

TURNING-OVER OF THE ELECTRIC DIPOLE IN A POLYMER^{*}

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Abstract The transition from the biexciton to the exciton can turn over the direction of the electric dipole of a polymeric molecule. This turning-over action combined with the photoinduced polarization reversion can be used as a switch. The switching speed is governed by the relaxation time of the turning-over process, which can be determined by a dynamical simulation.

Keywords Exciton, Biexciton, Electric dipole, Switch, Relaxation

INTRODUCTION

Recently it has been shown that a polymer can possess a novel photoinduced phenomenon, where the direction of the electric dipole of a polymeric molecule is reversed on absorbing a photon^[1]. This phenomenon is called photoinduced polarization reversion (PPR). Since it takes place in a single polymeric molecule, it can be used to design a molecular device with a switching effect.

PPR provides a mechanism to turn the electric dipole of the polymeric molecule from the direction of the electric field E to the opposite direction of E . To be used as a switch, besides the above action, it is necessary to have a reversed action, which turns the electric dipole from the opposite direction back to the original direction. This reversed action is a turning-over process, which can be realized by stimulated emission. This paper reveals the relaxation process of this turning-over by studying its dynamics.

There are two excitations in the polymeric molecule, one is the exciton^[2], another is the biexciton^[3, 4]. Since a polymeric molecule has a one-dimensional chain structure, self-trapping plays a very important role in the photoexcitation of the polymer, and the bond structure of the polymeric molecule depends on the excitation. When an electron is excited from the valence band to the conduction band, it results in an electron-hole pair. This photoexcitation induces a distortion of the bond structure shown in Fig. 1. Consequently, the lattice distortion creates two electronic bound states lying in the gap: the up-gap state Φ_u and down-gap state Φ_d , which are shown in Fig. 2. This is called the self-trapping effect. Due to this self-trapping, the state at the bottom of the conduction band moves into the gap to form the up-gap state Φ_u , and the state at the top of the valence band also moves into the gap to form the down-gap state Φ_d . Both Φ_u and Φ_d are occupied by one electron. Then the electron-hole pair is converted into a self-trapped exciton. When the polymeric molecule with a self-trapped exciton absorbs another photon, the electron sitting in the Φ_d is excited into the Φ_u , the bond structure is further distorted, and the

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energy difference between the Φ_u and Φ_d reduced. This reduction can be seen by comparing Figs. 2(a) and 2(b). After this photon absorption, the exciton becomes the biexciton, in which there are two electrons in Φ_u , and Φ_d is empty.

