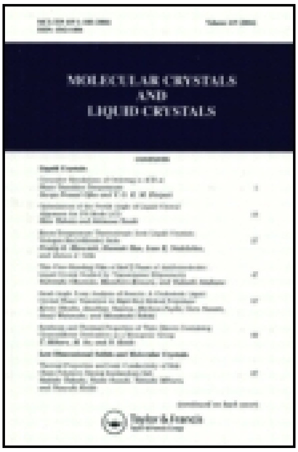

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Theory of Optical Absorption in Doped Conjugated Polymers

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

[a] Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, 305, Japan

To cite this article: Yukihiro Shimoi , Shuji Abe & Kikuo Harigaya (1995): Theory of Optical Absorption in Doped Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 329-334

To link to this article: http://dx.doi.org/10.1080/10587259508034012

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 329–334
Reprints available directly from the publisher
Photocopying permitted by license only

THEORY OF OPTICAL ABSORPTION IN DOPED CONJUGATED POLYMERS

YUKIHIRO SHIMOI, SHUJI ABE, and KIKUO HARIGAYA
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305, Japan

Abstract The optical absorption of polarons and bipolarons in doped conjugated polymers is investigated theoretically. The Pariser-Parr-Pople model in the present paper includes long-range electron-electron (e-e) interactions, electron-lattice coupling of the Su-Schrieffer-Heeger type, and modulation in transfer integral lifting the degeneracy of the ground state. The calculations by mean of the single configuration-interaction method with unrestricted Hartree-Fock molecular orbitals show that a polaron (bipolaron) gives rise to two (one) absorption peaks below the optical gap even in the presence of the e-e interaction. The peak positions depend on the interaction strength.

INTRODUCTION

Doping into conjugated polymers brings about drastic changes in their electronic and optical properties:[1] Electric conductivity rises up by several orders of magnitude. New absorption appears below the optical gap. These changes are associated with the formation of solitons, polarons, and bipolarons. In most of conjugated polymers, except for *trans*-polyacetylene, soliton formation is inhibited due to their non-degenerate ground state, so that polarons and bipolarons are the candidates of charge carriers. The Brazovskii-Kirova (BK) model indicated that a bipolaron is favorable energetically than two separated polarons in non-degenerate conjugated polymers.[2]

According to the BK model, the formation of a polaron or a bipolaron is accompanied by two localized single-particle levels in the gap. Three (two) optical transitions are allowed associated with these levels in the case of a polaron (bipolaron).[3] Many experiments showed that two sub-gap absorption peaks with comparable intensities are induced upon doping.[4] So far, the peaks have been ascribed to bipolarons. The BK model predicts that the oscillator strength of the highest transition is much weaker than the others,[3] in contradiction with the experiments. It was reported that the breaking of the charge-conjugation (CC) symmetry can change the ratio of absorption intensities.[5,6] Recently, Furukawa reexamined this problem experimentally by referring the absorption spectra of oligomers and assigned the two sub-gap peaks to the absorption of *polarons*.[7]

It is important to elucidate the role of electron-electron (e-e) interaction for the intensity problem, since the significance of the interaction (which is ignored in the BK model) has been pointed out in many aspects of conjugated polymers. Nevertheless, only few theoretical works on this issue have been carried out within a perturbational theory [8,9] or in a strong coupling limit.[8] However, these approaches are not suitable for the intermediate strength of the interaction. In this paper, we use the single configuration-interaction (S-CI) method with unrestricted Hartree-Fock (UHF) molecular orbitals (MO) to investigate the effects of e-e interaction on the optical absorption of a polaron and a bipolaron in the intermediate interaction regime.

