Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Exciton Effects and Nonlinear Optical Response in Soliton Lattice States of Doped Conjugated Polymers

Kikuo Harigaya [a], Yukihiro Shimoi [a] & Shuji Abe [a]

[a] Electrotechnical Laboratory, Tsukuba, Ibaraki, 305, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Kikuo Harigaya , Yukihiro Shimoi & Shuji Abe (1996): Exciton Effects and Nonlinear Optical Response in Soliton Lattice States of Doped Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 283:1, 271-276

To link to this article: http://dx.doi.org/10.1080/10587259608037899

Mol. Cryst. Liq. Cryst., 1996, Vol. 283, pp. 271–276
Reprints available directly from the publisher
Photocopying permitted by license only

EXCITON EFFECTS AND NONLINEAR OPTICAL RESPONSE IN SOLITON LATTICE STATES OF DOPED CONJUGATED POLYMERS

KIKUO HARIGAYA, YUKIHIRO SHIMOI, AND SHUJI ABE
Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan

Abstract Exciton effects on conjugated polymers are investigated in the soliton lattice system. We use the Su-Schrieffer-Heeger model with long-range Coulomb interactions treated by the single-excitation configuration-interaction method. The soliton band is present in the Peierls gap of the doped system. There appears a new kind of the exciton where an electron-hole pair is excited between the soliton band and the continuum states. We find that the oscillator strengths accumulate rapidly at this exciton as the soliton concentration increases. The contribution from the lowest exciton is more than 90% at the 10% doping. The third-harmonic generation (THG) at off-resonance frequencies is calculated as functions of the soliton concentration and the chain length of the polymer. The optical nonlinearity by the THG at the 10% doping increases by the factor about 10^2 from that of the neutral system.

INTRODUCTION

Recently, the roles and excitation structures of excitons in conjugated polymers have been investigated intensively, relating with the origins of nonlinear optical spectra.[1–4] The lowest energy excitation has the largest oscillator strength as the most remarkable consequence of correlation effects. This feature is observed when the correlations are taken into account by the single-excitation configuration-interaction (single-CI) method[1] and also by the time-dependent Hartree-Fock (HF) formalism.[4]

It is widely known that the soliton lattice state is realized[5] when the Su-Schrieffer-Heeger (SSH) model[6] is doped with electrons or holes. The soliton band develops 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 this paper, we consider exciton effects in the soliton lattice state. There is one kind of the 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 call this exciton as the "intercontinuum exciton". In the soliton lattice state, 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 name the "soliton-continuum exciton", appears when the electron-hole excitation is considered between the soliton band and one of the continuum bands. We look at variations of relative oscillator strengths of the new excitons, the soliton-continuum and intercontinuum excitons.

Next, we look at how the above changes of the characters of optical excitations are reflected in the nonlinear optical properties. We will be able to realize large optical nonlinealities in the soliton lattice system, because the energy gap is small in doped conjugated polymers. We consider the off-resonant nonlinear susceptibility as a guideline of the magnitude of the nonlinearity. We calculate the third harmonic generation (THG) at zero frequency, with changing the chain length and the soliton concentration. We show that the optical nonlinearity by 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.

MODEL AND METHOD

The SSH hamiltonian[6] is considered with the long-range Coulomb interactions, $1/\sqrt{(1/U)^2 + (r/aV)^2}$, whrere U is the strength of the onsite interaction, V means the strength of the long range part, r is the distance between atom sites, 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 lattice. The HF order parameters and dimerization amplitudes are determined selfconsistently using the iteration method. The details of the formalism have been explained in the previous paper.[7] A geometry of a ring with the radius $Na/2\pi$ is used for a polymer chain with N carbon sites. The electric field of light is in the molecular plane. The THG is calculated with the sum-over-states method. 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: $N_d = 5.24 \times 10^{22}\text{cm}^{-3}$.[8] We also use the average hopping integral $t = 1.8\text{eV}$ in order to look at numerical data in the esu unit. The system size is chosen as $N = 80, 100$, and 120, because the size around 100 is known to give well the energy gap value of the infinite chain. The excess electron number is taken upto the 10% doping. We take one combination of the Coulomb parameters $(U, V) = (4t, 2t)$ as the representative case. The parameters in the SSH model[6] are $t = 1.8\text{eV}$, the spring constant $K = 21\text{eV/Å}^2$, and the electron-lattice coupling $\alpha = 4.1\text{eV/Å}$. Most of the quantities of energy dimension are shown in the units of t.

