

Photoinduced carrier fission in polymers with a nondegenerate ground state

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Polarons and bipolarons are carriers in conducting polymers. A dynamical simulation in polymers shows photoinduced carrier fission where a positive carrier (polaron) is split into two carriers by photoexcitation. One carrier is a negative polaron and the other is a positive bipolaron. This fission is an ultrafast process of photoinduced charge generation without the aid of an electric field with a relaxation time of 100 fs.

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I. INTRODUCTION

Traditionally, polymers represent a key field of the chemical industry. However, in recent years, polymers have also become significant for physics in regard to both fundamental studies and applications. On the one hand, the discoveries of electroluminescence¹ and photovoltaics^{2,3} have provided new possibilities for optoelectronic applications. On the other hand, due to its chain structure, the polymer is an excellent material for testing theories and models based on a one-dimensional system. Earlier research on polymers has concentrated on ground-state and transport properties. Recently, many novel phenomena and applications based on excited states and dynamical process have been explored. Thanks especially to substantial progress in femtosecond laser spectroscopy, it is possible to reveal the details of various photoinduced dynamical processes in polymers.

Over the past decade, many photoinduced phenomena such as photovoltaics,^{2,3} photoinduced phase transition,⁴ charge transfer,^{5,6} and photoinduced polarization reversion⁷ have been under extensive investigation. Why is a polymer suitable for such processes? Due to its one-dimensional nature, the lattice configuration is sensitively dependent on the electronic state. Once this state is changed by photoexcitation, the bond structure of the polymer undergoes distortion. Subsequently, some new electronic bound states are formed by the lattice distortion, which is a process called self-trapping. Since the polymer possesses a quasi-one-dimensional structure, self-trapping in a polymer is much more prominent than in other systems. With this feature, many intriguing photoinduced phenomena can occur in polymers, and the aim of this paper is to explore such phenomena.

In a conducting polymer with a degenerate ground state such as polyacetylene, the carriers are charged solitons,⁸ while the carriers of most polymers with nondegenerate ground states NDGS are polarons, where the electron or hole is surrounded by bond distortion.⁹ This means that the carriers in polymers are composite particles with internal structure. Meanwhile, due to the confinement effect in NDGS polymers, the bipolaron with charge $\pm 2e$ is also stable.^{9,10} The internal structures of these composite particles can be easily changed by photoexcitation, where in some cases the

change of the internal structure is so dramatic that the composite particle itself can be split.

In this paper, we study the structural change of the carrier induced by photoexcitation in polymers. Our dynamical simulation shows a special photoinduced process whereby a positive polaron is split into two carriers—one a negative polaron and the other a positive bipolaron—where this photoinduced carrier fission does not need the aid of an external electric field. If an external electric field is applied, two resulting carriers will move in opposite directions along the polymer chain. Apparently, this carrier fission is a type of photoinduced charge generation.

II. FORMULATION OF DYNAMICS

The prominent self-trapping effect in a polymer is characterized by the one-dimensional electron-lattice interaction and does not depend on the details of the polymer. Hence the

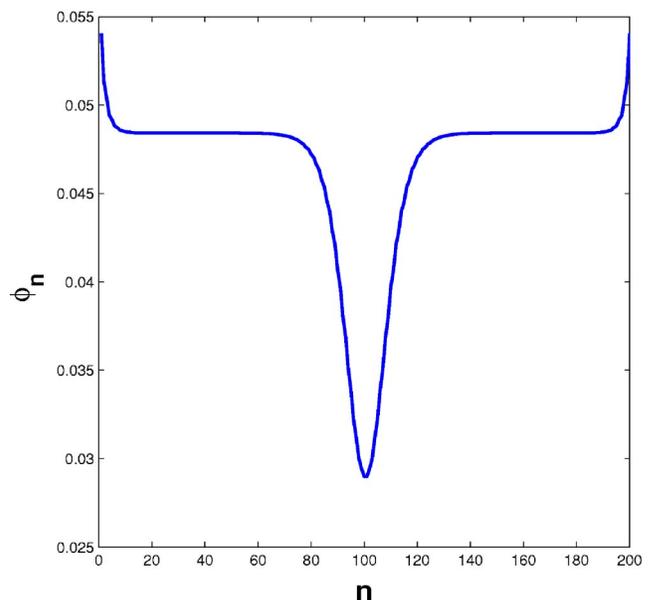


FIG. 1. Lattice configuration of a polaron with positive charge. The vertical axis is the lattice configuration, and n refers to the sites.

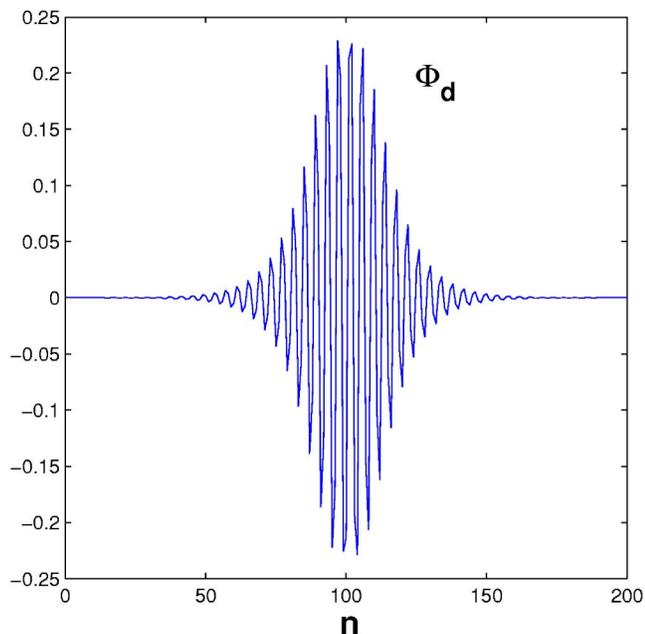
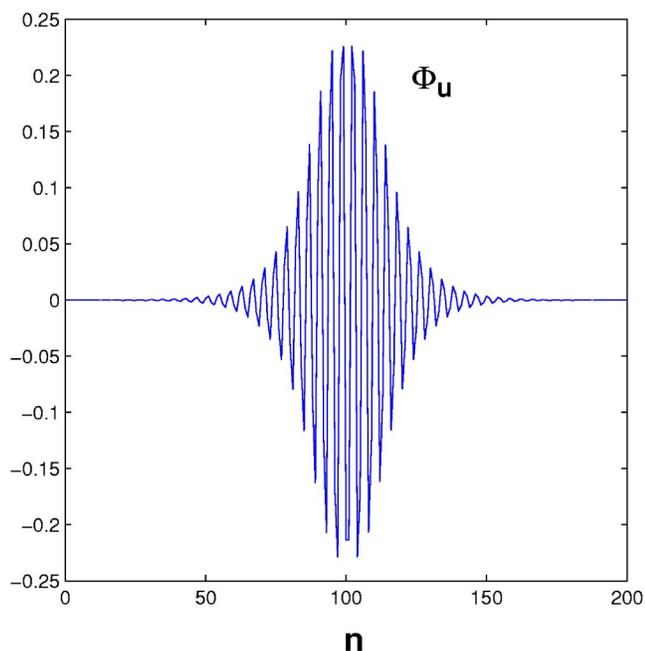


