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Photoinduced charge transfer in poly(p-phenylene vinylene)

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It has been suggested that excitation of poly(p-phenylene vinylene) (PPV) by photons above the absorption edge produces principally polaron pairs or split excitons. We show that such polaron pairs can account very well for the peaks in the observed picosecond photoinduced absorption, the width of the absorption, and other phenomena associated with photon absorption in PPV.

Exposure of poly(p-phenylene vinylene) (PPV) or its derivatives to light above the absorption edge creates excitons,[1] which, as inferred from the resemblance of their emission to that of PPV oligomers, occupy a single chain. Exposure to such photons might also be expected to create polarons, particularly for light polarized with electric vector perpendicular to the chains. To identify the excitations created a number of groups have carried out picosecond photoinduced absorption (PA) experiments.[2–5] Over the range investigated, the PA consists of two broad absorptions, peaked at ~1.5 and ~0.5 eV, the former region containing a weak secondary peak at 2.15 eV. Hsu *et al.*, whose studies eliminated a number of possible explanations, suggested that the PA is due to polaron pairs bound on neighboring chains by Coulomb attraction.[4] In later work Yan *et al.* estimated that 80–90 % of the excitations are polaron pairs, only 10–20 % being excitons.[6] More direct evidence that the excitations giving rise to the PA involve more than one chain was obtained by comparing the behavior of dilute solutions and thin films of poly[2-methoxy,5-(2′ ethyl-hexoxy)-1,4 phenylene vinylene] (MEH-PPV).[7] In the solution the ps PA dynamics match those of the photoluminescence (PL) indicating that the PA is due to singlet excitons. For the MEH-PPV thin film, however, the PL shows different, and overall more rapid, decay dynamics than the PA, which shows the long, plateaulike tail seen in the other PPV's.[7]

We have calculated the properties of polarons and polaron pairs in PPV as a function of chain (i.e., conjugation) length. Many different types of evidence have led to the picture of a typical PPV sample as an assembly of oligomers with average length of ~7, or perhaps as much as 10, monomers. When a photon of sufficient energy is absorbed, creating an electron and hole on a single chain, they may, as noted earlier, form an exciton. Alternatively the hole may be filled by an electron from a neighboring chain, creating a polaron P^- on the acceptor chain, P^+ on the donor chain. Another possibility, particularly for electric vector E perpendicular to the chains, is that electron and hole are created on separate chains and evolve into polarons. In fact more PA is seen for E perpendicular to the chains.[4] Note that the distance between inequivalent chains, which are the more strongly coupled ones, is 4 Å, typical of the distance between molecules that form charge-transfer states or excimers.[8] We will show that the peaks of PA predicted for such a polaron pair are in good agreement with the observed ones and their observed widths can reasonably be explained by this mechanism.

As background we enumerate what experiments have shown the ps PA is *not* due to. Early suggestions that this PA is due to a triplet exciton, which has an absorption centered at ~1.5 eV,[9] were eliminated by the discovery of the second PA peak at 0.5 eV with the same dynamics as the 1.5-eV peak.[4] The possibility that the excitations are singlet excitons is eliminated by the very different decay times for PA and PL, mentioned earlier for MEH-PPV films, and the observed competition between stimulated emission due to the excitons and the PA.[6] The fact that the ps photoconductivity of PPV is comparable to that of $(CH)_x$,[10] where it is acknowledged that only ~1 % of the photons create carriers,[11] indicates that the 80–90 % of the excitations we are discussing cannot be single polarons. [Note that we expect comparable drift mobility in PPV and $(CH)_x$; the polaron masses are similar, as will be shown.] Also, if there were so many polarons we would expect them to decay by polaron-polaron recombination[12] but there is no intensity dependence in the PA decay.[4] The possibility of the excitations being bipolarons is eliminated by the fact that they are formed within fs.[4] It has been suggested that the excitations are biexcitons.[5,13] This, however, is in contradiction with the results on MEH-PPV in solution, where it is shown that the excitations are not formed on isolated chains.

