Electronic and vibrational properties at the ZnPc/Ag(110) interface

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The geometrical, electronic, and vibrational properties of one monolayer of Zinc-phthalocyanine (ZnPc) adsorbed on Ag(110) are studied by low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and high-resolution electron energy-loss spectroscopy (HREELS). STM and LEED revealed that the molecules lie flat on the surface, ordered in a compact arrangement with a supercell defining a coincidence mesh with the substrate lattice. By comparing the HREELS spectra of one monolayer to those of a multilayer film, in which the molecules are weakly interacting, it was found that the electronic and vibrational properties of the molecular film are sensibly perturbed at the interface. The Q and B bands corresponding to optical interband excitations measured for the multilayer are not detected for the monolayer film and an intense low-energy Drude-like plasmon loss in the infrared region is observed. The vibrational features are also modified: several Raman modes of the isolated molecule were found to become infrared active for the monolayer because of the lowering of the molecular symmetry induced by the interaction with the substrate. Moreover a sizeable vibrational softening was measured for the selected modes indicating a charge transfer from the substrate to the molecules. Finally the strong asymmetric line shape observed for one of the Raman modes is discussed in terms of interfacial dynamical charge transfer and electron-phonon coupling.

I. INTRODUCTION

The interface formation between large pi-conjugated molecules and inorganic surfaces has stimulated an important scientific interest over the last decade because of their potential applications in the field of optoelectronics.[1–4] Nevertheless a better fundamental understanding of interfacial physical phenomena is needed to improve the design of organic molecule-based devices. To this end it is necessary to study the electronic and geometric structures of adsorbed molecular films which are responsible for the charge injection ability, the charge transport, and light emission/absorption processes.

From an applied point of view it has been shown that well-ordered films grown with high structural quality are the most relevant for electronic devices.[5] Highly ordered two-dimensional (2D) molecular films can be realized by exploiting the self-assembly properties of organic molecules upon adsorption on crystalline surfaces.[5–10] Many studies have in fact shown the possibility to realize molecular films having original geometrical structures and optoelectronic properties with respect to the molecular solids.[7,11,12] Among the technologically relevant organic molecules the metallophthalocyanines (MPc) are very extensively studied for their chemical and optoelectronic properties. They can be employed as building blocks for a wide range of applications such as gas sensors, field effect transistors, organic light emitting diodes, or data storage devices.[5,13] In particular Zinc-phthalocyanine (ZnPc) is one of the most simple, stable, and widely studied MPc. Its electronic and vibrational structures are well documented and it appears as a model molecule for a fundamental study on an adsorption system.

In the last few years MPc have been the subject of increasing interest due to the possibility of changing their electronic properties through doping by alkali-atom intercalation.[14–16] Similar to fullerenes the electronic structure of MPc can also be modified by the interaction with a metal substrate. For instance the metal-molecule interaction can be exploited to induce a charge transfer at the interface thereby changing the molecular electronic gap of the monolayer.[11,17–20] Noble metal surfaces are natural candidates to host self-assembled organic monolayers since their moderate reactivity toward pi-conjugated systems enables an adequate balance between molecule-molecule and molecule-substrate interaction resulting in the achievement of a well-ordered organic monolayer.[7,9,21–23] Moreover silver and copper often show to transfer charge to the adsorbed molecules because of their relatively low work function.[12,18,19,21,24,25] In the present paper we employed the Ag(110) surface to investigate how the substrate anisotropy (a twofold symmetry) can influence the molecular arrangement in the first monolayer and, in the perspective of electron doping, to study how the charge state of the ZnPc is modified by the interaction with the metal substrate.

The core of this paper is the study of one monolayer (ML) of ZnPc on Ag(110). To analyze the physical modifications of the molecular film at the interface, the properties of 1 ML ZnPc/Ag(110) are compared with those of a film of about 20 ML, the latter presenting very similar properties of that of the bulk molecular crystal. The organic/metal interface characterization was performed by a multitechnique approach. Low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) were used to determine the surface geometric structure and molecular orientation of the first layer. High-resolution electron energy-loss spectroscopy (HREELS) was employed to probe the vibrational and electronic properties of the system.

LEED and STM showed that the monolayer film is long-range ordered and presented a coincidence mesh with the substrate indicating the presence of preferential adsorption sites. HREELS measurements evidenced strong modifications of the properties of the molecular film in contact with the metal surface. The most striking effect with respect to the multilayer film is the quenching of the interband π-π^* transitions accompanied by the appearance of an intense and structured electronic background. This feature is discussed in terms of the metallic character of the interface. The measurements of the vibrational properties also revealed strong modifications upon adsorption, since a number of new vibrational modes appear for the monolayer film. These are interpreted as intrinsically Raman-active modes of the free molecule which become dipole active following a molecular symmetry breaking due to the molecule-substrate interaction. One of these new modes displays an asymmetric line shape, which is interpreted in terms of electronic damping of the molecular vibrations and interfacial dynamical charge transfer (IDCT).

