Reverse polarization in charged π-conjugated oligomers by single-optical excitation

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Abstract. A doped electron or hole will exist in a self-trapping state even in a π-conjugated oligomer. It can be excited by absorbing photons. Two possible optical-excitation modes, which are respectively called low-energy excitation and high-energy excitation are demonstrated in this paper. It is found that the high-energy excitation will result in a reverse polarization of the molecule. The polarizability is calculated and it is obtained that the strength of the reverse polarization is dependent upon the conjugation-length of the molecule.

1. INTRODUCTION

It has been well known that π-conjugated organic semiconductors have become very promising functional materials in optoelectronics devices[1-7] since light-emitting diodes (LEDs) based on conjugated polymers were demonstrated[8]. As quasi-one-dimensional (1D) systems, π-conjugated organic semiconductors have the characteristic of low-dimensional instability, and the lattice configuration is sensitively dependent on the electronic state. Once the electronic state is excited, the bond structure undergoes distortion, subsequently, some new electronic bound states form in these systems. The developments of femtosecond and photoinduced absorption technologies have provided powerful tools for us to study the physical properties and the dynamical processes of the excited states. It has been found that the excited states induced by photoexcitation possess many unique phenomena, which do not exist in the ground state[9], and a field called “photoinduced phenomenon” has become an active frontier in the interdisciplinary area of physics, chemistry, and material science.

With a perfect π-conjugated polymer chain, Sun et al. has found a new photoinduced phenomenon which is called photoinduced polarization reversion (PPR) by studying the single- and double-optical excitation[10,11]. They found that the polarizability of the chain with one exciton is positive, while that with a biexciton is negative. A sequential investigation including temperature and defect effects on the stability of reverse polarization was also reported[12]. Recently, a theoretical report has ever predicted that a π-conjugated polymer chain with a polaron may also be reverse polarized by single-optical excitation[13]. However, most of the work up to now has been done in a perfect one-dimensional chain, where the confinement effect of the chain ends is absent.

A π-conjugated polymer should be viewed as a string of effectively independent segments, separated by chemical or physical defects. While a π-conjugated oligomer can be obtained with a well-defined chemical structure and has a finite conjugation-length (CL). Lots of studies have demonstrated that the CL can produce much influence on some physical properties of π-conjugated oligomers such as the low-energy transition[14], spin-dependent exciton formation rates[15], and the stabilization of the
lowest excited state [16]. In this paper, conjugation-length dependence of the reverse polarization in charged \(\pi\)-conjugated oligomers will be discussed. The presentation is organized as follows. The model Hamiltonian is established and the scheme of a self-consistent calculation is also outlined in section 2. In section 3 we describe and discuss the results of our numerical computation. Finally, in section 4 our conclusions are summarized.

2. MODEL

Neglecting the interchain coupling of \(\pi\)-conjugated oligomers, in the framework of a tight-binding approximation, the extended SSH model is proposed [17]:

\[
H = H_0 + H_E + H_{e-e}, 
\]

\[
H_0 = -\sum_{n,s} \left[ t_0 - \alpha(u_{n+1} - u_n) \right] (c^+_{n,s} c_{n+1,s} + c^+_{n+1,s} c_{n,s}) + \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2 + K' \sum_n (u_{n+1} - u_n),
\]

\[
H_E = \sum_n eE (n a + u_n) (c^+_{n,s} c_{n,s} - 1),
\]

\[
H_{e-e} = U \sum_{n,s} c^+_{n,s} c_{n,s} c^+_{n-1,s} c_{n-1,s} + V \sum_{n,s,s'} c^+_{n,s} c_{n,s} c^+_{n+1,s'} c_{n+1,s'},
\]

where \(H_0\) describes the electron-lattice interactions, in which \(c^+\) and \(c\) are the creation and annihilation operators of an electron at site \(n\) with spin \(s\). \(u_n\) is the displacement of an unit at site \(n\), \(t_0\) the hopping constant, \(\alpha\) the electron-lattice interaction constant, and \(K\) the elastic constant. The linear term \(K'\) is introduced [18] to remedy the unstability of the model in the case of an open-end oligomer. For a \(\pi\)-conjugated oligomer containing \(N\) units of (CH) groups, \(K'\) is given by,

\[
K' = -\frac{2\alpha}{N - 1} \sum_{\mu,n,s} Z_{\mu,n,s} Z_{\mu,n+1,s},
\]

where \(\sum\) means summing over the occupied states. \(H_E\) is the interaction of electrons with the external electric field \(E\). \(H_{e-e}\) is the electron-electron interaction. For simply, \(H_{e-e}\) is treated by the Hartree-Fock approximation. The electronic wave function \(\psi_{\mu,s} = \sum_n Z_{\mu,n,s} |n\rangle\) is obtained by solving the Schrödinger of the electronic hamiltonian, which is dependent upon the bond displacement \((u_n - u_{n+1})\). On the other hand, by minimizing the total energy, displacement \((u_n - u_{n+1})\) is determined by the eigenstate,

\[
u_n - u_{n+1} = \frac{2\alpha}{K} \sum_{\mu,n,s} Z_{\mu,n,s} Z_{\mu,n+1,s} + \frac{K'}{K} \left( \sum_{\mu,n,m=1}^n Z_{\mu,m,s}^2 - n \right).
\]

Therefore, displacement \((u_n - u_{n+1})\) and eigenstate \((Z_{\mu,n,s})\) depend upon each other, which can be calculated iteratively.

