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Modification of the Cu(110) Shockley surface state by an adsorbed pentacene monolayer

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The modification of the Cu(110) Shockley-type surface state by an adsorbed pentacene layer was determined using high-resolution angle-resolved photoelectron spectroscopy. It was found that the surface state is shifted by 80–120 meV to higher binding energies, depending on the pentacene coverage. In addition, an increase in the surface-state population is measured for the sample adsorbed with one monolayer of pentacene. The modification of the surface state by the adsorption of pentacene is put into relation to a complex interplay of different phenomena such as the hybridization and mixing of electronic states, the polarization of the adsorbate in the surface dipole, and the Pauli repulsion. Thus, this observation of a molecular adlayer shifting a surface state away from the Fermi energy sheds more light on the adsorbate-adsorbent interactions.

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I. INTRODUCTION

In general, the chemistry and physics of metal surfaces is modified by the presence of surface and interface states which emerge from the discontinuation of the periodic bulk potential.[1] Such states have been studied spectroscopically and have also been visualized by standing-wave patterns in scanning-tunneling microscopy (STM).[2,3] Surface states can influence adsorbate-adsorbent interactions resulting in a modification of, e.g., the adsorption potential and the barriers for diffusion and dissociation.[4,5] Other effects which arise from the scattering of surface-state electrons are the stabilization of stepped surfaces[6] and the modification of adsorbate self-assemblies via Friedel charge-density oscillations.[7,8]

Organic molecular semiconductors such as pentacene ($C_{22}H_{14}$) with their intrinsically high charge-carrier mobility and their controllable electronic properties by doping are interesting materials for studying the interaction of molecules and metallic surfaces, also with relevance to organic electronic and optoelectronic devices.[9] In a recent study of the self-assembly of pentacene on Cu(110) Lukas *et al.*[10] observed long-range self-ordering by the formation of widely spaced rows of close-packed molecules. They proposed that this particular adsorbate structure is also mediated by Friedel charge-density oscillations produced by a surface state.

On the other hand, the presence of the adsorbates modifies the surface electronic structure of the substrate. Examples are the adsorption of rare gases discussed in the context of Pauli repulsion,[11,12] alkali metals discussed in the context of charge transfer,[13,14] and other more complex cases such as noble metals[15–17] on noble-metal surfaces.

Up to today only little has been published on the modification of surface states by the adsorption of large organic molecules. For example, a combined scanning-tunneling and photoelectron spectroscopy study of the PTCDA/Au(111) interface (PTCDA=3,4,9,10-perylene tetracarboxylic dianhydride, $C_{24}H_8O_6$) demonstrated that the Shockley surface state shifts about 40 meV to lower binding energy, i.e., closer to the Fermi energy.[18] Very recently, high-resolution angle-resolved photoelectron spectroscopy (ARPES) measurements at low temperatures showed a shifted surface state of about 160 meV toward the Fermi level after adsorption of PTCDA or 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) on Au(111).[19] In another study it was shown that for the adsorption of a characteristically different system, C_{60} on Cu(111), the surface state was also shifted toward the Fermi energy.[20]

The here presented paper deals with the modification of the $\bar{Y}$-localized Shockley state of the Cu(110) surface by pentacene adsorbed in two different adlayer structures, a slightly disordered (7×2) phase and a $(6\ -1,\ 1\ 4)$ phase. In contrast to the case of PTCDA on Au(111)[18] and C_{60} on Cu(111),[20] the adsorption of pentacene on Cu(110) leads to a shift of the surface state to higher binding energies. Different mechanisms for the modification of the surface state by adsorbates, such as Pauli repulsion, mixing and hybridization of electronic states, charge transfer, and polarization, will be discussed in the context of the large organic adsorbate pentacene. Notably, our study aims to reveal the role of the surface state in the pentacene on copper adsorption, which has been recently unraveled to deviate from the simple chemisorption/physisorption schemes for pentacene on Cu(119).[21] The modification of surface states depends on the properties of both the organic molecules and the metallic substrates and strongly relies on the nature and the strength of the bonding and the electronic coupling at the interface.

