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Citation: *The Journal of Chemical Physics* **140**, 244704 (2014); doi: 10.1063/1.4883735

View online: <http://dx.doi.org/10.1063/1.4883735>

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Metal-phthalocyanine ordered layers on Au(110): Metal-dependent adsorption energy

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(Received 23 April 2014; accepted 3 June 2014; published online 25 June 2014)

Iron-phthalocyanine and cobalt-phthalocyanine chains, assembled along the Au(110)-(1×2) reconstructed channels, present a strong interaction with the Au metallic states, via the central metal ion. X-ray photoemission spectroscopy from the metal-2*p* core-levels and valence band high-resolution ultraviolet photoelectron spectroscopy bring to light signatures of the interaction of the metal-phthalocyanine single-layer with gold. The charge transfer from Au to the molecule causes the emerging of a metal-2*p* core level component at lower binding energy with respect to that measured in the molecular thin films, while the core-levels associated to the organic macrocycle (C and N 1*s*) are less influenced by the adsorption, and the macrocycles stabilize the interaction, inducing a strong interface dipole. Temperature Programmed Desorption experiments and photoemission as a function of temperature allow to estimate the adsorption energy for the thin-films, mainly due to the molecule-molecule van der Waals interaction, while the FePc and CoPc single-layers remain adsorbed on the Au surface up to at least 820 K. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4883735>]

I. INTRODUCTION

A promising alternative route to inorganic semiconductor devices is the assembly of organic molecules on surfaces. Planar molecules with extended π -orbitals, like phthalocyanines, adsorb in a flat geometry on surfaces, they assemble in supramolecular ordered structures, and can represent a new class of systems to design electronic devices due to their interesting electronic, optical, and magnetic properties. In particular, transition metal phthalocyanines (MPc) have attracted a lot of theoretical and experimental research, thanks to the possibility of tuning their physical and chemical properties, also involving the design of new opto-electronic devices such as light-emitting diodes, field-effect transistors, solar cells, and spin-based devices.^{1–3} MPcs are $\pi - \pi$ conjugated molecules formed by an organic macrocycle composed by four pyrrolic and four benzene rings, symmetrically arranged around a central metal ion.⁴ The presence of a transition metal ion characterized by a different filling of the *d* orbitals,^{5,6} combined with a careful choice of the substrate, strongly influences the properties of the substrate-molecule interface.^{7,8}

Long-range ordering can be improved by exploiting the patterning of suitable metallic substrates. Ordered assembling can be obtained either by using metal vicinal surfaces as template,^{9–11} or by depositing the molecules onto naturally patterned surfaces, like the Au(110)-(1×2) reconstructed surface.¹² This metallic surface is widely used as a template

to follow a bottom-up approach in the formation of highly ordered molecular films, thanks to the twofold missing-row reconstruction along the [001] direction, that can drive the formation of one-dimensional (1D) molecular chains.^{13,14} MPc adsorption on Au(110)-(1×2) leads to the formation of ordered chains along the [1 $\bar{1}$ 0] direction, with the MPc molecular plane oriented parallel to the surface.^{15,16} The planar orientation, in particular for the first single-layer (SL), is due to an interaction between the metal-phthalocyanine orbitals and the Au electronic levels.^{16–19} Transition metal phthalocyanines with an open shell structure of the central ion molecular orbitals, strongly interact with the metal substrates, affecting the electronic, optical, and magnetic properties of the organic/metal interface, thus influencing the performances of the molecular device.^{10,20,21}

In this paper, we determine the adsorption energy of FePc and CoPc adsorbed on Au(110), with respect to CuPc/Au(110), as estimated by Temperature Programmed Desorption (TPD). The interfacial charge transfer between FePc and CoPc, and the Au(110)-(1×2) metallic surface, has been studied by means of core-level and valence band photoemission spectroscopy. We observe a charge transfer to the first MPc layer, the appearance of interface states due to the filling of open-shell molecular empty levels located on the central metal atoms, and we estimate a lower limit for the adsorption energy of the CoPc and FePc single layers. On the other hand, the core-levels associated to the organic macrocycle (C 1*s* and N 1*s*) are less influenced by the adsorption, although the organic macrocycles contribute to stabilize the interaction process inducing a strong interface dipole.

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II. EXPERIMENTAL

X-Ray Photoemission Spectroscopy (XPS) measurements of the Fe and Co $2p$ core-levels were carried out at the LoTUS Surface Physics Laboratory (Sapienza, University of Rome) in an Ultra High Vacuum (UHV) chamber, with a base pressure in the low 10^{-10} mbar range. XPS spectra were acquired with Al $K\alpha$ radiation ($h\nu = 1486.7$ eV), and electrons measured with the hemispherical analyser VG Microtech Clam-2, in constant Pass Energy (PE) mode set at 100 eV, with an overall energy resolution of 1 eV. The Binding Energy (BE) was calibrated with respect to the clean substrate by measuring the Au- $4f_{7/2}$ core-level at a BE = 84.0 eV. XPS measurement of the N- $1s$ and C- $1s$ core-levels were performed at the Aloisa beamline of the Elettra synchrotron radiation facility in Trieste.²² Experiments have been done in an UHV chamber with base pressure better than 1×10^{-10} mbar using a photon energy of 500 eV, with high energy-resolution of 180 meV. The binding energy scale was calibrated with respect to the Au- $4f_{7/2}$ core level at the clean substrate.

Ultraviolet Photoemission Spectroscopy (UPS) measurements were performed at the LoTUS laboratory. The high-resolution-UPS spectra were collected by means of a Scienta SES-200 hemispherical analyser (energy resolution of 16 meV). The UV radiation (He $_{I\alpha}$, 21.22 eV), was provided by a Scienta VUV-5050 monochromatic high flux source. The TPD experiments have been performed by heating the sample through a linear temperature ramp with constant heating rate $\beta = 0.3$ K/s, and the mass products of desorption were followed using a quadrupole mass spectrometer (Stanford RGA300). Due to limitations of the instrument to 300 amu, fragments of the MPC molecules originated in the spectrometer by the ionization process have been measured. In particular, also according to a previous analysis showing the most intense ones,²³ we followed the evolution of $m/z = 128$ amu (from the benzene and pyrrol rings).

