Final-state diffraction effects in angle-resolved photoemission at an organic-metal interface

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In this paper it is shown that angle-resolved photoemission performed using low-energy photons on an organic-metal interface allows to clearly distinguish genuine interface states from features of substrate photoelectrons diffracted by the molecular lattice. As a model system an ordered monolayer of Zn-phthalocyanine is used as a diffraction lattice to probe the electronic band structure of a Ag(110) substrate. Photoemission close to normal emission geometry reveals strongly dispersive features absent in the pristine substrate spectra. Density functional theory modeling helped identifying these as bulk sp direct transitions undergoing surface-umklapp processes. The present results establish the important role of final-state diffraction effects in photoemission experiments at organic-inorganic interfaces.

Angle-resolved photoelectron spectroscopy (ARPES) is a preferred tool to study the electronic band structure of single crystals.[1] When performed with low photon energy, bulk band-to-band direct transitions may dominate the spectrum.[2] Energy and momentum conservation laws allow the band structure to be mapped, for instance, by changing the detection angle and photon energy and by referring to band-structure calculations.[3] This renders the technique to be particularly adapted to probe energy regions relevant for the optical properties of solids. Recently, ARPES was successfully used to investigate the interface properties of conjugated organic nanostructures self-assembled on single-crystal surfaces, which form a new class of materials of steadily growing importance.[4–7] ARPES of single-domain structures reveals interface states dispersion, thus enabling access to the electronic properties of two-dimensional (2D) systems such as the quasiparticle bandwidth, their effective mass, and correlation effects.[4,5] Alternatively, Fourier-transform analysis of ARPES spectra was recently used to reconstruct the interface molecular orbital densities, including adsorbate-substrate hybridization effects.[6,7]

The presence of organic-inorganic hybrid states is not the only aspect relevant to the interpretation of ARPES spectra at interfaces, though. In fact, the adsorption of ordered arrays of atoms[8] or nanostructures[9] on a surface can modify the escape conditions of substrate photoelectrons. The resulting spectra are sensibly affected and reveal the substrate electronic structure via an additional diffraction process often referred to as surface umklapp.[8,9] Within the one-step photoemission model a bulk Bloch wave is optically excited into a damped state extending into the vacuum as a time-reversed low-energy electron diffraction (LEED) state.[1] The presence of an adsorbate-induced lattice on the substrate crystal surface promotes new LEED states and, consequently, a new set of final states outside the surface. As a result, features observed by ARPES around a given direction may actually originate from bulk direct transitions that are excited one surface reciprocal lattice vector apart.

Once deposited on noble-metal substrates, self-assembled organic molecules display a large variety of structures. The degree of order, lattice parameter, and molecule-substrate distance sensibly depend on the intermolecular and molecule-substrate interactions[10,11] and can often be tuned by acting on overlayer coverage, sample temperature, molecular functionalization, etc. In this context, the use of self-assembled organic networks as the diffracting adsorbate appears as a promising way to probe different regions of the substrate reciprocal space.

In the present Rapid Communication an ordered monolayer (ML) of chemisorbed zinc-phthalocyanine (ZnPc) is used to modify the photoemission at low photon energy from a Ag(110) substrate. Its band structure is studied by ARPES near normal emission (NE). New spectral features, absent for the pristine sample, are induced by the molecular adsorbate. The angular dispersion of these features is compared to modeled bands obtained from density functional theory (DFT) band-structure calculations of the silver substrate.

The experiment was carried out at the BaDElPh beamline at the Elettra synchrotron radiation facility (Trieste).[12] The sample was prepared *in situ* in ultrahigh vacuum condition. Standard sputtering and annealing treatments resulted in a clean substrate with a high structural order as checked by LEED and surface state photoemission. The molecules were evaporated from a resistively heated tantalum crucible at a rate of 0.1 ML per minute. Annealing at 500 K improved the order of the adlayer, resulting in a sharp LEED pattern.[13] ARPES measurements were performed with horizontally polarized light in the 7–12 eV photon energy range impinging onto the sample at 50° from the surface normal. The photoelectrons were collected by a Phoibos 150 electron analyzer with a 2D CCD detector keeping the sample at NE and oriented along the $\Gamma KLUX$ plane direction of the Brillouin zone. Measurements were performed at room temperature, giving an overall energy broadening of 100 meV; angular resolutions was set to 0.3°.

