

Electronic structure of conjugated polymers and interfaces in polymer-based electronics

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Abstract

Electron emission, in resonance with soft X-ray absorption, appears to provide a measure of the dispersion of the highest occupied and the lowest, core-hole distorted, unoccupied π -bands in poly(*p*-phenylenevinylene).

Key words: X-ray absorption, electron emission, photoelectron spectroscopy, poly(*p*-phenylenevinylene).

1. Introduction

The Surface Physics and Chemistry group in Linköping has studied the surfaces and interfaces of conjugated molecules, polymers, and interfaces there of over almost two decades. Much of the work has been documented in review articles [1–6] and books [7,8]. This oral presentation consisted of a mini-review of the research areas covered by the work in Linköping, and then the presentation of some new results on the electronic structure of unsubstituted poly(*p*-phenylenevinylene), or PPV. Given the space restrictions, and, because some of even the newer works have been reviewed else where [9,10], only a brief over view of the new data, on the electronic structure on PPV, is presented here [11].

2. The ground- and core-excited π -electronic structure of non-oriented poly(*para*-phenylenevinylene) studied by resonant photoelectron spectroscopy

The (quasi-) one-dimensional nature of conjugated polymers, with their rather simple band structure, allows the exploration of new aspects of non-traditional high-energy spectroscopies applied to solids. Poly(*para*-phenylenevinylene) or PPV has such a π -band structure, which, in its lowest binding energy portion, consists of a strongly dispersing band, denoted as π_4 , and a localized, flat band, π_3 , which intersect each other close to $k = \pi/a$, that is, near the edge of the 1D Brillouin zone [12]. In model calculations of the ground state of the polymer system, the band structure is very symmetrical, that is, the unoccupied bands mirror the occupied bands.

3. Experimental

Soft X-ray absorption (Near Edge X-ray Absorption Fine Structure spectroscopy, or NEXAFS) and Resonant Photoelectron Spectroscopy (RPES) measurements [13–15] were carried out at the MAX Laboratory for Radiation Research, Lund, Sweden. The NEXAFS spectra were obtained at beam line I411 and the RPES spectra at beam line I311. The PPV samples were prepared, via thermal elimination using a poly(*p*-xylylene- α -tetrahydrothiophene-chloride) precursor, as thick (> 10 nm) films, which were spin coated on clean gold substrates [16]. Although it is believed that there is a tendency for the resultant polymer (PPV) chains to lie more-or-less parallel to the surface of a spin coated film, the sample are not ordered.

4. Results and discussions

The new NEXAFS spectrum obtained in this study is shown in Fig. 1. In the present absorption spectrum [11], fine structure is observed in the region of the first resonance with π^* -final state symmetry, between 284.1 eV and 285.8 eV, as shown in Fig. 1, which was not observed in previously published works [17,18]. By tuning the photon energy within the first resonance, electronic transitions from the non-dispersed C(1s) level to specific parts of the unoccupied band structure are generated. The X-ray absorption corresponds to the electronic structure accessed in the presence of the C(1s) core hole. Specifically, for a dispersing valence band, in the presence of a core-hole, a given photon energy corresponds to an excitation into a state with a distinct wave vector k within the 1D Brillouin zone. In this respect, the soft X-ray absorption (the NEXAFS) should map out the dispersion of the initially empty π^* -band structure. However, the absorption is excitonic, in the presence of the core hole, and therefore the transitions do not reflect directly the band structure of the neutral system in the ground state. This will have

the effect of reducing the apparent energy of the X-ray absorption, and a deduction of the binding energy of the otherwise empty π -band will appear too high. The question as to whether or not the shape of the excited band is distorted (or just shifted to apparently higher binding energies) is still open. Qualified theoretical input is needed.

Following the excitation of an electron from the C(1s) level into an otherwise empty π^* -band, the excited electron loses energy by falling back to the original hole. This is known as participator core-hole decay of this state, identified as discussed below. The energy released by the de-excitation is transferred (in resonance) to another electron, in the occupied band structure, which then is excited to a high-energy free electron. The resonance emission (RPES [19]) may be seen clearly in the narrow photon energy region from 284.4 to 285.8 eV. The energy released is just equal to the photon energy needed to initially create the excited state (*i.e.*, $h\nu$), and the second electron subsequently released in the process has a kinetic energy determined by $E_K = h\nu - E_B$, as in conventional photo-electron emission. Thus the final state in the process, X-ray absorption followed by resonant participator electron emission, is identical to the single-hole-state generated in conventional valence band photoelectron spectroscopy, such as UPS; see, for example [7]. Plotting the electron emission spectra as a function of binding energy ($h\nu - E_K$) is used to identify the transitions as participator, rather than spectator (which would scale according to the kinetic energy, rather than binding energy). These issues have been discussed in detail by other authors elsewhere [13]. The spectra of emitted electrons, following X-ray absorption, are shown for different X-ray absorption energies, in Fig. 2 [11].

