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Hybridization and charge transfer at the anthracene/Cu(110) interface: Comparison to pentacene

F. Bussolotti* and R. Friedlein
School of Materials Science & Research Center for Integrated Science, Japan Advanced Institute of Science and Technology (JAIST),
1-1, Asahidai, Nomi, Ishikawa 923-1292, Japan

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The electronic structure of an ordered anthracene monolayer prepared at 293 K on Cu(110) has been investigated using angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). Spectral features observed in the binding energy region of 2–4 eV are assigned to interfacial states formed by hybridization with Cu (3*d*) orbitals. In the vicinity of the Fermi level, a charge-transfer state involving the lowest unoccupied molecular and Cu (4*s*) orbitals is formed and most likely supported by a non-negligible hybridization with 3*d* orbitals. The comparison to pentacene on the same surface [H. Yamane *et al.*, Phys. Rev. B **76**, 165436 (2007)] reveals a clear relation between the strength of hybridization and the energetic separation between the Cu (3*d*) band and the original molecular levels.

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I. INTRODUCTION

For the functioning of any organic electronics device structures employed in photovoltaic cells and thin film field effect transistors, the control of structural and electronic properties at hybrid interfaces to the metallic electrodes is most essential.[1–7] Correspondingly, a substantial amount of fundamental research has been generated with the aim to understand the properties of such interfaces. So far to a major extent the focus has been on the mechanisms of the alignment of the energy levels of substrate and the organic films, with very different models applied to the cases of weak and strong interactions at the interface.[8–12] Only some more recent experimental and theoretical results have provided a more detailed description of the interfacial states present in strongly interacting system.[13–18]

The adsorption of organic molecules onto metallic substrates is generally accompanied by a vacuum level (VL) shift at the organic/metal interface due to the formation of an interfacial dipole layer. This is in contrast with predictions from the Schottky-Mott model where a perfect VL alignment is assumed. Several and concurring mechanisms have been proposed in order to rationalize the origin of the dipole layer at such interfaces,[9] such as (i) the reduction of the tailing of the metal wave function into the vacuum via Pauli repulsion of the molecular electron density ("push-back effect"), (ii) polarization of the molecules by interaction with the image charge formed in the metal ("mirror effect"), and (iii), the formation of various types of bonds between the molecules and the substrate involving i.e., a (partial) charge transfer, hybridization and the formation of interfacial states. Despite the substantial amount of data collected for a large number organic/metal interfaces, however, the delicate interplay and relative importance of the various effects is far away from being completely understood representing a source of an intense scientific debate. Recently, particular attention has been paid to the role of electronic states derived from the metal and the molecules in determining the final alignment between the Fermi level of the metal and the molecular states.[13,18]

In this context, the study of thin organic films of linear oligoacene molecules such as anthracene and pentacene, the chemical structures shown in Fig. 1(a), turned out to be of special importance.[14,15,19] On one hand, among the huge variety of organic compounds they belong to the most interesting ones from a technological aspect.[4–6] On the other hand, the relative structural simplicity of oligoacenes combined with the strong tendency to form long-range ordered structures with well-defined adsorption geometries on single-crystalline metal surfaces[14,15] provides highly suitable reference systems for the understanding of the physics at organic/metal interfaces. Importantly, by tuning the molecular size between benzene and pentacene, the molecule-substrate interactions are changed leading to interface states with either weak[20] or strong[18] metal contributions, respectively. In this context, the recent finding of a strong mixing of molecular and metal electronic states for pentacene monolayer films deposited onto various single-crystalline copper surfaces has demonstrated the invalidity of simple physi- or chemisorption models in describing interactions between π coniugated and aromatic molecules and metals.[14,17] In particular, a strong increase of the electronic density of states at the Fermi level is observed and understood in terms of hybridization involving Cu (3*d*) orbitals and a non-negligible charge transfer into the lowest unoccupied molecular orbital (LUMO).

