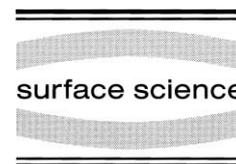




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The influence of the counterion on the electronic structure in doped phenylene-based materials

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Abstract

The mechanisms of charge storage and transport in doped conjugated organic materials are a topic of interest in both fundamental and application-oriented research. We investigated the valence electronic structure of n-doped *p*-sexiphenyl (6P), a model molecule for the electroluminescent polymer poly(*p*-phenylene). Different alkali metals and an alkaline earth metal were deposited stepwise in situ on thin films of 6P. After each step ultraviolet photoemission spectra were recorded using synchrotron radiation. The evolution of characteristic new features within the formerly empty energy gap of 6P was observed. We conclude from our observations that negative bipolarons (dianions) are the only charged species on a 6P surface. However, the lineshape and energetic positions of the new intragap features varied for each dopant used. By comparing the experimental data with quantum-mechanical calculations on model systems, we discuss the mechanisms that could explain this phenomenon. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Conjugated organic materials exhibit properties that make them very attractive for both fundamental physical investigations and application-oriented research. Such properties include electrical conductivity [1,2] and photo- or electroluminescence [3–7]. Especially in the context of the application of organic materials in devices, the nature of charge

storage and transport is of paramount importance. Many attempts to elucidate this issue have been undertaken by studying the changes in the valence electronic structure of conjugated systems as a function of doping using photoelectron spectroscopy [8–11]. Possible changes in the electronic structure upon in situ deposition of alkali or alkaline earth metals include the formation of negative polarons (anions) or negative bipolarons (dianions). The origin of these new electronic states is the filling of the former lowest unoccupied molecular orbital (LUMO) with one (polaron) or two (bipolaron) electrons. The so-formed new

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highest occupied molecular orbital (HOMO) is located energetically within the energy gap of the pristine molecule. Furthermore, also the HOMO-1 (the HOMO in the pristine molecule) can be found within the former energy gap. It must be anticipated that the binding energy of these new states is not independent of the dopant applied. However, very little effort has been made to gain a deeper insight into the role of the counterion in doped organic materials. To redress that situation, we have doped one organic system with different low-work-function metals. *Para*-sexiphenyl (6P) was chosen for our studies, as it has a huge potential for application in organic light-emitting devices [7,12,13]. We deposited potassium, caesium and calcium under ultrahigh vacuum conditions on thin films of 6P and followed the changes in the valence electronic structure by ultraviolet photoelectron spectroscopy (UPS). For a better understanding of the experimental data, quantum-mechanical calculations were performed on model systems that included the presence of counterions.

2. Experimental

UPS measurements were performed at the FLIPPER II experimental set-up in HASYLAB, Hamburg. In this multi-chamber system all sample preparation steps were done in situ, and ultrahigh vacuum conditions were sustained during transfers between the preparation and analysis chambers [14]. After careful outgassing, 6P (purchased from Tokyo Chemical Ind. Co. Ltd) was evaporated from a pinhole source on to stainless steel and gold substrates at a pressure lower than 10^{-8} mbar. The film thickness (200 Å to 500 Å) was monitored with a quartz microbalance. Alkali metals were deposited in carefully timed steps from SAES S.p.A. dispenser sources, and calcium from a Knudsen-type cell, the pressure being below 5×10^{-9} mbar during evaporation. The thickness of the calcium film was monitored with a quartz microbalance. The base pressure of the system and during data acquisition was 2×10^{-10} mbar. In order to maximize the photoelectron cross-section for the π -electron-derived molecular orbitals of 6P, a photon energy of 32 eV was chosen [15].

3. Theoretical methodology

For the calculations terphenyl (3P) was chosen, as we consider it a good compromise between reasonable modelling of a conjugated oligomer and manageable computational effort. The calculations were performed using the Dmol density-functional theory (DFT) package [16,17]. We chose a high-quality numerical basis set (double numeric plus polarization, DNP) and the Vosko–Wilk–Nusair expression [18] for the local correlation potential, together with the Slater local exchange functional.