FIG. 2. Localized wave functions in the gap, which have been normalized. n labels the sites of the polymer chain.

self-trapping in conjugated polymers can be described by the common Hamiltonian

$$H = H_e + \frac{K}{2} \sum_l (u_{l+1} - u_l)^2, \quad (1)$$

$$H_e = H_0 + H', \quad (2)$$

$$H_0 = - \sum_{l,s} \{ t_0 + \alpha(u_{l+1} - u_l) + (-1)^l t_e \} [a_{l+1,s}^+ a_{l,s} + \text{H.c.}], \quad (3)$$

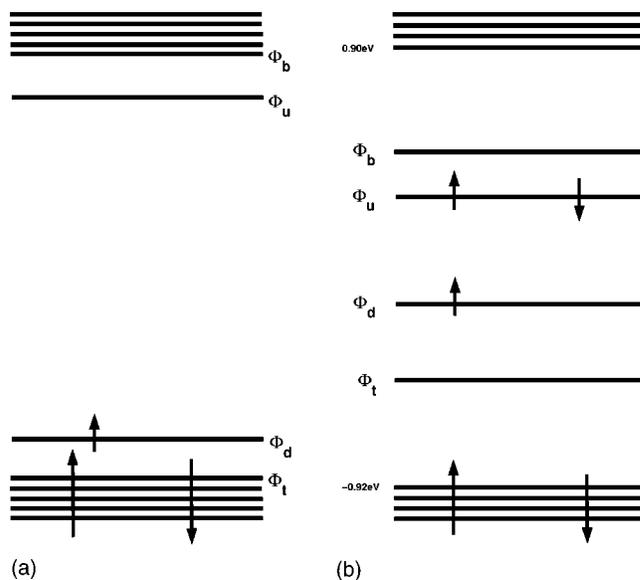


FIG. 3. Electron spectrum before (a) and after (b) carrier fission.

$$H' = U \sum_{l,s} n_{l,\uparrow} n_{l,\downarrow} + V \sum_{l,s,s'} n_{l,s} n_{l+1,s'}. \quad (4)$$

Here, u_l is the displacement of atom l with mass M , and K is an elastic constant; H_0 describes the electron–lattice interaction; t_0 is a hopping constant; and α is an electron–lattice coupling constant; the t_e term in H_0 reflects the confinement effect in polymers with NDGS, which ensures that composite particles like excitons, bipolarons, etc., in the polymer are stable; and H' is the electron–electron interaction. Since the bandwidth $W > 10$ eV of the polymer is much larger than the strength $U \sim 3-5$ eV of the electron–electron interaction, the polymer is not a strongly correlated system, and H' can be treated by the Hartree-Fock approximation. All the parameters in the Hamiltonian H take common values.⁹

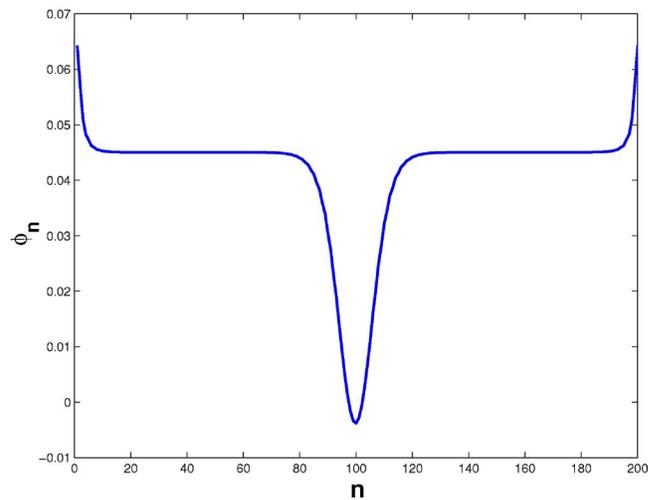


FIG. 4. Lattice configuration of a positive polaron n labels the sites of the polymer chain.

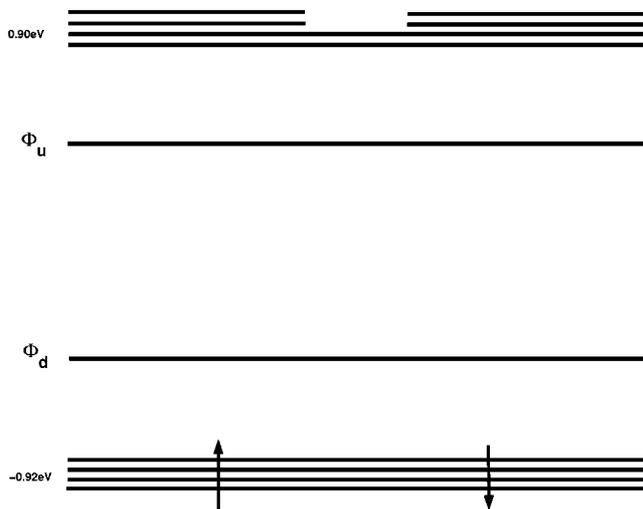


FIG. 5. Electron spectrum of a bipolaron.

