Excitons and Interband Excitations in Conducting Polymers Based on Phenylene

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A microscopic model for the photoexcitations of polyphenylenes is introduced. It allows for the effects of the "correlation-energy gap" U between charged and charge-neutral excitations and the dipole-dipole interaction V between neighboring monomers. It leads to the generic appearance of three dispersing absorption bands whose relative spacings in energy are largely set by U and the electronic bandwidth W, thereby establishing direct experimental access to these microscopic parameters.

The undoped forms of the conducting polymers based on phenylene form a wide and interesting class of organic semiconductors [1]. They include poly(paraphenylene) (PPP), poly(phenylene vinylene) (PPV), and the atomically bridged polyphenylenes such as polyaniline and poly(phenylene-oxide) (PPO). Their relevant π-electron bandwidths W range from $W < \Delta$ to $W \ll \Delta$, respectively, where Δ is the mean spacing between the molecular orbital (MO) energy levels of the isolated phenylene monomer [2,3].

In this Letter we introduce a simplified but analytically explicit microscopic model which we believe elucidates the essential physics of the excitations of these polymers. The model recognizes that the primary excitations are derived from the local excitations of the phenylene monomer and includes two effects which are not ordinarily considered in the usual band models of the polymers [4]. These are the "correlation-energy gap" U between charged and charge-neutral excitations [5] and the dipole-dipole interaction V between local excitations on neighboring monomers [6]. U is the energy required, in the limit $W \to 0$, to dissociate a local monomer excitation into a well-separated electron and hole. This effect is crucial as it leads, for $W \neq 0$, to the transfer of oscillator strength from interband transitions to exciton excitation *even before* the long-range electron-hole Coulomb attraction V_{eh} is allowed for. In fact, the symmetry of the local phenylene excitations is shown to lead to three excitons whose relative spacings in energy are largely set by U and W, and corrected by V and V_{eh}, thereby establishing experimental access to the values of these parameters. The significance of the two excitons that we find in the ultraviolet (uv) has not been recognized in the current debate [7] on the origin of the first absorption band in PPV. While the complex conductivity $\sigma(\mathbf{Q}, \omega)$ we calculate is in good qualitative agreement with that derived from the existing electron energy loss spectra (EELS) of the polymers [2,8], we call for new EELS studies in order to investigate the anisotropy of the conductivity and the exciton dispersion due to V that we predict in the uv.

Our model, based on PPP as the prototypical polymer, consists of a chain of N ($N \to \infty$) interacting phenylene monomers. Each monomer is assumed to have two degenerate (e_{1g}) hole states, labeled a and c, with "excita-

tion" energy E_h, and two degenerate (e_{2u}) electron states, labeled b and d, with excitation energy E_e. The orbital patterns of these states under an assumed D_{6h} symmetry of the *monomer* are shown in Fig. 1(a) [9]. If we introduce the fermion operators $a_{j\sigma}^\dagger$, $b_{j\sigma}^\dagger$, $c_{j\sigma}^\dagger$, and $d_{j\sigma}^\dagger$, which create, respectively, an electron or hole with spin polarization σ in the latter orbitals of the monomer j ($j = 1, \ldots, N$), the four possible dipole allowed $e_{1g} \to e_{2u}$ excitations of the monomer are described by the operators $B_{j\sigma}^\dagger = b_{j\sigma}^\dagger a_{j,-\sigma}^\dagger$, $D_{j\sigma}^\dagger = d_{j\sigma}^\dagger c_{j,-\sigma}^\dagger$, $A_{j\sigma}^\dagger = d_{j\sigma}^\dagger a_{j,-\sigma}^\dagger$, and $C_{j\sigma}^\dagger = b_{j\sigma}^\dagger c_{j,-\sigma}^\dagger$. These unsymmetrized component excitations are illustrated in Fig. 1(b). They may be combined to form the four ($n = 1, 2, 3, 4$) following singlet excitations of the phenylene monomer:

