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Polaron and bipolaronlike states in n-doped bithiophene

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Bithiophene is studied with varying Cs dosing as a model for the n-doping of thiophene-based conducting polymers. The evolution of the electronic structure with increasing Cs concentration is followed both indirectly, by electron-energy-loss spectroscopy (EELS), and directly by ultraviolet-photoemission spectroscopy (UPS). In both spectroscopies the behavior of the states formed in the gap indicates two doping regimes. The EELS results parallel the optical-absorption results for the p-doping of longer thiophene oligomers and polythiophene, and suggest a polaron (anion) to bipolaronlike (dianion) transformation. The UPS results are consistent with this interpretation, showing first in the low-doping regime the appearance of two states in the band gap which move closer together in the higher-doping regime. This constitutes direct observation of a transition from polaron to bipolaron states, albeit in a model system. Consideration of the photoionization cross sections indicates that the deeper (bi)polaron level has C $2p$ character while the shallow level, filled by donation from the Cs, has significant S $3p$ character.

I. INTRODUCTION

In the field of conducting polymers, those based on thiophene are attracting particular attention due to their processability and stability. The polymers are usually prepared in air and are then introduced into a vacuum system to investigate their physicochemical properties, e.g., by electron spectroscopic techniques. The neutral polythiophene (PT) polymers are semiconducting, but upon doping they become remarkably conducting. Doping experiments on PT (and its derivatives) have been reported in the literature with electron acceptors (p doping),[1,2] but there appear to be no experimental data to date of the n doping of the full polymers, although theoretical studies have been published.[3] Investigation of the electronic processes occurring on doping encounters a number of experimental problems associated with the necessity of an ultrahigh-vacuum (UHV) environment for the most direct (electron) spectroscopic techniques, and in general *in situ* sample preparation is preferable. This is clearly difficult with polymeric samples. An additional drawback with polymer samples is their inherently high-defect density, which may obscure some of the electronic effects expected on doping. This has led to studies of conjugated oligomers which are considered as models for the polymers and which can be prepared by thin-film techniques in a UHV environment. Following our work on model complexes for polymers,[4–7] the evolution of new states in the band gap on doping of such a model system for thiophene-based polymers is presented. In this paper the valence-band electronic structure of Cs-doped bithiophene is described, extending our previous work on the same charge-transfer complex[6] where the core and unoccupied levels have been probed by x-ray photoemission spectroscopy (XPS) and near-edge x-ray-absorption fine structure (NEXAFS) with results in agreement with the theoretical predictions for PT.[3] While this system is of course still far from a polymer in many respects, it expresses, nevertheless, essential features of the electronic structure on doping. Moreover, apart from their model aspects, the thiophene oligomers are intrinsically interesting as they have been shown to have technologically exploitable characteristics themselves.[8,9]

The effect on the model system of n doping, given the theoretically predicted evolution of the electronic structure for PT (Refs. 3, 10, and 11) is displayed in Fig. 1, where a schematic of the electronic structure for different stages of n doping is presented with (a) a vacuum-level reference and (b) a Fermi-level reference. The doping of the molecule is effectuated by charge transfer from the Cs. The thus ionized molecule undergoes a geometric relaxation from an aromatic to a quinoidlike structure which in turn leads to significant changes in the frontier orbitals. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) will move into the gap. For low doping, the upper energy level is half-filled, crossing the Fermi level, while the lower energy level is fully occupied; this is said to be a polaron state. On further doping, the two new gap states move closer together, forming a so-called bipolaron with both states fully occupied and with a concomitant shift of the Fermi energy towards the vacuum level.[3] In this work the evolution of these gap states for different n-doping levels is followed by direct and indirect electron spectroscopic techniques, ultraviolet photoemission spectroscopy (UPS), and electron-energy-loss spectroscopy (EELS), respectively. In addition to merely establishing the presence of doping-induced gap states, we also directly observe modifications in these states as a function of dopant (Cs) concentration. This will be discussed in

