Valence band photoemission from the Zn-phthalocyanine/Ag(110) interface: Charge transfer and scattering of substrate photoelectrons

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The electronic properties of Zn-phthalocyanine vacuum deposited on Ag(110) are studied by high-resolution valence-band photoelectron spectroscopy. Submonolayer, one ordered monolayer, and molecular layers of increasing thickness present spectral features that can be related to the molecule-substrate interaction as well as to the effect of the overlayer on the escape conditions of the substrate photoelectrons. For the first-ordered molecular layer, an interface state related to a charge transfer from the substrate to the molecules is detected through the appearance of a new feature at low binding energy. Such feature, appearing already at submonolayer coverage, is interpreted as the partial filling of the lowest unoccupied molecular orbital (LUMO) and to possible hybridization of the LUMO with substrate states. Because it is the major change observed in the molecular electronic structure after adsorption, the filling of the LUMO is likely to have a major role in the molecular chemisorption. The spectral line shape of the filled part of the LUMO is discussed in terms of electron-vibron coupling and electron correlation effects. Molecular states lying at higher binding energy show spectral modifications as a function of coverage implying a weaker contribution in the molecule-substrate interaction. Important changes are found in the spectral region of the Ag 4d band after the deposition of a submonolayer and as a function of coverage although no interface states are detected. It is shown that these features can be entirely explained by considering the effect of the molecular overlayer on the escape conditions of the substrate photoelectrons. The major effect is the emerging of the substrate three-dimensional density of states. Such evidence is not simply related to the present case but it is expected to apply to other systems where an organic layer is deposited on a single-crystal substrate.

I. INTRODUCTION

The electronic and optical properties of organic thin films depend sensitively on the interface nature between the active layer and the hosting support.[1–3] This recognition has stimulated important efforts in the study of model systems among which the interface of pi-conjugated molecules vacuum deposited on single-crystal noble-metal surfaces is a natural starting point.[4] On these surfaces, the formation of ordered molecular layers is currently obtained. Moreover, at room temperature (RT), the molecules may diffuse on the substrate surface and nanostructuration is possible via intermolecular interactions.[5,6]

Electron spectroscopies are fundamental tools to explore the electronic properties of interfaces. For instance, the modification of frontier molecular orbitals and the appearance of hybrid states at the interface can be detected by valence-band (VB) ultraviolet photoelectron spectroscopy (UPS) probing, to a first approximation, the density of states (DOS) of the first surface atomic layers.[3] Furthermore, combining UPS with interface DOS calculations is a powerful means since hybrid states can be projected on the atoms at the interface thus revealing the origin and nature of UPS features.[7–9]

Recent experiments have shown that a deeper understanding of the phenomena occurring at the organic-inorganic interface can be achieved by analyzing the interface-band energy dispersion as a function of electron wave vector.[10–12]

The study of low-energy excitations is also of great relevance. The modification of the rich vibrational structure of pi-conjugated molecules can give a measure of the bonding strength as well as reveal electron-vibron couplings having important consequences on the interface electronic properties.[13–15]

Metal-phthalocyanine (M-Pc) have been the subject of particular attention[16,17] because of their thermal stability, optoelectronic properties, and the presence of the central metal atom whose orbital and spin moments can be exploited to magnetic purposes.[18] Moreover, the presence of a doubly degenerate lowest-unoccupied molecular orbital (LUMO) renders M-Pc a peculiar case among medium-size organic molecules. Theoretical studies have suggested that electron doping of nonmagnetic-metal-Pc may result in electron systems whose correlation properties would resemble those of fullerides.[19] Particularly, close to the LUMO half filling a metallic state would be precursor of a superconducting phase at low temperature. Nevertheless, although doping of M-Pc is successfully achieved by alkali-atom intercalation of thick films, the presence of a metallic state is still under debate and, up to now, has not been observed by UPS.[20,21]

Ordered layers of M-Pcs on noble metal substrates show a great variety of behaviors depending on the metal atom at the center of the molecule,[22–24] the possible molecular peripheral functionalization[25,26] or the crystallographic face of the substrate. Interestingly the charge transfer from the substrate in such systems may represent an alternative way to electron dope the M-Pc.[15,26,27]

The ZnPc/Ag(110) interface, the subject of the present paper, shows some intriguing behaviors. In a recent study, high-resolution electron energy-loss spectroscopy (HREELS) performed on one ordered monolayer (ML) and a thick film of ZnPc/Ag(110) showed that the interface formation induces important modifications of the molecular electronic and vibrational properties.[15] Namely, at ML coverage the infrared part of the loss spectra showed the presence of Raman-active modes strongly coupled with molecule-metal interface states.

The present study reports on the UPS measurements of the ZnPc/Ag(110) interface electronic properties. High-resolution UPS on molecular layers of growing thickness enable to discern the spectral features characteristic of the clean substrate, the thick molecular film and the interface. In the following, after having described the experimental conditions, the valence-band spectra in two different energy ranges will be presented. In the wide range spectra, a crucial role is played by the intense Ag 4*d* bands even after molecular adsorption. In the zoom of the low binding-energy (BE) region, the behavior of the frontier orbital will be addressed.

