Dynamics of Photogenerated Polaron in Conjugated Polymers

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Within a tight-binding electron-phonon interacting model, we investigate the dynamics of photexcitations 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 (>105 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 (IRA V) absorption, it has been found that the photocarriers (charged polarons) are generated within 100 fs after photoexcitations with a quantum efficiency (∼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 ∼100 fs with a quantum efficiency ∼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 (∼106 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 π−π* 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 symmetry-
breaking term [20]:

\[
H = -\sum_{l,s} t_l (c_{l,s}^+ c_{l+1,s} + c_{l+1,s}^+ c_{l,s}) + \frac{1}{2} K \sum_t (u_{t+1} - u_t)^2 \\
+ \frac{1}{2} M \sum_t \dot{u}_t^2,
\]

where \( t_l = t_0 - \alpha (u_{t+1} - u_t) + (-1)^l t_c \) with \( t_0 \) being the transfer integral of \( \pi \) electrons in a regular lattice, \( \alpha \) the electron-lattice coupling constant, and \( u_t \) the lattice displacement of the \( l \)th site from its equidistant position. \( t_c \) is introduced to lift the ground-state degeneracy for non-degenerate polymers. The operator \( c_{l,s}^+ (c_{l,s}) \) creates (annihilates) a \( \pi \) electron with spin \( s \) at the \( l \)th site, \( K \) the elastic constant due to the bonds, and \( M \) the mass of a CH group. Although these parameters used here are determined by the equation of motion for a CH group. The ground-state degeneracy for non-degenerate polymers. The operator \( c_{l,s}^+ (c_{l,s}) \) creates (annihilates) a \( \pi \) electron with spin \( s \) at the \( l \)th site, \( K \) the elastic constant due to the \( \sigma \) bonds, and \( M \) the mass of a CH group. The ground-state degeneracy for non-degenerate polymers. The operator \( c_{l,s}^+ (c_{l,s}) \) creates (annihilates) a \( \pi \) electron with spin \( s \) at the \( l \)th site, \( K \) the elastic constant due to the \( \sigma \) bonds, and \( M \) the mass of a CH group. 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 \( \epsilon_{i}^v \) to \( \epsilon_{4}^v \), 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 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.

Starting from the initial ground state, we excite an electron originally occupying the energy level \( \epsilon_{m}^v \) to the level \( \epsilon_{k}^v \) 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 \( \delta_i \equiv (-1)^l (u_{t+1} - u_{t+1} - 2u_t) / 4 \) for the four lowest lying photoexcited states (\( \epsilon_{i}^v \) \( \rightarrow \) \( \epsilon_{i}^f \), \( i = 1 - 4 \)) are shown in Fig. 1.

In the case of photoexcitation from \( \epsilon_{1}^v \) to \( \epsilon_{1}^f \), 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 \( \epsilon_{1}^v \) shifts upward while \( \epsilon_{1}^f \) 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 is 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 \( \epsilon_{1}^v \) to \( \epsilon_{1}^f \), 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 for the polaron exciton is shown in Fig. 2(a). For such a photoexcited state, four energy levels (\( \epsilon_{1}^v, \epsilon_{2}^v, \epsilon_{1}^f, \) and \( \epsilon_{2}^f \)) enter into the energy gap and become localized states. However, it should be stressed that \( \epsilon_{1}^v \) and \( \epsilon_{2}^v \) (\( \epsilon_{1}^f \) and \( \epsilon_{2}^f \))
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 evolitional wavefunctions \( \{ \Phi_{L,R}(l,t) \} \) 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, \( \chi_L^u, \chi_L^d, \chi_R^u, \) and \( \chi_R^d, \) 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 \( e_i^u \rightarrow e_i^e (i = 1, 3, 5, \cdots) \), 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 \( e_i^u \rightarrow e_i^j (i = 2, 4, 6, \cdots) \), though they undergo different transient structures. For example, Fig. 1(c) and 1(d) show the temporal evolution of the states \( e_1^u \rightarrow e_1^j \) and \( e_4^u \rightarrow e_4^j \), 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 \( e_1^u \rightarrow e_1^j \) in the case of 200-site chain, but it is reduced to 100 fs for \( e_4^u \rightarrow e_4^j \) 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 \( e_n^u (e_n^e) \) 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 \( (e_1^u \rightarrow e_1^j) \) and \( (e_2^u \rightarrow e_2^j) \) undergo a similar lattice relaxation to that of the states \( (e_3^u \rightarrow e_3^j) \) and \( (e_4^u \rightarrow e_4^j) \), respectively.

For a given excitation with photon energy above the electronic \( \pi - \pi^* \) gap, the transitions \( e_i^u \rightarrow e_i^j (i \in \text{odd}) \) and \( e_i^u \rightarrow e_i^j (i \in \text{even}) \) 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 \( e_1^u \rightarrow e_1^j \) and \( e_2^u \rightarrow e_2^j \) have the similar transition probability, because they have comparable transition dipole moments (11.6 e\( \AA \) for \( e_1^u \rightarrow e_1^j \) and 11.1 e\( \AA \) for \( e_2^u \rightarrow e_2^j \)) and similar transition energies (1.76 eV for \( e_1^u \rightarrow e_1^j \) and 1.78 eV for \( e_2^u \rightarrow e_2^j \)). 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 \( e_1^u \rightarrow e_5^e \), the transition is forbidden by dipole selection rule, but it can be realized through a two-phonon process. The temporal evolution of bond order parameters is shown in Fig. 4. One can find that the lattice forms two localized distort, similar to that in Fig. 1(b), i.e., the photoexcited state from \( e_2^u \rightarrow e_5^e \). The other photoexcitations through a
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 $e_1^+ \rightarrow e_2^+$ to $e_1^-$. One can find that it takes $\sim 900$ fs for the 100-site chain and $\sim 300$ 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 undergo 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.

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1. *Primary Photoexcitations in Conjugated Polymers*, edited by N.S. Sariciftci, (World scientific, Singapore, 1997), and references therein.