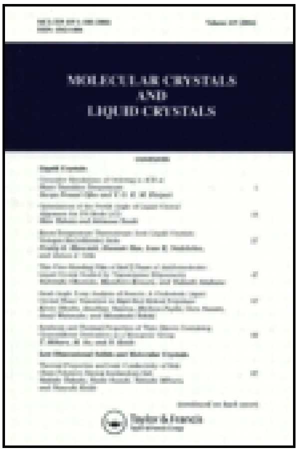

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Two- and Three-Photon Resonances in Conjugated Polymers

Chang-Qin Wu [a]
[a] Department of Physics, Fudan University, Shanghai, 200433, China

To cite this article: Chang-Qin Wu (1994): Two- and Three-Photon Resonances in Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 637-642

To link to this article: http://dx.doi.org/10.1080/10587259408039303

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 637–642
Reprints available directly from the publisher
Photocopying permitted by license only

TWO- AND THREE-PHOTON RESONANCES IN CONJUGATED POLYMERS

CHANG-QIN WU
Department of Physics, Fudan University, Shanghai 200433, China

Abstract There are two peaks observed in the third-harmonic generation (THG) of polyacetylene. The first peak at 0.6 eV is a three-photon resonance enhancement due to the first one-photon excited state 1^1B_u. What's the nature of the second peak at 0.9 eV? Within an interacting-electron model, we investigated the excitonic states in conjugated polymers. Our calculation suggests that the second peak is a three-photon resonance enhancement due to the edge of the continuum excitation band.

INTRODUCTION

It has been known that organic conjugated polymers have a great potential in practical use due to their peculiar electrical, magnetical, and optical properties.[1] Recent experimental studies further demonstrated that conjugated polymers, especially *trans*-polyacetylene, possess exceedingly large third-order susceptibility, $\chi^{(3)} \sim 10^{-9}$ esu, and extremely short response time, $\sim$ 0.1 ps.[2] Such significant properties suggest that the conjugated polymers are a promising candidate for high-speed nonlinear optical materials. However, many important phenomena in the nonlinear optical susceptibilities of conjugated polymers have not been understood yet. One of them is that the spectrum of third-harmonic generation (THG) $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of *trans*-polyacetylene has two peaks near $\hbar\omega = 0.6$ and 0.9 eV.[3] While the main peak at 0.6 eV is obviously the three-photon resonance enhancement, since the optical gap of *trans*-polyacetylene is about 1.8 eV[4], the understanding of the second peak is a controversial issue.

At first sight, the second peak at 0.9 eV of THG seems a two-photon resonance enhancement. However, a careful analysis shows that two-photon absorption in such a one-dimensional rigid lattice is forbidden by the momentum conservation.[5] A recent study gave that the dispersion of the optical nonlinearity could be fitted quite well by use of a three- or four-level model[6], which shows that only a few excited states are responsible for the observed third-order optical nonlinearity of the polymeric materials. Futhermore, the exact numerical solutions for very short chains suggested that these essential states are 1^1B_u, m^1A_g (always lays between 1^1B_u and 2^1B_u), and n^1B_u (the band threshold state).[7] But the understanding of THG spectrum needs a more careful study on the excited states, specially these excitonic states. Although, there have been many works on the excited states in a linear polyene, but most of them are for a very short polyene (a typical length is about 20 sites).[8] However, a much longer polyene is needed for an excitonic state of an interacting electron system.

In this paper, we employ a random phase approximation (RPA) to treat bound-exciton states in a one-dimensional Peierls-extended Hubbard model. Our calculation within the RPA can be performed for the system with any sizes. We found only one excitonic state (1^1B_u) with the resonable interaction strength for the conjugated polymers, and the second excitonic state (2^1A_g) appears for a relative strong interaction. The spectrum of third-hamonic generatioin within such a picture shows that the first two resonance peaks are three-photon resonance enhancements due to the first one-photon state 1^1B_u and the edge states of the continuum excitation band.

RADOM PHASE APPROXIMATION

We start from the one-dimensional Peierls-extended Hubbard model

$$H = -t\sum_{i,\sigma}(1 \pm z)(c^\dagger_{i,\sigma}c_{i+1,\sigma} + h.c.) + U\sum_i n_{i,\uparrow}n_{i,\downarrow} + V\sum_i n_i n_{i+1}, \tag{1}$$

where $c^\dagger_{i,\sigma}$ creates an electron of spin σ at site i, $n_{i,\sigma} = c^\dagger_{i,\sigma}c_{i,\sigma}$, $n_i = \sum_\sigma n_{i,\sigma}$, U and V are the on-site and nearest-neighbor interactions, t the hopping integral between the nearest-neighbor sites, and z the gap order parameter, and + for short bonds and − for long bonds. In the below, we will take $t = 1$ as the unit of energy.

