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Polaron and bipolaron excitations in doped polythiophene

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An energetic study of the excitation spectrum in doped polythiophene is presented within the framework of the Hückel approximation. The calculations show that localized states like polarons and bipolarons are produced by doping, the formation of doubly charged bipolarons being energetically more favorable than the formation of two polarons charged singly. It is then shown from the analysis of available magnetic and optical data that the bipolarons are the dominant charge states while the features due to the polarons appear under certain circumstances at low doping levels.

I. INTRODUCTION

In recent years, doped organic polymers have been the focus of considerable research interest because of the remarkable increase in their electrical conductivity upon doping with appropriate donor or acceptor compounds. In particular, these polymers are interesting because they should be excellent materials in battery applications and also in electrochromic displays. The electrical, magnetic, and optical properties of conducting polymers contrast markedly with those of doped semiconductors. This situation is mainly due to the charge-transfer mechanisms, which are very different in organic materials because of the existence of a large coupling between the lattice deformations and the electronic excitations. In the traditional semiconductor picture of doping, an electron (or hole) is given to the conduction (or valence) band of the material and no significant structural change occurs. In linearly conjugated polymers, the extra charge leads to a local deformation of the chain which consists in a length change of the bonds. This modification in turn strongly affects the electronic structure of the polymers and leads to defects like polarons. Each of these defects induces localized electronic states in the gap, which may accommodate another charge carrier to give a doubly charged excitation. Unlike *trans*-polyacetylene[1,2] the other conducting polymers such as polyparaphenylene (PPP), polypyrrole (PPy), and polythiophene (PT) do not have a degenerate ground state, and nonlinear excitations cannot exist in the form of topological solitons or domain walls separating the two dimerized phases. Thus, the doping processes in linear conjugated polymers lead to the formation of polarons and bipolarons, which are the dominant charged species.[3-6]

Recently, polythiophene has turned out to be one of the most interesting conjugated organic polymers.[7-9] High-quality films are now available and the possibility of carrying out reversible electrochemical doping suggests that it may be used as a cathode-active material in rechargeable storage batteries. Further, the change of color of polythiophene under the doping processes indicates that it may be a good material for the realization of electrochromic devices.[8-9]

Measurement of the absorption spectra of PT (Refs. 7–10) during electrochemical doping processes has been recently reported for a large range of concentration. The absorption spectra of neutral polythiophene is that of a semiconductor with an energy gap at about 2 eV, associated with the interband π-π^* transition. At low levels of doping, $y \sim 0.3$ mol %, three absorption features appear in the gap region at 0.6, 1.3, and 1.5–1.8 eV. For a larger concentration of about 3–4 mol %, the spectra shows two absorption maxima at about 0.7 and 1.5 eV. As the dopant level increases, the peak intensities also increase, the higher-energy structure shifts toward the high energies, and the interband transitions weaken. Experimental studies on the photoexcited absorption spectra have been reported by Kaneto *et al.*,[10] and a photoinduced absorption peak has been observed at 1.96 eV. By analogy with recent studies on other conducting polymers and particularly polypyrrole, the main features observed in the absorption spectra are interpreted as originating from transitions between the valence or conduction bands and the localized levels associated with the presence of polarons and bipolarons on the chain. Thus, the detailed evaluation of the optical properties are of direct interest in order to interpret the experimental results.

In this paper we present a theoretical study of the formation of polarons and bipolarons on polythiophene chains. In the framework of a generalized version of the adiabatic Su-Schrieffer-Heeger Hamiltonian, a Green's-function recursive method is used to obtain the density of states and the minimum energy of the system. In Sec. II the model Hamiltonian and our method of resolution are detailed. The energetic study and the properties of polaron and bipolaron excitations are presented in Sec. III. Section IV includes a comparison with experimental results and the conclusion.

II. MODEL HAMILTONIAN

Polythiophene consists of chains of successive rings which alternate in such a way that the sulfur atoms point in opposite directions. As shown in Fig. 1, a resonance form can be derived for PT by the permutation of single and double bonds between the atoms. As for the polyparaphenylene and polypyrrole, the two structures are not energetically equivalent.

