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Explicit evidence for bipolaron formation: Cs-doped biphenyl

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Thin condensed layers of biphenyl have been studied by ultraviolet photoelectron spectroscopy (UPS) and electron-energy-loss spectroscopy (EELS) as a function of Cs doping in order to model the situation in a doped conducting polymer. The UPS spectra show the growth of gap states which are assigned to bipolaron formation. This is the first direct observation of emission from states thought to be important for conduction in conducting polymers. While EELS also implies the formation of gap states their evolution with doping cannot be simply interpreted. The valence-band emissions clearly show shifts in the Fermi energy due to the bipolaron states and movements due to increased polarizability on the formation of the Cs-biphenyl complex.

Biphenyl can be considered as a model for *p*-polyphenylene (PPP) which belongs to the class of nondegenerate ground-state polymers that become conducting on "doping" either by acceptors or donors.[1] A great deal of effort has been focused on trying to understand the nature of the conducting mechanism in such systems. On the theoretical side the formation of gap states, due to charge-induced changes in the local molecular geometry, has been postulated.[2-5] To date the experimental evidence for these polaron-bipolaron states, such as indications of spinless conduction or transitions involving the gap states in optical absorption or electron energy loss on doped polymers, has been indirect. In this paper we present both ultraviolet photoelectron spectroscopy (UPS) and electron-energy-loss spectra (EELS) results for condensed biphenyl as a function of a Cs dose. In both spectroscopies features are observed which can be attributed to the formation of bipolaron states within the gap. In EELS transitions from these levels are clearly seen, but their behavior as a function of a Cs dose is difficult to assign unambiguously. In contrast UPS shows the formation and growth of the gap states directly, with energy positions in good agreement with those predicted for bipolarons in the calculations of alkali-metal doped quarterphenyl of Brédas *et al.*[3] UPS shows not only the predicted bipolaron states but also, on doping, initial energy shifts of the emissions from the deeper, essentially unaffected molecular orbitals, which are in line with a movement of the Fermi energy (E_F) from a midgap position to a position pinned by the induced gap states between the highest bipolaron level and the bottom of the conduction band.

A number of phenylene oligomers have been shown to form conducting complexes on doping with alkali metals.[6] Although biphenyl is the smallest of the phenyl oligomers it is known to adopt a quinoidlike geometry in the biphenyl–alkali-metal complexes and can be viewed as a model system for conducting PPP.[5] Experiments on such model systems have a number of advantages over those on the polymers themselves: Firstly they allow preparation *in situ,* which is desirable for alkali-metal doping and for surface sensitive techniques, secondly it makes it easier to adjust the doping levels, and thirdly such model systems better replicate the theoretical constrictions which, for computational ease, are performed on the smaller oligomers. As such, they afford a useful feedback for furthering theoretical developments and offer an aid to the interpretation of the necessarily more complicated polymer experiments.

To date there has been little in the way of UPS studies on the conducting polymers and what has been performed has been directed towards *p*-type doping.[7-9] These studies have not been particularly spectacular with the doping-induced effects being somewhat subtle and open to interpretation as the gap states are empty in the case of acceptor-doped bipolarons. Recently, a small density of states at E_F, along with a shift in E_F has been reported for saturation *p*-type-doped poly(3-methyl)thiophene which has been attributed to a reversion from bipolaron to polaron bands.[9]

Samples were prepared *in situ* in an ultrahigh-vacuum electron spectrometer (VG ADES 400) with facilities for angle-resolved UV photoelectron spectroscopy using a discharge lamp, low-energy electron diffraction (LEED), Auger spectroscopy, EELS, thermal desorption spectroscopy (TDS), and work-function measurements via the secondary-electron cutoff. The substrate was a Pd(110) surface which could be cooled to 80 K or heated resistively. Dosing of the biphenyl onto the substrate was carried out at 80 K with a molecular-beam doser and Cs doping was performed using a SAES getter source within a heated glass collimator.[10] Dosing was calibrated for biphenyl and Cs by TDS and work-function measurements respectively, and is quoted in terms of single molecular and atomic layers (ML) on the Pd(110) surface. Saturation of the biphenyl with Cs occurred at a ratio of one layer of Cs to two layers of biphenyl, which is approximately three Cs atoms per biphenyl molecule.

The TDS clearly indicated the formation of a biphenyl-Cs complex. Whether Cs multilayers were built up on biphenyl multilayers or vice versa, essentially identical TDS spectra were obtained with the Cs and biphenyl desorbing at the same temperature, 368 K, which is significantly higher than both pristine biphenyl, 218 K, and pristine Cs, 310 K, from this substrate. Even at 80 K diffusion of Cs into the biphenyl multilayer structure is indicated by UPS studies and complete mixing, without desorption, could be achieved by warming the substrate to 200 K. Spectra from such mixed layers were identical to that formed by sandwiching monolayers (ML) of biphenyl and Cs.

