Relevance of the electron energy-loss spectroscopy for *in situ* studies of the growth mechanism of copper phthalocyanine molecules on metal surfaces: Al(100)

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Reflection electron energy-loss spectroscopy (EELS) in specular and off specular geometry has been employed to study the early stage of the copper phthalocyanine (CuPc) growth on Al(100) substrate. EEL spectroscopy has been a useful tool in order to study the electronic structure of molecular films also in the submonolayer regime. The electronic structure of the first deposited layer of CuPc is strongly influenced by charge transfer from the Al substrate to the lowest unoccupied molecular orbital (LUMO). The strong molecule-substrate interaction gives rise to a coverage dependent frequency shift of the Al surface plasmon. Successive layers have essentially the electronic structure of the molecular solid. Momentum resolved EELS measurements reveal that, in the case of the thicker film investigated (22 Å), the plane of the molecule is almost perpendicular to the surface of the substrate.

I. INTRODUCTION

Metal phthalocyanines, denoted MPc's (Pc = phtalocyanine $C_{32}H_{16}N_8$), have been synthesized using elements from any group of the periodic table. They are planar molecules, closely related to biological molecules such as porphyrins, constituted by a porphyrazin ring (porphyrinlike) bonded to four benzene rings. Main features of this class of molecules are a metal atom in the center (usually one of the first transition series) and an extended π-electron delocalization. MPc's exhibit an high chemical and thermal stability and exist in different forms; among the various polymorphs,[1] the α and β ones are the best known and the most widely studied. In both crystalline forms the phthalocyanine units are positioned in columnar stacks with the ring tilted with respect to the stacking axis (tilt angle), which cohere to form the molecular crystal. The two forms display identical interplanar distance (3.4 Å) consistent with a van der Waals bond, but they differ for the tilt angle: 26.5° in the α form and 45.8° in the β form. Furthermore their lattice parameters are different (23.9 Å in the α form and 19.6 Å in the β form) as well metal-metal distance. The different aggregation geometry results in changes of the electrical conductivity along the stacking direction. From an electronic point of view, MPc are semiconductors whose gap width depends on the central atom (typically 1.5–1.8 eV) and slightly on the geometrical arrangement (a variation of 60–70 meV between the α and β form in the absorption spectra has been observed[2]). After p doping by oxidizing agents and stabilization of a face to face stacking,[3] MPc's become electrical conductors, thus enlarging their field of applications. All these properties allow several technological applications in different fields such as nonlinear optics, molecular electronics and highly specific gas-sensor fabrication [such as NO_2 (Refs. 4 and 5)]. Therefore the knowledge of MPc spatial and electronic structure, both as bulk crystals and as adsorbates on well-defined substrates, is much relevant. Over the past decade MPc overlayers have been studied interfaced

with metals,[6–9] semiconductors,[8,10–12] and layered compounds.[9,13,14] Attempts have been made to grow them in an ordered manner (heteroepitaxy) on various substrates, some of them of high technological interest.[15,16] Substrate materials which have been shown to support the epitaxial growth of phthalocyanine ultrathin films now include single-crystal metals, layered semiconductors (SnS_2, MoS_2, HOPG), surface-passivated three dimensional semiconductors (Si, GaAs, GaP), and insulators such as freshly cleaved single-crystal halide salts.[17] In some cases an overgrowth evolution characterized by different molecular orientations has been observed. In particular, the adsorption starts with planar arrangement at low coverages, when substrate-molecule interaction is believed to dominate, to change into out-of-plane orientation at higher coverages where molecule-molecule interaction is expected to become relevant.[18]

Recently, substrate surface reconstruction has been observed induced by molecular deposition and it has been speculated that it might be determined by strong molecule-substrate interaction. In particular, for the CuPc/Ag(110) interface, Ag surface reconstruction has been ascribed to the presence of facets.[19] More recently, for a gold (110) surface a clear long-range reordering of the substrate due to adsorption of CuPc (Ref. 20) has been detected. The capability of π-conjugated molecules to induce displacements of surface atoms in conjunction with self-organized molecular growth[21] appears then to be a general characteristic that is relevant from a technological point of view and makes adsorption of this class of molecules, in perspective, an attractive option for nano manipulation of surfaces.[22]

Among metals aluminum represents the archetypal for nearly-free-electron systems; therefore the Al surface constitutes an interesting alternative to the more extensively investigated transition metal substrates. In particular the absence of occupied d orbitals might highlight the role played by localization of the states in influencing the electronic structure of an organic-inorganic interfaces. To the best of our knowledge the Al surface has never been studied as a substrate for CuPc film deposition, apart from the case in which

it was used to support thick films of CuPc. In this latter case, the aim was to analyze bulk interband molecular transitions[23] and the influence from the metal-molecule interface was not investigated.