For a half-filled system, the ground state is of a dimerized lattice, which belongs to C_{2h} point group so that only two symmetries – symmetric A_g and antisymmetric B_u – exist under the central mirror reflection for a polyene. At thermodynamic limit, it is easy to distingush the excitonic states, which must appear as separete levels while the extended states forms a continuum excitation band. Here, we take a radom phase approximation (RPA)[9] to treat electron-hole excitations from the mean-field ground state. Due to the nature of RPA, the continuum excitation band will remain unchanged as the HF result. The correlation effect on this continuum band has been considered earlier.[10] In this section, we only concentrate on these bound-excitons. So we fix the gap order parameter $z (= 0.18)$ as an effective quantity, which gives a resonable band gap $(4z)$ for conjugated polymers. These bound-excitons appear in the band gap and their positions are considered to be relative to the band gap.

Within the RPA, the singlet electron-hole excitation

$$\varsigma^{\dagger}(l) = \frac{1}{\sqrt{N}} \sum_{n} (a^{\dagger}_{n+l,\uparrow} b^{\dagger}_{n,\downarrow} + a^{\dagger}_{n+l,\downarrow} b^{\dagger}_{n,\uparrow}) \tag{2}$$

satisfies the boson commutation relation. The electrons $a_{n,\sigma}$ and holes $b_{n,\sigma}$ are eigen-operators at the mean field approximation, l is the electron-hole separation and N is the number of carbon atoms. Then the Hamiltonian under the RPA will be

$$H_{\text{RPA}} = \sum_{l_1,l_2} \{\varepsilon(l_1,l_2)\varsigma^{\dagger}(l_1)\varsigma(l_2) + \frac{1}{2}u(l_1,l_2)[\varsigma^{\dagger}(l_1)\varsigma^{\dagger}(l_2) + \varsigma(l_1)\varsigma(l_2)]\} \tag{3}$$

where

$$\begin{aligned} \varepsilon(l_1,l_2) &= 2\epsilon(l_1 - l_2) + \frac{1}{2}(U - 4V)\delta_{l_1,0}\delta_{l_2,0} - V\{g(l_1)g(l_2) \\ &\quad + g(-l_1)g(-l_2) + g(l_1 - 1)g(l_2 - 1) + g(-l_1 - 1)g(-l_2 - 1)\}, \qquad (4) \\ u(l_1,l_2) &= \frac{1}{4}(U - 4V)\delta_{l_1,0}\delta_{l_2,0} + V\{g(l_1)g(-l_2) + g(l_2)g(-l_1) \\ &\quad + g(-l_1 - 1)g(l_2 - 1) + g(-l_2 - 1)g(l_1 - 1)\}, \qquad (5) \end{aligned}$$

and $\epsilon(l)$ is the Fourier transformation of the single electron energy spectrum and $g(l)$ is the correlation function in the mean-field ground state. The approximative hamiltonian could be easily diagonalized by the Bogoliubov transformation.

RESULTS AND DISCUSSIONS

In the last section, we have established the formulas for the electron-hole excitations within the RPA. The numerical calculations are easily performed for the system of up to several thousand sites. The results and discussions are given as follows.

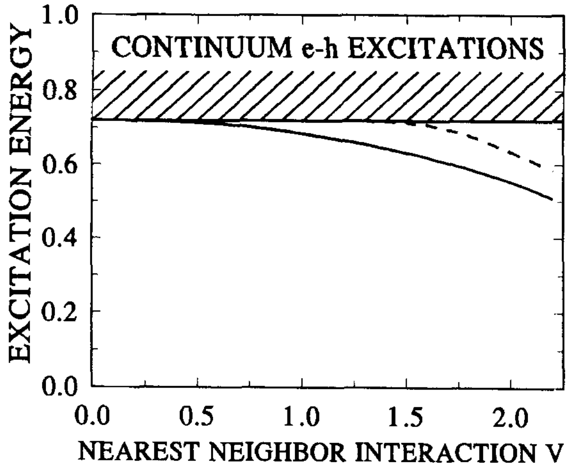

FIGURE 1 The excitation energies of 1^1B_u (solid line) and 2^1A_g (dashed line) states as a function of the interaction V for $U = 4V$.