$$P_{j,1}^\dagger = \sum_\sigma (B_{j\sigma}^\dagger - D_{j\sigma}^\dagger)/2, \quad E_{1u}(x), \qquad (1)$$

$$P_{j,2}^\dagger = \sum_\sigma (A_{j\sigma}^\dagger + C_{j\sigma}^\dagger)/2, \quad E_{1u}(y), \qquad (2)$$

$$P_{j,3}^\dagger = \sum_\sigma (B_{j\sigma}^\dagger + D_{j\sigma}^\dagger)/2, \quad B_{1u},$$

$$P_{j,4}^\dagger = \sum_\sigma (A_{j\sigma}^\dagger - C_{j\sigma}^\dagger)/2, \quad B_{2u}.$$

The first and second E_{1u} excitations have transition dipole moments of magnitude μ_0 in the monomer x and y directions, respectively, while the B_{1u} and B_{2u} excitations are dipole forbidden [9]. The Hamiltonian H defining the model is

$$H = \sum_{j\sigma} [E_h(a_{j\sigma}^\dagger a_{j\sigma} + c_{j\sigma}^\dagger c_{j\sigma}) + E_e(b_{j\sigma}^\dagger b_{j\sigma} + d_{j\sigma}^\dagger d_{j\sigma})]$$
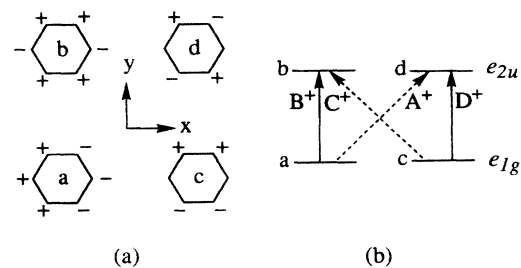

FIG. 1. (a) The orbital patterns of the e_{1g} and e_{2u} molecular orbitals, and (b) the four component $e_{1g} \to e_{2u}$ transitions of the phenylene monomer.

$$+ H_d + H_{ee},$$

where

$$H_d = -\sum_{j\sigma}\{t_{bb}(b^\dagger_{j+1,\sigma}b_{j\sigma} + \text{H.c.})$$

$$+ t_{aa}(a^\dagger_{j+1,\sigma}a_{j\sigma} + \text{H.c.})$$

$$+ t_{ab}[(b^\dagger_{j+1,\sigma} - b^\dagger_{j-1,\sigma})a^\dagger_{j,-\sigma} + \text{H.c.}]\}$$

describes the delocalization of the b and a orbitals due to the intermolecular hopping integrals t, while

$$H_{ee} = -\sum_{jn} U_n P^\dagger_{jn} P_{jn} - V_{eh}$$

$$- \sum_{jnm} V_{nm}(P^\dagger_{j+1,n} + P_{j+1,n})(P^\dagger_{jm} + P_{jm}) \quad (3)$$

specifies the leading contributions arising from Coulomb interactions. The first term in Eq. (3) specifies the *energy gain* U_n, when an electron and a hole in a singlet state are simultaneously present on the *same* monomer in the symmetry combination n. Since in the hypothetical dissociation process the number of intramonomer inter-electron distances increases precisely by 1, U_n can be qualitatively understood as the *repulsive* Coulomb interaction associated with this extra "bond" [10]. Note that the local monomer excitation energies E_n are $2\alpha_0 - U_n$, where $2\alpha_0 = E_e + E_h$. We may, crudely, estimate U_n from $U_n \sim (I - A - 2E_p) - E_n$, where I, A, and E_n are the ionization potential, electron affinity, and singlet excitation energies, respectively, of benzene and E_p the electronic polarization energy [11] of the singly charged monomer in the dielectric medium of the polymer. If, for PPP, we take $E_p = 1.5$ eV, we obtain from the benzene data [12] $U_1 = U_2 \sim 1$, $U_3 \sim 1.8$, and $U_4 \sim 3$ eV. For $U_1 \neq U_3$, the first term of Eq. (3) leads to an intra-monomer coupling of the $B^\dagger$ and $D^\dagger$ excitations, while for $U_2 \neq U_4$ it leads to a coupling of the $A^\dagger$ and $C^\dagger$ excitations. The second term of Eq. (7) describes the delocalization of the charge-neutral intramonomer excitations via the dipole-dipole interaction. For the actual case of PPP, the phenylene x axis coincides with the polymer axis so that V_{nm} is diagonal with $V_{11} = V > 0$ for the $E_{1u}(x)$ excitation and $V_{22} = -V/2$ for the $E_{1u}(y)$ excitation [13]. Following Salem [14] we arrive at the estimate $V \sim 0.25$ eV. For the atomically bridged polyphenylenes, the hopping integrals in H_d represent *virtual* hopping over the bridging atom. For PPV, both the electron hopping in H_d and the excitation hopping in H_{ee} represent virtual hopping processes over the vinylene unit. The term V_{eh} in Eq. (3) represents the long-range Coulomb interaction between an electron and a hole. Reasonable estimates put $V_{eh} \sim 0.1$ to 0.3 eV for neighboring monomers in PPP and PPV. In the present discussion of our model, the effects of electron-phonon interaction, lattice relaxation and disorder are not explicitly included.