II. EXPERIMENT

All experiments were performed under UHV conditions. The experimental setup was made of three interconnected vacuum chambers. The base pressure in each chamber was in the low 10^{-10} mbar range. The first chamber was dedicated to sample preparation, to molecule deposition, and LEED measurements. The second and the third chambers were dedicated to STM and HREELS analysis, respectively. STM measurements (OMICRON VT SPM) were performed in constant-current mode. No processing was applied to the STM images presented here except for a planar background subtraction. The HREELS spectra (VSI DELTA 0.5 spectrometer) were acquired in specular geometry conditions with an incidence angle of 60° with respect to the surface normal and with primary electron energy of 5.3 eV allowing a high surface sensitivity. The energy resolution was 3 meV (24 cm^{-1}). The Ag(110) sample was prepared by repeated cycles of Ar ion sputtering ($U=1$ keV; $I=2$ μA) followed by annealing at 620 K until a sharp LEED pattern was obtained. STM was used to check the presence of large terraces which allow the formation of a long-range ordered film on the surface, while HREELS measurement allowed to verify the absence of contamination. ZnPc molecules were synthesized by classical methods[26] and further purified by outgassing in UHV. They were heated at 600 K at a deposition rate of ≈ 1 ML per minute onto the silver surface kept at room temperature. During the sublimation the pressure did not exceed 2×10^{-9} mbar. A single monolayer was achieved by successive short-time depositions of 15 s. With this procedure sharp LEED patterns due to the molecular superstructure as well as clearly resolved STM images that show ordered and homogenous molecular arrays on the substrate terraces were obtained. HREELS measurements confirmed that the obtained coverage is indeed very close to one monolayer. The coverage of the thick layer was roughly estimated from the evaporation time.
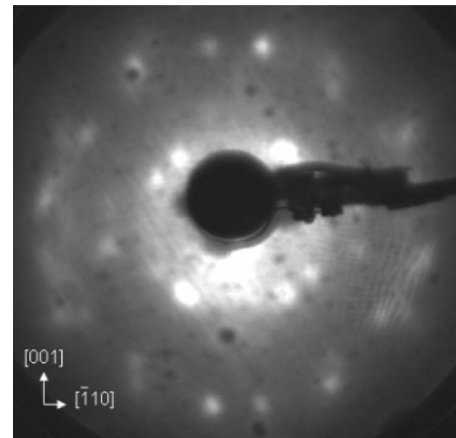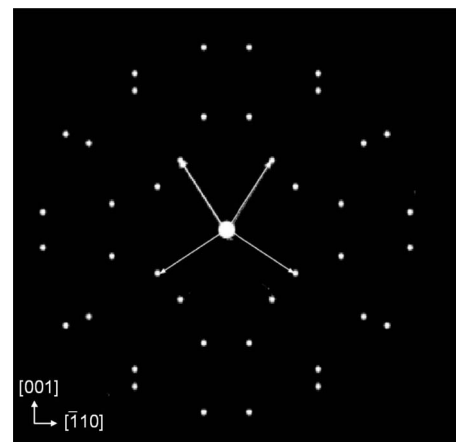
FIG. 1. (a) LEED pattern of the molecular superstructure of 1 ML ZnPc/Ag(110) taken with a primary energy of 11.2 eV. (b) Reconstructed pattern obtained with the two symmetric superstructures determined from the LEED pattern (see text).

III. RESULTS

A. 1 ML ZnPc/Ag(110): Geometrical structure

The LEED pattern obtained after the deposition of 1 ML of ZnPc on a freshly prepared Ag(110) is presented in Fig. 1(a). The diffraction pattern results from the superposition of two molecular lattices. Higher-energy patterns (not shown) including the substrate diffraction spots enabled to determine the length and direction of the molecular lattices. This was done by simulating the LEED pattern with different basis vectors in the reciprocal space until the best match between the simulated and the experimental pattern was found [Fig. 1(b)]. The best agreement is obtained for two coincidence superstructures defined by the matrices $M = (4 - 2, 2.5 \ 3)$ and $M' = (4 \ 2, 2.5 - 3)$. These matrices indicate that the lattices of the molecular film and the substrate coincide with every second unit cell of the superstructure. These two superstructures are symmetric with respect to the (001) and (-110) mirror planes which include the substrate high-symmetry directions $\langle -110 \rangle$ and $\langle 001 \rangle$, respectively. The length of the molecular lattice vectors are $A = 14.17$ Å and $B = 14.24$ Å and the angle between them is $\phi = 95°$.
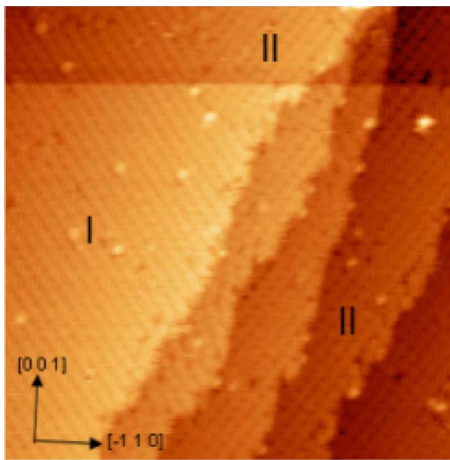
FIG. 2. (Color online) Large STM image (60×60 nm²) of the filled states ($U = -2.6$ V, $I = 0.1$ nA) of 1 ML ZnPc/Ag(110). We can distinguish different molecular domains (labeled I and II) whose orientations are symmetric with respect to the (001) and (−110) mirror planes which include the substrate high-symmetry directions $\langle -110 \rangle$ and $\langle 001 \rangle$, respectively.

Figure 2 displays a large-area STM image of 1 ML of ZnPc/Ag(110). The silver terraces are covered with ZnPc molecules forming a long-range ordered two-dimensional film in which two domains (I and II) can be distinguished. They are due to the two symmetric orientations of the molecular lattice. Figure 3(a) displays a high-resolution STM image of a smaller area which allows a closer view of the molecular arrangement. It reveals a compact film where the molecules lie flat on the surface. Their orientations within a domain is fixed with one arm of the cross-shaped molecules forming an angle of $\alpha = 25°$ with respect to the [001] of the substrate. Remarkably, for each molecule, one of the two arms of each cross-shaped molecule appears brighter than the other. To highlight this feature, Fig. 3(b) presents the intensity profile measured along the two arms of the molecules as shown in Fig. 3(a) by the red solid and black dashed lines. The mean height of the isoindoles moieties in the arm oriented along the red solid line is 0.1 Å higher than the center of the molecule. In the perpendicular direction (black dashed line) the apparent mean height of the other arm systematically appears about 0.2 Å higher than the center.

