Stability of Polarons in Conducting Polymers

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Theory predicts that an electron or hole added to a conjugated polymer chain causes the chain to distort, forming a large polaron. Recent calculations of the three-dimensional band structure of *trans*-polyacetylene, *t*-PA, and poly(phenylene vinylene), PPV, have obtained values for the interchain coupling that are large enough to destabilize the polaron. Nevertheless, there is evidence that polarons exist in these materials. We show that the existence of chain endings and other conjugation breaks can stabilize the polaron in actual samples.

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The one-dimensional treatment of conjugated polymers has had some notable successes, including accounting for *t*-PA being a semiconductor rather than a metal, and predicting the existence and properties of solitons in *t*-PA [1]. However, it was suggested some years ago, on the basis of calculations for the large polaron in the Holstein molecular crystal model (MCM) [2], that interchain coupling is too strong in conducting polymers for a large polaron to be stable [3,4]. The condition for stability is usually stated in terms of the transfer on resonance integral, t, the overlap (over all space) of the wave function on one site with the product of the Hamiltonian, and the wave function on the next-neighbor site. Specifically, the MCM calculations gave as the condition for stability $t_\perp/t_\parallel < 0.01$, where $t_\perp$ and $t_\parallel$ are the transfer integrals perpendicular and parallel to the chain direction, respectively. A good average value of $t_\parallel$ for conducting polymers is 2.5 eV. The value of $t_\perp$ depends on the space group. For *t*-PA and PPV the possibilities are $P2_1/a$ or $P2_1/n$, the former having the dimerization in phase, the latter out of phase, on the two chains in the unit cell. Recent calculations of the three-dimensional (3D) band structure of *t*-PA and PPV gave for $P2_1/a$ $t_\perp \simeq 0.12$ eV in the former case [5] and 0.08 eV in the latter case [6]. For $P2_1/n$, $t_\perp = 0.6$ eV for both polymers [5,6]. All of these values would be large enough to destabilize polarons in the MCM. More direct evidence for the instability of the conducting polymer polaron was provided by the failure of calculations to find polaron levels in the gap in the *t*-PA lattice in the $P2_1/a$ structure, which on the basis of total-energy calculations was taken to be the ground state [5]. Because electron-phonon coupling is not large enough in these polymers to create a small polaron, instability of the large polaron would mean that an electron (hole) added to the polymer remains in the conduction (valence) band as in an ordinary semiconductor [3,4].

Nevertheless, there is good evidence that polarons have been seen in actual *t*-PA and PPV samples. For lightly doped PPV the evidence comes from comparison of resonant Raman spectra of bulk samples with those of anions of model compounds equivalent to segments of PPV with different lengths [7]. For *t*-PA a broad infrared absorption seen some ps after irradiation has been attributed to polarons created by the light [8]. Also, values of mobility μ estimated from the measured ps photoconductivity, when the carriers are expected to be drifting along the chains, are in agreement with expectations for polarons, but not free carriers. Based on reasonable estimates for the number of carriers, μ for *t*-PA is found to be in the range 2 to 10 $\mathrm{cm}^2/\mathrm{V\,s}$ [9,10], in good agreement with the calculated value [11], while for PPV μ is 8×10^{-2} $\mathrm{cm}^2/\mathrm{V\,s}$ [12]. However, μ of free electrons at the band edge scattered by phonons has been calculated as 600 $\mathrm{cm}^2/\mathrm{V\,s}$ in polyparaphenylene [13], and should be comparable in *t*-PA and PPV.