4. Results and discussion

For each dopant used, the UPS spectrum of the pristine film was practically identical to previously reported spectra of 6P [15]. The alkali or alkaline earth metal was evaporated in increasing small steps until no further change in the UPS spectrum was observed, or, in the case of calcium, a metallic overlayer was formed. As reported elsewhere [19], we observed the evolution of new occupied electronic states in the formerly empty energy gap of 6P. The lineshape of these new emissions did not change throughout all doping levels. For the completely doped samples (i.e., no further change in the spectrum for longer exposure to the dopant flux), the Fermi level is located above any occupied electronic states. In accordance with earlier published results [8,9,11] we conclude that negative bipolarons are formed in 6P upon the deposition of potassium, caesium and calcium. The new approach in this work is to compare the energy positions and lineshapes of these doping-induced intragap states as a function of the dopant, i.e., the counterion.

In order to compare the properties of the intragap emissions induced by the deposition of potassium, caesium and calcium, they are plotted in Fig. 1 aligned to the maximum of the emission with lowest binding energy. The zero energy in this plot is chosen arbitrarily. These three spectra correspond to approximately complete doping of the sample, as judged from the relative intensities of the doping-induced peaks. While the low-bind-

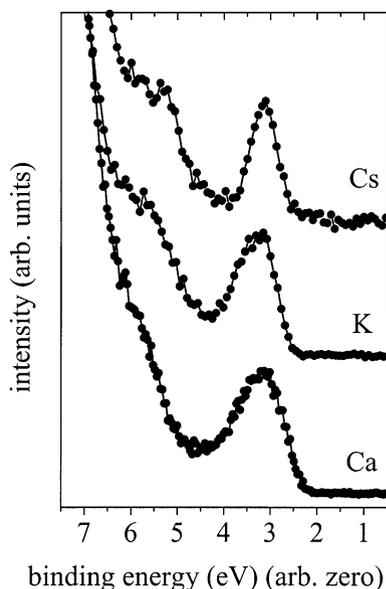


Fig. 1. UPS spectra of the doping-induced intragap states in 6P; dopant as indicated.

ing-energy peak (the new HOMO) observed for caesium doping is very sharp and symmetric, this feature is less defined for potassium and calcium deposition, and exhibits a pronounced asymmetric broadening towards higher binding energy. The second new feature (now the HOMO-1) in these spectra is clearly resolved for caesium doping (at about 5.3 eV on this energy scale). For potassium it still can be recognized, but its separation to the maximum of the HOMO is increased. The same is true for calcium; however, this second new emission is even less apparent in that case. The differences in the photoemission spectra of 6P doped with potassium, caesium and calcium imply that the counterion plays an important role in determining the electronic structure of the charge-transfer complex formed. In order to gain better insight into the origin of the experimentally observed dependence of the valence electronic structure on the dopant, we have performed quantum-mechanical calculations on model systems.

The 6P films that we used must be considered as polycrystalline with many stacking faults and grain boundaries [20]. The metals used in our studies exhibit diffusion on the 6P surface and into the bulk [19,21], but the diffusion coefficients

might vary. Therefore it is reasonable to assume that there might exist a variety of different 6P/metal atom geometries in a sample. This approach was pursued by calculating optimized equilibrium geometries of Ca/3P complexes with different starting geometries. The Ca/3P complexes thus obtained are shown in Fig. 2A–C. For configuration A the calcium atom was placed near the central phenyl ring of 3P in the starting geometry. After optimization it is also located there. This central ring appears strongly distorted, whereas the outer rings are only slightly affected. However, an analysis of linear combination of atomic orbital (LCAO) coefficients shows that the HOMO is delocalized over both the 3P molecule and the calcium atom. This is reflected by an analysis of the Mulliken atomic charges, which implies that

