Polaron Lattice in Highly Conducting Polyaniline: Theoretical and Optical Studies

S. Stafström [a] and J. L. Brédas

Laboratoire de Chimie Théorique Appliquée, Centre de Recherches sur les Matériaux Avancés,
Facultés Universitaires Notre-Dame de la Paix, B-5000 Namur, Belgium

A. J. Epstein

Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

H. S. Woo and D. B. Tanner

Department of Physics, University of Florida, Gainesville, Florida 32611

and

W. S. Huang and A. G. MacDiarmid

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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We present optical-absorption data together with band-structure calculations for the polaron lattice and bipolar lattice for the highly conducting form of polyaniline, proton-doped polyemeraldine. We show that the polaron-lattice band structure fully accounts for the observed optical transitions. These results are in marked contrast to the electronic structure of other doped conducting polymers, in that only one single broad polaron band appears deep in the gap together with a very narrow band nearly degenerate with the conduction-band edge.

Polyaniline[1,2] is a family of polymers that is of increasing current interest because the electronic properties can be modified through variation of either the number of protons, the number of electrons, or both. The emeraldine base form of the polymer, Fig. 1(a), is a semiconductor. Upon protonation of the formerly unprotonated $-N=$ sites, the conductivity increases by a factor of 10^{10}, reaching 1 S/cm, despite the unchanged electron concentration.[2] The Pauli susceptibility is essentially linearly proportional to the percentage of protonation,[3] in agreement with the proposal[3] that protonation ("proton doping") leads to phase segregation of unprotonated and fully protonated domains. A model based upon a two-step transition from isolated, doubly charged, spinless bipolarons to a polaronic metal [Figs. 1(b)–1(d)] has therefore been suggested[3]: (i) The first step relates to the instability of a bipolaron on a polyemeraldine chain [Fig. 1(b)] with respect to formation of two polarons[4] [Fig. 1(c)], and (ii) the second step is their separation to yield a polaron lattice.

In this Letter, we present for the first time combined theoretical and optical studies aimed at describing the electronic structure of the polaron lattice in protonated polyemeraldine. We demonstrate that the band structure for the polaron lattice fully accounts for the optical transitions which are experimentally observed. In contrast, our calculation for the bipolaron-lattice band structure is in disagreement with the optical, Raman,[5] and magnetic[3] data. Differently from all other known conducting polymers (polyacetylene,[6] polyparaphe-

nylene,[7] polypyrrole,[8] and polythiophene[9]), in polyaniline a single broad polaron band appears deep in the gap instead of two, and a second very narrow band appears near the conduction-band edge. These features can be explained by a detailed analysis of the polyaniline electronic structure. Our results afford a strong support for the applicability of the polaronic-metal model.[10]

Our electronic-structure calculation scheme has been previously used with great success for conducting polymers.[11] Lacking experimental data on the geometric structure of protonated polyemeraldine, we first proceed to geometry optimizations of long (three or five rings) aniline oligomers containing a polaron or a bipolaron using the MNDO (modified neglect of differential overlap) semiempirical self-consistent–field Hartree-Fock technique.[12] The torsion angles between two adjacent benzene rings are set at 30°, all the nitrogens being in the same plane, in order to be consistent with x-ray diffraction structure reported for single crystals of doubly charged aniline tetramers.[13] All the other geometric parameters are then fully optimized. For the polaron, the structural relaxation around the radical cation is allowed to extend only to the middle of the phenyl rings adjacent to the protonated nitrogen, consistent with x-ray photoelectron spectroscopy (XPS) data.[14]