The aim of this work is to study the growth mode and the molecular orientation of the overgrown film as a function of its thickness, and to characterize the geometric and electronic structure of monolayer and submonolayer CuPc films, deposited by thermal evaporation on an Al(100) substrate. CuPc is a dye pigment that is thermally very stable, thus allowing purification by sublimation and deposition by thermal evaporation or organic molecular beam epitaxy (OMBE).[17] Electron energy-loss spectroscopy (EELS) performed both in reflection geometry and as a function of the ejection angle are the main spectroscopic tools applied in this work.

The literature reports on a limited number of EELS experiments on MPc films in general and on CuPc films in particular, most of them made in transmission geometry on thick films, with high primary electron energy. Low-energy electron energy-loss spectra in reflection conditions have been measured on policrystalline films of H_2Pc, CuPc, VOPc, and PbPc (Refs. 24 and 25) (prepared by sublimation under high vacuum 10^{-7}–10^{-8} mbar) on a Si substrate, with a primary electron energy of 100 eV. The spectra of all phthalocyanine complexes examined have similar structures and the observed peaks in the $\pi \rightarrow \pi^*$ excitations region are always in good agreement with the correspondent optical absorption data.[2,26]

Although a limited number of works have made use of EEL spectroscopy to study MPc films, this technique is particularly attractive because it allows us to examine an energy range corresponding to a range from the ir to soft-x-ray regions in the electromagnetic spectrum by using a laboratory-based spectrometer that can be easily conjugated to a growth chamber for *in situ* investigation of the growth mechanism. The main target of this paper is to give evidence of the possibility of monitoring the growth of thin films of CuPc, ranging from submonolayer to a few monolayers, by the use of EEL spectroscopy and emphasize the potentiality of EELS technique in measuring the electronic properties of these films. Furthermore, the possibility to determine the orientation of the molecule with respect to the substrate has been shown. The latter result has been reached exploiting the relative orientation of transition dipole moment (i.e., the symmetry of the $\pi \rightarrow \pi^*$ transition at 3.7 eV) and momentum transferred in the collision. A similar experiment, based on core transition, has already been performed in the case of simpler organic molecule adsorbed on metallic substrate.[27]

II. EXPERIMENT

The experiments reported in this paper have been performed at the LASEC laboratory (Dip. di Fisica and Unità INFM, Università Roma Tre) with an apparatus that allows us to study thin films, grown *in situ*, by a variety of electron spectroscopies, thus providing complementary information on both electronic and geometric structure of the overlayer. In particular, the apparatus consists of two separate UHV chambers. The experimental chamber, equipped with an electron gun, a x-ray source, and two hemispherical analyzers, is devoted to spectroscopic investigations. A 5 degrees of freedom sample manipulator allows us to control position in space and temperature of the sample. A comprehensive description of this apparatus is given elsewhere.[28]

The preparation chamber features an electron bombardment evaporator Tricon[29] and a quartz crystal microbalance (QCM) used to control the growth rate of the films. The specific nature of CuPc, i.e., the high condensability of the evaporated and its tendency to sublimate forming needle-shaped crystals, made necessary to modify the evaporator source.[30] The thickness of the molecular overlayer is not univocally determined by the rate of deposition onto the QCM as it depends upon the sticking coefficient and the deposition mode. Hence from the QCM measurements, a nominal thickness, corresponding to uniform coverage of the surface, is deduced. Furthermore, the preparation chamber features an ion gun for sputtering substrates and a magnetically coupled linear feedthrough for transferring samples.