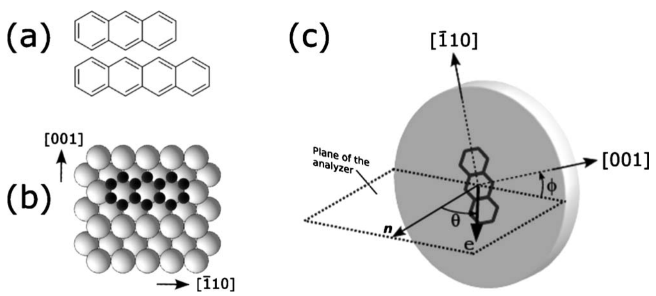

FIG. 1. (a) Chemical structures of anthracene (up, $C_{14}H_{10}$) and pentacene (down, $C_{22}H_{14}$) molecules. (b) Schematic representation of the Cu(110) surface plane and the molecular orientation. (c) Sketch of the experimental geometry indicating the polar and azimuthal photoelectron emission angles, θ and ϕ, respectively, as evaluated with respect to the [001] (ϕ=0°) and [$\bar{1}$10] (ϕ=90°) Cu main crystallographic directions.

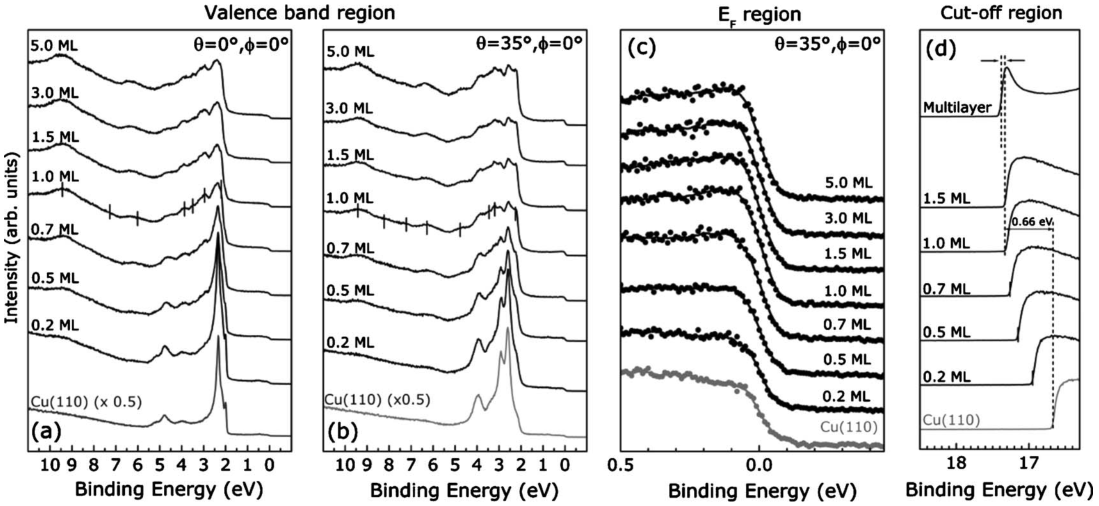

FIG. 2. UPS spectra of anthracene/Cu(110) as a function of the nominal film thickness, acquired at $\theta=0°$ (a) and $\theta=35°$ (b) along [001] of the Cu substrate surface ($\phi=0°$) The corresponding spectra of the clean Cu(110) surfaces are included as well. (c) Magnification of the spectra shown in panel (b), in the region in the vicinity of the Fermi level. (d) Evolution of the spectra in the cutoff region as a function of the nominal film thickness. The corresponding spectrum of a multilayer obtained by deposition at 140 K is shown for comparison.