In Fig. 4 a tentative model for the geometrical structure of 1 ML ZnPc/Ag(110) is presented. It exploits the LEED and STM results just described, that is the molecule-substrate commensurability and the molecular orientation with respect to the substrate high-symmetry directions. It is interesting to notice that since the overlayer forms a coincidence lattice, the molecular lattice points are located at two substrate sites only. For the sake of clarity only one of the two symmetric lattices present on the surface is shown. The adsorption sites were arbitrarily chosen so to place the Zn atom in high-coordination sites.

B. Electronic properties of ZnPc adsorbed on Ag(110)

In Fig. 5 the HREELS spectrum of a multilayer of ZnPc (about 20 ML) is displayed together with the ones of 1 ML
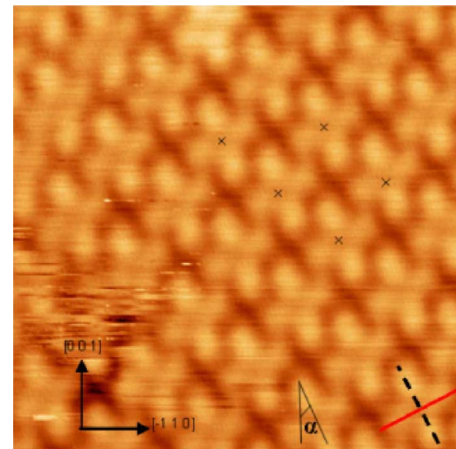
(a)
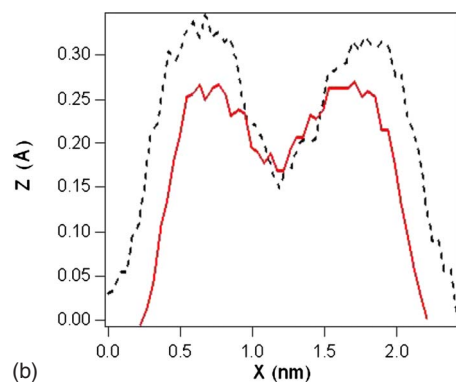
(b)

FIG. 3. (Color online) (a) STM image (10×10 nm²) of the empty states ($U = +1.6$ V, $I = 0.25$ nA) of 1 ML ZnPc/Ag(110). The angle between the direction given by the isoindoles units and the [001] direction of the silver surface is $\alpha = 25°$. (b) Line profiles along the two perpendicular directions given by the isoindoles units of the molecules as shown by the red and black dashed lines in Fig. 3(a) (bottom right corner). The line profiles are averaged over the five molecules marked by a cross in Fig. 3(a).

ZnPc/Ag(110) and of the clean Ag(110) surface. This superposition allows detecting the modification of the electronic properties between a thick layer and one monolayer of ZnPc adsorbed on Ag(110).

The multilayer spectrum is very similar to the ones previously reported for other MPc.[27–29] The losses in the energy range from 0 to 0.5 eV correspond to the vibrational excitations and above 0.5 eV they are due to the electronic transitions. In the inset (Fig. 5) the region of the electronic transitions of this HREELS spectrum is compared to the UV-Vis absorption spectrum of ZnPc diluted in a solution of dimethylformamide (DMF). The latter spectrum is representative of the weakly interacting molecules and will serve as a reference for the interpretation of the HREELS spectrum of the multilayer film. The two spectra show the low-energy electronic transitions between occupied and unoccupied molecular orbitals and accordingly concern features related to the same kind of transitions. The spectra display two distinct absorption bands: the Q band around 1.8 eV and the B band around 3.6 eV. In the case of the UV-Vis spectrum the Q band shows a strong absorption line that is due to the
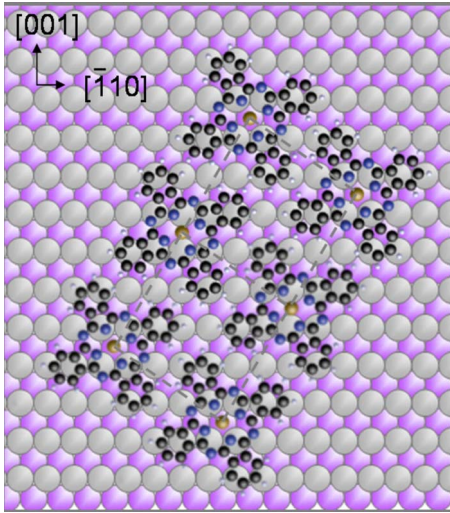
FIG. 4. (Color online) Model of the structural arrangement of the molecular film deduced from LEED and STM. Two unit cells are represented. The zinc atoms of the molecules are placed on top and on short-bridge positions (see text).
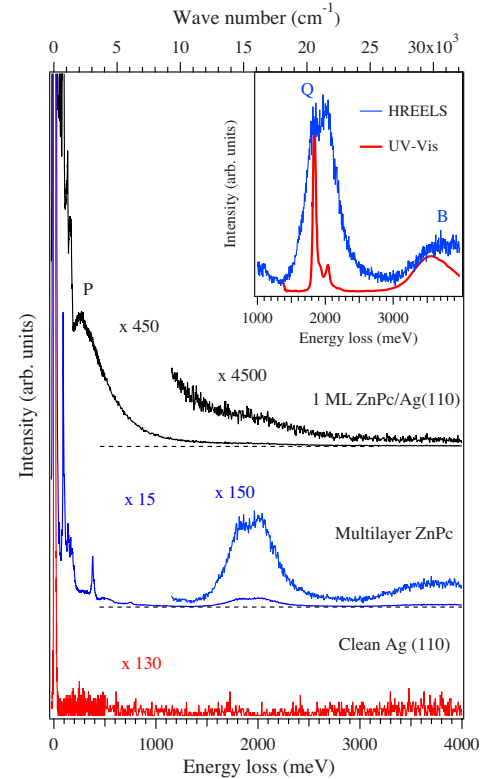

