Direct Observation of Charge-Induced π-Electronic Structural Changes in a Conjugated Polymer

M. Lögdlund, R. Lazzaroni, S. Stafström, and W. R. Salaneck
Department of Physics, Institut für Fysik och Mätteknik, Linköping University, S-581 83 Linköping, Sweden

J.-L. Brédas
Service de Chimie des Matériaux Nouveaux, Département des Matériaux et Procédées, Université de Mons, B-7000 Mons, Belgium

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Ultraviolet photoelectron spectroscopy (UPS) has been used to observe changes in the π-band structure in poly(3-hexylthiophene) induced by doping using $NOPF_6$. The charge-induced movement of the Fermi energy and a finite density of electronic states at the Fermi energy in the most highly doped (saturated) material are seen unambiguously with UPS for the first time in a conjugated polymer. The results imply the existence of a new, recently predicted theoretically, but hitherto unobserved, polaron-lattice state of this conjugated polymer at the saturation-doping level.

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Charge-induced changes in the local molecular geometry of conjugated polymer chains is a central issue in understanding the electronic properties of electrically conducting organic polymers, whose electronic structures are generally one dimensional. Most previous experimental studies of the electronic structure have been carried out using optical-absorption spectroscopy, where essentially only differences in electron energy levels are observed as optical transitions. Other more indirect experimental studies include, e.g., measurements of unpaired electronic spins which occur as a consequence of self-localized electronic states associated with such charge-induced structural relaxation effects in conjugated polymers.[1,2]

In this Letter, we report the direct observation of charge-induced electronic structural changes in the π system of a prototypical conjugated polymer, a polyalkylthiophene, using ultraviolet photoelectron spectroscopy (UPS). We have observed directly the movement of the Fermi energy, E_F, associated with new electronic states within the otherwise forbidden energy gap, E_g. These states are associated with the charge-induced geometrical changes in the conjugated polymer chain. In addition, we observe a finite density of states at the Fermi energy, $\rho(E_F)$, unambiguously for the first time using UPS. Whereas, in general, other types of measurements yield *indirect* evidence for a finite density of states at the Fermi energy, for example, in polyacetylene[3] and polyaniline,[4] photoelectron spectroscopies are, in principle, capable of yielding the electronic structure at and near the Fermi energy *directly*. Although previous attempts have been made to observe a finite $\rho(E_F)$ using x-ray photoelectron spectroscopy (XPS), the results have been at best ambiguous due to the existence of three factors: lower inherent resolution of XPS relative to UPS; interference of x-ray satellites if nonmonochromatic x-ray sources are used; and above all the inherent low cross sections for photoionization of energy levels with $C(2p)$-derived wave functions, i.e., those states nearest the Fermi energy in conjugated polymers. UPS, on the other hand, has a high cross section for photoionization of $C(2p)$-derived π orbitals.

The movement of E_F and the existence of a finite $\rho(E_F)$ indicate the existence of (although not alone definite proof of) a polaron lattice as the highest conducting (*saturation* doped) state of this conjugated polymer,[2,5] a state which has been predicted theoretically but hitherto not observed experimentally in this nondegenerate ground-state polymer. At "intermediate" doping levels (see below), bipolarons are known to be the charge-carrying species in the polythiophenes, according to the results of optical-absorption studies,[6-9] consistent with the one-dimensional nature of the system. Since the polaron lattice is expected to be unstable towards a Peierls distortion in a conducting system in *strictly one dimension,*[5] our new results imply the existence of higher-dimensional interactions, namely through charge-transfer interactions with the counterions, in the doped state of this polymer system,[10] which up to now had been generally considered to be a highly one-dimensional system. Moreover, this work provides a reference framework for the further refinement of theories of the metallic regime in conducting polymers.