II. EXPERIMENT

The ARPES measurements have been performed at the high-resolution photoelectron spectroscopy (HRPES) end station of the surface/interface spectroscopy (SIS) beamline at the Swiss Light Source (SLS), Paul Scherrer Institut, Villigen, Switzerland. The data have been recorded with a Scienta SES 2002 electron energy analyzer in the angular mode with the sample kept at room temperature. The analyzer was oriented in such a way that the angular dispersive direction was perpendicular to the polar rotation axis of the sample manipulator (i.e., the theta axis). Therefore, a full two-dimensional (2D) Fermi-surface (FS) map of the surface state was obtained by performing subsequent theta scans with the azimuth of the sample kept fixed along the $\bar{\Gamma}$-$\bar{Y}$ direction. All data presented in this paper were obtained with a photon energy of 40.8 eV using *p*-polarized light. This particular photon energy was selected for optimum signal-to-background ratio of the surface state. The energy and angular resolution were estimated to be about 20 meV and 0.3°, respectively.

The Cu(110) single crystals were cleaned by repeated cycles of Ar^+ sputtering and subsequent annealing to 750 K until no carbon and no oxygen were found in photoemission spectra. The pentacene was thermally evaporated onto the Cu(110) crystals while they were kept at room temperature. After preparation and characterization by low-energy electron diffraction (LEED) and STM, the pentacene-covered samples were transferred in a portable vacuum chamber to the HRPES end station. Typical transfer times were 5–6 h, during which the pressure stayed in the low 10^{-10} mbar range.

During the ARPES measurements the exposure time of the sample to the synchrotron light was optimized in order to avoid radiation damage. Additionally, for each new theta value the sample was moved by 0.1 mm along the theta axis to always provide a fresh sample surface. After the ARPES measurements the sample quality was checked again by STM and LEED, which confirmed the absence of significant sample degradation. Further, laboratory-based x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were performed to determine the pentacene coverage and the work function.

III. PHASE BEHAVIOR OF PENTACENE ON Cu(110)

The here reported STM study on the adsorption of pentacene on Cu(110) agrees well with earlier results[22,23] and discloses a complex multiphase behavior at room temperature, described in more detail elsewhere.[24] In contrast to earlier studies on pentacene on Cu(110) the samples have always been kept at room temperature, both during and after the pentacene deposition. For coverages below 0.6 monolayers (ML), STM reveals a disordered phase of highly mobile pentacene molecules. At 0.8 ML coverage extended, ordered molecular layers with limited long-range order can be identified in which the molecules are oriented with their long axis parallel to the $[1\bar{1}0]$ direction. The side-by-side distance of the molecules is twice the substrate lattice spacing, which is confirmed by sharp LEED half-order spots. Along the $[1\bar{1}0]$ direction the spacing of the molecules shows some variation with an average distance of 7 Cu-Cu atom distances. Hence, LEED shows a (7×2) structure where the superstructure spots along $[1\bar{1}0]$ are smeared out along [0 0 1]. At higher coverage (1 ML), a well-ordered (6 −1, 1 4) structure is formed, which appears in two mirror domains tilted by ±9° with respect to the [0 0 1] direction. The STM and LEED data as well as the corresponding structural models of these two phases are shown in Fig. 1.