II. EXPERIMENT

The experiment was performed in ultrahigh vacuum at the BaD ElPh beamline of the Elettra synchrotron radiation facility (Trieste). The beamline[28] is especially designed for low-energy, high-resolution photoemission experiments. The photons from a figure-8 undulator are energy selected by a normal incidence monochromator with a resolving power up to 40 000 at about 21 eV.[28] All measurements were performed with the sample at RT and using photons of 21 eV. The spectra were collected in normal emission and constant pass energy by a Phoibos 150 electron energy analyzer with an angular acceptance of $\pm 7°$. In all spectra, the electron binding energies are referred to the sample Fermi level. The energy resolution of the photoemission (PE) spectra is about 100 meV, limited by the thermal broadening. The Ag(110) sample was cleaned by repeated cycles of sputtering and annealing. The surface cleanliness and order was evaluated by low-energy electron diffraction (LEED) and by monitoring the Shockley-type surface state located at $\bar{Y}$ in the reciprocal space. The ZnPc molecules were deposited *in situ* by sublimation from an electronically bombarded molybdenum crucible. The depositions were performed at low rate so that 1 ML coverage was reached after about 2 min deposition. The Ag(110) sample was mounted on a vertical manipulator with 4 degrees of freedom, three translational and the rotation around the vertical axis. The sample azimuthal orientation was such that the Γ-*K*-*L*-*U*-*X* plane was in the horizontal scattering plane, i.e., that of the linear synchrotron light polarization. The angle between the synchrotron radiation and the electron energy analyzer is 50°.
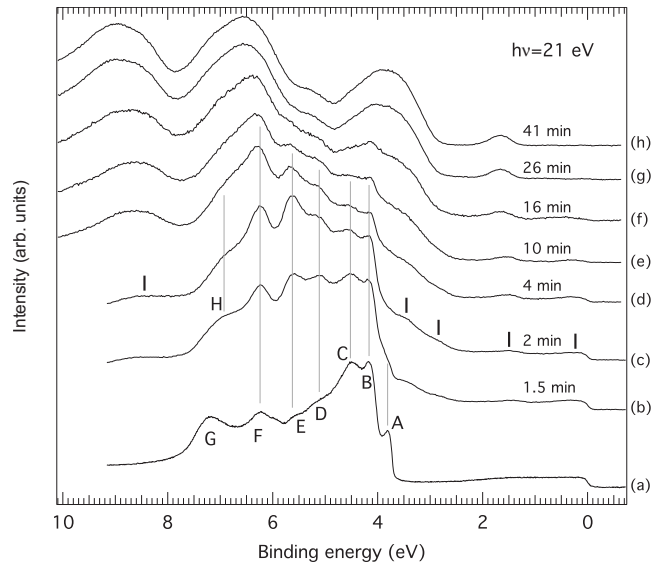

FIG. 1. Normal emission, valence-band spectra taken with 21 eV photons of the clean Ag(110) surface (a), and subsequent depositions of ZnPc/Ag(110). Gray vertical lines are intended as a guide to the eyes to follow the evolution of the Ag 4*d* features as a function of coverage. Spectrum (c) correspond to 1 ML ZnPc/Ag(110) where a LEED pattern was observed; short bars identify molecular states for 1 ML coverage; their evolution is discussed in the text. The uppermost spectrum corresponds to a thick film.

III. RESULTS

A. Valence band: The high binding-energy region (BE=2.5–10 eV)

Figure 1 shows a series of valence-band spectra of ZnPc/Ag(110) taken at 21 eV photon energy. The bottom spectrum (a) is the clean Ag(110) substrate; the region between 3.8 and 8.0 eV is dominated by the Ag 4*d* bands whose main features will be described later on in the present section; the *sp* bands dominate the energy distribution curve (EDC) at lower binding energies. The other reported spectra are those of ZnPc/Ag(110) at increasing film thickness. The uppermost spectrum corresponds to a thick film where the molecules are interacting weakly among each other without any sign of the molecule-substrate interaction. The spectrum is then completely due to ZnPc molecular orbitals; these are broader than the Ag 4*d* states and extend to a wider energy range.

Both the Ag(110) and ZnPc thick film spectra are in very good agreement with previous measurements.[29,30] As in the case of other closed *d*-shell metal-Pc, the ZnPc thick film spectrum (h) presents a sequence of smooth features largely due to the organic macrocycle. A detailed description of the ZnPc VB in terms of atomic composition can be found elsewhere.[29] In the following, we will only focus on the two pi-type features at low BE (centered at about 1.7 eV and 3.9 eV, respectively) since they are likely to be more sensitive to the molecule-substrate contact and because they are clearly discernible being superposed to the low-intensity Ag *sp* band. The peak at the lowest BE is the nondegenerate highest occupied molecular orbital (HOMO) having a 1*u* symmetry. Because it is well detached from the rest of the VB its BE

and shape are often studied as a function of coverage or doping to get insight on the electronic-structure evolution. The wave function of HOMO is mostly due to carbon atoms of the benzene and pyrrole cycles; in spectrum (h) its BE is 1.66 eV and its full width at half maximum is 0.47 eV. At higher BE ($\sim$3.9 eV), there is a strong feature that partially overlaps in energy with the Ag 4d bands of the clean substrate. It is due to electronic states coming from the organic macrocycle as well as from the states having some contribution from the central metal atom.[22,29,31,32]