We assume that one can neglect the interchain coupling

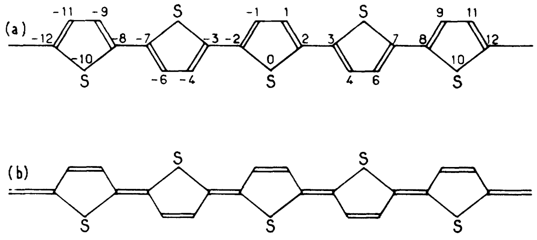


FIG. 1. Two equivalent structures for polythiophene. The form (a) is more stable than the form (b).

and we consider the PT chain in a manner somewhat analogous to that of Bredas for PPP and PPy.[5,6] Also, we assume that the σ electrons can be described in the adiabatic approximation while the π electrons can be treated in the tight-binding or Hückel-type approximation with a hopping (or resonance) integral which is given by a relationship of the Coulson type:[11]

$$\beta(r) = -A\exp(-r/B) , \tag{1}$$

where r is the bond length.

The σ-bonding energy for a bond is determined by the relation

$$f(r) = C\beta(r)(r - r_0 + B) . \tag{2}$$

The parameters A, B, C have to be optimized in order to fit the calculated results to certain experimental data of neutral polythiophene. As usual, r_0 is chosen to be equal to the length of a pure sp^2 bond. Because of the presence of a sulfur atom, the effective energy of an electron (or Coulomb integral) depends on the chemical nature of the atom. The variation of the effective energy $\Delta\alpha$ between two electrons bonded to a sulfur core and to a carbon core, respectively, is considered as an adjustable parameter. We have optimized the various parameters in order to reproduce (i) the experimental band gap of 2 eV; (ii) a 5-eV bandwidth of the two highest occupied π bands; (iii) the bond lengths which are obtained by an *ab initio* calculation of the geometry of the neutral chain,[12] and (iv) the distribution of the π charges on the heteroatom as calculated by the Hartree-Fock method.[14] All the bond lengths are in good agreement with electron diffraction data available on gaseous bithiophene.[13] The values are within the rings, $r(\mathrm{C{=}C}) = 1.36$ Å, $r(\mathrm{C{-}C}) = 1.43$ Å, $r(\mathrm{S{-}C}) = 1.72$ Å; and between the rings, $r(\mathrm{C{-}C}) = 1.48$ Å. This parametrization neglects sulfur $3d$ orbitals which are rather weak. The Coulomb interactions are not explicitly taken into account though they are partially included by using optimized values of parameters. Under all these conditions, the values determined for the parameters are $A = 20.3$ eV, $B = 0.86$ Å, $C = 3.79$ Å^{-1}, and $\Delta\alpha = 0.55$ eV. They are similar to those used for PPP and PPy.

As we discussed above, excitations like polarons or bipolarons can be associated with a local deformation of the polymer chains. By analogy with solutions of the continuum model, the bond-length variation of the s-type bond between the atom located at x and one of its nearest neighbors is described with the following trial function:[3,4]

$$\Delta r(s) = \frac{\Delta_0(s)}{2}\left[\tanh\left[\frac{x + D/2}{L}\right] - \tanh\left[\frac{x - D/2}{L}\right]\right] . \tag{3}$$

Such a function, plotted in Fig. 2, may be viewed as a soliton and an antisoliton with the same width L, centered at $x = \pm(D/2)$, respectively. L and D are considered as adjustable parameters to be varied so as to minimize the total energy of the system. $\Delta_0(s)$ denotes the maximum bond-length difference with respect to the bond lengths in neutral PT. We have chosen for the $\Delta_0(s)$ values those corresponding to the variation of the bond lengths that turn structure (a) in Fig. 1, into structure (b), which is the quinoidlike resonance form: within the rings, $\Delta_0(\mathrm{C{=}C}) = 0.13$ Å, $\Delta_0(\mathrm{C{-}C}) = -0.13$ Å, $\Delta_0(\mathrm{S{-}C}) = 0.11$ Å; and between the rings $\Delta_0(\mathrm{C{-}C}) = -0.22$ Å.

The total energy of the system can be written as the sum of an elastic and an electronic contribution. The elastic term is obtained by a simple summation over all the bonds of terms given by Eq. (2). The electronic energy E is given by

$$E_{\mathrm{el}} = \int_{-\infty}^{\varepsilon_F} zN(z)dz . \tag{4}$$

Here ε_F is the Fermi level and $N(z)$ the electronic density of states which may be calculated as

$$N(z) = -(2/\pi)\mathrm{Im}\mathrm{Tr}G(z) , \tag{5}$$

where $G(z)$ is the Green's function corresponding to the electronic part of the Hamiltonian H_e,

$$G(z) = (z - H_e)^{-1} . \tag{6}$$

Polythiophene is a one-dimensional system of rings with nearest-neighbor interactions. The Hamiltonian can be expressed in block tridiagonal form:

$$\begin{aligned} H_e = {} & \sum_n |n\rangle h_{n,n}\langle n| + \sum_n |n\rangle V_{n,n+1}\langle n-1| \\ & + \sum_n |n+1\rangle V_{n+1,n}\langle n| . \end{aligned} \tag{7}$$