EXCITON EFFECTS IN OPTICAL SPECTRA

Figure 1(a) shows the optical absorption spectrum at the 2% soliton concentra-

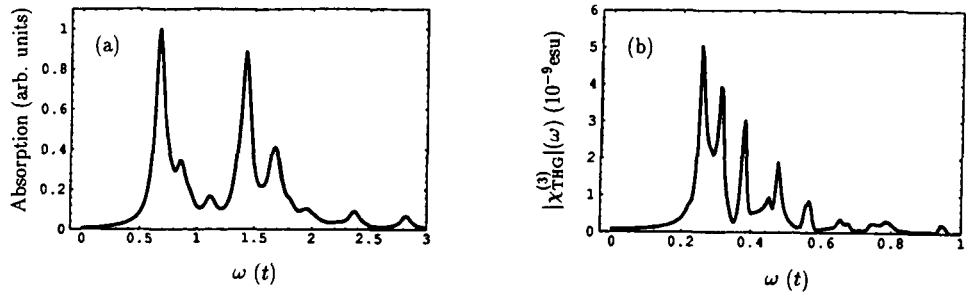

FIGURE 1 (a) The optical absorption spectrum and (b) the absolute value of the THG, for the system size $N = 100$, the electron number $N_{el} = 102$, and $(U, V) = (4t, 2t)$. The broadening $0.05t$ is used in (a), and $0.02t$ is used in (b).

tion. The broadening $0.05t$ is used. 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

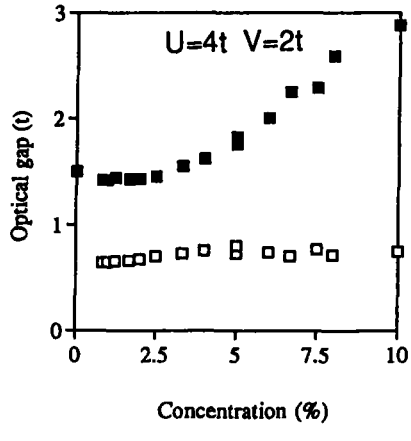

FIGURE 2 The optical gaps in the single-CI of the "intercontinuum exciton" (filled squares) and of the "soliton-continuum exciton" (open squares), plotted against the soliton concentration.

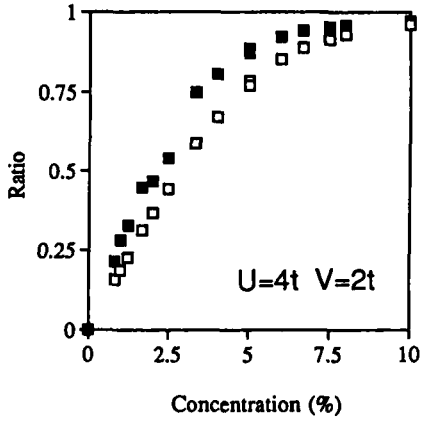

FIGURE 3 The ratio of the total oscillator strength of the "soliton-continuum exciton" as a function of the soliton concentration. The open squares are the data for the HF absorption, while the filled ones for the HF-CI absorption.

by Fig. 4 of ref. 4. The difference of the distribution of the THG strengths might come from the difference of the approximation method for electron correlations.

Figure 2 summarizes the optical gaps of the two kinds of excitons. The optical gap of the soliton-continuum exciton is almost independent of the concentration. The gap of the intercontinuum exciton increases rapidly when the concentration is larger than 2.5 percent. This is due to the fact that the number of states in the soliton band increases, and thus the energy gap between continuum states increases.

