

Bipolaron-induced third-order optical nonlinearity in conjugated conducting polymers

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A mechanism, due to the presence of bipolarons, for large resonant $\chi^{(3)}$ in doped *cis*-polyacetylene and other conjugated conducting polymers is presented. Under optical pumping, the electronic occupations of the two intragap energy levels of the bipolarons will vary, resulting in a shift in their energies, which in turn causes a dramatic change in the absorption spectrum. Even for moderate doping concentrations of bipolarons, $\chi^{(3)}$ is found to be as high as 10^{-8} esu. [S0163-1829(96)06648-9]

In recent years a great variety of conjugated polymers have been found to exhibit large optical nonlinearity in succession, and enormous attention¹ has therefore been focused on the understanding of the mechanisms of these effects, and the discovery of new ones for potential applications. In particular, there has been extensive interest in their resonant third-order optical susceptibility ($\chi^{(3)}$), due to demand from optical switching applications, as well as the desire to clarify the underlying quasiparticle dynamics.²

In this paper we present a mechanism of large resonant $\chi^{(3)}$ for non-degenerate-ground-state (NDGS) conjugated polymers. The idea is simple. Positive bipolarons with two empty intragap energy levels of NDGS conjugated polymers are produced by doping.³ No linear optical absorption due to transitions from the lower to the upper level is possible, because the former is empty. However, with an intense pump some electrons will be excited to the lower level from the valence band, such that the transition from the lower level to the upper becomes possible. This new absorption channel causes a peak in the photoinduced absorption spectrum. Moreover, the energies of the levels (and therefore the peak position) depend on their electronic occupations, and therefore the pump intensity. Due to the discreteness of the intragap levels, the peak can be, in principle, arbitrarily high. The corresponding large photoinduced change of refraction index implies large nonlinear optical susceptibility.

Since *cis*-polyacetylene (*cis*-PA) is the simplest NDGS conjugated polymer, it is an ideal prototype for the realization of our ideas. We base our study on the continuum limit⁴⁻⁶ of the Su-Schrieffer-Heeger (SSH) Hamiltonian.^{7,8} The lattice displacement is described by the gap parameter $\Delta(y)$:

$$\Delta(y) = \Delta_i(y) + \Delta_e, \quad (1)$$

where $\Delta_i(y)$, sensitive to electron-lattice coupling, is the intrinsic order parameter, Δ_e is a constant extrinsic order parameter,⁶ and y is the coordinate along the chain direction. The well-known bipolaron solution⁹ for the gap parameter is

$$\Delta_p(y) = \Delta_0 - K_0 v_F \{ \tanh[K_0(y + y_0)] - \tanh[K_0(y - y_0)] \}, \quad (2)$$

with the geometrical size y_0 determined by $\tanh(2K_0 y_0) = K_0 \xi_0$ of the perfectly dimerized chain. Two localized intragap eigenstates appear with energies

$$\epsilon_{\pm} = \pm \omega_0, \quad \omega_0 = (\Delta_0^2 - K_0^2 v_F^2)^{1/2}, \quad (3)$$

where v_F is the Fermi velocity. The constraint that the bipolaron profile in (2) satisfies the self-consistent gap equation^{7,8} imposes the relation

$$\frac{\pi}{4} (n_+ - n_- + 2) - \gamma_e K_0 v_F / \omega_0 - \sin^{-1}(K_0 v_F / \Delta_0) = 0, \quad (4)$$

with $\gamma_e = \Delta_e / (\lambda \Delta_0)$. $\lambda \equiv 4\alpha^2 a / (\pi K_0 v_F)$ is the dimensionless electron-lattice coupling constant. n_+ , n_- are the electronic occupations of the upper and lower intragap states, respectively.

For *p*-type bipolarons, there is no electron on either of the two intragap levels. Therefore transitions between those two levels do not occur, i.e., the linear absorption spectrum does not have a peak at $\omega = \epsilon_+ - \epsilon_- = 2\omega_0$. However, under intense pumping light the electronic occupation will be altered. The photoexcited electrons from the valence band will occupy the intragap levels, such that n_+ and n_- are not equal to zero any more. A sharp absorption peak is then expected to appear in the optical absorption profile $\alpha(\omega)$ of a weak probe beam. Moreover, the variation of n_+ and n_- changes the lattice distortion parameters K_0 and y_0 , such that the energies of the discrete intragap levels are shifted. The reason is that the change of the electronic occupations requires readjustment of the lattice distortion to minimize the total energy.