The ket vector $|n\rangle$ is associated with the five basis orbitals of the nth ring. $h_{n,n}$ and $V_{n,n+1}$ are 5×5 matrices. The $h_{n,n}$'s describe the intraring interactions and the

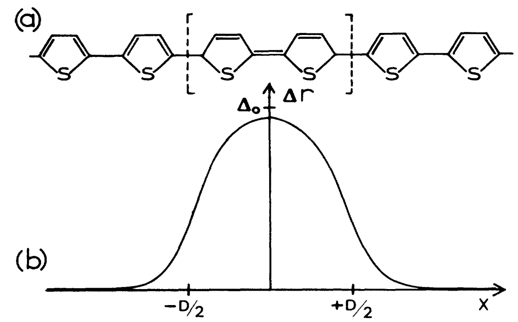


FIG. 2. (a) Structure diagram of a polythiophene chain with a polaron or a bipolaron. (b) Trial function describing the variation of the bond lengths.

$V_{n,n+1}$'s the inter-ring ones. The exact solution for the Green's functions of a generalized tridiagonal Hamiltonian whose elements are themselves block matrices has been obtained by Dy *et al.*[15] When the Green's functions are partitioned into blocks so that each elements $G_{n,n'}$ is a block matrix with the same dimension as the blocks in H, the diagonal elements are given by

$$G_{n,n}=(z-h_{n,n}-V_{n,n+1}\Delta_{n+1}^{+}V_{n+1,n}-V_{n,n-1}\Delta_{n-1}^{-}V_{n-1,n})^{-1}\,, \tag{8}$$

where the $\Delta_n^{\pm}$ verify the following recursion relations:

$$\Delta_n^{\pm}=(z-h_{n,n}-V_{n,n\pm1}\Delta_{n\pm1}^{\pm}V_{n\pm1,n})^{-1}\,. \tag{9}$$

Thus, once a starting $\Delta_n^{\pm}$ is determined by the boundary conditions imposed on the problem, all the other Δ's can be obtained using the recursion relations (9). In this case, the periodicity of the Hamiltonian far from the polarons and bipolarons entails that the Δ's are those corresponding to the perfect polymer. Equations (5)—(9) then allow the determination of the electronic density of states. To determine the electronic energy of the system, we must carry out the sum in Eq. (4) over the energies of occupied states. When the states in the energy gap are counted separately from the states within the bands, Eq. (4) becomes

$$E=\int_{\mathrm{VB}} zN(z)dz+\sum_i n_iE_i\,, \tag{10}$$

where the integral extends over the occupied valence bands (VB) and n_i is the number of electrons occupying the localized level with the E_i energy. The electronic energy of the system depends on the occupancy of gap states and in fact, on the charge of defects. Usually for the polaronlike defects, two levels appear in the gap and neutrality corresponds to double occupancy of the lower level ($n_1=2$, $n_2=0$). When an electron is transferred to the defect, a negative polaron P^- is formed and $n_1=2$ and $n_2=1$. For two electrons transferred, the created defect is a bipolaron BP^{2-} with $n_1=2$ and $n_2=2$. Analogous relations hold for p doping, and five kinds of defects can be expected in this system. However, as polythiophene is made up of odd-membered rings with two sorts of atoms, this can prevent the existence of electron-hole symmetry as for *cis*-polyacetylene or polyparaphenylene and the appearance of two symmetric doping-induced levels.

To investigate the stability of these defects, we have defined the binding energy of a defect as the energy gain obtained through the formation of a defect with respect to the corresponding vertical ionization process.

III. POLARON AND BIPOLARON EXCITATIONS

For each charge state of defects, the equilibrium configuration has been determined by minimizing the total energy of the system with respect to the two parameters of the trial function (3). Results for different defects are now presented.

In the case of the neutral defects, the minimum energy is obtained for a vanishing deformation. Such a defect cannot be stable apart from particular conditions, as, for instance, chemical impurities or isomerization defects.