The Au(110)-(1 \times 2) reconstructed surface was prepared by means of several sputtering-annealing cycles (800 eV Ar⁺, followed by annealing at 820 K, subsequently 400 eV Ar⁺, annealing at 570 K). Surface cleanness and order were checked using UPS and low energy electron diffraction (LEED), respectively.

FePc and CoPc deposition was performed using homemade quartz crucibles, resistively heated up to the sublimation temperature of the molecules. The nominal thickness of the molecular films was checked using a quartz microbalance, referring to a bulk-like film with density of 1.62 g/cm³. Completion of first SL is achieved at a nominal coverage of about 3.4 Å,⁶ and has been checked by LEED.¹⁸ The Scanning Tunneling Microscopy (STM) images of the CoPc single-layer adsorbed on Au(110) were taken at the STM UHV apparatus connected to the ID08 (present ID32) beamline at the European Synchrotron Radiation Facility (ESRF).

III. RESULTS AND DISCUSSION

The CoPc molecules adsorbed on Au(110) form an ordered chain structure along the gold reconstructed channels, as shown in the STM image reported in Fig. 1. We clearly

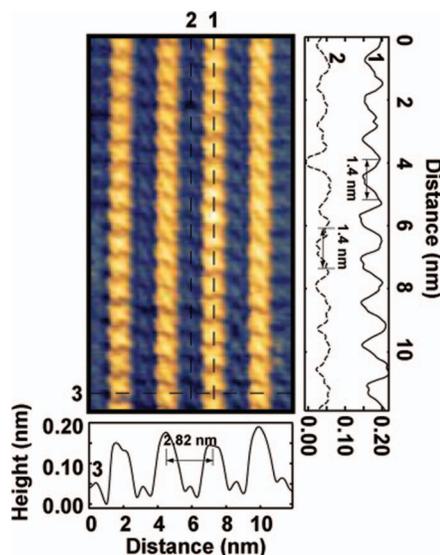


FIG. 1. Single-layer of CoPc molecules self-assembled onto Au(110). STM topographic image taken in constant current mode (-0.98 V bias voltage, 0.70 nA tunneling current) at $T = 300$ K. Three different line-profiles (marked as 1, 2, 3) across the image are traced, and reported aside.

observe long and parallel CoPc chains assembled along the $[1\bar{1}0]$ direction. The inter-chain distance along the $[001]$ direction corresponds to $7 \times a_0$ (2.82 nm, see profile 3 in Fig. 1), where a_0 is the Au(110) surface lattice parameter. The chain structure is driven by the underlying Au structure with a $\times 7$ periodicity, constituted by sequences of $\times 4$ - $\times 3$ Au chains,¹⁸ such as to allocate the molecules into the widened gold channels. This adsorption geometry is comparable to that recently observed for FePc single-layer adsorbed on the Au(110) substrate,¹⁸ where the parallel chains showed the same arrangement observed here. A row of bare Au atoms is directly lying below the topmost molecular chains, hence the MPC molecules are in direct contact with the gold substrate.¹⁸

The XPS Fe- $2p_{3/2}$ core level spectra for the FePc molecules adsorbed onto the Au(110) surface kept at room temperature, as a function of FePc coverage up to the formation of a 20 nm thick film (TF), are shown in Fig. 2 (left panel). XPS data taken on the FePc-TF after subsequent steps of annealing temperatures, are reported in Fig. 2 (right panel). The core-level lineshape in the TF is characterized by a main peak centered at 708.7 eV BE, whose asymmetric lineshape can be associated to a multiplet structure due to the interaction of unpaired electrons in the photoemission final states of the Fe²⁺ ion, typical of the metal-phthalocyanine and metal-porphyrin molecules.²⁴⁻²⁷ At lower FePc coverages, a further peak is present at 707.2 eV, dominant at 3 Å molecular coverage.

Several approaches have been used for evaluating the multiplet structure of the Fe $2p$ core-level, either applying a Zeeman-like final state effect^{25,26} based on the four levels splitted $m_j = 3/2, 1/2, -1/2, -3/2$ components of the $2p_{3/2}$ level, or in splitted states based on their total angular momentum ($J = 5/2, 3/2, 1/2$).²⁷ The Zeeman-like approach can be adopted thanks to the rather high spin-orbit splitting (13 eV), and to the orbital magnetic moment, as measured for FePc single layer adsorbed on Au.¹⁹ Thus, we fit the Fe- $2p_{3/2}$

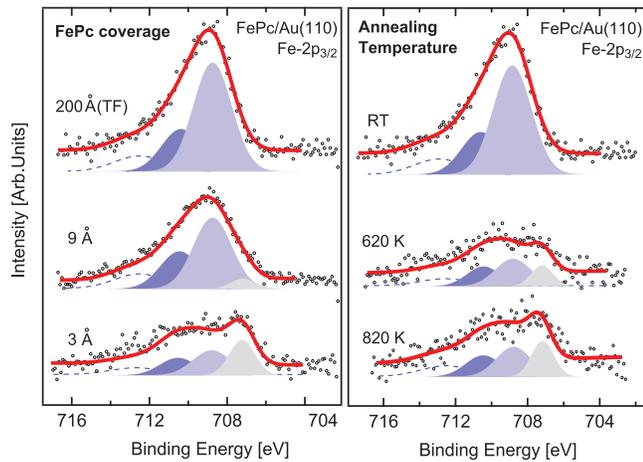


FIG. 2. XPS of the Fe- $2p_{3/2}$ core-level for FePc deposited on Au(110), as a function of FePc coverage, till formation of a 20 nm-thick film (left panel); and for the FePc-TF after annealing at increasing temperatures (right panel). Spectra are vertically stacked for clarity. The bluish and gray curves represent the single fitting curves of the data, the continuous red line the fitting sum.

core-level for the 20 nm-thick FePc film using an empirically modified Zeeman-like analysis,^{25,26} which is a simplified model where the four m_j sublevels are partially unresolved and modeled using two peaks centered at 708.7 and 710.4 eV. Furthermore, a broad higher binding energy satellite at 712.5 eV has been considered, in agreement with all previous observations and fitting approaches.^{24–27} The fitting curves are gaussian peaks with 1.4 eV full-width at half-maximum (FWHM), taking into account both the unresolved splitting and the overall experimental resolution (1 eV). However, it is evident the rise of an interface Fe- $2p$ component for low coverage, associated to FePc molecules directly interacting with the underlying Au atomic chains, present at the interface.

