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PHOTOEXCITATIONS IN POLY(PARAPHENYLENE VINYLENE)

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ABSTRACT Within a theoretical approach including both electron-phonon and electron-electron interaction terms, we investigate the relaxation processes of photoexcited states in oligomers and long chains of poly(paraphenylene vinylene), PPV. Our direct calculations indicate that in PPV the difference in relaxation energy between two polarons and one singlet [triplet] polaron-exciton decreases [increases] with the Hubbard U term; the long-range interaction V terms stabilize both the singlet and triplet polaron-excitons. The theoretical simulation of the photoinduced absorption spectra both for singlet and triplet states are in very a good agreement with experiment.

INTRODUCTION

Poly(paraphenylene vinylene) [PPV] is currently one of the most thoroughly investigated electro-active polymers because of its remarkable luminescence properties[1]. It is therefore essential to obtain a clear picture of the characteristics of the low-lying electronic excitations, responsible for the luminescence, and their associated lattice relaxations. Within single electron theory[2], Brazovskii and Kirova (BK), and Fesser, Bishop, and Campbell (FBC) have extended the Su-Schrieffer-Heeger model by adding an extrinsic gap term to describe the ground-state nondegeneracy present in polymers such as PPV. However, a direct calculation for PPV (and polydiacetylene) by Choi and Rice[3] pointed out that the BK or FBC models are not appropriate for PPV. Furthermore, there is much experimental evidence indicating the importance of electron-electron interaction. Rauscher et al even conclude that PPV can basically be described by a molecular exciton model ($U/t>>1$)[4].

In this work, we present the results of theoretical investigations where we consider the influence of both electron-phonon and electron-electron terms. We first study the photoexcited states and lattice relaxations in oligomeric and polymeric PPV in a one-electron Longuet-Higgins-Salem (LHS) model[5]; then, within an extended-Hubbard model, we analyze the electron correlation effect.

LHS MODEL

The LHS Hamiltonian reads:

$$H_{LHS}=-\sum_{<n,n'>} t_{nn'}(c_n^+c_n+h.c.)+\sum_{<n,n'>} f_{nn'} \quad (1)$$

where

$$t_{nn'}=A\exp(-|r_n-r_{n'}|/B) \quad (2)$$

$$f_{nn'}=-\frac{2}{R_1-R_2}t_{nn'}(|r_n-r_{n'}|-R_1+B) \quad (3)$$

R_1 and R_2 are the bond lengths for pure single (1.54 Å) and double (1.33 Å) bonds between carbons, respectively. Eq. 3 represents the self-consistent condition for optimizing the (macro)molecular geometry. The A and B parameters were obtained previously[6]: A=243.5 eV, B=0.3075 Å. The same self-consistent condition is applied to optimize the polaron and polaron-exciton states. We obtain that, in the center of the polaron exciton defect: (i) the geometry modifications for the phenyl bonds are about half those for the vinylene units; and (ii) there is no bond-alternation reversal within the vinylenes (this is in sharp contrast to the results from BK or FBC models, which do not take explicit account of the two-dimensional-like phenyl rings). In Table I, we give the binding energies for the polaron and polaron-exciton in different oligomers. The binding energy difference between two polarons and one polaron-exciton is 0.19 eV in a long oligomer with 21 phenyl rings, which is much less than that of BK model and indicates again the importance of the phenyl rings.

TABLE I. Relaxation energies (in eV, within LHS model) of polaron (p) and singlet polaron-exciton (pe) as a function the number of phenyl rings (Nr) in the PPV chain.