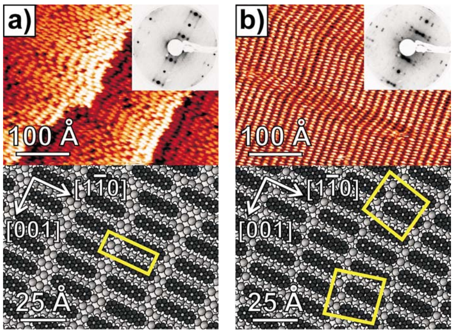

FIG. 1. (Color online) Observed adlayer structures for submonolayer and monolayer coverages of pentacene on Cu(110): (a) 0.8 ML; (b) 1.0 ML. Top: STM images 30×40 nm^2. Insets: corresponding LEED patterns taken at (a) 53.5 and (b) 63.0 eV. Bottom: structural models with unit cells marked in pale gray (yellow).

IV. Cu(110) SURFACE-STATE MAPPING AS A FUNCTION OF PENTACENE PHASE

In Fig. 2 we present the ARPES data of the surface state around the $\bar{Y}$ point of the surface Brillouin zone (SBZ) obtained on the clean Cu(110) surface. A parabolic shape of the surface-state band is observed along both high-symmetry directions $\bar{\Gamma}$-$\bar{Y}$ and $\bar{Y}$-$\bar{S}$ with a binding-energy minimum of $E_0 \approx 400$ meV. Different effective masses were measured in the two high-symmetry directions: $m_X^*/m_e = 0.40 \pm 0.01$ and $m_Y^*/m_e = 0.28 \pm 0.01$ along $\bar{Y}$-$\bar{S}$ and $\bar{\Gamma}$-$\bar{Y}$ directions, respectively (see Fig. 2). These values are in good agreement with data available in the literature[25] and reveal an anisotropy in the FS contour appearing in elliptical shape with the long axis along $\bar{Y}$-$\bar{S}$, which was also confirmed by STM studies.[26] The FS anisotropy is closely related to the Cu(110) surface

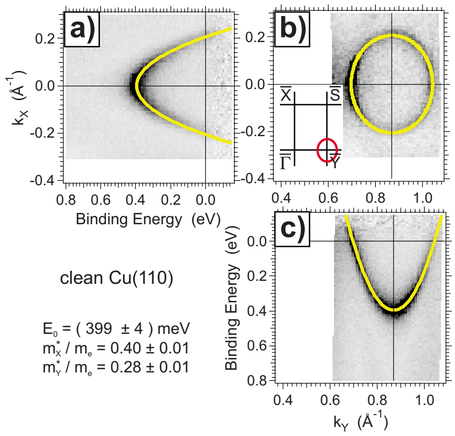

FIG. 2. (Color online) Dispersion of the $\bar{Y}$ surface state of the clean Cu(110) surface. (a) Dispersion along $\bar{Y}$-$\bar{S}$. (b) Cut through the $\bar{Y}$ surface state at the Fermi energy. Inset: sketch of the upper-right quadrant of the surface Brillouin zone with the Fermi line of the surface state marked in gray (red). (c) Dispersion along $\bar{\Gamma}$-$\bar{Y}$. The grayscale plots represent the photoelectron intensity after normalization by a Fermi step function and conversion to *k*-vector scale (dark corresponds to high intensity). The pale gray (yellow) lines mark the fit of a paraboloid to the experimental data.