FIG. 5. (Color online) Comparison between the specular HREELS spectra of 1 ML ZnPc/Ag(110) (top curve), the ZnPc multilayer (middle curve), and the clean Ag(110) (bottom curve) ($E_i=5.3$ eV, $\theta_i=60°$). The horizontal dashed lines indicate the offset added for each spectrum and the amplification factors relative to the height of each elastic peak are indicated. Inset: superposition of the HREELS spectrum of the multilayer and of the UV-Vis spectrum of isolated ZnPc (see text). The letters Q, B, and P indicate the most important features discussed in the text.

highest-occupied molecular orbital (HOMO)-lowest-unoccupied molecular orbital (LUMO) transition followed by some vibronic losses.[30] At higher energy the B band is assigned to transitions from levels close to the HOMO-1 to the LUMO and to HOMO-LUMO+1 transition.[30] Although very similar, the HREELS spectrum is broader compared to the UV-Vis spectrum and an additional feature appears at about 2 eV in the Q band. Those differences, already observed for other MPc thin films,[31–35] are due to solid-state effects. The peak at 2 eV is due to the creation of physical dimers leading to a Davydov splitting of the π-π^* transition.[31–35] The optical region of the HREELS spectrum confirms that the molecules in the multilayer are weakly interacting and substantially retain the electronic properties of pristine ZnPc. The film is then semiconducting with well-defined intramolecular excitations.

In the spectrum of the monolayer no loss features are observed in the energy region of the multilayer Q band and B band. Their quenching is accompanied by the appearance of a broad and intense spectral intensity (labeled P) at low energy and up to 1.5 eV. This feature exhibits a strongly asymmetric line shape with a maximum of intensity at about 270 meV. As will be discussed below, such feature is characteristic of the electronic properties of the interface ZnPc/Ag(110). As it can be seen by comparing the spectrum of the ML to the one of the clean Ag(110), the contribution of the silver substrate to the spectrum of 1 ML ZnPc/Ag(110) is negligible and the spectrum is dominated by the response of the molecular monolayer.

C. Vibrational properties of ZnPc adsorbed on Ag(110)

By following the evolution of the molecular vibrations one can get important insights on the modifications of the molecular properties upon adsorption.[36,37] In Fig. 6 we compare the vibrational spectrum of the monolayer (upper curve) to that of the multilayer (lower curve). A precise assignment

of the spectroscopic features of the multilayer is necessary to interpret the modifications of the vibrational and electronic properties occurring at the interface. In the following we will briefly describe the multilayer spectrum and compare it to reference absorption measurements taken on isolated molecules and to density-functional theory (DFT) calculations.

Before going into the detail of the peak assignment, it is useful to recall the vibrational representation Γ_{vib} of the isolated ZnPc with a D_{4h} symmetry $\Gamma_{vib}=14\ A_{1g}(R)+13\ A_{2g}+14\ B_{1g}(R)+14\ B_{2g}(R)+13\ E_g(R)+6\ A_{1u}+8\ A_{2u}(IR)+7\ B_{1u}+7\ B_{2u}+28\ E_u(IR)$. This vibrational representation obtained in the framework of the group theory describes the number of expected vibrational modes, the symmetries of these vibrations, and their activities.[38] R refers to Raman and IR to infrared-active modes, the other modes being neither Raman nor IR active. A_{1g}, A_{2g}, B_{1g}, B_{2g}, and E_u are in-plane vibrations while the A_{2u} modes have an out-of-plane character.

When performed in specular geometry the HREELS spectrum is governed by the dipole selection rules and it is sensitive to the IR active modes.[36] It is then useful to compare our spectrum to IR data for which every absorption peak has been assigned to a particular vibrational mode with the help of DFT calculations. The main features of the IR spectrum of
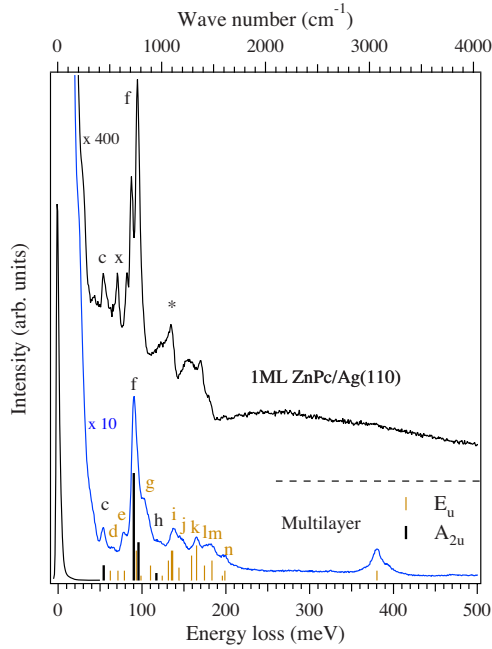
FIG. 6. (Color online) Comparison between the specular HREELS spectra of 1 ML ZnPc/Ag(110) (top curve) and of the multilayer of ZnPc (bottom curve) (E_i=5.3 eV, θ_i=60°). The horizontal dashed line indicates the offset added for the spectrum of the monolayer and the amplification factors relative to the height of each elastic peak are indicated. The vertical bars below the HREELS spectrum of the multilayer give the positions and intensities of the major IR-active modes of isolated molecules (Ref. 38). The thick (black) bars and the thin (orange) bars correspond, respectively, to the modes of A_{2u} and E_u symmetries. The letters as well as the asterisk refer to the most important features discussed in the text.