The degree of hybridization, the energetic position of the new interfacial states as well as the direction of the charge transfer has been found to be strongly dependent on the relative energy separation between the original metal and molecular states.[13,18] It may therefore be interesting to explore how interface states evolve as a function of relevant electronic parameters motivating studies on smaller oligoacene molecules adsorbed on the Cu(110) surface. Beside the separation between the Cu (3*d*) band and the energy level related to the original highest occupied molecular orbital (HOMO), it is a possible stabilization of the electron affinity level related to the LUMO providing a charge-transfer state at low binding energies that needs particular attention. Different to pentacene, the smaller anthracene molecule has a large gap of about 6.9 eV and a low affinity of only 0.55 eV.[21] It should therefore require a higher energy to stabilize charge transfer.

In order to address these questions, in this paper, are reported electronic properties of anthracene monolayer thin films deposited at room temperature onto Cu(110) surfaces [Fig. 1(b)] as studied using angular-resolved photoelectron spectroscopy (ARUPS). The experimental results are consistent with the formation of a chemisorbed monolayer of uniaxially aligned molecules that interact strongly, but weaker than pentacene molecules, with the metal surface. A number of metal-adsorbate interfacial states are formed by hybridization of molecular π with Cu (3*d*) orbitals. A partially filled, LUMO-derived hybrid state is detected near the Fermi level which is consistent with the occurrence of charge transfer from the metal substrate to the molecules.

II. EXPERIMENTAL

The experiments have been performed in a home-built, ultrahigh vacuum (UHV) setup (base-pressure $<2\times10^{-10}$ mbar) containing a sample preparation system specially designed to allow the deposition of small organic molecules under UHV conditions. Cu(110) single-crystal surfaces (99.999%, MaTecK GmbH, Germany) have been cleaned by repeated sputtering and annealing cycles. The quality of the metal surface has been evaluated by reflection high-energy electron diffraction (RHEED) and ARUPS as shown elsewhere.[22] Anthracene molecules have been deposited onto substrates being at room temperature (293 K), at a constant partial pressure of 5×10^{-8} mbar. Further details about the anthracene deposition procedure are reported elsewhere.[19] By following a procedure stated elsewhere,[11,14] the nominal thickness of the anthracene thin film expressed in monolayer (ML) units has been determined from the evolution of the work function as a function of the deposition time. Details are provided in the discussion below.

Photoelectron spectra have been acquired using a hemispherical analyzer (Scienta SES-100) and unpolarized HeI photons ($h\nu=21.218$ eV) incident at an angle of 70° with respect to the normal of the substrate plane (grazing incidence). The total energy and angular resolutions have been set to be better than 50 meV and 0.2°, respectively. Angular-integrated spectra have been acquired with an integration angle of about ±6° with respect to the normal emission direction $\boldsymbol{n}$ [polar emission angle $\theta=0°$, see Fig. 1(c)]. The origin of the in-plane azimuthal angle ϕ has been chosen to coincide with the [001] crystallographic direction of the Cu substrate [Fig. 1(c)]. The position of the VL representing the work function has been determined from the secondary electron cutoff, the sample being biased at −5 V.

III. RESULTS AND DISCUSSION

In Fig. 2 is reported the evolution of the valence band photoelectron spectra as a function of the nominal anthracene film thickness. The angular-integrated data presented in panel (a) and (b) have been acquired at both normal emission ($\theta=0°$) and $\theta=35°$, respectively, along the [001] Cu crystallographic direction. Corresponding data of the clean Cu(110) surface are shown for comparison.

Several modifications with respect to the substrate valence band structure are observed. In particular, the intensity of the substrate 3*d* signature is gradually quenched with progressing exposure to anthracene vapor. At the same time, additional spectral features, marked with vertical bars, appear at binding energies of about 2–5 eV in spectra taken along the [001] crystallographic direction. The relative intensity of these new features is strongly affected by superimposition with the dispersive Cu (3*d*) band. Note that, however, their binding energy positions are independent on the photoelectron emission geometry.

