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Spectroscopic observation of polaron-lattice band structure in the conducting polymer polyaniline

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Abstract

We present the results of soft x-ray emission measurements for undoped and protonated polyemeraldine. We show that the polaron-lattice band structure fully accounts for the observed x-ray transitions. A finite spectral intensity of C K α and N K α XES is observed at the Fermi level for protonated polyemeraldine, supporting the applicability of the polaronic-metal model for highly conducting polymers.

Interest in polyanilines has been reinforced by the discovery of their high electrical conductivity observed in doped phases, giving rise to a new class of conducting polymers [1]. Polyanilines are used as active electrodes in lightweight rechargeable batteries [2], as hole-injecting electrodes in electroluminescent flexible light-emitting diodes [3], as conductive adhesives and many other applications. Polyaniline is a generic term that refers to a family of polymer backbones $[(-B-NH-B-NH-)_y(-B-N=Q=N-)_{1-y}]$, which consist of alternating phenyl rings in the benzenoid (B) and quinoid (Q) form, and nitrogen heteroatoms in either amine ($-NH-$) or imine ($-N=$) form. Polyaniline can be prepared in three major forms which differ from one another by the degree of oxidation y (i.e., the ratio of amine nitrogens over the total number of nitrogen atoms): the fully reduced leucoemeraldine base (LEB) where $y = 1$, the half-oxidized emeraldine base (EB) where $y = 0.5$ (figure 1(I)) and the fully oxidized pernigraniline base (PNB) where $y = 0$. Each of these forms of polyaniline is an insulator with a band gap of 3.6 eV for LEB and EB and about 1.4 eV for PNB. These polymers can also exist in the corresponding protonated (salt) forms but only emeraldine salt (ES) is highly electrically conductive in this form. The largest conductivity reported to date is about 400 S cm^{-1} [4], which is 14 orders of magnitude higher than in the insulating emeraldine base form.

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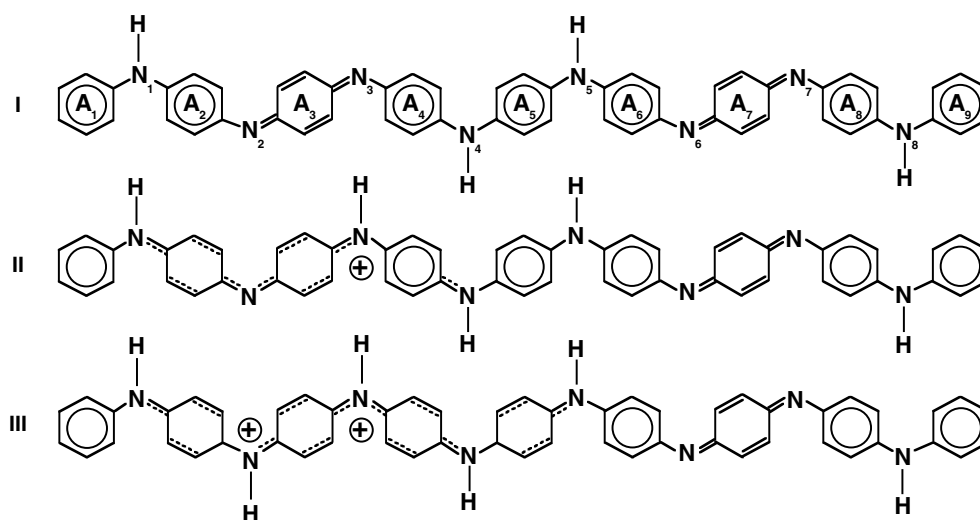


Figure 1. Chemical structures, atom and ring numbering of polyaniline in polyemeraldine form: (I) neutral molecule; (II) singly protonated (polaron) form; (III) doubly protonated (bipolaron) form.

The temperature dependence of the conductivity in the highly conductive state is described by Mott's 'variable-range hopping' law $\sigma(T) \propto \exp[-(T_0/T)^{0.5}]$. The exponent value of 0.5 can correspond to either one-dimensional localization in every chain or three-dimensional localization in the net of intersected chains with the Coulomb gap. The latter scenario seems to be more in agreement with the experimental data gained from DC and AC transport properties [5].

