

Photoinduced Polarization Inversion in a Polymeric Molecule

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The polymeric molecule can exhibit a new photoinduced phenomenon where the electric dipole of the molecule with a bipolaron is reversed by absorbing one photon. This photoinduced polarization inversion occurred in a single molecule is an ultrafast process with a relaxation time of 200 fs.

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In recent years femtosecond technology has provided a powerful tool to study an ultrafast process [1], especially to explore new properties of excited states. The lifetime of the excited states in molecules is on the nanosecond time scale (10^{-9} s); the time resolution of femtosecond technology can reach 10^{-15} s. Then the transient and dynamical process in the excited states can be revealed in detail. It has been found that the excited states induced by photoexcitation possess many novel properties, which do not exist in the ground state. The photoinduced phenomenon has thus become an active frontier in the interdisciplinary area of physics, chemistry, and material science. A particular field is luminescent polymers. Since 1990 electroluminescence in polymers demonstrated the significance not only in the device application, but also in understanding the nature of excitation in organic materials [2]. By using femtosecond spectroscopy, it is found that in polymers the primary photoexcitations are intrachain excitons [3]. And very recently, the biexciton, which is a sequential reexcitation of the intrachain exciton, is also observed in poly(paraphenylene vinylene) (PPV) [4]. In a dilute solution of PPV, photoinduced absorption and stimulated emission show that the lifetime of the exciton and biexciton in a single molecule are hundreds of picoseconds (10^{-12} s), which is a long time on the femtosecond scale, then it is made possible to investigate further the electric and optical properties of the exciton and biexciton in the polymeric molecule. Based on these findings, this paper predicts a new photoinduced phenomenon in the polymeric molecule: when a polymeric molecule absorbs one photon, its electric dipole is reversed. This switching effect can be called photoinduced polarization inversion (PIPI).

A prominent feature of the polymeric molecule is that its energy spectrum and bond distortion depend on the excitation. The reason is that the polymer chain is a quasi-one-dimensional system, under the electron-lattice interaction, its bond structure is easily distorted. With photoexcitation, the interaction between electron-hole pair and bond lattice causes self-trapping, which makes the bond structure distorted and creates two electronic bound states Φ_u and Φ_d near the center of the energy gap, which is about 2.5 eV. Consequently, the photoexcitation in the polymeric mole-

cule produces a neutral bipolaron (BP) [5], which is also called a self-trapped exciton (STE), where both Φ_u and Φ_d are occupied by one electron.

It is well known that the BP can be quantitatively described by the following Hamiltonian [5]:

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

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

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

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

$$H_E = E \sum_{l,s} e[la + u_l][a_{l,s}^\dagger a_{l,s} - n_0], \quad (5)$$

where H_0 describes the interaction between the electrons and bond lattice; H' is the electron-electron interaction, which is treated in the Hartree-Fock approximation; H_E is the interaction of the electrons with the electric field E , whose direction is from left to right. $a_{l,s}^\dagger$ and $a_{l,s}$ are the creation and annihilation operators of the electron at lattice site l with spin s , u_l the displacement of atom l , $n_{l,s} = a_{l,s}^\dagger a_{l,s}$, $t_0 = 2.5-3.0$ eV the hopping constant, $\alpha' = 40-60$ eV/nm the electron-lattice coupling constant, $t_e = 0-0.1$ eV the confinement constant, $K = 2000-3000$ eV/nm² the elastic constant, $U = 2.0-5.0$ eV and $V = 0.5-2.0$ eV the electron repulsion constants, $a = 0.122$ nm the lattice constant, n_0 the density of positive charged background.

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

$$H_e \Phi_\mu = \varepsilon_\mu \Phi_\mu. \quad (6)$$

The total energy is

$$E[\{u_l\}] = \sum_{\text{occ}} \varepsilon_\mu[\{u_l\}] + \frac{K}{2} \sum_l [u_{l+1} - u_l]^2. \quad (7)$$

The lattice distortion u_l is determined by

$$\frac{\delta E[\{u_l\}]}{\delta u(l)} = 0. \quad (8)$$

ε_μ , Φ_μ , and u_l can be obtained by self-consistently solving the combined equations (6) and (8). After getting the eigenstates Φ_μ , the charge distribution can be calculated by using the formula

$$\rho_l = \sum_{\text{occ}} |\Phi_\mu|^2 - n_0. \quad (9)$$

Then, the dipole and polarizability of the molecule can be determined from ρ_l .