ZnPc in DMF solution are extracted from Ref. 38 and superposed to the HREELS spectrum of the ZnPc multilayer in Fig. 6. The very good agreement between the two data sets in terms of energy position and intensity of every feature allows a precise assignment of every HREELS feature. The main features of the HREELS spectrum are marked with letters from a to o. Six of these peaks (a,b,c,f,h) correspond to out-of-plane A_{2u} modes whereas 11 of them (d, e and the modes from i to o) correspond to in-plane E_u modes. Finally the peak g is composed of some nonresolved losses probably due to the different polymorphic forms coexisting in the molecular film.[39] The rest of the IR-active modes predicted by the group theory are not detected because their intensities are too low.

Let us consider the main features of the multilayer vibrational spectrum in more details. The dominant structure (f) at about 730 cm^{-1} is in fact composed of three vibrational modes: the lowest and the highest ones have A_{2u} symmetry and are due to C-H out-of-plane bending while the middle one has E_u symmetry and corresponds to a macrocycle deformation mode. The features denoted by a, b, and c (200 cm^{-1}, about 320 cm^{-1}, and 435 cm^{-1}, respectively) also have A_{2u} symmetry and are due to out-of-plane deformation of the macrocycle. The remainder of the modes observed in the spectrum, that is the modes d and e (535 cm^{-1}

and 635 cm^{-1}, respectively) and all features above 1000 cm^{-1} are due to in-plane vibrations and have E_u symmetry. The intense isolated loss feature o (3070 cm^{-1}) has E_u symmetry and is due the to C-H stretching motion. Apart from the latter, all the E_u modes detected correspond to in-plane deformations of the molecular macrocycle.

Let us now turn to the differences between the vibrational properties of the multilayer and of 1 ML ZnPc/Ag(110). A striking difference between these two spectra concerns the C-H in-plane stretching mode (located at 3070 cm^{-1} in the thick film), which is totally quenched for 1 ML. The most intense features of the monolayer spectrum are still located at about 700–800 cm^{-1}. As discussed later, although their line shapes and energy positions have changed, they can be confidently assigned to the C-H out-of-plane bending (A_{2u}) modes (peak f of the thick layer). At lower frequencies the A_{2u} mode labeled c at 435 cm^{-1} is unchanged with respect to the multilayer spectrum. In the frequency range just below and above the C-H features f (550–680 cm^{-1} and 1000–1700 cm^{-1}) several loss features are detected and their intensities are comparable to what were measured in the case of the multilayer where they were assigned to E_u modes. We will see in the next section that because of the surface selection rules that apply in HREELS, in the case of the ML they cannot be attributed to E_u modes anymore. Among these modes we find the mode labeled x ($\sim$570 cm^{-1}) and the one labeled with an asterisk at 1100 cm^{-1}. We finally notice that the latter has a clear asymmetric line shape that differs from the symmetric Lorentzian or Gaussian line shape usually observed for vibrational losses.

IV. DISCUSSION

A. 1 ML ZnPc/Ag(110): Geometrical structure

The LEED and STM revealed the presence of a long-range ordered ML. The model of Fig. 4 summarizes the main ingredients of the interface geometric structure which are discussed in the following. The fact that we observe a compact film suggests that the intermolecular dispersive forces play an important role in the self-assembly process. On the other hand the influence of the surface on the arrangement of the molecular superstructure is clearly revealed by the two symmetric orientations of the molecular film with respect to the substrate high-symmetry directions and by the coincidence mesh between the superstructure and the substrate. This indicates the existence of specific adsorption sites for the large ZnPc molecule as suggested in Fig. 4.

In the high-resolution STM image presented in Fig. 3(a) intramolecular contrasts are also noticeable. In particular the apparent heights of the isoindole units measured at the two main arms of the cross-shaped molecule differ and a depression localized at the center of the molecule is observed [Fig. 3(b)]. Since the STM maps the local density of states, the apparent low height at the location of the Zn atom can be related to the almost negligible participation of this atom in the LUMO.[40–42] More interestingly the different apparent heights of the two arms suggest a lowering of the molecular symmetry from D_{4h} to a twofold symmetry upon adsorption. This twofold symmetry is likely to be due to the coupling of
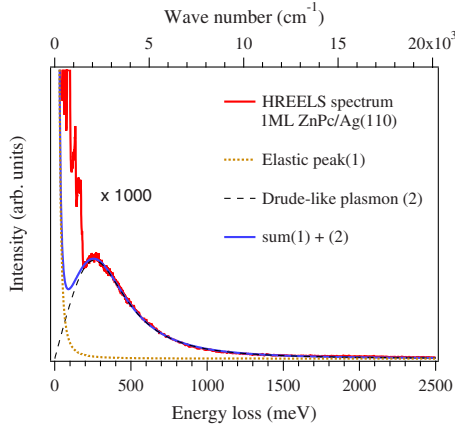
FIG. 7. (Color online) Specular HREELS spectrum (red curve) of 1 ML ZnPc/Ag(110) ($E_i = 5.3$ eV, $\theta_i = 60°$). (1) The (orange) dotted line corresponds to the shape of the contributions of the elastic peak and the most intense low-energy components; the (black) dashed line is the plasmon contribution. (2) The full (blue) line (3) results from the sum of (1) and (2).

the fourfold symmetric molecule with the Ag(110) substrate having a C_{2v} symmetry. The consequence of such symmetry lowering on the vibrational properties of the ML will be addressed later in the paper.