To study the properties of polaron pairs in PPV we first need a Hamiltonian suitable for describing polarons in that material. Because there are no explicit Coulomb interactions involved in the polaron, as there are in the case of the exciton or bipolaron, for example, we feel that good results can be obtained from a tight-binding Hamiltonian in the spirit of the Su-Schrieffer-Heeger Hamiltonian[14] with parameters chosen to fit experimental data. This was judged to be the case for polyacetylene and other conducting polymers,[15] where in fact results in reasonable agreement with experiment were obtained for even the upper bipolaron level. Further, as pointed out earlier for $(CH)_x$, choice of the parameters to fit experimental data does result in the inclusion of the effect of electron-electron correlation, possibly more reliably in this case than inclusion of terms with poorly known on-site Coulomb repulsion U and near-neighbor interaction potential V.[16] The Hamiltonian we used was

$$H=\sum_{m=1}^{M}\sum_{\langle ij\rangle}[-(t_0-\alpha u_{\langle ij\rangle})c_i^\dagger c_j+\tfrac{1}{2}K(u_{\langle ij\rangle}-C)^2+\mathrm{H.c.}], \tag{1}$$

where M is the number of monomers in the chain and $\langle ij\rangle$ indicates one of the pairs of nearest neighbors in the monomer. The sum is taken over all nine pairs. t_0 is the electronic coupling or transfer integral between neighboring π orbitals and $u_{\langle ij\rangle}$ is the change in length of the $\langle ij\rangle$ bond, referred to an imagined initial state with all bonds equal in length. α is the ratio between electronic coupling change and bond length change and K is the effective spring constant, due to the σ bonds. C is a stiffness constant adjusted to give the correct chain length in a self-consistent calculation.[17] The parameters t_0, α, and K were chosen so that calculations with Eq. (1) gave values within 1% for three quantities: (1) the difference between single bond length, 1.474 Å, and double bond length, 1.355 Å, of the vinyl group as determined by modified neglect of differential overlap; (2) the valence-band width, 5.47 eV, obtained by local-density functional (LDF) theory;[18] (3) the energy gap, 2.8 eV.[19] The values that satisfy the criterion just given are $t_0=2.66$ eV, $\alpha=10.29$ eV/Å, and $K=99.0$ eV/Å^2. Larger values than those familiar from polyacetylene, $(\mathrm{CH})_x$,[14] were expected because the band gap is twice as large, and the vinyl dimerization is 40% larger.

From a self-consistent calculation with the Hamiltonian (1) and the parameters just specified, the energy interval between the polaron level and the next level on a long chain of PPV ($\geqslant$ 20 monomers) was found to be 0.18 eV. It is larger, of course, for short chains.[20] The half-width of the polaron is ~4 monomers or ~26 Å. Significantly, a calculation of the polaron geometry using the unrestricted Hartree-Fock *PM*3 method gave results in good agreement with ours. This agreement is additional evidence for the validity of our Hamiltonian. Knowing the polaron geometry, we calculated the mass of the polaron m_p as was done for the soliton mass in Ref. 14.[20] The resulting m_p was $1.8m_e$, comparable to $m_p=1m_e$ in $(\mathrm{CH})_x$, m_e being the free electron mass.