An enhancement of anthracene-related electronic states is observed until a nominal thickness of 1 ML above which no further changes in the overall valence band line shape occurs. Since at large exposure times, the overall spectral intensity is still dominated by electronic states of the Cu(110) surface, and since the spectra do not change anymore, it is concluded that a growth of a multilayer film does not occur at room temperature. As observed in the case of other organic films deposited on metal substrates, even an inhomogeneous growth would eventually lead to a gradual and eventually to a complete suppression of the substrate-derived signal.[10,14,16] It has already been recently observed[19] and may easily be conceived that the formation of a multilayer film at 293 K is prevented because intermolecular interactions are weak as compared to those between larger aromatic compounds for which such a growth at room temperature is documented.[10,14,16] Single-crystalline multilayer films on Cu(110) form well at 140 K. Subsequent layers adopt a "standing" molecular configuration and are characterized by a square unit cell within the planes.[22]

Note that despite the progressive molecular coverage observed until about a nominal thickness of 1 ML, there is no reduction and even an enhancement of spectral weight at the Fermi level. In particular, as clearly shown in the off-normal UPS data reported in Fig. 2(c), a small peak centered at about 0.25 eV is observed whose intensity saturates after completion of the monolayer.

Additional evidence for the formation of a stable monolayer is found in the saturation of the VL shift with respect to the position observed for the Cu(110) surface, shown in Fig. 2(d). At saturation, the position of the VL corresponds essentially to that of a thick anthracene multilayer, as grown on the same surface at 140 K.[22] The saturation of the VL shift is similar in related organic/metal systems.[14,16] A more detailed discussion will be presented later in the context of the analysis of the complex phenomena occurring at the anthracene/copper interface.

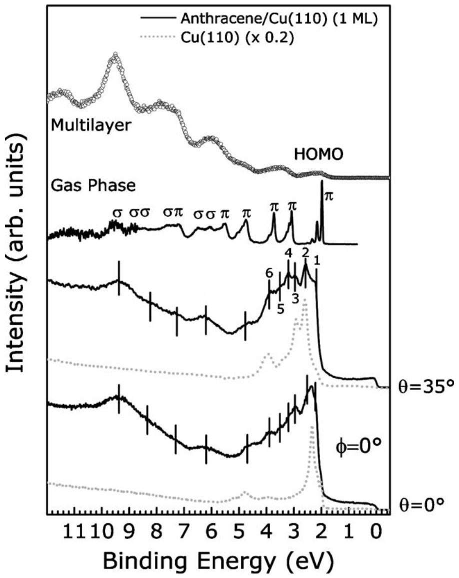

FIG. 3. Comparison of the monolayer spectra as acquired at $\theta=0^\circ$ and $\theta=35^\circ$ along [001] ($\phi=0^\circ$) with those of the clean substrate surface, of free anthracene molecules in the gas phase (shifted) (Ref. 24) and with the anthracene multilayer at 140 K.

For the anthracene monolayer on Cu(110), a long-range ordered, two-dimensional structure has been claimed on the basis of independent scanning probe microscopy (STM) results.[23] Similar to pentacene/Cu(110),[14,23] anthracene molecules are self assembled into equally spaced, [001]-oriented molecular rows, with the molecular plane parallel to the surface and the long molecular axis aligned along the $[\bar{1}10]$ main crystallographic direction of the Cu substrate. While in the present experiments, structural data could not been obtained directly by *in situ* RHEED measurements, anisotropic ARUPS data discussed below are consistent with an alignment of the long molecular axis along the $[\bar{1}10]$ main crystallographic direction of the Cu substrate as observed by STM.[23] While the molecular orientation appears to be unaffected by variations in the deposition conditions, the lateral extension of the two-dimensional domains, however, may depend on how the film is made.[14,23] In particular, for pentacene, the degree of order obtained at room temperature is significantly improved during a moderate annealing at 400 K. Obviously, by increasing the lateral mobility of the molecules, energetically more favorable adsorption sites may be found. According to Yamane *et al.*,[14] for the pentacene/Cu(110) layer, the transition into an ordered state leads to a significant variation of the spectral line shape. Annealing of the anthracene monolayer for 1 h at 400 K, just below the desorption temperature of the monolayer film, did not result in spectral changes supporting the idea that the room temperature molecular mobility of anthracene on Cu(110) may be already sufficiently high.