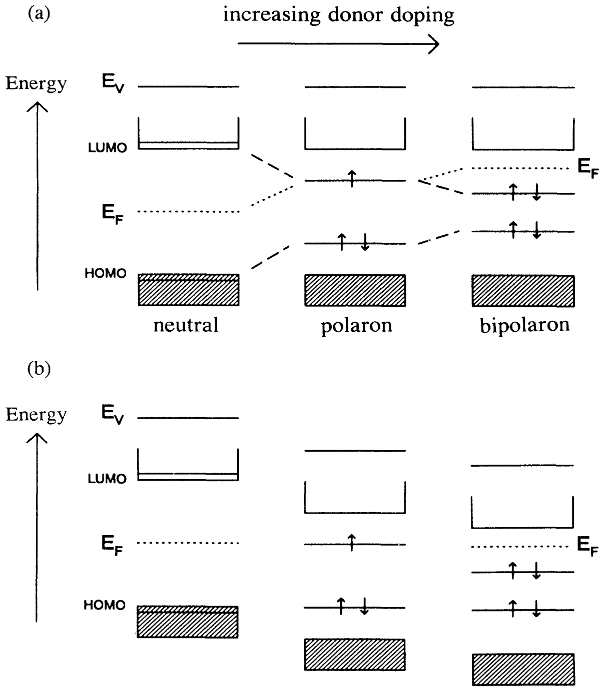

FIG. 1. Schematic of the predicted evolution of the valence and conduction bands as viewed with (a) a vacuum-level and (b) a Fermi-level reference.

terms of a polaron to bipolaronlike transition. Moreover, the atomic-orbital character of the gap states has been investigated using the photon-energy dependence of their ionization cross sections in synchrotron-radiation experiments. It is suggested that the molecular orbital which accepts the donor charge has a prominent S 3*p* contribution. Implications of this for the conductivity of *n*-doped PT are discussed.

II. EXPERIMENT

The experiments were performed in a VG ADES 400 spectrometer with a base pressure $<10^{-10}$ mbar. The system was equipped with a noble-gas discharge lamp allowing angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), an electron gun for electron-energy-loss spectroscopy (EELS), and a mass spectrometer for thermal desorption spectroscopy (TDS). The mass spectrometer was aligned in line of sight to the sample and was multiplexed by a computer allowing 10 mass units to be followed concurrently. Using He for the discharge lamp, unpolarized light with energies of 21.1 and 40.8 eV could be used for ARUPS. Work functions were determined via the secondary electron cutoff in ARUPS experiments. The experiments on the photon-energy dependence of the gap-state photoemission were performed in a vacuum system similar to the one described above attached to the TGM-2 beam line at the BESSY synchrotron in Berlin.

All thin-film surfaces were prepared on a Ni(110) single-crystal substrate, which could be cooled to liquid-nitrogen temperature (80 K) and heated resistively. The Ni crystal was used just as a substrate for the molecular layers under observation, and due to their thickness, no Ni features interfered with the spectra. However, the Fermi level of Ni provided a suitable energy reference for UPS.

Bithiophene was introduced via a pinhole doser out of a volume held at 370 K. The pressure in the molecule reservoir was kept at 0.05 mbar to obtain reproducible doses of bithiophene. Cs dosing was performed by evaporation from a SAES getter source with a heated glass collimator. The thicknesses of the molecular layers and the Cs doses were calibrated by TDS and work-function measurements, respectively, and are referred to in units of their respective monolayers on the Ni substrate.

III. RESULTS AND DISCUSSION

A. TDS

Figure 2 displays thermal desorption spectra from the Ni(110) substrate of (a) four layers of bithiophene, (b) a thick Cs film, and (c) four layers of bithiophene condensed on a thick layer of Cs. The bithiophene signal from the pristine multilayer (167 amu) shows a sharp desorption at 210 K, followed by a weaker desorption feature at around 250 K. These are assigned to a bithiophene multilayer (i.e., condensed bithiophene) and