Next, we have considered the case of single charged defects. The binding energy in the case of a hole polaron is plotted in Fig. 3(a) for different values of parameters of the trial function. A minimum appears for the values $D=3$ and $L=3$ (in units of number of cycles), and corresponds to the formation of a polaron whose binding energy $E(\mathrm{P}^+)=0.12$ eV, which is also the value obtained by Bredas *et al.* for polypyrrole.[6]

The deformation of the lattice is rather soft. The larger deformation lies in the middle of the defect being about 50% of the maximum value Δ_0. For instance, the length of the bond between the rings is found to be reduced by 0.10 Å with respect to the perfect chain. The presence of a polaron induces two localized states in the gap at 0.36 and 1.72 eV above the valence-band edge. These two levels are not symmetrically located with respect to the gap center because the contribution of the sulfur atoms breaks the electron-hole symmetry. However, the sulfur is weakly interacting with the π electrons of neighboring carbon atoms and the two levels appear at nearly the same distance from the valence- (0.36 eV) and conduction- (0.28 eV) band edges.

Similar results are obtained for the case of doped n-type polythiophene; they are given in Table I. The negative polaron is seen to be a little less stable than the hole polaron. The values for the polarons' size and for the energies of the two doping-induced levels are nearly the same for the two kinds of polarons. This similarity was to be expected from the weak influence of the sulfur.

Whatever the doping type, the minimum energy re-

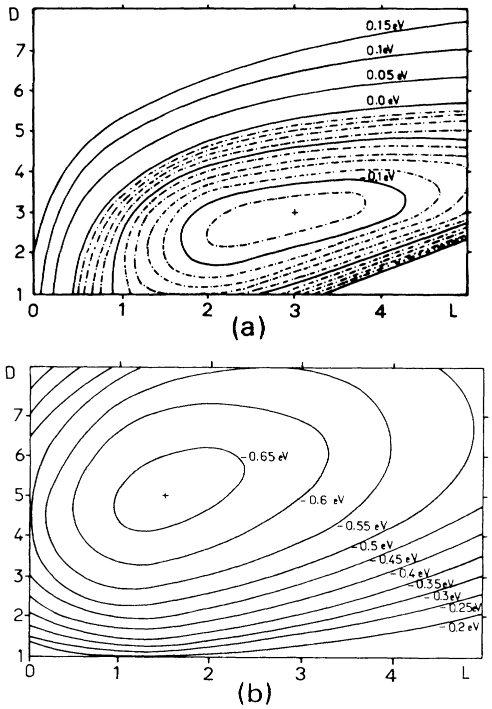


FIG. 3. Constant-energy contour for charged defects. The numbers labeling the lines indicate the energy values in eV. (a) Polaron (singly charged). (b) Bipolaron (doubly charged).

TABLE I. Characteristics of polaron and bipolaron excitations for polythiophene doped by donors or acceptors.

	Acceptor (p-type) doping		Donor (n-type) doping	
	Polaron	Bipolaron	Polaron	Bipolaron
Total binding energy (eV)	0.12	0.67	0.06	0.36
Position of the localized levels with respect to the top of the valence band (eV)	0.36 1.72	0.74 1.43	0.29 1.83	0.53 1.58
Width of deformation (units of number of cycles)	6	5	6	5
Amplitude of deformation (percent of maximal deformation)	46%	95%	38%	81%

quired to add one electron (or one hole) via the formation of a polaron is always lower than that necessary to inject the charge in the conduction (or valence) band.

Let us now consider the case of bipolarons which are doubly charged defects. First we will examine the hole polaron in some detail. From Fig. 3(b), one can see that a minimum appears for $D=5$ and $L=1.5$. From the results given in Table I, the bipolaron is seen to be more stable than two polarons; it follows that the formation of such a bipolaron is clearly more probable than that of two polarons by an amount of 0.43 eV. Moreover, the binding energy is sufficiently large so that it can be expected that the bipolaron may still be stable in the presence of interactions neglected in this calculation, as, for example, the Coulomb interactions between the electrons.

These results are rather similar to those of Bredas *et al.* on polypyrrole.[6] The bipolaron is a defect with the same width as polaron but the deformation of the bond length at the middle of the defect is larger, being 95% of the allowed maximum deformation and about twice that of the polaron. The presence of a hole bipolaron induces two localized states in the gap. These states (the energies of which are given in Table I) are not located in a symmetrical manner with respect to the center of the gap.

To investigate the electronic structure of polythiophene chains in the presence of positive bipolarons, we have calculated the changes in the densities of states. Let $|in\rangle$ be the orbital associated with the ith atom in the nth ring of polythiophene chain (see the central cell shown in Fig. 1, for the numbering); the density of states on the site is given by

$$N_{in}(E)=-(2/\pi)\mathrm{Im}G_{in,in}(E) ,$$

where $G_{in,in}(E)$ is the diagonal element of the Green's function defined in (6). The partial densities of states for a given type of atom are defined as

$$N_i(E)=\sum_n N_{in}(E) ,$$

where the sum extends all over the rings.

