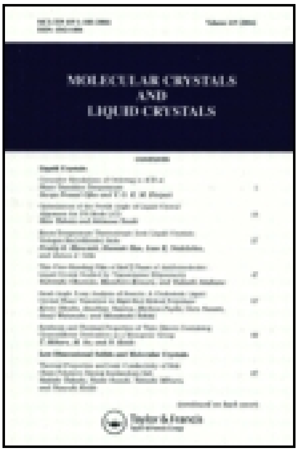

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THE ELECTRONIC STRUCTURE OF ALKALI DOPED ULTRA THIN SEXIPHENYL FILMS

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Abstract: The formation and evolution of the gap states formed with increasing Cs concentration in thin 6P films are followed with ultraviolet photoemission spectroscopy (UPS) and indirectly with energy loss spectroscopy involving electronic transitions (EELS). Two distinct doping regimes are apparent, in the lower doping regime bipolaron-like (dianionic) states are formed 0.8 and 2.9 eV above the valence band maxima. In the higher doping regime, approaching Cs saturation, a 0.5 eV splitting in the gap states is observed which is attributed to interacting bipolaron states, and as such is a precursor to bipolaron band formation.

INTRODUCTION

In the last few years there has been a growing interest in the oligomers of the conducting polymers. This has been fuelled by the need for well defined systems as experimental models to express the features of the ill characterised polymers. Also they have an intrinsic interest since the discovery that the oligomers can perform as well as, if not better than, their associated polymers in devices such as FETs and light emitting diodes[1,2]. The principal tool for studying the electronic structure of these materials is traditionally optical absorption spectroscopy where upon doping (n- or p-) excitations are observed within the band gap which are specific to the oligomer species (length and charge) but independent of dopant material[3,4]. Whilst the excitations observed clearly indicate that states are created within the gap on doping the exact nature of the excitations observed is still open to question. Ultra-violet photoemission spectroscopy (UPS) provides a more direct means of probing valence band (orbitals) and, in the case of n-doped materials, allows one to observe the states created and their evolution on doping as has been demonstrated for biphenyl[5], bithiophene[6] and a number of polyene molecules[7,8] on alkali metal doping.

p-Sexiphenyl (6P) provides a good model for polyparaphenylene (PPP) as it is long enough to support polarons and bipolarons thought to be important for the conduction mechanism in PPP. Indeed 6P has been shown to be conducting on alkali metal doping[9]. In this contribution we investigate 6P as a function of increasing alkali metal exposure following the electronic structure indirectly with electron loss spectroscopy and directly with UPS.

EXPERIMENTAL

The experiments were performed in a VG ADES 400 spectrometer containing facilities for angle-resolved UV photoelectron spectroscopy (ARUPS) using a He discharge lamp, electron energy loss spectroscopy (EELS) of the electronic levels with a resolution of 0.3eV, thermal desorption mass spectroscopy (TDS) and work function (ϕ) measurements via the secondary electron cut off in UPS. The electron spectroscopies used are extremely surface sensitive consequently the vacuum conditions are stringent and in the results presented here ultra high vacuum conditions ($<8\times10^{-10}$ mbar) were maintained even during the in situ evaporation of 6P. The thin 6P films were produced by evaporation in situ onto a Ni(110) substrate that could be cooled to 77K or resistively heated. The rate of evaporation was controlled with a quartz oscillator with rates of 0.03 monolayers per second typically used. The purity of the 6P was monitored with a mass spectrometer in line of site of the evaporator and by its characteristic π band in the UPS spectra. Cs was evaporated from an SAES getter source. Details of the experimental set-up and molecular evaporator can be found elsewhere [10]. In the following Cs exposures are expressed as a percentage of that required to saturate the 6P films with Cs i.e. the value beyond which no changes were observed by any of the spectroscopies. It should be noted that metallic Cs desorbs at room temperature and Cs diffuses through 6P films even at 77K.

RESULTS

EELS

In figure 1 a series of electron energy loss spectra (EELS) for a 13 monolayer thick 6P film for increasing exposure to Cs at room temperature is displayed . A low primary electron energy of 20eV has been used to minimise electron beam induced damage and to provide a surface sensitivity the same as for the UPS spectra. Also, as can be seen in the bottom spectrum, at this primary energy no significant features are introduced by the Ni substrate. EELS provides analogous information to optical absorption spectroscopy although strictly for such low incident electron energies non-dipole transitions can also be excited. The spectrum of pristine 6P is very similar to the transmission EELS results of Fink et al.[11] for PPP showing two main features at approximately 7 and 4 eV associated with π–π* transitions from the localised and delocalised π orbitals. The adsorption edge of 3 eV is also in agreement with the optical absorption results for 6P[12]. On initial exposures to Cs a single broad peak at 1.3 eV appears. With increasing exposure this feature grows in intensity at the expense of the neutral π–π* transitions and shifts slightly to higher energy settling at 1.6 eV. By an exposure of 50% the excitations of the neutral 6P are almost completely bleached out. Further exposure results in an increase in intensity to the high energy side of the now dominant mid-gap peak and the formation of a shoulder at about the former band edge. The appearance of a single excitation feature through the whole doping range suggests only one ionic species is formed predominantly.