The FePc TF deposited on Au(110) has been annealed at subsequent steps at increasing temperature, up to 820 K, the highest temperature compatible with the Au(110) surface, in order to preserve the surface structure.²⁸ The XPS Fe- $2p_{3/2}$ core levels measured after each annealing step, are shown in Fig. 2, right panel. The low-BE peak associated to the single-layer in direct contact with Au reappears above 600 K, and it is dominant at 820 K, while the multiplet structure of the TF is strongly reduced. These data are compatible with the desorption of the multi-layer film, which has been recently shown to take place at about 580 K,²³ while the first single-layer remains bound to the Au surface. This picture is consistent with the FePc TF constituted by a molecular film of planarly stacked face-on molecules on Au(110), as recently determined by linearly polarized x-ray absorption spectroscopy,¹⁵ and by scanning tunnelling microscopy and low-energy electron-diffraction.¹⁶

The $3d$ orbitals of the central Fe ion in the D_{4h} molecular symmetry, are ligand-field splitted in a double e_g (d_{xz} , d_{yz}), single b_{2g} (d_{xy}), single a_{1g} (d_{z^2}), and single b_{1g} state ($d_{x^2-y^2}$). The first layer of FePc molecules adsorbed on the bare Au(110)-(1 \times 2) surface presents the central Fe ions in direct contact with the underlying reconstructed Au surface.¹⁶ Thus, a mixing of Fe and Au electronic states with redistribu-

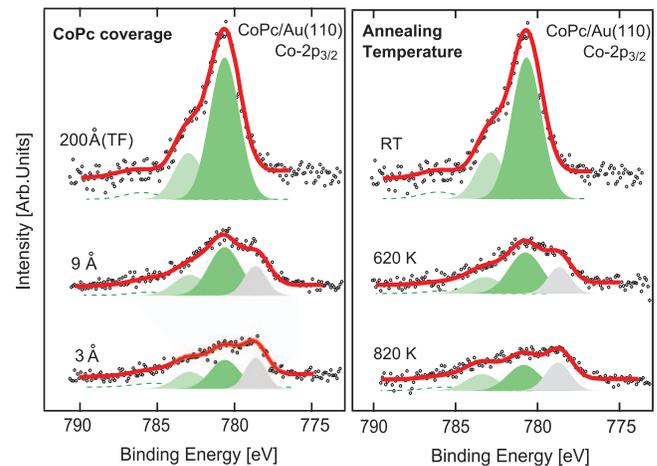


FIG. 3. XPS of the Co- $2p_{3/2}$ core-level for CoPc deposited on Au(110), as a function of CoPc coverage, till formation of a 20 nm-thick film (left panel); and for the CoPc-TF after annealing at increasing temperatures (right panel). Spectra are vertically stacked for clarity. The greenish and gray curves represent the single fitting curves of the data, the continuous red line the fitting sum.

tion of the density of states that mainly involves the a_{1g} level takes place, with its partial occupation.¹⁷ On the basis of these considerations, the appearance of the peak at lower binding energy in the XPS Fe- $2p_{3/2}$ data when a single molecular layer or less is adsorbed on Au(110), can be explained by charge transfer and orbital mixing between the substrate and the molecule. The charge transfer could either influence the final excited state, causing a more efficient screening of the hole,²⁹ or could directly affect the initial state of the metal ion, involving a change in the effective oxidation state of the ion itself. The width of the interface core-level peak shown in the figures, which is mainly related to the m_j splitting, is narrower (1 eV) than the width obtained for the fitted TF peaks. This feature is compatible with the general picture of charge transfer with change in the molecular spin state,¹⁹ and consequently in the m_j splitting, due to the interaction of Fe central atoms with Au. The interaction induces a strong reduction of the FePc magnetic moment values at the SL configuration suggesting a $S = 1/2$ configuration, as reported in Ref. 19.

The Co- $2p_{3/2}$ core level XPS data for the CoPc/Au(110) system, as a function of molecular coverage (left panel) and desorption temperature (right panel), are reported in Fig. 3. The CoPc-TF presents two main structures at 780.6 and 783.0 eV, associated to the partially resolved m_j splitting, due to a Zeeman-like effect, as discussed for the case of FePc molecule. Also in this case, an unresolved satellite is present, at about 785.3 eV. In analogy with the FePc/Au(110) system, in the low coverage spectra a lower-BE component appears at about 778.5 eV, associated to the first CoPc layer in contact with Au. The SL-peak reappears, as a dominant peak after the thermal annealing of the CoPc-TF at 820 K. The CoPc-TF prepared on Au(110) is constituted by few layers of flat molecules¹⁵ in perfect analogy with the case of FePc on Au(110). The smaller width (1 eV) of the interface core-level peak with respect to the TF-components (1.4 eV) can be explained by a change in the spin state of the molecules at direct contact with the Au surface.¹⁹ The presence of both

the bulk-like and interface components for the Co- $2p_{3/2}$ core-level at the CoPc/Au(110) system, along with the SL morphology shown in the STM image (Fig. 1) suggest that the CoPc molecules assembled on Au(110) present comparable structural configuration and interaction process as the FePc molecules. In particular, the appearance of the Co- $2p$ core-level interface component is a consequence of the charge transfer from the metal substrate to the out-of-plane Co- d states.

A higher adsorption energy and shorter distance to the Au(110) surface for FePc and CoPc than for CuPc, have been recently found by density-functional theory (DFT) calculations,¹⁹ which also brought to light the charge transfer and charge density redistribution from Au to the MPC molecular orbitals. In particular, for FePc and CoPc the bonding charge involves the a_{1g} orbitals with the d_{z^2} component, while for CuPc the interfacial reorganization only partially influences the b_{1g} orbital. This charge redistribution takes place because the MPC molecules adsorb onto Au metal atoms at the SL coverage,¹⁹ and these molecules are responsible of the observed chemically shifted Fe and Co $2p$ core-level components.

The different interaction of CuPc/Au(110) with respect to FePc and CoPc on Au(110) also leads to different adsorption energies. The adsorption energies as calculated through the central ion contribution to the bonding amount to 0.73 eV, 0.54 eV, and 0.37 eV for FePc, CoPc, and CuPc, respectively.¹⁹ The van der Waals contribution to the adsorption energy is not considered in the calculation, but it is common to all the MPCs being associated to the organic macrocycles, even if may be stronger for FePc and CoPc than for CuPc due to the closer distance to the surface (2.7 Å, 2.8 Å, and 3.2 Å, respectively).

