, which is independent of the excitation energies, in good agreement with results from experiments. Effects of the conjugation length are also discussed.

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During the last decade, there have been a lot of efforts devoted to understanding the properties of conjugated polymers because of their attractive performance in optoelectronic devices, e.g., light-emitting diodes, lasers, and photovoltaic cells. It has been well known that light emission arises mainly from the singlet exciton and that the charge carriers are charged polarons in polymers. However, the mechanism for photogeneration of charge carriers remains controversial [1]. Based on the experimental facts that the increase in photocurrent and the corresponding decrease in photoluminescence are not proportional at a high electric field ($>10^5$ V/cm), Moses *et al.* [2] suggested that the photocarriers are charged polaron pairs created directly, which is known as a band model. On the other hand, the charge carriers are regarded as a result of the field-induced dissociation of excitons which are firstly formed by photoexcitations, this is the so-called exciton model [3–7]. More recently, by use of transient photoinduced infrared-active vibrational (IRAV) absorption, it has been found that the photocarriers (charged polarons) are generated within 100 fs after photoexcitations with a quantum efficiency ($\sim$10%), and they are clearly not the result of exciton dissociation in prototypical luminescent polymers, poly(phenylenevinylene) (PPV), and its derivatives [8–10]. Additionally, Ruseckas *et al.* [11] also found that charged polarons are generated within $\sim$100 fs with a quantum efficiency $\sim$20% in a polythiophene derivative. All these experimental results show that both neutral excitons and charged polarons are independently formed at the same time. However, their branching ratio and formation dynamics are not clearly understood yet.

The lattice dynamics [12–18] has been widely used to simulate formation of these nonlinear excitations within the tight-binding Su-Schrieffer-Heeger (SSH) model [19] as well as its extended versions [20] for nondegenerate ground-state polymers. Based on an adiabatic scheme, a soliton-antisoliton pair has been found in degenerate polymer, [12] and the neutral polaron exciton has been identified in nondegenerate polymers [17] when an electron in the valence band is excited to the conduction band. Furthermore, it has been found that the neutral polaron exciton could be dissociated into a pair of charged polarons only in a high electric field ($\sim 10^6$ V/cm) [18]. Therefore, the possibility of carriers resulting from the field-induced dissociation of exciton should be low. However, most of these works focused on the excitation at band edges, i.e., an electron is excited from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Since the photon energy applied in photoexcitation experiments is usually greater than the $\pi - \pi^*$ gap, an electron-hole pair is created above the band edge. The electron-hole pair will relax to lower energy states accompanied with lattice distortions, which is believed to be of fundamental importance for generations of photocarriers.

It is the aim of this study to describe this process and to address the branching ratio of its products. In this Letter, we present results from a numerical study of the lattice relaxation of various photoexcited states, such as those via a dipole-allowed transition and those via a two-photon absorption. The dynamics is treated within the mean-field approximation where transitions between instantaneous eigenstates are allowed [14] in contrast to the adiabatic dynamics with fixed level occupation [12]. The results show that, in the earlier stage after photoexcitation, the lattice undergoes different transient distortions for different excited states, but only two kinds of stable states are formed at last; one is the neutral polaron exciton in which an electron and a hole are bound together by a lattice deformation, and the other is a mixed state of polaron exciton and oppositely charged polaron pair which possesses a bond configuration including two separated local deformations. This result implies that both neutral exciton and charged polarons are directly created by photoexcitation.