A local distortion of the chemical bonds gives rise to the appearance of polymer conductivity since protonation does not change the electronic concentration. These distortions are commonly referred to as either polaron, which stores the extra positive charge when only one nitrogen is protonated, or bipolaron, in which both imine nitrogens are protonated [6] (see figure 1(II) and (III)). To explain the conductive state of ES, two models have been proposed. A regular distribution of polarons leaves the electronic band half-filled [7, 8] or the random bipolaron structure leads to the formation of extended electronic states at the Fermi energy [9, 10]. It has been shown recently by direct quantum-chemical calculations that polarons are likely to be the most stable defects in ES, and, in particular, they are energetically more stable than bipolarons [11]. It has been found that not only the conductivity but also the Pauli contribution to the magnetic susceptibility increases with the degree of protonation. This is consistent with the assumption that the charge carriers in ES are polarons rather than bipolarons and conductivity results from the formation of a polaron lattice with a half occupied polaron band [8]. This picture is supported by band-structure calculations [8, 12, 13] as well as optical [8], electron-spin-resonance (EPR) and transport [5] studies. Therefore the regular distribution of polarons can be used as a basic model for developing a more microscopic theory of charge and energy transport. Up to now, there has been no direct spectroscopic information regarding the electronic structure of ES, which is essential for selecting an adequate picture. The question regarding which model is favourable is not trivial, since for other conjugated polymers spectroscopic evidence is in favor of a bipolaron-type nature of the current carrier [14].

In this paper we study the differences in the electronic structure of protonated and undoped polyemeraldine by means of soft x-ray emission spectroscopy (XES). Our results show that the

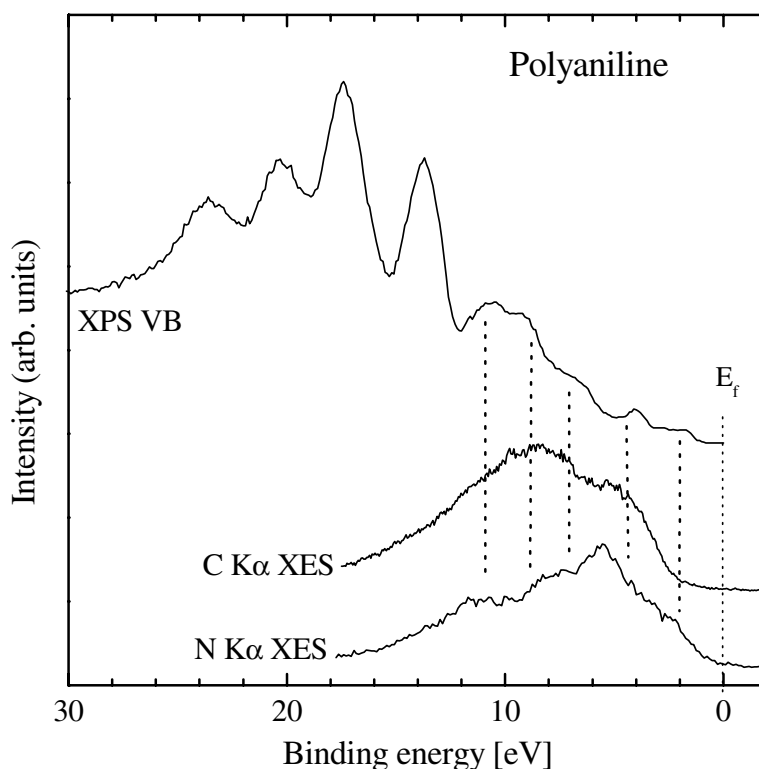


Figure 2. Comparison of carbon and nitrogen $K\alpha$ emission spectra of undoped polyemeraldine ($\gamma = 0.5$) with XPS VB of leucoemeraldine ($\gamma = 1$).

conclusions drawn from the calculated band structure for the polaron lattice fully account for the experimentally observed x-ray transitions of protonated polyemeraldine. These findings support the applicability of the polaronic-metal model [7, 15] for highly conducting polymers.