B. 1 ML ZnPc/Ag(110): Electronic and vibrational properties

In the previous section it was shown that the ML film shows remarkable spectroscopic differences with respect to the weakly adsorbed multilayer film. In spite of what is observed for the thick film, in the case of one-ordered ML no optical gaps (Q band and B band) could be detected. Such feature is a clear evidence that the electronic properties are severely modified at the interface because of the molecule-substrate interaction. As the optical gaps disappear, a broad and intense low-frequency structure (P) emerges which extends from 0 to 1.5 eV. Such low-energy feature was already observed for other similar systems or alkali-doped molecular films, and has often been assigned to collective intraband electron-hole excitations (intraband plasmon).[21,43,44] In order to elucidate the origin of the low-energy electronic feature in the present case we tried to reproduce the experimental spectrum by the loss function of a Drude-like plasmon of a free-electron gas.[45] After a background subtraction to account for the contribution of the elastic peak the following function was used to fit the spectrum

$$I_{\text{loss}}(\omega) = \frac{(I_{ip}\omega_{ip}^2\omega\Gamma)}{(\omega^2 - \omega_{ip}^2)^2 + (\omega\Gamma)^2} \propto \text{Im}\left(-\frac{1}{\varepsilon(\omega) + 1}\right), \quad (1)$$

where ε is the dielectric function, I_{ip} is the maximum intensity of the loss function ω_{ip} and γ are the plasmon frequency and the plasmon width, respectively. The result displayed in Fig. 7 shows that the spectral intensity of the low-energy feature is well reproduced by the model loss function. The parameters employed for the plasmon energy and width are 368 and 585 meV, respectively. These values are similar to what was observed in some related systems such as PTCDA/Ag(111) or C_{60} on transition metals.[21,43,44,46]

As for other similar interfaces the presence of an interface plasmon and the quenching of optical gap features reveal the metallic character of the ZnPc/Ag(110) system.[21,43,44,46] Such metallic behavior is accompanied by a charge transfer from the substrate to the molecules, which are good electron acceptors.[11,18] Nevertheless a metallic character for a Pc/transition metal interface is not always observed and even if some charge is transferred the interface can be semiconducting as observed for instance for $ZnPcCl_8/Ag(111)$.[11,18,37,47] In the present case the metallicity likely stems from the partial filling of the LUMO and its hybridization with the substrate electrons (s electrons and/or surface states) to form well-delocalized interface states crossing the Fermi level.[48,49] The observed interface plasmon is then the result of collective electron-hole pair excitations of vanishing energies from the now partially filled LUMO.[21] In the following the consequences of the molecule-substrate interaction and namely the presence of a metallic interface on the vibrational properties of the ML will be analyzed.

The HREELS spectrum of a thick layer of ZnPc taken in specular geometry (Fig. 6) essentially probes the dipole-active modes. Among these, the modes with E_u symmetry lie in the molecular plane whereas those with A_{2u} symmetry display an out-of-plane character. The simultaneous observation of these two perpendicularly oriented modes in the thick film evidences that the molecules are not oriented parallel to the metal surface.[28,29,31]

When one monolayer of ZnPc is adsorbed on Ag(110), E_u C-H stretching mode (peak o) is completely quenched (Fig. 7). It is important to notice that this mode is indeed observed in off-specular geometries (not shown) proving that its quenching in the spectrum of Fig. 7 is due to the surface selection rules and the molecular orientation. In fact this IR mode has an in-plane character and since the molecules lie flat on the surface the variation in the dipolar moment created by this vibration is effectively screened by the metallic substrate.[27,36] Accordingly the detection of all modes with E_u symmetry, i.e., IR-active modes that have the same symmetry like that of the C-H stretching mode, is not allowed by the surface selection rules for the monolayer. Otherwise the A_{2u} modes producing an out-of-plane variation in the dipole moment can still be observed.[27,36]

The other molecular vibrations having E_u symmetry are the modes d and e (~ 535 cm^{-1} and 635 cm^{-1}, respectively), and the modes above 1000 cm^{-1} measured for the thick layer. Because of the just-mentioned surface selection rules, one would expect a quenching of these vibrational bands as well. Nevertheless several modes are still observed in this energy region. As outlined below the reason is the peculiar chemical interaction between the molecules and the silver surface.

Indeed the electronic structure of the monolayer indicates an important molecule-substrate interaction when the molecules are adsorbed on the Ag(110) surface. The system may then be viewed as a molecule-substrate complex, where the D_{4h} symmetry of the isolated molecule is reduced upon adsorption due to the symmetry of the surface.[36,37,50] Accordingly in the STM image presented in Fig. 3 the molecules appear with a twofold symmetry suggesting a $D_{4h} \rightarrow C_{2v}$ symmetry lowering. Through the surface selection rules it is
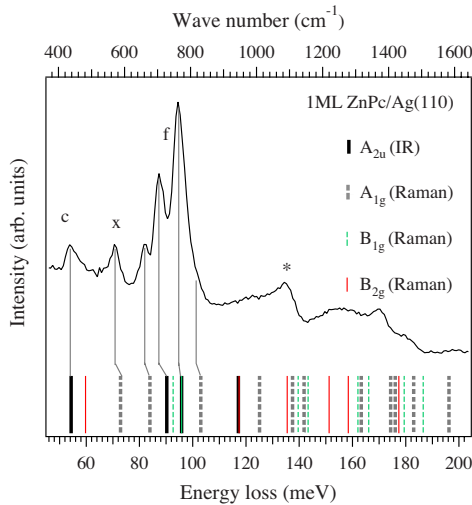
FIG. 8. (Color online) Specular HREELS spectrum of 1 ML ZnPc/Ag(110) (black line) (E_i=5.3 eV, θ_i=60°). The frequencies of A_{2u} (thick black vertical line), A_{1g} (thick dashed gray vertical line), B_{1g} (thin dashed green vertical line), and B_{2g} (thin red vertical line) modes of the isolated molecule are represented below the HREELS spectrum. The letters c and f correspond to the A_{2u} modes observed for the thick layer.

possible to track the origin of the modes allowed within the new symmetry. This is outlined in the correlation tables in Ref. 36. Under the C_{2v} symmetry the modes that belong to A_1 representation are dipole allowed. They correspond to the A_{2u} IR-active modes and to the A_{1g} and B_{1g} or B_{2g} (Ref. 51) Raman-active modes of the isolated molecule. The presence of several vibrational modes in the energy region of the now inhibited E_u modes can then be explained by the symmetry reduction in the molecules: upon symmetry lowering several Raman modes of the isolated molecule become dipole allowed. It is interesting to note that the IR activity of the vibrational modes is very sensitive to the strength of the molecule-substrate interaction. For instance, in the case of the weakly adsorbed CuPc/Au(100) system, where the molecules are also oriented parallel to the surface, the specular HREELS spectrum displays the dipole allowed A_{2u} out-of-plane modes whereas all E_u modes are quenched.[27] However at variance with the present study no Raman-derived modes are observed indicating that the molecular symmetry essentially remains unaffected by molecule-substrate interaction. This comparison confirms that in the case of 1 ML ZnPc/

Ag(110), several modes not having a A_{2u} symmetry become IR-active because of chemical interactions with the substrate and the consequent lowering of the molecular symmetry.