Figure 3 shows the ratio of the oscillator strengths of the soliton-continuum exciton with respect to the total oscillator strengths, plotted against the soliton concentration. The closed and open squares are the results of the HF-CI and HF calculations, respectively. The closed squares have the larger ratio than the open ones. This is one of exciton effects. When the concentration is near zero, the ratio varies almost linearly. This would be the natural consequence for low concentrations, because interactions among solitons are exponentially small and thus the ratio is proportional to the number of solitons. The increase of the ratio saturates at about 7 percent. The soliton-continuum exciton becomes like a free exciton at larger concentrations owing to the formation of the soliton band.

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.

Figure 4 displays the variations of the absolute value of $\chi^{(3)}_{\rm THG}(0)$ for $(U, V) = (4t, 2t)$. The deviations of the plots from the expected smooth behavior might come from the quantum effect due to the finite system size.[9] The linear absorption has

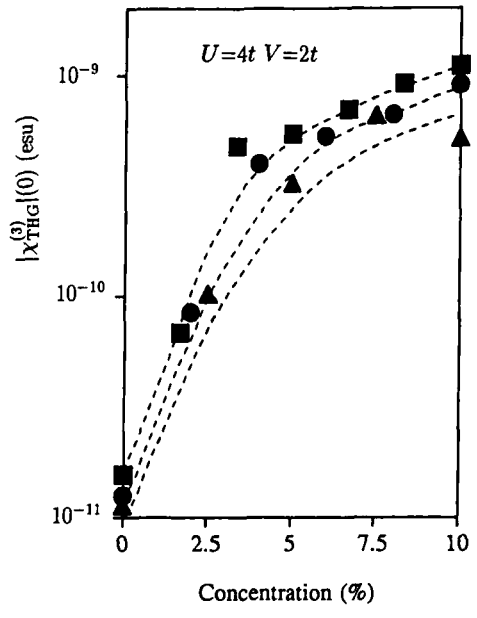

FIGURE 4 The absolute value of the THG at $\omega = 0$ v.s. the soliton concentration for $(U, V) = (4t, 2t)$, shown in the esu unit. The numerical data are shown by the triangles ($N = 80$), circles ($N = 100$), and squares ($N = 120$), respectively. The dashed lines are the guide for eyes.

the size consistensy, so the plots of the relative oscillator strengths vary smoothly as functions of the soliton concentration as shown in Fig. 3. However, the THG is not size consistent, and spectral shapes depend on the system size when N is as large as 100.[9] 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.[9] 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.

Then, why such the large increase of the THG would occur upon doping of the polymers? In the soliton lattice theory by 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. 2, the lowest optical gap is almost independent of the concentration, and thus the change of the optical gap would not be the main reason. However, 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.

SUMMARY

Exciton effects have been investigated in the soliton lattice system. There appears a new kind of the exciton where an electron-hole pair is excited between the soliton band and the continuum states. 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 optical nonlinearity at the 10 percent doping increases by the factor about 10^2 from that of the neutral system. We have discussed that this is owing to the accumulation of the oscillator strengths at the lowest exciton with increasing the soliton concentration.

REFERENCES

1. S. Abe, J. Yu, and W. P. Su, Phys. Rev. B, 45, 8264 (1992).
2. S. Abe, M. Schreiber, W. P. Su, and J. Yu, Phys. Rev. B, 45, 9432 (1992).
3. D. Guo, S. Mazumdar, S. N. Dixit, F. Kajzar, F. Jarka, Y. Kawabe, and N. Peyghambarian, Phys. Rev. B, 48, 1433 (1993).
4. A. Takahashi and S. Mukamel, J. Chem. Phys., 100, 2366 (1994).
5. B. Horovitz, Phys. Rev. Lett., 46, 742 (1981).
6. W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B, 22, 2099 (1980).
7. K. Harigaya, Y. Shimoi, and S. Abe, J. Phys.: Condens. Matter, 7, 4061 (1995).
8. C. R. Fincher, C. E. Chen, A. J. Heeger, A. G. MacDiarmid, and J. B. Hastings, Phys. Rev. Lett., 48, 100 (1982).
9. S. Abe, M. Schreiber, W. P. Su, and J. Yu, J. Lumin. 53, 519 (1992).