The adsorption energy can be experimentally determined by estimating the activation energy through a TPD experiment on the MPC layers adsorbed on Au(110). We performed a first TPD experiment on 20-nm thick films of FePc, CoPc, and CuPc, the same thickness used for the XPS experiment as a function of annealing temperature. The TPD data for the MPC TFs reported in the supplementary material³⁰ present a desorption peak at 570 K for all TFs, in agreement with a previous TPD experiment of FePc-TF on Au(110).²³ The desorption peak is due to desorption of the MPC multilayer, and the desorption temperature is independent from the specific central metal ion, as expected for a multilayer where the interaction is mainly driven by molecule-molecule dipolar van der Waals interaction between the molecular planes.

We now focus on the high temperature region, above the desorption of the molecular multi-layers. We report in Fig. 4 the TPD data for FePc, CoPc, and CuPc, starting from both a MPC TF (right panel) and a MPC SL (left panel) deposited on Au(110). The CuPc molecular layer presents a desorption peak at 700 K, while not any desorption peak is observed for FePc and CoPc up to 820 K, the maximum annealing temperature compatible with the Au(110) substrate stability.²⁸

Thus, while the FePc and CoPc SLs remain adsorbed on the Au(110) surface, the CuPc SL desorbs, demonstrating that a different interaction between these MPCs and Au(110) takes place in the SL coverage phase. Since the interaction of the

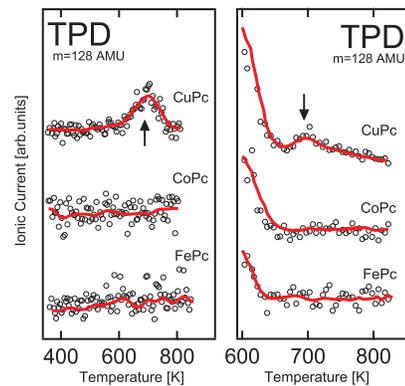


FIG. 4. Temperature-programmed desorption experiments for FePc, CoPc, and CuPc, starting from single-layer films (left panel) and from films of 20-nm thickness (right panel). Circles represent original data and the red line is an eye guideline obtained by smoothing the rough data.

molecules with the substrate is mainly driven by the charge transfer from metal states to the central metal ion, a dependence on the filling of the d -states is expected. In particular, in CuPc the d -states are filled and a lower interaction can be observed, while for FePc and CoPc characterized by partially filled d -states, the charge transfer determines a stronger molecule-substrate interaction.

The desorption temperature peaks measured by TPD allow to estimate the activation energies (E_a), by means of the Redhead approach³¹

$$E_a = k_B T_{max} \left[\ln \left(\frac{\nu T_{max}}{\beta} \right) - 3.64 \right],$$

where T_{max} is the temperature of the maximum of desorption peak, k_B is the Boltzmann factor, β is the heating rate (0.3 K/s in the present experiment), and ν is a pre-exponential factor.³² We assume the pre-exponential factor $\nu = 10^{18} \text{ s}^{-1}$. Its value can depend on the molecular size and it is in general much higher for large than for small molecules, due to their internal degrees of freedom.³³ This value of ν , compatible with large aromatic molecules,^{33,34} has been chosen because it brings to an activation energy for the CuPc TF on Au(110) in agreement with the measured sublimation enthalpy of CuPc thin-films,³⁴ where only van der Waals interactions ensure the film cohesion.

Within these assumptions, the estimated activation energies for the MPC TFs and SLs on Au(110) are reported in Table I.

The estimated activation energy for the TFs ($\simeq 2.3 \text{ eV}$) is fully compatible with a dipolar interaction between the molecular layers and with the enthalpy variation during sublimation of bulk molecular films,³⁴ independent from the

TABLE I. Temperature of the maximum of desorption peak (T_{max}), estimated activation energy (E_a) as calculated using the Redhead equation,³¹ with pre-exponential factor $\nu = 10^{18} \text{ s}^{-1}$.

| | $(T_{max} \pm 15) \text{ K}$ | | | $(E_a \pm 0.05) \text{ eV}$ | | |
|--------------|------------------------------|------|------|-----------------------------|-------|------|
| | FePc | CoPc | CuPc | FePc | CoPc | CuPc |
| Thick film | 576 | 576 | 576 | 2.27 | 2.27 | 2.27 |
| Single layer | >820 | >820 | 700 | >3.30 | >3.30 | 2.74 |

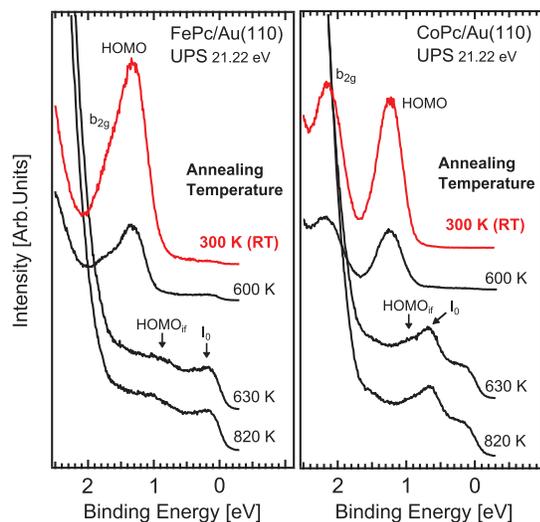


FIG. 5. High-resolution UPS of the VB for FePc (left panel) and CoPc (right panel) thin-films on Au(110), as a function of annealing, at increasing temperature steps. Spectra are vertically stacked for clarity.

central metal atom. As it concerns the first molecular layer, we observe that only the CuPc single-layer desorbs from Au(110), while both FePc and CoPc do not desorb till the highest temperature reachable without affecting the Au(110) surface integrity. For the CuPc SL on Au(110), we estimate 2.74 eV of activation energy, compatible with a dominant van der Waals interaction of the aromatic macrocycle on the metal surface, considered the large molecular surface area.³³ For FePc and CoPc SLs on Au(110), we estimate a lower limit for the activation energy of 3.3 eV. This high value of E_a can be explained by taking into account the influence of the central metal ion, that gives the most important contribution to the adsorption energy differences. Finally, we briefly notice that, even modifying ν by two orders of magnitude, the absolute energy values would change by less than 10%, without affecting the relative energy difference between the various MPCs.

