Photoinduced phenomenon in polymers

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Numerical simulation has shown that a polymeric molecule can possess a photoinduced phenomenon—photoinduced polarization reversion—in which the electric dipole of the polymeric molecule is reversed by absorbing one photon. This paper provides an analytic theory by means of a response function to prove that a polymeric molecule with a bipolaron has a negative static polarizability and explains the physical origin of this photoinduced phenomenon in detail. This paper also presents a dynamical calculation for the photoinduced polarization reversion, from which the relaxation time for the dipole reversion can be determined.

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I. INTRODUCTION

The development of femtosecond technology [1,2] has changed our idea about time scales. We used to think that the lifetimes of excited states of molecules, which are about 1 ns (10^{-9} s), are so short that the excited states are usually considered as unstable, and it is difficult to study transient and dynamical processes of the excited states. Now the situation is changed by femtosecond technology, which provides a powerful tool to study ultrafast processes. Today, the time resolution has reached several femtoseconds (10^{-15} s), compared to which the lifetimes of the excited states are so long that the transient and dynamical processes in molecular excited states can be revealed in detail. It has been found that the excited states induced by photoexcitation possess many unique phenomena, which do not exist in the ground state, and a field called "photoinduced phenomenon" has become an active interdisciplinary frontier cutting across the areas of physics, chemistry, and material science. This present paper studies the photoinduced phenomenon in polymeric molecules. It is shown that a polymeric molecule with a bipolaron can possess a negative static polarizability [3], which can never appear in the ground state of any kind of molecule [4].

Studies of photoexcitation in polymers demonstrate its significance not only for device applications, such as electroluminescence and optoelectronic display [5,6], but also for understanding the nature of excitations in organic materials [7–14]. By using femtosecond spectroscopy, it is found that the primary photoexcitations in conjugated polymers are intrachain excitons [15]; also biexcitons [16–19], which are characterized as a sequential reexcitation of intrachain excitons, have been observed recently in poly(paraphenylene vinylene) (PPV) [20]. In a dilute solution of PPV, photoinduced absorption and stimulated emission show that the lifetimes of excitons and biexcitons in a single molecule are hundreds of picoseconds (10^{-12} s), which is very long compared to the femtosecond scale, and thus makes it possible to investigate further the electric and optical properties of excitons and biexcitons in polymeric molecules. Based on these findings, the photoinduced phenomenon is predicted by a numerical simulation: when a polymeric molecule absorbs one photon, its electric dipole is reversed. A sketch of this phenomenon is shown in Fig. 1. This switching effect is called "photoinduced polarization reversion (PPR)," which has been briefly described earlier [3]. Substantial supplements and further explanations are presented in this paper, mainly, (1) an analytic theory by means of a response function is provided to prove that the polymeric molecule with a bipolaron has a negative static polarizability, (2) the physical origin of the PPR is explained in detail, and (3) the dynamical process for dipole reversion is simulated.

The polarization after reversion in Fig. 1 looks strange, where the positive charge in the molecule moves towards the anode and negative one towards the cathode, which seems in conflict with Coulomb's law. Why such polarization is reasonable will be explained in Sec. III. Before that, the energy spectrum of excitation and the bond structure of the polymeric molecule are described in Sec. II. Section IV gives an analytic theory to calculate the polarizability by means of the Green's-function method. Section V presents a numerical calculation of the dipole moment induced by an external electric field. Section VI shows the dynamical process of PPR, and its relaxation time is determined. The conclusion and discussion are presented in Sec. VII.
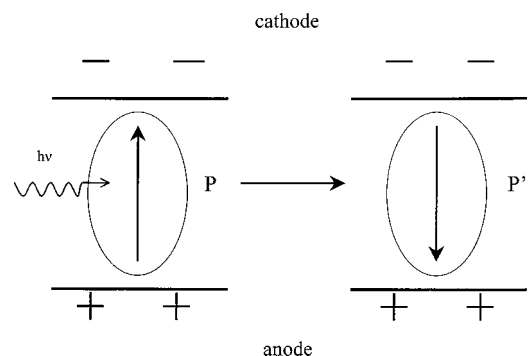

FIG. 1. Photoinduced polarization reversion.