In fact, all the functions $N_i(E)$ are not independent, as can be seen by symmetry considerations. When the defect is centered at the middle of a ring, the system is symmetrical with respect to a mirror perpendicular to the chain axis. In this symmetry operation, the atoms 1 and -1 on one hand and 2 and -2 on the other hand correspond with each other. The sulfur atom which is located on the mirror is not modified by this operation. As a consequence, the partial density of states relative to two equivalent atoms are the same and only three different functions must be calculated. The changes in the partial densities of states $\Delta N_0(E)$, $\Delta N_1(E)$, and $\Delta N_2(E)$ due to the presence of hole bipolaron are plotted in Fig. 4 for the upper valence band and in Fig. 5 for the conduction band. The main changes in partial density of states arise from the band edges. In the two bands, the variations ΔN_1 and ΔN_2 for the two types of carbon atoms are rather similar; they are equal in the valence band and nearly the same in the conduction band. The sulfur density of states ΔN_0 increases over the whole valence band. That is consistent with the fact that the presence of defect is equivalent to the introduction of some rings of quinoid type on the chain. In this structure the sulfur is less tightly bound to the neighboring carbons. Its atomic character is more pronounced and the sulfur contribution around the energy of the atomic level increases.

Figure 6 shows the probability densities $|\psi|^2$ of the two localized states which appear in the gap in the case of hole bipolaron. These are roughly similar and have the form expected for band-edge wave function cut off by a localizing envelope. Assuming an envelope $y(x)$ of the form proposed by SSH,[1]

$$y(x)\sim(1/L)\mathrm{sech}(x/L) ,$$

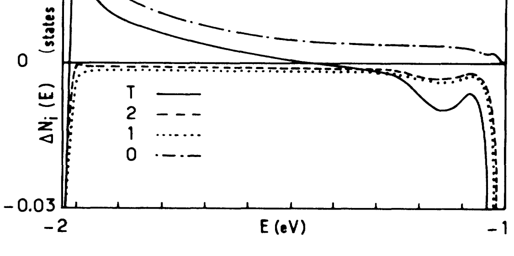


FIG. 4. Change in the partial densities of states $\Delta N_i(E)$ due to the presence of a hole bipolaron, plotted for the upper valence-band region. The change in the total density of states is also plotted (solid line).

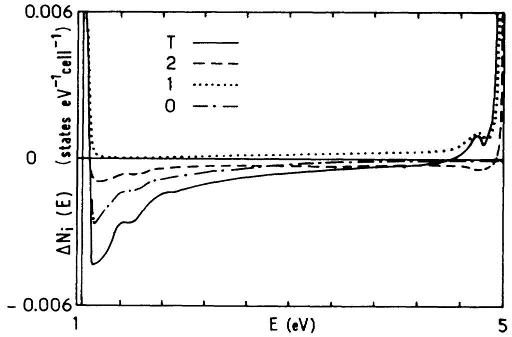


FIG. 5. Change in the partial density of states $\Delta N_i(E)$ due to the presence of a hole bipolaron plotted for the lower conduction band region. The change in the total density of states is also plotted (solid line).

where L is the defect half-width expressed in numbers of rings, we obtain $L \sim 5$ for the extension of the wave function of each localized state in the gap. The main difference between these two wave functions lies in their symmetry properties. The lower level has an antisymmetrical wave function, while the upper level one is symmetric. That is due to the position of the bipolaron which is located on a ring center. Thus, the defect is mirror symmetric about its center and the wave functions must be symmetric or antisymmetric under this transformation. However, the position of the levels may appear surprising in comparison with the usual view of bonding and antibonding levels. These symmetry considerations have important consequences on the oscillator strengths of the optical transition, as calculated by Fesser *et al.*[4]

We have also studied the formation of a negative bipolaron which may be created when electrons are injected by an n-type doping. The results are found to be fairly similar to those obtained for the hole bipolaron. However, the negative bipolaron is less stable. From Table I, we can see that regardless of doping type, the formation of a bipolaron is always favored over the formation of two polarons. The gain is equal to 0.43 eV for the case of p-type doping and 0.27 eV for n-type.