The experiments were carried out at Beamlines 7.0 and 8.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory employing the Uppsala University [16] and University of Tennessee at Knoxville [17] endstations. Photons with an energy of 300–302 eV, well above the carbon K edge, and with an energy 412–430 eV, well above the nitrogen K edge, were delivered to the endstations via undulator beamlines employing their spherical grating monochromators. The x-ray fluorescence spectrometers provide an energy resolution of 0.30 eV and 0.65 eV for the carbon and nitrogen measurements, respectively.

For our measurements we have chosen the basic form of undoped and protonated polyemeraldine. The doped samples were prepared by protonation with 60% camphorsulphonic acid (CSA). The protonation with H^+ adds holes to the imine groups around the quinoid ring.

The non-resonant x-ray emission process can be described as a two-step one with the emission process decoupled from the excitation process. The first step corresponds to an electron transition from a core level to the conduction band when the sample absorbs an incoming photon. The second step is the emission of an outgoing photon when electrons undergo transitions from the valence band to fill the core holes created during the photon absorption. Both steps are governed by the dipole selection rule $\Delta l = \pm 1$ leaving the 1s core

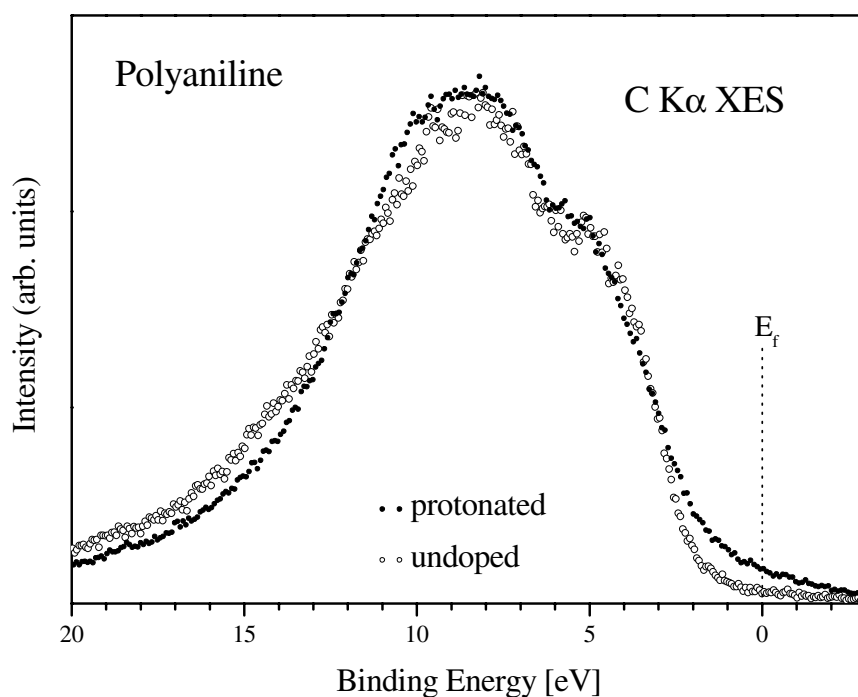


Figure 3. Carbon $K\alpha$ emission spectra of undoped and protonated polyemeraldine displayed on a binding energy scale.

level holes in carbon and nitrogen to be filled by 2p valence electrons only. Therefore the emission spectra are probing the density of p states of the particular atomic site. The location of the Fermi level in x-ray emission spectra is determined by x-ray photoelectron spectroscopy (XPS) measurements of the core level binding energies.

Figure 2 displays $C K\alpha$ and $N K\alpha$ emission spectra of undoped polyemeraldine ($y = 0.5$) compared with an XPS valence band spectrum of leucoemeraldine ($y = 1$) reproduced from [18]. The XES spectra are displayed on the common binding energy scale by using the C 1s and N 1s binding energies [19]. Carbon and nitrogen $K\alpha$ emission spectra are located close to the top of the valence band in the range of 0 to 12 eV. Strong overlap of these spectra implies strong hybridization of C 2p and N 2p states due to the formation of C–N bonds. This is in accordance with band structure calculations [8, 12]. In the energy range of 12 to 24 eV C 2s and N 2s states form four subbands due to C–C, C–N and N–N bonding. The subbands are not observed in x-ray emission due to the fact that $2s \rightarrow 1s$ transitions are dipole forbidden.