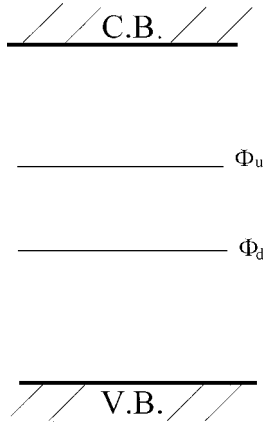*Corresponding author. Email address: xinsun@fudan.edu

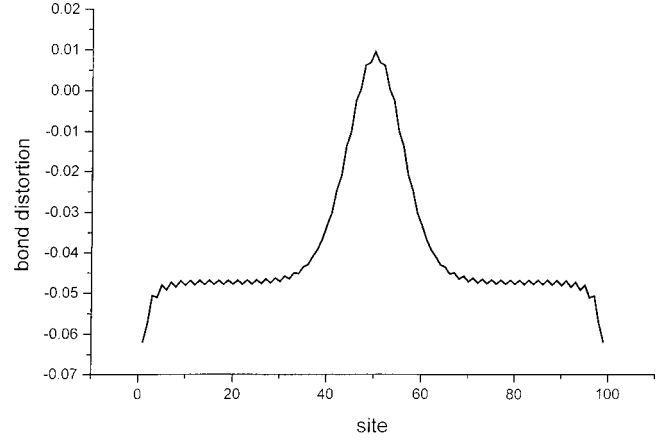FIG. 2. Spectrum of a polymeric molecule with a neutral bipolaron.

FIG. 3. Bond distortion of a polymeric molecule with a neutral bipolaron. The abscissa is the atom's site in a polymer chain and the ordinate is the order parameter describing the change of the bond length.

II. EXCITATIONS IN POLYMERS

A prominent feature of the polymeric molecule is that its electronic energy spectrum and bond distortion depend on the excitation. The reason is that the polymer chain is a quasi-one-dimensional system, whose bond structure is easily distorted under electron-lattice interaction. With the photoexcitation, the interaction between an electron-hole pair and bond lattice causes self-trapping and produces a neutral bipolaron (BP) [21], which is also called a self-trapped exciton (STE). For the bipolaron, the bond distortion creates two gap states: an up-gap state Φ_u and a down-gap state Φ_d, shown in Fig. 2, whose wave functions are orthogonal to each other. The bond distortion associated with the bipolaron is shown in Fig. 3, where the polymer chain consists of 100 units. In the neutral BP or STE, both Φ_u and Φ_d are occupied by one electron.

It is well known that the BP can be quantitatively described by the Hamiltonian [21]

$$H = H_e + \frac{K}{2} \sum_l (u_{l+1} - u_l)^2, \quad (2.1)$$

$$H_e = H_0 + H' + H_E, \quad (2.2)$$

$$H_0 = -\sum_{l,s} \{ t_0 - \alpha'(u_{l+1} - u_l) + (-1)^l t_e \}$$

$$\times [a_{l+1,s}^\dagger a_{l,s} + \text{H.c.}], \quad (2.3)$$

$$H' = U \sum_{l,s} n_{l,s} n_{l,-s} + V \sum_{l,s,s'} n_{l,s} n_{l+1,s'}. \quad (2.4)$$

Here, 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; $H_E = -PE$ is the interaction of the electrons with the electric field E, whose direction is from left to right, where P is the electric dipole; and $a_{l,s}^\dagger$ and $a_{l,s}$ are the creation and annihilation operators of an electron at lattice site l with spin s, u_l is the displacement of atom l, $n_{l,s} = a_{l,s}^\dagger a_{l,s}$, $t_0 = 2.5-3.0$ eV is the hopping constant, $\alpha' = 40-60$ eV/nm is the electron-lattice coupling constant, $t_e = 0-0.1$ eV is the confinement constant, $K = 2000-3000$ eV/nm^2 is the elastic constant, and $U = 2.0-5.0$ eV and $V = 0.5-2.0$ eV are the electron repulsion parameters.