Valence-band photoemission of conjugated organic molecular samples is often performed in a fixed-photon mode at

21 eV or higher photon energies. On noble-metal surfaces the measured valence band normally displays broad molecular features superimposed on the flat *sp* band and structured *d* bands lying at a higher binding energy (BE). The appearance of low BE features close to E_F often evidences electron transfer from the metal to the molecule, in the simplest models due to the filling of the lowest unoccupied molecular orbital (LUMO).[6,10,14] A relatively small ($\leqslant$0.5 V) in-plane 2D dispersion of electronic states with molecular lattice periodicity was observed for systems displaying single orientational domains.[5]

In the present study the use of low photon energies reveals a rather different picture. Figure 1 displays NE spectra taken in angle-integrated mode at different photon energies. An interface state is indeed detected in the direct vicinity of the Fermi level as the filled LUMO band due to charge transfer from the substrate to the molecules. The other molecular feature present in the spectra is the highest occupied molecular orbital (HOMO) of the pristine molecules at 1.5-eV BE. Most interestingly, a strong dispersing peak is also present in the spectra. For comparison, the angle-integrated clean Ag(110)
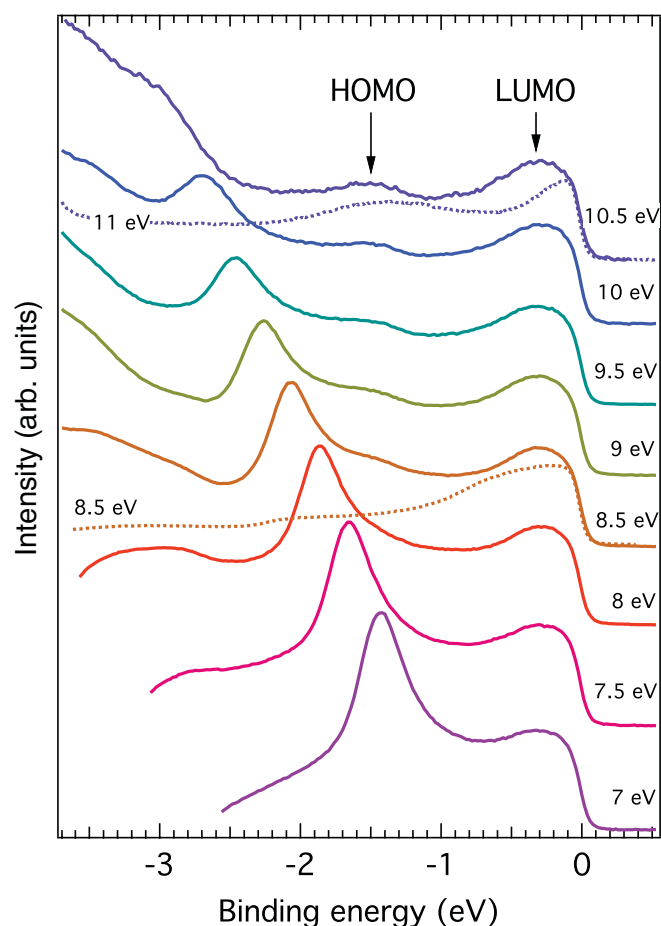

FIG. 1. (Color online) Normal emission, angle-integrated ($\pm 7°$) photoemission spectra of 1-ML ZnPc/Ag(110) for varying photon energies. The molecular states are the broad features at 1.5 eV (HOMO) and close to the Fermi level (LUMO). From top to bottom an intense peak disperses to a lower binding energy. Also shown (dashed lines) are the clean Ag(110) spectra taken at 11- and 8.5-eV photon energy.

spectra taken with $h\nu =$ 8.5 and 11 eV are also reported. They display an enhanced intensity in the vicinity of the Fermi level, followed by a smooth background at higher BE. These features are due to the dispersing *sp* band away from normal emission and are detected because of the wide angle of integration, as will be explained following in the text. The intense dispersive peak present for 1-ML ZnPc/Ag(110) must then be induced by the presence of the molecules. On the other hand, referring to former low-energy photoemission studies,[2] the dispersing feature is reminiscent of *sp* bulk direct transitions observed in normal emission (NE) from the Ag(111) surface along the Γ-L direction. This intuitively suggests that the molecular adsorption allows the observation of a bulk direct transition that is absent in the clean substrate spectrum. Modification of the substrate emission due to molecular adsorption was already observed recently in photoemission at 21 eV,[14,15] where the angular dependence of *d* band emission is observed to be averaged out due to scattering of substrate photoelectrons by the molecular lattice. Consequently, the *d*-band substrate contribution to the photoelectron spectrum is that of a polycrystalline sample. In the present case the modification of the escape conditions of substrate photoelectrons can be precisely addressed.