A confirm of the adsorption energy and of the molecule-substrate interaction of the first layer of FePc and CoPc in contact with Au(110), can be obtained by analyzing the evolution of the spectral density of electronic states in the valence band (VB) energy region, as a function of temperature. The VB of FePc and CoPc TFs grown on Au(110) at RT, and after annealing at subsequent steps of temperature, are shown in Fig. 5, left and right panels, respectively.

The MPC thin-films are characterized by intense molecular levels, the highest-occupied molecular-orbital (HOMO of a_{1u} character), mainly associated to π states delocalized on the pyrrole rings, and the b_{2g} orbital mainly associated to d -like orbitals of the central metal ion,⁵ in agreement with previous experimental observations.⁶ The higher BE of the b_{2g} orbital for CoPc than for FePc is due to the higher occupation of the d -orbitals in CoPc with respect to the FePc.⁵ The MPC thin films have been annealed at increasing temperatures, the molecular orbital intensity reduces due to multi-layer desorption, which is basically completed for both molecular layers above 600 K. At the highest temperature reachable with-

out affecting the Au crystalline surface (820 K),²⁸ the typical HOMO of the TF is disappeared, while an energy-shifted orbital is present at about 1 eV for both FePc and CoPc, which we attribute to an interface HOMO (HOMO_{if}), and a further peak (I_0) emerges between the HOMO_{if} and the Fermi level. The HOMO_{if} is at almost the same energy for both FePc and CoPc SLs and it has been attributed to the macrocycle interaction through the πa_{1u} orbitals with the Au d states.⁶ It is worth noticing that FePc on graphene/Ir does not show a shift in the a_{1u} molecular orbital,⁸ owing to the very low interaction of FePc with the graphene/Ir substrate. The interface I_0 peak lies at 0.21 eV and 0.73 eV BE for the FePc-SL and the CoPc-SL, respectively. Due to the BE-dependence on the d -state occupation of the central metal ion, the I_0 state has been related to interaction of the d_{z^2} orbital, which receives charge from the gold states, in the molecule-surface interaction process.¹⁷ We also notice that an analogous interface state has been recently observed at 0.3 eV BE for FePc adsorbed on graphene/Ni,³⁵ where the Fe- d_{z^2} orbital directly interacts with the nickel states underlying graphene.

The VB data evolution is in agreement with the multi-layer desorption temperature measured by TPD (580 K).³⁰ The estimated activation energy (2.27 eV) is in very good agreement with the activation energy obtained for MPCs multi-layer desorption from graphene/Ir (2.2-2.4 eV), where the MPC molecules also pile-up face-on onto the graphene surface.^{8,36,37} Thus, the TF desorption temperature is independent of the central metal ion, and of the substrate, once the MPC molecules assemble in planar layers.

Electronic state mixing between the Au states and the d -like orbitals associated to the central metal ion (Fe and Co) can explain the higher adsorption energy of the FePc and CoPc molecules in the SL on Au, with respect to the lower molecule-molecule van der Waals interaction in the molecular multi-layers. The I_0 interface state in the VB of the FePc and CoPc SLs on the Au(110) substrate remains even at the highest heating temperature (820 K), which corresponds to an activation energy of 3.3 eV.³¹ This fact indicates that the single-layer desorption is expected to occur at a higher temperature, incompatible with the Au(110) substrate stability.²⁸ The VB data of the SLs confirm the strong molecule-substrate interaction, driven mainly by the central metal Fe and Co ions. Since CuPc presents the d_{z^2} orbital completely filled, at contrast with FePc and CoPc, its interaction with Au(110) is weaker, and as a consequence the CuPc SL desorbs at a lower temperature from the Au(110) surface.

The interaction of FePc and CoPc on Au(110) has been further analyzed by studying the role of the macrocycle atoms, namely, N and C. The N-1s and C-1s core levels for the FePc and CoPc single-layers adsorbed on Au(110), in comparison with those from the corresponding TFs, are displayed in Figs. 6 and 7, respectively. The N-1s core level is due the photoexcitation from the two non-equivalent nitrogen atoms (N_1 and N_2) in the pyrrole rings and in the bridge position, respectively, in agreement with previous observations on a variety of MPCs.³⁷⁻⁴² We fit the N-1s core-level with pseudo-Voigt-profiled peaks, all presenting a gaussian width of 0.19 eV (representing the overall energy resolution). The two main components with 0.4 eV energy difference, and the broad

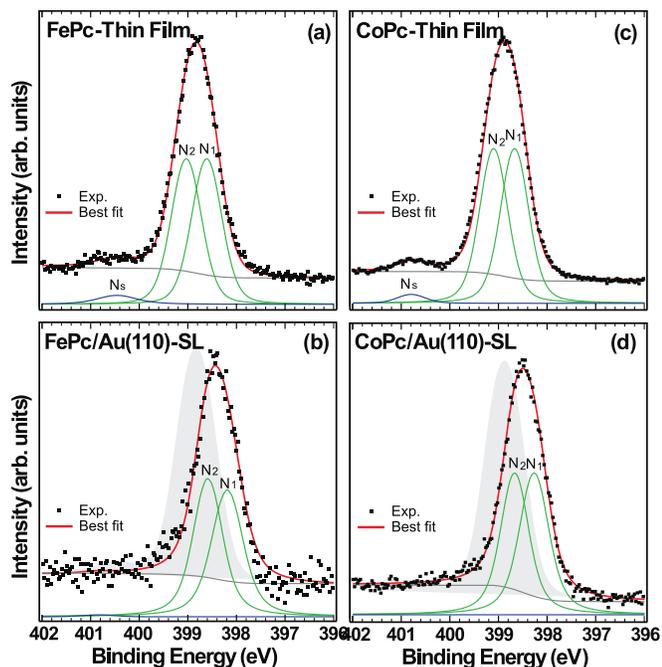


FIG. 6. XPS spectra of the N $1s$ core level for a FePc TF (a), FePc SL (b), CoPc TF (c), and CoPc SL (d) on Au (110). The gray shadowed curves in SL-data (c) and (d) represent the TF-data from (a) and (b), respectively. Superimposed to the data the best fit is shown, obtained with the Voigt-profiled curves due to the N_1 and N_2 components, associated to nitrogen atoms belonging to benzene and pyrrole rings, respectively, also considering the N_s satellite structure (see detail in the text).