Excitonic States

The dependence of the excitation energies on the interaction V for $U = 4V$ is displayed in Figure 1. It is clear that the interaction V serves as an attraction potential between electrons and holes. No matter how small V is, at least one bound-exciton (1^1B_u) exists. This is a character of one-dimensional systems. The second bound-exciton (2^1A_g) will emerge at $V = 1.32$, which is independent of the parameter U at the RPA.

For a long-range electron interaction, such as the Ohno's formula for the interaction $V_{ll'}$ between the electrons at sites l and l',[10] we can do a similar calculation, which gives the same picture of excitonic states but a few more levels very close to the edge of continuum excitation band. This result is similar with that of the calculation within a single electron-hole subspace.[11]

Third Harmonic Generation

For conjugated polymers, there have been many evidences that the nearest neighbour electron interaction V is not larger than the value of the hopping integral t_0.[10] With this interaction, we believe that the second excitonic state 2^1A_g does not appear or appears very close to the edge of the continuum excitation band. In any cases, the first two important states are the 1^1B_u excitonic state and the edge states of the continuum excitation band.

Under the picture of these excitation states, the spectrum of third harmonic generation $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ gives that the first two peaks are the three-photon resonance enhancements at $E_g/3$ (E_g the optical gap) due to the excitonic state 1^1B_u and at $E_b/3$ (E_b the band gap) due to the edge states of the continuum excitation band, respectively. A possible two-photon resonance peak due to the second excitonic state 2^1A_g is at a much higher position ($\sim E_b/2$).

Remarks

The experiments[3] indicate that the position of the two peaks at the third harmonic generation of polyacetylene has a ratio 2 : 3, however, the ratio of the first two peaks we found is $E_g : E_b$, a much small value. The fact implies that we should consider more effects, such as electron correlation and lattice relaxation, to reach a quantitative agreement. We have known that the electron correlation will increase the value of E_b[10] and the lattice relaxation will decrease the value of E_g. These effects are considering carefully in further work.

ACKNOWLEDGEMENTS

The author would like to thank the National Natural Science Foundation of China for the research fellowship at T.D. Lee Physics Laboratory of Fudan Univerrsity. The supports from the Shanghai Qi-Ming-Xing Plan for Young Scientists and the State Education Commission of China are acknowledged.

REFERENCES

1. Yu Lu, Solitons & Polarons in Conducting Polymers (World Scientific, Singapore, 1988); A.J. Heeger, S. Kivelson, J.R. Schrieffer, and W.P. Su, Rev. Mod. Phys. 60, 7781(1988).
2. See, for example, Organic Molecules for Nonlinear Optics and Photonics, edited by J. Messier, F. Kajzar, and P. Prasad, NATO Advanced Study Institute Series Vol. E194(Kluwer, Dordrecht, 1991).
3. F. Kajzar, S. Etemad, G.L. Baker, and J. Messier, Synth. Met. 17, 343(1987); W.S. Fann, S. Benson, J.M.J. Madey, S. Etemad, G.L. Baker, and F. Kajzar, Phys. Rev. Lett. 62, 1492(1989).

4. N. Suzuki, M. Okazaki, S. Etemad, A.J. Heeger, And A.G. MacDiarmid, Phys. Rev. Lett. 45, 1209(1980).

5. C.Q. Wu and X. Sun, Phys. Rev. B41, 12845(1990); B42, 9736(1990).

6. A.K. Agrawal, S.A. Jenekhe, H. Vanherzeele, and J.S. Meth, J. Phys. Chem., 96, 2837(1992).

7. D. Guo, S. Mazumdar, and S.N. Dixit, Synth. Met. 49-50, 1(1992).

8. Z.G. Soos, G.W. Hayden, P.C.M. McWillams, and S. Etemad, J. Chem. Phys. 93, 7439(1990).

9. J. Lorenzana, M.D. Grynberg, L. Yu, K. Yonemitsu, and A.R. Bishop, Phys. Rev. B47, 13156(1993).

10. C.Q. Wu, Phys. Rev. B47, 4204(1993).

11. S. Abe, J. Yu, and W.P. Su, Phys. Rev. B45, 8264(1992); S. Abe, M. Schreiber, W.P. Su, and J. Yu, *ibid.* B45, 9432(1992).