We consider the *p*-type bipolarons created by acceptor doping. For low dopant concentrations (i.e., low bipolaron concentrations), the bipolarons are independent of each other, and the descriptions discussed in the preceding section are good for each of the bipolarons. An independent bipolaron, with two discrete intragap states, can be viewed as a two-level system in contact with a particle reservoir (the valence band). These two levels are denoted by index a (ϵ_+ level) and b (ϵ_- level), respectively. We denote the electronic pumping rate from the valence band to the i th state as

λ_i , and the decay rate from the i th state to the valence band as γ_i , here $i = a, b$. Since the bipolaron concentration is low, the electronic occupation of the valence band is assumed to be approximately unaffected by the pump, as long as the pump photon energy is below the band gap. The pumping light is treated as a classical electromagnetic wave $E(t) = \frac{1}{2} \mathcal{E} e^{i\omega_p t} + \text{c.c.}$, and we consider the density matrix for the two-level system:

$$\rho = \begin{pmatrix} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{pmatrix},$$

where ρ_{aa} is the probability that the upper level is occupied, and ρ_{bb} the probability that the lower level is occupied. For isolated two-level systems, the density matrix satisfies the standard optical Bloch equations.^{10,11} The effect of the reservoir (valence band) is included by introducing pumping and decay terms into the equations. The result is the following:¹⁰

$$\dot{\rho}_{ab} = -(2i\omega_o + \gamma)\rho_{ab} + i\mathcal{V}_{ab}(\rho_{aa} - \rho_{bb}), \quad (5)$$

$$\dot{\rho}_{aa} = \lambda_a(1 - \rho_{aa}) - \gamma_a\rho_{aa} - (i\mathcal{V}_{ab}\rho_{ba} + \text{c.c.}), \quad (6)$$

$$\dot{\rho}_{bb} = \lambda_b(1 - \rho_{bb}) - \gamma_b\rho_{bb} + (i\mathcal{V}_{ab}\rho_{ba} + \text{c.c.}), \quad (7)$$

where γ is the phenomenological dipole dephasing rate, the interaction energy \mathcal{V}_{ab} is equal to $-\frac{1}{2}\wp\mathcal{E}e^{i\omega_p t}$ (in the rotating-wave approximation), and $\wp \equiv \langle a | e\hat{r} | b \rangle$ is the dipole matrix element. Note that the pumping term is proportional to $(1 - \rho_{ii})$, which is the probability that the level is empty, while the decay term is proportional to ρ_{ii} , the probability that the level is occupied. After the introduction of the terms (terms proportional to λ_i , γ_i , and γ), the occupation number ρ_{ii} can be arbitrary, and the constraint $\rho_{aa} + \rho_{bb} = 1$ for an isolated system is relaxed. In most semiconductors, the dipole dephasing time $(1/\gamma)$, which is related to the relaxation time of coherent transients, is much smaller than the occupation decay time $(1/\gamma_i)$ of each level. Therefore we can take ρ_{aa} and ρ_{bb} as approximately constants in (5) and integrate $\rho_{ab}(t)$ to get

$$\rho_{ab}(t) = -i \frac{\wp\mathcal{E}}{2} e^{-i\omega_p t} \frac{\rho_{aa} - \rho_{bb}}{\gamma + i(\omega_p - 2\omega_0)}. \quad (8)$$

Substituting this into (6) and (7), and solving them in steady state condition ($\dot{\rho}_{aa} = \dot{\rho}_{bb} = 0$), we get the population difference

$$\rho_{aa} - \rho_{bb} = \frac{\lambda_a/(\lambda_a + \gamma_a) - \lambda_b/(\lambda_b + \gamma_b)}{1 + \tilde{I}_p \mathcal{L}(\omega_p - 2\omega_0)} = \frac{1}{2}(n_+ - n_-), \quad (9)$$

where the dimensionless Lorentzian $\mathcal{L}(\omega_p - 2\omega_0)$ and the dimensionless pumping intensity \tilde{I}_p are given by

$$\mathcal{L}(\omega_p - 2\omega_0) \equiv \frac{\gamma^2}{\gamma^2 + (\omega_p - 2\omega_0)^2},$$

$$\tilde{I}_p \equiv |\wp\mathcal{E}|^2 \frac{1}{2\gamma} \left(\frac{1}{\gamma_a + \lambda_a} + \frac{1}{\gamma_b + \lambda_b} \right).$$

Note $n_+ - n_- = 2(\rho_{aa} - \rho_{bb})$; the factor of 2 is due to spin degeneracy.