The electron's energy spectrum ε_μ and wave function Φ_μ are functionals of the lattice displacement u_l and determined by the eigenequation

$$H_e \Phi_\mu = \varepsilon_\mu \Phi_\mu. \quad (5)$$

The total energy is therefore given by

$$E[\{u_l\}] = \sum_{occ} \varepsilon_\mu[\{u_l\}] + \frac{K}{2} \sum_l [u_{l+1} - u_l]^2, \quad (6)$$

and the charge distribution is

$$\rho_l = \sum_{occ} |\Phi_\mu|^2 - n_0, \quad (7)$$

where n_0 is the density of the positively charged background. Since atoms are much heavier than electrons, an atom's movement can be described by classical dynamics,

$$M \frac{d^2 u_l}{dt^2} = - \sum_{\mu}^{occ} \frac{\partial \varepsilon_\mu}{\partial u_l} + K(2u_l - u_{l+1} - u_{l-1}). \quad (8)$$

Thus the dynamical behavior of the polymer chain is formulated in terms of these coupled equations and can be numerically solved in a stepwise fashion.¹¹ Consequently, the evolution of the lattice displacement $u_l(t)$ and charge distribution $\rho_l(t)$ can be determined.

III. PHOTOINDUCED CARRIER FISSION

In NDGS polymers, the carriers are polarons with a single positive or negative charge $\pm|e|$ and bipolarons with a double charge $\pm 2|e|$. In the case of a positive polaron, one hole is injected into the chain of the polymer, which means that one electron is removed from the top of the valence band (HOMO, i.e., highest occupied molecular orbital). As mentioned in the Introduction, the polymer's chain is a quasi-one-dimensional system whose lattice structure depends on the electronic state. Before the electron is removed, the lattice configuration is a homogeneous dimerization, with the

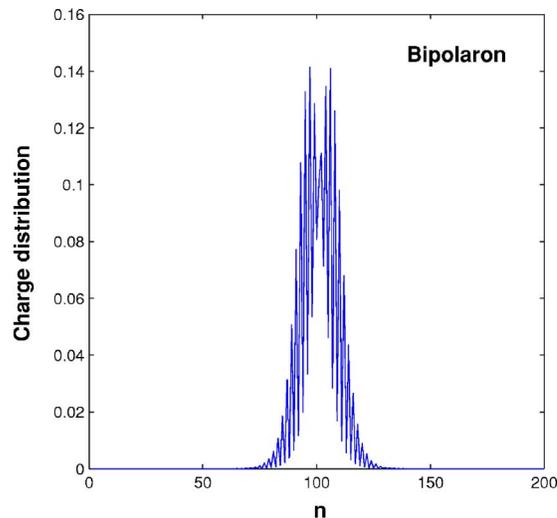
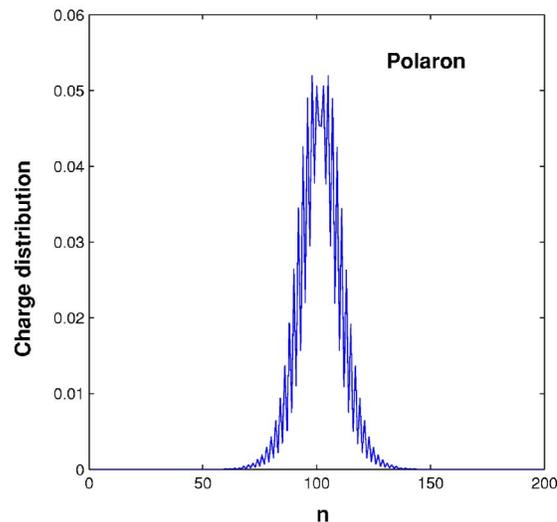


FIG. 6. Charge distribution of a positive polaron and charge distribution of a positive bipolaron. The vertical axis is the distribution at the n th site of the polymer chain, whose unit is a single positive charge $+|e|$. n refers to the sites.

lattice distortion $\phi_n = (-1)^n u_n$ being a constant ϕ . Once the electron is removed, the original lattice configuration is no longer stable and the bond structure is distorted. The resultant lattice configuration is shown in Fig. 1 for a chain whose length is 200 sites. Such a distorted lattice produces two localized electronic states Φ_u and Φ_d in the gap, whose wave functions are depicted in Fig. 2. Actually, the HOMO is raised from the top of the valence band into the gap to form Φ_d , and the lowest unoccupied molecular orbital is lowered from the bottom of the conduction band into the gap to form Φ_u . The energy spectrum and electron occupation of a positive polaron is shown in Fig. 3(a), where Φ_u is empty and Φ_d is occupied by only one electron.

If the electron sitting in the gap state Φ_d in Fig. 3(a) is also removed, the lattice configuration of the original polaron shown in Fig. 1 is unstable once again. The lattice will further relax to reach a new configuration as shown in Fig. 4. This is a positive bipolaron with double charge $\pm 2|e|$, and its energy spectrum and electrons' occupation is shown in Fig.