We note that if $H_d = 0$, H describes two dispersing Frenkel excitons, one derived mainly from the $E_{1u}(x)$ monomer excitation and the other from the $E_{1u}(y)$ exci-

tation. We now illustrate the generic way in which this picture is changed for $H_d \neq 0$, by calculating the complex conductivity $\sigma_{\alpha\alpha}(Q, \omega)$ ($\alpha = x$ or y) for the case of PPP. Denoting by Q an arbitrary wave vector along the x direction, the paramagnetic conductivity is given by the Kubo formula [15]

$$\sigma_{\alpha\alpha}(Q, \omega) = (i\omega ANb)^{-1} \int_0^\infty dt \exp(i\omega t)\langle[J^\alpha_Q(t), J^\alpha_{-Q}(0)]\rangle,$$
$$(4)$$

where $J^\alpha_Q = \sum_j \exp(iQR_j)J^\alpha_j$ is the current fluctuation operator for the α direction, b the lattice constant of the chain, and A the transverse area corresponding to one chain. The interband current densities J^α_j are

$$J^x_j = ie\Big\{v_0(P^\dagger_{j,1} - P_{j,1}) + (v_1/2)\sum_\sigma$$

$$\times [(b^\dagger_{j+1,\sigma} + b^\dagger_{j-1,\sigma})a^\dagger_{j,-\sigma} - \text{H.c.}]\Big\}, \quad (5)$$

$$J^y_j = iev_0(P^\dagger_{j,2} - P_{j,2}),$$

where $v_0 = \mu_0 E_1/e\hbar$ arises from the transition dipole moments of the E_{1u} excitations and v_1 arises from the "oblique" interband hopping terms in H_d. For PPP $t_{aa} = t_{bb} = t_{ab} \equiv t$, and for the planar polymer, MO theory gives $v_1 = v_0/3$ [16]. More generally, the ratio v_1/v_0 may be regarded as a parameter of the model. The evaluation of (4) is greatly simplified if two effects in H are ignored. The first are the terms in H_{ee} describing the creation and destruction of *pairs* of excitations. The second are the oblique hopping terms in H_d after they have been retained in J^x_j. The neglect of these two terms introduces errors of order $V/2\alpha_0$ and $(t/\alpha_0)^2$, respectively. Since $t < \sim 1$, $2\alpha_0 \sim 7$, and $V < \sim 0.25$ eV typically, these corrections are small. Then the final state problem reduces to the problem of a *single* electron interacting with a *single* hole, and the Kubo formulas are readily evaluated in terms of standard ladder diagrams only [15]. The results can be expressed in a closed analytical form if the long-range V_{eh} is set to be zero. (We will discuss the effect of V_{eh} later in the paper.)