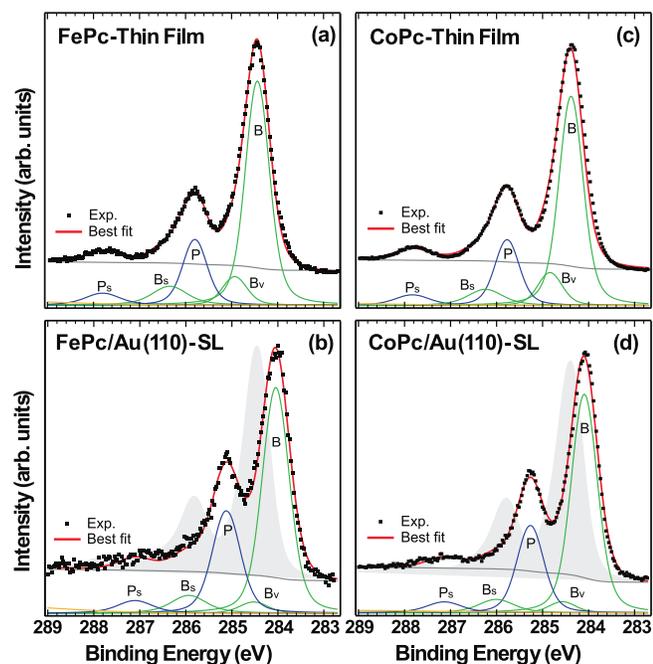


FIG. 7. XPS spectra of the C $1s$ core level for a FePc TF (a), FePc SL (b), CoPc TF (c), and CoPc SL (d) on Au (110). The gray shadowed curves in SL-data (c) and (d) represent the TF-data from (a) and (b), respectively. Superimposed to the data the best fit is shown, obtained with the following Voigt-profiled curves: B and P denote carbon atoms belonging to benzene and pyrrole rings, respectively, B_s and P_s are the shake-up satellites of the benzene and pyrrole components, respectively, and B_v is a vibrational mode (see detail in the text).

TABLE II. N $1s$ fitting parameters for the FePc (left) and CoPc (right) thin-films (top) and single-layers (bottom). Binding Energy (BE, in eV), full-width at half-maximum, FWHM (W, in eV), and relative percentage peak area (I).

| | BE (eV) | W (eV) | I (%) | BE (eV) | W (eV) | I (%) |
|-------|---------|--------|-------|---------|--------|-------|
| | FePc TF | | | CoPc TF | | |
| N_1 | 398.61 | 0.73 | 0.48 | 398.68 | 0.69 | 0.49 |
| N_2 | 399.03 | 0.73 | 0.48 | 399.11 | 0.69 | 0.49 |
| N_s | 400.73 | 0.73 | 0.04 | 400.80 | 0.69 | 0.02 |
| | FePc SL | | | CoPc SL | | |
| N_1 | 398.19 | 0.77 | 0.50 | 398.27 | 0.72 | 0.51 |
| N_2 | 398.59 | 0.72 | 0.50 | 398.67 | 0.69 | 0.49 |

shake-up satellite structure (N_s) at higher BE, are in agreement with the literature on MPCs,^{38,41,42} and the fit parameters are reported in Table II. The satellite structure present in the TF is quenched at the SL coverage on Au(110) and a rigid 0.4 eV energy shift of all components towards higher BE is measured for the TF with respect to the SL.

The C- $1s$ spectra for both systems (SL and TF) presented in Fig. 7 have been fitted with five pseudo-Voigt-profiled components (0.19 eV gaussian width), associated to the carbon atoms in the benzene rings (B), in the pyrrole rings (P), to their relative shake-up satellites (B_s and P_s , respectively), due to the transition from the HOMO to the lowest-unoccupied molecular-orbital (LUMO). The fifth component (B_v) is related to the excitation of a vibrational mode for carbon atoms belonging to the benzene rings.^{39,42–44} Fit parameters are reported in Table III. An overall energy shift by a few tenths of eV towards higher BE is observed comparing both SLs with respect to their corresponding TFs, shift observed also for the shake-up satellites. An important issue is the reduction of the energy difference between the benzene and pyrrole components, upon going from the TF (1.37 eV) to the SL (1.07 eV), and the B-to-P intensity ratio lowering for the SLs with respect to the TFs. The structure associated to the vibrational

TABLE III. C $1s$ fitting parameters for the FePc (left) and CoPc (right) thin-films (top) and single-layers (bottom). Binding Energy (BE, in eV), full-width at half-maximum, FWHM (W, in eV), and relative percentage peak area (I).

| | BE (eV) | W (eV) | I (%) | BE (eV) | W (eV) | I (%) |
|-------|---------|--------|-------|---------|--------|-------|
| | FePc TF | | | CoPc TF | | |
| B | 284.44 | 0.62 | 0.61 | 284.32 | 0.63 | 0.60 |
| B_v | 284.93 | 0.63 | 0.08 | 284.83 | 0.63 | 0.09 |
| P | 285.81 | 0.63 | 0.18 | 285.77 | 0.63 | 0.18 |
| B_s | 286.35 | 0.91 | 0.08 | 286.24 | 0.91 | 0.08 |
| P_s | 287.81 | 0.91 | 0.05 | 287.83 | 0.91 | 0.05 |
| | FePc SL | | | CoPc SL | | |
| B | 284.04 | 0.7 | 0.58 | 284.09 | 0.67 | 0.61 |
| B_v | 284.52 | 0.72 | 0.03 | 284.56 | 0.69 | 0.03 |
| P | 285.11 | 0.72 | 0.27 | 285.26 | 0.69 | 0.25 |
| B_s | 285.93 | 0.91 | 0.07 | 286.00 | 0.91 | 0.06 |
| P_s | 287.10 | 0.91 | 0.05 | 287.13 | 0.91 | 0.05 |

mode (B_v) is reduced in intensity and does not present energy variation within 5% with respect to the main peak.

