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Two-step dissociation of a polaron in conjugated polymers*

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We have studied the electric-field-driven motion of a polaron by solving the time-dependent Schrödinger equation nonadiabatically and the lattice equation of motion simultaneously. It is found that the polaron may experience two sequent transitions under high fields; one is the transition from the subsonic to the supersonic state, and the other from the supersonic to dissociated state. The acoustic mode is decoupled from the charge when the polaron moves at a speed faster than the sound speed, and then the optical mode is decoupled at the second transition to make the polaron dissociate completely.

Keywords: conjugated polymer, polaron, dynamics
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1. Introduction

Charge transport properties in conjugated polymers have attracted much attention since the trans-polyacetylene was found to be able to be doped and exhibited a very high electrical conductivity in 1977. Many electronic devices[1,2] have been fabricated based on these conjugated polymers. One of the processes appearing in functioning these devices is the motion of the charge carriers along the polymer chain under an external electric field.

It is well known that removing (adding) electrons from (to) conjugated polymers can induce localized charged defects in the form of polarons or solitons[3−6] (the latter takes place only in the case of trans-polyacetylene), i.e. localized charges associated with a lattice distortion due to the strong electron–phonon interactions. It is generally believed that these excitations are related to the charge carriers in conjugated polymers. The dynamical processes of these excitations are one of the major and fundamental issues of interest in the organic electronic devices such as organic light-emitting diodes (OLEDs) and organic spintronics.

So far, many extensive studies on polaron dynamics in conjugated polymers have been carried out.[7−19] Rakhmanova and Conwell[7,8] have considered the motion of a polaron under low and high electric fields, respectively. Their results show that the polaron can form and move in its entity in low electric fields but dissociate in high fields. The highest electric field strength under which the polaron can sustain, referred to as dissociation electric field, is about 6×10^5 V/cm. Basko and Conwell[9] have also analysed the dynamical process of a polaron and found that the speed of a steadily moving polaron cannot exceed the sound speed (V_s). This conclusion is consistent with that from the numerical results presented by Arikabe *et al* [15] but inconsistent with those given by Johansson and Starfström.[10,11] In Johansson and Starfström's work, the maximum saturation speed is about four times the sound speed. Both acoustic and optical deformations have been defined to describe the behaviour of the polaron under an external electric field. They have found that, around a critical strength of electric field 0.14 mV/Å, the saturation speeds of the polaron under various fields have a step-like transition from sonic to supersonic. All the present investigations are focused on the field strength dependence of a polaron. In fact, a polaron is a state of an electron coupled with a lattice. The electron moves under the action of an external field, and the lattice has to follow the motion if the polaron keeps in its entity,

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which means that the polaron transport includes the response of the slow lattice deformation to the fast moving electron. Therefore, it is necessary to study the behaviour of a polaron with different speeds, especially, the characterization of a moving polaron that is important for understanding its dissociation.

2. Method

A conjugated polymer chain may be described with the Su–Schrieffer–Heeger (SSH) model.[20−22] The electric field is introduced through the vector potential appearing in a complex phase factor in the transfer integral. The Hamiltonian is written as

$$H = H_{\rm el} + H_{\rm lattice}, \tag{1}$$

where $H_{\rm el}$ is the Hamiltonian relating to electron and electric field, which can be described as

$$H_{\rm el} = -\sum_{n,s} t_n {\rm e}^{{\rm i}\gamma A} \hat{c}^{+}_{n,s}\hat{c}_{n+1,s} + {\rm e}^{-{\rm i}\gamma A}\hat{c}^{+}_{n+1,s}\hat{c}_{n,s}), \tag{2}$$

in a periodic boundary condition, where $t_n = [t_0 - \alpha(u_{n+1} - u_n)]$ is the hopping integral of π electrons between sites n and $n+1$, α is the electron–phonon coupling constant, u_n the displacement coordinate of the nth site and $\hat{c}^{+}_{n,s}(\hat{c}_{n,s})$ the electron creation (annihilation) operator on site n with spin s. Coefficient γ in the exponent is defined as $ea/\hbar c$, with e, a, c being electron charge, lattice constant and speed of light, respectively. Vector potential $A = A(t)$ is related to the external electric field through $E = -\partial_t A(t)/c$.

