

## The electronic structure of adsorbed aromatic molecules: Perylene and PTCDA on Si(111) and Ag(111)

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The electronic structure of valence orbitals of adsorbed big organic molecules has been studied by means of UV photoemission and calculations using various semiempirical methods. The aromatic molecules perylene and its derivative PTCDA (perylene-tetracarboxylic dianhydride) have been adsorbed as oriented mono- and multilayers on two different, well-defined surfaces, Si(111) and Ag(111).

### 1. Introduction

The present study is part of an extended investigation of the electronic, geometric, and kinetic properties of various organic materials as adsorbates and thin films on different surfaces. Such adsorbates serve as model systems for a basic understanding of organic/inorganic interfaces which play an important role for several applications, for instance in the field of molecular electronics. As an interesting example, PTCDA (perylene-tetracarboxylic dianhydride) has been chosen since it is a stable, plane and highly symmetric aromatic molecule (see inset in fig.1) with potentially useful electric properties [1]. It can easily be processed and grows epitaxially on some surfaces under certain conditions [2]. In order to elucidate the influence of the reactive anhydride groups of PTCDA on the bonding properties we also studied perylene for comparison which is the kernel

of PTCDA and a pure aromatic molecule without functional groups. For comparison, we also investigated two different substrates, Si(111) as reactive semiconductor surface and Ag(111) as relatively inert metal surface. Other results of our investigations on these systems using photoemission (XPS, UPS), TPD, and NEXAFS are and will be published elsewhere [3-6].

Here we concentrate on one particular aspect, the study of the valence structure of PTCDA and perylene by means of angle- and polarization-resolved UV photoemission (ARUPS) and of ad hoc calculations. The aim is to get more information about the rather complicated multi-orbital valence spectra such that they can be interpreted in more detail and utilized for a further understanding and control of the interface. It turns out that for this purpose a comparison of experiments and calculations is inevitable, and that the results of different approaches must be taken into account.

## 2. Technical aspects

The experiments were performed in UHV chambers comprising normal surface science equipment. The perylene and PTCDA spectra on Si(111) were taken using polarized synchrotron radiation (TGM1 at BESSY, Berlin) and a rotatable 180° spherical sector analyser (VSW) for angle-resolved ( $\pm 2^\circ$ ) measurements. The PTCDA/Ag(111) data were recorded with a laboratory source (HeI) employing a fixed analyser (VG ESCALAB MkII) with minor angular resolution ( $\pm 8^\circ$ ). After cleaning and characterizing the substrates adsorbate layers were deposited by vacuum sublimation from Knudsen cells; the coverages were controlled by a quadrupole mass spectrometer or by a quartz oscillator and calibrated by XPS, TPD and/or NEXAFS measurements. More details are given elsewhere [4-6].

Calculations were made for both molecules and for different geometries. The geometrical parameters (bond lengths, angles) were taken (a) from x-ray structure data of single crystals [7], (b) from geometry optimization calculations using different approaches (MNDO, PM3 from MOPAC [8]), and (c) from the bond lengths of benzene. The comparison of different geometries appeared necessary as the parameters from crystals may not be representative for an adsorbate or thin film as the interaction of the reactive anhydride groups leads to significant distortion of the PTCDA molecules in a crystal [7].

As calculational methods we employed both ab-initio and semiempirical methods. Since our molecules are relatively large (requiring simple calculations), and since subtle differences may play

an important role we compared the results of various approaches (double-zeta ab-initio, CNDO/S, INDO/S, MNDO, PM3). Details of the calculations and comparisons will be given elsewhere [9]; here we concentrate on the results of the semiempirical PM3 calculations as with these the most extensive data set was obtained, and as these yielded the best agreement with experiment.

## 3. Results and discussion

In fig.1 ARUPS spectra from three different adsorbate layers on Si(111) are compared, a perylene multi-, a PTCDA mono- and a PTCDA multilayer. For each adsorbate the results of two different measurement geometries are displayed representing s- and p-polarization, respectively. Together with normal electron emission ( $\theta \approx 0^\circ$ ) this choice of parameters offers the application of selection rules provided that the molecules are adsorbed in a preferential orientation of high symmetry. Indeed one observes a strong polarization dependence of some of the peaks in fig.1, for instance of peaks 1 and 3, and in particular of peak 2. This observation clearly indicates that the peak with strongest angular dependence (peak 2) represents (at least partly) a  $\pi$ -orbital with high symmetry ( $B_{1u}$  for the  $D_{2h}$  point group), and that the molecules are preferentially **oriented parallel** to the surface in the mono- and in the multilayer. However, the question whether the non-vanishing intensity for s-polarization is due to some disorder or to a contribution of orbitals of other symmetry cannot unambiguously be