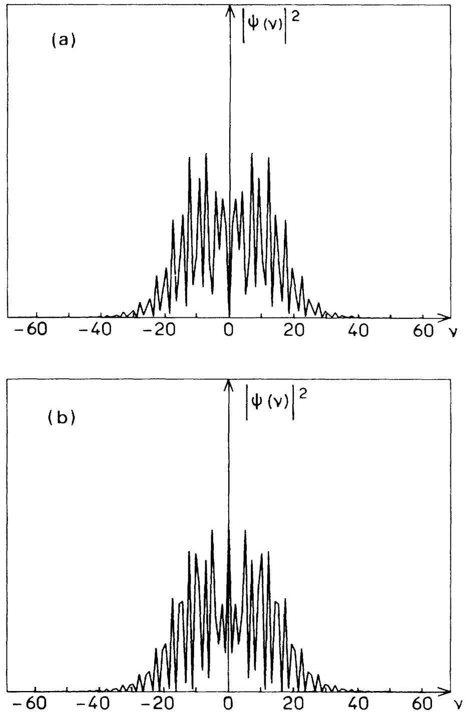


FIG. 6. Probability densities of the localized levels in the gap arising from the presence of a hole bipolaron. The functions are plotted versus the atomic site number defined in Fig. 1. (a) Lower level. (b) Upper level.

Our results are compared in Table II with the theoretical results concerning polarons and bipolarons for other polymers with a nondegenerate ground state. Calculations

TABLE II. Theoretical results for polaron and bipolaron excitations for polymers.

	Polaron (P^+)					Bipolaron (BP^{2+})				
	PDA[a]	*cis*-CH_x [b]	PPP[c]	PPy[d]	PT	PDA	*cis*-CH_x	PPP	PPy	PT
Total binding energy (eV)	+ 0.052	+ 0.034	+ 0.03	+ 0.12	+ 0.12	+ 0.363	+ 0.27	+ 0.40	+ 0.69	+ 0.67
Width of deformation (Å)		15	21	17	26		15	21	17	26
Amplitude of the deformation (% of the maximal deformation)		25%	50%	80%	46%		70%	100%	100%	95%
Position of the lower localized level with respect to the valence band (eV)	0.16	0.102	0.2	0.49	0.36	0.48	0.36	0.56	0.75	0.73
Position of the upper level with respect to the conduction band (eV)	0.16	0.102	0.2	0.53	0.28	0.48	0.36	0.56	0.79	0.57
Variation in energy between a bipolaron state and a two polaron state (eV)	−0.259	−0.205	−0.34	−0.45	−0.43					

[a] Reference 16.
[b] Reference 17.
[c] Reference 5.
[d] Reference 6.

on polyparaphenylene[5] (PPP), polypyrrole[6] (PPy), and polydiacetylene[16] (PDA) have been carried out within the framework of the Hückel approximation as in the present work. For *cis*-polyacetylene,[17] the Brazowskii-Kirova[3] continuum model has been used. Our results on polythiophene are rather similar to those obtained for the other polymers if account is taken of the differences of structures and possibly of the presence of a heteroatom. These similarities suggest that polythiophene can be viewed as being as slightly analogous to *cis*-polyacetylene with a structure formed by a sp^2 polyene chain with four carbon atoms in the unit cell and a sulfur heteroatom bound by covalent coupling to neighboring carbon atoms to form the heterocycle.

The influence of the sulfur atom on the electronic band structure mainly depends on the strength of the carbon-sulfur coupling. This one is weaker than the carbon-carbon coupling and the resonance integral C—S is about three times smaller than the (C—C) ones. Thus, the sulfur atom interacts weakly with the π electrons of the chain. However, its presence modifies the band structure, breaking the electron-hole symmetry.

In the case of doped *cis*-polyacetylene, two localized levels (corresponding to polaron or bipolaron states) appear in the gap and are symmetrically located with respect to the gap center. In doped PT, the sulfur atom acts in the same manner as in neutral PT, removing electron-hole symmetry. A dissymmetry then arises between the two levels in the gap. Our results show a departure from the symmetry which is equal to 0.08 eV. This is a rather weak value which must be compared to the mean symmetrical position of the energy levels (0.65 eV) with respect to the band edges.

The weak departure from the electron-hole symmetry given by our calculations is consistent with the absorption spectrum data obtained by Chung *et al.*[7] These authors note that the sum of the two observed transitions is equal to the energy gap that shows the existence of electron-hole symmetry. Although the presence of a heteroatom breaks the electron-hole symmetry which exists for a carbon chain such as *cis*-$(CH)_x$, the weakness of the coupling between the carbon atoms and the heteroatom leads only to a small departure to the symmetry, at least for a heteroatom such as sulfur and probably also for the nitrogen.