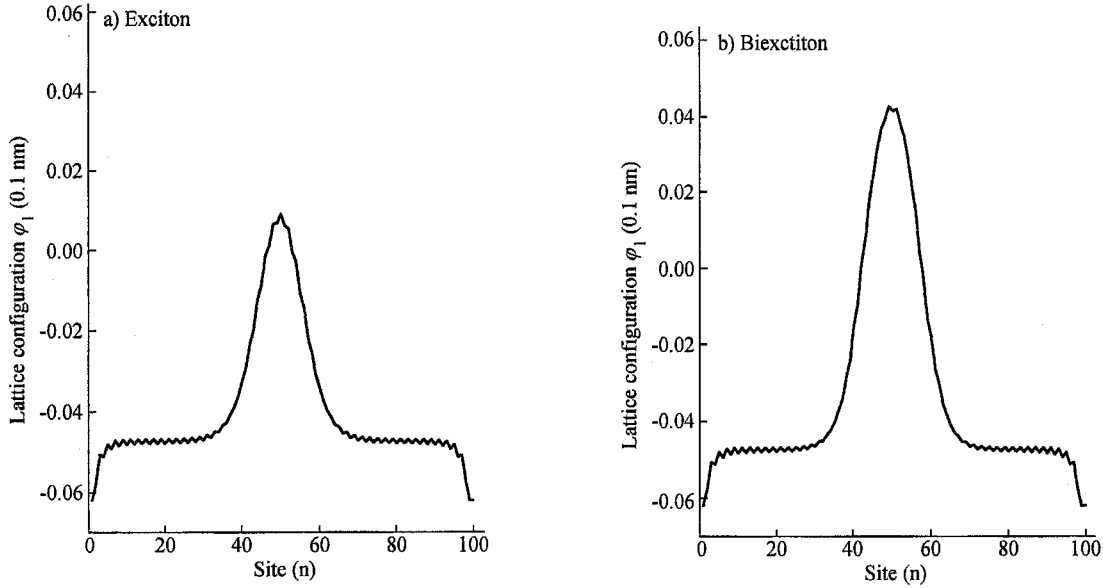


Fig. 1 The configurations of lattice distortion

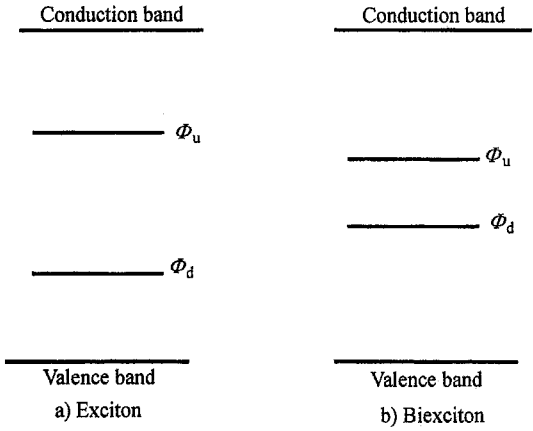


Fig. 2 The electronic spectra

It has been proved that the static polarizability of a polymeric molecule with a biexciton is negative, and that with an exciton is positive. Therefore, when a polymeric molecule with an exciton absorbs a photon, this exciton becomes a biexciton, and its static polarizability is changed from positive to negative. Consequently the electric dipole of the polymeric molecule is reversed from the direction of the electric field to the opposite direction.

The lifetime of the biexciton is hundreds of picoseconds (10^{-12} s)^[3], which is 3 orders of magnitude longer than the relaxation time of the PPR^[1]. One of the electrons in the up-gap-state Φ_u can be transferred to Φ_d by stimulated emission. After the transition, the biexciton becomes an exciton, and the static polarizability of the polymeric molecule changes from negative to positive. Then its electric dipole returns from the opposite

direction to the direction of the electric field. Therefore, the transition from biexciton to exciton is a turning-over process, and both photon absorption and stimulated emission are capable of turning over the electric dipole. These two processes complete the function of a switch. The photon absorption (from exciton to biexciton) is turning-on, and the stimulated emission (from biexciton to exciton) is turning-off. Since the separation between the Φ_u and Φ_d in the exciton is much larger than that in the biexciton, the photon energy in turning-on is higher than that in turning-off. This is the so-called Stokes shift. Then we can manipulate turning-on and turning-off with different photon energy.

DYNAMIC THEORY

The turning-over is a process of changing from the biexciton to the exciton, where the lattice distortion and the gap states Φ_u and Φ_d are changed. The evolution of the lattice distortion and gap states can be revealed by studying the relaxation process dynamically, from which the switch time of turning-over can be determined.

Since the self-trapping is a characteristic of a one-dimensional system, it does not depend on the details of the molecular structure, and the self-trapping effect in different conjugated polymers can be described theoretically by a common formulation, *i.e.*, the Su-Schrieffer-Heeger Hamiltonian^[5],

$$H = H_u + H_e \quad (1)$$

$$H_e = H_{e-l} + H' + H_E \quad (2)$$

$$H_u = \frac{K}{2} \sum_l (u_{l+1} - u_l)^2 \quad (3)$$

$$H_{e-l} = - \sum_{l,s} \{t_0 - \alpha'(u_{l+1} - u_l) + (-1)^l t_e\} \times [a_{l+1,s}^\dagger + H.c.] \quad (4)$$

$$H' = U \sum_{l,s} n_{l,s} n_{l,-s} + V \sum_{l,s,s'} n_{l,s} n_{l+1,s'} \quad (5)$$

$$H_E = - \sum_{l,s} e n_{l,s} E (l a + u_l) \quad (6)$$

where, H_u is the elastic energy of the bond lattice and H_e is the electronic part of the Hamiltonian, which includes three terms: H_{e-l} is the interaction between the electrons and the bond lattice; H' is the Hubbard model to describe the electron-electron interaction^[6], which is treated by the Hartree-Fock approximation; and H_E is the interaction of the electrons with the external electric field E . $a_{l,s}^\dagger$ and $a_{l,s}$ are the creation and annihilation operators of the electron at lattice site l with spin s ; u_l is the displacement of atom l ; $n_{l,s} = a_{l,s}^\dagger a_{l,s}$ is the density of the electrons; $t_0 = 2.5\text{--}3.0$ eV is the hopping constant; $\alpha' = 40\text{--}60$ eV/nm is the electron-lattice coupling constant; and $t_e = 0\text{--}0.1$ eV is the energy change for exchanging the single bond and double bond in the conjugated polymer. For polymers with degenerate ground states, $t_e = 0$. $K = 2000\text{--}3000$ eV/nm² is the elastic constant; $U = 2.0\text{--}5.0$ eV and $V = 0.5\text{--}2.0$ eV are the electron repulsion parameters; and $a = 0.122$ nm is the lattice constant.