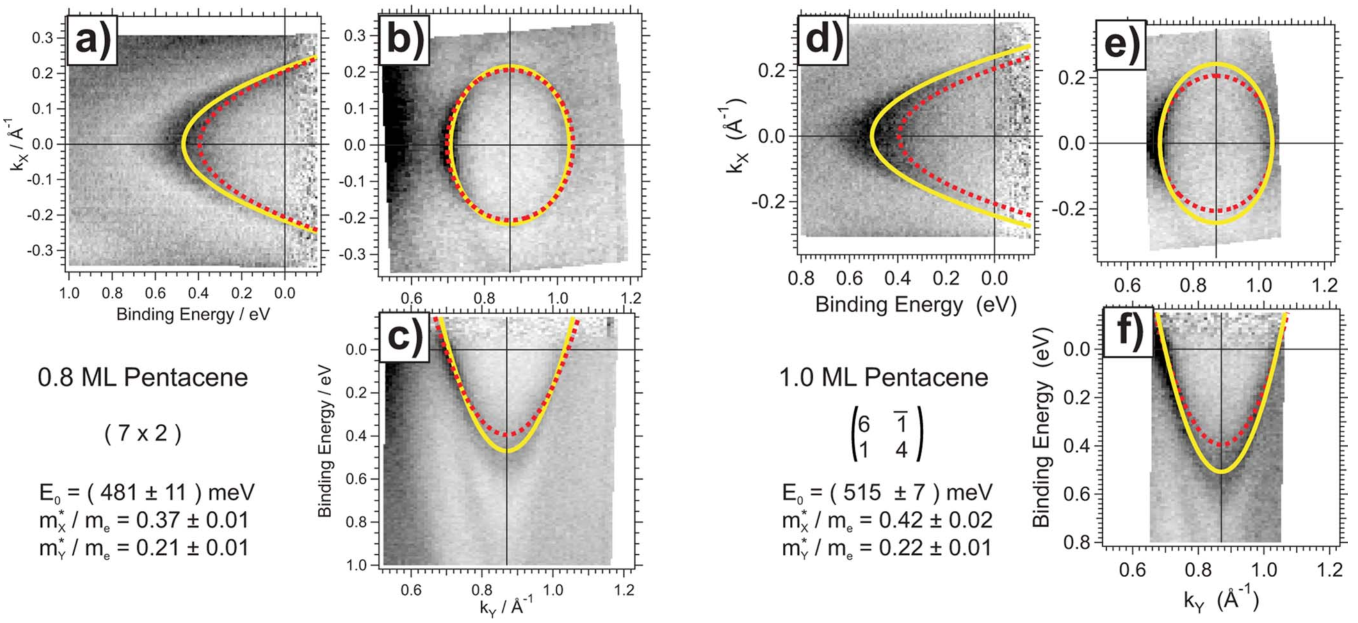

FIG. 3. (Color online) Dispersion of the $\bar{Y}$ surface state of a Cu(110) surface, covered with (a)–(c) 0.8 ML pentacene and (d)–(f) 1.0 ML pentacene. The straight lines marked in pale gray (yellow) mark the fit of a paraboloid to the experimental data. The dotted lines marked in gray (red) correspond to the paraboloid fitted to the experimental data of the clean Cu(110) surface from Fig. 2.

geometry presenting a twofold symmetry. Indeed, the bulk band gap projected on the (110) SBZ results in anisotropic behavior, i.e., a gap diameter shorter in the $\bar{\Gamma}$-$\bar{Y}$ direction than in the $\bar{Y}$-$\bar{S}$ direction.[25]

Adsorption of pentacene at coverages of 0.8 and 1 ML leads to a shift of the surface-state band to higher binding energies and to a change in the effective masses of the surface-state electrons. In Fig. 3 the corresponding ARPES data are presented. The bottom band energy was found at 481 meV for the (7×2) phase and at 515 meV for the (6 −1, 1 4) phase. While the effective mass in the $\bar{\Gamma}$-$\bar{Y}$ direction decreases for both the (7×2) and the (6 −1, 1 4) phases, the effective mass in the $\bar{Y}$-$\bar{S}$ direction decreases for the (7×2) phase and increases for the (6 −1, 1 4) phase. As a consequence, the Fermi wave vectors of the Shockley surface state are similar for the (7×2) phase compared to the ones obtained on clean surfaces, whereas for the (6 −1, 1 4) phase the Fermi wave vector increases along the $\bar{Y}$-$\bar{S}$ direction, leading to a higher anisotropy of the FS. Thereby the Fermi line for the (6 −1, 1 4) phase encloses a larger fraction of the SBZ than for the clean surface [Fig. 3(e)], which means that the population of the surface state is increased. These results are also confirmed by Martínez-Blanco *et al.*[27,28]

Provided that the area of the whole surface Brillouin zone corresponds to two electrons per surface copper atom (spin up and spin down), this increase corresponds to 0.034 ± 0.016 electrons per surface copper atom. Assuming for the pentacene surface density the value of 0.08 pentacene molecules per surface copper atom taken from the presented model [Fig. 1(b)], this would correspond to 0.43 ± 0.20 electrons per pentacene molecule.

