Polarons and bipolarons in polypyrrole: Evolution of the band structure and optical spectrum upon doping

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We present the results of tight-binding band-structure calculations on a deformable polypyrrole chain, as a function of doping. The states which are produced are polarons and bipolarons whose excitation spectrum explains the optical-absorption data.

A consistent description of the electrical transport mechanism in conducting polymers constitutes a critical problem in the understanding of these materials. In this paper we describe band-structure calculations on a deformable polypyrrole chain, which yield quantitative agreement with experiment results. We show that polarons and bipolarons are formed upon doping and that the resulting excitation spectrum accounts well for the existing optical-absorption data. Transport by bipolaron hopping explains the observation of high conductivity without a paramagnetic susceptibility in oxidized polypyrrole.

Doped polypyrrole (PP) is a conducting polymer usually obtained by electrochemical oxidation of pyrrole.[1] PP provides conductivities typically ranging between 10 and 100 $\Omega^{-1}cm^{-1}$, and is remarkable among conducting polymers because of its good stability in air.[1] Scott, Pfluger, Krounbi, and Street[2] have reported ESR measurements on samples of neutral PP and oxygen-doped PP. Very interestingly, in electrochemically cycled highly conducting PP films, no ESR absorption signal is detected. This observation led those authors to suggest that the absence of paramagnetism associated with the current carriers could be explained by relating charge carriers to doubly charged spinless bipolarons.[3] The localized deformation associated with a polaron or bipolaron consists of lengthening the double bonds and shortening the single bonds. Conceptually, this may be viewed as a soliton-antisoliton pair, bound by the energy which it costs to interchange single and double bonds in the ground state of the nondegenerate system.

Yakushi, Lauchlan, Clarke, and Street[4] have recorded the optical spectra of PP at various stages of oxidation, from the as-grown highly oxidized (one perchlorate anion per three pyrrole rings) film to the (electrochemically reduced) almost neutral film (see Fig. 1). At low levels of oxidation (lower curve, Fig. 1), there is a strong absorption maximum at 3.2 eV, associated with the interband $\pi \rightarrow \pi^*$ transition. Within the gap region, there are three additional features at 0.7, 1.4, and 2.1 eV. As the level of oxidation increases, the middle 1.4-eV absorption disappears, and the interband transition weakens and shifts to higher energy. In the fully oxidized sample (upper curve, Fig. 1), two intense, broad absorption bands are present at 1.0 and 2.7 eV and the interband transition appears as a shoulder at 3.6 eV.

In order to interpret these experimental results, we present in this Brief Report a theoretical study of the energetics of polaron and bipolaron formation on PP chains and the band-structure evolution upon oxidation. We use a technique based on a quantum-chemical version of the adiabatic Su-Schrieffer-Heeger Hamiltonian,[5] previously adapted

to treat nondegenerate ground-state polymers.[6] Our key result is to demonstrate that the evolution of the absorption spectra upon oxidation can be fully explained in terms of initial polaron formation and then bipolaron formation on the PP chains. In agreement with the ESR measurements,[2] our theoretical studies of the absorption spectra indicate that bipolarons are the spinless charge carriers in the highly conducting regime of doped PP.