The alkyl-substituted polythiophenes are some of the most studied conducting polymers today because of their high degree of processability.[11] In particular, the temperature dependence of the electronic structure of undoped poly(3-hexylthiophene), or P3HT, determined by UPS using He II (40.8 eV) radiation, has been presented previously in the characterization of the thermochromism in P3HT in terms of thermally induced conjugation defects in the aromatic backbone.[12] The chemical structure of P3HT is shown at the top of Fig. 1. The presence of the alkyl side groups does not have any direct effect upon the π system of the polymer at low temperatures.[13] In this work we have studied the effects on the electronic

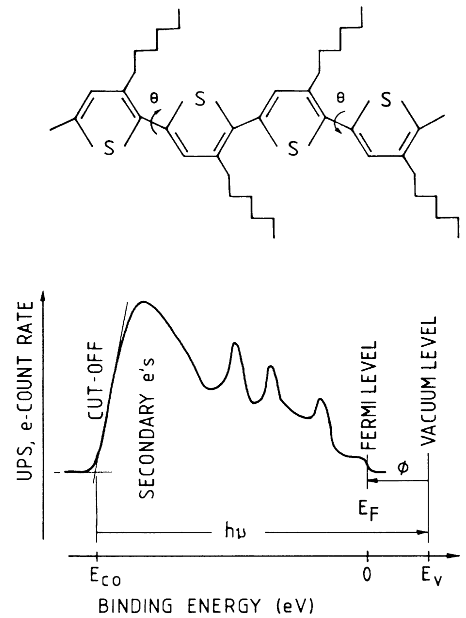

FIG. 1. Top: chemical structure of poly(3-hexylthiophene), or P3HT. Bottom: hypothetical UPS spectrum, with the parameters ϕ, E_F, and E_{CO} as defined in the text.

properties of P3HT caused by doping using $\mathrm{NOPF_6}$ dissolved in acetonitrile. We focus upon the structure of the π-electronic band, the so-called π_3 band, which lies closest to the Fermi level E_F, as a function of doping, as observed via UPS using He I (21.2 eV) radiation. Since data collection was carried out at $-40\,^{\circ}\mathrm{C}$, the results can be interpreted in the context of a planar geometry of the conjugated backbone.[2,12]

The *processability of the polyaklylthiophenes* makes possible the preparation of very pure and very clean ultrathin films, which enables the present study. The P3HT used here was of a molecular weight corresponding to polymer chains containing approximately fifty thiophene rings.[11] A great deal of effort was put into preparing very clean ultrathin films, as discussed previously.[14] Thin films were cast from chloroform in a saturated chloroform atmosphere, and inserted (through air in transport) directly into a closed $\mathrm{N_2}$ atmosphere in an "introduction chamber" of a specially designed and built photoelectron spectrometer.[15] The films were dried under 10^{-6} Torr, obtained by an oil-free turbo pump, and then moved directly into the main analysis chamber, at a pressure of less than 10^{-10} Torr, maintained by a special combination of ion- and cryo-pumping. The films were then heated to 180 °C to remove hydrocarbon contamination and any remaining solvent. Because of the surface sensitivity of UPS, the heating step was necessary, and shown to be sufficient, in obtaining high-quality spectra.[12,14] After working with films of various thicknesses, we have no experimental evidence (nor suspicions) that the effects reported here are of any surface origin.

Doping was done by moving the sample back into the introduction chamber, substituting the vacuum with a flowing dry $\mathrm{N_2}$ atmosphere, and applying a controlled amount of the doping solution, $\mathrm{NOPF_6}$ in acetonitrile, on the surface of the sample, which was tilted at 30° to the horizontal. The excess doping solution gathered in a special receptical built into the sample holder. Finally, the chamber was sealed, and the sample dried again under 10^{-6} Torr turbo-pumped vacuum, as above. The $\mathrm{N_2}$ atmosphere is very effective in keeping $\mathrm{O_2}$ and $\mathrm{H_2O}$ from the sample, as discussed previously.[14] The extent of doping appeared to increase uniformly up to a *saturation* point, beyond which the spectra did not change. For the saturation-doped samples, the samples were rinsed *in situ* with acetonitrile after doping but before pumping to 10^{-6} Torr, in order to remove any possible residual salt from the surface. Ultraviolet photoelectron spectra were recorded with He I (21.2 eV) radiation, with an analyzer resolution of 0.2 eV. Binding energies quoted are estimated to be good to within ± 0.1 eV.