According to the calculations [8, 12] the band structure of the bipolaron lattice exhibits a gap of 0.5–0.65 eV (between the highest occupied band and the bipolaron band). In the polaron lattice on the other hand the highest occupied band is only half filled by valence electrons. The electrons near the Fermi level are completely delocalized throughout the whole chain and can move freely in the band. This is of course correct only for the ideal chains. Disorder effects transform the metallic state into the ‘Fermi glass’ one where the electron motion is activated [5]. Conclusively only the polaron band picture, not the bipolaronic one, results in a finite density of states at the Fermi level. Experimental determining of the density of states at the Fermi level is of crucial importance in order to decide for either the polaronic or the bipolaronic band structure.

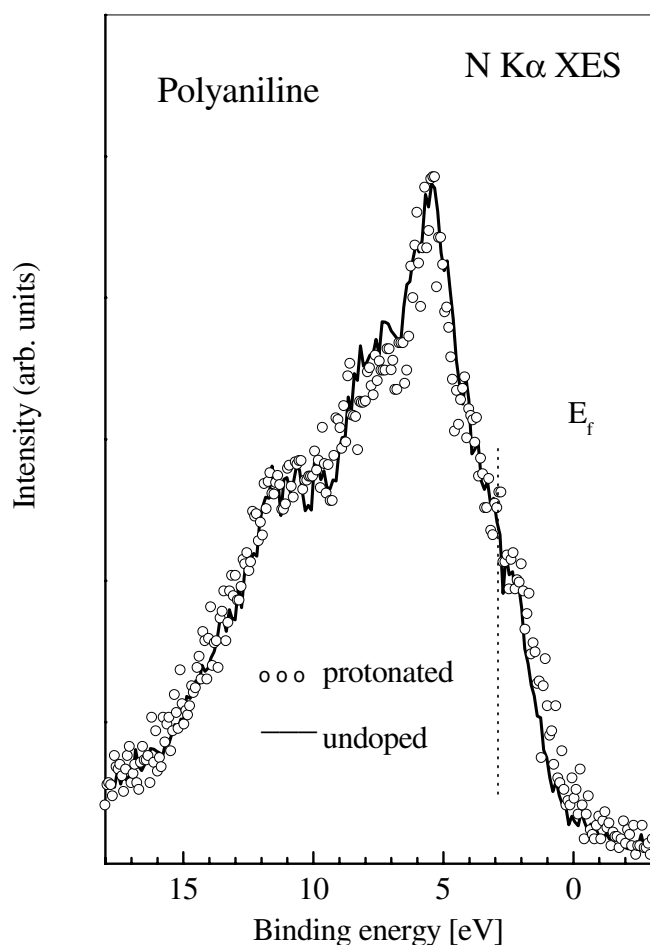


Figure 4. Nitrogen $K\alpha$ emission of undoped and protonated polyemeraldine displayed on the binding energy scale.

Figures 3 and 4 exhibit the carbon and nitrogen $K\alpha$ emission spectra of undoped and protonated emeraldine converted to a binding energy scale. The spectra are normalized to the same peak height at the intensity maximum. The intensity of the $C K\alpha$ emission in the vicinity of the Fermi level E_F is clearly increased for the protonated emeraldine compared to the undoped sample (figure 3). This finite density of states at the Fermi level evidences the metallicity of the doped phase. The same tendency of higher spectral intensity in the vicinity of the Fermi level for protonated polyemeraldine with respect to the undoped phase is observed in $N K\alpha$ XES (figure 4), though these measurements have been performed with a lower energy resolution (due to the higher emission energy) and statistics than the carbon data, the latter being due to the smaller content of nitrogen atoms in polyaniline. Protonation increases the finite density of states near the Fermi level and the origin of the increase is the formation of the polaron band. In the case of the bipolaron band structure, no finite density of states is expected near E_F . Recently, an extremely small finite density of states for protonated emeraldine has been observed in photoemission measurements [20]. Unfortunately the authors do not indicate the level of protonation.

To summarize, we have observed a finite density of states in protonated emeraldine in the vicinity of the Fermi level using soft x-ray emission measurements. This direct observation is in a full agreement with band structure calculations for the polaron lattice and therefore supports a polaronic-metal model for conducting polymers.

Acknowledgments

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