In order to allow a more detailed discussion of the interfacial electronic properties, angular-integrated UPS spectra of the anthracene monolayer, of the multilayer prepared at 140 K,[22] of the free molecule[24] and of the Cu(110) substrate have been separately plotted in Fig. 3. The gas phase spectrum has been shifted to align spectral features to those of the multilayer film.

At high-binding energies (>4 eV), the energy separation between spectral features related to σ and some of the π molecular levels match well with those in the spectrum of the free molecule and with those of the multilayer film. This matching is not preserved for the π orbitals in the region between 2 and 4 eV where six new interfacial states (numbered 1–6) are resolved in either one or both of the spectra taken at $\theta=0^\circ$ and $\theta=35^\circ$ instead of the original three related to the HOMO, HOMO-1, and HOMO-2. Note that the binding region in question is that of the Cu (3*d*) band.

With the breakdown of a description in terms of pure molecular states, the behavior is very different to the case of a "flat-lying" anthracene monolayer weakly physisorbed on the surface of highly oriented pyrolytic graphite for which a strong molecular character of the organic film persists.[19] On the other hand, the data are in agreement with recent theoretical calculations and experimental findings on related systems.[13,14,17,18] For larger aromatic molecules, such as pentacene and perylene-3,4,9,10-tetracaboxylic acid dianhydride (PTCDA), the interfacial electronic structure observed in the Cu (3*d*) binding energy region is qualitatively described to result from a relatively strong hybridization between the molecular and substrate wave functions leading to a splitting of the original molecular levels.

In this context, the appearance of a clear photoelectron emission peak near the Fermi edge, not present in the multilayer spectrum, deserves special attention. An increase of the density of states near the Fermi level may be attributed to a (likely partial) occupation of the former LUMO by charge transfer from substrate 4*s* states at the Fermi level. Given the low affinity of the anthracene molecule, charge transfer into the LUMO may be surprising. One should consider, however, that anthracene has a higher electron-accepting ability *per carbon atom* than pentacene.[21] Different to free molecules, where a transfer of a full charge is needed, at surfaces, partial charge transfer may be possible if stabilizing contributions such as an increase in the affinity due to screening in the solid state,[25] electrostatic interactions between the transferred charge and its image and the redistribution and relaxation of interfacial electron densities are sufficiently large.

Some degree of hybridization with metal orbitals may occur, as discussed for the interfaces of PTCDA on Ag(111) and Ag(110)[12] and for pentacene thin films deposited on various Cu single crystal surfaces.[16,17] Most importantly, the pentacene/Cu(110) monolayer system is discussed to be characterized by a non-negligible band dispersion of the interfacial states related to the HOMO and LUMO reflecting the two-dimensional, lateral periodicity of the molecular layer. The delocalized nature of these interfacial electronic states has been attributed to strong substrate-mediated intermolecular interactions, due to a significant hybridization between molecular and metal orbitals.[16,17]

In order to verify the occurrence of a similar scenario for the anthracene monolayer on Cu(110), the polar angle dependence of the LUMO-derived state at a binding energy of about 0.25 eV has been investigated. This peak can be well distinguished from the simple steplike Fermi edge of the clean substrate. Corresponding spectra resolved in θ, taken along high-symmetry directions, are reported in Fig. 4. Along the [001] symmetry direction [$\phi=0°$, Fig. 4(a)], the spectral intensity of the LUMO-derived state progressively increases with θ reaching a maximum in between 45° and 49°. Anisotropy in the photoelectron distribution is typical for adsorption geometries with the molecular plane parallel to the substrate surface,[26,27] and seems to still prevail even if unpolarized light has been used. Since the binding energy does not vary with θ, the LUMO-derived electronic state appears to be localized along the [001] symmetry direction. In the $[\bar{1}10]$ direction [$\phi=90°$, Fig. 4(b)], the intensity of the peak close to the Fermi level is significantly quenched and broadened but can only be properly evaluated in a small angular range between 38° and 48° limited by the appearance of superimposed substrate-derived features at lower angles and our present experimental set-up.