The MNDO geometries of the central parts of the oligomers, which we find to be independent of oligomer length, are used to describe the polymeric unit cells for a polaron lattice and a bipolaron lattice. In the bipolaron-lattice case, the benzene ring between the two
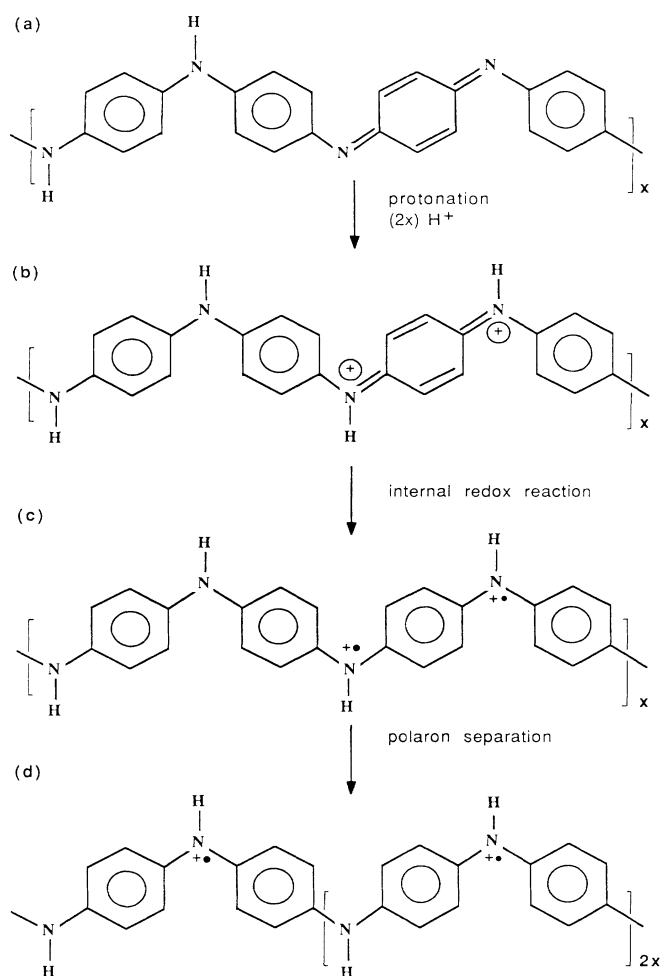
FIG. 1. Sketch of the geometric structure of polyemeraldine (a) before protonation and (b)–(d) after 50% protonation: (b) Formation of bipolarons and (c) of polarons; (d) the polarons separate, which results in a polaron lattice.

FIG. 2. Optical absorption spectra of protonated polyemeraldine. Inset: Near-ir and visible absorption for both emeraldine base (insulating) and emeraldine salt (metallic) forms.

proton-carrying nitrogens has a strongly quinoid geometry with double $C=C$ bonds of 1.362 Å and single $C-C$ bonds of 1.474 Å; the CN bonds around the charged nitrogens possess very different lengths: $r_{C=N} = 1.343$ Å and $r_{C-N} = 1.407$ Å. In the polaron-lattice case, those latter CN bonds are equal (1.411 Å), and only slightly shorter than those around the other nitrogen (1.414 Å); the benzene rings mostly adopt an aromatic geometry, the CC-bond lengths, as one goes away from the charged nitrogen, being equal to 1.440, 1.400, and 1.417 Å. Only the 1440-Å bonds are reminiscent of some residual quinoid character in agreement with resonance Raman studies.[5] As the final step in the calculation, the polymer unit cells for the polaron and bipolaron lattices are used as input for valence-effective Hamiltonian (VEH) pseudopotential band-structure calculations.[11,15]
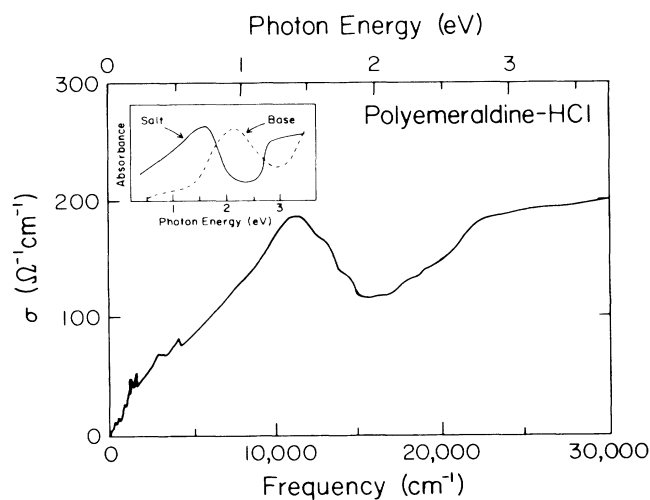
The emeraldine salt samples used for optical studies were free-standing films[2] made by the treatment of insulating emeraldine base films with HCl.[2] Transmission measurements were carried out between 50 and 300 cm^{-1}. The room-temperature reflectance was measured over 600–30 000 cm^{-1} (0.075–3.75 eV); the Kramers-Kronig analysis gave the frequency-dependent conductivity, $\sigma(\omega)$. The $\sigma(\omega)$ data for protonated polyemeraldine are presented in Fig. 2. The inset shows previously reported near-infrared and visible absorbance data for separately prepared samples of the emeraldine base and emeraldine salt forms. In the conducting (salt) form, the localized exciton peak at 2 eV associated[3,16] with the quinoid rings of the insulating phase has been eliminated. Instead there are two strong optical peaks at 2.8 eV and above, and a broad absorption at $\simeq 1.5$ eV, which we interpret as excitations to the polaron band. Note that this peak continues to the far infrared, implying intraband absorption at low frequency. The full width at half maximum of this peak gives an estimate of the polaron bandwidth of 1.0 eV. Finally, consistent with the predictions[17] for a polaron lattice, no strong doping-induced vibrational structure is seen in these spectra.