The lattice is modelled by

$$H_{\rm lattice} = \frac{K}{2}\sum_n (u_{n+1} - u_n)^2 + \frac{M}{2}\sum_n (\partial u_n/\partial t)^2, \tag{3}$$

where K is the elastic constant and M the mass of a CH group.

Evolution of the lattice configuration is determined by the equation of motion

$$\begin{aligned} M\ddot{u}_n =& -K(2u_n - u_{n+1} - u_{n-1}) \\ &+ \alpha[{\rm e}^{{\rm i}\gamma A}(\rho_{n,n+1} - \rho_{n-1,n}) + {\rm c.c}], \end{aligned} \tag{4}$$

where the density matrix ρ is defined as

$$\rho_{n,n'} = \sum_\nu \Psi^*_\nu(n,t) f_\nu \Psi_\nu(n',t). \tag{5}$$

Here, f_ν is the time-independent distribution function determined by the initial electron occupation, while the electronic wavefunctions are the solutions to the time-dependent Schrödinger equation

$$\begin{aligned} {\rm i}\hbar\frac{\partial}{\partial t}\Psi_\nu(n,t) =& -t_n {\rm e}^{{\rm i}\gamma A}\Psi_\nu(n+1,t) \\ &- t_{n-1}{\rm e}^{-{\rm i}\gamma A}\Psi_\nu(n-1,t). \end{aligned} \tag{6}$$

The spin index s has been omitted in the equations. The coupled differential equations (4) and (6) are solved with a Runge–Kutta method[23] of order eight with step-size control, which has been proven to be an effective approach to investigating the polaron dynamics[10] and photoexcitation dynamics[24] in conjugated polymers.

Acoustic and optical modes are described with the order parameters $y^{\rm a}_n$ and $y^{\rm o}_n$ defined as

$$y^{\rm a}_n = [(u_n - u_{n-1}) + (u_{n+1} - u_n)], \tag{7a}$$

$$y^{\rm o}_n = [(u_n - u_{n-1}) - (u_{n+1} - u_n)]. \tag{7b}$$

The centre of the charge density is defined as

$$\rho_{\rm c} = \begin{cases} N\theta_{\rm e}/2\pi, & \text{if} \quad \langle\cos\theta_{\rm e}\rangle \geq 0 \quad \text{and} \quad \langle\sin\theta_{\rm e}\rangle \geq 0; \\ N(\pi + \theta_{\rm e})/2\pi, & \text{if} \quad \langle\cos\theta_{\rm e}\rangle < 0, \\ N(2\pi + \theta_{\rm e})/2\pi, & \text{otherwise}, \end{cases} \tag{8}$$

where

$$\theta_{\rm e} = \arctan\frac{\sum_n \rho_{n,n}\sin(2\pi n/N)}{\sum_n \rho_{n,n}\cos(2\pi n/N)}.$$

Then the centres of the acoustic (optical) modes $y^{\rm a,o}_{\rm c}$ can be defined similarly, where

$$\theta_{\rm a,o} = \arctan\frac{\sum_n y^{\rm a,o}_{\rm c}\sin(2\pi n/N)}{\sum_n y^{\rm a,o}_{\rm c}\cos(2\pi n/N)}.$$

The widths of the charge density and the acoustic (optical) mode are estimated from the following formulas:

$$W_\rho(t) = \Big(\sum_n [n - \rho_{\rm c}(t)]^2\rho_{nn}\Big)^{1/2}, \tag{9}$$

$$W^{\rm a(o)}_y(t) = \Big(\sum_n [n - y^{\rm a(o)}_{\rm c}(t)]^2 |y^{\rm a(o)}_n - y^{\rm a(o)}_0|\Big)^{1/2}, \tag{10}$$

where $y_0^{a(o)}$ is the dimerized lattice displacement of the pristine chain.