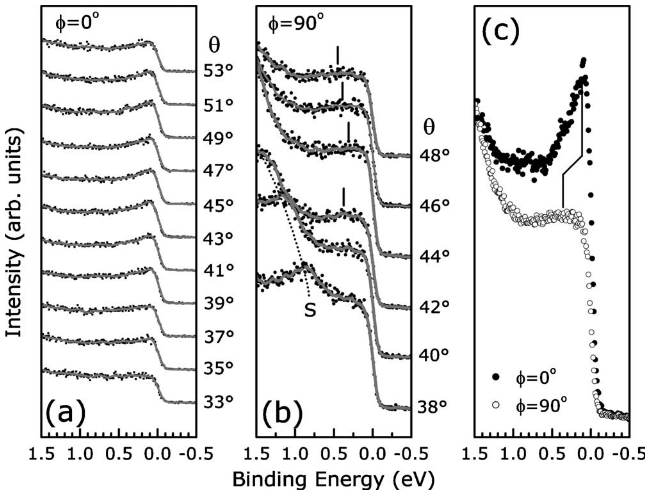

FIG. 4. Dependence of the ARUPS spectra of the anthracene/Cu(110) monolayer on the polar angle θ along the [001] ($\phi=0°$, panel a) and $[\bar{1}10]$ ($\phi=90°$, panel b) directions of the Cu(110) surface. A comparison between corresponding angle-integrated UPS data is given in panel (c) (see text for details).

Importantly, however, as clearly visible in the comparison of the two directions made in Fig. 4(c), the binding energy of the LUMO-derived feature in the $[\bar{1}10]$ direction is about 0.1–0.2 eV higher than along the [001] direction. For this comparison, the data have been integrated between $\theta=45°$ and 49°. There may be two explanations to account for the variation of the binding energy observed in the two crystallographic directions: either (i) there are actually two occupied, LUMO-derived interfacial states, or (ii) there is a slight dispersion of the LUMO-derived state along one of the two directions. In case of a localized state, the binding energy is expected to be completely independent of the particular crystallographic direction reflecting equality at the center of the Brillouin zone as measured at $\theta=0°$.

The different behavior observed for the two main crystallographic directions reflects a decisive role played by the molecular adsorption geometry in driving the substrate-mediated, intermolecular interactions. It may be conceived that electronic states are less localized along $[\bar{1}10]$ given the alignment of the long molecular axis along this direction. Note that for the similar pentacene/Cu(110) reference system, a significant dispersion of two LUMO-derived states has been observed along the same direction.[14] The larger band width with respect to the present anthracene case can be directly linked to the higher pentacene-substrate interaction strength.[28]

Further insight about the interfacial electronic properties of the anthracene monolayer on Cu(110) and, indirectly, on the molecular orientation may be derived from a more de-

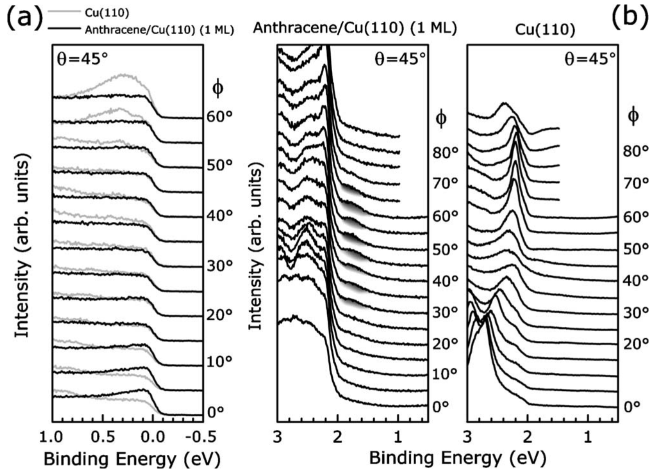

FIG. 5. Dependence of the ARUPS spectra of the anthracene/Cu(110) monolayer on the azimuthal angle ϕ in the binding energy regions in the vicinity of the Fermi level (panel a) and HOMO (panel b). The corresponding spectra of the clean substrate are also included for comparison.