The Al substrate is a single crystal ($5 \times 5 \times 2.5$ mm^3) with (100) orientation and is supported by a molybdenum sample holder. Two different cleaning procedures have been adopted to remove the thick oxide layer always present on samples stored in air. The Al surface was cleaned by electropolishing prior to introduction in the preparation chamber. The electropolishing was performed on an AB electropolishing cell, Buchler Std, using a solution constituted of 345 ml of 60% $HClO_4$ and 655 ml of $(CH_3CO)_2O$. The sample was then cleaned under vacuum by repeated cycles of sputtering with argon ions (4 keV, 67 μA) and annealing (450 °C).[31] The sample cleanliness and order was checked before every deposition by means of Auger electron spectroscopy (AES) and EELS. Commercial CuPc was obtained from Aldrich Chemical (97% dye content); it was purified by sublimation under vacuum (540–550 °C, 10^{-2}–10^{-3} mbar) and then introduced in the molybdenum crucible of the electron bombardment evaporator. The purity of the powder was checked by means of an elemental analyzer (CE Instruments, model 1110 CHNS-O). Calculated values for $C_{32}H_{16}CuN_8$ are C, 66.72; H, 2.80; N, 19.45. The values found are C, 66.58; H, 2.66; N, 19.34 (%). (The uncertainty was ± 0.3 for C and ± 0.1 for H and N). The molecule was sublimated onto the substrate at room temperature at a rate of approximately 0.5 Å/min. The film, prepared in such a way, has been found stable until 400 °C and under electron bombardment (impinging current of few nA) does not suffer evident radiation damage; in summary it stays clean, under UHV condition, for at least 48 h. The EEL spectra reported in the paper were collected at room temperature with one of the two hemispherical electron analyzers present in the experimental chamber. EELS measurements were performed at fixed incident kinetic energy and the overall energy resolution was 500 meV throughout the whole range of incident electron energies (140 eV to 500 eV); the angular resolution was ± 0.5°. Two different kinds of EEL spectra have been recorded in this work. In the first one the energy loss probability is measured in specular reflection conditions with a fixed incident angle of 34° from surface normal. In the second one the probability for a given energy loss was measured
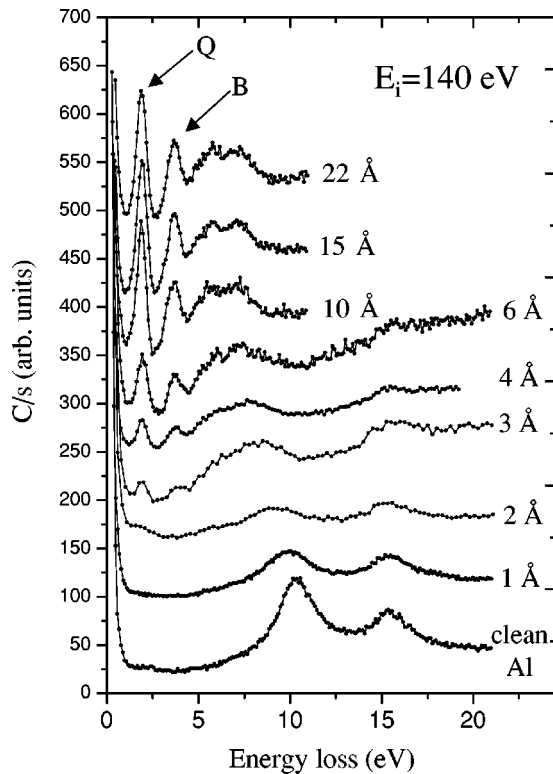
FIG. 1. EEL spectra as a function of CuPc film thickness performed in specular geometry with a primary energy of 140 eV. As a reference reported also is the EEL spectrum of the clean aluminum.
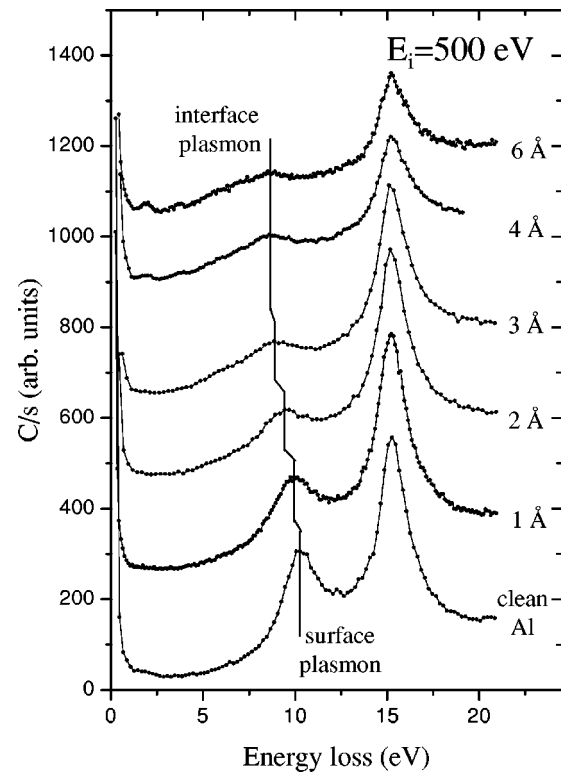
FIG. 2. EEL spectra as a function of CuPc film thickness performed in specular geometry with a primary energy of 500 eV. As a reference reported also is the EEL spectrum of the clean aluminum.