In actual polymer samples there are chain breaks and various conjugation defects, such as sp^3 bonds [14,15], cross-links, inclusions of catalyst or of precursor polymer, that act as chain breaks. For *t*-PA, analysis of Raman scattering results has provided good evidence that a sizable proportion of chains have 40 C-H's or fewer [16]. More recently photoluminescence studies of thermally isomerized *t*-PA samples have led to the conclusion that mean lengths of *t*-PA segments are probably less than 26 C-H's (with an isolated *cis*-PA inclusion), the segments being separated by sp^3 or other defects [17]. Note that *cis*-PA inclusions, neutral solitons (usually present in undoped samples), and sp^3 defects cause a reversal of the phase of dimerization. This may be the reason that experimental investigations of the *t*-PA structure have been divided on whether it is $P2_1/a$ or $P2_1/n$. The most recent experiments find that structure to be predominantly $P2_1/n$ with local regions of $P2_1/a$ [18]. In the case of PPV, interchain registration is sufficiently poor that x-ray studies have not been able to decide on $P2_1/a$ or $P2_1/n$ [19]. Also, PPV samples may have regions of short conjugation length due to a remaining precursor polymer.

To explore the effect of conjugation breaks on the existence of polarons we have done tight-binding calculations of the atomic displacements and energy levels resulting from the addition of an electron to a pair of parallel *t*-PA chains and to a cluster of *t*-PA chains in the actual herringbone structure. We used the tight-binding Hamiltonian [20] shown to fit the calculated 3D structure of t-PA:

$$H=\sum_j H_0^{(j)}+\sum_{ij,k} t_\perp^{ij,k}(c_{ij}^\dagger c_{i,k}+c_{i,k}^\dagger c_{ij}) , \tag{1}$$

where i is the site index, j and k chain indices, and H_0 the SSH Hamiltonian [21]:

$$H_0^{(j)}=-\sum_{\substack{i\\(\text{chain}\,j)}}[\{t_\parallel+\alpha(u_{i,j}-u_{i+1,j})\}(c_{i+1,j}^\dagger c_{i,j}+c_{i,j}^\dagger c_{i+1,j}) +(K/2)(u_{i+1,j}-u_{i,j})^2] . \tag{2}$$

Here $u_{i,j}$ is the displacement of the C at site i in the jth chain, α represents the electron-phonon coupling, taken as 4.1 eV/Å, and K an elastic constant, taken as 21 eV/Å^2. For the two chain calculation it was assumed that every C, rather than every other [5], is coupled to its opposite neighbor on the other chain. For 3D calculations the summations over j,k must reflect the fact that although the tight-binding Hamiltonian (1) includes only C atoms, the interchain interaction of the carbons is mediated by H atoms. As a result, the terms in the summation over j,k must connect each C with nearest-neighbor C's on two inequivalent chains. Adjacent sites on each chain are thus connected to different pairs of inequivalent chains [5,20]. In the calculations the C positions were allowed to relax parallel to the chain by minimizing the total energy with respect to $u_{i,j}$. The method used was similar to that of Stafström and Chao [22], but the chain ends were kept fixed. The latter measure was taken because the Hamiltonian (2) is unstable with respect to a uniform compression of all the bonds [23]. To avoid this it is possible to add a term linear in the displacements to the elastic energy [22,23], or to keep the chain ends fixed. The two procedures give results that are quite close [24].

The role of $t_\perp$ in polaron stability is demonstrated in Fig. 1, where the magnitude of each C displacement from its position in a uniform (undimerized) chain is plotted for different $t_\perp$ values versus site number for two parallel 100-site chains. In Fig. 1(a), where the two chains are unbroken, it is seen that for $t_\perp=0.01$ eV ($t_\perp/t_\parallel=0.004$) there is the usual t-PA polaron [25] completely on one chain, while the other chain is purely dimerized to the accuracy of the scale chosen. (Actually, in the limit of small $t_\perp$ the amplitude of the polaron on the second chain must grow linearly in $t_\perp$.) For $t_\perp=0.07$ eV the dip in the displacement characterizing the polaron decreases by ~25% on the first chain. As shown by a separate calculation, a decrease in the dip is correlated with a decrease in the amplitude of the polaron wave function. At $t_\perp\simeq0.07$ eV there appears on the second chain a small amplitude polaron. With increasing $t_\perp$ the dip, and therefore the amplitude, of the polaron on the first chain continues to decrease and that on the second chain to increase until $t_\perp\simeq0.15$ eV. Beyond that the two polarons are symmetric, with the same dip and the same amplitude. Calculations of the energy levels of the two-chain system show that as $t_\perp$ increases from 0 to 0.09 eV the conduction band edge moves down and the upper polaron level moves up. At 0.09 eV the spacing between these two levels is ~0.1 eV, of the order of the spacing between the conduction band levels. Thus it may be considered that at $t_\perp\simeq0.09$ eV the polaron level has joined the conduction band. The two chains are still deformed but, as seen in Fig. 1(a), the deformation extends the length of the chain.