The following parameters are selected from among those of polyacetylene in Ref.[25]: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21$ eV/Å^2, $a = 1.22$Å, and $M = 1349.14$ eV $\cdot$ fs^2/Å^2. Although these parameters used in calculation are for polyacetylene, the results are qualitatively valid for other conjugated polymers. In calculations, we use periodic boundary conditions to observe a polaron motion in a long time. The velocity of polaron is changed by adjusting the strength of the external field.

3. Results and discussions

A negatively charged polaron is produced on the chain ($N = 200$) centred on site 40 in the absence of the field at the beginning. The lowest unoccupied molecular orbital (LUMO) level occupied by an extra electron will fall into the gap to form a polaronic level, meanwhile a doubly occupied highest occupied molecular orbital (HOMO) level will also symmetrically appear in the gap. A polaron is characterized from three aspects: a localized lattice deformation or defect, a localized electronic state or charge density, and two discrete deep levels in a gap. A lattice defect may be induced by an extra electron due to the strong electron–lattice interactions in polymers, on the contrary, a lattice defect confines an extra electron to form a localized electronic state. Therefore, a polaron is a self-trapping state.

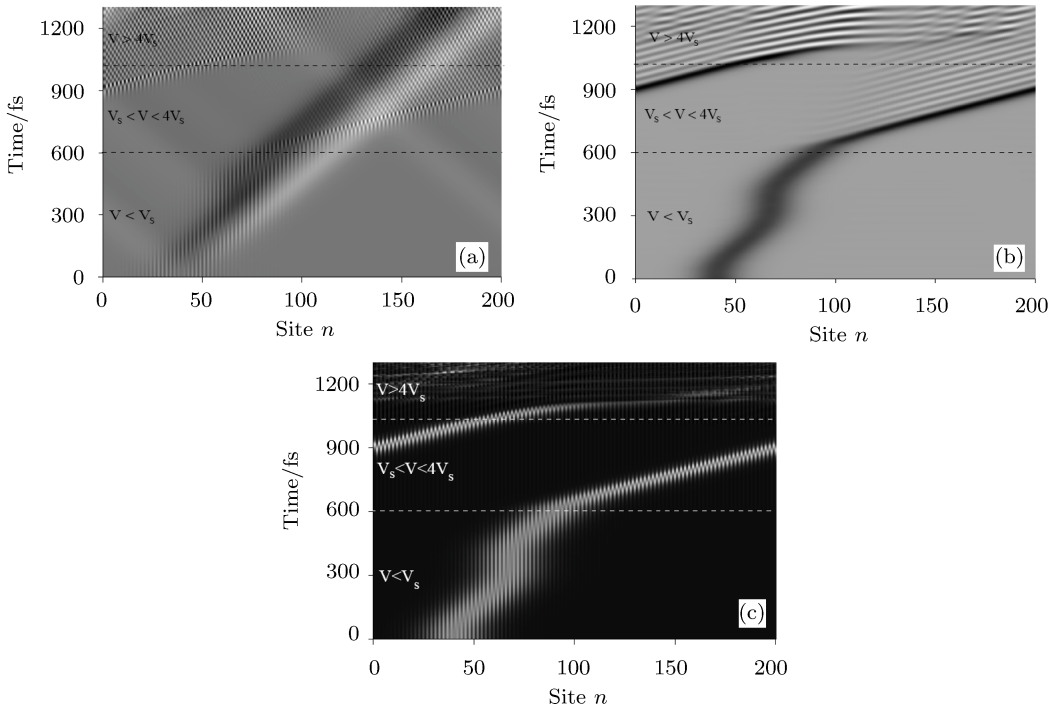


Fig.1. The dynamics of (a) the acoustic mode, (b) the optical mode and (c) the charge density in three periods of time each with a fixed applied field.