In addition to the ARPES measurements on the surface-state modifications, the change in the work function has been measured, by measuring the positions of the cutoff in the secondary electrons' background in the UPS spectra before and after adsorption of a pentacene monolayer. We observed a reduction in the work function of about 0.9 eV,[29] which is confirmed in Ref. 30 and indicates the formation of a surface dipole, likely induced by a charge transfer from the molecule to the substrate.

V. DISCUSSION

Only few systems have been reported yet where the surface state survives upon deposition of an adsorbate with considerable (e.g., π-metal) interaction, at the submonolayer up to the highly packed monolayer coverage. For example, it has recently been reported that adsorption of a PTCDA monolayer on Ag(111) leads to a huge shift of the surface state up to 0.6 eV above the Fermi level, induced by the strong bonding at the interface.[31] In contrast, the case of pentacene/Cu(110) shows a smaller shift, which indicates that the metallic electronic states are not strongly affected by the presence of the pentacene layer. On the other hand, the modification of the surface-state properties (binding energy and effective mass) implies that the interaction at the interface cannot be considered weak and therefore suggests a complex interaction between the metallic states and the molecular orbitals, being neither pure physi- nor chemisorption.

For the here presented experiments of pentacene on Cu(110) the modification of the surface state emerges from the complex interplay of different phenomena. In fact, when an adsorbate is resting on a surface, the surface dipole can be modified by (i) the different charge distributions of positive core and negative electronic charges (jellium model),[32] (ii) charge transfer,[13,14] (iii) mixing and hybridization of electronic states,[20,21,33] (iv) Pauli repulsion,[11,12] and (v) "mutual polarization."[34,35] These are all simplified interaction schemes which are interdependent and therefore difficult to separate. Additionally, coupling between neighboring adsorbates, which can influence the electronic states, may originate from (vi) the increasing delocalization of molecular states with increased molecular packing and (vii) band alignment and band bending.[36,37] The complex interplay of the different phenomena affecting both the geometry and the electronic structure in a large unit cell makes calculations very complex and time consuming. The relative importance of the factors influencing the surface state in our experiments is therefore discussed qualitatively in the following paragraphs.

In the first part of the discussion we are going to concentrate on the influence of the coupling between neighboring adsorbates on the surface state. The data presented in Fig. 3(e) exhibit an increase in the anisotropy in the Fermi-surface shape (increase in k_F along the $\bar{Y}$-$\bar{S}$ direction). This increase appears more significant at the full monolayer coverage than at 0.8 ML, an observation which can be related to the packing of the molecular adlayer. Specifically, as shown in Fig. 1(b), a well-ordered, long-range periodic structure is obtained at maximum packing density of the first pentacene monolayer. Along the [0 0 1] direction the distance between the pentacene molecules, i.e., the packing density, is the same for the (7×2) phase and the (6 −1, 1 4) phase, which corresponds to the separation of two Cu atoms in this direction. In the $[1\bar{1}0]$ direction, which corresponds to the $\bar{Y}$-$\bar{S}$ direction in SBZ instead, the packing density increases with increasing coverage, i.e., the distance between two neighboring molecules is 15.76 Å for the (6 −1, 1 4) structure compared to 17.9 Å for the (7×2) structure.