In order to infer the nature of the molecule adsorption-induced dispersing feature, band-structure calculations of the silver crystal were performed by DFT with the SIESTA 2.0 package using the generalized gradient approximation (GGA).[16] The computed band structure was used to extract the angular dispersion of low-energy photoelectrons above the Ag(110) surface.

Mapping an ARPES bulk direct transition from three-dimensional (3D) crystals requires knowledge of the energy and momentum of photoelectrons in the final state. Translational symmetry helps to determine $\mathbf{k}_\parallel$ for a given kinetic energy and detection angle, but due to the presence of the interface to vacuum $\mathbf{k}_\perp$ it is not conserved. This precludes the precise location of the photoinduced transition in the 3D Brillouin zone and complicates 3D band mapping. This difficulty can be overcome by determining a reasonable final-state dispersion for the photoelectrons by means of DFT band-structure calculations.

For a given photon energy $h\nu$, the DFT band structure allows to find the locations in $\mathbf{k}$ space where direct transitions are allowed and the corresponding $(E, \mathbf{k})$ final states. The photoelectron emission angle and corresponding binding energy of a given transition can then be computed assuming a realistic surface work function[17] giving a $E_B(\theta_e)$ curve to be compared to the ARPES spectrum.[18]

The approach sketched above suffers from the well-known self-interaction problem of DFT. For the purposes relevant here, a simple rigid shift applied to the calculated angular dispersion is sufficient to overcome this difficulty. The computed angular dispersion is found to be in good agreement with experiments on clean Ag(110). In Fig. 2(b) the ARPES image of Ag(110) that is relevant for the present study, taken along the $\Gamma KLUX$ plane, is displayed. The green lines are the modeled *sp* direct transitions, matching well with the experimental spectra when a $+ 0.32$ eV shift is applied.

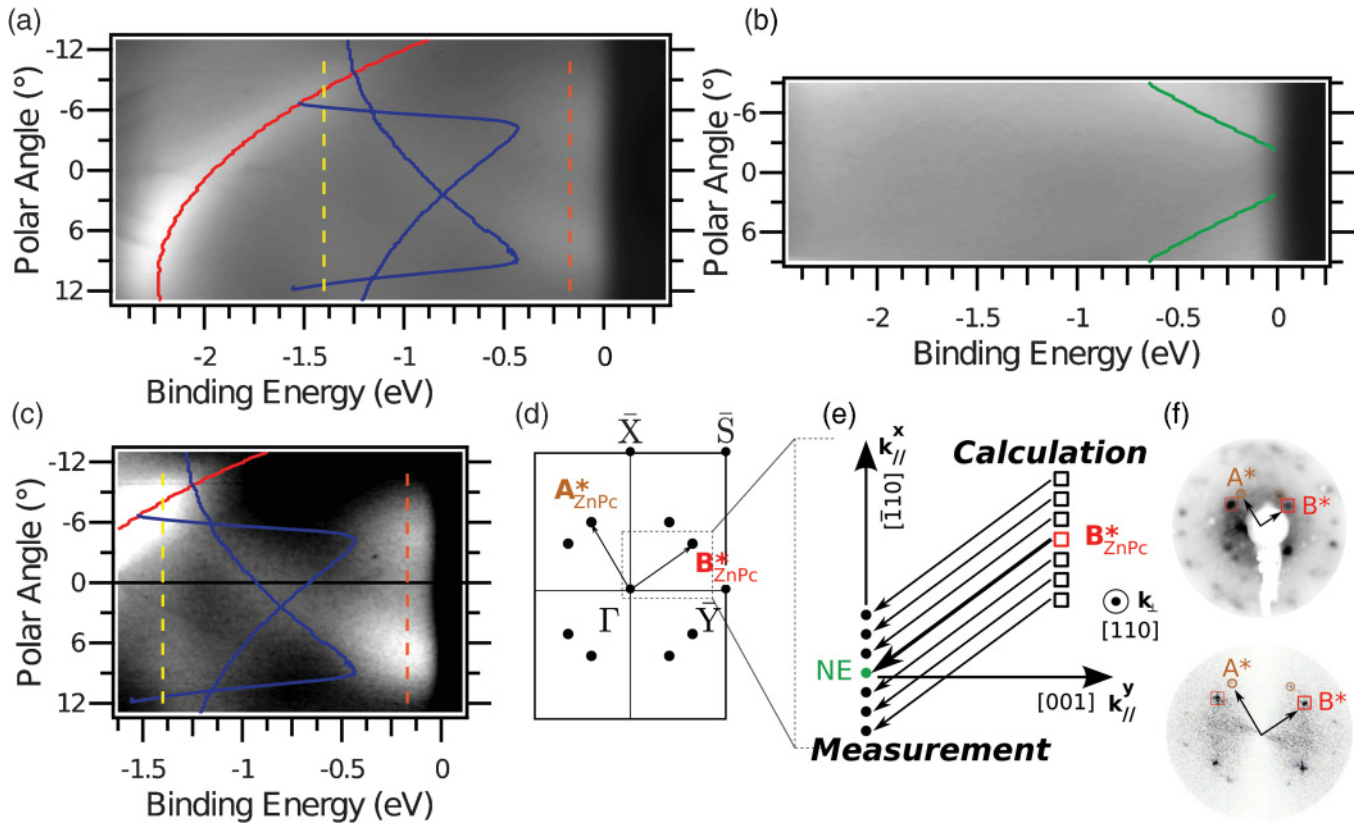As shown in Fig. 1, the adsorption of 1-ML ZnPc/Ag(110) reveals a previously absent feature in NE spectra. More