In fact, the meanings of the three terms on the right hand sides of (6) and (7) are now transparent: the first term is the transition rate from the valence band, the second is the decay rate into the valence band, and the third is the transition (or decay) rate from (into) the other discrete level. These three rates must balance each other in stationary conditions. Under such conditions, the mean occupation numbers n_{\pm} of the localized levels are, in general, nonintegers. The relations (2) and (4) between the bipolaron parameters K_0 , y_0 , and the electronic occupations n_{\pm} are assumed to be still correct after replacing n_{\pm} by their (noninteger) means. These parameters, in turn, determine the energies ϵ_{\pm} and the wave functions of the localized levels, and all the transition rates involving them. The underlying justification for this procedure is that the time scale for the fluctuations of the occupation number is of the order of the electronic transition time, which is usually much shorter than the lattice response time. Therefore, under stationary conditions, even though the electronic occupations change among 0, 1, and 2 constantly, the lattice remains basically fixed at the configuration determined by the mean electronic occupations.

For fixed pump intensity I_p and frequency ω_p , we determine the occupation number difference $n_+ - n_-$ by (9). As stated before, the lattice distortion parameters K_0 , y_0 are functions of $n_+ - n_-$, therefore the transition rates λ_a , λ_b are functions of $n_+ - n_-$ too. Equation (9) then becomes an implicit equation for $n_+ - n_-$, which can be solved numerically for arbitrary I_p and ω_p . Explicit expressions for $\lambda_{a,b}$ are worked out in Ref. 9. Once n_+ , n_- are determined, we can use the relations $\mathcal{P} = 2\wp^* e^{i\omega_p t} \rho_{ab} N$, and $\alpha(\omega) = \text{Im}[(k/2\epsilon)(\mathcal{P}/\mathcal{E})]$ to obtain the probe absorption coefficient due to transition between discrete levels for the entire probe wave spectral range. Here N is the bipolaron concentration and \mathcal{P} is the polarization. The result is

$$\alpha(\omega)_{\epsilon_- \rightarrow \epsilon_+} = -\frac{k|\wp|^2}{2\epsilon} (\rho_{aa} - \rho_{bb}) \frac{\gamma}{\gamma^2 + (\omega - 2\omega_0)^2}. \quad (10)$$

Remember that the peak position $2\omega_0$ is also a function of $\rho_{aa} - \rho_{bb} = \frac{1}{2}(n_+ - n_-)$, and therefore depends on the pump intensity. The total probe absorption $\alpha(\omega)$ is equal to the $\epsilon_- \rightarrow \epsilon_+$ absorption in (10) plus the absorption due to transitions from the valence band.

The absorption change $\Delta\alpha(\omega)$ due to pumping can be converted to the refraction index change $\Delta n(\omega)$ using the Kramers-Kronig relation¹¹

$$\Delta n(\omega) = \frac{c}{\pi} \text{P} \int_0^{\infty} d\omega' \frac{\Delta\alpha(\omega')}{\omega'^2 - \omega^2}, \quad (11)$$

where P indicates the principal value, and the third-order nonlinear susceptibility $\chi^{(3)}$ for Kerr effect can be evaluated by the relationship¹²

$$n_2 = \frac{dn}{dI_p}, \quad (12)$$

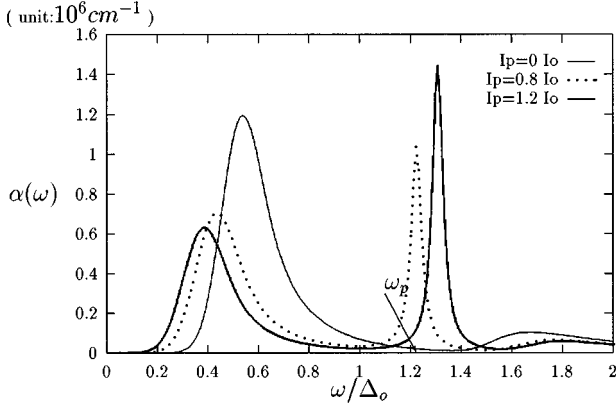


FIG. 1. The probe absorption spectra $\alpha(\omega)$ are shown for various pumping intensities I_p . I_0 is 1 kW/cm^2 . Decay rates are selected as $\gamma = 0.025\Delta_0$, $\gamma_a = 0.001\Delta_0$, $\gamma_b = 0.01\Delta_0$.

