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Field-induced charge generation in electroluminescent polymers

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Abstract

A novel phenomenon of the 'field induced charge generation' is observed recently in the electroluminescent polymers. The experiments show that the photoexcitation in the electroluminescent polymers can be converted into a pair of opposite charged carriers by the electric field. Our study presents the dynamical process of the charge generation in the polymer chain by solving the time-dependent Schrodinger equation, and the evolution shows that the field-induced charge generation is an ultrafast process produced in about 10 fs. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently two groups simultaneously reported the phenomenon of 'field-induced charge generation' in Ladder-type poly(*para*-phenylene)(LPPP): A strong external electric field may turn the neutral photoexcitation in the luminescent polymer into a pair of opposite charged carriers [1,2]. In 1997, Tasch et al. found that in electroluminescent polymer m-LPPP, when the electric field exceed 1.5 MV/cm, the luminescence was quenched, and the luminance fell sharply with increasing electric field [3]. All these experiments indicate that the exciton in luminescent polymers is dissociated into a pair of opposite charged polarons by a strong electric field [4].

In order to clarify the transient property of this field-induced charge generation, it's necessary to reveal its dynamic mechanism and show the evolution process of the charge generation. Today the femtosecond spectroscopy technology has got such a high time resolution as 10^{-15} fs, it's possible to observe the transient charge distribution during the course of charge generation. This paper performs a dynamic simulation on this course and present the evolution process of the exciton converting into a pair of opposite charged carriers, from which we can get the time-dependent charge distribution and determine the relaxation time of the charge generation.

2. Theory formula

The static and dynamical states of the electrons and lattice in the conjugated polymers can mainly be described by the well-known SSH model [5]

$$H_{\mathrm{SSH}} = -\sum_{n,\sigma}[t_0 + \alpha(-1)^n(\phi_n + \phi_{n+1} + t')](C^{+}_{n+1,\sigma}C_{n,\sigma} + H.C.) + \frac{K}{2}\sum_{n}(\phi_n + \phi_{n+1})^2 \tag{1}$$

where $K = 21$ eV/Å^2 is the harmonic spring constant; φ_n is the displacement of the atom at lattice site n; M is the mass of carbon atomic; $\alpha = 4.1$ eV/Å the electron-phonon coupling constant; $t_0 = 2.5$ eV the hopping integral; $\alpha t' = 0.06$ eV the energy difference of non-degenerated ground state; $C^{+}_{n,\sigma}$ and $C_{n,\sigma}$ the creation and annihilation operators of electron at site n with spin σ.

The photoexcitation in the conjugated polymer produces an electron-hole pair, which evolves to a self-trapped exciton [4]. In the self-trapped exciton, there are two electronic bound states ψ_u and ψ_d in the energy gap. Both ψ_u and ψ_d are localized in the central part of the polymer chain and occupied by one electron.

The self-trapped exciton is a neutral excitation. Before applying the electric field, there is no net charge distribution in the polymer chain. After the electric field is applied, the exciton is polarized, and there emerges the charge distribution in the central part of the chain. When the electric field is strong enough, the exciton is dissociated, the positive charge

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and negative charge are driven to the opposite ends of the chain. This dissociation of the exciton is the field-induced charge generation. In this paper, we study the dynamical process of this charge generation and present the evolution of the charge distribution.

The interaction between the electron and electric field is

$$H' = \sum_{n,\sigma} Ee\left(n - \frac{N+1}{2}\right) a C^{+}_{n,\sigma} C_{n,\sigma} \tag{2}$$

where Na is the length of the polymer chain, and $a = 1.22$ Å the lattice constant, in the present case, $N = 100$, and $E = 1.6$ MV/cm. Then, the total Hamiltonian is

$$H = H_{\mathrm{SSH}} + H' \tag{3}$$

For the static electric field E, H possesses the eigenfunctions $\Phi_{\mu,\sigma}$ and eigenvalues ε_{μ}, i.e.