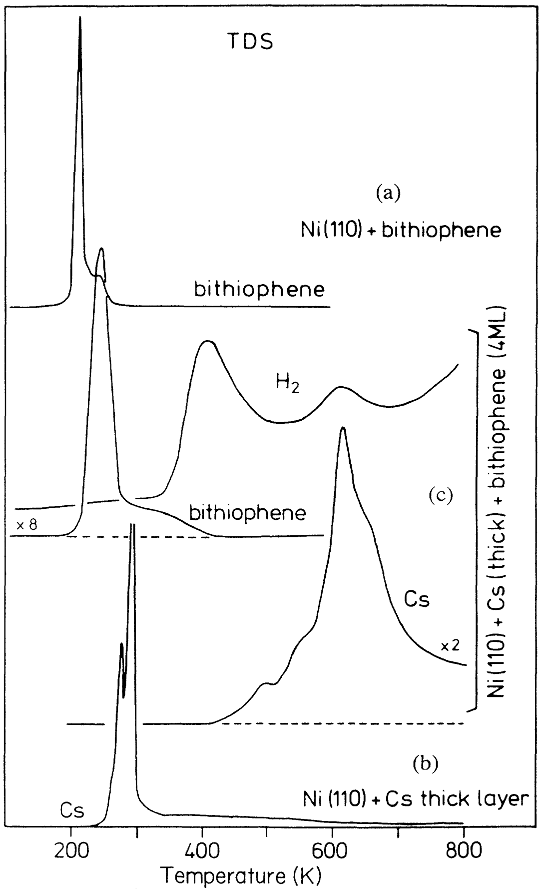

FIG. 2. Thermal desorption spectra from the Ni substrate of (a) four layers of bithiophene, (b) multilayer Cs, and (c) four layers of Cs absorbed on four layers of bithiophene.

bilayer desorptions, respectively.[12] Breakup of the molecular monolayer (i.e., the layer in direct contact with the Ni substrate), as determined by a strong increase in H_2 (2 amu, not shown here), occurs above 300 K. Metallic Cs shows a double peaked structure at 285 and 295 K, the first being smaller than the second, both followed by a small desorption signal of Cs up to 800 K. The two peaks around room temperature are due to condensed Cs metal as determined by the appearance of the Cs-metal Auger signal and the shape and energy position of the 5*p* emissions in ARUPS, typical of metallic Cs.

In the case of bithiophene on a Cs film [Fig. 2(c)], the thermal desorption signals of both bithiophene and Cs change dramatically relative to those of their respective pristine films. The bithiophene signal loses its original multilayer desorption peak totally; the only parent desorption left corresponds in energy position and intensity to the bilayer desorption from the clean Ni surface [note that the bithiophene signal in Fig. 2(c) is magnified by a factor of 8]. Breakup of the molecule, judged from the desorption of large amounts of hydrogen [H_2 signal in Fig. 2(c)] starts around room temperature. An equally dramatic change can be seen in the Cs signal. There is no desorption of Cs up to about 425 K, beyond which a large broad feature is observed, with a maximum at around 600 K. Again, a magnification of the Cs signal by a factor of 2 is used here.

Interestingly, there was no significant difference in the TDS spectra, whether a bithiophene multilayer was laid on a Cs substrate or Cs was evaporated onto a bithiophene film surface. This indicates that the Cs and bithiophene layers mix intimately before desorbing from the substrate. The strong differences in the TDS of bithiophene and Cs in the co-condensed layers as opposed to those of the pristine materials clearly indicate strong interaction between Cs and bithiophene and the formation of a bithiophene-Cs complex.

This complex formation is readily observed by the appearance of new features in the EELS and UPS spectra (see below). Unlike the previously investigated biphenyl case,[4] however, warming to beyond room temperature, but before complex desorption, results in a severe modification in the molecule-alkali complex, as evidenced by distinct changes in the electron spectra and by the hydrogen desorption before Cs desorption. Consequently, to avoid the complications arising from these chemical effects, in the following we will present results of experiments performed at around 100 K. It should be noted that Cs diffuses into the condensed bithiophene phase even at this low temperature and that the Cs-molecule complexes are therefore already established.

B. EELS

Figure 3 shows low-energy EELS spectra taken in reflection geometry at a primary energy of 20 eV with an energy resolution of better than 0.35 eV. This primary energy was chosen first to reduce damage to the molecule and second to gain high cross sections for the molecular features relative to the Ni substrate features (which are not observed at 20 eV). The figure shows a spectra series of about four layers of bithiophene with increasing amounts of Cs. All spectra are normalized to the height of the elastic peak at 20 eV electron energy. This is reasonable given that the electron gun current was constant and the surface was always a diffuse scatterer. The loss spectrum of pristine condensed bithiophene at the bottom of Fig. 3 shows a distinct HOMO-LUMO gap with zero loss intensity until about 3.5 eV. The principal loss (assigned to a $\pi \rightarrow \pi^*$ transition) is at 4 eV and there is weaker loss intensity, with less distinct features, stretching up to 8 eV loss energy. Dosing with Cs initially results in the appearance of two sharp loss features in the gap at 1.5 and 2.7 eV, which grow with increasing Cs exposure at the expense of the original $\pi \rightarrow \pi^*$ transitions. By one-layer Cs exposure on four layers of bithiophene (i.e., about one Cs atom per two bithiophene molecules), these two states in the gap dominate the loss spectrum with the original molecular losses being all but extinguished. On further exposure, the 1.5-eV feature wanes, while the 2.7-eV loss suffers a gradual shift to lower loss energy until it settles at 2.3 eV as a broad feature on a background at two to three layers of Cs exposure (i.e., more than one Cs atom per bithiophene molecule). Still higher exposures yield spectra that can be associated with a metallic Cs layer alone, showing a plasmon at 1.9 eV and a second-order plasmon at 4 eV loss energy and the $O_{23}VV$ Cs Auger feature at around 11