We will now shortly describe the spectrum of the clean Ag(110) surface, starting with the 4d bands whose main features are labeled from A to G. Previous studies[30,33] performed in normal emission reported spectra very similar to spectrum (a) in Fig. 1. Differences in the relative intensity of some features can be ascribed to matrix element effects due to different experimental geometries. Although some direct transition peaks are expected to occur in the spectrum,[33] all the features of the Ag 4d bands can entirely be explained in terms of one-dimensional DOS (1D-DOS) or Van Hove singularity features.[30] Indeed, the relative insensitivity of most of the structures to photon energies close to one employed in the present study precludes their attribution to the bulk k-conserving direct transitions only.[30] Rather, the PE spectra show a striking overall agreement with the 1D DOS of the bulk band structure in the direction normal to the surface. This is the so-called "surface photoelectric effect," which originates from the ∇A term in the Hamiltonian and the matrix element describing the interaction between the electromagnetic vector potential A and one electron in the solid.[34] Although in dipole approximation the dominant term $A\nabla$ gives rise to k-selective optical transitions (also referred as direct transitions or vertical transitions), the often neglected ∇A term cannot be ignored to properly account for the measured EDC in high-resolution spectra of single-crystal surfaces. This is due to the fact that at the surface, the strong dielectric change between vacuum and the metal induces a corresponding discontinuity in the component of the vector potential perpendicular to the surface. Consequently, the matrix element between any initial state and final states can be nonzero, provided that both states have a nonvanishing wave function at the surface. Since this second term is unselective in $k_\parallel$, the resulting PE spectrum in normal emission reflects the 1D DOS in the direction normal to the surface. Finally we remark that at these photon energies surface photoemission in normal emission is particularly important for Ag(110) face. In fact, energy-conserving final states are only available in bands centered at the $(1,1,1)$ and $(1,1,-1)$ lattice points and—at variance to what observed for (111) and (100) faces—emission at the surface normal can than take place only through secondary cones.[30,34] The lower-lying sp band extending down to the Fermi level will be described in more detail in Fig. 2.

We will now follow the intensity evolution with coverage of the different features just described. Concerning the features lying within the Ag 4d bands region this will be done by keeping the same nomenclature as in spectrum (a). In fact the new features appearing after the molecular adsorption have the same BE as those of the clean Ag(110) to which they are—as we will see—closely related.
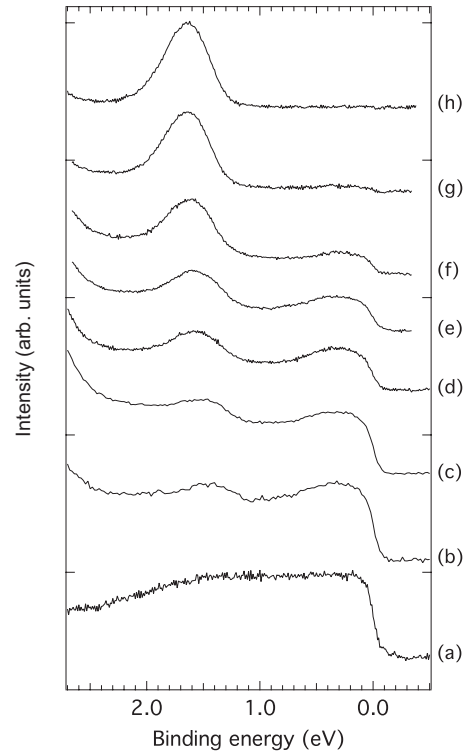

FIG. 2. Detail of the valence band at low binding energies. Spectra were taken in normal emission with 21 eV photons. As in Fig. 1, from bottom to top, the clean Ag(110) surface and subsequent depositions of ZnPc/Ag(110) are displayed.

In spectrum (b), an amount of molecules corresponding to less than 1 ML was deposited and no LEED pattern was observed at this stage. The first molecular layer is expected to grow in a disordered phase of increasing density up the monolayer completion in the proximity of which an ordered phase is observed.[15] By comparing the nominal coverage of spectrum (b) and (c) (the latter corresponding to one ordered ML, see below), one may estimate the coverage obtained with the first deposition to be close to 0.75 ML. Such estimation is confirmed by the spectral intensity of the molecular and substrate-related states (see discussion below).

After the first deposition, the valence band is severely modified. The spectral region of the Ag 4d bands has considerably changed: (i) three new features grew up at the same BE as D, E, and F; (ii) B and C remain mostly unchanged; (iii) A and G are almost suppressed with respect to the spectrum of the clean substrate; (iv) a new feature labeled H become apparent at high BE.

Molecular states are clearly detected aside from the Ag 4d region; they are highlighted by vertical bars in spectrum (c). At higher BE ($\sim$8.6 eV), we observe the appearance of a weak and broad feature. Because of its BE this structure clearly has a molecular origin. On the lower BE side, four features appear superposed to the Ag sp band; their origin can be inferred from the comparison with spectra of thicker films. The states lying between the Fermi level and 2 eV BE are due to a charge-transfer interface states and to the HOMO; they will be displayed and addressed more clearly in Fig. 2. Two more features appearing between 2 eV and the

onset of the Ag 4*d* bands region are visible at about 2.9 and 3.45 eV and can be related to the broad feature centered at 3.9 eV in the thick film spectrum (h).

The evolution of the spectral intensity within the energy region of the Ag 4*d* bands suggests that the effect of a molecular sub-ML is not simply a mere attenuation of the substrate photoelectrons peaks. In fact if that were the case the spectrum should be a linear combination between that of the clean Ag(110) and that coming from adsorbed molecules. Possibly, interface states due to molecule-substrate hybridization might also be observed at intermediate energies. Instead, some features of clean Ag(110) are suppressed and some others are, though to different extents, enhanced. Concerning the molecular states they are clearly detectable only aside from the Ag 4*d* bands region.

At slightly higher deposition time (c) the LEED pattern of 1 ML ZnPc/Ag(110) was observed (not shown).[15] As reported in Ref. [15], it corresponds to the presence of commensurate structural domains related by a mirror symmetry. Every domain consists of a coincidence superstructure in which a point-on-line commensurability with the substrate is met every two lattice vectors along one direction. In the corresponding spectrum (c), there is a further change in the intensity ratios of the Ag 4*d* region features. Namely, the peaks corresponding to features C and B of the clean substrate slightly decrease while those at higher BE increase in intensity the most pronounced being E. In fact in this energy region the measured spectrum is practically identical to that of polycrystalline Ag.[35] The molecular orbital states visible on both sides of the Ag 4*d* region show an evolution consistent with a higher molecular coverage. They all increase in intensity without any appreciable BE shift.