The electric field is turned on smoothly, which will drive the polaron to moving along the chain. It is found that the velocity of the polaron depends on the strength of the field. Figure 1 shows the evolutions of the acoustic, optical modes, and the net charge densities with different speeds by adjusting the strength of the field. In the initial 600 fs, the polaron is accelerated to a speed lower than the sound speed V_s under a weak field. It is found that the polaron moves in its entity and keeps its original shape. The black and white parts emerging in the acoustic mode represent the emitted acoustic phonons. Increasing the field strength to drive the polaron to moving at a higher speed, say, 600 fs, it is found that, from Fig.1(a), the polaron moves at a supersonic speed, which means that it gains enough energy and overcomes the potential trap of the acoustic mode. In this region, the polaron emits acoustic as well as optical phonons. From the evolution, one can see that the acoustic mode lags behind the charge, but the optical mode still moves

together with the localized charge. The polaron moving at supersonic speeds is different from the static or subsonic polaron, and it is still localized but characterized by the optical mode. With the further increase of the external field at 1000 fs, the charge will be free of the confinement of the optical mode and become extended. As shown in the third region of Fig.1(a), the chain presents a uniform distribution of black and white parts except for the left acoustic and optical modes. As a polaron needs a time of $T = 2a/v_{\rm p}$ to across a lattice period, if the lattice atoms can keep the response to the charge motion, one should have $T \geq \omega_{\rm Q}^{-1}$, where $\omega_{\rm Q} = \sqrt{4K/M}$ is the bare optical phonon frequency. Therefore, a polaron will dissociate into an extended state when its speed $v_{\rm p} \geq 2a\omega_{\rm Q}$ or $v_{\rm p} \geq 4V_{\rm s}$, where $V_{\rm s} = a\omega_{\rm Q}/2$ is the sound speed.

Figures 2 (a) and 2(b) give the developments of the centres and the widths for the acoustic and optical modes as well as the charge density, respectively. The optical mode keeps well together with the charge in the case of the subsonic motion. Owing to the emission of the acoustic phonons, the centre of the acoustic mode departs from that of the charge and its width also becomes wider and wider. It is also interesting to note that the speed of the charge oscillates even at a fixed field as shown in Fig.2(a) or more clearly in Fig.3. In the first period of time, the charge moves at a subsonic speed, and its width keeps unchanged, which means a unitary polaron. In the second period of time, the charge moves at about $3V_{\rm s}$, with the present parameters used. The trap of the lattice on the charge takes place through the optical mode. The decrease of the charge width in this region is due to the fact that it has a high speed. In the third period of time, the charge becomes free of the lattice confinement and moves as a quasi-free particle.

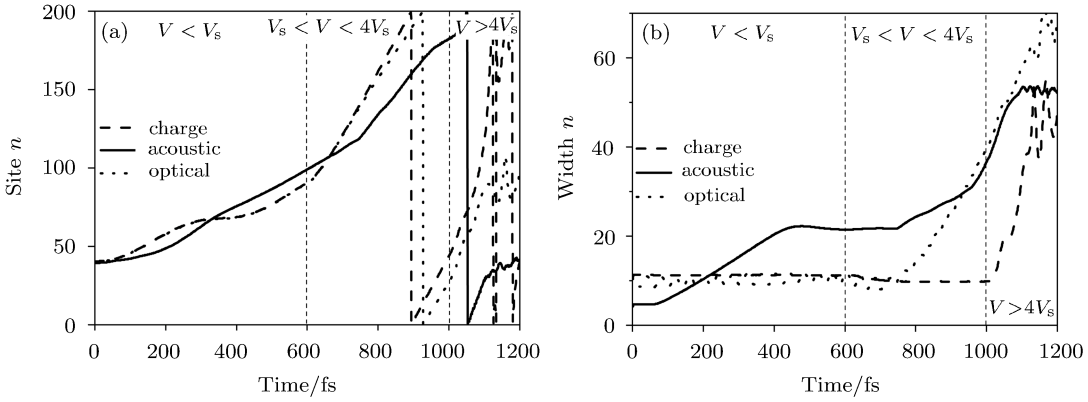


Fig.2. (a) Centre motions of the optical (dot) and the acoustic (dash) modes as well as the charge density (solid) in three periods of time each with a fixed applied field. (b) Evolutions of the widths of the optical (dot) and the acoustic (dash) modes as well as the charge density (solid) in three periods of time each with a fixed applied field.