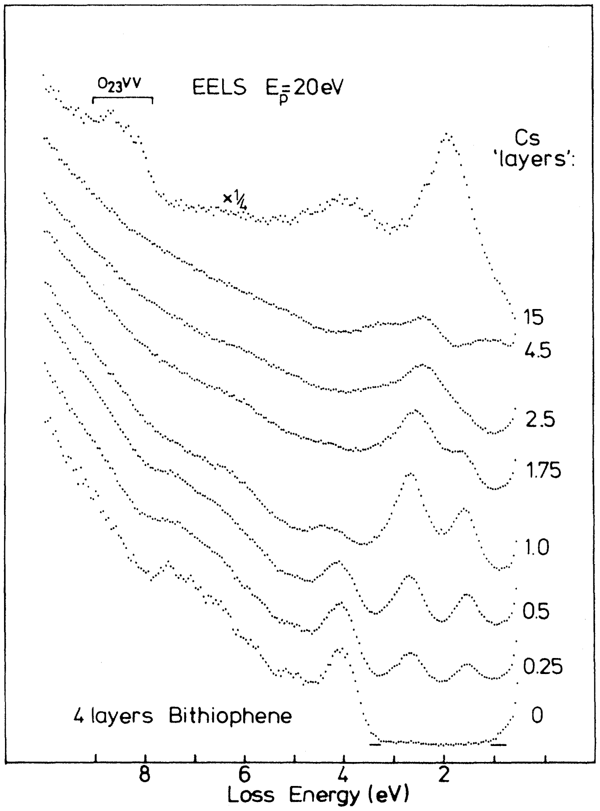

FIG. 3. Electron-energy-loss spectra, primary energy 20 eV in reflection geometry, of four layers of bithiophene with increasing amounts of Cs absorbed on it.

eV kinetic energy. The signal of the top curve in Fig. 3 is reduced by a factor of 4 for ease of comparison to the other spectra, and it should be noted that there is no evidence for Cs valence-valence Auger emissions, despite high Cs concentrations, until a metallic Cs overlayer is formed. This gives support to the idea that a charge-transfer complex is formed with Cs.

The losses of the pristine molecule are in good agreement with results for the gas phase, where the $\pi \rightarrow \pi^*$ transition is at 4.12 eV.[13] The behavior of the loss spectra on *n* doping is similar to that observed for the *p* doping (with Br) of bithiophene, although the energies of the gap-state excitations are different for the two cases.[7] These results mirror the optical-absorption results of Fichou *et al.*[14] and Waragai and Hotta[15] for the *p* doping of larger conjugated thiophene oligomers. In these results, initial doping also induces two gap-state absorptions which transform at higher doping levels to spectra which are dominated by a peak lying between the two with a shoulder at the prior high-absorption-energy position. Furthermore, this transformation in the optical-absorption spectra is also accompanied by the disappearance of the $\pi \rightarrow \pi^*$ transition. The qualitative agreement between the *n*- and *p*-doping results is good given the inherently lower resolution of the EELS spectra. Quantitatively, the differences in the absolute energy positions are in line with expectations both because of the smaller band gap of the longer oligomers used in the optical-absorption experiments and because differences in excitation energies involving the gap states for *n*- and *p*-doped *n*-thiophenes are expected, if, as has been predicted, the gap states are not symmetrically positioned within the band gap.[11] The behavior of the absorption spectra has been interpreted in terms of a polaron-to-bipolaron transition as the transformation in the spectra on increasing doping occurs at approximately one dopant per thiophene ring[15] and because it has been observed to be concomitant with the disappearance of the ESR signal[14] consistent with a transition from polaron states (spin bearing) to bipolaron states (spinless).

