

Charge-conjugation symmetry breaking and the absorption spectra of polyphenylenes

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The effects on the absorption spectra of polyphenylenes of charge-conjugation symmetry breaking are studied within the framework of a recently introduced microscopic model. Breaking of this symmetry is shown to result in the appearance of a fourth distinct absorption band in the spectra of derivatized and atomically bridged polyphenylenes, providing further direct experimental information on the intramonomer contribution to the effective electron-hole interaction.

A fundamental problem in conjugated polymers, particularly in the polyphenylenes,¹ is understanding the origin and nature of their absorption bands. The crucial factor in this problem is the magnitude of the *effective* Coulomb interaction H_{e-h} between an electron and a hole relative to the π -electron bandwidth W . Practically, conclusions on this relative magnitude are made on the basis of indirect experimental evidence and are frequently controversial. A good example of the latter is the current intense debate on the nature of the lowest energy absorption band in poly(phenylene vinylene) (PPV),²⁻⁵ for which estimates of the excitonic binding energy range from thermal energies, $k_B T$,³ to the order of 1 eV.^{4,5}

Recently, two of the present authors have introduced⁶ a simplified but analytically explicit microscopic model (hereafter referred to as RG), which we believe elucidates the essential physics of the photoexcitations of the polyphenylenes. Since these polymers are essentially chains of linked phenylene monomers, the model recognizes that their singlet excitations are derived from the four singlet ($e_{1g} \rightarrow e_{2u}$) excitations of the local phenylene monomer. If the polyphenylene possesses charge-conjugation symmetry (CCS),⁷ that is, electron-hole symmetry, the model leads to the generic appearance of three principal absorption bands. The relative spacings and intensities of these bands are set by W and key parameters specifying the magnitude of H_{e-h} , thereby establishing direct experimental access to these microscopic parameters. Very interestingly, there is a *fourth*, dipole forbidden, singlet excitation band which is rendered allowed if the CCS of the polyphenylene is broken. The RG model has been studied analytically⁶ and numerically for oligomers^{8,9} and approximate fits to the three main absorption bands of PPV (Refs. 10-12) have indicated that the *lowest* energy exciton in PPV is weakly bound in the sense that the *relevant part* of H_{e-h} is small by comparison to W .

Here, we explicitly consider CCS-breaking terms in the RG model and demonstrate the appearance of the fourth absorption band as a natural consequence of them. We do this for derivatized polyphenylenes, where CCS is violated by side groups attached to the phenylene monomer, and atomically bridged polyphenylenes, where the electron-hole symmetry is broken by the presence of the bridging atoms [see examples in Figs. 1(a) and 1(b)]. Importantly, the appearance of the fourth peak in PPV derivatives can be explained con-

sistently with the estimates of the microscopic parameters deduced from our previous analysis^{6,8} of the three main absorption bands in this polymer. This is in sharp contrast to the consideration of Ref. 5, where the appearance of the fourth peak in the spectrum of MEH-PPV (Ref. 13) was attributed entirely to the strength of electron-electron correlations exceeding a threshold value in a Pariser-Parr-Pople-like model of PPV which, because it preserves CCS, makes no allowance whatsoever for the substitution of the phenylene monomer. Recently, a fourth peak in the absorption spectrum has also been observed¹⁴ in alkoxysulfonate-substituted poly(paraphenylene) (PPP),¹⁵ confirming that the symmetry-breaking-induced transition dipole moment we describe here is a general characteristic of substituted polyphenylenes.