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

$$H_e \Phi_\mu = \varepsilon_\mu \Phi_\mu. \quad (2.5)$$

The total energy is

$$E[\{u_l\}] = \sum_{occ} \varepsilon_\mu[\{u_l\}] + \frac{K}{2} \sum_l [u_{l+1} - u_l]^2. \quad (2.6)$$

The lattice distortion is determined by

$$\frac{\delta E[\{u_l\}]}{\delta u_l} = 0. \quad (2.7)$$

ε_μ, Φ_μ, and u_l can be obtained self-consistently by solving the combined equations (2.5) and (2.7). After getting the eigenstates Φ_μ, the charge distribution can be calculated by using the formula

$$\rho_l = \sum_{occ} |\Phi_\mu|^2 - n_0, \quad (2.8)$$

where n_0 is the density of positively charged background. Then, the dipole and polarizability of the molecule can be determined from ρ_l. The wave functions of the two gap states are the bound-state solutions of Eq. (2.5).

III. POLARIZABILITY

When a static magnetic or electric field is applied to a molecule, the molecule is magnetized or polarized. In magnetism, all molecules are divided into two categories: (1) a magnetic molecule, which possesses an inherent magnetic moment M consisting of electron's orbital and spin magnetic

moments, and (2) a nonmagnetic molecule, whose inherent magnetic moment is zero. After a static magnetic field H is applied, these two kinds of molecules have opposite responses. For the former, their magnetic moment M orients to the direction of the external magnetic field H. Then their magnetic susceptibility χ is positive, which is "paramagnetic." For the latter, although no inherent magnetic moment exists, an induced magnetic moment is produced by H. Since this induced moment comes from the precession of the electron's magnetic moments, its direction must be opposite to H, so their magnetic susceptibility is negative, which is "diamagnetic." Thus, the magnetic susceptibility of molecules can be either positive or negative.

In electricity, molecules can also be divided into two categories: (1) polar molecules, which have an inherent dipole P, and (2) nonpolar molecules without a dipole P. When a static electric field E is applied, for the former, their dipole P orients to the external electric field E, and their electric susceptibility polarizability α is positive. For the latter, an induced dipole is produced by the electric field E in such a way that the positive charge in the molecule shifts towards the cathode, and the negative one towards the anode. Then the induced dipole is in the direction of the external electric field E, so that their polarizability is also positive. Therefore, both the polar and nonpolar molecules possess positive polarizability [4], which is the reason why in electricity there is no "para-" and "dia-" terminology. Such asymmetry between magnetism and electricity is caused by the absence of magnetic charge.

Can the static polarizability of a molecule become negative? The negative polarizability requires the direction of the induced electric dipole to be opposite to that of the external electric field. This means that the positive charge in the molecule shifts toward the anode and the negative charge toward the cathode. Such polarization seems to violate Coulomb's law.

It should be pointed out that the above argument is based on classical electrodynamics. However, a molecule is a quantum system, and it can be seen that quantum effects can make the static polarizability negative in special cases.

As a quantum system, a molecule can stay in one of a series of eigenstates Ψ_μ. Quantum mechanics tells us that the static polarizability of a molecule in an eigenstate Ψ_μ is [22]

$$\alpha_\mu = \sum_\nu \frac{2|P(\nu,\mu)|^2}{\varepsilon_\nu - \varepsilon_\mu}, \qquad (3.1)$$

where $P(\mu,\nu)$ is a dipole matrix element between Ψ_μ and Ψ_ν. This formula indicates that all the other eigenstates give contributions to the static polarizability of the state Ψ_μ. For the ground state, all the denominators in Eq. (3.1) are positive, and its static polarizability is positive. Therefore, for any molecule, the static polarizability in its ground state is always positive. In this respect, the classical argument works. But something different can happen in excited states.

For any excited state Ψ_e, it can be seen from Eq. (3.1) that there are two types of contributions to its polarizability with opposite signs: The contributions from the states above

Ψ_e are positive, but those from the states below Ψ_e are negative. There are only several eigenstates below the state Ψ_e, but an infinite number of eigenstates above the state Ψ_e. Therefore, usually the positive contributions from above eigenstates are dominant. Thus, even for excited states, their polarizabilities are usually still positive, which is the reason why the negative static polarizability has not been seriously considered in physics.

