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 (HF) approximation and the single-excitation configuration-interaction (single-CI) method are used to obtain optical absorption spectra. The third-harmonic generation (THG) at off-resonant frequencies is calculated as functions of the soliton concentration and the chain length of the polymer. The magnitude of the THG at the 10 percent doping increases by the factor about 10^2 from that of the neutral system. This is owing to the accumulation

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of the oscillator strengths at the lowest exciton with increasing the soliton concentration. The increase by the order two is common for several choices of Coulomb interaction strengths.

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1. Introduction

Recently, effects of electron-electron interactions have been investigated in many aspects of conjugated polymers. For example, electronic excitation structures in the half-filled conjugated polymers with the 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 recently, relating with origins of nonlinear optical spectra [2-4]. The lowest energy excitation has the largest oscillator strength 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 term of the nondegeneracy [8] are doped with electrons or holes. The new bands related with the nonlinear excitations develop in the Peierls gap as the doping proceeds. When correlation effects are considered by the single-CI, the excitation structures exhibit the presence of excitons. In the previous paper [9], we have considered exciton effects in the soliton lattice states of the doped conjugated polymers. There is one kind of exciton 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 as the

"intercontinuum exciton" [9]. In the soliton 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., valence and conduction bands. Therefore, the number of the kind of excitons increases, and their presence is reflected in structures of the optical spectra. A new exciton, which we have named the "soliton-continuum exciton" [9], appears when the electron-hole excitation is considered between the soliton band and one of the continuum bands. We have looked at variations of relative oscillator strengths of the new excitons, the soliton-continuum and intercontinuum excitons. When the excess-electron concentration is small, the ratio of the oscillator strengths of the soliton-continuum exciton increases almost linearly with respect to the concentration. The oscillator strengths accumulate rapidly at this exciton as the concentration increases. The contribution from the soliton-continuum exciton is more than 90 percent at the 10% doping.

The purpose of this paper is to investigate how the above changes of the characters of optical excitations are reflected in the nonlinear optical properties. We might be able to realize large optical nonlinealities 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 of the doped polymers have not been reported so 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 as much as 10 percent. 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. We consider the off-resonant nonlinear susceptibility as a guideline of the magnitude of the nonlinearity. In this case, multi excitations, such as double (triple) excitations [11], do not contribute significantly, so we can assume that the single-CI well describes the characters of excitations at off-resonances. We will calculate the third harmonic generation (THG) $\chi^{(3)}_{\rm THG}(\omega) = \chi(3\omega;\omega,\omega,\omega)$ at the zero frequency $\omega = 0$, with changing the chain length and the soliton concentration. We will show that the magnitude of the THG at the 10 percent doping increases by the factor 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 the soliton concentration. The increase by the order two is common for several choices of Coulomb interaction strengths.

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

2. Model

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

$$H = H_{\rm SSH} + H_{\rm int}. \tag{1}$$

The first term of eq. (1) is:

$$\begin{aligned} H_{\rm SSH} &= -\sum_{i,\sigma}(t-\alpha y_i)(c^\dagger_{i,\sigma}c_{i+1,\sigma} + \text{h.c.}) \\ &+ \frac{K}{2}\sum_i y_i^2, \end{aligned} \tag{2}$$

where t is the hopping integral of the system without the 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 eq. (1) is the long-range Coulomb interaction in the form of the Ohno potential [10]:

$$\begin{aligned} H_{\rm int} &= U\sum_i (c^\dagger_{i,\uparrow}c_{i,\uparrow} - \frac{n_{\rm el}}{2})(c^\dagger_{i,\downarrow}c_{i,\downarrow} - \frac{n_{\rm el}}{2}) \\ &+ \sum_{i\neq j} W(r_{i,j})(\sum_\sigma c^\dagger_{i,\sigma}c_{i,\sigma} - n_{\rm el})(\sum_\tau c^\dagger_{j,\tau}c_{j,\tau} - n_{\rm el}), \end{aligned} \tag{3}$$

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

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

is the Ohno potential. The quantity $W(0) = U$ is the strength of the onsite interaction, V means 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 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]. A geometry of a ring with the coordinate of jth carbon atom ($1 \leq j \leq N$),

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

is used for 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 light is parallel to the x-y plane. The optical absorption spectra where light is along with the x- and y-directions are summed as shown by the following formula:

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

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 κth excitation, and $|g\rangle$ means the ground state.