At a higher coverage, spectrum (d) is obtained. The corresponding evaporation time is twice that necessary to obtain the first full ML. For spectrum (d) and (e), within the Ag 4*d* region, at least four features are still distinguishable at the BE range of B-F features of the Ag(110) substrate. They have increasing intensity for increasing BE. Looking at the higher coverage spectra one notices that the spectral weight of molecular-orbital states in this region become more and more pronounced and contribute considerably to the background in spectrum (d); as a consequence feature F becomes more important than feature E. Eventually for spectrum (f) only feature B is clearly distinguishable.

When the coverage is raised beyond the first ML, the molecular states detected aside from the Ag 4*d* features evolve in the following way: (i) the molecular feature at high BE progressively increases in intensity and shifts to higher BE; (ii) the two features, lying just above the Ag 4*d* onset on the low BE side, also increase in intensity but their evolution as a function of coverage is more involved. In fact, starting from spectrum (d) they merge together to form a single shoulder that eventually forms the low BE side of the strong and broad feature centered at 3.9 eV for the thick film; (iii) close to the Fermi level the Ag *sp* band contribution decreases gradually with coverage and the HOMO contribution increases correspondingly. A Fermi edge was still detectable for spectrum (f) while in spectrum (g), the lowest energy feature is the HOMO.

B. Valence band: The low binding-energy region (BE=0–2.5 eV)

In Fig. [2], a detail of the region of the VB close to the Fermi level is shown. These spectra were taken just after those of Fig. [1]. A better statistics allows getting more insight in the interface electronic structure. Close to the Fermi level, the spectrum of the clean Ag(110) appears as a plateau extending up to about 1.5 eV BE. At higher BE, the intensity decreases up to the 4*d* band edge.

Considering the band-structure calculation of Eckardt *et al.*,[36] direct transitions from band 8+ to bands 6− and 8− are possible with 21 eV photon energy and are expected to appear around 1.5 eV BE. The observed EDC in spectrum (a) of Fig. [2] can then be rationalized as a superposition of the *sp* direct transitions and a DOS contribution whose intensity increases toward the Fermi level.[37]

From the very first ZnPc deposition (b) and up to spectrum (g), in this energy range the spectra are characterized by two main features: one centered at 1.4–1.6 eV and another one very close to the Fermi level. By looking at the spectra at higher coverage, the higher BE feature can be identified as the HOMO of ZnPc. On the other hand, the feature at lower BE can be assigned to the filling of the ZnPc LUMO by charge transfer once in contact with the substrate, as observed for similar systems.[11,12,26,27,38,39] We will refer to this feature as to the filled-LUMO or LUMO-derived feature. Nevertheless we keep in mind that the charge transfer is likely to be accompanied by interface hybridization between the substrate *sp* band and the molecular orbitals.

At first sight, two main aspects are evident from the series of spectra in Fig. [2]: (i) the HOMO/filled LUMO intensity ratio changes with coverage; (ii) the HOMO shifts to higher BE for higher coverage. We will show in the following that both aspects are related to the charge transfer at the interface.

An intense feature due to the filled LUMO is present close to the Fermi edge from the lowest coverage, testifying that the charge transfer sets in before the completion of the first layer. Concerning the HOMO/filled-LUMO intensity ratio, we notice that the HOMO intensity itself increases with coverage. This is expected because an increasing amount of molecules is present on the surface and the inelastic mean-free path for the photoelectrons is such that the entire film thickness is probed, at least up to spectrum (g). The finite probing depth also explains the fact that the intensity close to the Fermi level decreases as a function of coverage: after the first deposition the Ag *sp* contribution is screened by the first-layer molecules, causing a reduction in the EDC close to the Fermi edge. Surprisingly, the intensity in the energy region of the filled LUMO is slightly higher than that of the HOMO. This can be understood by noticing that for spectrum (c) the ratio is inverted. This suggests that the substrate spectral intensity does also change from (b) to (c). The latter is expected to have a stronger contribution in the lowest coverage spectrum. For the Ag 4*d* band, we observed that the molecular adsorption causes a three-dimensional (3D)-DOS EDC to overcome 1D-DOS and bulk direct transitions of clean Ag(110). Accordingly, we can expect the direct transitions located around 1.5 eV BE to be quenched and 3D-DOS EDC to be favored: for the *sp* band of a free-electron

metal the 3D-DOS would be proportional to $\sqrt{(E-E_0)}$, where E is the initial state energy and E_0 is the bottom of the sp band. As a consequence, the filled-LUMO intensity may appear higher than the HOMO just because of the higher substrate contribution right below the Fermi edge. Another possible explanation would imply a higher charge transfer per molecule in the sub-ML regime as recently observed by core level photoemission for SnPc/Ag(111).[39]

Spectrum (c) is that of one ordered ML ZnPc/Ag(110). The intense LUMO-derived feature testifies of a charge transfer at the interface in agreement with HREELS measurements. As mentioned above, the intensity of the HOMO becomes stronger than the filled LUMO. Nevertheless, as observed in similar systems, the HOMO/filled-LUMO intensity ratio is surprisingly low,[26] suggesting a sizable hybridization of the filled LUMO with substrate states.

