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Nonlinear optical response from excitons in soliton lattice systems of doped conjugated polymers

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Abstract. Exciton effects on conjugated polymers are investigated in soliton lattice states. We use the Su–Schrieffer–Heeger model with long-range Coulomb interactions. The Hartree–Fock approximation and the single-excitation configuration-interaction method are used to obtain optical absorption spectra. The third-harmonic generation (THG) at off-resonant frequencies is calculated as a function of the soliton concentration and the chain length of the polymer. The magnitude of the THG at 10% doping increases by a factor of about 10^2 from that of the neutral system. This is due to the accumulation of the oscillator strengths at the lowest exciton with increasing soliton concentration. The increase by the order two is common for various choices of Coulomb interaction strengths.

1. Introduction

Recently, many aspects of effects of electron–electron interactions have been investigated in conjugated polymers. For example, electronic excitation structures in half-filled conjugated polymers with constant bond alternation have been theoretically investigated by using the exciton formalism [1] and the exact diagonalization method [2], and also by solving the time-dependent Hartree–Fock (HF) equations [3]. The roles of excitons were pointed out earlier, but excitation structures have been considered intensively still only recently, as they relate to origins of nonlinear optical spectra [2–4]. The lowest-energy excitation has the largest oscillator strength, which is as the most remarkable consequence of correlation effects. This is clearly seen when the optical spectra calculated by using the HF wavefunctions are compared with the spectra with the correlation effects. This feature is observed when the higher correlations are taken into account by the single-excitation configuration-interaction (single-CI) method [1] and also by the time-dependent HF formalism [3].

It is widely known that the soliton, polaron and bipolaron lattices are present [5] when the SSH model [6], its continuum version [7] and the extended model with the nondegeneracy term [8] are doped with electrons or holes. New bands related to the nonlinear excitations develop in the Peierls gap as the doping proceeds. When correlation effects are considered using the single-CI, the excitation structures exhibit the presence of excitons. In a previous paper [9] we have considered exciton effects in the soliton lattice states of doped conjugated polymers. One kind of exciton occurs in the half-filled system, where the excited electron (hole) sits at the bottom of the conduction band (top of the valence band). We have called this exciton the ‘intercontinuum exciton’ [9]. In the soliton

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lattice states of the doped SSH model for degenerate conjugated polymers, there are small gaps between the soliton band and the continuum states, i.e., between the valence and conduction bands. Therefore, as the number of this kind of exciton increases their presence is reflected in the structures of the optical spectra. A new exciton, which we have called the 'soliton-continuum exciton' [9], appears when the electron-hole excitation between the soliton band and one of the continuum bands is considered. We looked at variations in relative oscillator strengths of the new excitons, the soliton-continuum excitons and the intercontinuum excitons. When the excess electron concentration was small, the ratio of the oscillator strengths of the soliton-continuum exciton to the total oscillator strengths increased almost linearly with the concentration. The oscillator strengths accumulated rapidly at this exciton as the concentration increased. The contribution from the soliton-continuum exciton was more than 90% at the 10% doping.

The purpose of this paper is to investigate how the above changes in the character of the optical excitations are reflected in the nonlinear optical properties. We might be able to realize large optical nonlinearities in soliton lattice systems because the energy gap is small in doped conjugated polymers and the oscillator strengths accumulate rapidly at the soliton-continuum exciton as the doping proceeds. Even though experimental facts concerning the doped polymers have not been reported much, it would be quite interesting to demonstrate theoretically how large optical nonlinearities would be obtained when conjugated polymers are doped with electrons or holes up to concentrations of as much as 10%. The SSH model with the long-range Coulomb interactions of the Ohno expression [10] is solved with the HF approximation, and the excitation wavefunctions of electron-hole pairs are calculated by the single-CI method. We consider the off-resonant nonlinear susceptibility as a guideline to the magnitude of the nonlinearity. In this case multiexcitations, such as double (triple) excitations [11], do not contribute significantly, so we can assume that the single-CI method describes the character of the excitations at off-resonances well. We will calculate the third-harmonic generation (THG) $\chi_{\text{THG}}^{(3)}(\omega) = \chi^{(3)}(3\omega; \omega, \omega, \omega)$ at zero frequency $\omega = 0$, changing the chain length and the soliton concentration. We will show that the magnitude of the THG at 10% doping increases by a factor of about 10^2 from that of the neutral system. This is owing to the accumulation of the oscillator strengths at the lowest exciton with increasing soliton concentration. The increase by the order two is common for several choices of Coulomb interaction strengths.