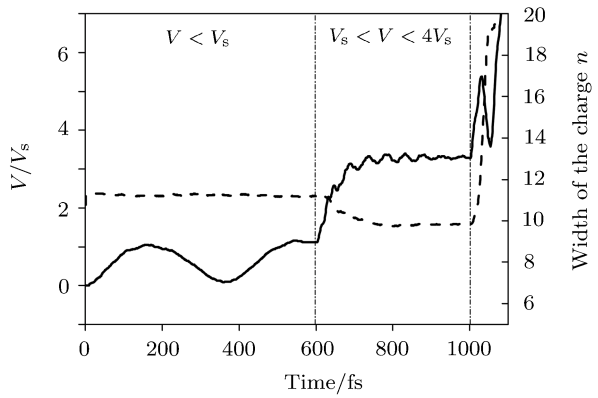


Fig.3. The ratio of charge speed (V) to the sound speed ($V_{\rm s}$) (solid) and the charge width (dot) versus time in three periods of time each with a fixed applied field.

Figure 4 shows the evolution of the instantaneous levels defined as $\varepsilon_\nu(t) = \langle \Psi_\nu(t)|H(t)|\Psi_\nu(t)\rangle$. It can be seen that the polaronic levels keeps nearly unchanged before dissociation. Only a small oscillation appears when the charge moves at a speed faster than the sound speed but slower than four times the sound speed. The levels will go into the bands when the polaron gains enough energy from the field and dissociates. It is also noted that the variation of the valence band levels and the conduction band levels appear in the figure. In the case of a weak field, the lattice potential dominates the behaviour of electrons and the energy levels keep unchanged in the first 600 fs. An intermediate field will compete with the lattice potential of electrons, which results in weakening the effect of lattice on electrons. Therefore, the subbands become

narrow in the interval of 600–1000 fs. In the case of a strong field, the effect of the lattice potential can be neglected and all the instantaneous levels appear oscillatory as shown in the third interval of Fig.4.

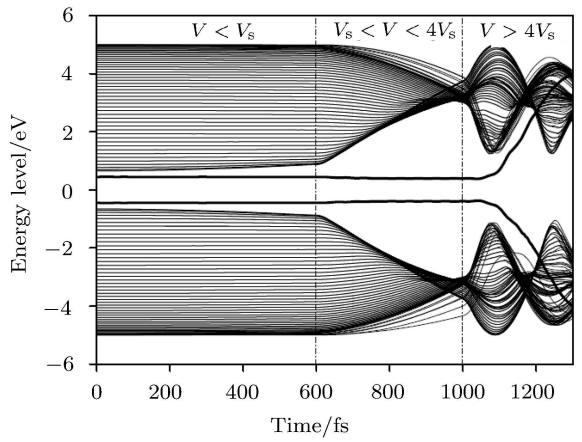


Fig.4. Evolution of the instantaneous energy levels.

4. Summary

Recently, polaron dissociation has been experimentally proved by the mobility transition at an electric field strength of about 15 mV/Å.[26] In this paper, we have traced in detail the whole process of motion of a polaron from a slow to a fast moving state and from a unitary to a dissociated state. Both optical and acoustic modes are introduced to describe the polaron behaviour. A polaron experiences two abrupt changes, one is the transition from the subsonic to the supersonic state at V_s and the other from the supersonic to the dissociated state at about $4V_s$. The charge couples with both the acoustic and optical modes in the case of the subsonic motion. When the polaron moves at a speed above V_s but below $4V_s$, the acoustic mode lags behind the charge, but the optical mode still moves together with the localized charge. The polaron is still localized but characterized by the optical mode. The polaronic energy level is well separated from the bands in this region, so we consider the motion of the polaron in this region to be stable. When the polaron moves at a speed above $4V_s$, the electronic states, the acoustic and the optical modes become extended. The critical speed of the polaron dissociation is estimated by the bare optical phonon frequency to be about $4V_s$ and found to be consistent with the numerical simulation results available from the literature and present work. The velocity of a polaron is dependent on the external electric field before it dissociates, while the mobility of the dissociated charge is unchanged, which has been observed experimentally.[26] Therefore, the characteristics of a polaron can be investigated through adjusting the strength of a driving field.

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