Recent optical absorption studies of various oligomers containing aromatic rings suggest that the absorption finger print of the anions (cations) are two peaks roughly symmetrically placed within the gap whilst the di-anions (di-cations) are characterised by a single broad and intense peak at around mid-gap[3,4,13]. Consequently one would infer

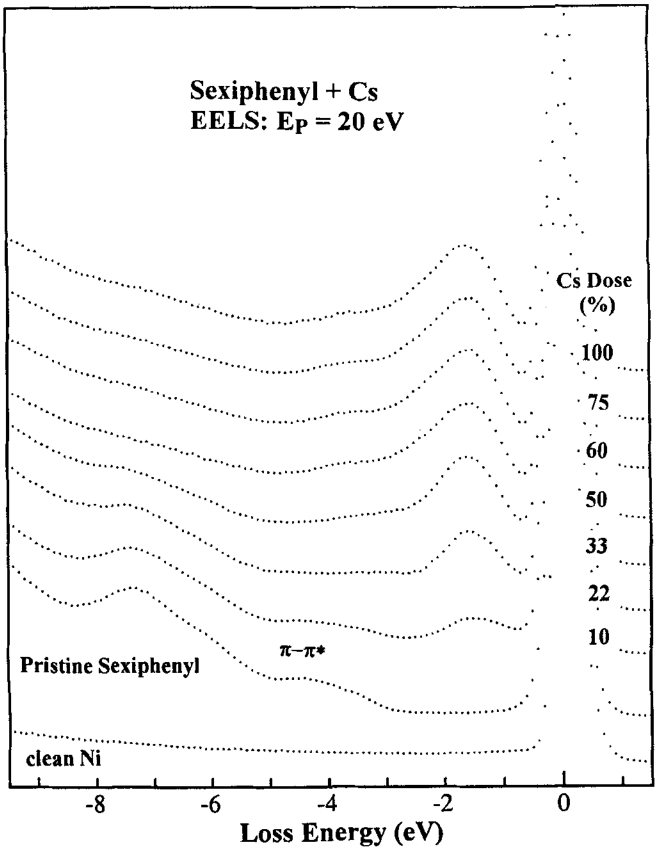

FIGURE 1: EELS spectra of 13 monolayers of sexiphenyl on exposure to Cs at room temperature.

from the results of figure 1 that dianion species predominate; even at low exposures where the π–π* transitions of the neutral molecule are dominant only a single broad excitation is evident. Exhaustive attempts to no avail were made to duplicate the optical absorption results of Furukawa et al. which show two peaks at 2.2 and 0.8 eV for Na doped 6P in solution[4]. It should be noted however that the mono-ionic fingerprint has been observed for both bithiophene and biphenyl at low Cs exposures in similar EELS experiments to that presented here[5,6]. The loss energy at low Cs exposures of 1.3 eV is in reasonable agreement to the 1.1 eV obtained by Furukawa et al. for highly Na doped 6P in solution[4] and the 1.25 eV for p-doped (AsF_5) 6P[12], both of which have been attributed to bipolaron states. On the other hand the shift to 1.6eV and the strong asymmetry induced at higher doping levels has, to the authors knowledge, no counterpart in optical absorption studies of the oligomers. Suggestions of such behaviour, however, can be found in Fink et al.'s transmission EELS results of PPP at high (50 monomer %) n-doping levels[11].

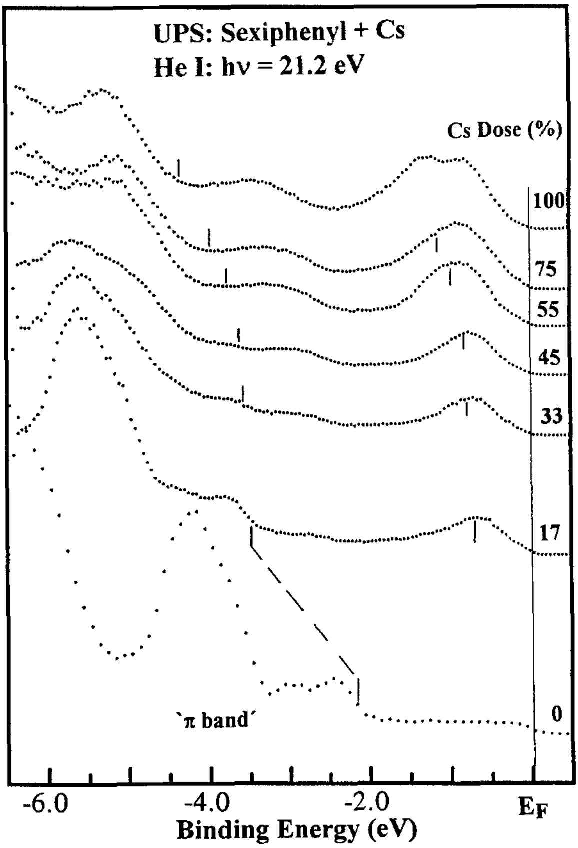

Figure 2: UPS spectra of 10 monolayers of sexiphenyl on increasing exposure to Cs. Tick marks indicate positions of constant binding energy w.r.t. the vacuum level.