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

$$\begin{aligned}
\chi^{(3)}(3\omega;\omega,\omega,\omega) &= e^4 N_{\rm d} \sum_{\kappa,\lambda,\mu} f_{g,\mu} f_{\mu,\lambda} f_{\lambda,\kappa} f_{\kappa,g} \\
&\times [\frac{1}{(E_{\mu,g} - 3\omega)(E_{\lambda,g} - 2\omega)(E_{\kappa,g} - \omega)} \\
&+ \frac{1}{(E^*_{\mu,g} + \omega)(E_{\lambda,g} - 2\omega)(E_{\kappa,g} - \omega)} \\
&+ \frac{1}{(E^*_{\mu,g} + \omega)(E^*_{\lambda,g} + 2\omega)(E_{\kappa,g} - \omega)} \\
&+ \frac{1}{(E^*_{\mu,g} + \omega)(E^*_{\lambda,g} + 2\omega)(E^*_{\kappa,g} + 3\omega)}],
\end{aligned} \tag{7}$$

where, $N_{\rm d}$ is the number density of the crystalline polymer, and this is material-dependent. For demonstration of the magnitude of the THG, we use the value of the number density of the CH unit, which is taken from *trans*-polyacetylene: $N_{\rm d} = 5.24 \times 10^{22}{\rm cm}^{-3}$ [16]. We also use $t = 1.8$eV in order to look at numerical data in the esu unit. In eq. (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 mu-

tual cancellation among them [17]. Also, we include a small imaginary part in the denominator: for example, $E_{\kappa,g} \to E_{\kappa,g} + \mathrm{i}\eta$ and $E^*_{\kappa,g} \to E^*_{\kappa,g} - \mathrm{i}\eta$. 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 $N_{\rm el} = N, N+2, N+4, N+6, N+8, N+10$ to $N+12$), because the size around 100 is known to give well the energy gap value of the infinite chain. More larger system size becomes tedious for doing 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 arbitrary 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/Å^2, and $\alpha = 4.1$eV/Å, are fixed in view of the general interests of this paper. All the quantities of energy dimension are shown in the units of t.

3. Numerical Results and Discussion

Figure 1(a) shows the optical absorption spectrum at the 2% soliton concentration for $(U, V) = (4t, 2t)$. The broadening $\gamma = 0.05t$ is used. The same data have been used in Fig. 3(b) of the ref. [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(b) displays the absolute value of the THG against the excitation energy ω. The abscissa is scaled by the factor 3 so that the features in the THG locate at the similar points in the abscissa of Fig. 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 higher than $0.5t$ is not large relatively. The point, 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 in higher energies is still larger as shown by Fig. 4 of the ref. [3]. The difference of the distribution of the THG strengths might come from the difference of the approximation method for electron correlations.

The THG data like in Fig. 1(b) are calculated for the three system sizes, $N = 80$, 100, 120, and for the soliton concentrations up to 10%. As clearly seen for example in Fig. 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.

Figures 2(a) and (b) display the variations of the absolute value of $\chi^{(3)}_{\rm THG}(0)$ for $(U, V) = (2t, 1t)$ and $(4t, 2t)$, respectively. The plots are the numerical data, and the dashed lines are the guide for eyes, showing the overall behavior for each system size. The deviations of the plots from the expected smooth

behavior might come from the quantum effect due to the finite system size [18]. The linear absorption has the size consistensy, 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 even if $|\chi^{(3)}_{\rm THG}|(0)$ is sensitive to the system size and the soliton concentration. The THG increases as the system size increases. This behavior 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 for a few percent to 10% soliton concentration. The behavior is similar for the two sets of the Coulomb interactions for Figs. 2(a) and (b). The THG in Fig. 2(b) is about ten times smaller than that of Fig. 2(a). This is due to the difference of the interaction strengths. The increase by about the factor 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 to optical excitation of the system. The experiments of nonlinear optics on doped conjugated polymers have not been reported so many times. However, the present theory could used as one of guidelines for strengths of optical nonlinearities in doped systems.

Then, why such the large increase of the THG would 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 first that the decrease of the energy gap is one of the reasons. But, as shown in the Fig. 4 of the ref. [9], the lowest optical gap due to the single-CI calculations is almost independent of the 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 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 the factor 10^2 is due to the fact that the oscillator strengths accumulate rapidly at the lowest exciton with increasing the soliton concentration.

4. Summary

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

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Figure Captions

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

Fig. 2. The absolute value of the THG at $\omega = 0$ v.s. 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 the guide for eyes.