Calculations of the energetics of polaron and bipolaron formation on PP chains are performed using tight-binding Hückel theory with σ bond compressibility and bond-order–bond-lengths relationships. In this model, β transfer
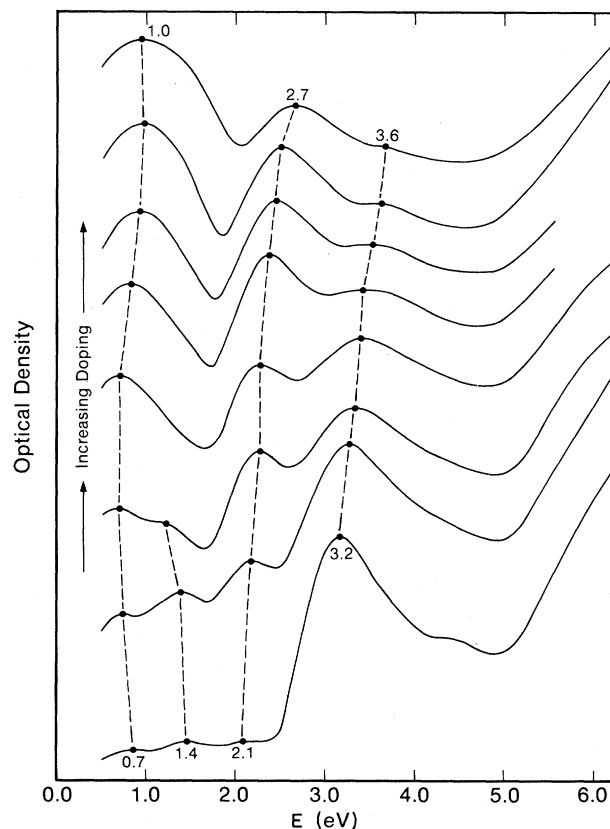

FIG. 1. Evolution of the optical-absorption spectrum of polypyrrole as a function of doping level. The concentration of perchlorate anions increases from bottom curve (almost neutral PP) to top curve (33 mol% doping level).

integral values are expressed as a function of the bond length r as

$$\beta(r) = A \exp(-r/B) \ .$$

The energy of the σ framework is

$$f(r) = C(r - r_0 + B)\beta(r) \ .$$

We have optimized the parameters A, B, and C on neutral polypyrrole in order to reproduce (i) the ~ 3.2-eV optical transition, (ii) the ~ 3.5-eV bandwidth for the highest occupied π band (corresponding to the ab initio calculated value[7]), and (iii) the geometry recently optimized by ab initio Hartree-Fock calculations:[8] within rings, $r_{C-N} = 1.385$ Å, $r_{C-C} = 1.363$ Å, and $r_{C-C} = 1.424$ Å; between rings, $r_{C-C} = 1.474$ Å. Such a parametrization implicitly accounts for some of the effects of Coulomb correlations, which are not otherwise considered in the one-electron Hückel method. We obtain parameter values similar to those optimized on polyparaphenylene:[6] $A = 50.0$ eV, $B = 0.53$ Å, $C = 5.0$ Å^{-1}. The highest occupied level is calculated at -0.60 eV, and the lowest unoccupied at 2.56 eV.

We model possible lattice deformations upon oxidation by allowing bond lengths (and thus transfer integrals) to vary over a number of pyrrole rings N in the following way:[6,9]

$$r_{n,n+1} = r^0_{n,n+1} + \alpha \tanh(n/l) \tanh[(4N-n)/l] \ .$$

Here, $r^0_{n,n+1}$ is the undistorted bond length between atoms n and $n+1$, n is the site location from one end of the defect, $(4N-n)$ is then the separation from the other end (the factor of 4 being the number of carbon atoms in one ring), α scales the deformation (depending on the type of bond), and l modulates the amplitude of the deformation and indicates the abruptness of the defect edges. Maximum deformations are taken in accordance with the previously optimized ab initio values for the highly doped chain:[8] within rings, r_{C-C} can at most go up to 1.46 Å ($\alpha = 0.097$ Å), r_{C-N} up to 1.428 Å ($\alpha = 0.043$ Å), and r_{C-C} down to 1.36 Å ($\alpha = -0.064$ Å); the bond between rings, down to 1.34 Å ($\alpha = -0.137$ Å). Calculation on a chain having the fully distorted structure indicates that the gap goes down to 0.7 eV and the total energy per ring is ~ 5.8 kcal/mol larger than in the undistorted lattice. This stability difference is about one-fifth smaller than in the polyparaphenylene case[6] (in agreement with ab initio results[10]) and means the PP lattice is softer.

We study the energetics of polaron formation along the chain by removing one electron and optimizing the N and l values that lead to the smallest total energy for the ionized system. A polaron is formed when the increase in π plus σ energy due to the lattice deformation is more than compensated by a lowering in ionization energy, the difference corresponding to the polaron binding energy.

