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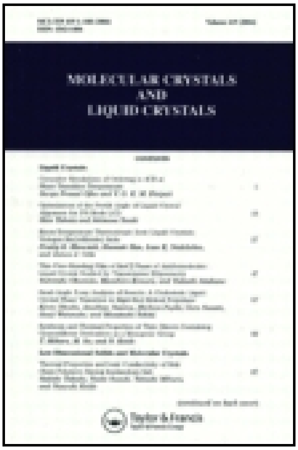

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Theory on Photoinduced Absorption from Singlet Excited States in Conjugated Polymers

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Version of record first published: 04 Oct 2006

To cite this article: Yukihiro Shimoi, V. A. Shakin & Shuji Abe (1998): Theory on Photoinduced Absorption from Singlet Excited States in Conjugated Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 77-82

To link to this article: http://dx.doi.org/10.1080/10587259808042459

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Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 77–82
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Theory on Photoinduced Absorption from Singlet Excited States in Conjugated Polymers

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Photoinduced absorption from singlet excited states in conjugated polymers are theoretically studied by a Pariser-Parr-Pople type model. Full valence-bond calculations indicate that, when the two possible lowest singlet excited states (the so-called $2A_g$ and $1B_u$ sates) are nearly degenerate, absorption from them are quite similar in their spectral features, in spite of much different characters of these two states.

Keywords: conjugated polymers; photoinduced absorption; electron-electron interaction

INTRODUCTION

Conjugated polymers have attracted much attention in the field of photophysics because of their outstanding optical properties such as large third-order nonlinear susceptibility and the high efficiency of electroluminescence. Natures and energy positions of excited states in these systems are much influenced by electron-electron interaction. Extensive theoretical investigations have shown that, in the case of strong interaction, the lowest singlet excited state is an optically forbidden state with the same symmetry as that of the ground state (the so-called $2A_g$ state), resulting in no or very weak luminescence [1-3]. On the other hand, it becomes optically allowed ($1B_u$ state) in weak interaction regime. The $2A_g$ and $1B_u$ states have mutually different characters: The covalent $2A_g$ state is characterized by a bound pair of triplet excitations whereas the ionic $1B_u$ state has excitonic nature [2,4].

Photoinduced absorption (PA) spectroscopy provides information on excited states. So far, transient PA observed in several conjugated polymers such as polydiacetylenes (PDAs) has been ascribed to a transition from $1B_u$ excitons

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after lattice relaxation [5]. A recent alternative assignment is a transition from the $2A_g$ state for polymers like PDAs and polythienylenevinylene [6], since their no- or very weak fluorescence suggests that $2A_g$ lies below $1B_u$.

In the present paper, we study theoretically absorption from the $2A_g$ and $1B_u$ states in connection with the aforementioned assignments. We demonstrate that, despite much different characters of these states, absorption from them has quite similar spectra when the two states are nearly degenerate. Therefore, it seems difficult to determine, only from spectral features, which state is responsible for PA spectra. In final section, we also comment on the effects of the lattice relaxation of an $1B_u$ exciton on PA spectra.

MODEL

Interacting π electrons on a linear polymer chain are described by the following Hamiltonian.

$$H = -t\sum_{n,s}[1-(-)^n\delta](C^\dagger_{n,s}C_{n+1,s} + C^\dagger_{n+1,s}C_{n,s})$$
$$+U\sum_{n}\rho_{n\uparrow}\rho_{n\downarrow} + \sum_{n>m}\sum_{s,s'}V_{m,n}\,\rho_{n,s}\rho_{m,s'}\ . \tag{1}$$

Here, $C^\dagger_{n,s}$ creates a π electron with spin s at n-th carbon atom and $\rho_{n,s}$ = $C^\dagger_{n,s}C_{n,s}-1/2$. We assume a perfect dimerization δ in the transfer integral appeared in the first term of Eq.(1) and neglect lattice deformation effects upon excitation. We use three different functional forms for long-range Coulomb interaction, $V_{m,n}$: the Ohno and Mataga-Nishimoto (MN) potentials for the Pariser-Parr-Pople (PPP) model and the extended Hubbered model where the interaction is truncated at the nearest neighbor sites. In the PPP models, we take $t = 2.4$ eV.

In order to describe the $2A_g$ state appropriately, it is necessary to take account of correlation effects sufficiently. Therefore, we solve the Hamiltonian (1) exactly by means of diagrammatic valence bond basis [7]. We can calculate the fairly high excited states (the lowest fifty states) in each symmetry spaces, by diagonalizing a state to already obtained lower excited states and by applying the

Lanczos method. Our system size N is up to twelve sites with the open boundary condition.