Photoelectron spectra of solids are recorded relative to the Fermi energy E_F by the manner in which a spectrometer functions. The *vacuum level,* however, is the reference energy of chemical significance. When E_F changes due to some chemical modification of a sample, e.g., in the interaction of graphite and other layered compounds,[16] and in the doping of conducting polymers,[17] then it is necessary to account for this change, E_F, *before* interpreting spectra.[14] The work function, ϕ, can be determined from the width of a UPS spectrum, using the following simple equation: $E_{\mathrm{CO}} - E_F + \phi = h\nu$, where $h\nu = 21.2$ eV for the He I radiation used in the experiments reported here, E_F is the Fermi energy, and E_{CO} is the cutoff energy of the secondary electrons in the UPS spectrum, as sketched at the bottom of Fig. 1. The binding energy is taken as a positive number. In this work, we estimate ΔE_F from the change in the work function, $\Delta\phi$, which is equal to ΔE_{CO}, and subsequently adjust all binding-energy values by this amount.[18]

In Fig. 2 are shown the He I UPS spectra of the π bands that occur nearest to E_F. Note the evolution of the band structure with doping. In particular, the so-called π_3-band edge is located at about -1 eV relative to E_F in the undoped material, as expected[19,20] for an intrinsic semiconductor with a band gap of about 2.1 eV. Upon doping to the saturation level, the π_3-band edge moves relative to E_F *and* E_F moves by about 0.8 eV relative to the vacuum level. The movement of the π-band edge (but not the ΔE_F) has been reported previously in poly(3-methylthiophene).[20] This is the first report of the direct spectroscopic observation of the shift of the Fermi level upon doping of a conjugated polymer. Most importantly, however, note that at saturation doping, a finite density of states is observed in the region of the Fermi

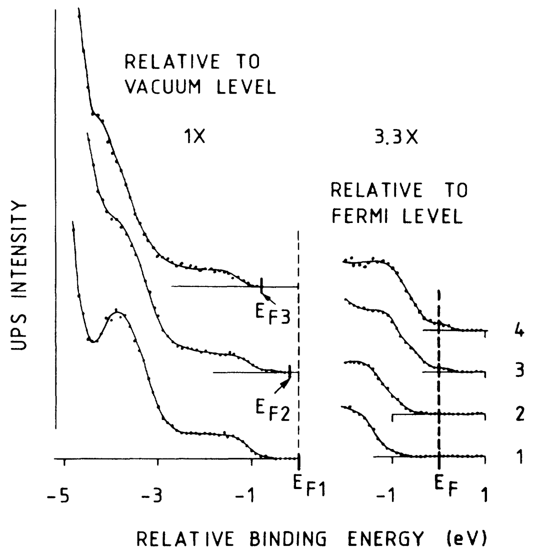

FIG. 2. The UPS spectra of the π bands of P3HT aligned relative to E_F (right) and adjusted for ΔE_F (left). The number 1 refers to undoped, 4 to *saturation* doped, and 2 and 3 to intermediate doping.

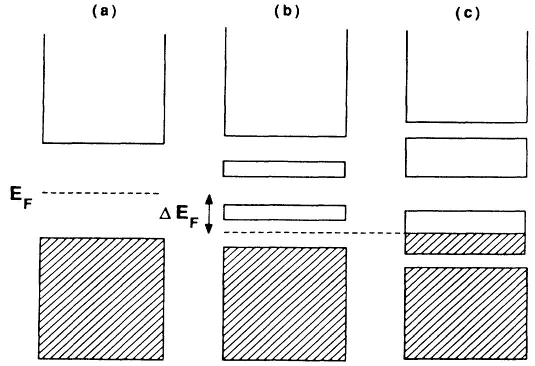

FIG. 3. Schematic representations of the band structures of (a) undoped, (b) bipolaron-lattice, and (c) polaron-lattice forms of polythiophene, after Ref. 2.

energy. These combined results are significant in several ways, as indicated below.

