Molecular states of polyacenes grown on noble metal surfaces

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Abstract.
Here we present a combined photoemission (UPS), metastable deexcitation (MDS) and optical absorption (NEXAFS) at C K-edge study of molecular states of polyacenes grown on Ag(111) and Au(111), from submonolayer to multilayer thicknesses. We focus on the evolution of the HOMO and LUMO molecular states induced by the adsorption from submonolayer to monolayer thickness and we find a different redistribution of these states in the various systems formed at RT: while a strong redistribution of the molecular states takes place in Pn/Ag(111) and Tc/Ag(111) interface, a weaker interaction is indicated for Tc/Au(111).

1. Introduction
Organic field effect transistors (OFETs) are among those devices with a large number of potential applications and thin films of various polyacenes have become widely used as molecular semiconducting materials in the field of organic electronics. A detailed understanding of the optical and electronic properties of polyacene thin films and their interfaces with metals implies the knowledge of their electronic structure. In this context thin films of tetracene (Tc, C_{18}H_{10}) and pentacene (Pn, C_{22}H_{14}), appear most promising candidates for the building of molecular organic semiconductors. Their transport properties in well-ordered organic thin films is highly anisotropic and is related to the structural, optical and electronic properties of the first layer [1,2,3,4,5,6]. Both Tc and Pn adsorb in a nearly flat configuration on noble metal (111) surfaces. Different ordered phases are found for Tc and Pn adsorption on noble metals (Pn/Au(111) [6], Pn/Ag(111) [2,3] Tc/Ag(111) [4]) and in some cases the phase diagram appears complex.

This work is based on the combined use of optical absorption (NEXAFS) at the C K-edge, photoemission (UPS) and metastable deexcitation spectroscopy (MDS): NEXAFS gives access simultaneously to local structure and empty electronic states, UPS complements the information with filled electronic states; MDS is sensitive only to the protruding part of orbitals, and an indication on the surface, subsurface or interface localization of the orbitals is obtained. We find differences in the various systems formed at RT: while a strong redistribution of the molecular states takes place for Pn/Ag(111) and Tc/Ag(111) interface, a weaker interaction is indicated for Tc/Au(111).

2. Experimental
Tc and Pn adsorption on Ag(111) and Au(111) were studied in two different ultra high vacuum UHV systems: NEXAFS and angular resolved UPS were measured at the BEAR beamline of the ELETTRA synchrotron radiation facility in Trieste [7] and Angle Integrated UPS and MDS at University of
Modena and R. Emilia, lab. of Physics of Materials and Surfaces (Dept. of Materials Engineering) [8]. The Ag(111) and Au(111) samples were treated with sputtering and annealing cycles. The base pressure in the chambers was \(3 \times 10^{-10}\) mbar. Surface cleanliness was checked by photoemission spectroscopy. No detectable C and O 1s core level emissions were present after the cleaning procedure and sharp Ag(111) and Au(111) LEED patterns were observed. Polyacenes were deposited onto the clean substrates at RT. The molecular coverage was determined by a quartz thickness monitor. XPS quantitative analysis of the Ag 3d or Au 4d and C 1s photoemission was carried out following standard procedures [2,3,4]. The same results were obtained by measuring the C 1s X-ray absorption edge jump. During Pn and Tc sublimation the pressure rose up to \(9 \times 10^{-10}\) mbar. The multilayer indicated corresponds to 2-3 monolayer (ML), a nominal coverage (read at the quartz balance) of 12-18 Å. Angular resolved UPS at normal incidence was measured with a hemispherical electron analyser (radius 66 mm) at constant energy resolution (~70 meV) and with a photon energy of 30 eV. Angular Integrated UPS was measured with a cylindrical mirror analyser (CMA), with a resolution of 100 meV and a discharge He lamp source, providing HeI photons. MDS spectra were taken with a He*metastable atom source, as described in reference [9], and measuring the electron emission with the CMA with a resolution of 300 meV. The NEXAFS spectra were normalized to the incident photon flux. Intensities were monitored by measuring the current drained by a tungsten grid inserted in the beam path. The photon energy resolution was 80 meV at the C K-edge, and the typical photon flux on the sample was of the order of \(10^{10}\) photons/second. The NEXAFS spectra have been measured in the Auger electron yield mode (sampling depth \(\sim 10\) Å). Spectra were taken at 80° of incidence with elliptically polarized light (0.28 of ellipticity) with the electric field (major axis) forming an angle of 53° with the surface normal (see also [3]).