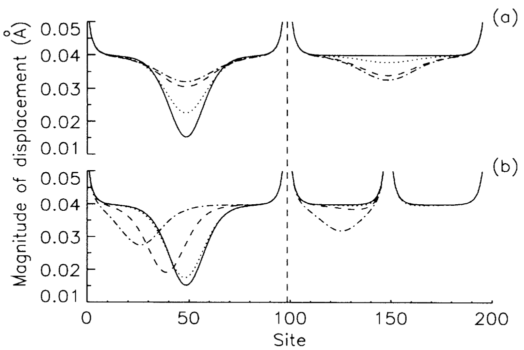

FIG. 1. Magnitude of C displacement vs site number for two parallel 100-site chains opposite each other, both unbroken in (a), with a missing bond between sites 49 and 50 on the second chain in (b). The $t_\perp$ values are indicated by ——, 0.01 eV; ····, 0.07 eV; ---, 0.09 eV; -·-·, 0.15 eV.

To study the effect of a chain break on the polaron stability we introduced a break by removing a single bond, leaving two chain segments terminated by double bonds. The elastic term between the decoupled atoms was retained, however, to keep the chain segments from shrinking. The energy minimization condition was modified accordingly. We verified for some cases that this procedure led to results indistinguishable on the scale of Figs. 1 and 2 from those treating the two segments as two independent chains, the Hamiltonian for each including the term linear in the displacements discussed above. Comparison of Figs. 1(a) and 1(b) shows that a chain break at the center of the second chain decreases the effectiveness of the interchain coupling. At $t_\perp=0.07$ eV the polaron is barely visible on the second chain. The dip and, therefore, the amplitude of the polaron continue to grow more slowly with increasing $t_\perp$ than when the chain is not broken. Equality of the amplitudes on the two chains is not reached at $t_\perp=0.15$ eV. It is also seen that with increasing $t_\perp$ the polaron on the unbroken chain shifts toward the left, where it can be opposite the polaron on the left hand 50-site chain to minimize its energy.

The result of incorporating additional breaks in the second chain, which (arbitrarily) was done so as to create chain segments of equal length, is shown in Fig. 2. It is seen that the polaron amplitude on the chain that initially has the polaron decreases more slowly the larger the number of chain segments. Correspondingly, the initial

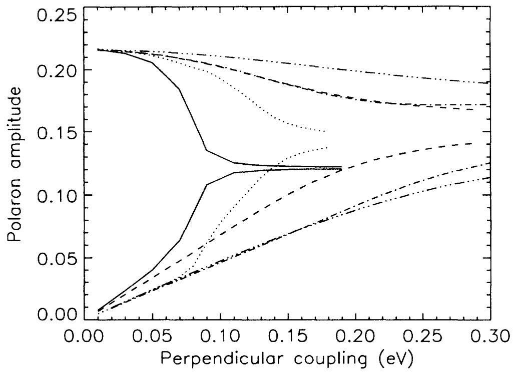

FIG. 2. Polaron amplitude as a function of $t_\perp$ for two 100-site chains opposite each other, the second chain broken into equal size segments. ——, one segment; ····, two segments; ---, three segments; -·-·, four segments; – · · · – · · · –, five segments.