Nevertheless, it cannot be concluded that the molecule in an excited state can never have negative static polarizability, since Eq. (3.1) cannot guarantee the positive part is always larger than the negative one. In fact, it can be shown that some low-lying excited states possess negative static polarizability, where one example is the up-gap state Φ_u of the exciton. By solving the eigenequation (2.5), the wave functions of the eigenstates can be obtained. In the external electric field E, all the eigenstates are polarized, and the gap states Φ_d and Φ_u of the exciton in an electric field $E = 10^3$ V/cm are shown in Fig. 1 of Ref. [3]. In that figure, the direction of the electric field E is from left to right, and it means that the anode is on the left side and the cathode on the right side. A notable feature is that the polarizations of the down-gap and up-gap states are opposite. There are two peaks in the wave functions of both the down-gap and up-gap states. Before the electric field is applied, these two peaks have equal heights; in the electric field, the wave functions are polarized. For the down-gap state Φ_d, Fig. 1A in Ref. [3] shows that the left peak is higher than the right one, and indicates that the electron shifts to the anode on the left side with a hole remaining on the right side (the cathode). So the polarization of the down-gap state is normal and its polarizability is positive. But Fig. 1B in Ref. [3] shows that, in the up-gap state Φ_u, the right peak becomes higher, which means that the electron shifts to the cathode on the right side, and the polarization of Φ_u becomes anomalous and its polarizability is negative. Such polarization behaviors are understandable. In this case, two gap states Φ_u and Φ_d are close to each other, and the dipole matrix element $P(d,u)$ between Φ_u and Φ_d is much larger than others. Then Eq. (3.1) tells us that, for the down-gap state, the dominant contribution to its polarizability α_d comes from the up-gap state, and the other contributions from the conduction band and valence band are much smaller. In this case, the denominator of the leading term is positive, and α_d is positive; for the up-gap state, the dominant contribution to its polarizability α_u comes from the down-gap state, where the denominator is negative, so that α_u becomes negative.

Thus, based on quantum mechanics, the negative static polarizability can be realized, and does not conflict with Coulomb's law. In classical physics, the electron has a specified position at any moment, and the electric field exerts a force directly on the electron to move it. This means that the movement of the electron is only decided by the electric field. In quantum mechanics, the electron's state is described by a wave function which is an eigenfunction of the Hamiltonian describing the molecule. The polarization is the change of the wave function caused by the electric field. The effect of the electric field is first to change the Hamiltonian by adding one more term describing the interaction between

the electric field and electrons $-PE$. The change in the Hamiltonian causes a modification of the wave function, which determines the electron's movement and the polarization. Therefore, the movement of electrons is not only controlled by the electric field, but also by some constraints on the wave functions, for example, the orthogonality between eigenfunctions. In our case, the two gap states Φ_d and Φ_u are always orthogonal to each other with or without the electric field. After E is applied, in order to keep the orthogonality of their wave functions, the left peak of Φ_d becomes higher and the right peak of Φ_u higher, where these two states possess opposite polarizations.

Such anomalous polarization also happens in highly excited states of the sodium atom, the Rydberg states [23]. Since the np states lie slightly above the $(n-1)d$ states and much below the $(n+1)s$ states, the np states can also have negative polarizability. For the Rydberg states, the energy intervals between adjacent states are on the order of meV, which is in the microwave region. By contrast, the level separation in polymers is about 1 eV, and these photoinduced phenomena in polymers are in the optical region.

It should be mentioned that we are interested in the "static" rather than the dynamical polarizability. It is well known that the dynamical polarizability is the frequency-dependent polarizability

$$\alpha_\mu(\omega) = \sum_\nu \left[\frac{|P(\mu,\nu)|^2}{(\varepsilon_\nu - \varepsilon_\mu) - \hbar\omega - i\Gamma/2} + \frac{|P(\mu,\nu)|^2}{(\varepsilon_\nu - \varepsilon_\mu) + \hbar\omega + i\Gamma/2} \right], \qquad (3.2)$$

where Γ is damping factory, which determines the width of absorption line.