We first present the results for $v_1 = 0$. The latter does *not* affect the form of the excitation spectrum. We obtain

$$\sigma_{\alpha\alpha}(Q, \omega) = (e^2 v_0^2/2Abi\omega)[F_\alpha(Q, \omega + i\Gamma)$$

$$+ F_\alpha(-Q, -(\omega + i\Gamma))],$$

where

$$F_\alpha = [\chi^\alpha_1 + \chi^\alpha_2 - 2(U_{\alpha,Q} - V_{\alpha,Q})\chi^\alpha_1\chi^\alpha_2]/D_\alpha, \quad (6)$$

$$D_\alpha = (1 - U_{\alpha,Q}\chi^\alpha_1)(1 - U_{\alpha,Q}\chi^\alpha_2) - (V_{\alpha,Q})^2\chi^\alpha_1\chi^\alpha_2,$$
$$(7)$$

in which $\chi^\alpha_i = \chi^\alpha_i(Q, \omega)$ are the propagators for the four component $e_{1g} \to e_{2u}$ monomer transitions. The quantity $\Gamma = \hbar(1/\tau_e + 1/\tau_h)$, where τ_e and τ_h are phenomenologically introduced, momentum independent, lifetimes of

the individual electron and hole states. Γ is also supposed to simulate disorder induced broadening and other microscopic processes, such as phonon excitation, that redistribute the oscillator strength of the absorption bands. Γ merges the exciton and interband absorption bands into a *single* dispersing band peak at the exciton energy. According to Eqs. (1) and (5), $\sigma_{xx}(Q, \omega)$ describes absorption and polarization due to the excitations derived from the $B^\dagger$ and $D^\dagger$ transitions [Fig. 1(b)]. The corresponding propagators are, respectively,

$$\chi_1^x = \chi_B = N^{-1} \sum_k [2\alpha_0 - 4t \cos(kb) \cos(Qb/2) - \omega]^{-1}$$

$$= [(2\alpha_0 - \omega)^2 - W_Q^2]^{-1/2}, \tag{8}$$

and $\chi_2^x = \chi_D = (2\alpha_0 - \omega)^{-1}$. Here $W_Q = W \cos(Qb/2)$, and the bandwidth $W = 4t$. Further, $U_{x,Q} = (U_1 + U_3)/2 + V \cos(Qb)$, $V_{x,Q} = (U_1 - U_3)/2 + V \cos(Qb)$. Now, we note that if $V_{x,Q}$ were zero, the $B^\dagger$ and $D^\dagger$ derived excitations would be decoupled. It follows from Eqs. (6)–(8) that the $B^\dagger$ derived excitations would then consist of a continuum of interband transitions with energies $2\alpha_0 - W_Q \leq \omega \leq 2\alpha_0 + W_Q$, with an excitonic bound state ("$B^\dagger$ exciton") below this continuum with energy

$$\hbar \omega_{Q,1} = 2\alpha_0 - (U_{x,Q}^2 + W_Q^2)^{1/2}. \tag{9}$$

The fraction of the total oscillator strength of the $B^\dagger$ excitations assumed by this exciton would be $f_Q = U_{x,Q}/(U_{x,Q}^2 + W_Q^2)^{1/2}$. On the other hand, the $D^\dagger$ derived excitations would consist of a single dispersing Frenkel-like exciton ("$D^\dagger$ exciton") with energy

$$\hbar \omega_{Q,2} = 2\alpha_0 - U_{x,Q} \tag{10}$$

and one-half of the oscillator strength of the original $E_{1u}(x)$ excitation. In general, the two types of excitations are coupled to each other by $V_{x,Q} \neq 0$ and lead generically to a lower energy and higher energy absorption band in $\mathrm{Re}\,\sigma_{xx}(Q, \omega)$. This coupling is reflected in the function D_x, Eq. (7), the zeros of which determine the energies $\hbar \omega_Q$ and lifetimes of the $B^\dagger$ and $D^\dagger$ excitons.