$$\chi^{(3)} = \frac{3n_0^2}{(4\pi)^2} n_2. \quad (13)$$

In the following, parameters suitable for *cis*-PA are used for our final numerical calculations: the NDGS confinement parameter $\gamma_e = 0.31$, and band gap $2\Delta_0 = 2.1 \text{ eV}$.⁸ Figure 1 shows the probe absorption spectra $\alpha(\omega)$ for 0.1% dopant concentration under various pumping intensities I_p . The pumping frequency ω_p is selected to be slightly larger than the resonant frequency $\epsilon_+ - \epsilon_- = 1.01\Delta_0$ at zero pumping. As is clearly seen in the figure, the absorption band on the left for ω/Δ_0 below 0.8 is due to the electronic transitions from the valence band to the ϵ_- level, while the small band on the right for ω/Δ_0 larger than 1.5 is due to the electronic transitions from the valence band to the ϵ_+ level. The pump frequency ω_p is equal to $1.225\Delta_0$. We note that the peak position of the left band moves toward smaller photon energies as the pump intensifies. This is because the energy level ϵ_- moves down toward the valence band as its occupation increases. More importantly, when the pump is turned on, a sharp absorption peak shows up for ω/Δ_0 between 1 and 1.5.

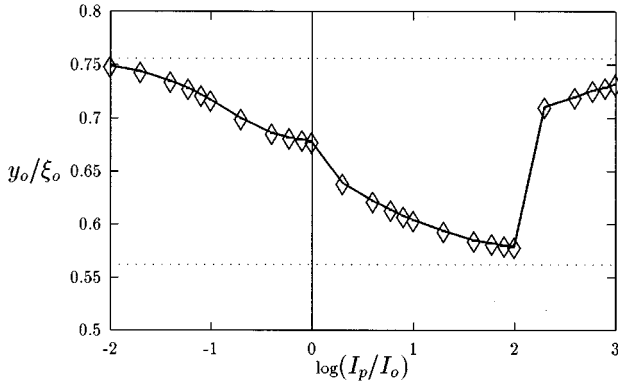


FIG. 2. The pumping dependency of the geometrical size y_0 of the lattice distortion of *p*-type bipolaron is plotted. ξ_0 is the correlation length of soliton kink. The upper dotted line is the pure bipolaron limit ($n_+ - n_- = 0$), and the lower dotted line is the pure polaron limit ($n_+ - n_- = -1$). The solid line is only a guide for the eyes.

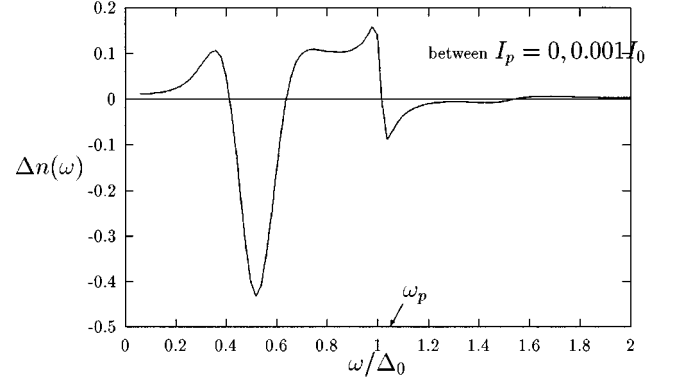


FIG. 3. The refraction index changes $\Delta n(\omega)$ are shown for 1% dopant concentration and $I_p = 0.001I_0$. The pumping frequency ω_p is fixed as $1.05\Delta_0$.