In Fig. 1 the He I ($h\nu = 21.2$ eV) spectra of ~4 layers of biphenyl are shown for increasing doses of Cs applied to the surface. The spectra have been aligned to E_F and indeed in this relatively thin layered structure the Pd substrate Fermi level is still evident, thus providing a good spectroscopic reference. The spectrum of the undoped condensed biphenyl is in very good agreement with that of the gas-phase molecule, for a detailed analysis of the pristine biphenyl UPS spectra and its relationship to the molecular geometry the reader is referred to Ref. 10, and references therein. The initial dose of 0.13 ML Cs (spectrum *b*) leads to a shift in the molecular orbitals to higher binding energy by an amount equivalent to the work-function change as measured from the secondary electron cutoff ($\Delta\phi = -1.47$ eV), and no new emissions are observed. At 0.25 ML Cs exposure (spectrum *c*) a further shift in the molecular orbitals, again equivalent to the work-function decrease, occurs. At this doping level the Cs $5p$ levels become evident and two new emissions in the gap between the highest occupied molecular orbitals (HOMO's) and E_F begin to appear. A further increase in the Cs dose to 0.38 ML leads to a growth in the Cs $5p$ and gap states, and the molecular emissions remain fixed in energy and become somewhat less well defined. Beyond this dosing level the Cs $5p$ and band-gap features grow in intensity with no shifts in energy position. However, in this 0.38–1 ML Cs doping region the deeper biphenyl orbitals (structures *B* and *C* in Fig. 1) undergo large shifts to lower binding energy which are not reflected by the small changes in work function. Spectra at a 1 ML dosing level (Fig. 1, spectrum *g*) can be considered as due to Cs saturated biphenyl within the probing depth of UPS; beyond this dose no changes in the spectra are observed until sharp Cs $5p$ emissions appear due to the formation of a metallic Cs surface layer (not shown). Saturation is defined as the dose of Cs beyond which metallic Cs $5p$ emission features are observed, even when the system is warmed to allow thorough mixing of Cs and biphenyl. The broad Cs $5p_{3/2}$ feature of Fig. 1 is typical of Cs in a dispersed state as is the lack of a Cs $O_{23}VV$ Auger signal in the region of 11 eV kinetic energy.

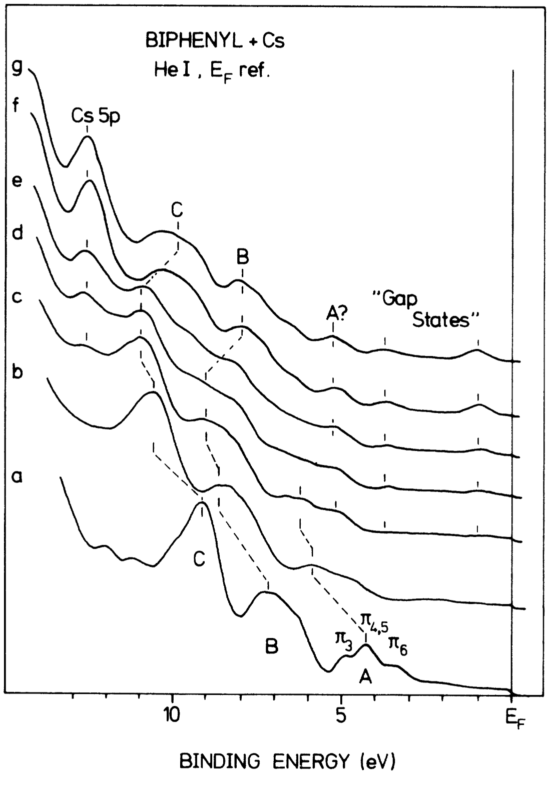

FIG. 1. He I ($h\nu = 21.2$ eV) UPS from ~4 layers of biphenyl on a Pd substrate for increasing amounts of Cs applied to the surface: spectrum *a*, 4 monolayers (ML) biphenyl (work function $\Phi = 3.9$ eV); spectrum *b*, +0.13 ML Cs ($\Delta\Phi = -1.47$ eV); spectrum *c*, +0.25 ML Cs ($\Delta\Phi = -1.78$ eV); spectrum *d*, +0.38 ML Cs ($\Delta\Phi = -1.89$ eV); spectrum *e*, +0.5 ML Cs ($\Delta\Phi = -1.89$ eV); spectrum *f*, +0.75 ML Cs ($\Delta\Phi = -2.06$ eV); spectrum *g*, +1 ML Cs ($\Delta\Phi = -2.14$ eV).