The Hamiltonian we consider in this paper is the SSH model [19] with a Brazovskii-Kirova-type symmetrybreaking term [20]:

$$H = -\sum_{l,s} t_l (c_{l,s}^{\dagger} c_{l+1,s} + c_{l+1,s}^{\dagger} c_{l,s}) + \frac{1}{2} K \sum_l (u_{l+1} - u_l)^2 + \frac{1}{2} M \sum_l \dot{u}_l^2, \tag{1}$$

where $t_l = t_0 - \alpha(u_{l+1} - u_l) + (-1)^l t_e$ with t_0 being the transfer integral of π electrons in a regular lattice, α the electron-lattice coupling constant, and u_l the lattice displacement of the lth site from its equidistant position. t_e is introduced to lift the ground-state degeneracy for nondegenerate polymers. The operator $c_{l,s}^{\dagger}(c_{l,s})$ creates (annihilates) a π electron with spin s at the lth site, K the elastic constant due to the σ bonds, and M the mass of a CH group. Although these parameters used here are taken as those chosen for polyacetylene [17], $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $t_e = 0.05$ eV, $K = 21$ eV/Å^2, and $M = 1349.14$ eV $\times$ fs^2/Å^2, the results are expected to be qualitatively valid for other conjugated polymers with a nondegenerate ground state.

The temporal evolution of the lattice configuration is determined by the equation of motion

$$M\ddot{u}_l = -K(2u_l - u_{l+1} - u_{l-1}) + 2\alpha(\rho_{l,l+1} - \rho_{l,l-1}), \tag{2}$$

where the density matrix ρ is defined as

$$\rho_{l,l'}(t) = \sum_k \Phi_k(l,t) f_k \Phi_k^*(l',t), \tag{3}$$

f_k is the time-independent distribution function determined by the initial electron occupation, and the electronic wave functions $\Phi_k(l,t)$ are the solution to the time-dependent Schrödinger equation

$$i\hbar\dot{\Phi}_k(l,t) = -t_l \Phi_k(l+1,t) - t_{l-1}\Phi_k(l-1,t). \tag{4}$$

The coupled differential Eqs. (2) and (4) could be solved with a Runge-Kutta method of order eight with step-size control [21], which has been proven to be an effective approach in investigating polaron dynamics [22] and photoexcitation dynamics [14] in conjugated polymers.

In most of our simulations, a 200-site chain is considered, which is long enough to eliminate the chain-end effect. At a half-filling case, it is easy to verify that the lattice has a bond alternation structure and the electronic band is quasicontinuum with a gap of about 1.8 eV. We denote $\varepsilon_m^v (m = 1, 2, 3, \cdots)$ to the mth energy level in valence band counted from the top, and $\varepsilon_n^c (n = 1, 2, 3, \cdots)$ to the nth energy level in conduction band from the bottom. By a simple calculation, one can find that the most probable dipole-allowed transitions are those from ε_i^v to $\varepsilon_i^c (i = 1, 2, \cdots)$, for example, the transition dipole moments between ε_i^v and $\varepsilon_i^c (i = 1 - 4)$ are 11.6, 11.1, 10.4, and 9.5 eÅ, and their transition energies are 1.76, 1.78, 1.81, and 1.85 eV, respectively.

Starting from the initial ground state, we excite an electron originally occupying the energy level ε_m^v to the level ε_n^c to describe a photoexcitation process. Then the temporal evolution of both the lattice and the wave functions are obtained by solving the coupled Eqs. (2) and (4). Firstly, we have simulated the dynamic relaxation of these dipole-allowed photoexcited states. As examples, the temporal evolutions of the staggered bond order parameter $\delta_l \equiv (-1)^l (u_{l-1} + u_{l+1} - 2u_l)/4$ for the four lowest lying photoexcited states ($\varepsilon_i^v \to \varepsilon_i^c$, $i = 1 - 4$) are shown in Fig. 1.

In the case of photoexcitation from ε_1^v to ε_1^c , see Fig. 1(a), the lattice relaxes rapidly to form one local deformation. This process needs about 75 fs, which is similar to that of a soliton pair formation in *trans-polyacetylene* [12]. Correspondingly, the energy level ε_1^v shifts upward while ε_1^c shifts downward into the gap, and they become two localized states. As a result, the electron and hole are trapped in the region of lattice distort. This self-trapping bound state of the electron-hole pair has been known as a polaron exciton. The bond configuration and the schematic diagram of energy levels for the polaron exciton are shown in Fig. 2(a). Sun *et al.* [18] have studied the effect of an electric field on such a polaron exciton, and found that it needs a high electric field (about 10^6 V/cm) to dissociate the polaron exciton into a pair of charged polarons. Therefore, it is not realistic that the charged polarons result from the dissociation of polaron exciton when the applied electric field is lower than 10^6 V/cm.