The movement of E_F must be taken into account before interpreting x-ray photoelectron spectra of the core electrons in terms of initial-state, charge-induced (doping), chemical shifts.[16,17] This aspect of the present work will be reported separately.[18] We note in passing, however, that upon doping, *before* correction for ΔE_F, both the as-recorded C(1s) and S(2p) core-level binding energies appear to shift in the *wrong direction* for an initial-state chemical shift resulting from electron transfer *from* the polymer *to* the dopant species. After correction for ΔE_F, the XPS chemical shift results agree with the analysis presented below.[18]

The present UPS data can be interpreted in terms of the results of recent extensive quantum chemical calculations by Stafström and Brédas,[2] based upon the valence effective Hamiltonian (VEH) pseudopotential method. Electronic charges (holes or electrons) can be added to a conjugated polymer via charge transfer with dopant molecules.[1] In the case of the present nondegenerate ground-state conjugated polymer, there are three doping regimes to be considered. Upon initial *lowest doping,* the individual charges (holes, in the present case) must initially go into polaron states, by definition. At *intermediate and high doping* levels, mobile polarons combine to form doubly charged bipolarons, which are expected to be the lowest-energy, stable, charge-carrying species in the polythiophenes.[2,8] Indeed, optical studies on poly(3-methylthiophene) are in complete agreement with the existence of polarons as the initial charge-carrying states, and with the existence of bipolarons at higher doping concentrations.[7] At *saturation doping,* however, VEH results indicate a possibility that the bipolaron lattice may revert to a polaron lattice, under certain conditions.[2]

The molecular wave functions of both polarons and bipolarons are spread out over many (~6) thiophene rings.[2,9] At the highest concentration, corresponding to *saturation* doping, these wave functions overlap, leading to the formation of either a polaron lattice or a bipolaron lattice.[2] Schematic representations of the band structures for undoped polythiophene, as well as the calculated polaron and bipolaron lattices (corresponding to saturation doping), are shown in Fig. 3. Only the polaron lattice exhibits a finite $\rho(E_F)$. Moreover, the difference in E_F expected between the undoped and the polaron-lattice forms of polythiophene is calculated to be 0.7 eV,[2] in very good agreement with the measured value of about 0.8 eV. We stress that the finite $\rho(E_F)$, the observed ΔE_F, and the XPS chemical-shift analysis[18] all agree with the polaron-lattice model.[2] Note that in self-consistent-field calculations,[2] the polaron lattice provides for significant charge polarization along the polymer chains, in agreement with the strong ir activity observed at high doping levels.[21]

The results of these present studies imply (but do not prove) the existence of a polaron lattice at the high (saturation) doping level in polythiophene. The polaron lattice, which corresponds to a half-filled band, is expected to be unstable in a one-dimensional system.[5,22] Thus, these results imply that additional interactions (higher dimensional, or locally with the counterions) occur, which are necessary to stabilize the polaron lattice. It should be noted, however, that there are other models of the high-doping regime which predict a metallic state in other conjugated polymers. In addition to a polaron-lattice model,[23] both disorder[24] and Coulomb interactions with dopant ions and charges on neighboring chains[25] have been suggested to produce a finite $\rho(E_F)$ in polyacetylene. Further calculations would be necessary in order to check the validity of these models for the case of the polythiophenes. We note, however, that the evolution of the Fermi level upon *p*-type doping predicted by the latter model[26] leads to a shift of the Fermi level towards lower binding energy, because of the interactions of the electrons on the polymer chains with the negative counterions, i.e., Coulomb repulsion. This effect goes in the *opposite* direction to what we observe experimentally in polythiophene. Furthermore, the presence of significant disorder would prevent the very observation of the UPS peak at the Fermi level.[1,27]

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[1] For a review, see *Handbook of Conducting Polymers,* edited by T. Skotheim (Dekker, New York, 1986).