$$H\Phi_{\mu,\sigma} = \varepsilon_{\mu}\Phi_{\mu,\sigma} \tag{4}$$

when the electron is not in the eigenfunction $\Phi_{\mu,\sigma}$, its time-dependent wave function $\psi_{\nu,\sigma}(t)$ can be obtained by solving the Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\left|\psi_{\nu,\sigma}(t)\right\rangle = H\left|\psi_{\nu,\sigma}(t)\right\rangle \tag{5}$$

Since the electric field E is switched on at $t = 0$, the initial wave functions are $\psi_{\nu,\sigma}(0)$, which are the electronic states of the self-trapped excitation with $E = 0$, i.e. $\psi_{\nu,\sigma}(0)$ are the eigenfunctions of the Hamiltonian, Eq. (1), with an exciton.

Since the atoms are much heavier than the electrons, the relaxation of the lattice is much slower than that of the electrons. During the relaxation of electrons' redistribution, the change of the lattice configuration is very small and can be neglected, then the Hamiltonian H does not depend on the time, and the solution of Eq. (5) is

$$\left|\psi_{\nu,\sigma}(t)\right\rangle = \exp\left(-\frac{i}{\hbar}Ht\right)\left|\psi_{\nu,\sigma}(0)\right\rangle \tag{6}$$

Expanding $\psi_{\nu,\sigma}(0)$ with the eigenfunctions $\Phi_{\mu,\sigma}$

$$\left|\psi_{\nu,\sigma}(0)\right\rangle = \sum_{\mu}\left\langle\Phi_{\mu,\sigma}\middle|\psi_{\nu,\sigma}(0)\right\rangle\left|\Phi_{\mu,\sigma}\right\rangle \tag{7}$$

and substituting the Eq. (7) into the Eq. (6), we can get

$$\left|\psi_{\nu,\sigma}(t)\right\rangle = \sum_{\mu}\exp\left(-\frac{i}{\hbar}\varepsilon_{\mu}t\right)\left\langle\Phi_{\mu,\sigma}\middle|\psi_{\nu,\sigma}(0)\right\rangle\left|\Phi_{\mu,\sigma}\right\rangle \tag{8}$$

In the Wannier representation, the basis of the electron state is

$$|n,\sigma\rangle = C^{+}_{n,\sigma}|0\rangle \tag{9}$$

and the wave functions $\Phi_{\mu,\sigma}$ and $\psi_{\nu,\sigma}(0)$ can be written as

$$\left|\Phi_{\mu,\sigma}\right\rangle = \sum_{n} Z^{\sigma}_{\mu,n}(E)|n,\sigma\rangle \tag{10}$$

$$\left|\psi_{\nu,\sigma}(0)\right\rangle = \sum_{n} Z^{\sigma}_{\nu,n}|n,\sigma\rangle \tag{11}$$

Then, in the Wannier representation, the time-dependent wave functions are

$$\begin{aligned}&\langle n,\sigma|\psi_{\nu,\sigma}(t)\rangle\\ &= \sum_{\mu}\exp\left(-\frac{i}{\hbar}\varepsilon_{\mu,\sigma}t\right)\langle n,\sigma|\Phi_{\mu,\sigma}\rangle\sum_{m}\left\langle\Phi_{\mu,\sigma}|m,\sigma\right\rangle\langle m,\sigma|\psi_{\nu,\sigma}(0)\rangle\\ &= \sum_{\mu}\exp\left(-\frac{i}{\hbar}\varepsilon_{\mu,\sigma}t\right)Z^{\omega}_{\mu,n}(E)\sum_{m}Z^{\omega}_{\mu,m}(E)Z^{\omega}_{\nu,m}\end{aligned} \tag{12}$$

Finally, we get the time-dependent charge distribution $\rho_{\mathrm{n}}(t)$

$$\rho_n(t) = \sum_{\nu,\sigma}{}'\left|\langle n,\sigma|\psi_{\nu,\sigma}(t)\rangle\right|^2 \tag{13}$$

where the summation $\sum'$ only takes the occupied states.

3. Results and discussions

First, solving the eigenequation, Eq. (4) numerically to calculate $Z^{\sigma}_{\mu,n}(E)$, ε_{μ} and $Z_{\nu,n}$. Then using the Eqs. (12) and (13) to get the time-dependent charge distribution $\rho_n(t)$.