Following these arguments in the case of Cs-doped bithiophene, the electron-loss spectra can be simplistically interpreted in the following way: the loss feature at 1.5 eV can be assigned to a transition from the singly occupied polaron level at the Fermi level to the conduction band. The 2.7-eV peak corresponds then to the excitation from the deeper- (in energy) lying doubly occupied gap state. With increasing doping, the higher-energy gap state is filled by a second electron and the two gap states move closer together, so that the excitations from these states appear as one broad feature in the loss spectra at higher doping levels, as seen in Fig. 3. The quenching of the original $\pi \rightarrow \pi^*$ transitions on creation of the gap states is due to the conservation of oscillator strength implied by the sum rule of oscillator strength.[1]

Studies of *p*-doped materials dominate the literature due to the need for *in situ* studies for the *n*-doped systems. As the gap states are empty in the case of *p* doping, these states cannot be directly observed, and the electronic energy levels can only be inferred from excitation spectra such as optical absorption or EELS. As pointed out in our previous study where both indirect (EELS) and direct (UPS) observations of the gap states induced on *n* doping of biphenyl were compared,[4] inferences regarding the gap states from excitation spectra alone are very dangerous. Investigations of the *n*-doped samples therefore has a decisive advantage since the more direct UPS method can be applied, as is done in Sec. III C.

C. UPS

The UPS spectral series corresponding to the EELS series of Fig. 3 is displayed in Fig. 4. It shows the multilayer spectrum from about four layers of bithiophene with increasing amounts of Cs exposure up to a spectrum of metallic Cs obtained after exposure of 15 Cs monolayers. The binding energy is referenced to the Fermi level (E_F) determined from the Ni substrate and, as can be seen in the figure, this coincides with the Fermi level of the condensed metallic Cs layer that forms on top of the complex after it is saturated. The pristine condensed bithiophene spectrum correlates well to those reported for the gas[13] and condensed phases[16] with the prominent nonbonding $\pi_2(2b_1)$, at 5.1 eV, and bonding $\pi_3(1a_2)$, at 3.7 eV, derived orbitals well resolved (here we have adopted the commonly accepted practice of using the nomenclature of the orbitals of the monomer). The He I

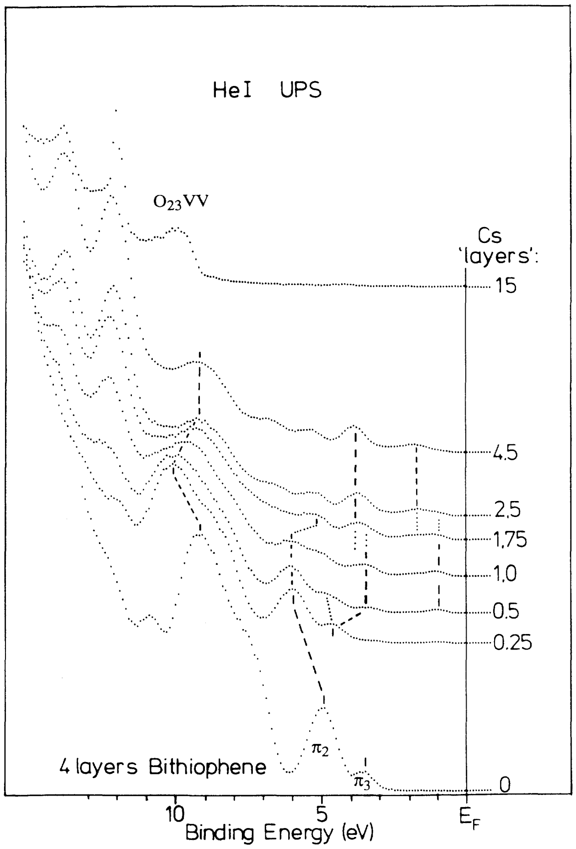

FIG. 4. He I ultraviolet photoemission spectra, $h\nu = 21.2$ eV, of four layers of bithiophene with increasing amounts of Cs absorbed on it.

and He II spectra reported by Tourillon and Jugnet,[16] however, appear at 0.5 eV lower binding energy than the He I spectra reported here. This discrepancy is also noticeable in the study of Fujimoto *et al.*,[17] whereby the energy shifts they required to obtain good agreement between experimental and calculated UPS spectra were 0.5 eV less for bithiophene and terthiophene than for the longer oligomers ($n=4$ to 8). We believe this is due to radiation-induced damage as shifts in the molecular orbitals to lower binding energy are seen in the spectra recorded with He I radiation ($h\nu=21.2$ eV) after short exposures to He II ($h\nu=40.8$ eV) light. The maximum shift of 0.5 eV, obtained in the order of minutes of He II exposure, is also reflected in an identical work-function (Φ) change, implying that there is no change in the binding energies relative to the vacuum level (E_V). This movement can be thus attributed to shifts in E_F relative to E_V due, for example, to photon-induced defect states pinning E_F. It is not due to charging, as hours of He I radiation, despite a much greater photon flux, do not induce these shifts.