UPS

Figure 2 displays the UPS spectral series in the region of the highest lying π band and band gap for increasing Cs exposure. The natural reference level for solid state UPS is the spectroscopic Fermi energy as the sample and spectrometer are in thermodynamic equilibrium. It is possible to reference the spectra to the vacuum level by adjusting the energy by the work function as determined from the secondary electron cut-off of the photoemission spectra. This must be done circumspectly as it is only appropriate (useful) when the change in work functions are due to shifts in the Fermi energy within the band gap, as for instance on creating gap states. If the change in ϕ contains significant surface effect, for instance a surface dipole layer, adjusting the spectra by $\Delta\phi$ would be very misleading. Careful analysis of our data suggests that the latter occurs on higher exposures and as a consequence we have displayed the spectra as obtained, i.e. with an E_F reference; indeed the Fermi level of the underlying Ni substrate can be discerned in figure 2. In going from the neutral molecule to the Cs saturated system ϕ decreases from 4.3 to 2 eV. The changes in ϕ are indicated by the tick marks on the figure, which therefore show positions of equal binding energy with respect to the vacuum level.

Initial exposures to Cs induces a large decrease in the work function which is reflected by equivalent shifts in all molecular orbital emissions to higher binding energy w.r.t. E_F. This is due to a repositioning of E_F arising from the creation of gap states on the charge transfer from Cs to the 6P LUMO. The latter is seen as an orbital emission appearing initially at 0.6 eV below E_F. Despite shifting and loss of intensity the distinctive UPS line shape of the neutral molecule is clearly retained up to 33% exposure. Additional features are also observed to grow at 0.6 and 2.7 eV w.r.t. E_F (2.9 and 0.8 eV above the valence band edge respectively). For exposures above this level distinct but different changes in both the gap state features and the molecular orbital emissions are observed. The latter undergo a rigid shift of 0.5 eV to lower binding energy. This is due to enhanced final state relaxation, a spectroscopic effect due to an improvement in the screening of the photo holes on formation of the charge transfer complex. This shift is completed at ≈60% exposure, well before the 6P film is saturated with Cs. The evolution of the 2.7 eV feature cannot be followed clearly as it merges with the shifted valence band edge. The behaviour of the shallow gap state is particularly intriguing. This feature shifts with the work function change (i.e. remains at constant binding energy w.r.t. the vacuum level) and reaches its maximum intensity at around 50% exposure. Beyond this level a second emission grows at 0.5 eV higher binding energy. At saturation this new peak has the same intensity as the original state and we are left with a partially overlapping doublet structure at 0.8 and 1.3 eV w.r.t. E_F. Of particular significance is the fact that the original charge transfer state does not lose intensity to the second state.

DISCUSSION

Work function measurements, thermal desorption mass spectroscopy (not shown), EELS and UPS results all indicate two doping regimes for 6P films with the breakpoint at around 50% of saturation doping. Up to 50% the EELS shows a single broad excitation at 1.3-1.6 eV while in the UPS two states develop in the gap at 0.6 and 2.7 eV. In the spirit of the interpretation of optical absorption studies the EELS indicates the formation of a dianionic species with the excitation being associated with transitions from the now doubly occupied ex-LUMO (upper bipolaron state) to the conduction band. The position of the ex-LUMO at 0.6-0.8 eV w.r.t. E_F in UPS is not incompatible with this interpretation. The observed energy positions with respect to the valence band edge for the two doping induced gap states are in agreement with the energies for the bipolaron states predicted by Bredas et al [14,15]. In this lower doping region the excitation finger print of EELS and the lack of a density of states at E_F in the UPS both suggest that the anionic (polaron) state is not formed.

The transition from the low doping to high doping regime cannot be interpreted as a polaron (anion) to bipolaron (dianion) transition. Such a transition has been observed in bithiophene on increasing doping with Cs [6] where the EELS showed the appropriate change in the excitation fingerprint and UPS showed the two gap states moving closer together, with the lowest gap state evolving to a peak at higher binding energy than that of the lower doping regime and with twice its intensity in agreement with expectations[6]. In contrast, in the present results the upper gap state clearly forms a doublet. This result is not due to incomplete doping as identical UPS spectra result if sub-monolayer exposures of 6P are applied to a metallic Cs surface[10]. A possible explanation for such behaviour is the interaction of bipolaron states where the doublet is interpreted as a bonding and anti-bonding combination. The resulting splitting of states would also explain the shifting and broadening in the EELS data and account (at least partially) for the changes in work function in the high doping regime. The result can thus be viewed as the precursor to bipolaron band formation. It can be imagined that this interaction is either between states of neighbouring 6P dianions or interactions between bipolaron states on the same 6P chains. The authors favour the latter as (i) the dimers condensed biphenyl and bithiophene do not show this splitting or work function changes in the high doping regime,(ii) sub-monolayer coverages of 6P on metallic Cs do show the splitting, and (iii) estimates suggest that the doping level at saturation is >100 monomer %, more than adequate to inject four electrons into the molecule.

Acknowledgements
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