Different from the above case, when an electron is photoexcited from ε_2^v to ε_2^c, two polaronlike defects are found in the dynamic relaxation, see Fig. 1(b). We have examined this case for a few picoseconds, and find that the two local deformations do not merge into one entity to form a polaron exciton, so such a state is dynamically stable. Because the two local deformations are separated far enough, they are actually two independent quasiparticles. The bond order parameters and the schematic diagram of energy levels are shown in Fig. 2(b). For such a photoexcited state, four energy levels (ε_1^v, ε_2^v, ε_1^c, and ε_2^c) enter into the energy gap and become localized states. However, it should be stressed that ε_1^v and ε_2^v (ε_1^c and ε_2^c)

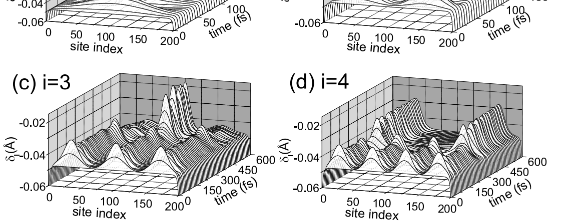

FIG. 1. Temporal evolutions of staggered bond order parameter $\{\delta_l\}$ for photoexcited states from ε_i^v to ε_i^c ($i = 1 - 4$).

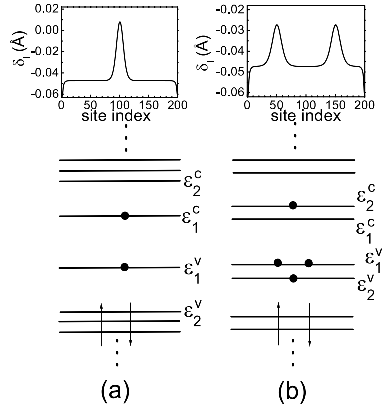

FIG. 2. The configuration of bond order parameter δ_l and the schematic diagrams of electronic levels for the polaron exciton (a) and for the mixed state of exciton and charged polarons (b).

become closer and closer as the two lattice deformations become more and more localized in the relaxation process, until, at last, they become two-fold degenerate levels when the wave functions of the two lattice deformations do not overlap any longer. It should be mentioned that the result in short-chain cases is different from that in the long chain case; we will discuss it later.

Since the two deformations are independent of each other, we can obtain their eigenstates $\{\chi_L\}$ (for the left particle) and $\{\chi_R\}$ (for the right particle), separately. Then, we project the evolutional wavefunctions $\{\Phi_k(l, t)\}$ into these eigenstates to determine their species. We find that such a structure with two local deformations is a mixture of four possible states, which are shown in Fig. 3 (only the gap states, χ_L^u, χ_L^d, χ_R^u and χ_R^d, which determine the charge distributions, are shown). Figures 3(a) and 3(b) correspond to the neutral exciton and the ground state, while figs. 3(c) and 3(d) are two separated oppositely charged polarons. Moreover, the probability of each case is obtained to be about 25%, so half of the yield should be the charged polaron pairs for such a photoexcitation.