Results

We change the relative stability between $2A_g$ and $1B_u$ by varying the strength of the dimerization δ [3], instead of the electron-electron interaction. In the PPP-Ohno model with system size N=12, the energy-level crossing occurs at about $\delta = 0.2$. At smaller (larger) δ, the $2A_g$ ($1B_u$) state is stable. In Fig. 1 we present calculated absorption spectra from these two singlet states in the PPP-Ohno model with $\delta = 0.1, 0.2$, and 0.3. Dashed lines in the figure indicate the position of the optical gap E_g, that is, the excitation energy of the $1B_u$ state from the ground state. Note that large transition energies are partially due to a finite system-size effect and partially due to the parametrization of the model.

The PA spectra from $1B_u$ will have a single major peak below the optical gap, if some broadening is taken into account. The main contribution to this peak is the transition to the so-called mA_g exciton which has a large dipole coupling with $1B_u$. A small absorption peak develops at high energy side of the major PA peak with increasing δ.

In absorption spectra from $2A_g$, oscillator strength is further concentrated on a transition, resulting in a sharp single PA peak below the optical gap. The final state of this transition is $3B_u$ in the PPP-Ohno model with N=12. This quantum number is independent of δ in $0.1 \leq \delta \leq 0.3$. In each δ, the peak-intensity in the PA from $2A_g$ is about the half of the sum of those from $1B_u$ to mA_g and the states located nearby in energy. As shown in Fig. 2(a), the transition energy from $2A_g$ to $3B_u$ normalized by the optical gap, $[E(3B_u)-\mathrm{E}(2A_g)]/E_g$ drastically decreases with increasing δ, in contrast to $[E(mA_g)-\mathrm{E}(1B_u)]/E_g$ which is only weakly dependent on δ. The two transition energies coincide near $\delta = 0.2$, that is, when $1B_u$ and $2A_g$ are almost degenerate. At this δ, the PA spectra from $2A_g$ and $1B_u$ have quite similar spectral features with same order of intensity, as shown in Fig. 1. We plot in Fig. 2(b) the normalized transition energies against the system size N in the PPP-Ohno model. The transition energies depend on N very weakly. Therefore, the positions of PA peaks against the optical gap are

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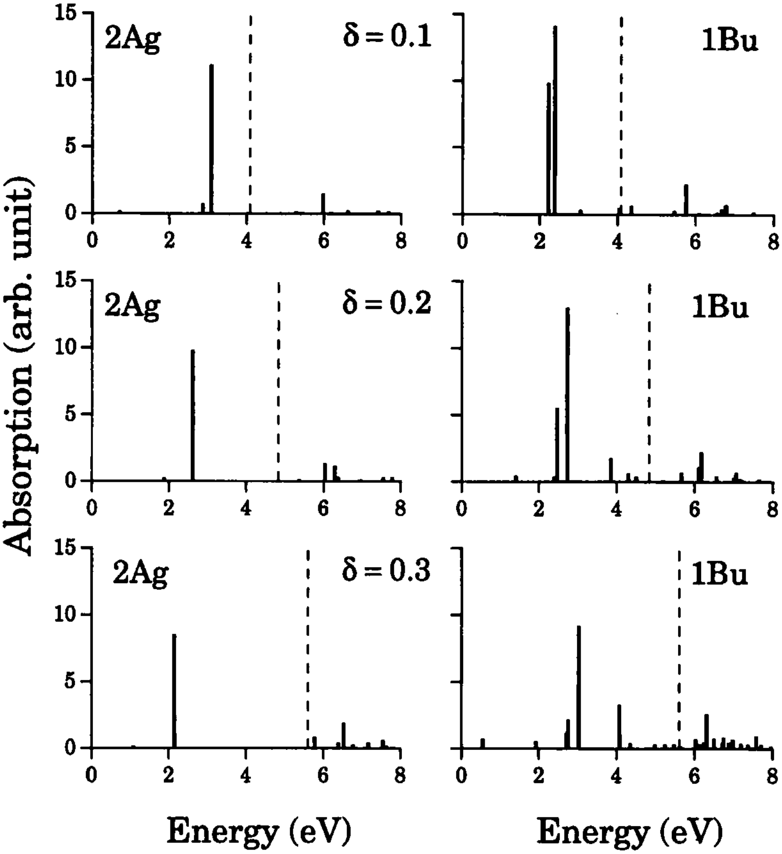

FIGURE 1 Calculated induced absorption spectra from the $2A_g$ (left) and $1B_u$ states (right) in the PPP-Ohno model with system size $N = 12$. Dimerization δ is 0.1, 0.2, and 0.3 from top to bottom. The dashed lines indicate the position of optical gap in the linear absorption spectra.

expected to be located in similar energy region even in the infinite system for the PPP-Ohno model.In Fig. 3, we show absorption spectra in the other two models with δ at which $1B_u$ and $2A_g$ states are almost degenerate ($\delta = 0.4$ for the PPP-MN model and $\delta = 0.2$ for the extended Hubbard model with $U = 3t$ and $V = t$). The absorption spectra from $2A_g$ and $1B_u$ are similar to each other also in these models, although the high energy peak in PA spectra from $1B_u$ fairly develops in the PPP-MN model. The position of the PA peak depends on the models.