3. Results
Fig. 1 shows the NEXAFS C K edge of Tc on Ag(111) and Au(111) at subML and ML coverages. The multilayer Tc spectrum is shown for comparison. The \(\pi\) resonances are well pronounced, showing a fine structure due to initial state effects of the different C emitters in the molecule. The feature A of the NEXAFS Tc multilayer have been attributed to transitions involving central C atoms [10], as is also the case for the Pn multilayer [3]. Fig. 1 indicates that the LUMO fine structure changes with Tc thickness in the low coverage range. Similarly, in the absorption spectra of 1 ML Pn deposited on Ag(111) [3], the \(\pi\) resonances assigned to the molecule central atoms at about 284 eV are absent as in the case here, of 0.6 ML of Tc/Ag(111); these changes of the LUMO transitions with respect to the gas phase or the multilayer suggest a molecular modification due to the redistribution of the oscillator strengths in the C 1s LUMO excitations for low coverages of polyacenes on Ag(111) surfaces at RT. The spectrum taken after the completion of a single ML (1.3 ML) is similar to the multilayer one, as
expected because of intra-layers Van der Waals bond. An analysis of the morphology the Pn/Au(111) system molecular films and a NEXAFS study are presented in ref. [5], where for low coverages a redistribution of the lineshape is found. Concerning the Tc/Au(111) system, the configuration of empty states appears less modified with respect to the multilayer spectrum, suggesting a weaker modification of the acene molecular states implying a weaker interaction with the gold substrate.

The filled electronic states have been studied by MDS and UPS. In case of MDS the He* interacts with the most protruding portion of surface orbitals [9, 11] providing information predominantly on the charge and energy distributions of outermost orbitals. Here the comparison of UPS with MDS is used to get, beside binding energies, information on the space distribution of electron charge, and to provide a picture of the charge clouds of the electronic states in terms of inward and outward direction of the orbitals [9 and refs therein, 11].

Fig. 2 shows UPS valence band states of Pn/Ag(111) taken at normal emission at different coverages (indicated). The Pn multilayer spectrum shows a broad peak at about 1.5 eV of binding energy that can be assigned to the HOMO (3b_{2g}) state [12] and features at higher energies that can be assigned to π filled states. The MDS Pn multilayer spectrum has been taken from ref.[11] and has been reported in here for comparison. For subML coverages up to the completion of 1ML, the 3b_{2g} peak is shifted at higher binding energy at about 1.9 eV, revealing a redistribution of the filled molecular states. This result is further confirmed by angular integrated UPS spectra (not shown) where the shifted HOMO feature has much stronger intensity. On the other hand, in the HOMO region hardly any emission is detectable in MDS, while broad and intense features are present at higher binding energies (3b_{3g} and 2a_{2u} states).

Fig. 3 shows UPS and MDS spectra of Tc/Ag(111) and the UPS of Tc/Au(111), together with the difference curve of the sub-ML with respect to the clean substrate. The Tc multilayer spectrum has been taken from ref.[13] and is shown for comparison. The HOMO peak in the multilayer results at 2.1 eV, in agreement with [14]. For the Tc/Ag(111) system at 1 ML, the HOMO results at the same binding energy, even though a shoulder is measured at 1.9 eV. For lower coverages only the peak at
1.9 eV is measured, with low intensity. Angular Integrated spectra confirm this energy position. This state is much depressed in MDS. In the Tc/Au(111) case the valence band changes due to Tc deposition are masked by the Au strong emission. The difference curve between the 0.5 ML film and the clean Au surface shows both the broaden b2g and b1g states.

The comparison between UPS and MDS, at coverages up to 1 ML, shows that in MDS the HOMO peak is undetectable while the π states at higher binding energy are observed. This fact is taken as an indication that the charge of the HOMO orbital is not distributed outward allowing to conclude that the HOMO is perturbed by the bond formation with the substrate.

The modification of the HOMO and LUMO molecular states can be related with Density Functional Theory calculations performed on Pn/Al(100) [15], Pn/Au(100) [16] and on Pn/Cu(119) [17] indicating a similar modification of the π molecular states of adsorbed polyacenes on the Ag(111) substrate. Further work is in progress. In any case we can indicate a progression of the bond strength, from the Tc/Au(111) to the stronger Pn/Ag(111).

4. Conclusions
The Tc and Pn adsorption on Ag(111) and Au(111) surfaces is studied at RT by complementary spectroscopic techniques. At this interfaces the polyacenes have a nearly flat orientation that are likely to allow the π conjugated molecular orbital to overlap and hybridize at different degree with the metal electronic states. We singled out differences in the HOMO and LUMO states of Tc and Pn adsorbed in subML coverages up to the completion of 1 ML. The modified HOMO state is not detected by MDS, showing that the most protruding molecular states are those at higher binding energy, with the HOMO participating in the interface redistribution of the electronic structure. The LUMO results strongly modified in the cases of Tc and Pn deposited on Ag(111) substrate and less perturbed on Au(111).

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