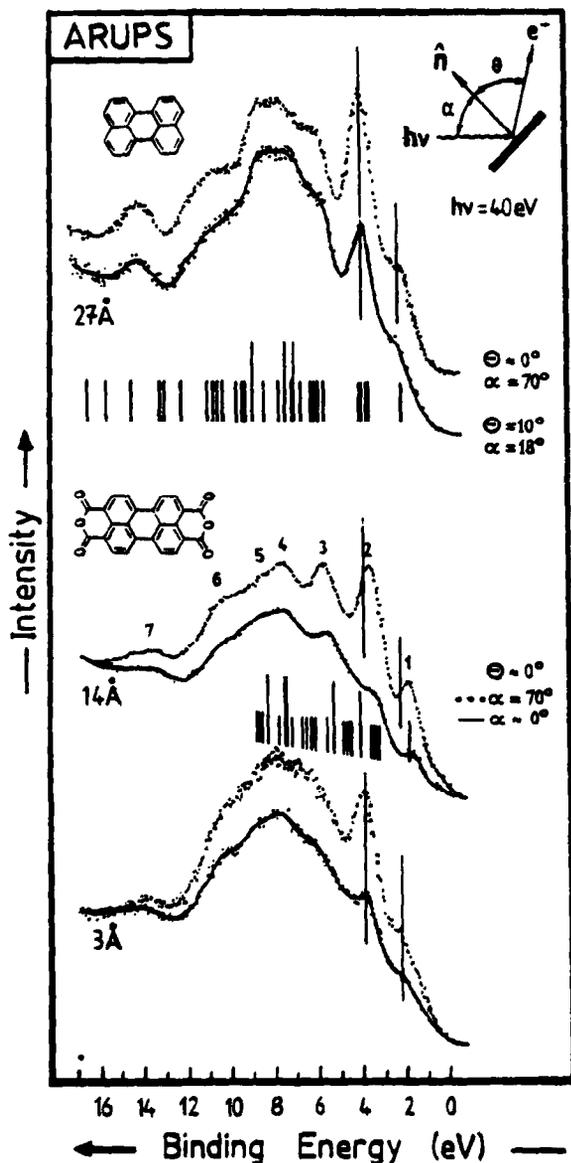


Fig.1 ARUPS spectra of perylene (top) and PTCDA (bottom and middle) adsorbate layers on Si(111) for different layer thicknesses as indicated. Two different measuring geometries are compared: s- ( $\alpha = 0^\circ$ ) and p-polarization ( $\alpha = 70^\circ$ ). Binding energies are referred to the Fermi level of the Si substrate. The bar spectra represent calculated energies using PM3.

answered by experiments but requires calculations (see below).

A second point of major interest is the bonding to the substrate, in particular in the case of the more reactive PTCDA. Fig.1 also contains monolayer spectra (middle) which exhibit significant differences as compared to the multilayer spectra, in particular around peaks 1 and 3. In fact, the monolayer PTCDA spectra are rather similar to those of perylene indicating that the anhydride groups are strongly involved in the bonding to the Si surface or that partial decomposition occurs.

More experimental insight can be gained by comparison of different

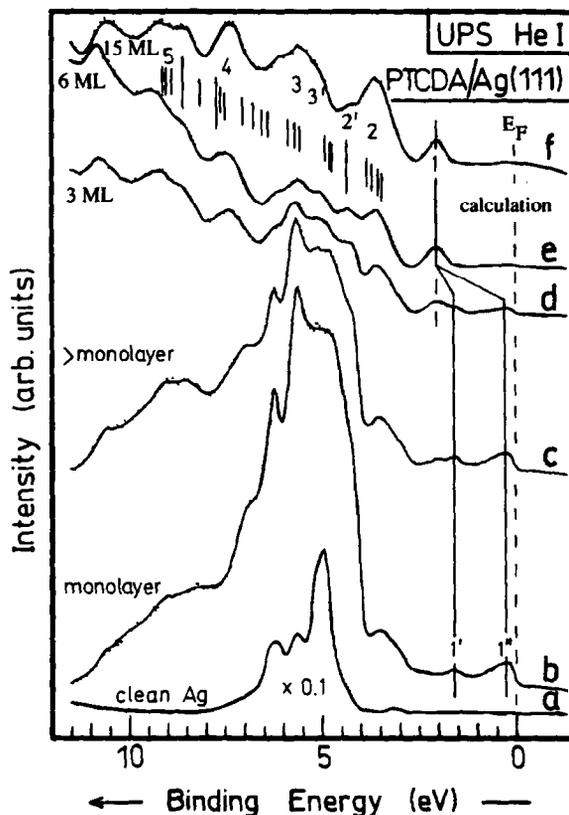


Fig.2 UPS ( $h\nu = 21.2\text{ eV}$ ) spectra of PTCDA on Ag(111) for various coverages. The bar spectrum represents calculated energies using PM3.

substrates. Fig.2 shows UPS spectra of PTCDA adsorbed on a Ag(111) surface taken for various coverages as indicated. Apart from the intense Ag d-band which extends from 4 - 8 eV below the Fermi level and is strongly attenuated by the organic overlayer one observes very similar valence features as for PTCDA on Si. The most significant differences between adsorption on Si and Ag (apart from relative intensity changes which may be due to the experimental parameters) are ( $\alpha$ ) the appearance of peaks 2' and 3' in the multilayer spectra, especially in spectra d and e, and ( $\beta$ ) the splitting and shift of peak 1 in the monolayer regime (spectra b and c of fig.2). At present we believe that observation ( $\alpha$ ) may be connected to a different order of the PTCDA layer in each case. The order is known to be strongly dependent on substrate surface and preparation parameters [2]. Observation ( $\beta$ ) indicates the formation of a covalent bond between PTCDA and the substrate, but for a more detailed understanding calculations concerning the character of the involved orbital(s) are required.