tailed analysis of the azimuthal dependence of the photoelectron spectra. The corresponding ARUPS data, integrated $\pm 6^{\circ}$ around $\theta=45^{\circ}$ have been acquired with an angular step of $\Delta\phi=5^{\circ}$, and are reported in Fig. 5(a). In particular, the intensity of the LUMO-derived state near the Fermi level is highest in the [001] direction and rapidly suppressed with increasing ϕ. At the same time, a new peak not recognizable in the spectra obtained in the high-symmetry directions shown so far has been observed at 1.5 eV, within a range between $\phi=50^{\circ}$ and 70° [shaded area in Fig. 5(b)]. This feature has no counterpart for the clean Cu(110) surface and is therefore attributed to an additional interfacial hybrid state. Note that an enhanced photoelectron emission intensity at particular azimuthal and polar angles is expected to occur in the case of a long-range ordered, organic monolayer, and interpreted by invoking quantitative symmetry arguments applied to selection rules for photoionization.[29] According to these arguments, no angular variation is expected in the case of an in-plane rotationally disordered film. Even if in the present study unpolarized light was employed, the data are very consistent with the formation of a two-dimensional long-range ordered anthracene monolayer, with a structure possibly the one observed by STM.[23]

With all particular interface states discussed, a qualitative model of the anthracene/Cu(110) interface can now be formulated. To provide a conclusive summary taking into account the azimuthal dependence of the intensity of adsorbate-induced features, ARUPS data acquired at a polar angle of $\theta=45^{\circ}$ for both $\phi=0^{\circ}$ and $\phi=60^{\circ}$ are reported in Fig. 6(a). In total, seven hybrid interface states are identified that do not find their counterpart in the multilayer spectrum. If one follows the arguments by Kawabe *et al.*,[13] the final energy position of the interface states shall be strongly dependent of the energy separation between molecular levels and the centroid of the Cu (3*d*) band. For anthracene, given the energetic overlap of the HOMO and the Cu (3*d*) band, states marked as "B" and "C" are most likely hybrid states formed by the corresponding orbitals.

As illustrated in Fig. 6(b), differences between anthracene and pentacene are larger for states derived from the LUMO.[30] For the pentacene monolayer on Cu(110), the formation of two LUMO-derived states has been observed[14] while for anthracene feature "A" is located closer to the Fermi level and formed upon charge transfer from the substrate. Given the strong coupling between pentacene and the metal surface, and the relatively small energy separation between the pentacene affinity level (in the solid state) and the Cu (3*d*) band, it may be conceived that these two LUMO-