The model of RG explicitly regards each phenylene monomer as providing two hole states, labeled a and c , and two electron states, labeled b and d . In an undistorted phenyl ring under an assumed D_{6h} symmetry, the states in each pair are degenerate and have e_{1g} and e_{2u} orbital patterns.¹⁶ Explicitly, their respective molecular orbitals (MO's) are $\psi_a = (12)^{-1/2} \times (2, 1, -1, -2, -1, 1)$, $\psi_b = (12)^{-1/2} \times (-2, 1, 1, -2, 1, 1)$, $\psi_c = 2^{-1} \times (0, -1, -1, 0, 1, 1)$, and $\psi_d = 2^{-1} \times (0, -1, 1, 0, -1, 1)$, where each component of the MO specifies the atomic $C(2p)$ site amplitude in the order of the numbering of the carbon atoms given in Fig. 1. The corresponding singlet excitations of the monomer are described by the operators $B_{j\sigma}^\dagger = b_{j\sigma}^\dagger a_{j,-\sigma}^\dagger$, $D_{j\sigma}^\dagger = d_{j\sigma}^\dagger c_{j,-\sigma}^\dagger$, $A_{j\sigma}^\dagger = d_{j\sigma}^\dagger a_{j,-\sigma}^\dagger$,

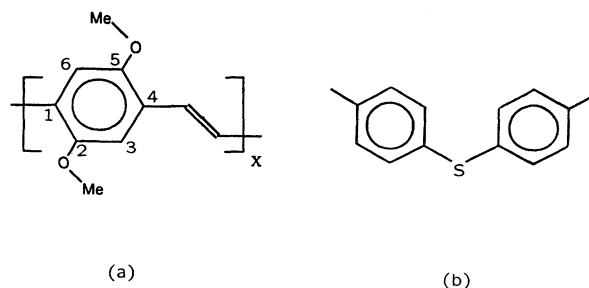


FIG. 1. Schematic structures of (a) dimethoxy PPV and (b) an atomically bridged polyphenylene. The numbering of carbon atoms used in the text is shown.

and $C_{j\sigma}^\dagger = b_{j\sigma}^\dagger c_{j,-\sigma}^\dagger$, where the fermion operators $a_{j\sigma}^\dagger$, $b_{j\sigma}^\dagger$, $c_{j\sigma}^\dagger$, and $d_{j\sigma}^\dagger$ create, respectively, an electron or hole with spin polarization σ in the specified orbitals of the monomer j ($j=1, \dots, N$). These excitations may be combined to form the four ($n=1,2,3,4$) following singlet excitations of the phenylene monomer:¹⁷

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

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

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

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

The excitations of Eqs. (1) and (2) have transition dipole moments in the monomer x and y directions, respectively, while the excitations of Eqs. (3) and (4) are dipole forbidden under D_{6h} symmetry.¹⁶

In a general form, the Hamiltonian H defining the RG model⁶ is

$$H = \sum_{j\sigma} \{E_h^a a_{j\sigma}^\dagger a_{j\sigma} + E_h^c c_{j\sigma}^\dagger c_{j\sigma} + E_e^b b_{j\sigma}^\dagger b_{j\sigma} + E_e^d d_{j\sigma}^\dagger d_{j\sigma}\} + H_d + H_{e-h}, \quad (5)$$

where the E 's are the excitation energies of electrons and holes in the orbitals mentioned,

$$H_d = - \sum_{j\sigma} \{t_{bb}(b_{j+1,\sigma}^\dagger b_{j\sigma} + \text{H.c.}) + t_{aa}(a_{j+1,\sigma}^\dagger a_{j\sigma} + \text{H.c.}) + t_{ab}((b_{j+1,\sigma}^\dagger - b_{j-1,\sigma}^\dagger)a_{j,-\sigma}^\dagger + \text{H.c.})\} \quad (6)$$

describes the delocalization of the b and a orbitals due to the intermolecular hopping integrals t (the c and d orbitals remain localized), while