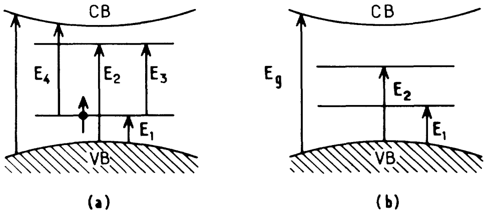
In any case, polarons and bipolarons are energetically favored when charges are introduced in the material. The deformations associated with bipolarons are stronger than in the polaron case and therefore the associated localized states induced in the gap are deeper.

IV. COMPARISON WITH EXPERIMENT: CONCLUSION

Recent ESR measurements on electrochemically ClO_4^--doped PT (Ref. 10) have shown that the spin density increases upon doping up to about 0.5 mol %. In the same manner, for PT films doped by BF_4^-,[10] the ESR spin density increases by more than two orders of magnitude until a maximum of 2×10^{20} spins/g is reached, observed at 3 mol %. These data yield a spin number comparable to the number of injected charges and are consistent with the creation of polarons. When the doping exceeds 2 or 3 mol %, the ESR signal decreases, suggesting a recombination of polarons to form bipolarons. Measurements on iodine-doped samples between 1.4 and 9 mol % I_3 (Ref. 18) indicate Curie spin concentration which is independent of the doping level. This feature shows that only a small fraction of charge transferred to the chain is stored in the form of excitations with spin $\frac{1}{2}$ such as polarons. This can result from the recombination of polarons to form bipolarons.

An experimental verification of this picture is also possible by investigation of the optical absorption spectra. As we discussed above, polarons and bipolarons induce localized states in the gap. In Fig. 7, we give the energy-level diagram and the transitions expected for polythiophene when one of the two types of excitation is created upon p-type doping (the discussion in the case of n-type doping may be led in a similar manner). In the case of a polaron located on a chain, we can expect four transitions originating from the valence band and the lower localized state, besides the interband transitions. The calculated absorption spectra show absorption peaks at $E_1=0.4$ eV, $E_2=1.7$ eV, and $E_4=1.6$ eV, and a sharp structure at $E_3=1.35$ eV corresponding to a transition between the two localized states. Changes of absorption spectra in a weakly doped polythiophene film have been measured at 0.4 mol % by Kaneto *et al.*[10,19] Absorption peaks arise in the gaps at 0.6 eV, 1.3 eV, and 1.5—1.8 eV. The theoretical predictions in the case of an isolated polaron are seen to be in good agreement with the experimental spectrum of a low-doped sample. The number and the positions of the observed transitions are consistent with the formation of polarons at weak doping.

For a chain with a hole bipolaron, the two levels in the gap are empty and the two transitions E_3 and E_4 do not exit any more. Only the two transitions E_1 and E_2 originating from the valence band are possible. The calculated values are, respectively, 0.7 and 1.4 eV. Studies of the absorption spectra during the electrochemical doping have been carried out by Kaneto *et al.*[10,19] for a dopant concentration of 3 mol % and by Chung *et al.*[7] over a large range of voltage. For example, around 3 mol %, which is a concentration where the bipolarons are not interacting, two peaks appear in the band gap at 0.65—0.7 eV and at 1.5 eV. The correct prediction of the number of transitions and the good agreement between our results and the experimental data show that the optical-absorption spectra is consistent with the concept of doping through bipo-



(a) (b)

FIG. 7. Energy level diagram and possible optical transitions for a PT chain with (a) hole polaron and (b) hole bipolaron. CB is the conduction band, VB the valence band.

laron formation in this concentration range.

By analysis of these experimental results obtained on a large range of concentrations, a description of doping processes may be suggested. The doping proceeds through the creation of polarons for light doping (~ 0.4 mol %), while at higher concentration (~ 3 mol %), the formation of bipolarons is favored.

In contrast with these results, recent photoexcited ESR data reported by Vardeny *et al.*[20] indicate no spins in the low concentration regime and the authors conclude that the dominant charged photoexcitation in PT are bipolarons rather than polarons. A relatively small number of spin $\frac{1}{2}$ excitations are also observed. As this number decreases after improvement of the structural order by annealing, these excitations are expected to be polarons trapped on defects. Moreover, the photoinduced absorption spectrum[20] reveals two asymmetric bands at $E_1 = 0.45$ eV and $E_2 = 1.25$ eV, which are identified with bipolaron transitions from the continuum states to the gap states. These values are about 0.2 eV lower than the ones calculated in this work and measured when the bipolarons are generated by doping.[7,10,19] On the other hand, the energy difference $E_2 - E_1 \sim 0.8$ eV, which gives the splitting between the two gap states, is independent of the generation process.