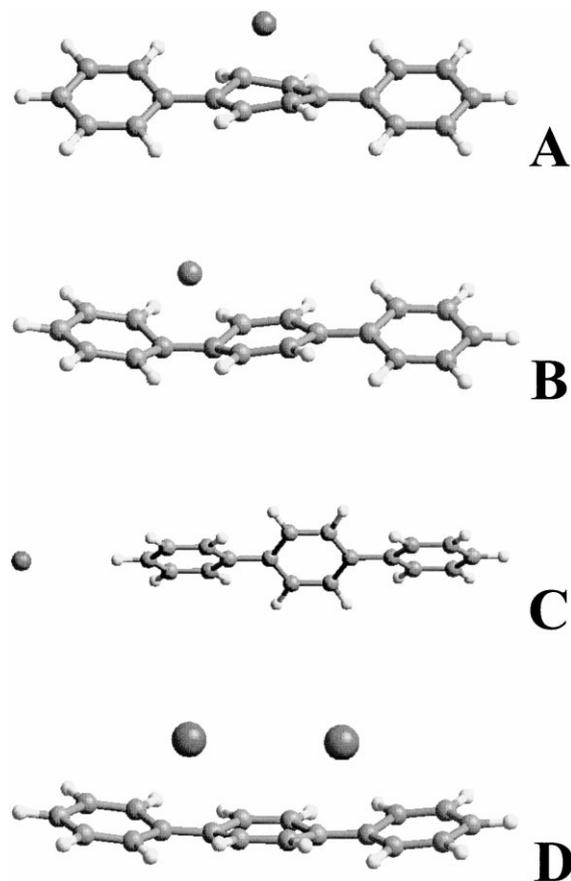


Fig. 2. Optimized equilibrium geometries of 3P/metal complexes, as discussed in the text.

the calcium atom is only partially charged and has not donated both of its 4s electrons. From the total energy point of view, complex B appears to be the most stable one. There, the calcium atom is located above the inter-ring bond between two phenyl rings. Again, a strong geometrical distortion of the 3P molecule is only observed in the vicinity of the calcium atom. The HOMO is delocalized over the whole complex. As for conformation A, there is only partial charge transfer from the calcium atom to the organic molecule. For A and B the closest Ca–C bonds are between 2.342 Å and 2.410 Å. Configuration C can be considered as the ‘non-interacting’ one. The calcium atom almost does not affect the geometry of the 3P molecule. The smallest Ca–C distance here is 4.442 Å. No interaction between metal and molecule is expected in this case. This is supported by the fact that the inter-ring torsional angles of 23.4° and 23.3° are very reminiscent of those in the pristine 3P molecule. Additionally, the HOMO of this complex C is localized on the calcium atom. For comparison, we present results on a complex of 3P and two potassium atoms (D), which would also allow the formation of a ‘bipolaron’. The potassium atoms are located above the two inter-ring bonds. The energy eigenvalues of HOMO and HOMO-1 of this complex are listed in Table 1, Δ being the energy separation between these two orbitals, as well as the corresponding values for complexes A and B. The eigenvalues are given as obtained from the calculation, and are not corrected for any solid-state effects. From a comparison of these values we can conclude a strong influence of the position of the counterion on the energetic positions of the energy levels and on the overall electronic properties in doped organic systems. For instance, the energies of the HOMO-1 in A and B are quite similar, whereas there is a

significant offset in the HOMO positions. Given a certain distribution of various organic molecule/metal atom geometries in our experiments, this could explain why, in the case of Ca/6P and K/6P, the low-binding-energy emission is not one sharp peak, but a broad asymmetric one. This implies that, in a well-ordered organic film with a homogeneous distribution of dopant atoms, this asymmetry should vanish. Indeed, in the case of Cs/6P, we observed the new HOMO as one single sharp symmetric peak. However, another reason for the well-defined emission for caesium doping might be that in this system not only a partial charge transfer occurs, but a complete one. This could mean that, for this system, the position of the counterions relative to the organic molecule is not as crucial as in the other systems.

5. Conclusion

We have compared photoemission data from thin 6P films that were doped with potassium, caesium and calcium with results from quantum-mechanical calculations on model systems. In the experiments a strong dependence of the lineshape of the doping-induced intragap states on the individual dopant was found. Calculations on complexes of the model molecule 3P with calcium and potassium show that not only the type of dopant, but also to a large extent the geometry of the complex can strongly modify its electronic structure. These findings imply that the peak asymmetry found in the photoemission experiments may originate from the presence of different molecule/counterion geometries in the samples.

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Table 1
Energy eigenvalues of the highest occupied molecular orbitals of the complexes from Fig. 2, and their separation Δ

System	HOMO (eV)	HOMO-1 (eV)	Δ (eV)
A 3P/Ca	3.14	5.55	2.41
B 3P/Ca	3.42	5.49	2.07
D 3P/2K	2.82	5.16	2.34

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