This paper is composed as follows. In section 2, the model is introduced and the numerical method is explained. Results of the optical nonlinearity are reported and a discussion is given in section 3. The paper is summarized in the final section.

2. Model

We use the SSH hamiltonian [6] with the Coulomb interactions:

$$H = H_{\text{SSH}} + H_{\text{int}}. \quad (1)$$

The first term of equation (1) is:

$$H_{\text{SSH}} = - \sum_{i,\sigma} (t - \alpha y_i) (c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{HC}) + \frac{K}{2} \sum_i y_i^2 \quad (2)$$

where t is the hopping integral of the system without bond alternation; α is the electron-phonon coupling constant which changes the hopping integral linearly with respect to the bond variable y_i ; $c_{i,\sigma}$ is an annihilation operator of the π -electron at the site i with spin σ ; the sum is taken over all the lattice sites of the periodic chain; and the last term with

the spring constant K is the harmonic energy of the classical spring simulating the σ -bond effects. The second term of equation (1) is the long-range Coulomb interaction in the form of the Ohno potential [10]:

$$H_{\text{int}} = U \sum_i \left(c_{i,\uparrow}^\dagger c_{i,\uparrow} - \frac{n_{\text{el}}}{2} \right) \left(c_{i,\downarrow}^\dagger c_{i,\downarrow} - \frac{n_{\text{el}}}{2} \right) + \sum_{i \neq j} W(r_{i,j}) \left(\sum_{\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - n_{\text{el}} \right) \left(\sum_{\tau} c_{j,\tau}^\dagger c_{j,\tau} - n_{\text{el}} \right) \quad (3)$$

where n_{el} is the number of π -electrons per site, $r_{i,j}$ is the distance between the i th and j th sites, and

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/aV)^2}} \quad (4)$$

is the Ohno potential. The quantity $W(0) = U$ is the strength of the on-site interaction, V is the strength of the long-range part, and a is the mean bond length.

The model is treated by the HF approximation and the single-CI method for the Coulomb potential. The adiabatic approximation is applied to the bond variables. The HF order parameters and bond variables are determined selfconsistently using the iteration method [12]. The details of the formalism have been explained in the previous paper [9]. The geometry of a ring with the coordinate of j th carbon atom ($1 \leq j \leq N$)

$$\left(R \cos \frac{2\pi j}{N}, R \sin \frac{2\pi j}{N}, 0 \right) \quad (5)$$

is used to represent a polymer chain, in order to remove edge effects. Here, $R = Na/(2\pi)$ is the radius of the polymer ring, N is the system size, and a is the lattice constant. The electric field of the light is parallel to the x - y plane. The optical absorption spectra where light is parallel to the x and y directions are summed as shown by the following formula:

$$\sum_{\kappa} E_{\kappa} P(\omega - E_{\kappa}) (\langle g|x|\kappa \rangle \langle \kappa|x|g \rangle + \langle g|y|\kappa \rangle \langle \kappa|y|g \rangle). \quad (6)$$

Here, $P(\omega) = \gamma/[\pi(\omega^2 + \gamma^2)]$ is the Lorentzian distribution (γ is the width), E_{κ} is the electron-hole excitation energy, $|\kappa\rangle$ is the κ th excitation, and $|g\rangle$ indicates the ground state.

The THG is calculated with the conventional formula [13-15]:

$$\begin{aligned} \chi^{(3)}(3\omega; \omega, \omega, \omega) &= e^4 N_d \sum_{\kappa, \lambda, \mu} f_{g,\mu} f_{\mu,\lambda} f_{\lambda,\kappa} f_{\kappa,g} \left[\frac{1}{(E_{\mu,g} - 3\omega)(E_{\lambda,g} - 2\omega)(E_{\kappa,g} - \omega)} \right. \\ &+ \frac{1}{(E_{\mu,g}^* + \omega)(E_{\lambda,g} - 2\omega)(E_{\kappa,g} - \omega)} + \frac{1}{(E_{\mu,g}^* + \omega)(E_{\lambda,g}^* + 2\omega)(E_{\kappa,g} - \omega)} \\ &\left. + \frac{1}{(E_{\mu,g}^* + \omega)(E_{\lambda,g}^* + 2\omega)(E_{\kappa,g}^* + 3\omega)} \right] \quad (7) \end{aligned}$$