When $v_1 \neq 0$, the total interband current contributed by the excitation $b_{k+Q/2,\sigma}^\dagger a_{-k+Q/2,-\sigma}^\dagger$ is changed from $v_0/2$ to $v_{k,Q}/2 = v_0/2 + v_1 \cos(kb) \cos(Qb/2)$. The net effect is to increase the oscillator strength of the lower energy band relative to the higher energy one (see Fig. 2, where $v_1 = 0.25 v_0$). It is straightforward to obtain the formula replacing Eq. (6) for this case. Space prevents us from considering it here, and it will be presented in the full version of this paper [17]. We will use it, however, to obtain the calculated plots of $\sigma_{xx}(Q, \omega)$ to be shown in Figs. 2 and 3.

$\sigma_{yy}(Q, \omega)$ describes the excitations derived from the $A^\dagger$ and $C^\dagger$ $e_{1g} \rightarrow e_{2u}$ excitations of the monomer [Eq. (2), Fig. 1(b)]. The formula (6) in which $U_{y,Q} = (U_2 + U_4)/2 - V \cos(Qb)/2$, $V_{y,Q} = (U_2 - U_4)/2 - V \cos(Qb)/2$ is
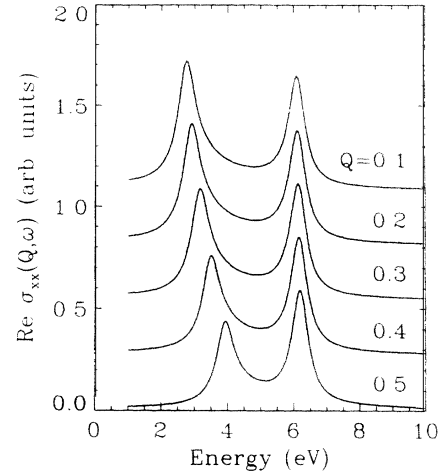

FIG. 3. $\mathrm{Re}\,\sigma_{xx}(Q, \omega)$ vs the energy $\hbar \omega$ for given values of the wave vector Q (in units of π/b) calculated for PPP, employing the parameters given in the text. For each Q the curves are displaced vertically by an arbitrary amount.

simplified because both propagators are equal

$$\chi_1^y = \chi_A = \chi_2^y = \chi_C = N^{-1} \sum_k [2\alpha_0 - 2t \cos(kb) - \omega]^{-1}$$

$$= [(2\alpha_0 - \omega)^2 - (W/2)^2]^{-1/2},$$

so that $F_y = 2\chi_A/(1 - \tilde{U}_{y,Q} \chi_A)$, where $\tilde{U}_{y,Q} = U_2 - V \cos(Qb)$, and the resulting absorption is not split into higher and lower energy bands. In these excitations either the electron is in an extended state while the hole is in a localized monomer state or vice versa. In the limit $\Gamma \rightarrow 0$, we see that the original $E_{1u}(y)$ excitation has spread into a continuum of interband excitations with
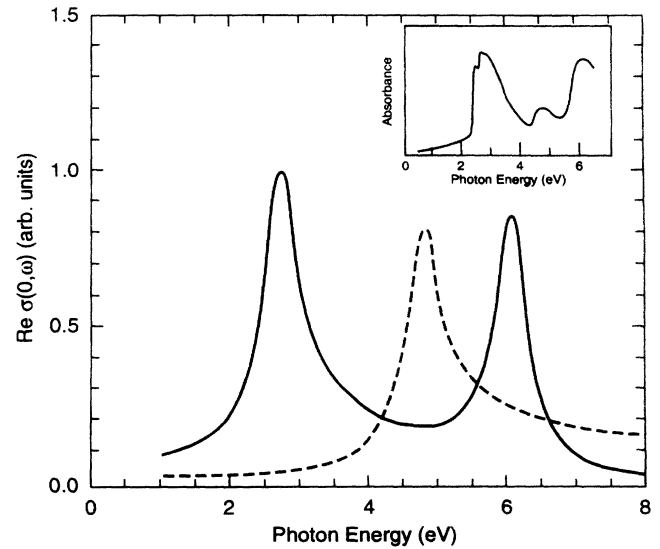