From this equation, it can be seen that there are many absorption bands corresponding to the resonant frequencies. For any molecule on the blue side of each absorption band the dynamical polarizability $\alpha(\omega)$ must be negative, which is called anomalous dispersion. Therefore, the dynamical polarizability can readily be negative, but it is rare for the static polarizability to be negative.

IV. RESPONSE FUNCTION

The polarization is the response of a system to an electric field, and the polarizability is the response function, which can be calculated by means of the Green's-function method [24]. The definition of the response function $\chi(t,t')$ in state $|s\rangle$ is

$$\delta\langle s|P(t)|s\rangle = \int dt' \chi(t,t') \delta E(t'), \qquad (4.1)$$

where $P(t)$ is dipole and $E(t)$ the electric field. According to the Kubo theorem [25], the linear-response function can be expressed in terms of the correlation function with $E=0$ as

$$\chi(t,t') = \frac{i}{\hbar} \theta(t-t') \langle s|[P_I(t), P_I(t')]|s\rangle, \qquad (4.2)$$

where $P_I(t)$ is the dipole operator in the interaction picture. Setting $t'=0$, in the representation of H_e,

$$\langle s|[P_I(t), P_I(0)]|s\rangle = \sum_n |\langle s|P|n\rangle|^2 [e^{i(\varepsilon_s - \varepsilon_n)t/\hbar} - e^{-i(\varepsilon_s - \varepsilon_n)t/\hbar}], \qquad (4.3)$$

where ε_s is the energy of the system at state $|s\rangle$.

The Fourier transformation of the response function is

$$\chi(\omega) = \int_{-\infty}^{\infty} \chi(t) e^{(i\omega - \eta)t} dt$$
$$= \sum_n |\langle s|P|n\rangle|^2 \left(\frac{1}{\varepsilon_n - \varepsilon_s - \hbar\omega - i\hbar\eta} - \frac{1}{\varepsilon_s - \varepsilon_n - \hbar\omega - i\hbar\eta} \right). \qquad (4.4)$$

The imaginary part of $\chi(\omega)$ is

$$\chi''(\omega) = \pi \sum_n |\langle s|P|n\rangle|^2 [\delta(\hbar\omega + \varepsilon_s - \varepsilon_n) - \delta(\hbar\omega - \varepsilon_s + \varepsilon_n)], \qquad (4.5)$$

and the real part is

$$\chi'(\omega) = P \int_{-\infty}^{+\infty} \frac{\chi''(\omega)}{\pi(\omega' - \omega)} d\omega' = \sum_n |\langle s|P|n\rangle|^2$$
$$\times \left[\frac{1}{\varepsilon_n - \varepsilon_s - \hbar\omega} - \frac{1}{\varepsilon_s - \varepsilon_n - \hbar\omega} \right], \qquad (4.6)$$

which is the dynamical polarizability $\alpha(\omega)$. The static polarizability α is

$$\alpha = \chi'(\omega = 0). \qquad (4.7)$$

In our case, the dipole operator is

$$P = \sum_{l,\sigma} ea \left(l - \frac{N+1}{2} \right) a_{l,\sigma}^\dagger a_{l,\sigma} = \sum_{\mu,\nu,\sigma} B_{\mu\nu} a_{\mu\sigma}^\dagger a_{\nu,\sigma}, \qquad (4.8)$$

$$B_{\mu\nu} = ea \sum_l \langle u|l\rangle \langle l|v\rangle \left(l - \frac{N+1}{2} \right), \qquad (4.9)$$

where e is the electronic charge, $a=0.122$ nm is the lattice constant; $|\mu\rangle$ is the Bloch wave function, and $|l\rangle$ is the atom wave function at site l. The dipole operator $B_{\mu\nu} a_{\mu\sigma}^\dagger a_{\nu\sigma}$ is for the transition of one electron from the occupied state $|\nu\rangle$ with energy $\hbar\omega_\nu$ to the unoccupied state $|\mu\rangle$ with energy $\hbar\omega_\mu$, and

$$\varepsilon_n - \varepsilon_s = \hbar(\omega_\mu - \omega_\nu). \qquad (4.10)$$