The relevance of the above scenario can be evaluated by comparing our results with the Raman and IR measurements performed on the isolated molecule. In Fig. 8 the HREELS spectrum of 1 ML ZnPc/Ag(110) in the energy region 400–1700 cm^{-1} is compared to the Raman and IR-active modes of ZnPc.[38] The A_{2u} and A_{1g} modes are represented by thick bars whereas the B_{1g} and B_{2g} modes are represented by thin bars. As one can see that the main features of the HREELS spectrum in the region below 900 cm^{-1} is composed of well-resolved peaks corresponding almost entirely to the A_{1g} and A_{2u} modes. This energy region will be discussed in more detail below. At higher frequencies the assignment is more involved. The HREELS features are not due to A_{1g} and A_{2u} only but also due to the B_{1g} or B_{2g} modes. It is also possible that some vibrational modes may be shifted with respect to the isolated molecule.

It is also interesting to note that for the isolated molecule, C-H stretching Raman modes with A_{1g}, B_{1g}, and B_{2g} symmetries are present in the energy region of the C-H stretching mode of E_u symmetry (peak o).[38] Regarding their symmetries, these vibrations would be susceptible to contribute to the monolayer spectrum but they clearly do not. This shows that not all of the originally Raman-active modes predicted to be dipole allowed induce a dynamic out-of-plane variation in the dipole moment strong enough to be probed. The absence of the C-H stretching modes probably indicates that this part of the molecule is weakly coupled with the metal surface and consequently this may also reflect that no (or very weak) distortion of the C-H bonds occurs upon adsorption.

Coming back to the peaks at about 435 cm^{-1}, 704 cm^{-1}, and 762 cm^{-1}, they are identified as the A_{2u} mode labeled c and as the two A_{2u} modes building up the feature f in the multilayer spectrum, respectively [see Fig. 5(a)]; the two other modes at 569 and 663 cm^{-1} correspond to the A_{1g} Raman-active modes of the free molecule. In Table I the six vibrational features of the monolayer below 800 cm^{-1} are compared to Raman or IR measurements performed on an isolated ZnPc and corresponding to the thick vertical bars in Fig. 8.[38] The agreement in term of wave number position between the observed monolayer modes and the corresponding modes of the isolated ZnPc is very good. All the concerned modes are related to vibrations of the whole macrocycle.

TABLE I. Main vibrational structures below 800 cm^{-1} as measured by HREELS for 1 ML ZnPc/Ag(110) (this study) and by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy for isolated molecules. The left column indicates the assignment of the vibrational modes according to Ref. 38.

Vibrational mode	Symmetry	HREELS (cm^{-1})	FTIR (cm^{-1})	Raman (cm^{-1})
Benzene out-of-plane bending	A_{2u}	435	438	
C-H out-of-plane bending	A_{2u}	704	728	
C-H out-of-plane bending	A_{2u}	762	773	
Ring breath., N-Zn stretch, Benzene expt.	A_{1g}	569		588
C-N-Zn-C in-plane bending, Isoindole expt.	A_{1g}	663		677

Very interestingly this comparison also shows that, as a general trend, the frequencies of the vibrational modes of the ZnPc molecules appear slightly redshifted upon adsorption on the Ag(110) surface. These shifts to lower energies can reasonably be interpreted as resulting from a charge transfer from the metal surface to the ZnPc. Such effect was already observed in the case of C_{60} thin films doped by alkali intercalation or by charge transfer from the substrate.[43,52,53] More recently, Craciun *et al.*[54] have measured sizeable charge-transfer related redshifts for different Raman lines in polycrystalline *K*-doped CuPc samples. From a theoretical point of view, a detailed study was recently performed on electron-doped MgPc molecules.[55] It was found that by adding one electron to the LUMO of an isolated molecule the vibrational modes tend to shift to lower wave numbers by about 10 cm^{-1}. This phenomenon is generally interpreted as a weakening of the intramolecular bonds and the consequent lowering of the vibrational frequencies upon charge transfer to some antibonding states. It has to be noticed that in the present case the molecular structure is certainly affected by the interaction with the substrate lattice and that a correlation between the shift in the vibrational modes and the molecular charge state is not straightforward. Nevertheless the similarity of the observed shifts in the present (-15 cm^{-1}) and in the mentioned theoretical study (-10 cm^{-1}) of the parent MgPc suggests that in the case of ZnPc/Ag(110) the charge transferred to the adsorbed layer is on the order of one electron per molecule. It is then interesting to relate the present results to the bulk electron-doped MPc systems.

In a recent theoretical work it was predicted that near half-filling the $MPc^{-\delta}$ system should exhibit singular electronic properties, including superconductivity.[14] The main ingredient is the presence of a highly correlated metal with orbital degeneracy as in the case of A_3C_{60} (where *A* is an alkali atom). However the experimental results on the electronic properties of doped Pc appear controversial and the possibility to make these systems metallic is still under debate. On one hand transport measurements showed that molecular films become metallic upon *K* intercalation.[54] On the other hand some photoemission and HREELS studies have shown that the molecular films remain insulating for all investigated doping levels.[16,56,57] The results presently found for the ZnPc/Ag(110) interface appear very important in this context since they suggest a different way to synthesize a metallic MPc-based system.