The lineshape differences for the C-1s core-level in the FePc and CoPc SLs on Au(110) with respect to their corresponding TFs, has been previously observed in analogous systems, i.e., CoPc/Cu(111), where a comparable reduced energy difference has been recently measured between the benzene and pyrrole C-1s signals.⁴⁰ In the present case of adsorption on Au(110), the experimentally observed B-to-P energy difference in SLs and TFs (1.07 eV and 1.37 eV, respectively) can be attributed to a slight modification of the molecular configuration when the FePc and CoPc molecules are adsorbed on the underlying reconstructed Au surface. This slight distortion is compatible with the STM observation of CoPc and FePc molecules adsorbed on Au(110) in the SL coverage stage, being the central metal atom directly adsorbed onto a Au row.¹⁶ In particular, *ab initio* calculations brought to light a distortion of the molecules in contact with the Au atomic rows, associated to the macrocycle bending. Indeed, two opposite phenylene rings bend up and the perpendicular ones bend down with respect to the surface, causing a breaking of the fourfold molecular symmetry.¹⁶ This angular deformation has been previously observed for MPcs on semiconductor surfaces,^{39,45–47} where the molecular distortion induced by the substrate covalent bondings is more pronounced. This slight molecular distortion can explain the energy shift between the benzene and pyrrole components of the C 1s core-levels when the central metal atoms of FePc and CoPc interact with Au. Thus, we attribute the B-to-P energy difference in the C 1s core-level components between TF and SL (0.3 eV) to the molecular distortion upon adsorption, which mainly affects the extremal C atoms present in the distorted macrocycle, and not the N atoms. Furthermore, the overall C 1s energy shift is associated to a balance between dipolar change and charge transfer. The work function upon molecular adsorption lowers by 0.79 eV, 0.83 eV, and 0.95 eV for FePc, CoPc,⁶ and CuPc,⁴² respectively. The overall work function change ($\Delta\Phi$) is due to the contribution of both dipolar change and charge transfer. The present measurements, bringing to light the chemically shifted core-level components, give an explanation to those previously observed^{6,42} $\Delta\Phi$ variations: in fact, the lower $\Delta\Phi$ variation for FePc and CoPc than for CuPc is actually due to the charge transfer at the interface which counterbalances the surface dipole that is mainly associated to the organic macrocycles and thus almost independent of the specific MPc.

IV. CONCLUSION

The presence of metal-2p interface core-level components observed by XPS for FePc and CoPc single-layers adsorbed on Au(110), with respect to the typical 2p binding energy of their respective thin-films, gives clear indication of charge transfer involving the central metal ion interacting with the underlying gold states. TPD and photoemission measurements on MPcs adsorbed on Au(110), show that the single-layer of CuPc (with filled d_{z^2} states), fully desorbs at 760 K, while the stability of the single-layers of FePc and CoPc (with partially empty d_{z^2} levels) on Au is demonstrated by the per-

sistence of the single-layers up to the highest temperature reachable without affecting the Au(110) crystalline stability (820 K). Thanks to the TPD and photoemission measurements as a function of temperature, we can estimate an adsorption energy of 2.74 for the CuPc SL on Au(110), while FePc and CoPc present a lower limit of 3.3 eV. The presence of an interface state (d_{z^2} -like) in the valence band at FePc and CoPc SLs after desorption of the multi-layer, is a further proof of their interaction with Au driven by central metal atom. Moreover, the N and C 1s core-levels reveal the role in the interaction of the organic macrocycle common to all MPcs that contributes to the interface dipole, stabilizing the adsorption on Au(110). Aromatic oligomers like MPcs with the same organic macrocycle ensuring face-on anchorage to a metal surface, different occupation of the *d*-states in the central metal ion and different interaction states, may be used as potential components of a nano-scale device.

ACKNOWLEDGMENTS

We are grateful to the staff members of the ALOISA beamline at the Elettra synchrotron radiation source (Trieste) and of the ID08 (present ID32) beamline at the ESRF (Grenoble) for their support. We thank Riccardo Frisenda for the experimental assistance. This work was funded by MIUR PRIN Grant No. 20105ZZTSE “GRAF,” by Sapienza University funds, and by the Elettra Sincrotrone Trieste support for users.

- ¹Z. Bao, A. J. Lovinger, and A. Dodabalapur, *Appl. Phys. Lett.* **69**, 3066 (1996).
- ²D. Hohnholz, S. Steinbrecher, and M. Hanack, *J. Mol. Struct.* **521**, 231 (2000).
- ³L. Bogani and W. Wernsdorfer, *Nat. Mater.* **7**, 179 (2008).
- ⁴S. R. Forrest, *Chem. Rev.* **97**, 1793 (1997).
- ⁵M.-S. Liao and S. Scheiner, *J. Chem. Phys.* **114**, 9780 (2001).
- ⁶P. Gargiani, M. Angelucci, C. Mariani, and M. G. Betti, *Phys. Rev. B* **81**, 085412 (2010).
- ⁷F. Sedona, M. Di Marino, D. Forrer, A. Vittadini, M. Casarin, A. Cossaro, L. Floreano, A. Verdini, and M. Sambi, *Nat. Mater.* **11**, 970 (2012).
- ⁸M. Scardamaglia, S. Lisi, S. Lizzit, A. Baraldi, R. Larciprete, C. Mariani, and M. G. Betti, *J. Phys. Chem. C* **117**, 3019 (2013).
- ⁹L. Gavioli, M. Fanetti, M. Sancrotti, and M. G. Betti, *Phys. Rev. B* **72**, 035458 (2005).
- ¹⁰A. Annese, C. Viol, B. Zhou, J. Fujii, I. Vobornik, C. Baldacchini, M. G. Betti, and G. Rossi, *Surf. Sci.* **601**, 4242 (2007).
- ¹¹J. Götzen, S. Lukas, A. Birkner, and G. Witte, *Surf. Sci.* **605**, 577 (2011).
- ¹²F. Evangelista, A. Ruocco, D. Pasca, C. Baldacchini, M. G. Betti, V. Corradini, and C. Mariani, *Surf. Sci.* **566**, 79 (2004).
- ¹³C. Baldacchini, C. Mariani, and M. G. Betti, *J. Chem. Phys.* **124**, 154702 (2006).
- ¹⁴A. Kühnle, L. Molina, T. R. Linderoth, B. Hammer, and F. Besenbacher, *Phys. Rev. Lett.* **93**, 086101 (2004).
- ¹⁵M. G. Betti, P. Gargiani, R. Frisenda, R. Biagi, A. Cossaro, A. Verdini, L. Floreano, and C. Mariani, *J. Phys. Chem. C* **114**, 21638 (2010).
- ¹⁶S. Fortuna, P. Gargiani, M. G. Betti, C. Mariani, A. Calzolari, S. Modesti, and S. Fabris, *J. Phys. Chem. C* **116**, 6251 (2012).
- ¹⁷M. G. Betti, P. Gargiani, C. Mariani, S. Turchini, N. Zema, S. Fortuna, A. Calzolari, and S. Fabris, *J. Phys. Chem. C* **116**, 8657 (2012).
- ¹⁸M. G. Betti, P. Gargiani, C. Mariani, R. Biagi, J. Fujii, G. Rossi, A. Resta, S. Fabris, S. Fortuna, X. Torrelles *et al.*, *Langmuir* **28**, 13232 (2012).
- ¹⁹P. Gargiani, G. Rossi, R. Biagi, M. Pedio, S. Fortuna, A. Calzolari, S. Fabris, J. C. Cezar, N. Brookes, and M. G. Betti, *Phys. Rev. B* **87**, 165407 (2013).
- ²⁰C. Stadler, S. Hansen, I. Kroger, C. Kumpf, and E. Umbach, *Nat. Phys.* **5**, 153 (2009).