Thus, there is creation of different kinds of excitations at low charge concentrations according to the excitation process. This fact cannot be explained in the framework of the above theoretical calculations. In our simplified model, we have neglected the Coulomb effects which depend on the charge state of the excitation and which are not the same when the charges are injected by electrochemical doping or created by photogeneration. Therefore, a more careful estimation of the binding energy has to be done.

First, for the bipolaron, the Coulomb repulsion between the two associated charges modifies the binding energy E_B^0 by an amount V_B, which is the difference in Coulomb energy between the state with a double charge and the state with a single charge, the lattice deformation being the same in two cases. Moreover, the transition energies are shifted by the same amount. This shift has been observed by Vardeny *et al.*[20] for the photoinduced bipolarons and leads to the value $V_B = 0.25$ eV. When this first Coulomb effect is taken into account, the binding energy of a bipolaron is reduced to $E_B = E_B^0 - V_B = 0.42$ eV.

In comparison with the formation of two polarons, which requires an energy $2E_P^0 = 0.24$ eV, the creation of a bipolaron is still favored by an energy difference $\Delta E = +0.18$ eV. When the bipolarons and polarons are generated by doping, there is an additional Coulomb interaction between the dopant molecules and the defect charges. Some estimations[21-23] of the binding energy have been obtained for a similar problem in polyacetylene concerning polarons and solitons, but accurate calculation is difficult because of the lattice relaxation and of the strong influence of the model used.

As the spatial extent of polarons and bipolarons is the same, the bipolaron binding energy is approximately twice as large as the polaron one, E_d. When all the Coulomb effects are considered, the total binding energy is $E_B' = E_B^0 - V_B + 2E_d$ for a pinned bipolaron and $2E_P' = 2E_P^0 + 2E_d$ for two pinned and largely separated polarons. Since E_B' and E_P' are shifted the same amount, there is no change of their difference ΔE. The coupling with the dopant species has the same influence on the two configurations and the difference between the creation energy of a bipolaron and the one of two largely separated polarons is still equal to 0.18 eV.

On the other hand, the doping process involves the creation of a polaron for each charge transferred from doping molecules to the PT chain. These polarons are metastable and relax to one bipolaron following the process (in case of p doping) $P^+ + P^+ \rightarrow BP^{2+}$.

At the thermal equilibrium, it has been shown[24,25] that the ratio of polaron to bipolaron concentration depends on their formation energy as $\exp[(E_B - 2E_P)/2kT]$.

Although the bipolaron configuration has the lowest energy, polarons can be present and their concentration will be much greater than the one calculated neglecting the Coulomb interactions.

The decay of a pair of polarons into a bipolaron is only possible if the two polarons appear on a single chain and if they are free to diffuse. This is not necessarily the case for polarons created by doping because they are bound to the dopant molecules of opposite charge by a Coulomb interaction. Consequently, if the diffusion of the dopant species is neglected, there is a barrier to recombination of a pair of widely separated polarons because the charge on one polaron localized at first near a dopant ion must be removed from this Coulomb interaction before being pulled up to the second pinned polaron. This barrier recombination is hard to evaluate because the lattice relaxation is important. Generally, diffusion of the dopant molecules is relatively fast and makes easier the recombination of polarons into bipolaron by reducing and removing the barrier. However, this diffusion is very sensitive to the presence of defects and imperfections which restrict the polaron mobility and prevent their recombination. This would allow the existence of polarons in lightly doped PT.

In summary, within the framework of the Hückel approximation, we have presented an energetic study of polarons and bipolarons in doped polythiophene. We have shown that a polaron and a bipolaron are stable defects with respect to the direct transfer of electrons or holes from the dopant molecules to the conducting or valence band. The states containing the extra charges are localized on about five rings. Our results are rather similar to those obtained for other polymers with a nondegenerate ground state and in particular, the bipolaron excitation is found to be more stable than two polarons. The Coulomb contribution to the bipolaron energy decreases the difference between the formation energy of a bipolaron and the one of two polarons, but bipolarons are still the more stable excitations. The ESR and optical-absorption data has been used to obtain information on the presence of polarons and bipolarons. The analysis of the results suggests that bipolarons are the dominant charge states in PT. However, under certain circumstances, polarons have been observed at low doping levels. Bipolarons, resulting from the combination of polarons, dominate at higher levels. The polarons and the bipolarons appear to play a fundamental role in the properties of doped polythiophene.

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