The nature of the defect states is beyond our scope here; however, a number of observations can be made. The defects are induced by photons with energy greater than about 30 eV, as evidenced from synchrotron-radiation studies; at 30 eV the full shift is accomplished in the order of tens of minutes. At liquid-nitrogen temperatures the effected area is isolated to the spot impinged by the higher-energy photons, and the desorption temperature at this spot is higher than that for the unirradiated areas or those areas irradiated with lower-energy photons (i.e., He I radiation). Thiophene is known to polymerize under x-ray radiation with the process thought to be mediated by the creation of cationic radicals.[18] It can thus be imagined that the E_F here is pinned by such cationic radicals, and certainly the direction of shifts is correct for such an effect.

The region of greatest interest is that of the highest-lying π orbitals and of the HOMO-LUMO gap, shown in expanded format in Fig. 5 for the same set of experiments. To interpret what is happening in this region, one must be aware of the various shifts that occur on doping. On following the UPS spectra as a function of Cs dose, care must be taken as the molecular orbitals first shift to higher binding energy and at higher exposures shift back to lower binding energy. These shifts have been reported before in our work on the core levels of this system, where the XPS signals of the carbon and sulfur of bithiophene on doping have been followed.[6] As the sizes of the shifts at low doping levels to higher binding energy correspond exactly to changes in the photoelectric work function, Φ, these can be assigned to movements of E_F within the gap, i.e., movements of E_F relative to the vacuum level. The shifts to lower binding energy at higher doping levels (with no concomitant changes in Φ) are likely to be due to changing from spectra associated with the pristine molecule to spectra principally due to the bithiophene-Cs complex. In the latter, although the deeper orbitals may not be greatly affected by complex formation, a relaxation shift to lower binding energy is observed in the photoemission spectra due to enhanced screening, effectuated by the valence electrons donated by the Cs atoms, i.e., the complex is more polarizable than the pristine molecule. It should be noted that the above reference level and relaxation shifts are only observed for the orbitals associated with the molecule and are not seen in either the Cs orbital emissions nor in the gap states induced on doping, as expected given that these features are only associated with the complex formed.

At low doping levels the 1-eV shift to higher binding energy is very distinct, as there is little loss of resolution. The nonbonding and bonding π's now appear at 6.1 and 4.7 eV binding energy, respectively; additionally, between these and E_F two new features at 1.1 and 3.5 eV are discernible. These gap features increase in intensity with dose at the expense of the π orbitals. More specifically, when the effect of relaxation on further doping is considered, the bonding π_3 orbital no longer exists in its original form. Interestingly, the energy difference between the higher-binding-energy gap state and the lower-energy one decrease with Cs coverage. The low-binding-energy gap state at 1.1 eV is gradually supplanted by a new feature appearing at 2.1 eV. At high doping levels the 1.1-eV feature is no longer visible and the gap states are observed at 2.1 and 4 eV. Significantly, this transition in the UPS spectra occurs at the same doping level as the transformation in the EELS spectra. The narrowing of the separation between the gap states (2.4 → 1.9 eV) on going from low to high doping is in agreement with the