Figure 3 shows the VEH band structures of protonated polyemeraldine for the bipolaron lattice [Fig. 3(a)] and the polaron lattice [Fig. 3(b)]. Note that the unit cell of the bipolaron lattice is twice as big as that of the polaron lattice (see Fig. 1), leading to twice as many bands in the first Brillouin zone. It is important to mention that there are two (four) extremely flat unoccupied bands, so close in energy that they appear to be a single curve, located around -0.1 a.u. of energy (-2.7 eV) in the band structure of the polaron (bipolaron) lattice. This reflects the absence of any significant wave-function
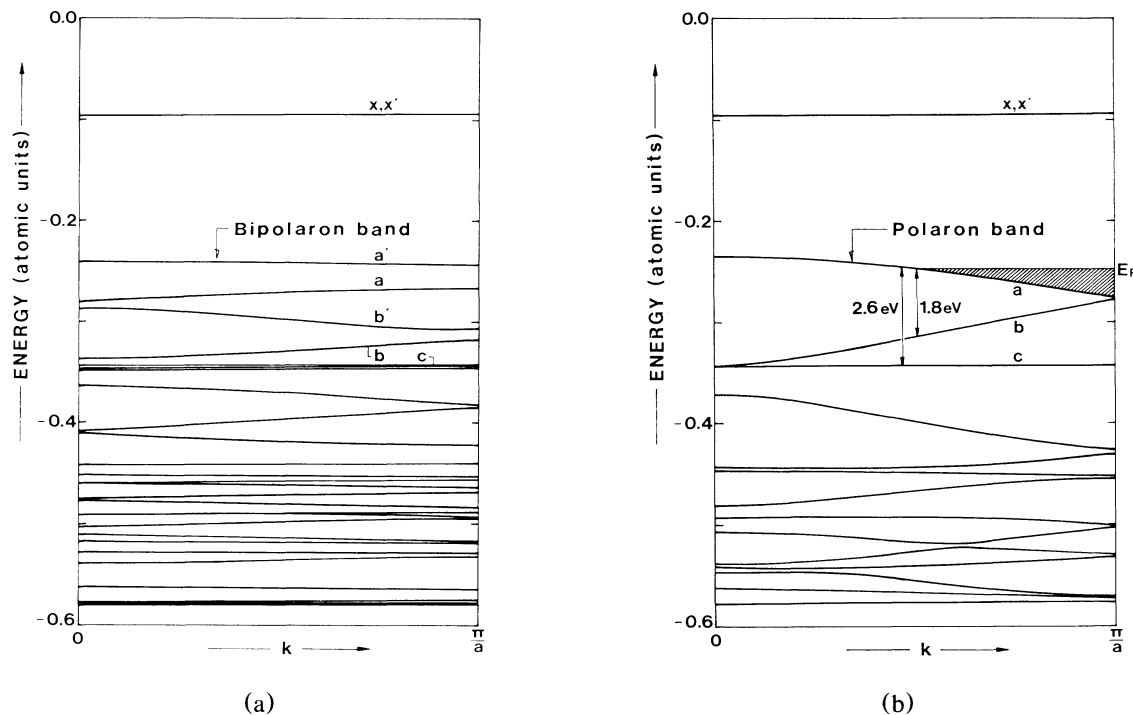
FIG. 3. VEH band structures for 50% proton-doped polyemeraldine in the case of (a) bipolaron lattice and (b) polaron lattice.