With regard to the dynamic relaxations of higher lying photoexcited states, we find that the lattice will relax to form one localized defect, i.e., polaron exciton, for the photoexcited states $\varepsilon_i^v \rightarrow \varepsilon_i^c (i = 1, 3, 5, \cdots)$, while it will develop into the structure with two independent local deformations, i.e., the mixed state of exciton and charged polarons, for the photoexcited states $\varepsilon_i^v \rightarrow \varepsilon_i^c (i = 2, 4, 6, \cdots)$, though they undergo different transient structures. For example, Fig. 1(c) and 1(d) show the temporal evolution of the states $\varepsilon_3^v \rightarrow \varepsilon_3^c$ and $\varepsilon_4^v \rightarrow \varepsilon_4^c$, respectively. It should be stressed that the formation time is related to the overlap of the wave functions localized in the transient deformations and then the conjugation (chain) length. For example, it is 320 fs for $\varepsilon_4^v \rightarrow \varepsilon_4^c$ in the case of 200-site chain, but it is reduced to 100 fs for $\varepsilon_4^v \rightarrow \varepsilon_4^c$ in the case of 120-site chain. For these transient structures which are highly specific to the exciting frequency, they result from the lattice responses to the potential surface of the final (initial) eigenstate connected in the absorption at the initial stage. The origin of this behavior is easily understood by the fact that the wave envelope of $\varepsilon_m^v(\varepsilon_m^c)$ takes a standing-wavelike form which has m maximum amplitudes, thus there are m maximums in the driving forces inducing lattice distortions [13]. Furthermore, it should be mentioned that, for other possible dipole-allowed states, we have obtained the same physical pictures. For example, the states $(\varepsilon_1^v \rightarrow \varepsilon_3^c)$ and $(\varepsilon_2^v \rightarrow \varepsilon_4^c)$ undergo a similar lattice relaxation to that of the states $(\varepsilon_3^v \rightarrow \varepsilon_3^c)$ and $(\varepsilon_4^v \rightarrow \varepsilon_4^c)$, respectively.

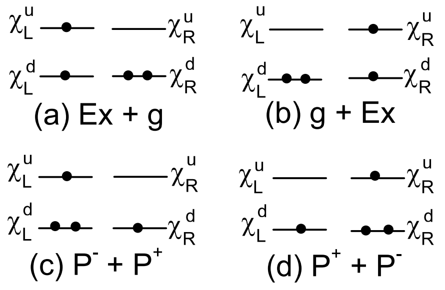

FIG. 3. The possible states corresponding to the bond configuration with two separated local deformations.

For a given excitation with photon energy above the electronic $\pi - \pi^*$ gap, the transitions $\varepsilon_i^v \rightarrow \varepsilon_i^c (i \in \text{odd})$ and $\varepsilon_i^v \rightarrow \varepsilon_i^c (i \in \text{even})$ have almost same probability, because they have comparable transition dipole moments at a certain transition energy. For example, for the excitation at 1.77 eV, both $\varepsilon_1^v \rightarrow \varepsilon_1^c$ and $\varepsilon_2^v \rightarrow \varepsilon_2^c$ have the similar transition probability, because they have comparable transition dipole moments (11.6 eÅ for $\varepsilon_1^v \rightarrow \varepsilon_1^c$ and 11.1 eÅ for $\varepsilon_2^v \rightarrow \varepsilon_2^c$) and similar transition energies (1.76 eV for $\varepsilon_1^v \rightarrow \varepsilon_1^c$ and 1.78 eV for $\varepsilon_2^v \rightarrow \varepsilon_2^c$). This is also valid for higher excitation energies. Therefore, both the single deformation polaron exciton and the mixed states corresponding to the two lattice deformations should have a similar formation probability. Considering that half of the yield is the charged polaron pairs in the mixed state, the quantum efficiency of charged polarons is about 25%, which is independent of the excitation energies. Our results are basically consistent with the experimental results, ~10% observed in poly[2-methoxy-5-(2'-ethyl)hexyloxy-1,4-phenylene vinylene] (MEH-PPV) through transient IRAV measurement [9] and ~20% found in a polythiophene derivative by transient absorption spectroscopy [11].