Nr	2	3	4	5	6	7	8	21
p	0.19	0.15	0.13	0.11	0.097	0.087	0.080	0.046
pe	0.74	0.58	0.51	0.46	0.42	0.38	0.36	0.28

LHS/EXTENDED HUBBARD MODEL

We now consider the electron-electron interaction effects and take the extended-Hubbard approach by introducing U and long-range V terms:

$$H=H_{LHS}+U\sum_i c_{i\uparrow}^{+}c_{i\uparrow}c_{i\downarrow}^{+}c_{i\downarrow}+\sum_{i<j,\sigma,\sigma'} V_{ij}c_{i\sigma}^{+}c_{i\sigma}c_{j\sigma}^{+}c_{j\sigma'} \qquad (4)$$

where $V_{ij}=V/d_{ij}$, d_{ij} is the distance between i and j. Within first-order perturbation, the singlet and triplet excitation energies are evaluated as:

$$E^{S(T)}=\varepsilon_s-\varepsilon_a+(-1)^{\delta_s}U\sum_i |\phi_a(i)|^2|\phi_s(i)|^2+\sum_{i<j} V_{ij}[4(1-\delta_s)\phi_a(i)\phi_a(j)\phi_s(i)\phi_s(j)$$

$$-|\phi_a(i)|^2|\phi_s(j)|^2-|\phi_s(i)|^2|\phi_a(j)|^2] \qquad (5)$$

where the δ_s is the spin of the excitation, $\varepsilon_{s(a)}$ is the one-electron virtual (occupied) orbital energy, and $\phi(i)$ is the LHS wavefunction. The molecular geometries of the excitons are optimized according to a tanh parameterized form[6]. We stress that, we define the binding energy of the polaron-exciton as the creation energy difference between one polaron-exciton and two uncorrelated polarons (opposite in charge), rather than as the difference between the exciton level and the continuum; this binding energy is that responsible for charge separation.

When only the effect of U is included, we find that the relaxation energy of the singlet polaron-exciton decreases with electron-electron interaction strength; the reverse is obtained for the triplet polaron-exciton (Fig. 1a). For long (polymer) chains, the binding-

energy of the singlet polaron-exciton decreases from 0.19 eV [U=V=0 eV] to 0 eV at [U=8 eV; V=0 eV] (*i.e.*, for an intermediate U/t value of about 3). The consideration of the long-range interaction V terms stabilizes both the singlet and triplet polaron-excitons. In Fig. 1b, we present the relaxation energy of the singlet polaron-exciton in a long chain (Nr=21) as a function of V for a fixed U=8 eV value. For V larger than 2 eV, the binding energy of singlet polaron-exciton becomes again equal to that of the single-electron calculations. The precise stabilization of the singlet polaron-exciton thus depends on the competition between these terms (we note that screening effects would tend to reduce the V terms); for reasonable estimates of U=3V=8 eV, we obtain a binding energy of *ca.* 0.4 eV. This value is in excellent agreement with a number of measurements, including the temperature dependence of the quantum yield in photovoltaic devices at zero field[7] and the electric-field-induced quenching of the photoluminescence[8]; it also matches the results from classical semiconductor calculations[9]. The strong binding of the triplet polaron-exciton rationalizes the very long lifetimes that are observed[10]; also, the results of Optically-Detected Magnetic Resonance measurements[11] require that the triplet polaron-exciton be strongly localized.