In spectrum (d), the intensity is lower than in spectrum (c) all through the observed range, the valley between filled-LUMO and HOMO becomes deeper and the HOMO/filled-LUMO ratio increases. This is likely to be due to the presence of second-layer molecules. In fact, since the charge transfer is expected to be confined at the interface, from the second layer on molecules will have their LUMO completely empty. Accordingly also the substrate sp band contribution is reduced. Such behavior is confirmed at higher coverage.

The above arguments, together with the observation of the LEED pattern after the second deposition, confirm that spectrum (c) roughly corresponds to one monolayer of ZnPc/Ag(110). This conclusion is also supported by the behavior of the Ag 4d bands. In fact, the interface-related features, namely, the 3D DOS observed since the first deposition [spectrum (b) in Fig. 1], grow in intensity for the second deposition [spectrum (c)] due to the fact that a higher fraction of the substrate photoelectrons contribute to the 3D DOS EDC. For higher coverage, the molecular states become important. At first, they affect the background and subsequently smear out the Ag 3D DOS features. The latter eventually disappear at the same time as the molecular features close to the Fermi level.

Let us now analyze in more detail the behavior of the HOMO. By following the HOMO BE position as a function of coverage one notices that there is a continuous shift to higher BE in going from the interface to the thick film. This actually holds also for the molecular orbital lying at higher BE for which the shift is even larger. In fact to interpret the data two regimes need to be considered. The first concerns the molecules in direct contact with the substrate. In that case the molecular orbital BE is reduced by the screening of the electrons at the interface. As a consequence the HOMO-LUMO energy difference (about 1.5 eV) appears considerably reduced with respect to that of a thick film [about 3.1 eV (Ref. 40)]. For the second and further layer molecules, the screening is less effective. Moreover, since the molecular orbitals of the thick film are expected to be aligned to the vacuum level, they gradually shift to higher BE.

Interestingly the HOMO width (0.47–0.5 eV) does not change appreciably in going from spectrum (c) to higher coverage spectra. This negligible broadening of the HOMO at the interface testifies a very weak contribution of the HOMO in the molecule-substrate interaction.

IV. DISCUSSION

A. Valence band: The high BE region (BE=2.5–10 eV)

The data presented in the previous section show that once the ZnPc/Ag(110) interface is created, the spectral signature of either the clean substrate or the pristine molecule change considerably.

The spectral modifications occurring within the energy region of the Ag 4d bands render the spectrum of 1 ML ZnPc/Ag(110) extremely similar to that of polycrystalline silver, i.e., it primarily reflects the Ag 4d DOS. Remarkably, the effect is already visible at sub-ML coverage. The molecular orbitals certainly contribute to the EDC but they are not clearly discernible in this energy range because of their low intensity compared to the Ag-derived peaks. On the other hand, the presence of the molecules deeply affects the photoemission from the substrate. This is not surprising since even in the case of a weak interaction, the presence of the adsorbate is expected to modify the escape conditions for substrate photoelectrons. Provided that the adsorbate forms a regular lattice, a new set of k-conserving transitions become available. The process is sometimes referred to as "surface-umklapp" and can be seen as the diffraction of substrate photoelectrons by the periodic potential induced at the interface by the molecule-substrate interaction, accompanied by a $\boldsymbol{G}_\parallel$ momentum transfer so that $\boldsymbol{k}_\parallel^{Ext}=\boldsymbol{k}_\parallel^{in}+\boldsymbol{G}_\parallel$. The result here is the appearance of new spectroscopic features that were inhibited in the clean substrate spectrum. The presence of these features can be predicted by considering the new periodicity induced by the presence of the adsorbate. This has been done, for instance, in the case of Cu(111)/Xe or CO[$\sqrt{(3)}\times\sqrt{(3)}$]$R$30.[41] The presence of the adsorbate lattice allows probing reciprocal-lattice rods other than the $\bar{\Gamma}$-L by normal-emission photoemission.[42–44] On the other hand, when the adsorbate forms a disordered overlayer an incoherent scattering process may occur and consequently an angle averaging effect of the substrate photoelectron spectrum is observed.[45]

In the present case, after the adsorption of 1 ML of molecules, the ZnPc arrange in an ordered lattice and a coherent scattering effect (diffraction) is expected. However, because of the large lattice parameter and the presence of mirror domains, a large number of adsorbate 2D $\boldsymbol{G}_\parallel$ vectors are able to affect the escaping photoelectron, which emerges with a range of $\boldsymbol{k}^{Ext}$. In contrast to what happens for small adsorbates, several directions perpendicular to the surface are sampled, a number of direct transitions localized throughout a large range of the bulk Brillouin zone are able to contribute to the PE spectra, and a PE line-shape characteristic of a bulk 3D DOS emerges.