as a function of the transferred momentum by rotating the sample while keeping fixed the included angle between the incoming and scattered beams.

III. RESULTS AND DISCUSSION

In Fig. 1 are reported the constant momentum transfer EEL spectra measured in specular reflection as a function of CuPc coverage; the nominal thickness (from now on coverage) ranges from 1 Å up to 22 Å. All the spectra have been collected in specular reflection geometry and with a primary energy of 140 eV in order to take advantage of the reduced mean free path and then to be sensitive to the molecular film. The EEL spectrum of clean aluminum is also reported for reference.

A. Interface plasmon

The clean Al spectrum is dominated by two structures at 10.5 eV and 15 eV that correspond to the surface (SP) and bulk plasmon (BP), respectively. The intensity of the bulk plasmon drops with increasing coverage and almost disappears already for a coverage of 6 Å. In contrast the surface plasmon shows a more articulate evolution. For the lowest coverages the centroid of this structure shifts towards lower loss energy; the shift increases as the thickness grows up to 3 Å: in this situation it is not any more possible to resolve the surface plasmon from the molecular transitions appearing in the 5–8 eV region with similar intensity. The evolution of

the SP with coverage is more evident in Fig. 2, where the EEL spectra on the CuPc/Al(100) system are reported but with a primary energy of 500 eV, in order to highlight the interface excitations rather than the overlayer ones. It is then easier to follow the evolution of surface plasmon at very low coverages; we find that it shifts toward lower loss energy when increasing the coverage and it reaches a steady value (8.5 eV) already at 4 Å, well before bulklike conditions are fulfilled. It is therefore plausible to ascribe the SP peak to an interface plasmon such as those observed by Raether[32] in the case of thin films deposited on metallic substrate. More recently, a peak at 7 eV in the EEL spectrum of an Al surface exposed to O_2 has also been attributed to plasma oscillations localized in the metal substrate.[33] To ascertain whether or not the observed SP transition corresponds to an interface plasmon, it can be considered that the energy of such a collective mode is expected to disperse with the overlayer thickness unless the following condition is fulfilled:[32]

$$q_s d \gg 1, \tag{1}$$

where q_s is the momentum associated with the plasma oscillation, i.e., the surface component of the momentum exchanged in the inelastic scattering (q), and d is the thickness of the film. Dispersion of the plasma frequency as a function of the thickness of the overlayer was already observed for a thick Al film (150 Å) covered with oxide layer.[34] In our case q_s can be evaluated on the basis of the double collision model that is known to be valid[28,35,36] for the energy loss

processes in specular reflection geometry. According to this model, the inelastic scattering is followed or preceded by an elastic one and the inelastic cross section can be assumed different from zero only for scattering angle falling within a cone of aperture $\Theta_0 = \Delta E / 2E_0$, where E_0 is the energy of primary beam and ΔE is the energy lost in the collision. Consequently the maximum q_s allowed is of the order of $\Theta_0 k_i \simeq 1.2$ Å^{-1}, where k_i is the incident momentum. This explains the dispersion of the interface plasmon observed in Fig. 2, in particular the asymptotic value is reached for a coverage of 4 Å, which is the minimum coverage to satisfy inequality 1 ($q_s d = 4.8$). Moreover, making the assumption that the Al conduction electrons are well described by a free-electron gas, the interface plasmon frequency is related to the dielectric constant of the molecular film by the relation[32]

$$\hbar \omega_s = \frac{\hbar \omega_p}{\sqrt{1 + \varepsilon}}. \tag{2}$$

From the measurements reported in Fig. 2 we estimate for $\omega_s = 8.5$ eV and for $\omega_p = 15$ eV hence obtaining a value of 2.1 for the dielectric constant of the CuPc, a value that well agrees with those measured for other planar organic molecules, with an extended delocalization of π electrons, like benzene. All these findings support the hypothesis that the dispersing structure observed in Fig. 2 is to be ascribed to a surface plasma wave propagating within the aluminum substrate whose frequency is modified by the dielectric response of the molecular adlayer. To the best of our knowledge this is the first observation of an interface plasmon induced by organic molecule in aluminum.