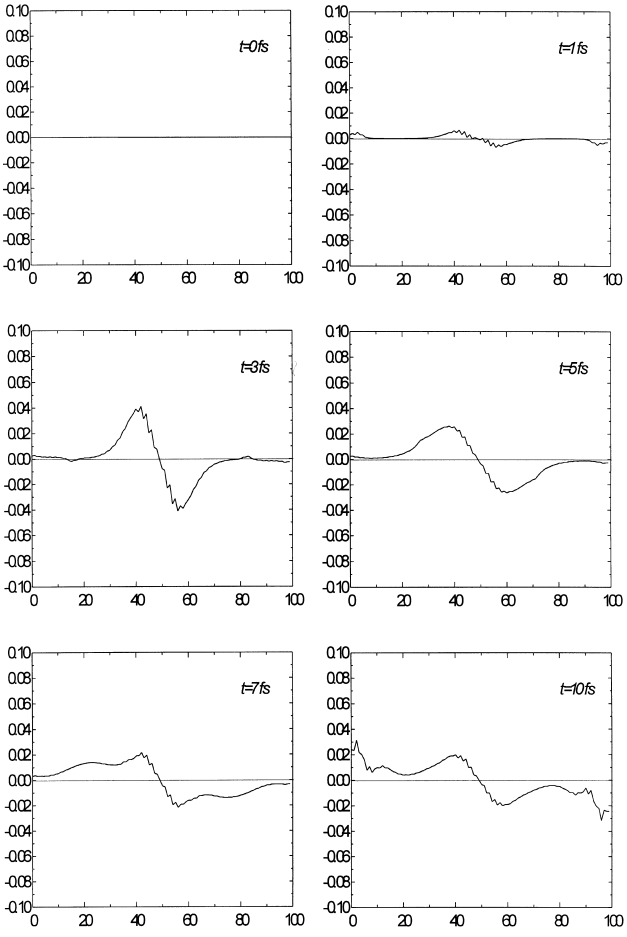

Fig. 1. The charge distribution at different times. The abscissa is the site n in the chain, and the ordinate is the charge in the unit of electron's charge e.

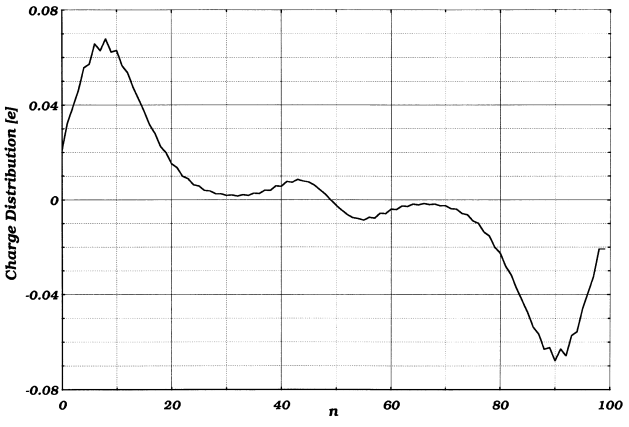

Fig. 2. The static charge distribution in the electric field E.

Fig. 1 shows the evolution of the charge distribution $\rho_n(t)$ at $t = 0$, 1, 3, 5, 7 and 10 fs, and Fig. 2 shows the static charge distribution in the electric field E. It can be seen that, after 10 fs, the electron has been driven to the left end of the chain, and the hole to the right end. This is the field-induced charge generation.

This evolution indicates that the relaxation time for the field-induced charge generation is about 10 fs. It confirms that the relaxation process of the electrons is much faster than that of the lattice, which takes about 200 fs.

Notice that the size of the exciton is about 20 sites in the central area of the chain and the electric field causes both exciton polarization and charge separation, so these are two positive and negative peaks, the inner one is polarization and the outer one is charge separation. After 10 fs, the polarized charge in the inner peak is further separated by the electric field, and the charge distribution gradually reaches that in Fig. 2, which is the static distribution at $t \rightarrow \infty$, where the further separation of the electron and hole is stopped by the ends of the finite chain.

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