DYNAMICAL STUDY ON THE BEHAVIOR OF ELECTROLUMINESCENT POLYMERS UNDER APPLIED ELECTRIC-FIELDS*

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Abstract   The behaviors of the electroluminescent polymers under applied electric fields were studied by using the tight-binding model of electron-lattice coupling and solving the real-tmie Newton dynamical equation. It was discovered that (1) the extra electron and hole injected by the applied electric field make the lattice relaxation, and bipolaron-excitons are formed. (2) there exists a critical electric field. When an applied field is equal to or larger than the critical field, the bipolaron-exciton will be dissociated into positive and negative polarons, leading to photoluminescence quenching. The result is consistent with the relevant experiments, and it also implies that the bipolaron-exciton is a kind of luminous species in polymers.

Key words   dynamical study, applied electric field, polymer.

Introduction

Much attention has been focused on the electroluminescence (EL) of polymers since the EL in polymers[1] was discovered by Cambridge University of UK in 1990. Today the EL study of polymers has become one of the frontier subjects in the world. Being different from conventional inorganic semiconductors, the polymer is a quasi-one-dimensional system[2] and has the characteristic of low-dimensional instability. The extra electron and hole will induce the variations of both lattice structures and electronic states in low-dimensional systems, leading to the formation of bipolaron excitons[3~4]. Recently Kersting et al[5] and

Tasch et al[6]. have observed experimentally the electric-field-induced photoluminescence (PL) quenching in electroluminescent conjugated polymers. In order to understand the PL and other optical phenomena of polymers under applied electric fields, we study the behavior of electroluminescent polymers with extra electron and hole under applied fields by the real-time dynamical methodology. Our results are compared with the relevant polymer experiments[5~7].

1.   Method

Electroluminescent polymers consist of carbon-hydrogen atoms groups. By simplifying a carbon-hydrogen atom's group as a lattice point, we can regard an electroluminescent conjugated polymer as a finite chain with N lattice points. The electronic Hamiltonian of the system under an applied field will be

$$H_e = - \sum_{n,s}[t_0 - \alpha(\varphi_{n+1} - \varphi_n) + (-1)^n t_e](C_{n+1,s}^+ C_{n,s} + HC) + \sum_n eEnaC_{n,s}^+ C_{n,s} \quad (1)$$

where $C_{n,s}^+(C_{n,s})$ is the creation (annihilation) operator of an electron on site n with spin s; t_0 is the electron hopping probability, and α, the electron-lattice interacting constant; φ_n represents the displacement from the equilibrium configuration of lattice points; t_e is the symmetry-breaking term, determined by the energy difference between phase A and phase B of the nondegenerate ground states since electroluminescent polymers have nondegenerate ground states; and E is the electric field strength.

The electronic wave function Ψ_μ and eigenvalues ε_μ are determined by the electronic eigenequations

$$H_e\Psi_\mu = \varepsilon_\mu\Psi_\mu. \quad (2)$$

Because the mass of a carbon-hydrogen atoms' group is much heavier than that of an electron, we need not consider the phase difference between electron's shift and atom's shift. So it is reasonable to use an adiabatic approximation. Thus for any instantaneous configuration $\{\varphi_n(t)\}$ of atoms' positions, electrons are instantly in the eigenstates of the potential field brought about by atoms configuration. Therefore, the instantaneous electronic spectra $\varepsilon_\mu(\{\varphi_n(t)\})$ and electronic states $\Psi_{n,\mu}(\{\varphi_n(t)\})$ are functionals of the instantaneous configuration $\{\varphi_n(t)\}$ of atoms' positions. When atoms are in a configuration $\{\varphi_n(t)\}$, the total energy of an electroluminescent polymer is

$$E_{total}(\{\varphi_n(t)\}) = \sum_\mu^{occ.} \varepsilon_\mu(\{\varphi_n(t)\}) + \frac{1}{2}K\sum_n(\varphi_{n+1} + \varphi_n)^2 + \sum_n K'(-1)^{n+1}(\varphi_{n+1} + \varphi_n) \quad (3)$$

The first term on the right of Eq. (3) is the electronic energy, the second and the third terms are elastic energies, K is elastic constant. $K' = -1.25032\alpha$ for a finite chain with 100 lattice points[8].