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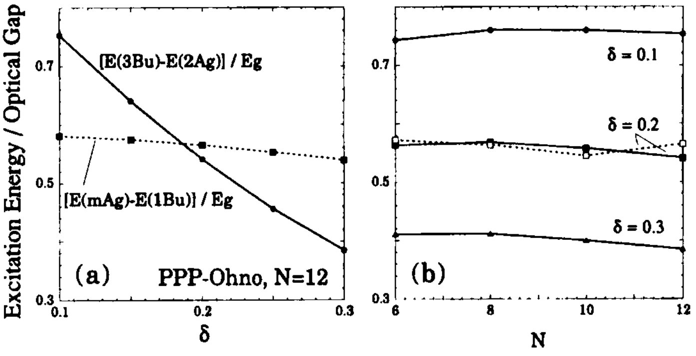

FIGURE 2 The transition energy between $2A_g$ and $3B_u$ which have a strong dipole-coupling is plotted against the dimerization δ (a) and against the system size (b), in the PPP-Ohno model (solid lines). The energy is normalized by the optical gap. The transition energy from $1B_u$ to mA_g is also included (dashed lines). $N = 12$ in (a) and $\delta = 0.1, 0.2$, and 0.3 in (b).

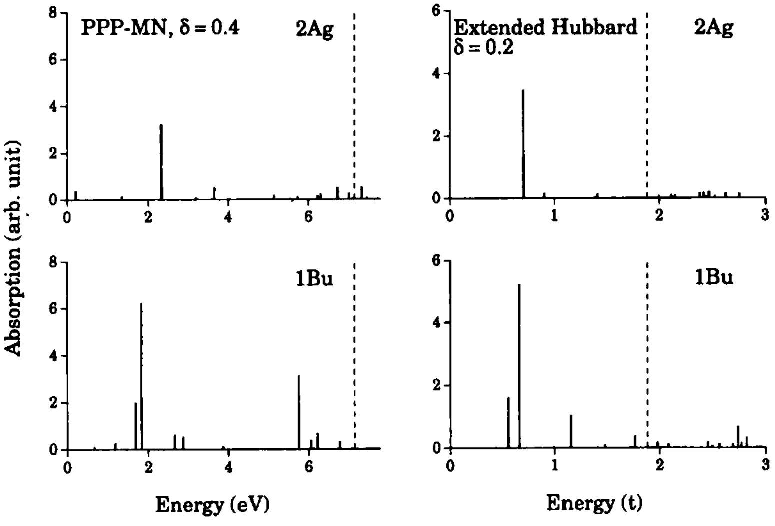

FIGURE 3 Calculated induced absorption spectra from the $2A_g$ (upper panel) and $1B_u$ states (lower panel) in the PPP-MN model with dimerization $\delta = 0.4$ and the extended Hubbard model with $U = 3t$, $V = t$, and $\delta = 0.2$. The system size $N = 12$. The dashed lines indicate the optical gap in the linear absorption spectra.

Concluding Remarks

In conclusion, we demonstrate that theoretical PA spectrum from the $2A_g$ state has a sharp peak below the optical gap. Recently, a large dipole coupling between 2Ag and a Bu state is also reported within the intermediate neglect of differential overlap multireference double configuration-interaction (CI) calculation [8]. The spectra are quite similar between PA from $2A_g$ and $1B_u$ when they are nearly degenerate. Since the observed transient PA spectra in PDAs have broad peak, it seems difficult to determine only from spectral features, the excited state responsible for the observed PA spectra.

Another significant aspect in the PA is the lattice relaxation process, forming the singlet exciton-polarons. Recently, we also investigated the polaronic effect on the PA from $1B_u$ exciton state within the single-double CI treatment for a model which includes both electron-electron interaction and electron-lattice coupling [9]. In this model, the main PA peaks are located in relatively low photon-energy region both for relaxed and unrelaxed geometrical configurations. As demonstrated in ref. 9, the lattice relaxation further concentrates the oscillator strength on a single peak and increases drastically the double excitation component in the two-photon excited states relevant to the PA spectra.

Acknowledgments

One of the authors (Y.S.) learned a lot on the valence bond method from the discussions with Prof. S. Mazumdar. The authors acknowledge Prof. T. Kobayashi for fruitful discussions.

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