The dipole moment \(P\) is given by,

\[
P = -e \sum_{n=-N/2}^{N/2} \left( \rho_n - \rho_{-n} \right) (n a + u_n) = -e \sum_{n=-N/2}^{N/2} \Pi_n (n a + u_n)
\]

where \(\rho_n = \sum_{\mu,s} |Z_{\mu,n,s}|^2 - 1\) is the charge density distribution, and \(\Pi_n = \frac{1}{2} (\rho_n - \rho_{-n})\) is called the polarized charge density in this paper. The dipole moment \(P\) is dependent upon the external electric field \(E\) and the linear expanding coefficient \(\chi\) is called the polarizability.
3. RESULTS AND DISCUSSION

The parameters in the calculation take the values $t_0=2.5\text{eV}$, $\alpha=41.0\text{eV}/\text{nm}$, $a=0.122\text{nm}$ and $K=2100.0\text{eV}/\text{nm}^2$. Due to the strong electron-lattice coupling, the bond length in a pristine $\pi$-conjugated oligomer molecule is alternated. There is a gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). When the molecule is doped with one electron or hole, it is found that the electron or hole is not extended over the whole molecule but confined in a finite region. Two deep levels $\varepsilon_d$ and $\varepsilon_u$ will appear in the gap. In the case of an electron doping, $\varepsilon_d$ is doubly occupied and $\varepsilon_u$ singly. Experimentally one finds two optical transitions[19] that are interpreted as the $P_1$ and $P_2$ transitions as shown in Fig 1. For $P_1$, the electron with energy $\varepsilon_u$ is excited into the LUMO with energy increasing $\Delta - \Delta^2 / 2$ ($\Delta$ is half of the energy gap); For $P_2$, the electron with energy $\varepsilon_d$ is excited into level $\varepsilon_u$ with energy increasing $\Delta / 2^2$.

From the reverse polarization of a biexciton, it can be obtained that the key point to get the reverse polarization is to produce two deep levels (up-one $\varepsilon_u$ and down-one $\varepsilon_d$) which are close to each other, and the electrons occupying in $\varepsilon_u$ are more than that in $\varepsilon_d$. It is obvious that the high-energy excitation $P_2$ can lead to the reverse polarization of a charged oligomer molecule. Now let us consider the instantaneous states after excitation $P_2$. Due to the strong electron-lattice interaction, the excited electron-hole pair will induce the deformation of the molecule structure and result in a redistribution of the charged state. If we check the charge density distribution $\rho$, it will be found that there are two wave packets after excitation, where the charged state has a higher electrical energy than that before excitation. To see the polarization of the charged oligomer, an external electric field $E=10^{-2}\text{V/nm}$ is applied with the direction from left to right along the molecule chain. Fig 2 shows the polarized charge density $\Pi = \frac{1}{2}(\rho_+ - \rho_-)$ in a singly negatively charged molecule with the conjugation-length $64a$. The dashed line indicates the polarized charge density before excitation and the solid line for the high-energy excitation. It is found that an apparent reverse polarization appears after high-energy excitation $P_2$. Before photoexcitation, the doped electron is confined to the left side of the molecule, where there is a lower electric potential. After high-energy excitation $P_2$, the doped electron will spread towards to the direction of the higher electric potential, which results in the reverse polarization of the molecule. The increasing of the energy due to the excitation behaves in the reverse polarization. Furthermore, the dipole moment $P$ of the charged molecule is calculated from Eqs.(7), from which the polarizability $\chi$ is obtained. We get $\chi_H = -85.96\text{e} \cdot \text{nm}^2/\text{N}$ for the high-energy excitation in present parameters. Therefore the high-energy excitation will result in a reverse polarization.

However, the strength of the polarization is found to be conjugation-length dependent. Fig 3 shows the dependence of the polarizability $\chi$ on the conjugation-length, in which the square represents $\chi_B$ (polarizability before excitation) and the triangle $\chi_H$ (high-energy excitation). Due to the strong confinement effect of the chain ends, either before or after excitation, the charge density distribution is not easily changed by an external electric field in a small molecule. Therefore, before excitation, the polarization keeps nearly unchanged when the molecule chain is short ($L < 40a$ as shown in Fig 3). When the chain is long enough, the polarizability $\chi_B$ increases naturally with the conjugation-length and the increasing tendency becomes linearly ($L \geq 40a$ as shown in Fig 3).
After the high-energy excitation, it is found that the polarization will be reversed when the oligomer molecule is short. The strength of the reverse polarization has a maximum value at a suitable conjugation-length. For example, at present parameters, the maximum reverse polarization will appear at $L \sim 72a$, which is about the length of molecule $T_{18}$. With the further increasing of the chain length, it is found that the local charge distribution of the doped electron will keep unchanged. Therefore the polarization of the whole molecule after $P_2$ becomes a normal polarization when the chain length is long enough.

4. CONCLUSION
Reverse polarization is a peculiar property of $\pi$-conjugated molecules. It has been predicated that a photo-switch device could be designed by the reverse polarization of a biexciton in high-conjugated polymers. Here we study the single-optical excitation of a charged oligomer. A reverse polarization is obtained through the high-energy excitation $P_2$ which only needs to be photoexcited once. Strength of the reverse polarization is conjugation-length dependent. Only at a suitable conjugation-length, the molecule shows an apparent reverse polarization.

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Figure 2. Polarized charge density of a charged oligomer molecule as a function of atomic site $n$. The applied electric field $E=10^{-2}$ V/nm with the direction from left to right along the oligomer chain. The dashed line: before excitation; the solid line: high-energy excitation.

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Figure 3. Dependence of polarizability $\chi$ on conjugation length $L$. The square represents $\chi_B$ (polarizability before excitation) and the triangle $\chi_H$ (high-energy excitation) respectively.
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