MODEL

We consider π electrons on a liner chain consisting of N sites. The operator $C^\dagger_{n,\sigma}$ creates a π electron with spin σ at site n. We use the Pariser-Parr-Pople model given by,

$$\begin{aligned} H = &-\sum_{n,\sigma} t_{n,n+1}(C^\dagger_{n+1,\sigma}C_{n,\sigma} + C^\dagger_{n,\sigma}C_{n+1,\sigma}) \\ &+\sum_{n} U\rho_{n\uparrow}\rho_{n\downarrow} + \sum_{n\neq m}\sum_{\sigma,\sigma'} \frac{V}{2|n-m|}\rho_{n,\sigma}\rho_{m,\sigma'} + \sum_{n}\frac{K}{2}(u_{n+1}-u_n)^2 . \end{aligned} \tag{1}$$

Here, $\rho_{n,\sigma} = C^\dagger_{n,\sigma}C_{n,\sigma}$ and u_n is the displacement of n-th site. The first line in the r.h.s. of Equation (1) indicates the hopping of a π electron among nearest neighbor sites. The hopping integral $t_{n,n+1}$ includes the BK term δ_0 which lifts the degeneracy of the ground state and the electron-lattice coupling α of the Su-Schrieffer-Heeger (SSH) type:[10]

$$t_{n,n+1} = [1+(-1)^n\delta_0]t - \alpha(u_{n+1}-u_n). \tag{2}$$

The first and second terms in the second line of Equation (1) indicate on- and off-site e-e interactions, respectively. The last term is the elastic energy of lattice. The periodic boundary condition is imposed to the system. In this paper, we take the dimensionless coupling constant $\lambda = 2\alpha^2 / \pi t K = 0.2$, which is the original value of the SSH model.[10] A smaller value, e.g., $\lambda = 0.136$ in our previous papers,[11,12] is more realistic, but we use $\lambda = 0.2$ to allow a HF self-consistent solution for a bipolaron in the case of intermediate e-e interaction.

The UHF approximation is applied to the Hamiltonian (1) in order to obtain electronic states in the ground state of doped chain. (For a bipolaron, an obtained solution is identical to a restricted HF solution with a closed shell.) The equilibrium lattice structure with a polaronic or bipolaronic configuration is determined by use of the Feynman-Hellmann theorem with keeping the total chain length unchanged. Excited states, that is, final states of optical transitions, are obtained by the S-CI method with the bases of the UHF-MO.

The optical absorption at photon energy ω is proportional to $\sum_m \omega^{-1} |\langle m|j|0\rangle|^2 \times\delta(E_m - \omega)$. Here, $|0\rangle$ and $|m\rangle$ denote the ground state and m-th excited state, respectively, and E_m is its excitation energy. The current j is expressed as

$$j \propto \mathrm{i} \sum_{n,\sigma} t_{n,n+1}(C_{n+1,\sigma}^{\dagger} C_{n,\sigma} - C_{n,\sigma}^{\dagger} C_{n+1,\sigma}). \tag{3}$$

RESULTS

Figure 1 shows the calculated absorption spectra of a hole polaron with up spin ((a) and (c)) and a hole bipolaron ((b) and (d)) in the system with N=120 sites. Figures 1(a) and (b) are the case of U=3t, V=1.5t, and $\delta_0 = 0.05$. For comparison, in Figures 1(c) and (d) we also show the non-interacting case (U=V =0), corresponding to the tight-binding version of the BK model. Sub-gap absorption due to the polaron and bipolaron is shaded. An electron polaron and an electron bipolaron give the same spectra as those of hole ones in our model.

In Figures 1(a) and (b), a strong absorption peak at ω=1.6t is due to the transition to a *free* exciton state in the spatial region of the regular bond order wave (BOW) outside the polaron or the bipolaron.[13] In the non-interacting case, interband transitions take part of this and give rise to successive peaks starting at ω=0.9t, which will merge into a continuous spectrum in the limit of infinite system size.