To treat the case of a polaron pair on adjacent chains we added to Eq. (1) the term giving the potential at the ith atom on one of the chains due to the charge on the other chain:

$$V_i=-\sum_j ee_j/\varepsilon_\perp[(d_\parallel)_{ij}^2+(\varepsilon_\parallel/\varepsilon_\perp)(d_\perp)_{ij}^2]^{1/2}, \tag{2}$$

where the summation is over all the sites on the other chain, e_j is the charge on the jth site (determined self-consistently), $(d_\parallel)_{ij}^2$ and $(d_\perp)_{ij}^2$ the parallel and perpendicular components, respectively, of the distance between the site i and the site j, $\varepsilon_\parallel$ and $\varepsilon_\perp$ the dielectric constants parallel and perpendicular to the chain direction, taken as 8 and 3, respectively. We obtained $\langle t_\perp\rangle$, the average interchain transfer integral, by taking the LDF calculated splitting due to interchain coupling, 0.32 eV (Ref. 18) as $4\langle t_\perp\rangle$ because each chain has four (inequivalent) chains as nearest neighbors. The interchain coupling for a pair of monomers is then $8\langle t_\perp\rangle$. To apportion this among the eight atom pairs of the monomer, each of which has different spacing, we took into account the exponential dependence of $t_\perp$ on the distance between the atoms of a pair,[20] known from crystallographic studies. The value of $\langle t_\perp\rangle$ is smaller than in polyacetylene and the polaron in PPV was found to be stable under this coupling. However, as in polyacetylene, the interchain coupling resulted in a portion, ~10%, of the polaron being shifted to the coupled chain.[21]

For our calculations of the energy levels of a P^+-P^- pair we give results only for the two chains of the same length. When the lengths were not matched, or did not totally overlap each other, the polarons still tended to sit opposite each other, due to the Coulomb attraction. The effect was essentially that of equal length chains, although the length might be smaller than that of either chain. To determine the stability of a polaron pair relative to that of an exciton we calculated the formation energy of the pair, i.e., the difference between the total (lattice plus electronic) energy of a pair of coupled PPV chains containing a P^+-P^- pair and that of the two coupled chains in their ground state. Each energy was determined self-consistently. The result was that the energy required to create a pair on adjacent chains varies little with chain length, from 2.1 eV for 2-monomer-long chains to a minimum of 1.9 eV for 5-monomer chains, then going to a constant value of 2.0 eV for chains up to 30 monomers. The energy required to create an exciton is given by the optical absorption edge, usually taken as 2.3 or 2.4 eV. The absorption tail to lower energies might conceivably be in part due to exciton creation on longer than average chains. For chains shorter than average exciton creation energy is higher than 2.3 or 2.4 eV.[22] Thus polaron pair creation is favored over exciton creation with the possible exception of very long chains. This result is not surprising; being on adjacent chains, thus only 4 Å apart, the electron and hole can take greater advantage of the Coulomb energy than they can in an exciton, which has a length greater than 6 monomers, or 40 Å (Ref. 23) if the chain length allows. The energy levels for the situation of the polarons exactly opposite each other are given in Fig. 1 for two 7-monomer chains. As expected, the levels on the chain with P^- are pulled down due to the attraction of P^+, while those on the chain with P^+ are moved up due to the repulsion of P^-. The polaron levels, with the polaron being localized opposite the polaron on the other chain, move more than the conduction- or valence-band levels, the distance of the top P^- level and the lower P^+ level from the band edge thus increasing from 0.2 to 0.4 eV. For a 5-monomer chain the distance increases to 0.54 eV. The lower P^- level and the upper P^+ level move into the valence and conduction bands, respectively. The introduction of the interchain coupling is seen to have little effect on the energy levels. The spacing between the P^- and P^+ levels in the gap is 1.39 eV for 10-monomer chains, 1.42 eV for 5-monomer chains, and goes up to 1.7 eV for 2- and 3-monomer chains. As is seen by comparison of Fig. 1 with the experimental data,[4] the transition between the P^- level and the conduction-band edge, or between the valence-band edge and the P^+ level, matches closely the experimental peak in the infrared, while the transition between the P^- and P^+ levels matches closely that of the visible PA. The weak secondary peak at 2.15 eV referred to earlier corresponds to the transition between the valence-band edge and the P^-