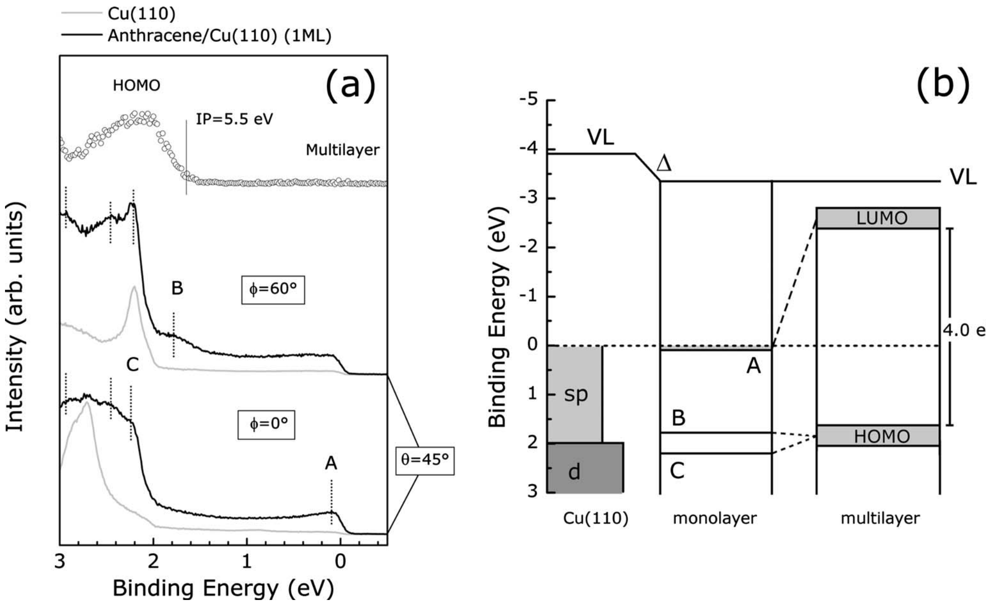

FIG. 6. Spectra of the anthracene/Cu(110) monolayer as acquired at $\theta=45^{\circ}$ in correspondence of different azimuthal angles ($\phi=0^{\circ}$ and $\phi=60^{\circ}$). LUMO and HOMO derived interfacial states are indicated by capital letters A, B and C respectively (b) Energy level diagram for the pentacene/Cu(110) interface. The HOMO-LUMO transport gap for the multilayer film has been estimated from Ref. 30.

derived interfacial states may well be formed as hybrids with 3*d* orbitals. In the case of anthracene, the affinity level is further away from the d band leading to a much weaker interaction. However, as the observation of the appearance of A at different binding energies shows, hybridization is not absent, and one is left with an electronic system that is formed by both charge transfer from 4*s* states and by a hybridization with 3*d* orbitals weaker than for pentacene. In other words, the complex behavior at the interface involves a major redistribution of orbitals and charges.

The formation of a partially filled state at the anthracene/Cu(110) interface relates to a charge re-distribution in space that should lead to the formation of an interfacial dipole providing a positive shift of the VL. This is, however, in contrast to the observed shift of −0.66 eV. For pentacene/Cu(110), with −0.9 eV the negative shift is even larger.[14] Obviously, the contribution of the charge transfer phenomena to the overall energy level alignment is completely overwhelmed by other effects such as the pushing back of metal electron densities or the image charge effect which both result in a negative shift of the VL at the interface. In particular, the larger negative shift for pentacene may be well related to a stronger push-back effect provided by a closer distance of the molecule to the substrate surface, as compared to anthracene.

In conclusion, the adsorption of anthracene molecules into ordered structures on Cu(110) is relatively strong and driven by both hybridization and (partial) charge transfer involving the metal 3*d* and 4*s* orbitals. Obviously, even for molecules smaller than pentacene, charge transfer at the interface can be stabilized by the electrostatic interaction between the transferred charge and its image and by a substantial redistribution and relaxation of interfacial electron densities. Similarities and differences to the pentacene monolayer on the same Cu(110) surface relate in particular to the strength of hybridization with Cu (3*d*) orbitals that depends strongly on the energetic separation between the 3*d* centroid and molecular levels, and on the distance of the molecule from the metal surface. Without charge transfer, this distance would certainly be larger affecting in turn also the strength of hybridization. A continuation of studies on related interface systems will be very helpful in further clarifying the parameters that drive the balance between charge transfer and hybridization at organic/metal hybrid interfaces.

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*Corresponding author. Present address: Graduate School of Advanced Integration Science, Chiba University, Yahoi-cho, Inage-ku, Chiba 263-8522, Japan; fabio@restaff.chiba-u.jp

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