In a recent calculation for two adjacent pentacene molecules held in the vacuum, the onset of intermolecular interaction in vacuum is found at a separation of 16.5 Å between the two molecules.[38] Thus, intermolecular interaction along the $[1\bar{1}0]$ direction has to be expected also for surface-supported molecules within the (6 −1, 1 4) layer and potentially leads to the formation of an electronic band. Such an electronic band may modify the electronic potential felt by the surface-state electrons and may thus affect the occupation of the surface state. The correspondence of the close-packed direction ($[1\bar{1}0]$) of strongest interaction with the induced change in the Fermi wave vector in the $\bar{Y}$-$\bar{S}$ direction provides support for such a relation.

Three distinct mechanisms have been proposed for the modification of noble-metal surface states by adsorbed rare gases (Pauli repulsion), alkali metals (charge transfer), and other noble metals (change of the noble-metal character).[39] For adsorbed rare gases on noble-metal (111) surfaces the Shockley surface state shifts to lower binding energy, which has been attributed to the Pauli repulsion between the surface-state electrons and the closed shell of the rare-gas atoms. This repulsion pushes the surface-state electrons toward the bulk, thereby destabilizing the surface state and thus lowering its binding energy.

For alkali metals adsorbed on (111) and (110) noble-metal surfaces, the surface state shifts to higher binding energies as long as there is no adsorbate-induced surface reconstruction formed.[14] The highly electropositive character of the alkali metals leads to an electron transfer from the adsorbate to the substrate, thereby decreasing the electrostatic potential in the surface region. Consequently, the electrons of the surface state are pulled toward the surface so that the surface state is stabilized and its binding energy increases.

Similar to the case of rare-gas adsorption, the surface-state electrons are repelled by the valence electrons of the pentacene adsorbed on Cu(110). However, this is not the main contribution to the modification of the surface state in this case, as it shifts to higher binding energies instead toward the Fermi level as is the case for rare gases. In contrast to rare-gas adsorption, the frontier orbitals in organic molecules are energetically closer to the Fermi level, which enables interaction with the electronic states of the substrate. Therefore, charge transfer, mixing of electronic states near the Fermi level, and covalent bonding between the adsorbate and the substrate are possible.

Our observation of an increased population of the surface state for the (6 −1, 1 4) phase may indicate a charge transfer between the pentacene molecules and the surface state. On the other hand, the population increase could also be induced by the highly packed molecular layers, which may only affect the mixing between surface and bulk states. Notably, the fact that the population of the surface state is not increased for the (7×2) phase with respect to the clean surface, although the binding-energy shift is almost as high as for the (6 −1, 1 4) phase, can be an indication that the shift of the surface state is more probably due to the mixing of the electronic states than due to pure charge transfer.

The direction of a possible charge transfer between the molecule and the surface can be estimated from the chemical potential of the adsorbate and the substrate as reported by Lindell *et al.*[40] This estimate, however, does not consider local surface physical properties, such as the surface and step states. The chemical potential of metals is the opposite of the work function, i.e., in the case of Cu(110)$\mu_{\mathrm{Cu}(110)}=-4.5$ eV.[29] For organic molecules the chemical potential can be estimated by $\mu=-(\mathrm{IP}+\mathrm{EA})/2$. For pentacene the ionization potential (IP) ranges from 5.9 to 6.6 eV.[41–43] The electron affinity (EA) is reported to be between 1.1 and 1.5 eV.[41,42] For these values the chemical potential of pentacene ranges between −4.05 and −3.50 eV. A possible electron transfer will occur in the direction from the species with higher chemical potential to the one with lower chemical potential, in our case in the direction from the pentacene to the Cu(110) substrate.

It is important to note that the charge transfer between the adsorbate and the substrate does not exclusively involve the surface state. Some charge could also be transferred directly to the bulk states; e.g., Baldacchini *et al.*[44] showed that there is a strong interaction of the pentacene π orbitals with Cu(100) and Cu(119) d bands. But this is a phenomenon which is only to be assessed in a detailed numerical study which goes far beyond the scope of this experimental report on a rather novel electronic interaction.