$$H_{e-h} = - \sum_{jn} U_n P_{jn}^\dagger P_{jn} + V_{dd} + V_{e-h} \quad (7)$$

specifies the leading contributions arising from Coulomb interactions. The first term in Eq. (7) defines 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 . $V_{dd} = - \sum_{jnm} V_{nm}(P_{j+1,n}^\dagger + P_{j+1,n})(P_{jm}^\dagger + P_{jm})$ describes the delocalization of the charge-neutral intramonomer excitations via the dipole-dipole interaction. In this paper we will use the simplified structure of PPP, in which case $V_{11} = V$, $V_{22} = -V/2$, while $V_{nm} = 0$ otherwise.⁶ The long-range Coulomb interaction is introduced as $V_{e-h} = V_c \sum_{j \neq l} \rho_j \rho_l / |2j - l|$, where $\rho_j = \sum_{\sigma} (a_{j\sigma}^\dagger a_{j\sigma} + c_{j\sigma}^\dagger c_{j\sigma} - b_{j\sigma}^\dagger b_{j\sigma} - d_{j\sigma}^\dagger d_{j\sigma})$ is the net charge density on the monomer j .

The interband transition dipole moments relevant to the optical absorption are discussed in Ref. 6 and, for the model in which the x axis of the phenylene monomer coincides with the polymer axis, are given by

$$P_j^x = \mu_0(P_{j,1}^\dagger + P_{j,1}) + (\mu_1/2) \sum_{\sigma} [(b_{j+1,\sigma}^\dagger + b_{j-1,\sigma}^\dagger)a_{j,-\sigma}^\dagger + \text{H.c.}],$$

$$P_j^y = \mu_0(P_{j,2}^\dagger + P_{j,2})$$

for the x and y directions, respectively. Here μ_0 arises from the transition dipole moments of the local E_{1u} excitations while μ_1 arises from the ‘‘oblique’’ interband hopping terms in H_d . The B^\dagger and D^\dagger transitions are polarized along the chain, while the A^\dagger and C^\dagger transitions are polarized perpendicular to it.

CCS is broken in the model of Eq. (5) when (a) the local monomer energies E satisfy $E_e^d - E_e^b \neq E_h^c - E_h^a$, and (b) the hopping integrals t_{aa} and t_{bb} are different.

It is easy to understand why the structures of Fig. 1 lead to breakdown of CCS. In the case of Fig. 1(a) we may, most simply, represent a side group by one electron level with energy E_s with respect to the atomic $C(2p)$ energy and introduce the matrix element t_s for the hopping of an electron between this level and the neighboring carbon atom. The perturbation Hamiltonian for a single monomer is then $V_p = V_{p2} + V_{p5}$, where $V_{p2} = t_s(a_2^\dagger s_2 + \text{H.c.}) + E_s s_2^\dagger s_2$, a_2^\dagger being the electron site creation operator for the carbon site 2, while s_2^\dagger is the site creation operator for the side group 2 (spin indices omitted). (V_{p5} is analogous to V_{p2} with indices 2 being replaced by 5.) Assuming the corrections to the energies E to be small, second-order perturbation theory in t_s yields them as $\delta E_h^a = \epsilon_1/6$, $\delta E_h^c = \epsilon_1/2$, $\delta E_e^b = \epsilon_2/6$, $\delta E_e^d = \epsilon_2/2$, where $\epsilon_1 = t_s^2/(\alpha_0 + E_s)$ and $\epsilon_2 = t_s^2/(\alpha_0 - E_s)$.¹⁸ It is important to note the following: (1) Electron and hole excitation energies within pairs of localized (c and d) and delocalizable (a and b) states are shifted by different amounts ($\epsilon_1 \neq \epsilon_2$). This results in either positive ($|E_s| < \alpha_0$) or negative ($|E_s| > \alpha_0$) shifts of the band absorption edges for x -polarized transitions. (2) Within each pair of electron (b and d) and hole (a and c) states, the corrections are different. This results in shifts *and* splitting of the band edges for y -polarized transitions. Note that the second effect also occurs if $t_s = 0$ but the energies of the $C(2p)$ orbitals on sites 2 and 5 are inductively modified by amounts $\Delta E \neq 0$. If the intermonomer hopping in Eq. (6) is a stronger interaction than the coupling to the side groups, the perturbing effect of the latter on the *band states* derived from the a and b orbitals must be calculated. Since the band levels closer to E_s experience larger shifts in energy, this can lead to different effective bandwidths for the conduction and valence bands. [Of course, in detailed calculations more than one energy level associated with a side group can be involved. See, e.g., the quantitative results of valence effective Hamiltonian¹⁹ and intermediate neglect of differential overlap²⁰ calculations for oligomers of PPV derivatives.] The principal effects of side groups in the model of Eq. (5) therefore may, in general, be taken into account by setting $t_{aa} \neq t_{bb}$ and