where N_d is the number density of the crystalline polymer, and this is material dependent. For a demonstration of the magnitude of the THG, we use the value of the number density of the CH unit, which is taken as that for *trans*-polyacetylene: $N_d = 5.24 \times 10^{22} \text{ cm}^{-3}$ [16]. We also use $t = 1.8 \text{ eV}$ in order to look at numerical data in esu units. In equation (7) $f_{\lambda,\kappa} = \langle \lambda|x|\kappa \rangle$ is the dipole matrix element with the electric field parallel with the x axis, $E_{\kappa,g} = E_{\kappa} - E_g$, E_{κ} is the energy of the excited state, and E_g is the energy of the

ground state. In the actual calculation, we change the order of terms so as to take into account the mutual cancellation among them [17]. Also, we include a small imaginary part in the denominator: for example, $E_{\kappa,g} \rightarrow E_{\kappa,g} + i\eta$ and $E_{\kappa,g}^* \rightarrow E_{\kappa,g}^* - i\eta$. This assumes a lifetime broadening and suppresses the height of the delta-function peaks. The THG at $\omega = 0$ does not sensitively depend on the choice of η . This can be checked by varying the broadening. In the next section, we report the results with the value $\eta = 0.02t$.

The system size is chosen as $N = 80, 100, 120$ when the electron number is even (it is varied from $N_{el} = N, N + 2, N + 4, N + 6, N + 8, N + 10$ to $N + 12$), because the size around 100 is known to give well the energy gap value of the infinite chain. Larger system size makes it tedious to do single-CI calculations which call for huge computer memories. In principle, we have to adjust parameters and find appropriate ones in order to reproduce experimental data such as the energy gap and the bond alternation amplitude. But, we will change parameters arbitrarily in a reasonable range in order to look at general properties of the optical nonlinearity. We take two combinations of the Coulomb parameters $(U, V) = (2t, 1t)$ and $(4t, 2t)$ as the representative cases. The other parameters, $t = 1.8$ eV, $K = 21$ eV \AA^{-2} , and $\alpha = 4.1$ eV \AA^{-1} , are fixed in view of the general interests of this paper. All the quantities of energy dimension are shown in units of t .

3. Numerical results and discussion

Figure 1(a) shows the optical absorption spectrum at 2% soliton concentration for $(U, V) = (4t, 2t)$. The broadening $\gamma = 0.05t$ is used. The same data have been used in figure 3(b) of [9]. There are two main features around the energies $0.7t$ and $1.4t$. The former originates from the soliton-continuum exciton, and the latter is from the intercontinuum exciton.

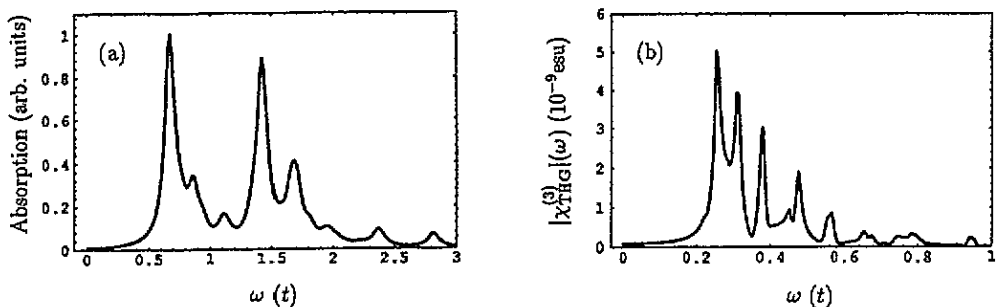


Figure 1. (a) The optical absorption spectrum and (b) the absolute value of the THG, for the system size $N = 100$, the electron number $N_{el} = 102$, and $(U, V) = (4t, 2t)$. The broadening $\gamma = 0.05t$ is used in (a), and $\eta = 0.02t$ is used in (b).

Figure 1(b) displays the absolute value of the THG against the excitation energy ω . The abscissa is scaled by a factor of 3 so that the features in the THG are located at similar points in the abscissa of figure 1(a). The small feature at about $\omega = 0.22t$ comes from the lowest excitation of the soliton-continuum exciton and the larger features at about $\omega = 0.24t$ and $0.32t$ come from the higher excitations. The features from the intercontinuum exciton extend from $\omega = 0.48t$ to the higher energies. In the present calculations, the THG in the energy region above $0.5t$ is not large relatively. The fact that the THG becomes smaller as the excitation energy increases has been seen in the calculations of the half-filled system [4]. However, in the time-dependent HF formalism, the THG at higher energies is still

larger, as shown by figure 4 of [3]. The difference in the distribution of the THG strengths might come from the difference of the approximation method for electron correlations.