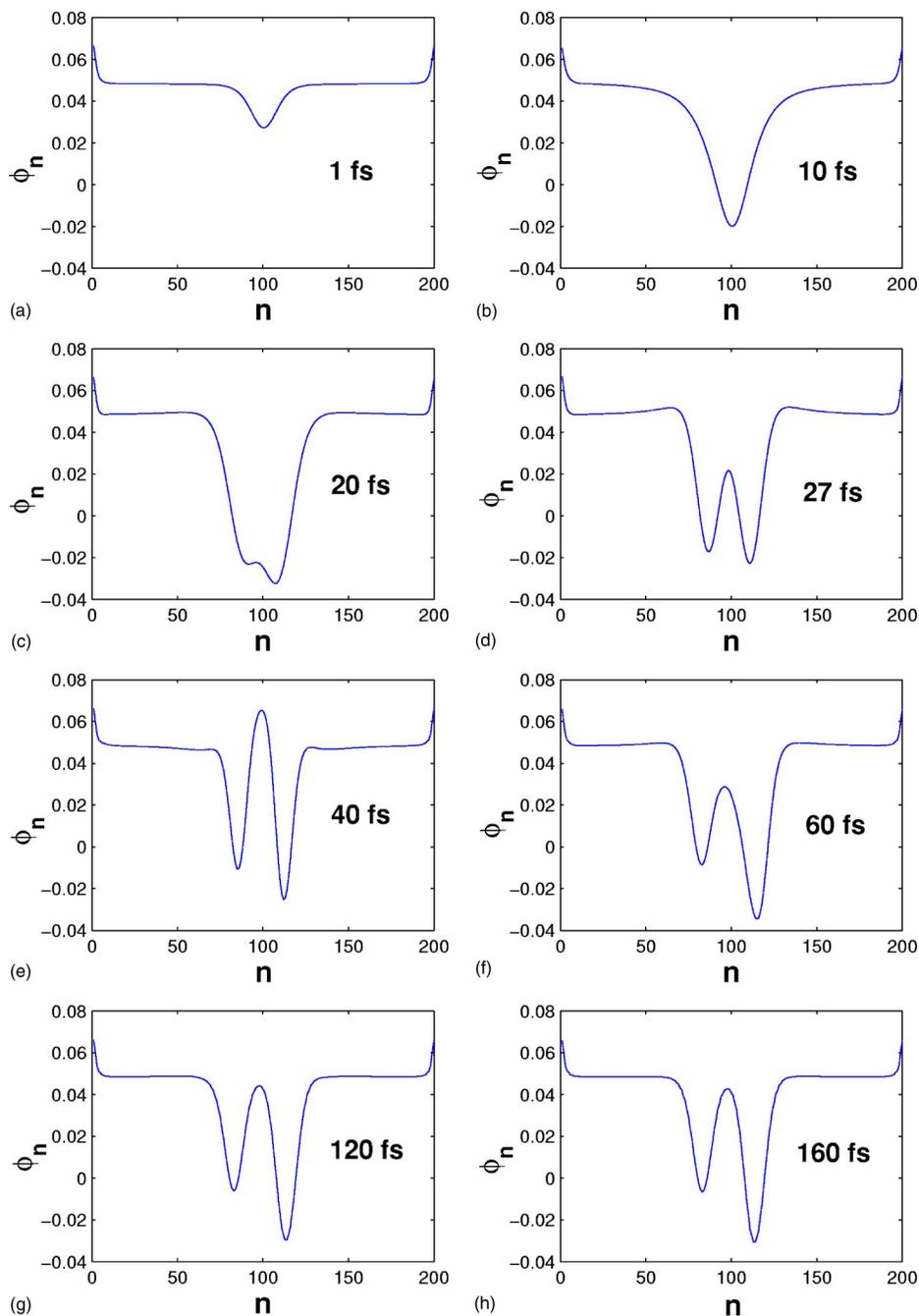


FIG. 7. Polymer chain's lattice relaxation after photoexcitation. The vertical axis is the lattice configuration, and n refers to the sites.

5. For the bipolaron, both gap states Φ_u and Φ_d are empty.

With these occupied electronic states, the charge distributions p_l of the polaron and bipolaron can then be calculated by using Eq. (7) and are shown in Fig. 6. The total charges are $+|e|$ and $+2|e|$, respectively, which are concentrated in the area where the lattice is distorted.

From Fig. 3, it is seen that the localized state Φ_u is empty; this state can accept two electrons with opposite spins. For certain photoexcitation, e.g., by means of STIRAP (stimulated Raman adiabatic passage),¹² two electrons in the valence band can be excited into Φ_u . Then the lattice configuration of the positive polaron shown in Fig. 1 is unstable again after the photoexcitation. The relaxation process of the lattice configuration followed by photoexcitation can be ob-

tained by solving the dynamical equations (8), and the evolution of the lattice configuration is shown in Fig. 7. At the beginning, there is only one valley corresponding to the original polaron [Fig. 7(a)]. In the first stage, this valley is deepened and broadened [Fig. 7(b)]. At $t=20$ fs, a hump appears in the bottom of the valley [Fig. 7(c)], indicating that the polaron starts to be split. The hump grows thereafter [Fig. 7(d)]. When $t=100$ fs, the original valley is fully divided into two new valleys [Fig. 7(g)], which means that the polaron splitting is complete. After that [Fig. 7(h)], this two-valley configuration basically does not change further, where the middle barrier between these two valleys just oscillates.

In order to identify these two valleys, we need to study the evolution of the charge distribution during the relaxation