When we introduce a single positive charge on the chain, we obtain the formation of a polaron with a 0.12-eV binding energy. The polaron extends over four rings ($N = 4$); the lattice distorts quite strongly ($l = 5$), the bond-length deformation in the middle of the defect being about 80% of the maximum values given above. The presence of a polaron on the chain introduces two localized electronic levels in the gap: a singly occupied bonding polaron state 0.49 eV above the valence band (VB) edge and an empty antibonding polaron state 0.53 eV below the conduction-band (CB) edge [Fig. 2(a)]. The polaron states in the gap account for the
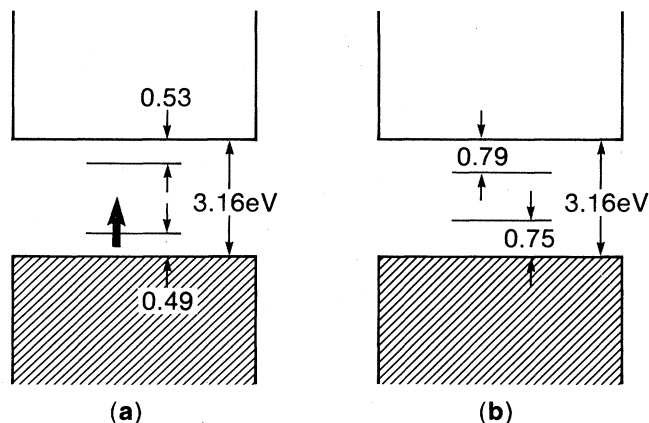

FIG. 2. Electronic structure diagrams for a polypyrrole chain containing (a) a polaron and (b) a bipolaron.

three transitions observed within the gap in very slightly oxidized PP (lower curve, Fig. 1). The first absorption peak at 0.7 eV can be related to a transition from the VB to the bonding polaron state; the peak at 1.4 eV is associated with a transition from the bonding to the antibonding polaron state; finally, the peak at 2.1 eV corresponds to a transition from the VB to the antibonding polaron state. Exact matching of calculated transitions to peaks in the absorption spectrum should not necessarily be expected, since the experimental data have not been Kramers-Kronig transformed due to their limited spectral range. Nevertheless, the semiquantitative agreement between calculation and data is quite satisfying. It must be stressed that the sum of the first two peak energies exactly corresponds to the peak energy for the third transition, as it should within a one-electron model.

Note that the peak positions indicate that the location of the antibonding polaron state is further away from the CB edge than the location of the bonding state from the VB edge. This asymmetric location arises because of the different nitrogen orbital contributions to the VB and CB states and is very difficult to reproduce within Hückel theory but had been predicted at the ab initio level.[8] In this case, a fourth transition, from the bonding polaron state to the CB, should be observed at ~ 2.5 eV. This energy value unfortunately corresponds to the disorder-broadened edge of the band-gap transition.

At higher oxidation levels, polaron states start interacting. The calculations indicate that two polarons, as they approach each other, become unstable with respect to the pairing of their spins and the formation of a doubly charged spinless bipolaron. The extent of the bipolaron is similar to that of the polaron ($N = 4$), but the l value is smaller ($l = 1$), showing that the bond lengths within a bipolaron defect are at their maximal deformation except at the edges of the defect.

With respect to two vertical ionization processes, the gain in total energy by forming the bipolaron is 0.69 eV. This indicates that the formation of a bipolaron is favored over that of two polarons by 0.45 ($= 0.69 - 2 \times 0.12$) eV. This is significantly larger than in polyparaphenylene[6] and reflects the increased softness, and thus electron-phonon coupling, of the PP lattice.

The above picture of polaron recombination to form bipolarons is in full agreement with ESR measurements on PP

chemically doped with oxygen.[2] An ESR signal corresponding to polarons is observed only at dopant concentrations less than about 0.5%. The intensity of that signal then falls indicating that spins pair above about 1%.