For the bipolaron, there are two gap states: up-one Φ_u and down-one Φ_d , whose wave functions are orthogonal to each other and shown in Fig. 1, where $E = 10^{-2}$ V/nm and the length of the molecule is $100a$. A notable feature is that the polarizations of Φ_u and Φ_d are opposite. For down-state Φ_d , Fig. 1(a) shows that the left peak is higher than the right one; it indicates the electron shifts to the anode in the left side, so the polarization of Φ_d is normal. But, Fig. 1(b) shows that, in Φ_u , the electron shifts to the cathode in the right side, so the polarization of Φ_u is anomalous.

How can one understand this polarization behavior? Quantum mechanics tells that the static polarizability of a molecule in eigenstate Φ_μ is [6]

$$\alpha_\mu = \sum_\nu \frac{2|P(\nu, \mu)|^2}{\varepsilon_\nu - \varepsilon_\mu}, \quad (10)$$

where $P(\mu, \nu)$ is the dipole between Φ_μ and Φ_ν . For the ground state, all the denominators in Eq. (10) are positive.

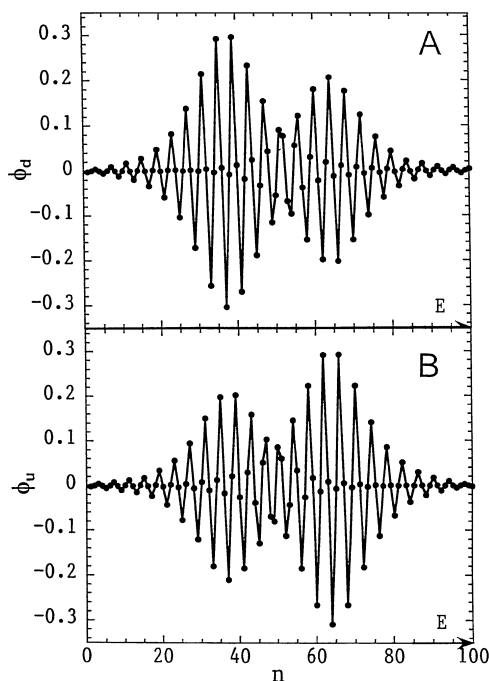


FIG. 1. The polarized wave functions of gap states: (a) Φ_d ; (b) Φ_u .

Therefore, for any molecules, the polarizability in ground state is always positive. So, the polarization is very different from the magnetization.

In magnetism, the molecules can be divided into two categories: with or without magnetic moment \mathbf{M} . When a static magnetic field \mathbf{H} is applied, these two kinds of molecules have opposite response. For the former, their \mathbf{M} orients to the direction of \mathbf{H} . Then their magnetic susceptibility χ is positive, they are called paramagnetic. For the latter, although no inherent magnetic moment, an induced moment is produced by \mathbf{H} . Since this induced moment comes from the precession of electron's magnetic moments, its direction must be opposite to \mathbf{H} , so their χ is negative, and called diamagnetic. Thus, the magnetic susceptibility of the molecule can be either positive or negative.

In electricity, the molecules can also be divided into two categories: (1) polar molecules, which have dipole \mathbf{P} ; (2) nonpolar molecules, which do not have \mathbf{P} , when a static electric field \mathbf{E} is applied. For the former, their \mathbf{P} is oriented to \mathbf{E} , and their electric susceptibility α is positive. For the latter, an induced dipole is produced by \mathbf{E} , the positive charge in the molecule shifts towards the cathodes, and the negative one toward anode, then the induced dipole is in the direction of \mathbf{E} , so that their polarizability is also positive. Therefore, in the ground state, both the polar and nonpolar molecules possess positive polarizability [6]. It is the reason why, in electricity, there is no "para" or "dia" terminology. Such asymmetry between magnetism and electricity is caused by the absence of magnetic charge.

However, from Eq. (10), it is seen that some special excited states can possess negative polarizability. In our case, two gap states Φ_u and Φ_d are close to each other, and the dipole $P(u, d)$ between Φ_u and Φ_d is much larger than others. Then Eq. (10) indicates that the dominant contribution to α_d comes from Φ_u , and α_d is positive; the dominant contribution to α_u comes from Φ_d , and α_u is negative.

So, the up-gap state Φ_u possesses negative polarizability, while the down one is positive. Such anomalous polarizability also happens in the high excited states of sodium atom—the Rydberg states [7], because the np states lie slightly above $(n-1)d$ states and much below $(n+1)s$ states, so np states can have negative polarizability. For the Rydberg states, the energy intervals between adjacent states are on the scale of meV, which is in the microwave region. By contrast, the level separation in polymer is about 1 eV, and these photoinduced phenomena are in the optical region.