The electron's energy spectrum ε_μ and the wave function Φ_μ which are functionals of the lattice distortion u_l , are determined by the eigenequation of the Hamiltonian H_e ,

$$H_e \Phi_\mu = \varepsilon_\mu \Phi_\mu \quad (7)$$

The total energy of all electrons is

$$\varepsilon(\{u_i\}) = \sum_{\mu}^{\text{occ.}} \varepsilon_{\mu}(\{u_i\}) \quad (8)$$

where the summation runs over just the occupied states, so that the total energy of the system is

$$E(\{u_i\}) = \varepsilon(\{u_i\}) + \frac{K}{2} \sum_l (u_{l+1} - u_l)^2 \quad (9)$$

The wave functions of these two gap states Φ_u and Φ_d are the bound states in the solutions of the eigenequations (7). It has been proved that, in the biexciton, the polarizations of Φ_u and Φ_d are opposite. The static polarizability α_d of Φ_d is positive, but α_u of Φ_u is negative.

As emphasized before, the bond structure of the polymeric molecule is not fixed, and its lattice configuration $\varphi_l = (-1)^l u_l$ is dependent on the electron's excitation. Once the electron is excited from one state to another, the original bond structure becomes unstable, and the lattice configuration φ_l changes. Since the atom is much heavier than the electron, it is reasonable to neglect the quantum effects of the lattice motion, and the atom's movement can be studied by using classical dynamics^[7], in which the l -th atom experiences a force f_l as

$$f_l = -\frac{\partial E[\{u_i\}]}{\partial u_l} = -\sum_{\mu}^{\text{occ.}} \frac{\partial \varepsilon_{\mu}[\{u_i\}]}{\partial u_l} + (2u_l - u_{l+1} - u_{l-1}) \quad (10)$$

and the atom's dynamic equation is

$$M \frac{d^2 u_l}{dt^2} = -\sum_{\mu}^{\text{occ.}} \frac{\partial \varepsilon_{\mu}}{\partial u_l} + K(2u_l - u_{l+1} - u_{l-1}) \quad (11)$$

where M is the mass of the atom.

By using the Hellman-Feynman theorem,

$$\begin{aligned} \frac{\partial \varepsilon_{\mu}}{\partial u_l} &= \frac{\partial}{\partial u_l} \langle \Phi_{\mu} | H_e | \Phi_{\mu} \rangle \\ &= \left\langle \Phi_{\mu} \left| \frac{\partial H_e}{\partial u_l} \right| \Phi_{\mu} \right\rangle \\ &= \langle \Phi_{\mu} | l \rangle [2\alpha' \langle l-1 | \Phi_{\mu} \rangle (1 - \delta_{l,1}) - \\ &\quad 2\alpha' \langle l+1 | \Phi_{\mu} \rangle (1 - \delta_{N,1}) + \langle l | \Phi_{\mu} \rangle eE] \end{aligned} \quad (12)$$

the calculation for the force can be facilitated. Substituting Eq. (12) into (11), the dynamic equation of the atom's movement can be solved numerically step by step. Each step should last a very short interval τ so that the change of the force within τ is negligible. Since the period of the lattice vibration is about 40 femtoseconds (fs), the step τ is chosen as 1 fs. In the numerical calculation, the final positions and the velocities of the atoms at each step are taken as the initial conditions of the next step. Then the relaxation processes caused by the stimulated emission can be simulated.

RELAXATION PROCESS OF TURNING-OVER

The relaxation process of the turning-over is a transition from the biexciton to the exciton, which consists of two parts: one is the evolution of the lattice distortion, another is the evolution of the gap states Φ_u and Φ_d . A three

dimensional view of the relaxation of the lattice distortion is shown in Fig. 3. At the beginning ($t = 0$), the peak of the distortion associated with the biexciton is quite high. During the relaxation process, the height of the peak oscillates, the period of the oscillation is about 40 fs. The amplitude of the oscillation is getting smaller, after several oscillations, the distortion is gradually stabilized. Finally, the peak of the distortion reaches the distortion configuration of the exciton. From the evolution, it can be estimated that the relaxation time of the turning-over is about 160 fs.