In the following we compare the case of PTCDA on Ag(111) and on Au(111) with our observations. In contrast to pentacene adsorption on Cu(110), for PTCDA adsorption on Au(111) the surface state is shifted to the opposite direction, i.e., to lower binding energy, and remains occupied.[18,19] For PTCDA adsorption on Ag(111) the surface state is strongly shifted above the Fermi level.[31] This shows that our observation of a binding-energy increase after adsorption of a large organic molecule is unexpected. For PTCDA on Au(111), LEED,[45] work-function measurements,[18] and x-ray standing-wave experiments[46,47] indicate that PTCDA is weakly physisorbed. Therefore, the interaction between the molecules and the substrate is considerably different compared to the pentacene/Cu(110) system. In contrast, PTCDA is strongly chemisorbed on Ag(111) via the central carbon ring,[48] which results in an electron transfer from the substrate to the molecule.[40,49] Notably, the UPS spectrum of PTCDA adsorbed on Ag(111) reveals an additional band near the Fermi level arising from the partially filled lowest unoccupied molecular orbital (LUMO) of the adsorbed molecules due to an electron transfer from the substrate to the molecules.[49] Moreover, it has been reported that free-electron-like unoccupied states are developed in the PTCDA overlayer mediated by the valence electrons of the Ag(111) substrate.[50] Later, these electronic states have been identified to be the Shockley states modified upon the adsorption of the PTCDA monolayer.[31] Thus, we conclude that the interaction strength of the pentacene with Cu(110) is stronger than the one of PTCDA/Au(111) and weaker than the one of PTCDA/Ag(111).

The complex interaction mechanisms of the pentacene with the Cu(110) surface make it difficult to classify the adsorption in terms of physisorption or chemisorption. On one hand, if there is a charge transfer between the molecule and the substrate or mixing of the substrate and adsorbate electronic states, this is typically associated to weak chemisorption. On the other hand, if the modification of the surface state is induced by mixing and hybridization of electronic bulk states with the surface state in the presence of the adsorbate, this may be associated to strong physisorption.

Besides direct measurements of the local density of states within the surface state by STM,[47] ARPES is an ideal probe for learning about the interaction at the interface and provides featured information. For PTCDA/Au(111), the major factor for the modification of the surface state is the Pauli repulsion leading to a shift of the bottom band by about 40 meV to lower binding energy. This energy shift is much higher for a PTCDA monolayer on the Ag(111) surface (of about 660 meV) due to the strong interaction at the interface. In the case of pentacene on Cu(110) the complex substrate-molecule and intermolecular interactions lead to a shift of the binding energy as well as to an increase in the occupation of the surface state for the 1 ML covered sample.

VI. CONCLUSION

In conclusion, the pentacene/Cu(110) interface provides a model system exhibiting a shift of the Cu(110) Shockley surface state to higher binding energies upon adsorption of a well-ordered molecular monolayer. Besides this binding-energy increase we also observe an increase in the population of the surface state for the (6 −1, 1 4) phase, which we associate either to an electron transfer to the substrate or to surface state/bulk state mixing.

The complex interplay of surface and molecular states has been related to the combination of a number of phenomena: Pauli repulsion, charge transfer, mixing and hybridization of electronic states, and polarization as well as coupling of neighboring molecules. The interrelation of these phenomena as they manifest themselves in the here presented experiments motivates *ab initio* calculations to deepen the understanding beyond the current discussion.

Furthermore, the measurement of surface-state modifications upon adsorption is a complementary and direct probe of the electronic processes occurring at the organic-metal interface compared to the more common investigations of molecular orbitals at surfaces by STM,[51] STS,[52] and (inverse) photoemission techniques.[53,54] The behavior of the surface state can thus be used as a probe for the adsorbate/substrate interaction, thereby providing additional information about the properties of electronic interfaces toward applications in organic electronic devices.

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