$$E_e^b = E_h^a = \alpha_1, \quad E_e^d = \alpha_2 + \delta, \quad E_h^c = \alpha_2 - \delta, \quad (8)$$

where in Eq. (8) we have redefined the zero of energy. Consequently, already in a band picture with $H_{e-h}=0$, four, rather than three, absorption bands occur in the polymer, and at the following threshold energies: $2\alpha_1 - 2(t_{aa} + t_{bb})$ for the B^\dagger transitions, $\alpha_1 + \alpha_2 - \delta - 2t_{bb}$ for the C^\dagger transitions, $\alpha_1 + \alpha_2 + \delta - 2t_{aa}$ for the A^\dagger transitions, and $2\alpha_2$ for the D^\dagger transitions.

The case of atomically bridged polyphenylenes [Fig. 1(b)] can be treated analogously. If E_s is now the pertinent energy level of the bridging atom and t_s is the hopping integral between the phenylene *end* carbons and this atom, then corrections to the excitation energies occur only for the delocalizable states: $\delta E_e^b = 2\epsilon_2/3$ and $\delta E_h^a = 2\epsilon_1/3$. The importance of this effect in understanding the $C(1s)$ - π^* excitation spectra of these polyphenylenes has been stressed by Crecelius *et al.*²² Of course, CCS is also broken through $t_{aa} \neq t_{bb}$ and the perturbation calculation yields $t_{aa} = |\epsilon_1|/3$ and $t_{bb} = |\epsilon_2|/3$.

When $H_{e-h} \neq 0$, the four independent transitions of the simple band picture are profoundly modified: they couple to each other and at the same time transfer oscillator strength to excitons.⁶ If the long-range Coulomb interaction V_{e-h} is neglected analytical expressions for the frequency- (ω) and wave-vector- (Q) dependent conductivity $\sigma_{\alpha\alpha}(Q, \omega)$ ($\alpha=x$ or y) of an infinite polymer chain may be derived from the Kubo formula. The result for $\sigma_{yy}(Q, \omega)$ is

$$\sigma_{yy}(Q, \omega) = (e^2/2Abi\omega)[F_y(Q, \omega + i\Gamma) + F_y(-Q, -(\omega + i\Gamma))], \quad (9)$$

where

$$F_y = [v_A^2 R_A + v_C^2 R_C + 2v_A v_C V_{y,Q} \chi_A \chi_C] / D_y, \quad (10)$$

$$D_y = (1 - U_{y,Q} \chi_A)(1 - U_{y,Q} \chi_C) - (V_{y,Q})^2 \chi_A \chi_C. \quad (11)$$

In Eq. (9), b is the lattice constant of the chain, A is the transverse area corresponding to one chain, and Γ is a phenomenologically introduced broadening parameter:

$$R_A = \chi_A(1 - U_{y,Q} \chi_C), \quad R_C = \chi_C(1 - U_{y,Q} \chi_A).$$

In Eqs. (10) and (11), $\chi_A(\omega)$ and $\chi_C(\omega)$ are the propagators for the A^\dagger and C^\dagger interband transitions:

$$\chi_A = N^{-1} \sum_k [\alpha_1 + \alpha_2 + \delta - 2t_{aa} \cos(kb) - \omega]^{-1} \\ = [(\alpha_1 + \alpha_2 + \delta - \omega)^2 - (W_a/2)^2]^{-1/2}$$