B. Molecular transition

Electronic transitions due to the CuPc molecule become evident in the EEL spectrum starting from a coverage of 3 Å; for this coverage two weak peaks centered at 1.9 and 3.7 eV (hereafter Q and B transitions, respectively) appear together with a broad structure between 5 and 8 eV that is more intense than the Q and B transitions. Increasing the coverage, the Q and B transitions are always present: their intensities increase as a function of the coverage while their shape, energy position, and relative intensity remain substantially unchanged. In contrast the broad structure at 5–8 eV shows a modest evolution, reaching its final shape at 6 Å. For coverages of this value and higher the structure shows two prominent features located at 5.8 and 7.1 eV that are weaker than the B and Q transitions. It is interesting to note that starting from 10 Å, the EEL spectrum does not show significant modifications, thus suggesting that the molecular film has reached a bulklike configuration. This is confirmed by the observation that the energies at which electronic transitions appear do correspond to those reported in a previous work on thick CuPc films.[24] According to the diagram level of the CuPc molecule as obtained from the four-orbital model,[37–39] the transitions at lower energies ($\Delta E < 5$ eV) appearing in Fig. 1 are assigned mostly to $\pi \rightarrow \pi^*$ electronic transitions of phthalocyanine molecules. In particular the peak at 1.9 eV, the Q band, is due to a mixture of $a_{1u}(\pi)$

$\rightarrow e_g(\pi^*)$ and $b_{2g} \rightarrow b_{1g}$ transitions; although the two transitions are almost degenerate in energy, the former has a dipole moment perpendicular to the molecular plane while the latter, mostly due to d orbitals from copper atom, has a dipole moment in the plane of the molecule. On the contrary the peak at 3.7 eV, the B band, is related to the single $a_{2u}(\pi)$ $\rightarrow e_g(\pi^*)$ transition, thus having a well defined symmetry with respect to the plane of the molecule. We also observe peaks at 5.8 eV, C band, and at 7.1 eV, X_1 band, both assigned to a $\pi \rightarrow \pi^*$ transition. It is worth noting that there is a good agreement between the transition observed by means of EELS for the bulklike coverages (10–22 Å) and those obtained in the optical absorption spectra for a thick film of CuPc.[26] Additionally, in absorption spectroscopy two other bands at 4.7 eV (N) and at 7.8 eV (X_2) have been identified. We speculate that the former transition (N) gives rise, in our spectra, to the low energy shoulder of the peak centered at 5.8 eV while the latter transition (X_2) is not detectable as already reported in a previous EELS work.[24]