- ²¹F. Petraki, H. Peisert, F. Aygül, U. Latteyer, J. Uihlein, A. Vollmer, and T. Chassé, *J. Phys. Chem. C* **116**, 11110 (2012).
- ²²L. Floreano, G. Naletto, D. Cvetko, R. Gotter, M. Malvezzi, L. Marassi, A. Morgante, A. Santaniello, A. Verdini, F. Tommasini *et al.*, *Rev. Sci. Instrum.* **70**, 3855 (1999).
- ²³C. Struzzi, M. Scardamaglia, M. Angelucci, L. Massimi, C. Mariani, and M. G. Betti, *Il Nuovo Cimento C* **36**, 51 (2013); online at <http://www.sif.it/riviste/ncc/econtents/2013/036/02/article/9>.
- ²⁴Y. Bai, M. Sekita, M. Schmid, T. Bischof, H.-P. Steinrück, and J. M. Gottfried, *Phys. Chem. Chem. Phys.* **12**, 4336 (2010).
- ²⁵C. Isvoranu, B. Wang, K. Schulte, E. Ataman, J. Knudsen, J. N. Andersen, M. Bocquet, and J. Schnadt, *J. Phys.: Condens. Matter* **22**, 472002 (2010).
- ²⁶C. Isvoranu, B. Wang, E. Ataman, J. Knudsen, K. Schulte, J. N. Andersen, M.-L. Bocquet, and J. Schnadt, *J. Phys. Chem. C* **115**, 24718 (2011).
- ²⁷M. Schmid, J. Zirzmeier, H.-P. Steinrück, and J. M. Gottfried, *J. Phys. Chem. C* **115**, 17028 (2011).
- ²⁸A. Hoss, M. Nold, P. von Blanckenhagen, and O. Meyer, *Phys. Rev. B* **45**, 8714 (1992).
- ²⁹O. Gunnarsson and K. Schönhammer, *Phys. Rev. Lett.* **41**, 1608 (1978).
- ³⁰See supplementary material at <http://dx.doi.org/10.1063/1.4883735> for discussion about temperature programmed desorption experiments and adsorption energy.
- ³¹P. Redhead, *Vacuum* **12**, 203 (1962).
- ³²J. Miller, H. Siddiqui, S. Gates, J. Russell, Jr., J. Yates, Jr., J. Tully, and M. Cardillo, *J. Chem. Phys.* **87**, 6725 (1987).
- ³³R. Zacharia, H. Ulbricht, and T. Hertel, *Phys. Rev. B* **69**, 155406 (2004).
- ³⁴T. Basova, P. Semyannikov, V. Plyashkevich, A. Hassan, and I. Igumenov, *Crit. Rev. Solid State Mater. Sci.* **34**, 180 (2009).
- ³⁵L. Massimi, S. Lisi, D. Pacilè, C. Mariani, and M. G. Betti, *Beilstein J. Nanotechnol.* **5**, 308 (2014).
- ³⁶M. Scardamaglia, G. Forte, S. Lizzit, A. Baraldi, P. Lacovig, R. Larciprete, C. Mariani, and M. G. Betti, *J. Nanopart. Res.* **13**, 6013 (2011).
- ³⁷M. Scardamaglia, C. Struzzi, S. Lizzit, M. Dalmiglio, P. Lacovig, A. Baraldi, C. Mariani, and M. G. Betti, *Langmuir* **29**, 10440 (2013).
- ³⁸M. Schmid, A. Kaftan, H.-P. Steinrück, and J. M. Gottfried, *Surf. Sci.* **606**, 945 (2012).
- ³⁹N. Papageorgiou, Y. Ferro, E. Salomon, A. Allouche, J. M. Layet, L. Giovanelli, and G. L. Lay, *Phys. Rev. B* **68**, 235105 (2003).
- ⁴⁰E. Annese, J. Fujii, I. Vobornik, and G. Rossi, *J. Phys. Chem. C* **115**, 17409 (2011).
- ⁴¹A. Ruocco, F. Evangelista, R. Gotter, A. Attili, and G. Stefani, *J. Phys. Chem. C* **112**, 2016 (2008).
- ⁴²F. Evangelista, A. Ruocco, R. Gotter, A. Cossaro, L. Floreano, A. Morgante, F. Crispoldi, M. G. Betti, and C. Mariani, *J. Chem. Phys.* **131**, 174710 (2009).
- ⁴³I. Kröger, B. Stadtmüller, C. Stadler, J. Ziroff, M. Kochler, A. Stahl, F. Pollinger, T.-L. Lee, J. Zegenhagen, F. Reinert *et al.*, *New J. Phys.* **12**, 083038 (2010).
- ⁴⁴A. Cossaro, D. Cvetko, G. Bavdek, L. Floreano, R. Gotter, and A. Morgante, *J. Phys. Chem. B* **108**, 14671 (2004).
- ⁴⁵N. Papageorgiou, E. Salomon, T. Angot, J.-M. Layet, L. Giovanelli, and G. L. Lay, *Prog. Surf. Sci.* **77**, 139 (2004).
- ⁴⁶T. Angot, E. Salomon, N. Papageorgiou, and J.-M. Layet, *Surf. Sci.* **572**, 59 (2004).
- ⁴⁷E. Salomon, T. Angot, N. Papageorgiou, and J.-M. Layet, *Surf. Sci.* **596**, 74 (2005).