Let us now turn our attention to the intrinsically Raman-active mode located at 1100 cm^{-1} and marked with an asterisk in Figs. 6 and 8 and to the origin of its asymmetric line shape. Such a line profile is not observed in the case of the thick layer nor for the other modes of the ML. This suggests that the asymmetric line shape of this mode in the monolayer film results from a singular interaction of a particular vibrational mode of the molecule with the underlying substrate. Similar features have already been observed in vibrational spectroscopy in the case of atomic or molecular adsorbates on metal surfaces and were found to have a characteristic Fano line shape (see, e.g., Refs. 21 and 58–61, and references therein). In those works it was shown that the presence of such features in IR or HREELS spectroscopy occurs when the vibrational motion of the adsorbate is damped by energy
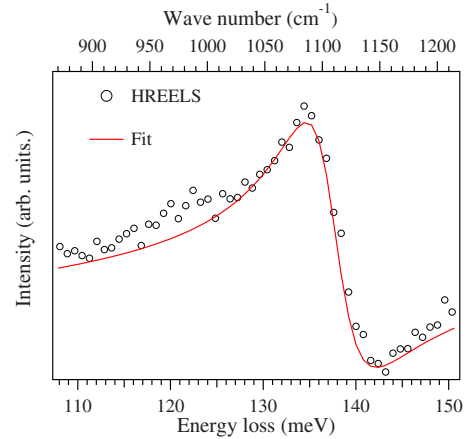

FIG. 9. (Color online) Zoom on the vibrational losses of the HREELS spectrum of 1 ML ZnPc/Ag(110) (black circles) in the region between 870–1200 cm^{-1}. Fano line-shape approximation (full red line) done with the help of Eq. (2).

transfer to the metal substrate.[60] Importantly the energy transfer mechanism can occur only if the lowest unoccupied orbital of the adsorbate has a considerable overlap with the Fermi level of the substrate. Some adsorbate vibrational modes can then couple with the electronic states and cause a dynamic energy shift in the partially filled orbital through the Fermi level of the substrate.[21,58–62] The electronic damping of the molecular vibration results in a breakdown of adiabaticity giving rise to the observed Fano line shape. This mechanism is also often referred to as interfacial dynamical charge transfer.[63]

In the present case the metallicity of 1 ML ZnPc/Ag(110) is proven by the presence of the low-energy plasmon due to intraband LUMO-derived transitions and by the absence of electronic gap features. The prerequisite condition for IDCT that is the overlap between the adsorbate's LUMO and the Fermi level at the interface is then fulfilled. To evidence that the line shape of the vibrational excitations is in this case effectively described by a Fano line shape the function given in Ref. 60 has been used to fit the experimental data

$$L(\omega) = c\,\gamma\omega_r\omega\,\frac{[1-(\tau/\gamma)(\omega^2-\omega_r^2)]^2}{(\gamma\omega)^2+(\omega^2-\omega_r^2)^2},\qquad(2)$$

where *c* is a constant used to adjust the height of *L* to the experimental data, γ corresponds to the damping measured by the full-width at half-maximum of the line shape, τ is the tunneling rate, and ω_r is the fully renormalized Born-Oppenheimer vibrational frequency. A background has been subtracted to the spectrum to take into account the low-energy excitations and the fitting procedure was realized in the range of 870–1200 cm^{-1}. The resulting curve fit is displayed in Fig. 9. It shows good agreement with the experimental data even if two weak additional contributions, probably originating from the two A_{2u} and A_{1g} modes, are also found in the range of 900–1000 cm^{-1}. The fitting parameters used were $\omega_r = 1109$ cm^{-1} and $\gamma = 60$ cm^{-1} and the asymmetry parameter given by $\omega_r\tau$ is 0.77. These parameters are quite close to the ones determined for W(110)-(1×1)H

and the value of the asymmetry parameter denotes the presence of strong nonadiabatic effects.[60,61] The frequency ω_r is also found to coincide with the A_{1g} vibration frequency of the isolated molecule. However this might be fortuitous since the vibration frequency of this mode is expected to be shifted with respect to the one of the isolated molecule. The vibrational mode involved in the coupling with the electron continuum likely comes from one among those lying within 1100 and 1160 cm^{-1}.

We then propose that the asymmetric line shape of the feature at 1100 cm^{-1} is the clear sign of a nonadiabatic coupling between electronic states and the molecular vibration and of an important electron-phonon coupling between an intrinsically Raman-active mode and the partially filled LUMO-derived state. It will be interesting to further investigate this aspect since the electron-phonon coupling is a crucial parameter foreseen by theoretical calculations on electron-doped MPc.[14] We also notice that such interactions are likely to be linked to the adsorption site recognition phenomenon.[8]

V. CONCLUSIONS

In this paper the structural order as well as the electronic and vibrational properties of 1 ML ZnPc/Ag(110) have been studied. STM and LEED measurements have revealed that the molecular monolayer forms a compact and ordered film. The equilibrium structure is coincidence mesh between the superstructure and the substrate lattices. HREELS measurements indicate that a specific chemical bond is formed between the molecules and the substrate as revealed by both electronic and vibrational features. A complete modification of the electronic properties is achieved at the interface as shown by the presence of a LUMO-related interface plasmon in the infrared region as well as the quenching of the π-π^* interband transitions of the neutral molecule. The appearance of vibrational intrinsically Raman-active modes in the monolayer spectrum is interpreted as the sign of a reduction in the molecular symmetry upon adsorption. The frequencies and line shapes of the vibrational modes confirm that the modification of the electronic structure is due to a partial filling of the LUMO leading to the metallicity of the interface and that this is accompanied by an interfacial dynamical charge transfer. The present study suggests a way to synthesize a metallic MPc-based system for which unconventional electronic properties can be expected.

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