Due to electron-lattice interactions, the eigenvalues (the first term of Eq. (3)) of elec-

tronic states, as the function of atoms configuration, are the additional potential of the lattice. So the total energy expression Eq. (3) is the total potential energy of the system when atoms configurations are $\{\varphi_n(t)\}$. Thus the force exerted on the n-th atom of electroluminescent polymers can, at any moment, be expressed as

$$f_n(t) = -\frac{\delta V}{\delta \varphi_n} = -\frac{E_{total}(\{\varphi_n(t)\})}{\delta \varphi_n} \tag{4}$$

Since the mass of a carbon-hydrogen atoms' group is much heavier than that of an electron, it can be regarded as a classical particle. Consequently, the real-time Newton dynamical equations for carbon-hydrogen atoms' groups are

$$M = \frac{dv_n(t)}{dt} = f_n(t) \tag{5}$$

$$\frac{d\varphi_n(t)}{dt} = v_n(t) \tag{6}$$

where M is the mass of a carbon-hydrogen atoms' group, φ_n and v_n are treated as classical displacements and velocities.

2　Main Results and Discussion

Since the applied field injects electrons and holes into the active layer of a polymeric light-emitting-device, there exist the extra electron and hole in the electroluminescent conjugated polymer. Taking the case that there exists a hole at the top of the valence band and an electron at the bottom of the conduction band as the initial condition, we solve the combined Eqs. (1～6) step by step. Each step lasts only a very short time interval. Therefore, during the time interval, the change of the forces can be ignored, and the original differential equations can be simplified to the difference equations. By numerical calculation, the lattice configurations, bond-length distributions, electronic charge densities and the total energy at any moment in the presence of an external field are obtained.

Figure 1 represents the variations of bond-length for $t_e = 0.05\text{eV}$ in the presence of the field $E = 0 - 7.7\text{V/cm}$. In the figure, the thin line is the ground state, and the thick line denotes the variations of bond-length along a finite chain after 150 femtoseconds (starting from the initial condition that there exists a hole at the top of the valence band and an electron at the bottom of the conduction band). Figure 1 shows that the extra electron and hole induce the local deformation of the lattice, and an electron-hole polaron is produced. Since the electron and hole are in the same area of real space, they can form an exciton. An elecrron-hole polaron exciton is called a bipolaron-exciton.

Figures 2 (a) and (b) depict, respectively, the variation of bond-length and the charge density distributions along a finite chain in the electric field $E \geq 7.8 \times 10^5\text{V/cm}$ and after 150 femtoseconds. Comparing Fig. 1 with Fig. 2 (a), we can clearly see that there

exists a critical field $E_{critical}$, which will induce a sudden change of bond-length as well as atomic configuration distributions since the bond-length equals the distance of the nearest lattice points.
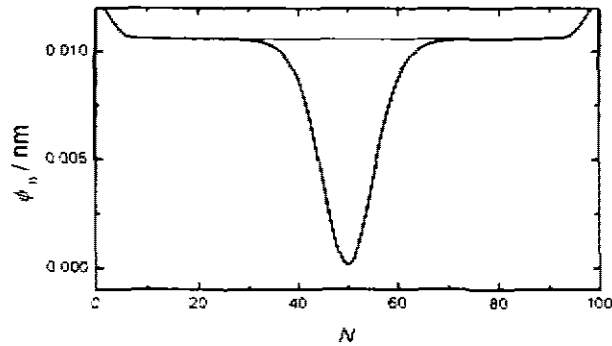

Fig. 1 When electric field E is in the range from 0 to 7.7×10⁵V/cm, the variation of bond-length along a finite chain of the electroluminescent polymer with the extra electron and hole. (the thin line represents t＝0, the thick line denotes t＝150fs)