[2] S. Stafström and J.-L. Brédas, Phys. Rev. B **38**, 4180 (1988).

[3] S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M. A. Druy, A. Sivak, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. **45**, 1123 (1980).

[4] A. J. Epstein, H. Rommelmann, M. A. Druy, A. J. Heeger, and A. G. MacDiarmid, Solid State Commun. **38**, 683 (1981).

[5] S. Kivelson and A. J. Heeger, Phys. Rev. Lett. **55**, 308 (1985).

[6] T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, Phys. Rev. B **30**, 702 (1984).

[7] G. Harbeke, D. Baeriswyl, K. Kiess, and W. Kobel, Phys. Scr. **T13**, 302 (1986).

[8] M. J. Nowak, D. Spiegel, S. Hotta, A. J. Heeger, and P. A. Pincus, Synth. Met. **28**, C399 (1989).

[9] J.-L. Brédas, F. Wudl, and A. J. Heeger, Solid State Commun. **63**, 577 (1987).

[10] C. Fite and P. Bernier, Phys. Rev. B **36**, 4574 (1987).

[11] J.-E. Österholm, J. Laakso, P. Nyholm, H. Isotalo, H. Stubb, O. Inganäs, and W. R. Salaneck, Synth. Met. **28**, C435 (1989).

[12] W. R. Salaneck, O. Inganäs, B. Thémans, J. O. Nilsson, B. Sjögren, J.-E. Österholm, J.-L. Brédas, and S. Svensson, J. Chem. Phys. **89**, 4613 (1988).

[13] B. Thémans, W. R. Salaneck, and J.-L. Brédas, Synth. Met. **28**, C359 (1989).

[14] M. Lögdlund, R. Lazzaroni, W. R. Salaneck, S. Stafström, J. O. Nilsson, X. Shuang, J.-E. Österholm, and J.-L. Brédas, in *Proceedings of the Third International Winter School on Conducting Polymers,* edited by H. Kuzmany, M. Mehring, and S. Roth (Springer-Verlag, Berlin, 1989).

[15] W. R. Salaneck, R. Bergman, J.-E. Sundgren, A. Rockett, T. Motooka, and J. E. Greene, Surf. Sci. **198**, 461 (1988).

[16] G. K. Wertheim, P. M. Th. van Attekum, and G. Basu, Solid State Commun. **33**, 1127 (1980).

[17] W. R. Salaneck, R. Erlandsson, J. Prejza, I. Lundström, and O. Inganäs, Synth. Met. **5**, 125 (1983).

[18] R. Lazzaroni, M. Lögdlund, S. Stafström, W. R. Salaneck, and J.-L. Brédas (to be published).

[19] C. R. Wu, J. O. Nilsson, O. Inganäs, W. R. Salaneck, J.-E. Österholm, and J.-L. Brédas, Synth. Met. **21**, 197 (1987).

[20] Y. Jugnet, G. Tourillon, and Tran Minh Duc, Phys. Rev. Lett. **56**, 1862 (1986).

[21] D. B. Tanner (private communication). See also, D. B. Tanner, G. L. Doll, A. M. Rao, P. C. Eklund, G. A. Arbuckle, and A. G. MacDiarmid, Synth. Met. **28**, D141 (1989).

[22] R. E. Peierls, *The Quantum Theory of Solids* (Oxford Univ. Press, London, 1955).

[23] S. Kivelson and A. J. Heeger, Phys. Rev. Lett. **55**, 308 (1985).

[24] E. J. Mele and M. J. Rice, Phys. Rev. B **23**, 5397 (1981).

[25] S. Jeyadev and E. Conwell, Phys. Rev. Lett. **61**, 361 (1988).

[26] E. M. Conwell, H. A. Mizes, and S. Jeyadev, Phys. Rev. B **40**, 1630 (1989).

[27] C. B. Duke, in *Extended Linear Chain Compounds,* edited by J. S. Miller (Plenum, New York, 1982), Vol. 2, Chap. 2, p. 59.