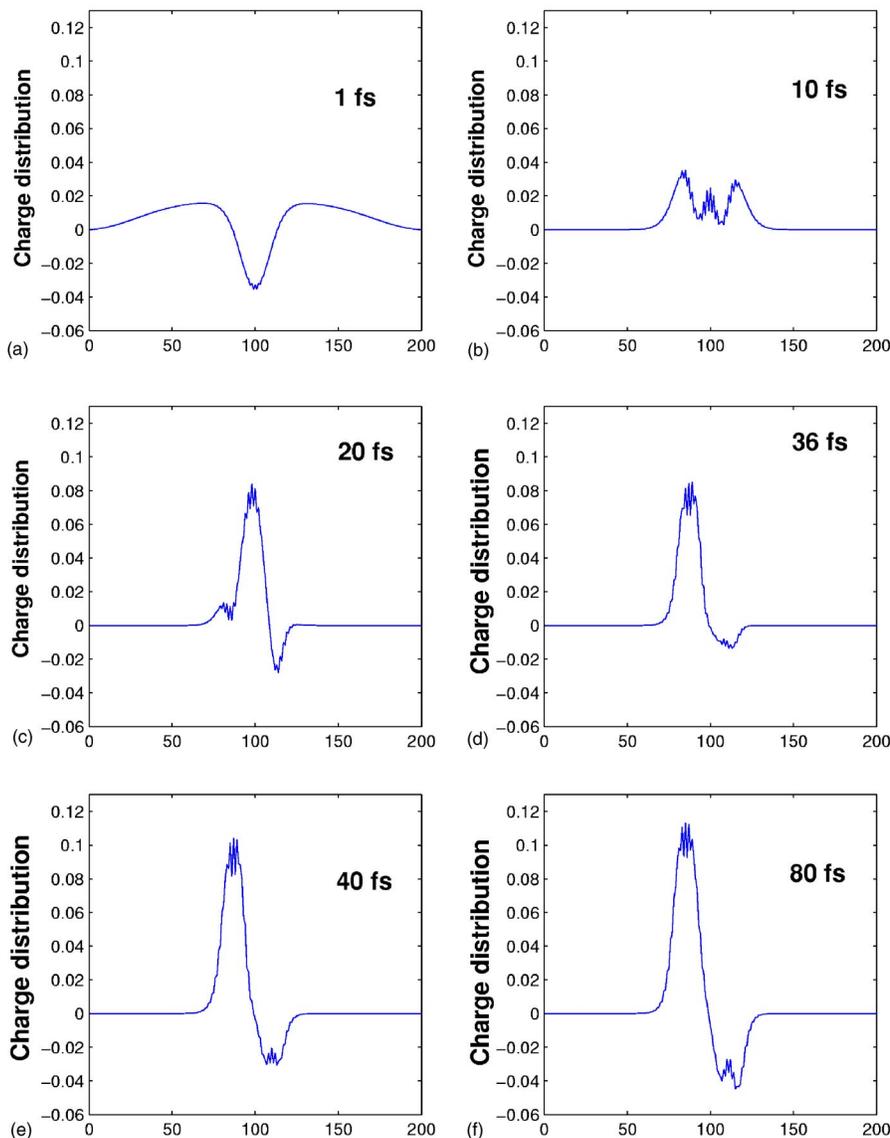


FIG. 8. Charge distribution in the polymer chain after photoexcitation with $U=4.0$ eV, $V=0.3$ eV, and $\alpha=4.0$ eV/Å. The vertical axis is the charge distribution at the n th site of the polymer chain, whose unit is a single positive charge $+|e|$. n refers to the sites.

process of the lattice configuration. By using Eq. (7), the time-dependent charge distribution $\rho_l(t)$ can be calculated, and the results are shown in Fig. 8.

Since Φ_u is a localized state and the wave functions in the valence band are extended states, when two electrons with opposite spins are excited from the valence band into Φ_u , negative charge is moved into the center part of the polaron, so that at the beginning there is a deep dip in the charge distribution [Fig. 8(a)].

TABLE I. Net charge of the bipolaron B^{++} and polaron P^- with different electron interactions.

| U (eV) | 4.0 | 5.0 | 5.6 | 6.0 | 5.0 |
|--|-------|-------|-------|-------|-------|
| V (eV) | 0.3 | 0.3 | 0.3 | 0.3 | 1.0 |
| Net charge of positive bipolaron B^{++} ($+ e $) | 1.81 | 1.74 | 1.66 | 1.57 | 1.59 |
| Net charge of negative polaron P^- ($- e $) | -0.81 | -0.74 | -0.66 | -0.57 | -0.59 |

Along with the relaxation of the lattice configuration, the charge is redistributed to a distribution that is no longer symmetrical about the center. Near $t=20$ fs, negative charge emerges on the right side [Fig. 8(c)]. Then the positive charge shifts further to the left side, leaving more negative charge on the right side [Fig. 8(d)], and the charge distribution becomes a profile with a peak of positive charge on the left side and a valley with negative charge on the right side. At a given instant in time, the total charge of the peak and valley is $+|e|$ (the charge of the original polaron). When $t=80$ fs, a peak with positive charge $+2|e|$ is established on the left side, while a valley with charge $-|e|$ is formed on the right side [Fig. 8(f)]. Afterwards, the main feature of the charge distribution is retained, where the only different aspect is a small oscillation. This indicates that two new carriers with opposite charges are formed by 100 fs.

By comparing the evolution of the lattice configuration (Fig. 7) with that of the charge distribution (Fig. 8), it can be found that they coincide with each other in both space and time. Therefore we can identify that the left carrier is a positive bipolaron and the right one is a negative polaron. Thus a