FIG. 2. $\mathrm{Re}\,\sigma_{xx}(0, \omega)$ (full curve) and $\mathrm{Re}\,\sigma_{yy}(0, \omega)$ (broken curve) vs the photon energy $\hbar \omega$ calculated for PPP, employing the parameters given in the text. The inset shows the absorbance spectrum of "standard" PPV (Ref. [18]).

energies $2\alpha_0 - W/2 \leq \omega \leq 2\alpha_0 + W/2$, together with an exciton below this continuum with energy

$$\hbar\omega_{Q,3} = 2\alpha_0 - [\tilde{U}^2_{y,Q} + (W/2)^2]^{1/2}. \quad (11)$$

The fraction of the total oscillator strength taken by this exciton is $f_Q = \tilde{U}_{y,Q}/[\tilde{U}^2_{y,Q} + (W/2)^2]^{1/2}$. Its energy lies in between those of the two $E_{1u}(x)$ derived excitations. The polarization of this "intermediate energy" exciton is different from that of the other two. Finally, we note from Eq. (7) for D_y that there is a *fourth*, dipole forbidden, singlet exciton with energy $\hbar\omega_4 = 2\alpha_0 - [U^2_4 + (W/2)^2]^{1/2}$. It is derived from the B_{2u} excitation.

When the polymer axis makes a finite angle θ with the phenylene x axis, all three bands will appear in $\sigma(Q,\omega)$ for a given polarization of the electric field vector. In the inset of Fig. 2 an experimental absorption spectrum [18] of PPV is shown, the three-peak structure of which we interpret as being due to these absorption bands. The relative spacings in energy of the three bands are largely set by U and W but are corrected by V and V_{eh}. It is important to notice that in the absence of *any* Coulomb interaction ($U = V = 0$), the intermediate energy peak would fall precisely in the middle of the lower and higher energy peaks [see Eqs. (9)–(11)]. The shift of the intermediate peak from such a position indicates the significance of the Coulomb interaction. In Fig. 2 we have calculated $\sigma_{xx}(0,\omega)$ and $\sigma_{yy}(0,\omega)$ vs $\hbar\omega$ for the PPP model, employing the parameter values $2\alpha_0 = 7$ eV, $U_n = U = 0.8$ eV (all n), $W = 4.2$ eV, $V = 0.1$ eV, $v_1 = 0.25v_0$, and $\Gamma = 0.3$ eV. These *trial* values of the parameters yield absorption peaks at the three exciton energies ~2.7, 4.8, and 6.1 eV close to the three peaks of the experimental data. Note that $V_{eh} \neq 0$ does not affect the higher energy peak (Frenkel-like exciton) but moves the two other peaks downward in energy. In independent calculations [19] on finite chains, we have included the long-range Coulomb interaction V_{eh} exactly and find that the corresponding two exciton energies can be lowered by ~0.1–0.2 eV. Of course, it is impossible to extract unambiguously all the values of the microscopic parameters from only three experimental peak positions. More could be done by analysis of EELS data. Figure 3 presents calculations of $\sigma_{xx}(Q,\omega)$ vs $\hbar\omega$ for increasing values of Qb/π. For clarity, the dispersing $E_{1u}(y)$ band (having a "negative" dispersion) is not shown. The calculated spectra are in good qualitative agreement with the EELS data of the Fink group [2,8] for PPP and PPV. However, the lack of good crystallinity of the materials studied in these experiments precludes a detailed fit of the present theory. EELS measurements on films of improved crystallinity would be able to test the detailed validity of our microscopic model.

Finally, from the spacing of all three bands [18] we are able to assess the relative importance of excitonic and interband excitation in the lowest energy band of

PPV: The $B^\dagger$ exciton assumes $\sim(U + V)/W \sim 20\%$ of the total oscillator strength of the delocalized electron-hole pair excitations and has a binding energy $\sim(U + V)^2/2W \sim 0.1$ eV. This places the exciton in the weak-coupling regime ($W \gg U$).

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