From Fig. 1, the Q and B transitions appear for coverages of 3 Å and higher. This threshold value corresponds, in the hypothesis of a flat lying adsorption geometry, to saturating the surface with one monolayer. In this framework molecules from the first layer do not contribute to Q and B bands. In order to understand whether at low coverages these structures are simply confused in the background, or an alteration of the electronic structure occurs that forbids them, the Q and the B band intensities are plotted as a function of CuPc coverage (see Fig. 3). For coverages below 10 Å we observe that the experimental data can be fitted with a straight line whose intercept to zero corresponds to a coverage between 2 and 3 Å. Hence, appearance of the optical absorption bands (Q and B) in the EEL spectrum has a clear threshold at a low nonzero coverage. It implies that the electronic structure of the first adsorbed molecules is different from that of the bulk ones. We also notice that the threshold coverage of 2–3 Å is consistent with the saturation value for one layer of flat lying absorbed molecules. This behavior is confirmed by a similar investigation performed at 500 eV of incident energy.[30] In other words we can make a clear distinction between molecules directly bonded to the Al substrate (coverage below 3 Å) and molecules not directly bonded to the substrate (coverage above 3 Å). In the latter case the electronic structure, as revealed by EELS, is identical to that of bulk CuPc while in the former case modification of the electronic structure is such to prevent transitions toward the lowest unoccupied molecular orbital (LUMO) orbital. Above 10 Å we observe a saturation of the Q and B band intensity. It is now important to understand why the optical transitions are inhibited for molecules directly bonded to the Al substrate. The simplest hypothesis to be made requires that, as a consequence of charge transfer, electrons from the Al substrate fill up the molecular π^* LUMO and the $3d_{x^2-y^2}$ orbitals. In order to fill the LUMO (doubly degenerate) and the $3d_{x^2-y^2}$ states, 5 electrons per molecule should migrate from the substrate. Roughly speaking, each CuPc molecule covers about 32 Al atoms, then each of these metallic atoms will contribute with about 0.16 electron to the charge transfer process. Considering the high density of nearly free electrons of the
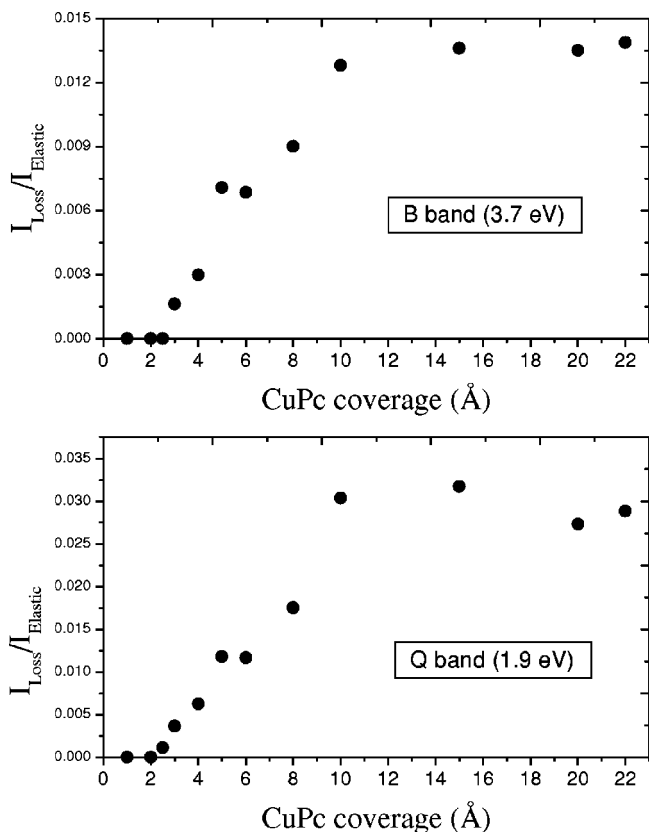
FIG. 3. Q and B band intensity, normalized to the related elastic peak intensity as a function of CuPc coverage.

FIG. 4. Experimental geometry for the EEL spectrum as a function of the exchanged momentum. Electron gun and the analyzer are fixed; α_p is the angle between the dipole moment of the molecular transition and the surface of the sample described by the plane aa'. The rotation of the surface is described by the angle θ and θ_o is the angle between the electron gun (the analyzer) and the normal to the surface when specular conditions are satisfied.

is as large as 2.67 eV. In conclusion a sizeable charge transfer from substrate to molecule explains the observed threshold in coverage for appearance of optical bands in the EEL spectra.

C. EEL spectra as a function of the exchanged momentum

The inelastic scattering in specular reflection geometry can be described by means of the double collision model (DCM) theoretically predicted[36] and experimentally verified[28,35] for energy losses in the range 10–30 eV. In this model the measured electrons suffer a double collision (one elastic and one inelastic) with the solid: in the elastic collision electrons are reflected from the surface, and in the inelastic one an energy loss occurs while scattering in forward direction. Concerning our experiment, the proposed model has two main implications: (i) the smallness of the momentum exchanged in the inelastic collision, compared with the momentum of the incident electrons, allows to apply the dipole approximation, (ii) two channels will incoherently contribute to the total cross section, that in which the elastic collision precedes $(D+L)$ and that in which it follows $(L+D)$ the inelastic collision. As previously pointed out the transitions at the lowest energies have a well defined symmetry; in particular the B band, due to its unambiguous $\pi \to \pi^*$ character, has dipole moment (**p**) perpendicular to the plane of the molecule. The spatial orientation of the molecule can then be probed by changing, in the experiment, the direction of dipole moment with respect to the momentum transferred in the inelastic collision. In this framework the cross section of EELS is proportional to $|\mathbf{p} \cdot \mathbf{q}|^2$; thus the molecule orientation can be derived studying the EELS probability of the transition B as a function of the angle included between **p** and **q**. In Fig. 4 is reported the kinematics of the experiment. According to the DCM, two inelastic exchanged momenta are drawn directed along the directions of the incoming beam ($\mathbf{q}_{L+D}$) and of the collected beam ($\mathbf{q}_{D+L}$). α_P