The effect described above is even more impressive when looking to spectra taken in different geometries, displayed in Fig. 3. In the upper panel, the Ag(110) VB spectra taken, from bottom to top, with an increasing incidence angle of the light beam are shown. In the bottom spectrum, the emission angle is 22° from the surface normal, probing the $\bar{Y}$ region. The middle spectrum is the one at normal emission while the top spectrum is measured 22° off-normal toward grazing incidence. The bottom panel shows the UPS spectra in the
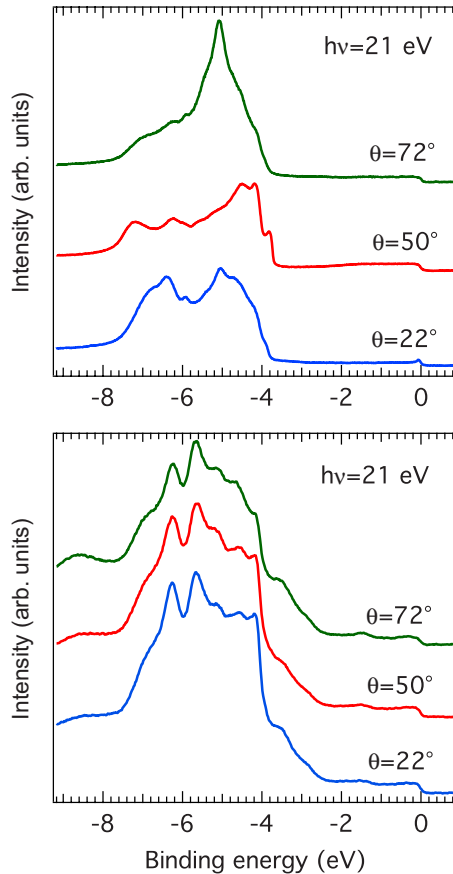
FIG. 3. (Color online) Valence-band UPS spectra taken with 21 eV photon energy of: (upper) clean Ag(110) and (bottom) 1 ML ZnPc/Ag(110). In both panels, the middle spectrum is taken at normal emission (light incidence angle $\Theta = 50°$), the upper spectrum at 22° off normal toward grazing incidence ($\Theta = 72°$) and the lower one at 22° toward normal incidence ($\Theta = 28°$).

same geometries after the deposition of 1 ML ZnPc/Ag(110). The angular dispersion effect observed in the clean Ag(110) spectra is here completely lost. This is coherent with the picture given above of a strong diffraction of the substrate photoelectrons by the adsorbate.

Interestingly, the effect of favoring 3D-DOS photoemission already appears at sub-ML coverage, where a LEED pattern was not yet observed. At that coverage, indeed very close to 1 ML, the molecules are likely forming a disordered layer and an incoherent scattering process should then be responsible for the appearance of 3D features.

Concerning the bottom spectrum of Fig. 3, a sharp feature is clearly visible close to the Fermi edge. This is the well-known Shockley-type surface state of Ag(110). After the molecular deposition, this state disappears from the spectrum. This was observed for other organic molecules deposited on silver single crystals and can be interpreted as a shift of the Shockley state to the empty states.[46]

It is interesting to note that, apart from feature H in Fig. 1, the 3D DOS peaks emerging after the adsorption of ZnPc/Ag(110) have their counterparts (approximately at the same BE) in the spectrum of the clean substrate. As mentioned in Sec. III A the normal photoemission spectrum of the Ag(110)

surface is dominated by 1D-DOS photoemission. Since these are part of the 3D-DOS transitions, it is not surprising that some of them may reinforce (D, E, F) and some other may not (A, G).

We point out that the modification of the substrate escape conditions should be observed whenever an organic molecule is deposited on a single-crystal surface and the organic-inorganic interaction is appreciable.[26] Taking into account the effect described above will be of help in discerning interface states due to molecule-substrate hybridization.

Figure 1 also allows appreciating the spectral evolution of electronic states belonging to the adsorbed molecules. The feature at high BE (at about 8.6 eV BE) is largely due to sigma orbitals,[29,32] therefore it is not expected to actively participate to the interface bond. The observed shift to higher BE for increasing thickness is probably due to a different amount of final-state screening for the thick film with respect to the interface. The two states lying on the low BE side of the Ag 4*d* region are not easy to assign. If one takes into account the just mentioned screening difference, the large and broad feature appearing at 3.9 eV in the thick film spectrum should indeed set at approximately 3.45 eV BE at ML coverage and should then be related to the two first-layer features. To precisely address the observed splitting at the interface would need appropriate electronic-structure calculation of the interface DOS. Nevertheless, we can speculate that some molecular orbitals forming the feature at BE = 3.45 eV are involved in the molecule-substrate interaction. These would concern the organic macrocycle but perhaps also the central metal atom as recently pointed out from M-Pc on Au(110).[22]

B. Valence band: The low BE region (BE = 0–2.5 eV)

The analysis of Fig. 2 has enlightened a charge transfer from the substrate to the molecules showing up as a new interface DOS derived from the partial filling of the formerly doubly degenerate LUMO. This is the most prominent modification of the molecular electronic structure at the interface. As a consequence the LUMO-derived feature is a clear signature of the molecule-substrate interaction, which is likely to be covalent with charge transfer.

A charge transfer to the molecules was invoked in a recent HREELS study[15] of the ZnPc/Ag(110) interface to account for the quenching of the *Q*-band losses, and the redshift of dipole vibrational modes. In the same study, the presence of an interface plasmon feature at low energy together with the appearance of intrinsically Raman-active modes showing a Fano line shape was interpreted through a dynamical charge transfer at the interface. A natural explanation of the asymmetry of the vibrational modes is that a nonvanishing DOS at the Fermi level exists for the molecular orbital to which the vibrational modes are coupled.

The strong intensity close to the Fermi level observed in the photoemission spectrum of 1 ML ZnPc/Ag(110) confirms the LUMO filling and the formation of interface states. On the other hand, because of the presence of substrate contribution to the measured EDC, it is not clear whether the DOS related to filled LUMO extends up to the Fermi level.

It is interesting to note that other charge-transfer systems of carbon-based molecules deposited on noble metals show different behavior. For instance, for C60 on noble metals the further EDC that appears at the Fermi level after the adsorption of first-layer molecules is well above the expected substrate contribution and room-temperature spectra show maxima at less than 0.2 eV from the Fermi level.[47–49] The same trend is also observed, for instance, for pentacene on vicinal Cu(119) (Refs. [7] and [11]) and porphyrin on Ag(110).[50]

In the case of 1 ML ZnPc/Ag(110), the LUMO-derived feature does not show a maximum in the vicinity of the Fermi level but rather appears as a hump centered at about 0.3 eV from it. This can be due to different causes. On one hand, as observed for other carbon-based molecules on noble metals, the actual DOS related to the partial filling of the LUMO is likely to be concerned by a sizable hybridization with the underlying substrate electronic states.[7,9,12,38,47] In the present case such interface DOS may be rather broad showing a resonance away from the Fermi level.