and

$$\chi_C = [(\alpha_1 + \alpha_2 - \delta - \omega)^2 - (W_b/2)^2]^{-1/2},$$

where $W_a = 4t_{aa}$, $W_b = 4t_{bb}$. The velocities $v_A = \mu_0(\alpha_1 + \alpha_2 + \delta)/e\hbar$ and $v_C = \mu_0(\alpha_1 + \alpha_2 - \delta)/e\hbar$. The function $D_y(Q, \omega)$, in which

$$U_{y,Q} = (U_2 + U_4)/2 - V \cos(Qb)/2,$$

$$V_{y,Q} = (U_2 - U_4)/2 - V \cos(Qb)/2,$$

expresses the coupling between $A^\dagger + C^\dagger$ and $A^\dagger - C^\dagger$ transitions. Its zeros as a function of ω determine the energies $\hbar\omega_Q$ of the $E_{1u}(y)$ - and B_{2u} -derived excitons. In systems where CCS is preserved $v_A = v_C$ both propagators are equal, $\chi_A = \chi_C$, and Eq. (10) is simplified: $F_y = 2v_A^2 \chi_A / (1 - U \chi_A)$, where $U = U_2 - V \cos(Qb)$, so that the resulting absorption is a single band, corresponding to $A^\dagger + C^\dagger$ excitations [Eq. (2)], while the $A^\dagger - C^\dagger$ B_{2u} -derived excitations [Eq. (4)] have vanishing transition dipole moment. The energy of the allowed $E_{1u}(y)$ -derived exciton is $\hbar\omega_3 = \alpha_1 + \alpha_2 - [\tilde{U}^2 + (W/2)^2]^{1/2}$ while the energy of the forbidden B_{2u} -derived exciton is $\hbar\omega_4 = \alpha_1 + \alpha_2 - [U_4^2 + (W/2)^2]^{1/2}$. Both exciton bands become allowed when $\chi_A \neq \chi_C$. In this case the function F_y shows that the B_{2u} -derived excitations borrow oscillator strength from the E_{1u} -derived excitations. If CCS is only weakly broken ($\delta \approx 0$, $W_a \approx W_b = W$) the energy of the B_{2u} -derived exciton is just $\hbar\omega_4$.

The corresponding formula for $\sigma_{xx}(Q, \omega)$ is given in Ref. 8 and expresses σ_{xx} in terms of the propagators χ_B and χ_D for the B^\dagger and D^\dagger transitions:

$$\chi_B = N^{-1} \sum_k [2\alpha_1 - 2(t_{aa} + t_{bb}) \cos(kb) \cos(Qb/2) - \omega]^{-1} \\ = [(2\alpha_1 - \omega)^2 - W_Q^2]^{-1/2},$$

$$\chi_D = (2\alpha_2 - \omega)^{-1}.$$

Here $W_Q = W \cos(Qb/2)$ and the bandwidth $W = (W_a + W_b)/2$. The energies of the two excitons $\hbar\omega_1$ and $\hbar\omega_2$ associated with these transitions are given by the zeros of the function $D_x(Q, \omega)$,

$$D_x = (1 - U_{x,Q} \chi_B)(1 - U_{x,Q} \chi_D) - (V_{x,Q})^2 \chi_B \chi_D, \quad (12)$$