substrate, such a charge transfer is not unreasonable. Besides, a comparably large charge transfer it has already been observed in the case of C_{60} overlayer grown on Al.[40] Further support to the charge transfer mechanism comes from considerations on the molecular energy levels. For molecular solids grown on solid surfaces it was commonly assumed that an organic-metal interface energy diagram can be obtained by aligning the vacuum levels of the two materials. Recently it has been demonstrated that this assumption is not always true for both metal[41] and semiconductor substrates.[42] Vacuum level alignment applies only when the interaction between molecular film and substrate is weak. As previously pointed out, this is not our case. The charge transfer with consequent formation of an ionic bond between CuPc and Al substrate implies the formation of a dipole barrier at the interface.[42] The presence of a surface dipole barrier is also supported by the consideration that the work function (WF) of aluminum is 4.3 eV while the electron affinity (EA) of the molecule (distance between LUMO and vacuum level) is only 3.1 eV. Then the 1.2 eV difference between the two levels should prevent any charge transfer in the case of noninteracting interfaces. Our EELS analysis suggests that LUMO is filled and then it is either aligned or it lies below the Fermi level; we then conclude that the LUMO state of the molecules directly bonded to the metal shifts at least by 1.2 eV. Similar results have been already observed for C_{60}/Au(110) (Ref. 43); also in that case the authors claim for a charge transfer from the metal to the molecule even though, in that case, the difference between the EA and WF
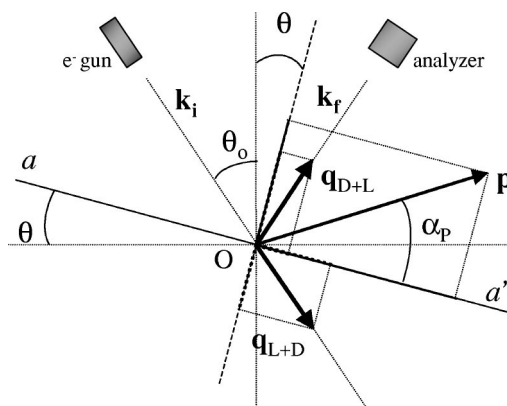
is the angle formed by vector **p** with respect to the surface and represents the orientation of the molecule. The experiment was performed with the higher coverage (22 Å), by scanning the angle θ, i.e., the angle between the normal to the surface and the bisector of the included angle between incoming and outgoing electron beams (see Fig. 4). The directions of incident and diffracted beams are fixed in the laboratory reference frame, thus also $(\mathbf{q}_{D+L})$ and $(\mathbf{q}_{L+D})$ have a fixed direction. By keeping fixed the energy of incoming and outgoing electrons, the rotation of the sample results in a rotation of **p** and thus in a variation of the scalar product $\mathbf{p} \cdot \mathbf{q}$ (q is not univocally determined, two values are present for each kinematics). It is more convenient to describe the process in the sample reference frame, where the scalar product between the exchanged momentum and dipole moment can be separately written for the two channels ($L+D$ and $D+L$) as

$$\mathbf{q} \cdot \mathbf{p}_{L+D} = [q_\perp p_\perp + \mathbf{q}_\parallel \cdot \mathbf{p}_\parallel]_{L+D}$$

$$= qp[\cos(\theta_o - \theta)\sin\alpha_p + \sin(\theta_o - \theta)\cos\alpha_p\cos\beta],$$

$$\mathbf{q} \cdot \mathbf{p}_{D+L} = [q_\perp p_\perp + \mathbf{q}_\parallel \cdot \mathbf{p}_\parallel]_{D+L}$$

$$= qp[\cos(\theta_o + \theta)\sin\alpha_p + \sin(\theta_o + \theta)\cos\alpha_p\cos\beta], \tag{3}$$