A bipolaron introduces two states in the gap, at 0.75 eV above the VB edge and 0.79 eV below the CB edge [Fig. 2(b)]. Very importantly, the bipolaron bonding state, in contrast to the polaron case, is empty. As a result, only two transitions within the gap are now possible. Thus the emptying of the bonding states in the gap accounts for the loss of the middle 1.4-eV absorption peak when going from slightly oxidized to highly oxidized PP.

In Fig. 3, we present the band structure calculated for 33% doping level (i.e., one bipolaron per six rings) as achieved in the as-grown film. The agreement with the corresponding absorption spectrum (upper curve, Fig. 1) is excellent. The band gap is correctly obtained at 3.56 eV, 0.40 eV larger than in the undoped case. The two intense absorptions within the gap are accounted for by the presence of two wide bipolaron bands. The two bipolaron bands are calculated to be, respectively, 0.45 and 0.39 eV wide. Furthermore, note that the intensity of the lower bipolaron absorption is largest; this is consistent with the oscillator strengths calculated by Fesser, Bishop, and Campbell[11] on the basis of a continuum coupled electron-phonon model adapted for nondegenerate ground-state polymers.

Finally, it is worth pointing out that the extent of bipolaron defects is in agreement with x-ray photoemission spectroscopy (XPS) observations,[12] indicating the presence of three types of nitrogen atoms in oxidized PP: uncharged, moderately charged, and strongly charged. These can be related to nitrogen atoms located, respectively, outside the bipolarons, in the two outer rings of each bipolaron, and in the two inner rings of each bipolaron. In neutral PP, only one kind of nitrogen is seen.

In summary, our theoretical studies on polypyrrole, combined with available optical, magnetic, and XPS data,
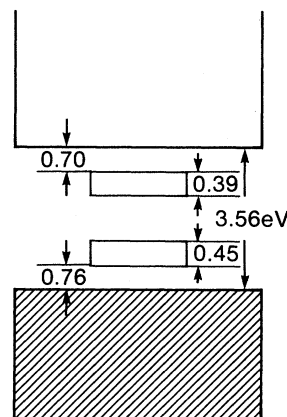

FIG. 3. Band structure for highly oxidized (33 mol% doping level) polypyrrole, showing the presence of two broad bipolaron bands in the gap.

demonstrate that (i) polarons are formed on the chains at low oxidation level, (ii) at higher oxidation levels, polarons combine to form spinless bipolarons, and (iii) wide bipolaron bands are present in the gap in the highly conducting regime, which confirms the predictions based on ESR experiments that spinless bipolarons are the current carriers. In contrast to highly doped trans-polyacetylene, the gap does not close.

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[1]K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak, Synth. Met. 1, 329 (1980); G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, Mol. Cryst. Liq. Cryst. 83, 253 (1982).

[2]J. C. Scott, P. Pfluger, M. T. Krounbi, and G. B. Street, Phys. Rev. B 28, 2140 (1983).

[3]S. A. Brazovskii and N. N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz. 33, 6 (1981) [JETP Lett. 33, 4 (1981)].

[4]K. Yakushi, L. J. Lauchlan, T. C. Clarke, and G. B. Street, J. Chem. Phys. 79, 4774 (1983).

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

[6]J. L. Brédas, R. R. Chance, and R. Silbey, Phys. Rev. B 26 , 5843 (1982).

[7]J. L. Brédas, B. Thémans, and J. M. André, J. Chem. Phys. 78, 6137 (1983).

[8]J. L. Brédas, B. Thémans, and J. M. André, Phys. Rev. B 27, 7827 (1983).

[9]As shown in Ref. 6 parametrization in terms of a product of tanh functions, rather than a difference, produces no substantial modification in the results of the variational procedure.

[10]J. L. Brédas, in Handbook on Conducting Polymers, edited by T. J. Skotheim (Marcel Dekker, New York, in press).

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

[12]P. Pfluger and G. B. Street, J. Chem. Phys. (to be published).