Moreover, we have also studied the lattice dynamics of photoexcited states via a two-phonon absorption process. For example, for the state excited from ε_1^v to ε_2^c, the transition is forbidden by dipole selection rule, but it can be realized through a two-photon process. The temporal evolution of bond order parameters is shown in Fig. 4. One can find that the lattice forms two localized distorts, similar to that in Fig. 1(b), i.e., the photoexcited state from ε_2^v to ε_2^c. The other photoexcitations through a

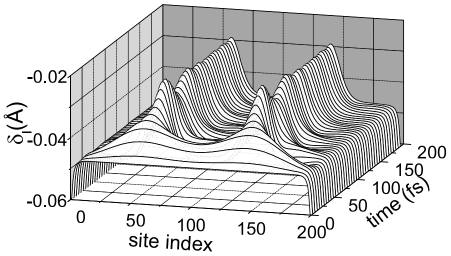

FIG. 4. Temporal evolutions of staggered bond order parameter δ_l for photoexcited state through two-photon absorption ($\varepsilon_1^v \to \varepsilon_2^c$).

two-photon process have similar results, i.e., the mixed state with two separated local deformations. Therefore, the photocarriers can also be formed directly through a two-photon process, which is in agreement with the experimental results [9]. It can be seen that the polaron-exciton state with one deformation will not be formed in a two-photon absorption process, so that the quantum yield of charged polarons will be 50%.

The conjugation length of polymers plays an important role in understanding the photogeneration of charge carriers. We have examined the dependence of dynamical relaxation processes on chain length. We find that the polaron exciton can always exist, independent of chain length. However, for the configuration with two separated local deformations, i.e., the mixed state of exciton and charged polaron pair, its behavior in the short chain case is different from that in long chain cases. Two deformations can be generated initially, but they will combine to form one lattice deformation, i.e., the polaron exciton, after a time period which depends on the chain length. This arises because the two lattice deformations cannot be separated far enough due to the confinement of chain ends in the short chain case, thus their wave functions are overlapping. For example, Fig. 5 shows the lattice evolutions of polymer chains including 100 sites [Fig. 5(a)] and 60 sites [Fig. 5(b)], respectively, photoexcited from ε_2^v to ε_2^c. One can find that it takes ~900 fs for the 100-site chain and ~300 fs for the 60-site chain to merge the two separated deformations into a polaron exciton. Thus the charged polarons have longer life times for longer chains. Indeed, Moses *et al.* [9] have found that the charge carriers have a longer life time in stretch-aligned PPV than that in the disordered MEH-PPV. It should result from that the aligned PPV has longer conjugation length than that in disordered MEH-PPV, though the different interchain interactions may also play a role.

In conclusion, we have adopted a nonadiabatic scheme to study lattice relaxation of various photoexcited states and addressed the generation mechanism of charged polarons. We have identified two kinds of stable lattice configurations, though they undergoes different transient distortions for different energy excited states. One of them is the well known polaron-exciton state, and the other is a state of two localized lattice distorts which is a mixture of charged polarons and exciton. Thus, our results indicate that both excitons and photocarriers (charged polarons) are ultrafast formed at the same time, and the quantum efficiency of charged polarons is obtained to be about 25%. Additionally, the dependence of conjugation length has been investigated.

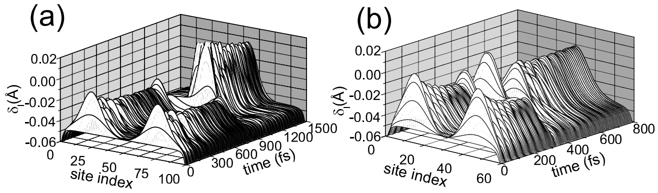

FIG. 5. Temporal evolutions of staggered bond order parameter δ_l for photoexcitation ($\varepsilon_2^v \to \varepsilon_2^c$) of different chain-length polymers, (a) $N = 100$; (b) $N = 60$.

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*Corresponding author.
Electronic address: cqw@fudan.edu.cn

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