Sub-gap absorption of a polaron (bipolaron) has *two* (*one*) peaks even in the presence of the e-e interaction. Their positions (normalized by the gap) shift to inside of the optical gap with increasing the interaction strength, as shown in Figure 2. In the case of a polaron, the oscillator strengths of the two peaks are comparable, and are not so sensitive to the interaction. Their line shapes are similar in Figures 1(a) and (c), in contrast to the change in the absorption profile of BOW. On the other hand, in the case of the bipolaron, the e-e interaction makes the absorption profile symmetric and broader.

The analysis of the S-CI wave functions reveals that the low- (high-) energy sub-gap peak in Figure 1(a) is characterized by the transition to the lowest unoccupied MO (LUMO) for down- (up-) spin electron. The absorption of a bipolaron in Figure 1(b) is due to the transitions to the LUMO for both spins. These levels are localized around the

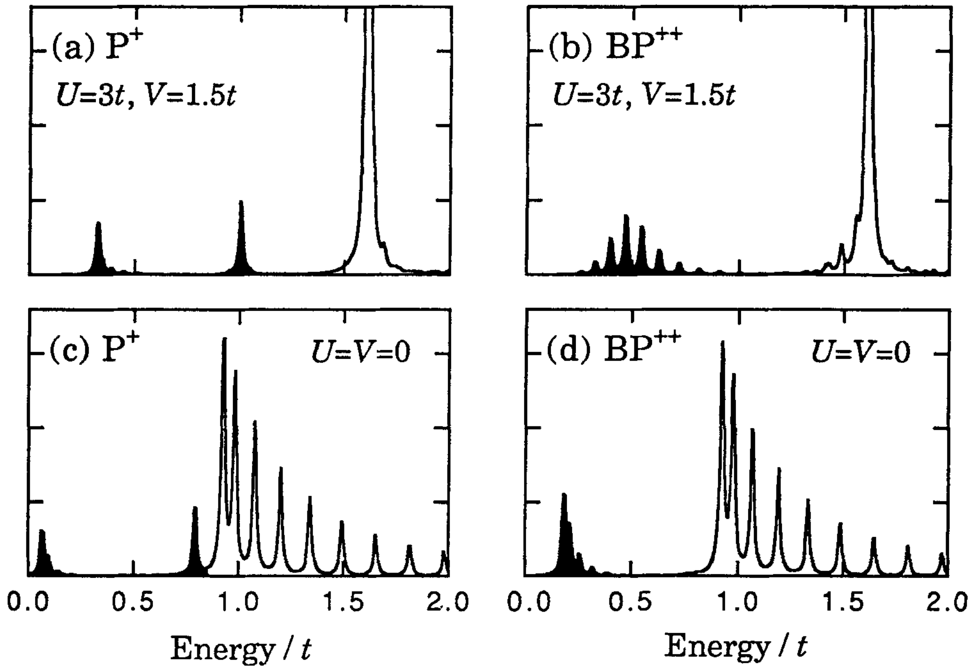

FIGURE 1 Calculated optical absorption spectra of a polaron ((a) and (c)) and a bipolaron ((b) and (c)). In (a) and (b), U=3t, V=1.5t, and $\delta_0 = 0.05$ are assumed. (c) and (d) are the non-interacting case with U=V=0 and $\delta_0 = 0.05$ for comparison. Sub-gap absorption due to the polaron and bipolaron is shaded. The life-time broadening with width 0.01t is assumed.

polaron and bipolaron. These characters of transitions are similar to those for the non-interacting BK model.

DISCUSSIONS

We have demonstrated that the e-e interaction mainly affects the positions of sub-gap peaks in the absorption spectra of the polaron and the bipolaron. However, the interaction does not change the number of sub-gap peaks. Therefore, concerning the absorption spectrum of a bipolaron, the e-e interaction does *not* improve the discrepancy between the experiments mentioned in the beginning and the theory, in