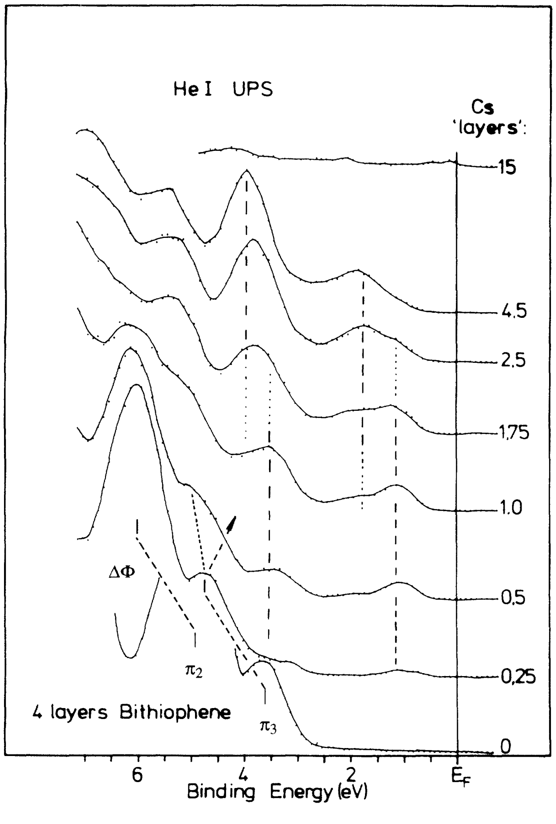

FIG. 5. The region near the Fermi energy of Fig. 4 in greater detail.

expectations for a transition between polaron and bipolaron states also. If, as suggested by the correlation of the EELS results with the optical-absorption results of p-doped systems, the transition observed is that of polaron-to-bipolaron gap states, the question that begs an answer is, "why does the highest polaron level, which should lie at the Fermi level, appear at 1.1 eV binding energy?"

A possible reason for this may be due to the inadequacy of our model system combined with the nature of the UPS experiment. In UPS when one speaks of observing features at E_F, we mean that we are observing photoemitted electrons with the maximum possible kinetic energy ($h\nu$ when the spectrometer work function is taken into account). This is achieved by the emission of electrons from E_F (binding energy zero) when the hole remaining is fully delocalized: equivalent to a fully screened or relaxed final state. This criterion can be imagined to be satisfied in an extended system, such as a conducting polymer, when the half-filled polaron *levels* can form polaron *bands* that straddle E_F. With our dimer model system, however, even if the half-filled polaronlike states are created, as the experimental results indicate, they have to be localized on the dimer and do not form bands. Final-state screening on this localized system is therefore expected to be incomplete, and photoemission from the half-filled states may consequently appear at higher binding energy. Such phenomena are known for absorbed molecules with half-filled HOMO's such as nitrogen monoxide, where UPS shows the orbital to be several eV below E_F, while inverse photoemission shows it several eV above E_F.[19] For the adsorbed molecular systems, however, the situation is complicated by hybridization with the substrate. Another recent example in the literature for larger molecules (lutetium-diphthalocyanine) also sheds some light on the extent of the conjugation length necessary to allow enough delocalization for complete screening of the orbitals.[20] In this case the conjugation length around the molecule is relatively large; despite this, the half-occupied HOMO is observed by UPS to lie below E_F.

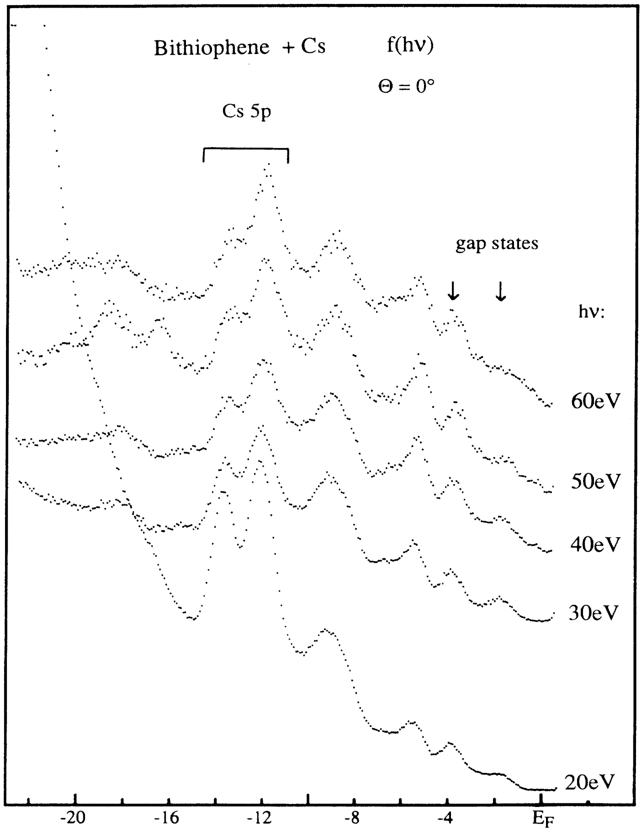

FIG. 6. UPS spectra of Cs-doped bithiophene for a range of incident photon energies.