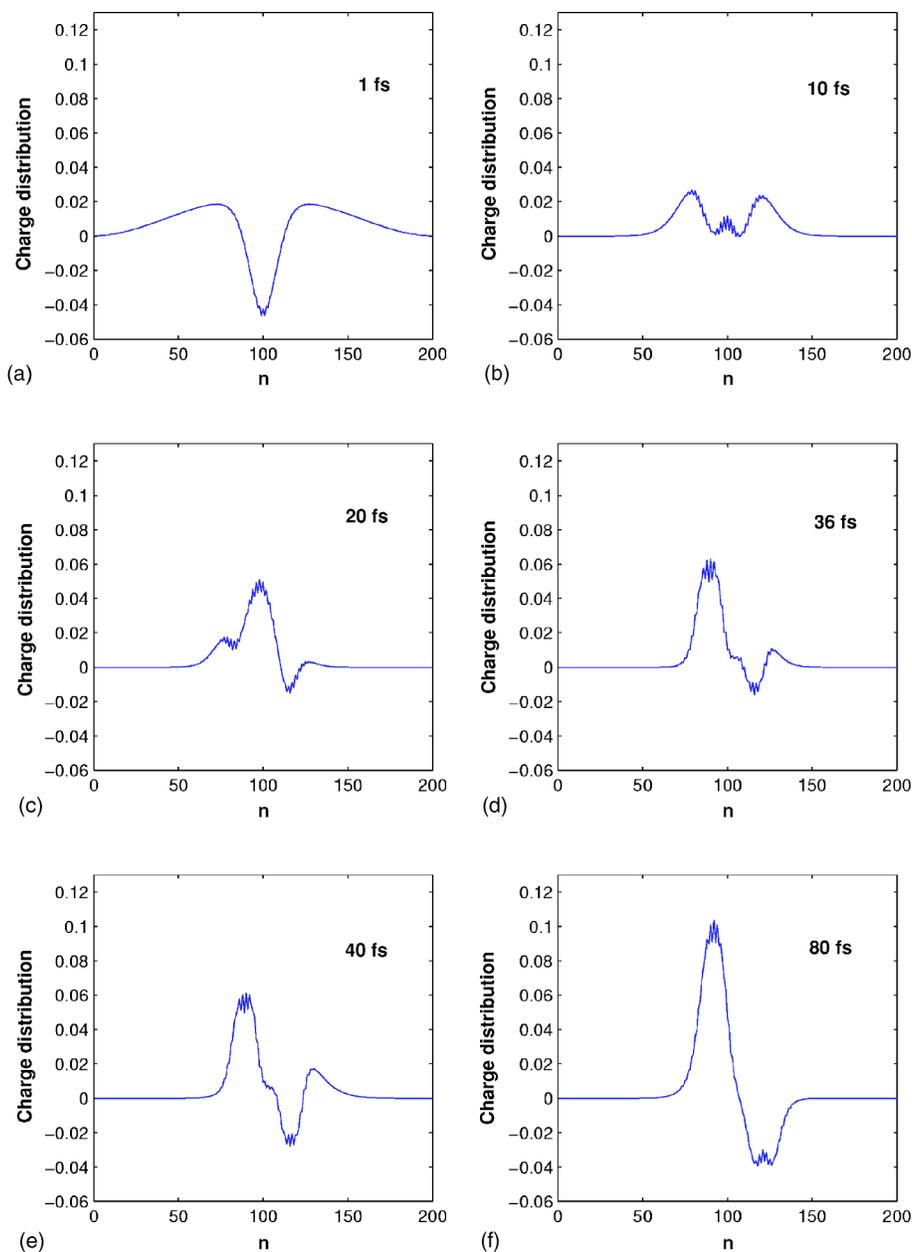


FIG. 9. Charge distribution in the polymer chain after photoexcitation with $U=6.0$ eV, and $V=0.3$ eV, and $\alpha=4.0$ eV/Å. The vertical axis is the charge distribution at the n th site of the polymer chain, whose unit is a single positive charge $+|e|$. n refers to the sites.

positive polaron is split into a positive bipolaron and a negative polaron by photoexcitation, where the splitting time is about 100 fs. Observation of this ultrafast dynamical process requires femtosecond laser spectroscopy, but the consequence of this splitting process may possibly be observed by measuring the conductivity. Since the fission not only doubles the number of carriers, but also doubles the charge of the positive carrier from polaron to bipolaron, the effect of carrier fission can be detected by observing enhancement of the polymer's conductivity.

In order to understand the effect of the electron interaction on the carrier fission, we have studied the dependence of the fission process on the parameters of the electron interaction U and V . After fission, since the bipolaron is positively charged and the polaron is negatively charged, under the electron interaction, they should attract each other. It is expected that when the electron interaction increases, the bipo-

laron and polaron come closer with more overlap. Once the configuration of the bipolaron overlaps with that of the polaron, part of the positive charge of the bipolaron will be neutralized by the overlapped part of the negative charge of the bipolaron, so that the net charges of both the bipolaron and polaron will decrease. This is shown in Table I, where we see that when U increases from 4 to 6 eV with fixed $V=0.36$ eV, the net charge of the bipolaron B^{++} decreases from $1.81 e$ to $1.57 e$, and that of the polaron P^- decreases from $-0.81 e$ to $-0.51 e$. Meanwhile, with fixed $U=5.0$ eV, when V increases from 0.3 to 1.0 eV, the net charges of B^{++} and P^- decrease from $1.74 e$ and $-0.74 e$ to $1.59 e$ and $-0.59 e$, respectively. It should be noted that when $U=5$ eV and $V=1$ eV, the electron interaction is sufficiently strong to account for such an interaction in a polymeric molecule, and yet the overlap between the bipolaron and the polaron is still quite small. This means that the photoinduced