The THG data shown, for example, in figure 1(b) are calculated for the three system sizes, $N = 80, 100, 120$, and for soliton concentrations of up to 10%. As clearly seen, for example in figure 1(b), the off-resonant THG at $\omega = 0$ is quite far from features coming from excitons. The contributions from double (triple and so on) excitations would be very small. Thus, the single-CI calculations could be used as a measure of the optical nonlinearities of doped conjugated polymers.

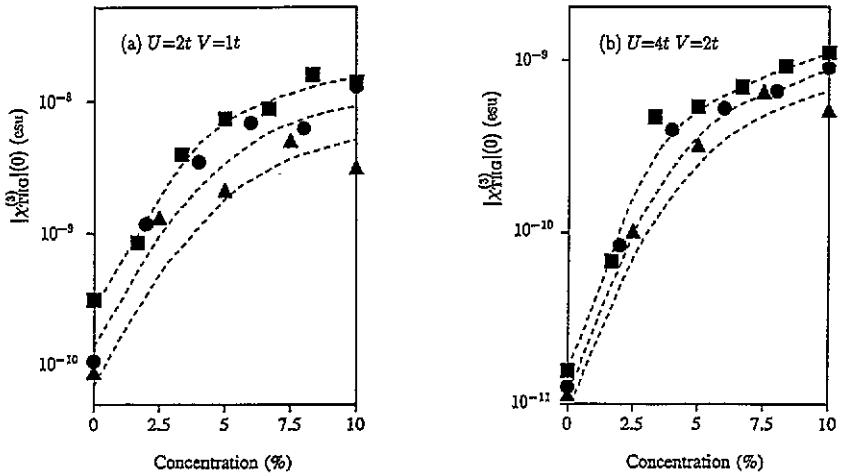


Figure 2. The absolute value of the THG at $\omega = 0$ versus the soliton concentration for (a) $(U, V) = (2t, 1t)$ and (b) $(4t, 2t)$. The numerical data are shown by the triangles ($N = 80$), circles ($N = 100$), and squares ($N = 120$), respectively. The dashed lines are a guide for eyes.

Figures 2(a) and (b) display the variations of the absolute value of $\chi_{\text{THG}}^{(3)}(0)$ for $(U, V) = (2t, 1t)$ and $(4t, 2t)$, respectively. The plots are the numerical data, and the dashed lines are a guide for the eyes, showing the overall behaviour for each system size. The deviations of the plots from the expected smooth behaviour might come from quantum effects due to the finite system size [18]. The linear absorption has size consistency, so the plots of the relative oscillator strengths vary smoothly as functions of the soliton concentration [9]. However, the THG is not size consistent, and spectral shapes depend on the system size when N is as large as 100 [18]. Therefore, it would not be strange for $|\chi_{\text{THG}}^{(3)}(0)|$ to be sensitive to the system size and the soliton concentration. The THG increases as the system size increases. This behaviour is the same as has been seen in the calculations of the half-filled systems [18].

The increase of the off-resonant THG near zero concentration is very rapid, but the THG is still increasing by a few percent up to 10% soliton concentration. The behaviour is similar for the two sets of Coulomb interactions for figures 2(a) and (b). The THG in figure 2(b) is about ten times smaller than that of figure 2(a). This is due to the difference of the interaction strengths. The increase by about a factor of 10^2 at the 10% doping from that of the neutral system seems to be a remarkable fact. This fact might be independent of Coulomb interactions strengths characteristic of optical excitation of the system. Nonlinear optics experiments on doped conjugated polymers have not been much reported. However, the present theory could be used as a guideline for strengths of optical nonlinearities in doped systems.

Why does such a large increase of the THG occur upon doping of the polymers? In the soliton lattice theory with the continuum model [5], the energy gap decreases as the soliton concentration increases. Therefore, it may seem at first that the decrease of the energy gap is one of the reasons. But, as shown in the figure 4 of [9], the lowest optical gap due to single-CI calculations is almost independent of concentration, and thus the change of the optical gap would not be the main reason. However, as we have discussed in [9], the ratio of the oscillator strength of the soliton-continuum exciton to the total oscillator strengths increases very rapidly. In view of this change of the exciton characters, it would be natural to conclude that the increase of the THG by a factor of 10^2 is due to the fact that the oscillator strengths accumulate rapidly at the lowest exciton with increasing soliton concentration.

4. Summary

We have considered off-resonant nonlinear susceptibility as a guideline to the strength of nonlinearity in doped conjugated polymers. We have calculated the off-resonant THG by changing the chain length and the soliton concentration. We have shown that the magnitude of the THG at 10% percent doping increases by a factor of about 10^2 from that of the neutral system. The increase by the order two is common for the various choices of Coulomb interaction strengths.

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