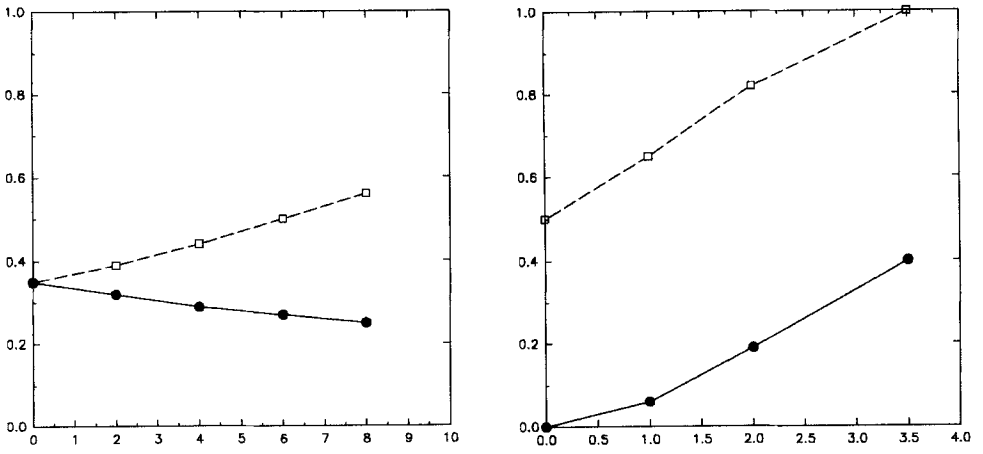

FIGURE 1 (left): Dependence of polaron-exciton relaxation energy on U for Nr=8, V=0; (right): Relaxation energy difference between a singlet polaron-exciton and two polarons (exciton binding energy) as a function of V for Nr=21, U=8 eV. All units are in eV. Solid line for the singlet, dashed line for the triplet.

PHOTOINDUCED ABSORPTION

To study the photoinduced absorption (PA) spectra, we partition the Hamiltonian in Eq. (4) into an Hartree-Fock part plus a fluctuation. We treat the latter within a single configuration interaction (SCI) approach, so that we can obtain the wavefunctions of the excitons for the evaluation of optical transition moments. For the parameters U=3V=8 eV, the PA theoretical spectra for the singlet and triplet states are presented in Fig. 2.

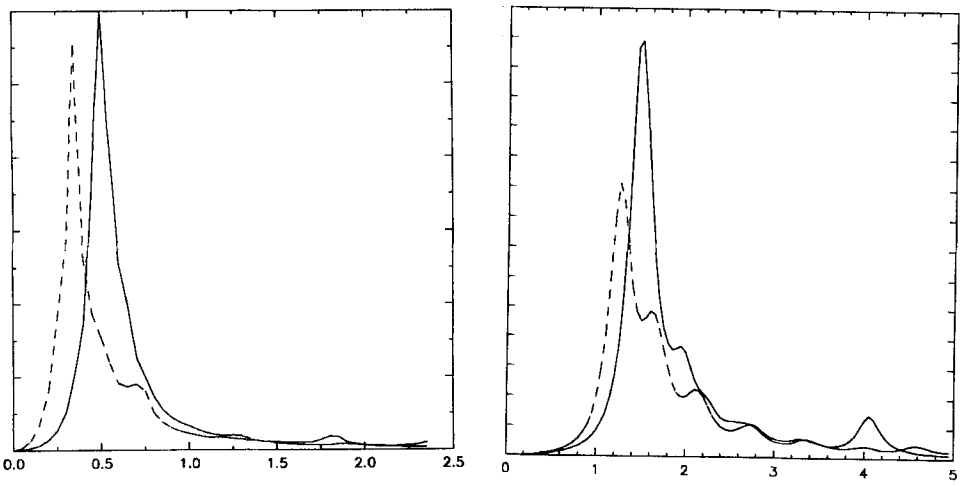

FIGURE. 2 Theoretical PA spectra of (left) singlet states and (right) triplet states for oligomer Nr=8 (U=3V=8 eV). Solid (dashed) lines represent the results when polaron-exciton geometries are relaxed (rigid).

It is important to point out that we can obatin reasonable PA spetra only when the geometries of excitons are relaxed. Both peaks are subject to blue-shifts upon geometry relaxation. The low energy peak at 0.5 eV and the high energy peak at 1.5 eV (actually quite common in conjugated systems such as polyenes) are attributed to singlet and triplet exciton absorptions, respectively. The peak at 1.85 eV (for singlet) suggested by *Leng et al.*[12], *is not* reproduced in our calculations since it is forbidden by symmetry. We

note that this peak is absent[13] in the PA measurements on well-ordered PPV samples.

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