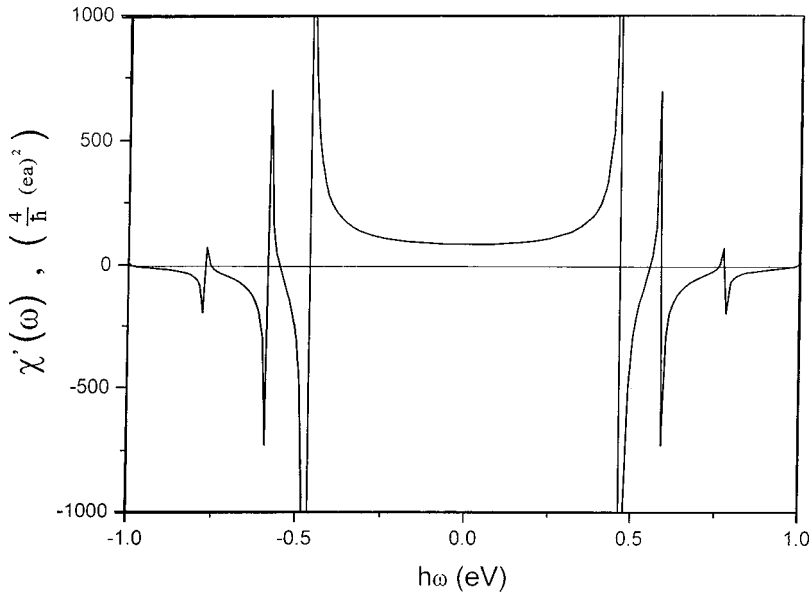Substituting Eqs. (4.8)–(4.10) to (4.5)–(4.7), we get

FIG. 4. Dynamical polarizability of a polymeric molecule with an exciton.

$$\chi''(\omega) = \frac{4\pi}{\hbar} \sum_{\mu}^{(unocc)} \sum_{\nu}^{(occ)} B_{\mu\nu}^2 [\delta(\omega - \omega_\mu + \omega_\nu)$$

$$- \delta(\omega + \omega_\mu - \omega_\nu)], \tag{4.11}$$

$$\chi'(\omega) = \frac{4}{\hbar} \sum_{\mu}^{(unocc)} \sum_{\nu}^{(occ)} B_{\mu\nu}^2 \left(\frac{1}{\omega_\nu - \omega_\mu - \omega} - \frac{1}{\omega_\mu - \omega_\nu - \omega} \right), \tag{4.12}$$

$$\alpha = \frac{8}{\hbar} \sum_{\mu}^{(unocc)} \sum_{\nu}^{(occ)} B_{\mu\nu}^2 / (\omega_\nu - \omega_\mu). \tag{4.13}$$

The occupied and unoccupied states are dependent on the excitations. For the exciton, both the up-gap and down-gap states are occupied by one electron. For the biexciton, the up-gap state is occupied by two electrons with opposite spins, and the down-gap state is empty. For both the exciton and biexciton, the valence band is filled and the conduction band is empty.

The dynamical polarizabilities of the polymeric molecule with an exciton and biexciton are shown in the Figs. 4 and 5. It is remarkable that the static polarizability of a polymeric molecule with an exciton is positive, but that with a biexciton is negative. The numerical calculation shows

$$\alpha(\text{biexciton}) = -5 \times 10^{-37} C \, m^2/V. \tag{4.14}$$

This is four orders of magnitude larger than that of the hydrogen atom ($\alpha_H = 7.4 \times 10^{-41} C \, m^2/V$) [22], where the reason is that the size of a biexciton is about 5 nm and π electrons have large delocalization along the polymer chain.