An important point is that electron emission, following the participator core-hole decay of this state, might be expected to occur from specific parts of occupied π -band, the details of which are governed by the momentum-dependent Coulomb interaction between the core-excited and valence band electrons. In Fig. 2a is shown the RPES spectra in the energy region near threshold. First, a non-dispersing peak at 3.85 eV binding energy, which is related to the flat π_3 -band, appears at a photon energy of 284.8 eV, that is, in the middle of the resonance. A second, strongly dispersing feature starts to appear at the threshold energy, at the low binding energy side of the spectrum. For higher photon energies, the peak disperses to higher binding energy, and merges with the non-dispersing peak. It appears that by sweeping the photon energy through the first resonance, the dispersing π_4 -band is mapped out. This, however, requires the conservation of the electron momentum k_{\parallel} in the Coulomb interaction between the electrons involved.

Further more, in this case, plotting the peak position versus the photon energy, as in Fig. 1b, the underlying core-hole excited state unoccupied band structure may be derived.

Further work is necessary. The nature of the RPES Coulomb matrix elements, key to the de-excitation process, must be theoretically rationalized. The nature of the core-excited state must be understood in detail in order to explore the possibilities and the and limitations of RPES spectroscopy for the study of the band structure of non-oriented or polycrystalline polymeric solids.

5. Summary and conclusions

By observing the resonant emission of electrons following the absorption of soft X-rays, two features appear to be mapped. The soft X-ray absorption follows the band dispersion in the otherwise unoccupied π^* -bands, and the electron emission spectra appear to follow the dispersion of the initially occupied π -bands. Since the soft X-ray absorption is believed to be excitonic, the location of the dispersed π^* -band in binding energy is uncertain, but is clearly not that for the neutral system in the ground state. The dispersion in the π^* -band, however, should correspond to that expected from calculations of the neutral system in the ground state, as studied by UPS. In order to firmly establish the interpretation of the data, more theoretical input, concerning the matrix elements involved in the de-excitation process, are required.

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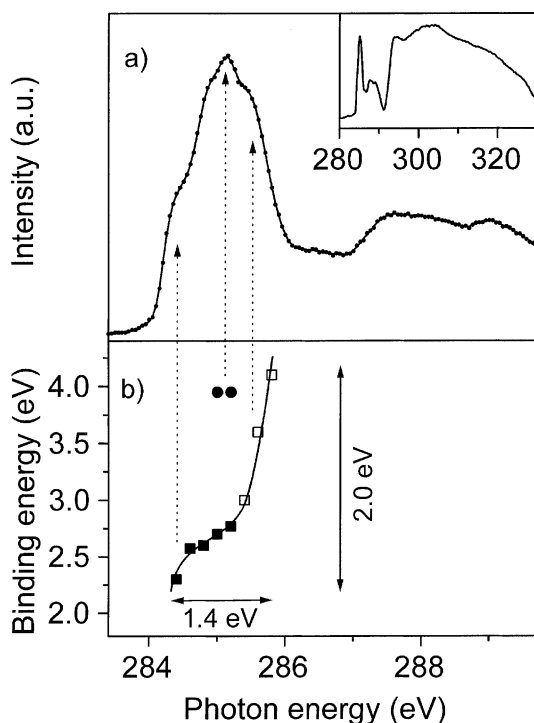


Fig. 1: (a) NEXAFS spectrum of PPV [11]. (b) The position of the RPES peaks of the π_3 - and π_4 -bands as a function of the photon energy.

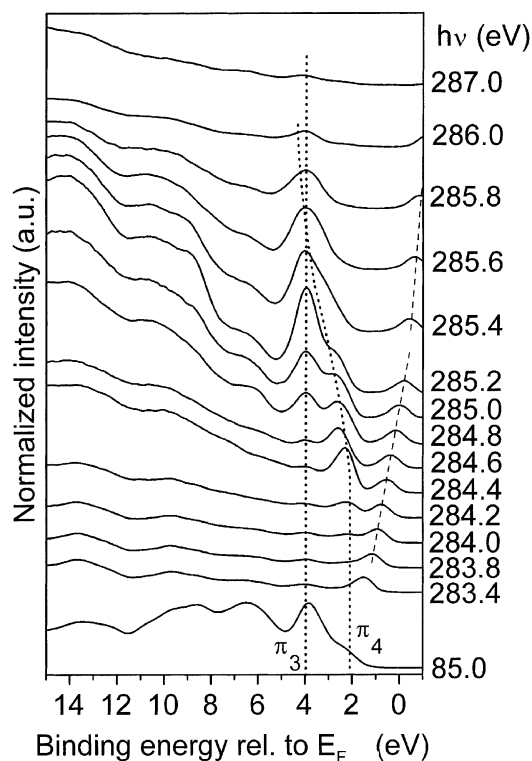


Fig. 2: The RPE spectra of PPV. The position of the C(1s) line excited by second-order light is indicated by a dashed line [11]. Although an artifact, this C(1s) feature is useful for energy calibration.