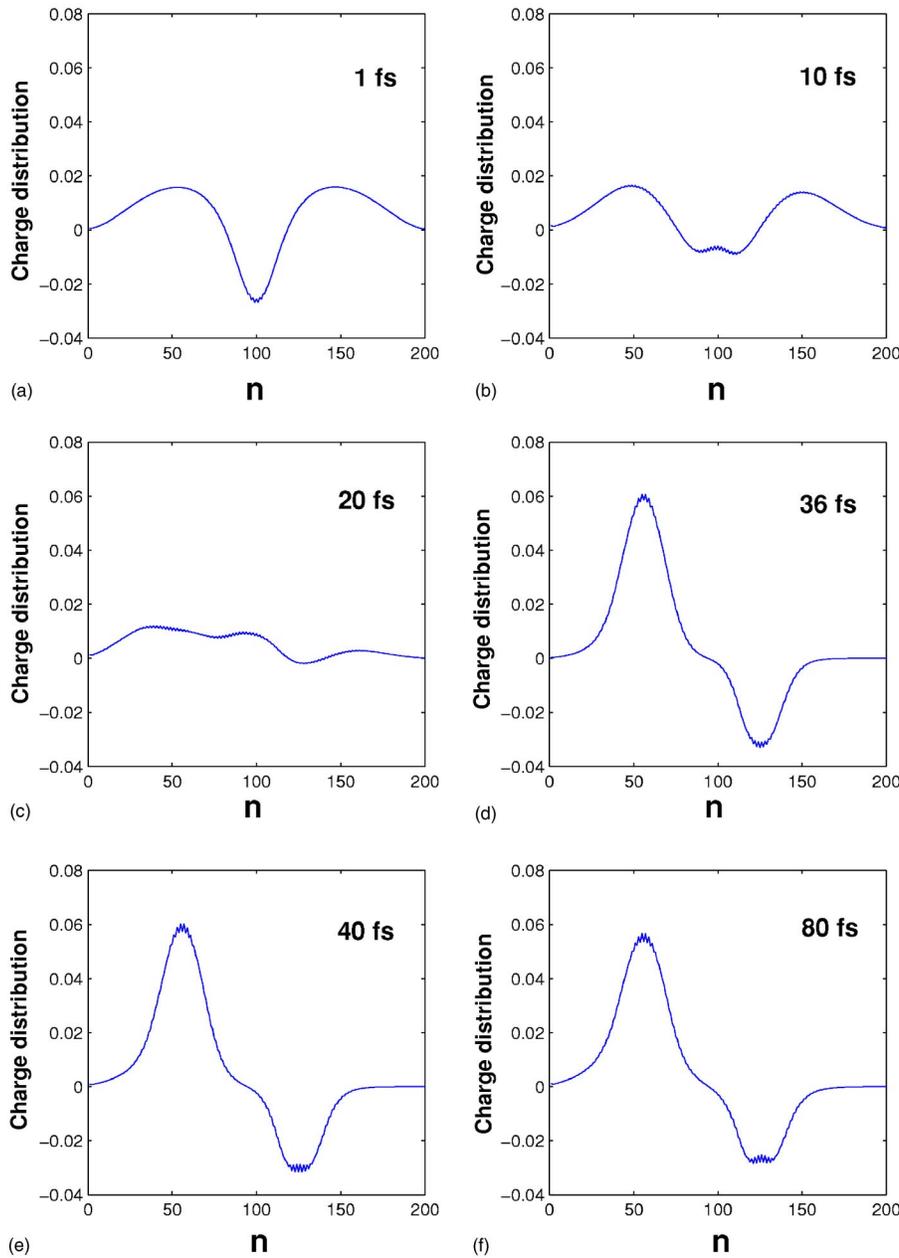


FIG. 10. Charge distribution in the polymer chain after photoexcitation with $U=4.0$ eV, $V=0.3$ eV, and $\alpha=3.0$ eV/Å. The vertical axis is the charge distribution at the n th site of the polymer chain whose unit is a single positive charge $+|e|$. n refers to the sites.

carrier fission can overcome the electron interaction.

We also have studied the influence of the electron interaction on the dynamic process of the carrier fission, where we choose two sets of parameters as $U=4.00$ eV, $V=0.3$ eV (Fig. 8) and $U=6.0$ eV, $V=0.3$ eV (Fig. 9). For charge redistribution, it is found that the speed of charge transport with weak electron interaction is a bit faster than that with strong interaction. However, the electron interaction does not qualitatively change the result.

Although polymeric molecules are not strong correlated systems, the interaction between electrons and phonons is a key factor for self-trapping in a polymer. We also have investigated the effect of the strength of the electron-phonon coupling α on the evolution process, where two values of the electron-phonon constant are chosen: $\alpha=4.0$ eV/Å (Fig. 8) and 3.0 eV/Å (Fig. 10). The results show that an increase in the electron-phonon coupling enhances the localization of

the carrier. This is expected since such an increase reduces the width of the polaron and bipolaron.

At room temperature, the heat energy is about $KT \sim 0.025$ eV. However, the energy gap of the polymer is about 2 eV, and the binding energies of the polaron and bipolaron are about 0.5 eV, which is far greater than the heat energy. Thus the heat energy is too small to influence the fission process, and the temperature is not an important factor.

During the lattice relaxation, the electron's spectrum also changes. The gap states Φ_u and Φ_d of the original positive polaron move further into a deeper part of the gap. In the meantime, the top state Φ_t of the original valence band is raised up into the gap to become a localized state, and the bottom state Φ_b of the original conduction band is lowered down into the gap. There appear four gap states after the carrier fission, as shown in Fig. 3(b). Here, Φ_u and Φ_d be-