amplitude at the nitrogen sites and the adjacent carbon atoms for these bands. For the bipolaron lattice [Fig. 3(a)], band a corresponds to the highest occupied band, whereas band a', the first unoccupied band, can be understood as being a bipolaron band by analogy with the situation in polypyrrole[8] or polythiophene.[9] For the polaron lattice, the half-occupied band a constitutes the polaron band. The width of this polaron band is calculated to be 1.1 eV, in excellent agreement with the 1.0-eV estimate from the low-frequency intraband optical absorption. In both cases, there is seemingly only one defect (polaron or bipolaron) band in the gap. In other conducting polymers,[6-9] there are always within the gap two distinct defect bands, arising from a destabilization of the highest occupied band (leading to the lower defect band) and a stabilization of the lowest unoccupied band (leading to the higher defect band).[18] The apparent presence of only a single defect band within the gap in 50% proton-doped polyemeraldine can be understood by consideration of fully reduced polyaniline, polyparaphenyleneamine,[19] where the highest occupied (lowest unoccupied) band corresponds to a combination of bands a (x) and b (x'). As pointed out above, band x is extremely flat with a width smaller than 0.05 eV.[20] Although formation of the polaron or the bipolaron lattice does lead to an upper defect band, band x', this band is hardly stabilized with respect to band x because of the flatness of this band. Hence, the flat upper polaron band, band x', is nearly degenerate with the conduction band, band x.

One of the consequences of this peculiarity of the upper defect band in protonated polyemeraldine is to be found in the optical absorption spectra. Whereas in other conducting polymers the doping-related subgap absorptions are due to electronic transitions involving both defect bands,[18] in polyemeraldine the transitions to the upper defect band x' cannot be distinguished from those to the conduction band x. Thus only one defect band, the lower defect band a, plays a role in the subgap absorption. (The upper band might lead to a minor diminution of the apparent optical gap.) Thus the detailed analysis of the polyemeraldine band structure establishes a modified picture for the transitions within the gap.

We now turn to a comparison of the optical spectra with the band structures presented in Fig. 3. This comparison rules out the presence of a bipolaron lattice in 50% proton-doped polyemeraldine for the following reasons. In the band structure of the bipolaron lattice, there is a gap of 0.65 eV between the highest occupied band a and the bipolaron band a'. This gap is inconsistent with the intraband absorption observed in the infrared. Furthermore, because all the electronic bands are either totally full or empty, there should be no observable Pauli susceptibility, which is contrary to the evolution of the magnetic data upon protonation.[7]

The polaron-lattice band structure, in contrast, yields electronic transitions which agree in four ways with the optical absorption data for 50% proton-doped polyem-

eraldine: (i) The polaron band is only half occupied, allowing for intraband absorption and thus for far-infrared absorption; (ii) direct optical transitions from band b to the polaron band a are calculated to be at 1.8 eV, which compares favorably with the first optical absorption at about 1.5 eV; (iii) direct optical transitions from band c to the polaron band a are calculated to be at 2.6 eV, which is in very good agreement with the second absorption observed at 2.8 eV; (iv) the first electronic transitions involving the upper defect band and the conduction band are predicted to occur at 4.1 eV, in agreement with the location of the third absorption. Furthermore, as mentioned above, the calculated polaron bandwidth is in good accord with the experimental estimates. The small differences between the predicted and observed spectra may be related to the disorder within the polymer as well as to effects due to the presence fo the interstitial Cl^- ions.

In summary, the band-structure calculations for the polaron lattice are in excellent agreement with the optical absorption data presented for proton-doped polyemeraldine and establish a modified picture for the electronic transitions appearing within the gap upon doping.

(a)Permanent address: IFM, Linköping University, S-581 83 Linköping, Sweden.

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[20]We add to the discussion that incomplete neglect of differential overlap–configuration-interaction calculations, including up to double excitations and performed on long (fully reduced) polyaniline oligomers, confirm that level x corresponds to · the first excited state in those compounds (S. Stafström and B. Sjögren, to be published).