linear rate of growth of the polaron on the second chain is for the most part smaller the larger the number of segments. The reason for this is that the energy required to create a polaron, which is proportional to the gap [23], increases with decreasing chain length. The increase is slow down to 50 sites, but grows progressively more steeply as the chain length decreases further. Thus, as more short chain segments are introduced it is energetically increasingly favorable for the polaron to remain on the 100-site chain. The smaller initial rate of growth for the two-segment case occurs because the motion of the polaron to the left on the unbroken chain keeps up its amplitude; in the three-segment case the polaron on the unbroken chain stays delocalized over the chain with increasing $t_\perp$ because the energy required to squeeze into 33 sites is too large. Note that for the cases of zero and one chain break, after the initial slow linear increase of the polaron on the second chain the polaron amplitude grows much more rapidly with increasing $t_\perp$.

For the 3D case we self-consistently calculated the atomic displacements and energy levels of a 19-chain section of t-PA with one added electron. The 19 chains were arranged so that the central chain and its six nearest neighbors were each correctly coupled to four inequivalent chains. The chains were all 50 sites long. The decision as to which $t_\perp$ value to use is complicated by there being both $P2_1/n$ and $P2_1/a$ regions present in actual samples, their alternation being possibly as rapid on the average as 26 sites [17]. Because the polarons are mobile it appears that stability would be generally determined by the larger $t_\perp$. We therefore calculated for $t_\perp = 0.12$ eV.

The result of the calculation with no chain break is that the polaron deformation is distributed over all 19 chains with the largest amplitude on the central chain. Even on the central chain, however, the minimum displacement was 0.0317 Å, thus close to the 0.04 Å on a purely dimerized chain. This minimum displacement is far from that for a full polaron on a 50-site chain, 0.0134 Å. Correspondingly, there were no energy levels in the gap for this case, although the lowest conduction band levels were pulled down by a few hundredths of an eV. If a larger cluster had been used it is clear that sites still further from the central chain would also show some polaronic distortion, further decreasing the amount of the polaron on the central chain. It is reasonable to expect that in the limit of a large number N of chains this would have become a symmetric polaron with $1/N$ of its amplitude on each chain, thus in essence a free electron.

The introduction of a break at the middle of every chain but the central one caused the polaron to grow greatly on the central chain and shrink on all other chains. The minimum displacement on the central chain went down to 0.0167 Å and the other chains were almost purely dimerized. Because the polaron amplitude is already so small on the outermost chains of the cluster it is expected that adding more chains would have little effect, i.e., that the polaron is stable in this case. Clear evidence that a stable polaron has been produced is the presence of a half-filled level in the gap, 0.19 eV below the conduction band edge [or lowest unoccupied molecular orbital (LUMO)]. Thus introduction of conjugation breaks has resulted in a stable polaron. It should be emphasized, however, that the properties are somewhat different from those of a polaron calculated for $t_\perp = 0$, for which, with our parameters, the polaron level would be 0.33 eV below the LUMO for a 50-site chain.

We have concentrated so far on stabilization due to conjugation breaks that give rise to chain segments shorter than ~50 sites. It is apparent, however, that on any length segment less severe conjugation defects, which do not constitute chain breaks but raise the energy required to create a polaron on the segment, can help localize the polaron on other chain segments.

In addition to establishing that polaron stability may be enhanced by the presence of defects, the above discussion makes it clear that the absorption spectrum of polarons is greatly affected by defects. Because the polaron has two levels in the gap, one of them half filled, the absorption should have three maxima, corresponding to transitions between the singly occupied level and the valence and conduction bands, and the transition between the two polaron levels. As discussed above, the location of the levels is affected by chain segments length, strongly for lengths of 40 sites and fewer, and also by the presence of non-conjugation-breaking defects. With many short chains and conjugation defects in the current samples [16,17], it is not surprising that the observed photoinduced polaron absorption was broad and featureless [8].

In conclusion, we have shown that the presence of conjugation defects, particularly chain segments of 50 sites and fewer, can account for the existence of polarons in current t-PA samples and probably other polymers as well. This suggests that, if conjugation defects could be eliminated, electron and hole transport in t-PA would be like that in silicon.

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