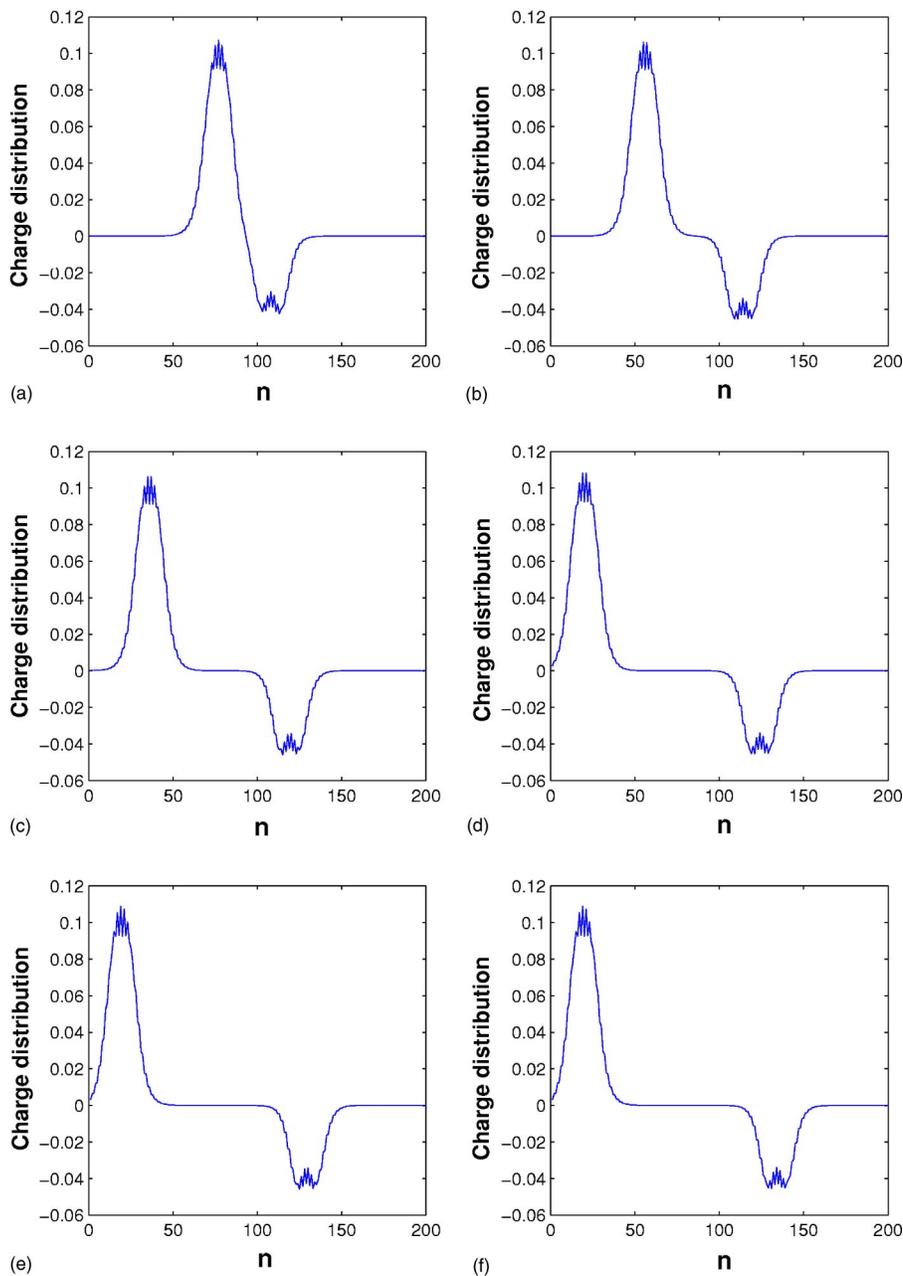


FIG. 11. Separation of the new negative polaron and positive bipolaron under an external electric field. The vertical and horizontal axes are the same as in Fig. 8.

long to the negative polaron, while Φ_b and Φ_t belong to the positive bipolaron.

In regard to Fig. 3, we should mention that since our calculation is unrestricted Hartree-Fock, and the electron in Φ_d is unpaired, the spectrum of spin-up is somewhat different from that of spin-down. In order to make the picture easier to be understood, Fig. 3 does not distinguish between the spectra of spin-up and spin-down.

IV. CONCLUSION AND DISCUSSION

Our main conclusion is that a positive polaron in conducting polymers can be split by certain photoexcitation into a negative polaron and a positive bipolaron. Below we review and discuss the features of this photoinduced carrier fission.

A. Carrier fission and charge separation

As shown in the previous section, this kind of carrier fission does not need an external electric field and is different from charge generation under a strong external electric field.^{13–15} An electric field E is applied, the negative polaron and positive bipolaron produced by the photoexcitation move in opposite directions, yielding charge separation. Figure 11 shows the evolution of the charge distribution in a field $E = 5 \times 10^4$ V/cm, where the valley with negative charge is the polaron moving toward the right side, and the peak with positive charge is the bipolaron moving toward the left side. From this figure it also can be seen that the bipolaron is moving more quickly than the polaron, since the charge of the bipolaron is twice that of the polaron.

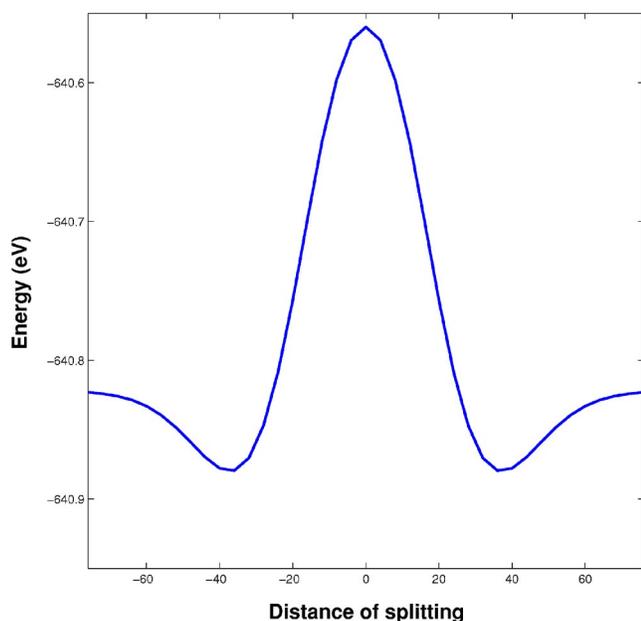


FIG. 12. Total energy vs distance of fission-produced new carriers (polaron and bipolaron). The horizontal axis is measured in units of the lattice of the polymer chain.

B. Broken symmetry

Since the lattice configuration of the original polaron possesses central symmetry about the middle point of the polymer chain, all the electronic states of the polymer have defi-

nite parities. Therefore, at the beginning of the carrier fission, both the lattice configuration and charge distribution are symmetrical about the center of the polymer chain [see Figs. 7(a) and 8(a)]. Although the Hamiltonian itself [Eqs. (1)–(4)] has inversion symmetry, the symmetry of the lattice configuration (and charge distribution) are broken during the relaxation process. After fissioning, a positive bipolaron emerges on the left side and a negative polaron on the right side. As is well known, symmetry breaking has a common feature in that the result is not unique. In our case, the fission has two possibilities: The bipolaron can sit either on the left or on the right side of the polaron. This means that the excited polaron's energy, which depends on the relaxing lattice configuration, has two equal minima, as shown schematically in Fig. 12, and the excited polaron can accidentally fall into one of these two minima. However, the polaron itself without photoexcitation has only one minimum, corresponding to the stable lattice configuration of the polaron. The addition of an infinitesimal external influence can lift such uncertainty. Here, if an infinitesimal electric field is applied, the relative positions of the polaron and bipolaron will be fixed.

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