Now let the BP (STE) be photoexcited, i.e., the electron at Φ_d is excited to Φ_u by absorbing one photon. Obviously, this excited bipolaron BP* is a biexciton. Remarkably, the polarization behavior of the polymeric molecule with a biexciton is totally different from that with an exciton. We can use Eq. (9) to calculate the charge distributions in the polymeric molecule, which are shown in Fig. 2. For the molecule with an exciton, Fig. 2(a) shows that the

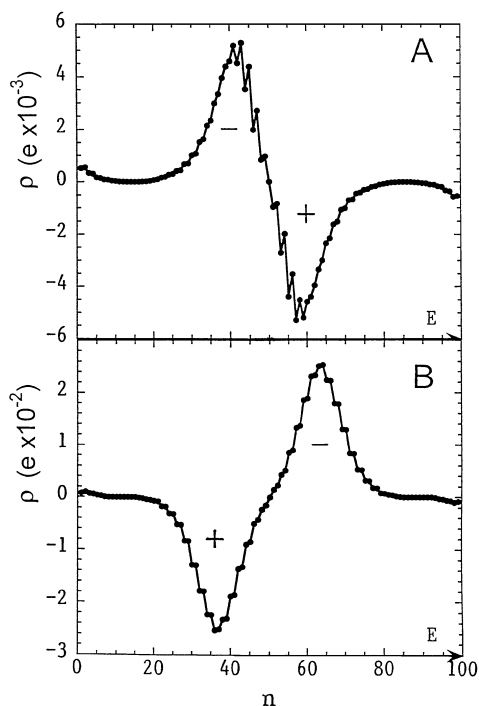


FIG. 2. The change distributions in the polymeric molecule with (a) BP; (b) BP*. The unit of the ordinate is electron's charge e .

negative charge is induced in the left side while the positive one is in the right. It indicates that the molecular dipole is in the same direction as the electric field E , and its polarizability is positive. Contrarily, for the molecule with a biexciton, Fig. 2(b) shows that the molecular dipole is opposite to E , and its polarizability becomes negative. The physics is clear, as is shown in Fig. 1, the up-gap state has anomalous polarizability while the down-gap state is normal, the biexciton is produced by exciting the electron from the down-gap state to the up-gap state.

The result shows that the polarizability of one polymeric molecule with one biexciton is very large. Its absolute value is 3 orders of magnitude larger than that of a hydrogen atom, since the size of the biexciton is about 5 nm and π electrons have big delocalization along the polymer chain.

It should be pointed out that here we are interested in the static polarization [see Eq. (10)] rather than the dynamical one, which is frequency-dependent polarizability $\alpha(\omega)$

$$\alpha_{\mu}(\omega) = \sum_{\nu} \left[\frac{P^2(\mu, \nu)}{(\varepsilon_{\nu} - \varepsilon_{\mu}) - \hbar\omega - i\Gamma/2} + \frac{P^2(\mu, \nu)}{(\varepsilon_{\nu} - \varepsilon_{\mu}) + \hbar\omega + i\Gamma/2} \right]. \quad (11)$$

From this equation, it can be seen, for any molecule, in the blue side of the absorption band, $\alpha(\omega)$ must be negative. Actually, it is anomalous dispersion. Therefore, for the dynamical $\alpha(\omega)$, it is trivial to get negative polarizability. But, for the static $\alpha(\omega = 0)$, it is rare to have negative α .

Therefore, in the electric field, when a polymeric molecule with a BP is photoexcited, its electric dipole is re-

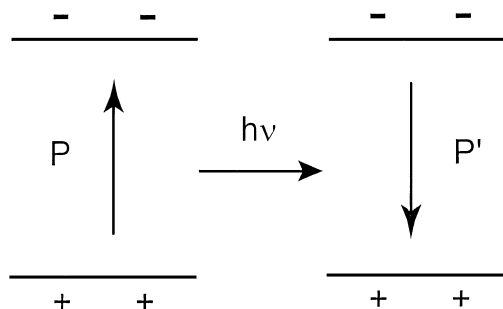


FIG. 3. The photoinduced polarization inversion (PIPI).

versed by absorbing one photon, which is shown in Fig. 3; this is PIPI. By using the lattice dynamics [8], the relaxation process of PIPI can be simulated, and the result shows that the relaxation time of PIPI is about 200 fs. So the PIPI is an ultrafast switching effect in a single molecule.

Since the lifetime of the biexciton is hundreds of picoseconds [4], which is 3 orders longer than the time to form the biexciton, PIPI can be observed by using a pump-probe method in a polymer solution. Shining a tunable laser pulse to the polymeric molecules with excitons, and tuning its frequency, when the photon is resonantly absorbed, the molecular dipole is reversed. At the same time, the scattering of the probing light is changed by the polarization reversion, and the PIPI is detected.

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