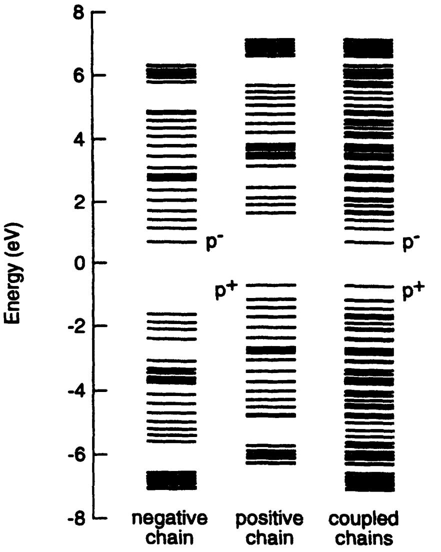

FIG. 1. Energy levels around midgap ($E = 0$) for a polaron pair on 7-monomer-long PPV chains.

level on the P^- chain or between the P^+ level and the conduction band on the P^+ chain. For PPV, for which we did our calculations, the secondary peak is at 2.3 eV. The data were, however, taken on methoxy PPV for which the absorption edge, and therefore the gap, are 0.2 eV lower in energy, resulting in the peak being moved down a little in energy. As a first approximation we could move the peak down by the difference between gaps, 0.2 eV, which would bring it to 2.1 eV, in good agreement with the observed value. However, to find the correct location we would have to go through the procedure of finding t_0, α, and K for a gap of 2.6 eV, etc.

Experimentally, the absorption was found to be much stronger for probe E vector parallel to the chain than perpendicular.[4] This is, of course, expected for the infrared band, which involves only a single polaron. We account for the polarization in the visible band by noting that the spatial part of the wave function must be symmetric, i.e., a superposition of P^+ on, say the left-hand chain and P^- on the right with the equally probable situation of P^- on the left and P^+ on the right. Thus for the visible band the component of the transition dipole perpendicular to the chains vanishes by cancellation. There is absorption for parallel E vector because the interchain coupling results in part of each polaron being on each chain. This suggests that the intensity of the visible peak will be smaller than that of the infrared peak. The ratio of intensities of the two peaks is not known because the experimental data for the infrared band were not carried to high enough frequency. If the intensities are actually comparable it could indicate that the polaron pairs are excimers, with some of the exciton state mixed in with the charge transfer state. In this situation there would be a borrowing of oscillator strength from the exciton transition.[24] It is not expected that the polaron pair state includes a large amount of the exciton state, however, because emission from the polaron pairs has not been detected.

In actuality the polarons are not stationary; each moves in the potential well due to the other, resulting in shifts of the energy levels and the frequencies absorbed. Using our Hamiltonian we found the well to be quadratic in the separation between the polarons to quite large separations, ±2 monomers. With the force constant derived from the shape of the well, and allowing not one but both polarons to execute zero point motion, we estimated the probability of a separation x of the polarons to be proportional to $\exp(-0.46x^2)$. Figure 2 gives the probability of a given separation, which is proportional to the probability of absorbing the frequency characteristic of that separation, vs that characteristic frequency for a pair of 7-monomer chains. Although the shape of the bands in Fig. 2 bears a distinct resemblance to the shape of the experimental PA bands,[4] it is necessary to make some corrections before the ordinate represents PA. Most important of these are introducing the optical transition probability characteristic of each separation and summing over all the conjugation lengths. Longer conjugation lengths will lead to a small extension of the curves to lower energies, while shorter ones will lead to a somewhat larger extension to higher energies. Finally, polarons on separate conjugation lengths of the same chain, which cannot come as close as polarons on different chains, should give additional absorption not far removed from the absorption of isolated polarons. Their absorption in the visible band would be masked, being in the neighborhood of or beyond the absorption edge. However, in the infrared band the lowest frequency for which absorption data are shown, ~0.25 eV, is close to the absorption frequency for an isolated polaron on a 10-monomer chain.