It is clear in the He I spectra of Fig. 5 that the 6s valence band of metallic Cs has a much lower photoionization cross section than the gap states in the complex. In order to assess the nature of the gap-state orbitals, the photoionization cross sections of the valence-band emissions were investigated as a function of photon energy using synchrotron radiation. In Fig. 6 a range of UPS spectra are shown for incident photon energies between 20 and 60 eV, with the spectra aligned to the Cs 5p emissions and normalized to the 9-eV binding-energy σ band. The surface used for this experiment is again a thick layer of bithiophene with approximately four to five layers of Cs exposed to it, corresponding to a heavily doped molecular multilayer, with the two gap states clearly observed at lower photon energies. It should be noted that the features observed at 16 and 18 eV for $h\nu=50$ eV are due to higher-order light from the monochromator and that the Fermi-level emissions observed at higher photon energies are due to the substrate's d band, whose cross sections increase with increasing photon energy. The most striking feature is a decrease in the low-binding-energy gap state on increasing photon energy with respect to all other valence-band emissions. The higher-binding-energy gap state, on the other hand, behaves in a qualitatively similar fashion to the deeper molecular-orbital emissions. It can be concluded therefore that the two gap states have different cross sections, implying different orbital characters. Since the other molecular bands are dominated by orbitals of C 2p character,[17] the low-binding-energy gap state is suggested to have significant sulfur 3p character. Comparison with the calculated ionization cross sections of Yeh and Lindau[21] supports this, as the rate of decrease in the sulfur 3p cross section with increasing photon energy is much greater than that for carbon 2p orbitals, for the photon-energy range investigated.

Such a result is consistent with the expectation that the highest gap state is formed by occupation of the LUMO, which for thiophene has a significant sulfur contribution.[3] It is also consistent with XPS and S_{L23} edge NEXAFS results that indicate that the charge transferred from the Cs is located on the sulfur sites.[6]

IV. SUMMARY

The modifications induced in the electronic structure of the valence band of bithiophene on Cs doping have been investigated both indirectly, with EELS, and direct-

ly, by UPS. With both spectroscopies, the formation of new states within the gap is observed with clear indication of two doping regimes. In EELS, with increasing Cs exposure, there is a bleaching out of the pristine molecule $\pi \rightarrow \pi^*$ transitions. Initially, two new low-energy excitations grow in the gap until, at high exposures, they transform to a single feature. This behavior is qualitatively similar to the optical-absorption results reported in the literature for acceptor doping of longer thiophene oligomers and can be related to a polaron- (anion)-to-bipolaronlike (dianion) transformation. The gap-state excitation energies obtained in this *n*-doping case are, however, different from those of *p*-doped bithiophene, indicating an asymmetry of the states within the gap. This latter result has implications for those attempting to interpret optically induced optical-absorption studies, as both hole and electron (bi)polarons are formed optically.

The UPS results presented are, to the authors' knowledge, the first direct observation of a polaron-to-bipolaron transformation. For initial Cs exposures, two states in the forbidden gap are observed with binding energies of 1.1 and 3.5 eV with respect to E_F; these grow in intensity and then are replaced, on increasing Cs concentration, by peaks at 2.1 and 4 eV. This evolution is fully consistent with the expectations for a polaron-to-bipolaron transformation, as expressed in Fig. 1, when the inherently localized nature of the model system is considered, whereby the poor screening afforded to the photoholes leads to an increase in the binding energies observed. While the Cs-bithiophene complex must be considered a model, the similarities of the excitation spectra to those of the longer systems suggest that similar behavior, albeit scaled to a reduced band gap, would be expected for the UPS spectra of the *n*-thiophenes of greater extent. Despite having observed the direct photoemission features of the gap states, the authors could not unambiguously assign the excitations involving these states as observed in the EELS spectra. Therefore, it is concluded that inferences made as to the positions of the gap states from indirect observations alone, such as is commonly done in optical-absorption studies, must be approached tentatively as final-state effects, such as electron-hole interactions, must be assumed to play an important role.

The orbital character of the bipolaron states were determined by consideration of their photoionization cross sections. The deeper level was concluded to have C 2*p*, while the very different photon-energy dependence of the shallower feature suggests it has considerable S 2*p* character. This implies that the charge transferred from the Cs resides around the S sites, and, given the relatively high electron affinity of S, the donor charge is expected to be localized at this site. As the importance of the carbon backbone to the conduction mechanism of the carbon-based conjugated polymers is considered paramount, this may suggest poor conduction for *n*-doped polythiophene. Indeed, there are as yet no reports of conduction in *n*-doped PT.

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