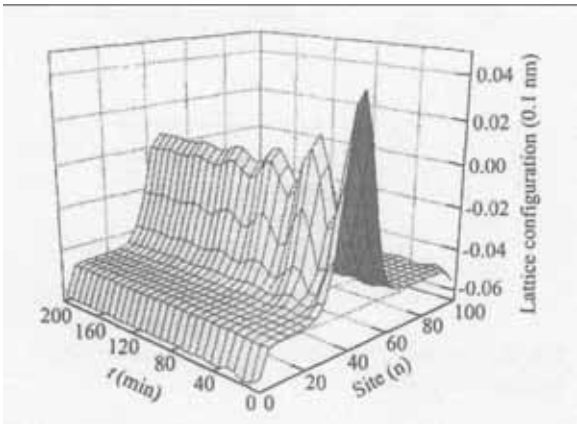


Fig. 3 The evolution of the lattice configuration in the turning-over process

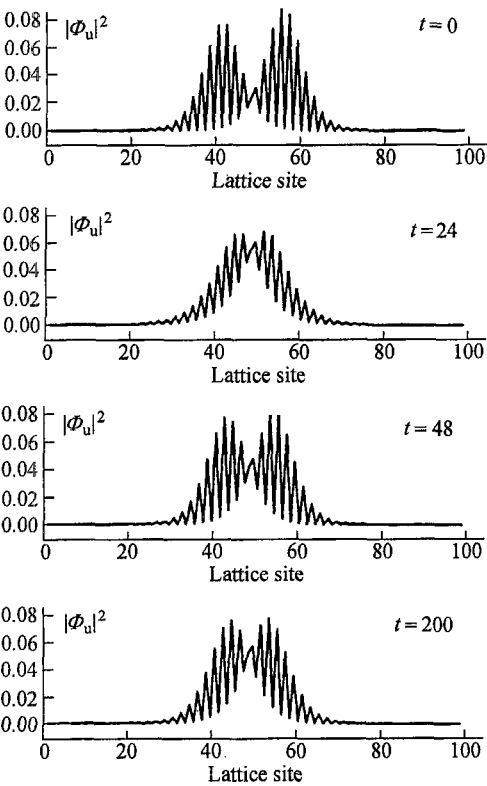


Fig. 4 The wave function Φ_u of the up-gap state at different times

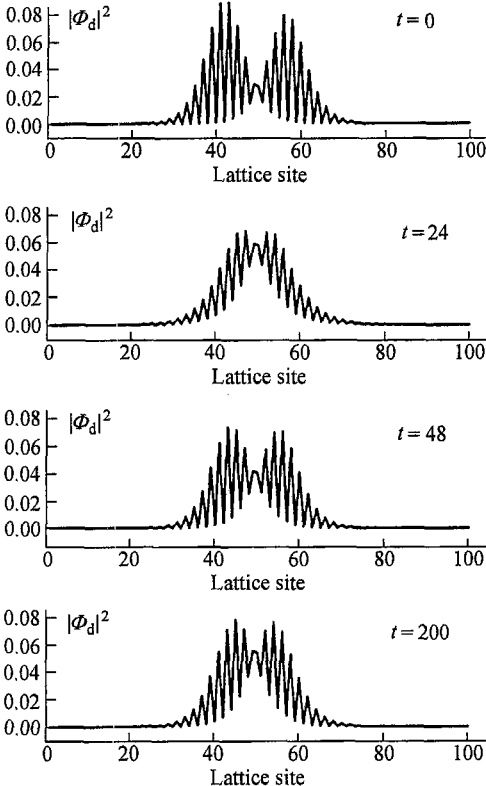


Fig. 5 The wave function Φ_d of the down-gap state at different times

The evolution of the electronic states in an electric field are shown in Figs. 4 and 5, they demonstrate $|\Phi_u(t)|^2$ and $|\Phi_d(t)|^2$ respectively at different times. At $t = 0$, $\Phi_u(0)$ and $\Phi_d(0)$ are the wave functions of the biexciton. At $t = 200$ fs, they are the wave functions of the exciton. From these evolutions, it can be seen that the width of the biexciton is larger than that of the exciton. It means that the exciton is bound more tightly.

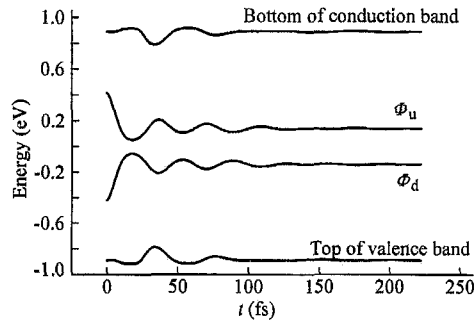


Fig. 6 The evolution of the electronic spectrum for the turning-over process

The energy levels of the up-gap and down-gap states are also changing during the relaxation process. Figure 6 demonstrates the evolution of the levels ε_u and ε_d . These evolutions also show that the relaxation time of the turning-over process is about 160 fs.

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