V. CHARGE DISTRIBUTION AND DIPOLE

Section IV provides an analytical method to calculate the dynamical polarizability and proves that a polymeric mol-
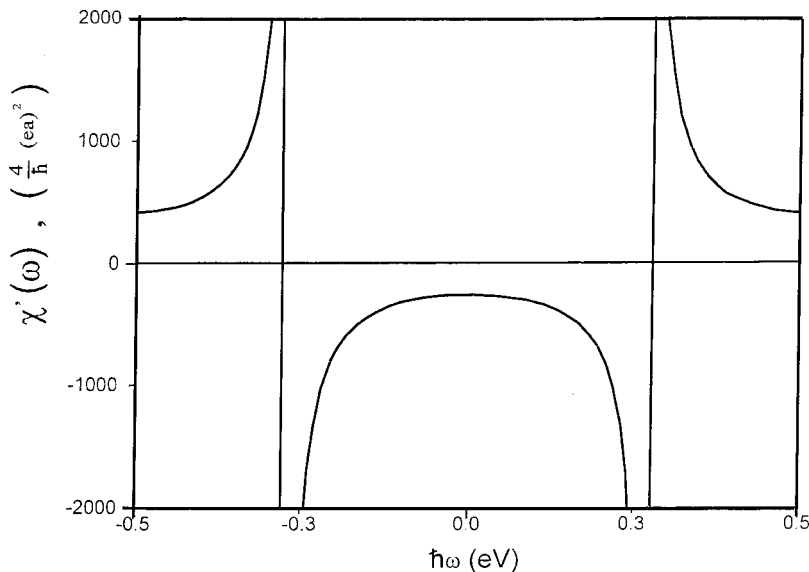

FIG. 5. Dynamical polarizability of a polymeric molecule with a biexciton.

ecule with a biexciton can possess a negative static polariz-ability. In this method, which is based on the Kubo theory of linear response, a prominent feature is that there is no elec-tric field applied to the molecule.

This section uses another method to directly calculate the static polarizability of the molecule with different excita-tions. Here a weak electric field is applied to the molecule, and the charge distribution and dipole moment in the mol-ecule induced by the electric field are numerically calculated. Then the static polarizability can be extracted from the linear relation $P = \alpha E$. The merit of this method is that the charge distribution along the polymer chain, which is induced by the electric field, can be explicitly demonstrated, and we can directly see the difference between the normal and anoma-lous polarizations.

First, with an applied electric field, the combined equa-tions (2.5), (2.6), and (2.7) are numerically solved to obtain the eigenfunctions Φ_μ, the energy spectrum, and lattice dis-tortion, which are dependent on the excitation. We see that the energy difference between two gap states of the biexciton is smaller than that of the exciton, where this reduction en-hances the effect for the up-gap state to reach a negative polarizability. Then, the charge distribution ρ_l can be ob-tained from Eq. (2.8) as

$$\rho_l(\text{exciton}) = \sum_{\text{VB}} |\Phi_\mu|^2 + |\Phi_d|^2 + |\Phi_u|^2 - n_0, \quad (5.1)$$

$$\rho_l(\text{biexciton}) = \sum_{\text{VB}} |\Phi_\mu|^2 + 2|\Phi_u|^2 - n_0. \quad (5.2)$$

The charge distributions along the molecular chain are shown in Fig. 2 of Ref. [3]. Figure 2A of Ref. [3] shows the charge distribution of a molecule with an exciton, where the polarization is normal and its static polarizability is positive; Fig. 2B of Ref. [3] shows the charge distribution with a biexciton, where the polarization is anomalous and its polar-izability is negative. The numerical results show that the static polarizabilities of the exciton and biexciton have the same values as those obtained in Sec. IV. This coincidence is expected, since these two methods are equivalent.

VI. RELAXATION PROCESS

For a one-dimensional system, the electronic excitation causes lattice distortion, and the lattice configuration is de-pendent on the excitation. In the polymeric molecule, the lattice configuration with an exciton is different from that of a biexciton. Then, the excitation from exciton to biexciton induces a lattice relaxation, which can be simulated by means of lattice dynamics [26]. Since an atom is much heavier than an electron, the atomic movement is described classically, and the adiabatic approximation is used to deter-mine the wave functions of the electrons.