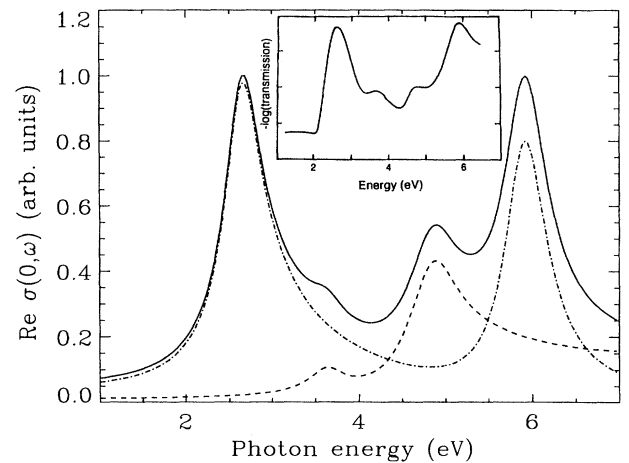


FIG. 2. Analytically calculated absorption spectra of a long polymer chain. The parameters used are listed in the text. The peak close to 3.7 eV arises as a consequence of broken charge-conjugation symmetry. The dash-dotted line is for the x -polarized absorption, the dashed line for the y -polarized one, and the solid line gives their sum representing unpolarized absorption. The inset shows an absorption spectrum of dimethoxy PPV taken from Ref. 20.

in which

$$U_{x,Q} = (U_1 + U_3)/2 + V \cos(Qb),$$

$$V_{x,Q} = (U_1 - U_3)/2 + V \cos(Qb).$$

Thus the energies of the polymer's family of four excitons are determined by Eqs. (11) and (12).

Figure 2 shows the absorption spectrum calculated from the analytical formulas for σ_{yy} and σ_{xx} employing the parameter values $\alpha_1 = 3.35$ eV, $\alpha_2 = 3.25$ eV, $t_{aa} = t_{bb} = 1$ eV, $U_1 = U_2 = 0.2$ eV, $U_3 = 1$ eV, $U_4 = 2$ eV, $\mu_1/\mu_0 = 0.45$, $\Gamma = 0.25$ eV, and $V = 0$. The CCS-breaking parameter is taken to be²¹ $|\delta| = 0.4$ eV and leads to the "fourth" absorption band close to 3.7 eV. The former set of parameter values is close to that of our previous analysis⁸ of the absorption spectrum of PPV. Note that the energy difference between the two central peaks is essentially determined by t , U_4 , and U_2 . The finite value of δ does correct this quantity but the main effect of δ is to provide the *intensity*, i.e., the transition dipole moment, of the "fourth" absorption band. For comparison, in the inset of Fig. 2, the experimental spectrum²⁰ of

dimethoxy PPV is shown. The experimental spectrum of MEH-PPV is very similar.⁵ It is apparent that the gross features of the experimental spectrum are well reproduced by the theoretical calculations. We have also performed numerical calculations for finite chains, which include the long-range Coulomb interaction V_{e-h} not taken into account in the analytical theory. For a chain of $N = 10$ monomers, e.g., we find that the calculated absorption spectrum closely resembles the analytic spectrum of Fig. 2.

The appearance of a fourth distinct band in the absorption spectra of derivatized polyphenylenes^{5,14,20} has therefore a natural explanation in terms of the breaking of the CCS of the unsubstituted polymer. The appearance of additional structure in the spectra of atomically bridged polyphenylenes observed by Crecelius *et al.*²² can similarly be interpreted as a signature of CCS violation in these systems. For them, the difference between the electron and hole bandwidths, $W_a - W_b$, is an important CCS-breaking parameter in addition to δ . Finally, we mention that an indistinct absorption feature at ~ 3.7 eV in unsubstituted PPV,¹¹ if unambiguously established as such,²³ may reflect weak CCS breaking occurring in the real polymer, e.g., due to interchain interactions.²⁴

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¹⁸In fact, the perturbation also induces transitions between $b \leftrightarrow d$ and $a \leftrightarrow c$ intramonomer orbitals, which is beyond H in the form of Eq. (5) and will therefore be ignored in the present paper. The effects of such transitions can be found in Refs. 19 and 20.

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²³We warn of a possible source of confusion on this point which arises from the results of recent calculations (Ref. 20) on PPV oligomers. Cornil *et al.* (Ref. 20) find a small "fourth" peak both in underivatized and derivatized PPV. The main point to realize here is that in their calculations the "fourth" peaks obtained in underivatized and derivatized PPV have entirely different origins: compare the assignments for peak II in Tables 1 and 2 in Ref. 20. Most probably, the peak they find for *underivatized* PPV is due to the short length of the oligomer ("finite-box" effect).

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