where the subscripts $L+D$ and $D+L$ take in account the presence of the two possible scattering channels previously discussed, β represents the orientation of the molecule in the azimuthal plane, and for $\beta=0$, **p** lies in the scattering plane. The differential inelastic cross section will then be, as already shown elsewhere,[28,35] the incoherent sum of the $D+L$ and $L+D$ cross sections. Hence, within first Born dipolar approximation the energy loss differential cross section factors out in a kinematical term times the optical oscillator strength of the transition involved, times the sum of the two orientation terms appearing in 3. Taking into account that none of the studied interfaces has displayed a low energy electron diffraction (LEED) pattern, an azimuthal random orientation of the adsorbed molecules can be safely assumed. This being the case, the dependence of the inelastic cross section upon the polar angle reduces to the modulus square of the orientation factors averaged over the azimuthal angle beta, which is

$$|\mathbf{q} \cdot \mathbf{p}|^2 \propto R \left[\cos^2(\theta_o - \theta)\sin^2\alpha_p + \frac{1}{2}\sin^2(\theta_o - \theta)\cos^2\alpha_p \right]_{L+D}$$

$$+ (1-R)\left[\cos^2(\theta_o + \theta)\sin^2\alpha_p \right.$$

$$\left. + \frac{1}{2}\sin^2(\theta_o + \theta)\cos^2\alpha_p \right]_{D+L}. \tag{4}$$

R is the relative weight of the two channels and it depends essentially on the amplitude of the elastic component of the cross section.[28] In Fig. 5 is reported the intensity of the transition B, normalized to the related elastic peak intensity, as a
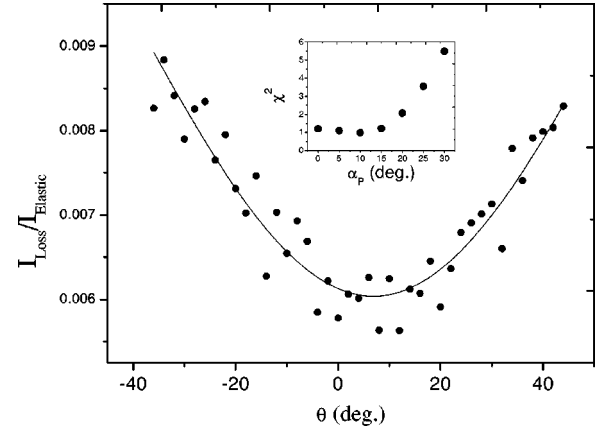
FIG. 5. B band intensity (●), normalized to the related elastic peak intensity, as a function of the polar angle. The continuous line is the best fit obtained with the trial function, Eq. (4), and $\alpha_p = 15°$. In the insert χ^2 values as a function of the α_p parameter are reported.

function of the polar angle. Equation (4) is a trial function with the scaling factor R used as a free parameter. The fitting procedure has been repeated for several value of α_p ranging from zero to 90°. In the insert of Fig. 5 is reported the χ^2 as a function of α_p from which it is possible to conclude that the proposed model can be accepted for values of α_p in the range 0°–15° where the χ^2 is almost constant and equal to 1. From the structural point of view this corresponds to having the plane of the molecule oriented almost perpendicular to the surface plane. The best R value is 0.54, which suggests an almost equal probability for $L+D$ and $D+L$ scattering channels. This finding is in agreement with previous similar experiments on clean surfaces[28] that support the hypothesis of incoherent superposition of the two, equally relevant, scattering channels contributing to the EEL spectrum. Once more, momentum resolved EELS from adsorbed molecules has been shown to be a sensitive, accurate tool for determining orientation with respect to the substrate surface of thin molecular films.

IV. CONCLUSIONS

In conclusion, the early stage of absorption of CuPc on the Al(100) surface has been studied by angle resolved EELS. The method has proven to be very sensitive and allows us to investigate coverages as low as 1 Å. The first monolayer of molecules suffers a massive charge transfer from the substrate inhibiting the optical B and Q absorption bands that are, instead, characteristic of bulk aggregation. This finding suggests that CuPc interacts with the Al substrate via a strong ionic bond. The molecule substrate interaction is also testified by the observed shift in frequency of the Al surface plasmon. For the thick overgrown film the molecular plane is oriented predominantly perpendicular to the substrate plane, and, in contrast to the first adsorbed layer, it does not show evidences for charge transfer from the substrate (B and Q band are restored).

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