The force f_n exerted on the nth atom is

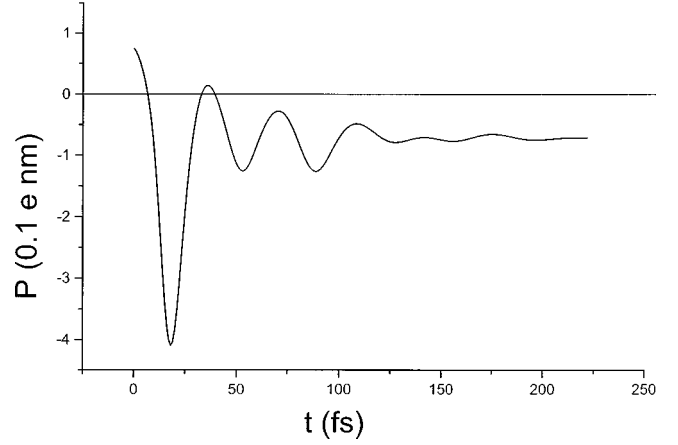$$f_n = -\partial E(\{u_n\})/\partial u_n, \quad (6.1)$$

FIG. 6. Time dependence of the dipole.

where $E(\{u_n\})$ is the total energy with the lattice configura-tion $\{u_n\}$, which is shown in Eq. (2.6). The calculation can be facilitated by using the Hellman-Feynman theorem,

$$\frac{\partial \varepsilon_\mu}{\partial u_n} = \left\langle \mu \left| \frac{\partial H_e}{\partial u_n} \right| \mu \right\rangle. \quad (6.2)$$

The evolution of the lattice configuration $\{u_n(t)\}$ can be worked out by numerically solving Newton's equation with the force f_n given in Eq. (6.1). Then the time dependences of the charge distribution and dipole can be obtained. Figure 6 shows the evolution of the dipole, which changes its direc-tion from positive to negative. It can be seen that the relax-ation time for the polarization reversion is about 150 fs.

VII. CONCLUSION AND DISCUSSION

As a quantum system a single molecule in some eigen-state can possess negative static polarizability, where one candidate is a polymeric molecule with a biexciton. The negative polarization can produce an ultrafast switching phe-nomenon known as photoinduced polarization reversal. This conclusion is based on the following physics.

The photoexcitation in a polymeric molecule induces a bond distortion in its molecular structure, which creates two electronic bound states in the gap: the up-gap state and the down-gap state. This self-trapping effect causes the electron-hole pair to become a neutral bipolaron or self-trapped exci-ton. The wave functions of the up-gap and down-gap states are orthogonal, with their levels close to each other. Then, for the down-gap state, the main contribution to its static polarizability comes from the up-gap state, and its static po-larizability is positive; for the up-gap state, the main contri-bution comes from the down-gap state, and its static polariz-ability is negative. When an electron is excited from the down-gap state to the up-gap state, the polarization changes its sign. When an electric field is applied to a polymeric molecule with an exciton, its polarizability is positive, and the dipole moment of the molecule points to the electric field. When the molecule with an exciton absorbs a photon, the electron in the down-gap state is excited to the up-gap state and the exciton becomes a biexciton, and its polariz-

ability becomes negative. Then, the dipole moment of the molecule is reversed by absorbing a photon, which is photo-induced polarization reversal (PPR). The dipole reversal is associated with lattice relaxation, and the relaxation time is 150 fs, which indicates that PPR is an ultrafast switching effect, which takes place in a single molecule.

PPR can be observed in many ways, where one is optical by using a pump-probe method in a polymer solution. This needs two laser pumps: the first produces the exciton, and the second is a tunable laser pulse to reexcite the exciton. Tuning the frequency of the second pump so that its photon energy equals the energy difference between the up-gap state and down-gap state, the second laser is resonantly absorbed by the exciton, which is excited into a biexciton, and the electric dipole of the polymeric molecule is reversed. In the meantime, a probing light pulse follows the second pump pulse, where the scattering of this light from the molecule is changed by the polarization reversal, and such scattering change gives a signal to detect PPR. Another way is electric, where the sample is put in a capacitor, which is connected to a circuit. When PPR takes place, the charges in the plates of the capacitor are changed, and some charge goes through the circuit.

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