Another possible explanation concerns the correlation effects on the adsorbed molecule. Although no precise measurements exist, the latter are supposed to be in the strong regime for the LUMO, given the value of unscreened intramolecular Coulomb repulsion (about 3 eV) with respect to the small expected bandwidth. When electronically doped by the substrate, the states occupying the originally doubly degenerate LUMO may form a lower Hubbard band separated in energy from its empty counterpart by action of the Coulomb repulsion. At the same time also the molecular vibrational modes and electronic states are known to be strongly coupled for ZnPc/Ag(110). As a result, the coherent part of the spectrum may suffer of an important renormalization and formation of polaronic states (due to electron-vibron coupling) at higher BE should be expected.[12] Both electron-electron and electron-phonon couplings may then contribute to the lack of quasiparticle peak in the vicinity of the Fermi level.

V. CONCLUSIONS

The valence band of thin films of increasing thickness of ZnPc/Ag(110) was studied by means of high-resolution UPS. The spectrum of the clean Ag(110) substrate and that of a thick film of molecules served as references to assign the spectroscopic features appearing after molecular deposition. Two distinct kinds of features are promoted by the molecular adsorption. The first is the appearance of the 3D density of states in the Ag $4d$ bands region. This is explained by the modification of the escape conditions for the substrate photoelectrons. The presence of the "chemisorbed lattice" creates a new set of reciprocal lattice vectors to which optical transitions toward states outside the surface become possible. Such effect, also known as surface umklapp process, can be seen as the diffraction of the substrate photoelectron by the chemisorbed molecular lattice. At submonolayer coverage, the 3D DOS features are also observed and are due the averaging effect of incoherent scattering from the disordered molecular layer.

The second feature is the appearance of new interface states, the most intense being related to a charge transfer from the substrate to the LUMO of first-layer molecules. Because this is the major modification of the electronic structure at the interface, the presence of the LUMO-derived states is a clear signature of the molecule-substrate interaction. The latter is likely covalent with charge transfer from the substrate to the molecules. Finally, at variance to what is observed for other pi-conjugated molecules adsorbed on metal substrates, the spectral line shape of the filled LUMO is not peaked in the vicinity of the Fermi level but at about 0.3 of BE. Such aspect is discussed in terms of electron-electron and electron-vibron interactions.

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[1] X.-Y. Zhu, Surf. Sci. Rep. **56**, 1 (2004).

[2] D. Cahen, A. Kahn, and E. Umbach, Mater. Today **8**, 32 (2005).

[3] N. Koch, J. Phys.: Condens. Matter **20**, 184008 (2008).

[4] S. Kowarik, A. Gerlach, and F. Schreiber, J. Phys.: Condens. Matter **20**, 184005 (2008).

[5] T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, and S. Mashiko, Nature (London) **413**, 619 (2001).

[6] G. Tomba, L. Colombi Ciacchi, and A. De Vita, Adv. Mater. **21**, 1055 (2009).

[7] A. Ferretti, C. Baldacchini, A. Calzolari, R. Di Felice, A. Ruini, E. Molinari, and M. G. Betti, Phys. Rev. Lett. **99**, 046802 (2007).

[8] C. Baldacchini, C. Mariani, M. G. Betti, I. Vobornik, J. Fujii, E. Annese, G. Rossi, A. Ferretti, A. Calzolari, R. Di Felice, A. Ruini, and E. Molinari, Phys. Rev. B **76**, 245430 (2007).

[9] M. Rohlfing, R. Temirov, and F. S. Tautz, Phys. Rev. B **76**, 115421 (2007).

[10] H. Yamane, D. Yoshimura, E. Kawabe, R. Sumii, K. Kanai, Y. Ouchi, N. Ueno, and K. Seki, Phys. Rev. B **76**, 165436 (2007).

[11] E. Annese, J. Fujii, C. Baldacchini, B. Zhou, C. E. Viol, I. Vobornik, M. G. Betti, and G. Rossi, Phys. Rev. B **77**, 205417 (2008).

[12] A. Tamai, A. P. Seitsonen, T. Greber, and J. Osterwalder, Phys. Rev. B **74**, 085407 (2006).

[13] M. Eremtchenko, D. Bauer, J. A. Schaefer, and F. S. Tautz, New J. Phys. **6**, 4 (2004).

[14] N. Ueno and S. Kera, Prog. Surf. Sci. **83**, 490 (2008).

[15] P. Amsalem, L. Giovanelli, J. M. Themlin, and T. Angot, Phys. Rev. B **79**, 235426 (2009).

[16] N. Papageorgiou, E. Salomon, T. Angot, J.-M. Layet, L. Giovanelli, and G. Le Lay, Prog. Surf. Sci. **77**, 139 (2004).

[17] F. Evangelista, V. Carravetta, G. Stefani, B. Jansik, M. Alagia, S. Stranges, and A. Ruocco, J. Chem. Phys. **126**, 124709 (2007).

[18] A. Zhao, Q. Li, L. Chen, H. Xiang, W. Wang, S. Pan, B. Wang, X. Xiao, J. Yang, J. G. Hou, and Q. Zhu, Science **309**, 1542 (2005).

[19] E. Tosatti, M. Fabrizio, J. Tobik, and G. E. Santoro, Phys. Rev. Lett. **93**, 117002 (2004).