Of major importance in the UPS results are the appearance of the gap states. The gap states cannot be directly assigned to emission from the Cs $6s$ levels. With He I radiation the cross section for the alkali-metal *s* levels is very low. The intensity of the $6s$ emission observed for the metallic Cs layers is approximately 1 order of magnitude lower than that for the gap states observed here. This clearly indicates that Cs has donated its valence electron on forming the complex. On donation to the π^* orbitals the *s* electron loses its *s* character and its cross section is greatly enhanced. The gap state at 1 eV below E_F is assigned, in the spirit of Brédas *et al.*,[4,5] to the lowest unoccupied molecular orbital (LUMO π_7) stabilized by geometric relaxation and filled by electron donation from Cs, while the 3.7 eV peak is the destabilized HOMO (π_6). The results here are in good agreement with bipolaron predictions of Brédas *et al.*[4] for alkali-metal doped quarterphenyl. The calculated bipolaron separation (2.65 eV), bipolaron to nonbonding π separation (2.2 eV), and bipolaron bandwidths (0.55 eV) compare favorably with the experimental results of 2.7, 2.5, and 0.6–0.7 eV, respectively. These results are to our knowledge the first direct observations of the levels thought to be critical in the conduction of doped organic polymers.

The formation of bipolaron states in the gap should lead to a substantial movement of the Fermi level with respect to the vacuum level. This is reflected experimentally by changes in the work function and changes in the binding energy of the deeper orbitals with respect to the Fermi level. Such an effect, and its significance to the interpretation of x-ray photoemission spectroscopy (XPS) data, has been recognized recently in a *p*-type-doped system.[9] This result is clearly shown in the initial doping of the biphenyl where bands *B* and *C* shift to higher binding energy by an amount equal to the work-function change (note the movement is in the opposite direction to *p*-type-doped systems where bipolaron bands are empty). Bipolaron bands are predicted to be roughly symmetrically placed in the gap, and the midgap is therefore placed between the bipolaron states.[3] As can be seen in Fig. 2, which is a close-up of Fig. 1, the midgap position is at a binding energy equivalent to the work-function change and thus doping has led to a change in E_F from a roughly midgap position to one between the upper bipolaron and the conduction band. It should be noted that the feature observed at low Cs doses at a binding energy of 2.4 eV and the density of states at the Fermi level are due to emissions from the Pd substrate and are not seen in experiments performed on thicker layers.

A second significant energy shift is observed near saturation doping for the deeper orbitals which is not related to any change in the gap states or movement in the Fermi-level position. This $\simeq 1.2$ eV shift to lower binding energy of bands *B* and *C* at near Cs saturation can be associated with relaxation due to electronic screening. Such a large shift reflects a large increase in the polarizability of the Cs-biphenyl complex relative to the biphenyl molecule. This is in agreement with the recent calculations of Brédas *et al.*[11] which have shown that donor doping of aromatic polymers (and oligomers) should result in marked increases in the polarizability with this change being due, in roughly equal proportions, to the geometric modification and charge transfer on doping. A corollary of this result is that it would be expected that on acceptor doping the change in polarizability would be much less due to the removal of polarizable π electrons. In the photoemission studies of *p*-type-doped systems this is apparently the case. No electronic relaxation has been suggested;[7-9] however, one must be cautious since relaxation will lead to energy shifts in the same direction as those arising from shifts in E_F for *p*-type-doped systems.

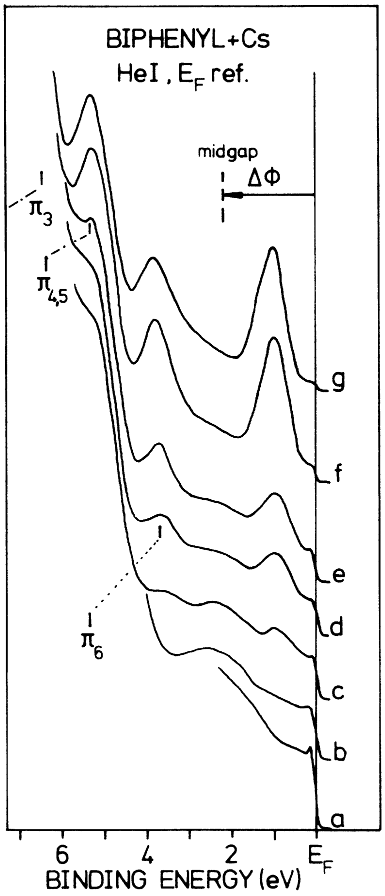

FIG. 2. The region of the gap states of Fig. 1 in a greater magnification.