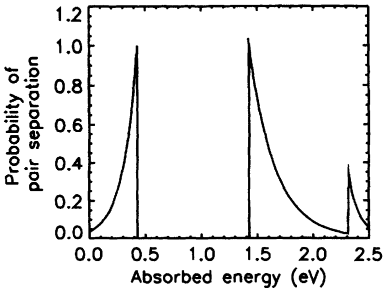

FIG. 2. Probability of a given separation of two polarons on separate 7-monomer chains vs the frequency that would be absorbed for that separation in PPV. The amplitude for the 2.3-eV peak was chosen arbitrarily.

In summary, we have shown that photoinduced charge transfer, which creates P^+P^- pairs on adjacent chains, can account for the ps photoinduced absorption observed in films of PPV (or its derivatives). The theory requires only that there be parallel sections of PPV chains 2 monomers or more in length (perhaps even 1 monomer) spaced at ~4 Å, which can occur even in amorphous samples. Clearly the number of such pairs and therefore the photoinduced absorption will be sample dependent. We can also predict that additional absorption will be found in the so far unexplored spectral region form 0.5 to 1.2 eV, specifically at ~0.9 eV, for example, due to the transition between the valence-band edge on the P^- chain and the P^+ level, or the P^- level to the conduction-band edge on the P^+ chain.

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[1] R. H. Friend, D. D. C. Bradley, and P. D. Townsend, J. Phys. D **20**, 1367 (1987).

[2] M. B. Sinclair *et al.*, Synth. Met. **50**, 593 (1992).

[3] I. D. W. Samuel *et al.*, Synth. Met. **55**, 15 (1993).

[4] J. W. P. Hsu *et al.*, Phys. Rev. B **49**, 712 (1994).

[5] J. M. Leng *et al.*, Phys. Rev. Lett. **72**, 156 (1994).

[6] M. Yan *et al.*, Phys. Rev. Lett. **72**, 1104 (1994).

[7] M. Yan. L. J. Rothberg, and T. M. Miller (private communication).

[8] See, for example, S. P. McGlynn, A. J. Armstrong, and T. Azumi, in *Modern Quantum Chemistry. Part III*, edited by O. Sinanoglu (Academic, New York, 1965).

[9] L. S. Swanson *et al.*, Phys. Rev. B **44**, 10 617 (1991); X. Wei *et al.*, Phys. Rev. Lett. **68**, 666 (1992).

[10] See, for example, D. D. C. Bradley *et al.*, J. Phys. C **21**, L515 (1986).

[11] See, for example, M. Sinclair, D. Moses, and A. J. Heeger, Solid State Commun. **59**, 343 (1986).

[12] L. Rothberg *et al.*, Phys. Rev. Lett. **65**, 100 (1990).

[13] F. Guo, M. Chandross, and S. Mazumdar, Synth. Met. (to be published).

[14] W. P. Su, R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[15] K. Fesser, A. R. Bishop, and D. K. Campbell, Phys. Rev. B **27**, 4804 (1983).

[16] See, for example, A. J. Heeger *et al.*, Rev. Mod. Phys. **60**, 781 (1988).

[17] S. Stafstrom and K. A. Chao, Phys. Rev. B **30**, 2098 (1984).

[18] P. Gomes da Costa, R. Dandrea, and E. M. Conwell, Phys. Rev. B **47**, 1800 (1993).

[19] P. Gomes da Costa and E. M. Conwell, Phys. Rev. B **48**, 1993 (1993).

[20] For details see H. A. Mizes and E. M. Conwell, Synth. Met. (to be published).

[21] H. A. Mizes and E. M. Conwell, Phys. Rev. Lett. **70**, 1505 (1993).

[22] R. Mahrt *et al.*, Makromol. Chem. Rapid Commun. **11**, 415 (1990).

[23] S. C. Graham *et al.*, Synth. Met. **41**, 1277 (1991).

[24] J. N. Murrell, Q. Rev. **15**, 191 (1961).