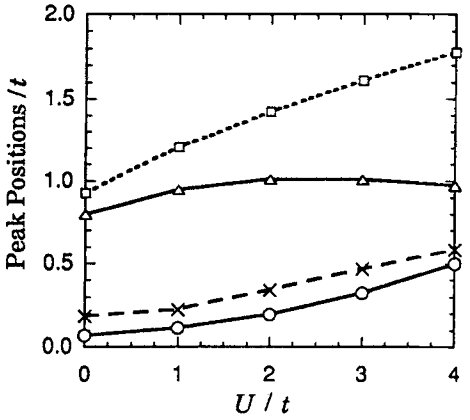

FIGURE 2 The positions of the sub-gap absorption peaks of a polaron (solid lines) and a bipolaron (dashed line) as functions of the strength of the on-site Coulomb interaction U. The optical gap is also depicted (dotted line). The relation $V=U/2$ and $\delta_0=0.05$ are assumed.

contrast to a perturbational calculation by Sum, Fesser, and Büttner,[9] who claimed that the high-energy peak becomes appreciably strong by the e-e interaction. However, this is questionable, because, as pointed out by themselves,[6] their effective Hamiltonian breaks the CC symmetry which is preserved in the original one.

Another, more natural interpretation of the experiments is to assign the charge carriers to polarons.[7] With this assignment, our model as well as the BK model can explain the observed two sub-gap peaks with comparable intensities. In our previous paper, we demonstrated that the e-e interaction suppresses strongly the stability of a bipolaron relative to two separated polarons and suggested that for a realistic interaction strength (U/t=2~3), a polaron is preferable configuration than a bipolaron at low doping concentration.[12] Therefore, the polaron interpretations is more natural. Optically detected magnetic resonance is a useful tool to assign the sub-gap absorption. Indeed, Wei *et al* reported that in poly(*p*-phenylene vinylene) a spin doublet state is associated with the two photo-induced absorption peaks which are similar to doping-induced ones.[14] This supports the polaron picture, in contrast to the opposite assignment by the authors.

Our model contains a phenomenological BK parameter δ_0. For a more quantitative comparison with experiments, it will be necessary to develop the theory by taking into account the molecular structures of individual polymers, as well as interchain coupling and electrostatic potentials from dopant ions.

REFERENCES

1. Conjugated Conducting Polymers, edited by H. G. Kiess (Springer, Berlin, 1992).
2. S. A. Brazovskii and N. N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz., 33, 6 (1981) [JETP Lett., 33, 4 (1981)].

3. K. Fesser, A. R. Bishop, and D. K. Campbell, Phys. Rev., B27, 4804 (1983).
4. For instance, T. -C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev., B30, 702 (1984); M. Tabata, M. Satoh, K. Kaneto, and K. Yoshino, J. Phys. Soc. Jpn., 55, 1305 (1986); D. D. C. Bradley, G. P. Evans, and R. H. Friend, Synth. Met., 17, 651 (1987); K. F. Voss, C. M. Foster, L. Smilowitz, D, Mihailovic, S. Askari, G. Srdanov, Z. Ni, S. Shi, A. J. Heeger, and F. Wudl, Phys. Rev., B43, 5109 (1991).
5. T. Martin and D. K. Campbell, Phys. Rev., B35, 7732 (1987).
6. U. Sum, K. Fesser, and H. Büttner, Phys. Rev., B38, 6166 (1988).
7. Y. Furukawa, to be published in Synth. Met..
8. D. K. Campbell, D. Baeriswyl, and S. Mazumdar, Synth. Met., 17, 197 (1987).
9. U. Sum, K. Fesser, and H. Büttner, Solid State Commun., 61, 607 (1987).
10. W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett., 42, 1698 (1979).
11. Y. Shimoi and S. Abe, Phys. Rev., B49, 14113 (1994).
12. Y. Shimoi and S. Abe, Phys. Rev., B (in press).
13. S. Abe, M. Schreiber, W. P. Su, and J. Yu, Phys. Rev., B45, 9432 (1992).
14. X. Wei, B. C. Hess, Z. V. Vardeny, and F. Wudl, Phys. Rev. Lett., 68, 666 (1992).