This peak is due to the electronic transition between the discrete levels ϵ_{\pm} . The peak position moves toward higher photon energies, because ϵ_+ and ϵ_- move apart as the electronic occupation increases. The evolution of the bipolaron shape under the same pumping frequency $\omega_p = 1.225\Delta_0$ is shown in Fig. 2. The bipolaron can be seen as a bound kink-antikink pair, ξ_0 is the correlation length of the kink, and y_0 is the distance between the kinks. The distortion profile first approaches a positive polaron (the lower dotted line) due to the gradual filling of the ϵ_- level ($n_+ - n_- \approx -1$). Then the profile evolves nearly into an *n*-type bipolaron (the upper dotted line) after both of the discrete levels are filled ($n_+ - n_- \approx 0$). This is because the occupation of the ϵ_+ level increases rapidly immediately after the ϵ_- level becomes nearly saturated (see the abrupt change at $I_p \approx 100I_0$ in Fig. 2), and $n_+ - n_-$ increases rapidly from -1 up to nearly 0, forming the *n*-type bipolaron.

Figure 3 shows the refraction index change $\Delta n(\omega)$ for 1% dopant concentration, calculated by (11), with $\alpha(\omega) \equiv \alpha(\omega; I_p) - \alpha(\omega; I_p = 0)$, as the pumping intensity increases from zero with $\omega_p = 1.05\Delta_0$. In Fig. 4, we fix

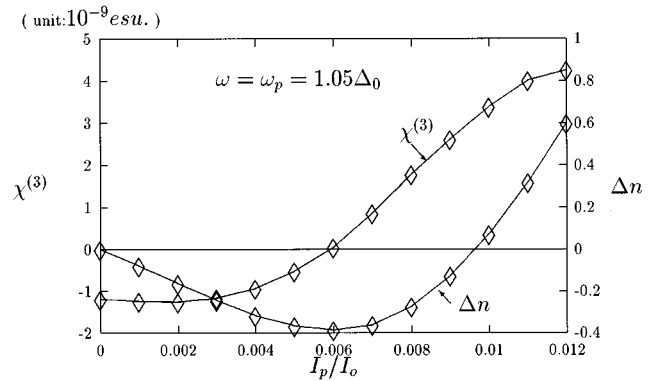


FIG. 4. The refraction index change Δn and the corresponding $\chi^{(3)}$ of *cis*-PA with 1% dopant concentration are plotted as a function of I_p . The frequency of probe light is fixed at the pump frequency (self-modulation) $\omega_p = 1.05\Delta_0$. The sharp absorption peak due to the electronic transition from ϵ_- to ϵ_+ level shifts through this frequency as I_p increases. Such an effect is essential to optimize the resonant nonlinearity.

$\omega_p = 1.05\Delta_0$ and plot $\Delta n(\omega_p)$, the self-phase modulation, as a function of I_p . Much smaller I_p is used in accordance with the conventional perturbative definition of $\chi^{(3)}$. ω_p is deliberately chosen to optimize $\Delta n(\omega_p)$ for this range of I_p . We numerically differentiate Δn with respect to I_p , and obtain the (intensity-dependent) nonlinear refraction index n_2 . Using (13), the corresponding nonlinear susceptibility $\chi^{(3)}$ is shown together with Δn . We find that the $\chi^{(3)}(\omega = \omega_p)$ of *cis*-PA here is of the order 10^{-9} esu for 1% doping. In some NDGS conjugated polymers (see Ref. 19, and references therein), the semiconductor-metal transition^{13–20} will not happen until the dopant concentration becomes as high as 29%. This indicates that the independent bipolaron approximation may be valid up to such dopant densities. Since $\Delta\alpha(\omega)$ and $\Delta n(\omega)$ are both proportional to the dopant con-

centration, $\chi^{(3)}$ may rise up to the order of 10^{-8} esu, or even higher.

In summary, the electronic occupations of the bipolaron-like topological defect are sensitive to the pumping intensity. In the *p*-type bipolaron, photoinduced change in the energies and electronic populations of the discrete intragap levels causes a remarkable third-order optical nonlinearity. $\chi^{(3)}$ can be at least of the order of 10^{-8} esu. Such a mechanism is a resonant mechanism utilizing the lattice repositioning under pumping, and is contrary to the off-resonant phenomena due to purely electronic correlation, as was mostly discussed in other works.

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