图 1 电场强度 E＝0—7.7×10⁵V/cm 时,具有额外电子和空穴的电致发光高分子的键长度和格点原子的关系(细线 t＝0,粗线 t＝150fs)
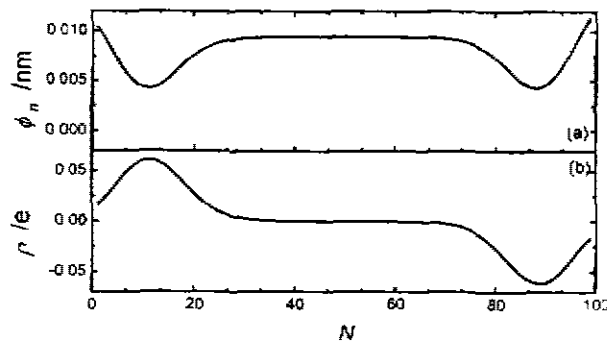
Fig. 2 When electric field E≥7.8×10⁵V/cm (the critical electric field E＝7.8 ×10⁵V/cm) and t＝150fs (a) the variation of bond-length along a finite chain of the electroluminescent polymer with the extra electron and hole (b) the charge density distribution

图 2 电场强度 E≥7.8×10⁵V/cm(临界电场强度 E＝7.8×10⁵V/cm)时, 具有额外电子和空穴的电致发光高分子,经 150fs 后(a) 键长分布, (b) 格点电荷密度分布

From the viewpoint of energy, the action of a strong enough field is to readjust the lattice structure and electronic states of electroluminescent polymers. Consequently, a bipolaron-exciton is dissociated and the total energy of the system decreases. Before the dissociation of a bipolaron-exciton, the electronic energy is $-327.653eV$ and the elastic energy is $8.110eV$. When a bipolaron-exciton is dissociated, i. e. at the critical field $E_{critical}$, the elastic energy is $7.783eV$ while the electronic energy is $-327.481eV$. Thus we can see that at a critical field the elastic energy decreases while the electronic energy slightly increases. The electronic Hamiltonian Eq. (1) and the total energy expression Eq. (3) show that the electron energy is linear with atomic displacements while the elastic energy is quadratic with atomic displacements. When a bipolaron-exciton is dissociated, the variations of atomic displacements are quite large, thus the elastic energy decreases a lot while the electronic energy increases a little. As a result, the decrease of the elastic energy is larger than the increase of the electronic energy. Consequently, the total energy is further lowered and the system is more stable after a bipolaron-exciton is dissociated.

From the viewpoint of nonlinear excited states, the energy required to create a bipolaron-exciton in a polymer is less than that for two polarons[2]. So extra electrons and holes generally form bipolaron-excitons in electroluminescent polymers. From a bipolaron-exciton to a hole-polaron plus an electron-polaron, the energy of the system increases. The energy difference between a bipolaron-exction and a hole-polaron plus an electron-polaron is offered by electric fields. The fact that a strong enough electric field dissociates a bipolaron-exciton means that there exists a critical field. When the electric field is less than the critical field, it can not provide enough electric-field -energy to dissociate a bipolaron-exciton. However, after $E \geq E_{critical}$, the electric field energy is large enough to split a bipolaron-exciton into a hole-polaron and an electron-polaron, which is consistent with the recent experiment[7].

The two dissociated polarons move at the opposite direction in an applied electric field and are well-separated, so they have little chance to recombine, leading to PL quenching. This result is consistent with the relevant experiments[5~7], in which the field-induced PL quenching[5~6] and charged polarons[7] are observed. The consistency also implies that the bipolaron-exciton is a kind of emitting species in electroluminescent polymers.

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电致发光聚合物在外电场中行为的动力学研究 *

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摘要　用电子-晶格耦合的紧束缚模型和求介实时牛顿动力学方程的方法研究了具有额外电子和空穴的电致发光高分子在外电场中的行为。发现外电场注入的额外电子和空穴使电致发光高分子晶格弛豫, 形成双极化子激子; 并存在一个临界电场, 当外电场大于或者等于临界电场时, 双极化子激子解离成正、负极化子, 导致发光猝灭. 该结果与电致发光高分子的光荧光被强电场猝灭的实验现象一致. 这个一致性反映了双极化子激子是电致发光高分子中的一种发光实体, 说明了电致发光高分子在强电场下光荧光猝灭的物理原因是在强电场作用下电致发光高分子中的双极化子激子被解离成正、负极化子.

关键词　动力学研究, 外电场, 高分子.