It is generally considered that, apart from the HOMO and LUMO, the molecular orbitals are not strongly modified on doping.[5] Indeed this is essentially the case for bands *C* and *B*; however, this is clearly not the case for the π orbitals of band *A* for doping higher than that of spectrum *c* of Fig. 1. The LUMO (π_6) is destablized and forms the gap state at 3.7 eV. In Fig. 2 it is clear that at its prior position of 5.4 eV the shoulder becomes a peak at high doping. This peak is assigned to the nonbonding ($\pi_{4,5}$) biphenyl orbitals whose emission is observed at a lower binding energy due to electronic relaxation similar to that of bands *B* and *C* at higher doping. The higher binding-energy bonding orbital (π_3) of band *A* in biphenyl is known to be sensitive to molecular geometry.[10] It is suggested that this orbital's binding energy increases relative to the nonbonding $\pi_{4,5}$ orbital due to increased interring interaction with its emission appearing as a shoulder between bands *A* and *B* at 6.5 eV (Figs. 1 and 2). This would be in accord with the decrease in the interring bond length on adoption of the quinoidlike structure.

In Fig. 3 a similar dosing series to that of the UPS spectra of Figs. 1 and 2 is shown for the reflection electron-energy-loss spectra. The series was taken for a primary energy of 20 eV with a resolution of 0.3 eV. This low primary energy has the advantages of reducing damage, minimizing features due to the Pd substrate, and providing a set of spectra with a similar sampling depth to that of the UPS spectra. The pristine biphenyl loss spectra show features at 4.6, 6.0, and 7.3 eV which can be directly related to the optical absorption spectra of biphenyl[12] and

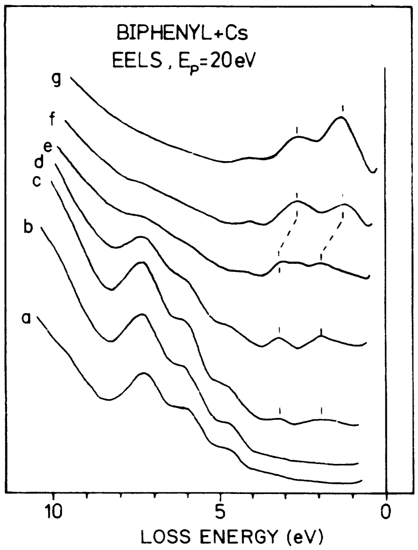

FIG. 3. Electron-energy-loss spectra (primary energy $E_p = 20$ eV) for ~4 layers of biphenyl with increasing doses of Cs; spectra *a*–*g* as for Fig. 1.

are not dissimilar to the transmission EELS results of PPP;[13,14] these can be attributed to $\pi \rightarrow \pi^*$ transitions. Initial doping leads to the appearance and growth of losses at 3.2 and 1.9 eV loss energy, which involve excitations of the gap states. Higher doping levels up to Cs saturation results in an almost total suppression of the $\pi \rightarrow \pi^*$ excitations, the appearance of a weak feature at 4 eV and an apparently rigid shift in the gap state losses by 0.6 eV to lower loss energy. The 4 eV loss is presumably the band-gap transition similar to that seen in transmission EELS of *n*-type-doped PPP.[14] The transition from initial to saturation doped spectra has the same onset as that for the UPS spectra (cf. spectra *e* of Figs. 1 and 3).

A more detailed analysis of the loss spectra is beyond the scope of this paper but a comparison of the observation of gap states by direct (UPS) and indirect (EELS) means is of particular significance. In both methods we see the appearance of the gap states, but in the direct measurement changes are observed with doping which could easily be misinterpreted as being due to changes in the gap states themselves. The UPS results, however, show no concomitant changes in the bipolaron levels. The rigid shift to lower loss energy ($\Delta E = -0.6$ eV) at high doping levels is difficult to rationalize with the present theoretical understanding of the electronic structure on doping. An explanation in terms of a lowering in the conduction band is ruled out as this would lead to a shift in E_F which, in turn, would result in lowering of the gap states binding energy of $\simeq 0.3$ eV, which is not observed in UPS. The shift in the EELS of the bipolaron excitations coincides with the electronic relaxation of the biphenyl orbital emissions in UPS. However, an increased screening ability with doping would result in an increase in the loss energy due to a decrease in electron-hole interaction. UPS clearly shows no shift in the initial state and the losses must therefore suggest a shift toward E_F of the final states or even a possible change to final states of the excitation involving the empty dopant levels.

In summary, UPS spectra have been presented which directly show emissions from bipolaron states in a doped organic system. Not only has the evolution of these states with dose been followed, but also energy shifts in the deeper levels which indicate, firstly, the shift of the Fermi energy by the bipolaron states, and secondly, electronic screening due to the increased polarizability of the complex formed. The results are in good agreement with theoretical predictions. EELS spectra for a similar dosing series to that of the UPS display excitations from the gap states. The changes with doping indicate that final-state effects strongly influence the excitation results and therefore such indirect observations cannot simply be related to the gap states alone.

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