[20] M. F. Craciun, S. Rogge, and A. F. Morpurgo, J. Am. Chem. Soc. **127**, 12210 (2005).

[21] L. Giovanelli, P. Vilmercati, C. Castellarin-Cudia, J.-M. Themlin, L. Porte, and A. Goldoni, J. Chem. Phys. **126**, 044709 (2007).

[22] P. Gargiani, M. Angelucci, C. Mariani, and M. G. Betti, Phys. Rev. B **81**, 085412 (2010).

[23] M. Casarin, M. Di Marino, D. Forrer, M. Sambi, F. Sedona, E. Tondello, A. Vittadini, V. Barone, and M. Pavone, J. Phys. Chem. C **114**, 2144 (2010).

[24] C. Stadler, S. Hansen, I. Kroger, C. Knumpf, and E. Umbach, Nat. Phys. **5**, 153 (2009).

[25] M. Koudia, M. Abel, C. Maurel, A. Bliek, D. Catalin, M. Mossoyan, J. C. Mossoyan, and L. Porte, J. Phys. Chem. **110**, 10058 (2006).

[26] L. Giovanelli, P. Amsalem, J. M. Themlin, Y. Ksari, M. Abel, L. Nony, M. Koudia, F. Bondino, E. Magnano, M. Mossoyan-Deneux, and L. Porte, J. Phys. Chem. C **112**, 8654 (2008).

[27] T. Schwieger, H. Peisert, and M. Knupfer, Chem. Phys. Lett. **384**, 197 (2004).

[28] L. Petaccia, P. Vilmercati, S. Gorovikov, M. Barnaba, A. Bianco, D. Cocco, C. Masciovecchio, and A. Goldoni, Nucl. Instrum. Methods Phys. Res. A **606**, 780 (2009).

[29] D. Schlettwein, K. Hesse, N. E. Gruhn, P. A. Lee, K. W. Nebesny, and N. R. Armstrong, J. Phys. Chem. B **105**, 4791 (2001).

[30] P. Heimann, H. Neddermeyer, and H. F. Roloff, Phys. Rev. Lett. **37**, 775 (1976).

[31] M.-S. Liao and S. Scheiner, J. Chem. Phys. **114**, 9780 (2001).

[32] N. Papageorgiou, Y. Ferro, E. Salomon, A. Allouche, J. M. Layet, L. Giovaneli, and G. Le Lay, Phys. Rev. B **68**, 235105 (2003).

[33] A. Goldmann, D. Westphal, and R. Courths, Phys. Rev. B **25**, 2000 (1982).

[34] S. Hüfner, R. Claessen, F. Reinert, Th. Straub, V. N. Strocov, and P. Steiner, J. Electron Spectrosc. Relat. Phenom. **100**, 191 (1999); G. V. Hansson and S. A. Flodstrom, Phys. Rev. B **17**, 473 (1978).

[35] M. G. Helander, M. T. Greiner, Z. B. Wang, and Z. H. Lu, Appl. Surf. Sci. **255**, 9553 (2009).

[36] H. Eckardt, L. Fritsche, and J. Noffke, J. Phys. F: Met. Phys. **14**, 97 (1984).

[37] G. Panaccione, G. Cautero, M. Cautero, A. Fondacaro, M. Grioni, P. Lacovig, G. Monaco, F. Offi, G. Paolicelli, M. Sacchi, N. Stojic, G. Stefani, R. Tommasini, and P. Torelli, J. Phys.: Condens. Matter **17**, 2671 (2005).

[38] Y. Zou, L. Kilian, A. Scholl, Th. Schmidt, R. Fink, and E. Umbach, Surf. Sci. **600**, 1240 (2006).

[39] M. Häming, C. Scheuermann, A. Schöll, F. Reinert, and E. Umbach, J. Electron Spectrosc. Relat. Phenom. **174**, 59 (2009).

[40] S. Krause, M. B. Casu, A. Schöll, and E. Umbach, New J. Phys. **10**, 085001 (2008).

[41] C. G. Larsson, J. Paul, and L. Walldén, Phys. Scr., T **T4**, 44 (1983).

[42] J. Anderson and G. J. Lapeyre, Phys. Rev. Lett. **36**, 376 (1976).

[43] V. L. Moruzzi, A. R. William, and J. F. Janak, Phys. Rev. B **8**, 2546 (1973).

[44] O. Rader and A. M. Shikin, Phys. Rev. Lett. **93**, 256802 (2004).

[45] S. A. Lindgren and L. Walldén, Phys. Rev. Lett. **43**, 460 (1979).

[46] C. H. Schwalb, S. Sachs, M. Marks, A. Schöll, F. Reinert, E. Umbach, and U. Höfer, Phys. Rev. Lett. **101**, 146801 (2008).

[47] L.-L. Wang and H.-P. Cheng, Phys. Rev. B **69**, 165417 (2004).

[48] C.-T. Tzeng, W.-S. Lo, J.-Y. Yuh, R.-Y. Chu, and K.-D. Tsuei, Phys. Rev. B **61**, 2263 (2000).

[49] A. Tamai, A. P. Seitsonen, F. Baumberger, M. Hengsberger, Z.-X. Shen, T. Greber, and J. Osterwalder, Phys. Rev. B **77**, 075134 (2008).

[50] C. Castellarin-Cudia, P. Borghetti, G. Di Santo, M. Fanetti, R. Larciprete, C. Cepek, P. Vilmercati, L. Sangaletti, A. Verdini, A. Cossaro, L. Floreano, A. Morgante, and A. Goldoni, ChemPhysChem **11**, 2248 (2010).