Summarizing the experimental observations one can clearly derive several conclusions, for instance about orientation, order in the molecular layer, and bonding to the surface, but many questions must remain open without accompanying calculations. Hence fig.3 presents a selected aspect of the data obtained from several different calculations which will be published in detail elsewhere [9]. This figure shows the ground state energy positions and symmetries of the topmost occupied orbitals of a single PTCDA molecule and the local contributions of the various atoms

to these orbitals, as calculated using MOPAC in the PM3 approximation [8]. Apart from the well-known

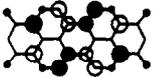
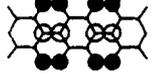
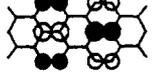
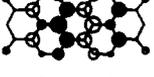
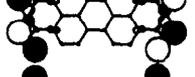
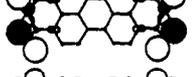
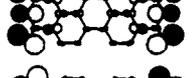
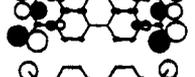
neutral ground state ionisation energy [eV]	D2h	
- 9.31	Au ( $\pi$ )	
- 10.69	B1u ( $\pi$ )	
- 10.74	B2g ( $\pi$ )	
- 10.95	B3g ( $\pi$ )	
- 11.05	B2g ( $\pi$ )	
- 11.56	B1g ( $\sigma$ )	
-11.56	B2u ( $\sigma$ )	
- 11.93	Ag ( $\sigma$ )	
- 11.97	B3u ( $\sigma$ )	
- 12.13	B1u ( $\pi$ )	
-12.29	B2g ( $\pi$ )	

Fig.3 Left: Ground state energies and symmetry assignments for the upper occupied orbitals of PTCDA from PM3 calculations. Right: Local distribution of these orbitals; the size of the lobes indicates the contributions of atomic orbital coefficients.

problem of such calculations to correctly predict the absolute energy positions one can clearly see that the agreement of relative energies for the measured and calculated data, respectively, is surprisingly good (see also the bar spectra in figs. 1 and 2).

The conclusions derived from the calculations and from the comparison with experiment are as follows:

(1) The topmost UPS peaks are well described by all calculations and hence can be assigned to orbitals of different symmetry character: peak 1  $\leftrightarrow$   $A_u$ , peak 2  $\leftrightarrow$   $B_{1u}$ ,  $B_{2g}$ ,  $B_{3g}$ ,  $B_{2g}$ , peak 2'  $\leftrightarrow$   $B_{1g}$ ,  $B_{2u}$ , peaks 3' and 3  $\leftrightarrow$   $A_g$ ,  $B_{3u}$ ,  $B_{1u}$ ,  $B_{2g}$ .

(2) The observation that peaks 2' and 3' only appear in the PTCDA spectra on Ag(111) could arise from epitaxial growth of PTCDA on Ag(111) [10]. Thus, the geometrical structure of the overlayer could be determined by the substrate geometry and different from that in PTCDA single crystals whereas a polycrystalline PTCDA layer is formed on Si(111) [4,5]. Very recent STM investigations [10] support this interpretation. Our calculations are consistent with this idea since especially the energy positions of peaks 2' and 3' are strongly dependent on the bond geometry within the PTCDA molecule. They are rather different for a "free" molecule and for one with geometry parameters as derived from the crystalline structure, respectively.

(3) Peak 2 represents a  $B_{1u}$  orbital, and hence its strong polarization dependence is understandable. However, three further orbitals of other symmetry are also located at this energy which may contribute intensity, in particular if the selection rules do not apply per-

fectly (e.g. for slight misorientation of the experimental geometry). Thus, disorder cannot unambiguously be concluded from the appearance of peak 2 for the "forbidden" geometry.

(4) Bonding to the substrate mainly occurs through the topmost (HOMO)  $A_u$  orbital (Ag, Si) and the orbitals contributing to peak 3 (Si). Some of these orbitals have significant O 2p character indicating the importance of the anhydride group for the surface bond. However, as especially the  $A_u$  orbital is dominated by  $p_z$  atomic orbitals of the perylene group one must conclude that the whole molecule participates in the covalent surface bonding.

#### 4. Conclusion

The present study of the complicated electronic structure of big organic adsorbates like PTCDA and perylene has shown that many details observed in the spectra, especially in the upper part of the valence band, can be understood by comparison to carefully performed calculations using different approaches. The combined information from calculation and experiment enables a deeper understanding of the electronic and geometric structure of organic overlayers and interfaces, and of the dependence of electronic data from parameters such as substrate, functional groups, order, and preparation conditions. The conclusions presented here are consistent with results from XPS, NEXAFS, TPD, and STM investigations published elsewhere [4-6,9,10].

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