FIG. 2. (Color online) (a) ARPES image of 1-ML ZnPc/Ag(110) taken around normal emission with $h\nu = 9$ eV along the $\Gamma KLUX$ plane of the Ag(110) substrate; red (gray) and blue (dark gray) $E_B(\theta_e)$ dispersion curves correspond to photoelectrons diffracted by $\mathbf{B}^{\star}_{\mathrm{ZnPc}}$ and $2\mathbf{B}^{\star}_{\mathrm{ZnPc}}$, respectively with a -0.3 eV shift; the dashed lines locate the nondispersive HOMO and LUMO features (from Fig. 1). (b) ARPES images of Ag(110) taken in the same experimental conditions as (a) but with doubled grayscale contrast; the green lines are the modeled sp direct transitions shifted by 0.32 eV. (c) Detailed view of (a) with enhanced contrasts to highlight the diffraction from $2\mathbf{B}^{\star}_{\mathrm{ZnPc}}$ reciprocal vectors. (d) The Ag(110) surface Brillouin zone with the molecular reciprocal lattice vectors. (e) Schematic view of the relation between experiments and calculations: The $E_B(\theta_e)$ curve is modeled by considering direct transitions occurring along $k_{\perp}$ rods (squares) parallel to the $\langle 110 \rangle$ direction; the electronic states being diffracted by $\mathbf{B}^{\star}_{\mathrm{ZnPc}}$ (surface umklapp) are measured around NE and along the analyzer dispersion direction; the arrows indicate the surface-umklapp vectors. (f) Upper part: VLEED pattern at 11.2-eV primary energy; lower part: FFT of a STM image of 1-ML ZnPc/Ag(110).

insight on its origins can be gained by looking at the angular dispersion. Figure 2 displays a detail of the ARPES spectra taken with 9-eV photon energy. Together with the HOMO- and LUMO-derived features (dashed lines), a strongly dispersive band is observed, which corresponds to the energy-dispersive feature observed in Fig. 1 and which is not observed for the pristine Ag(110) surface [see Fig. 2(b)]. A different set of final states needs to be considered to fully explain the observed spectrum.

The structural properties of the ZnPc/Ag(110) interface have been reported previously.[13] The molecules adsorb in a compact, flat-lying geometry, forming a coincidence mesh with the substrate. The primary reciprocal vectors of one of the two equivalent molecular domains allowed by the substrate symmetry are displayed in Fig. 2(d) within the substrate surface Brillouin zone. Also displayed are the first-order diffraction loci of the two domains.

The surface umklapp can be accounted for in the ARPES spectrum by considering direct transitions occurring along k rods lying parallel to the $\langle 110 \rangle$ direction (Γ-K) and centered at

the molecular reciprocal lattice. After undergoing the surface-umklapp process these photoelectrons will escape the surface around NE [Fig. 2(e)]. Their angular dispersion is modeled and—when relevant—is superposed to the experimental data [Figs. 2(a) and 2(c)]. The dominant dispersing feature is well reproduced by a sp direct transition diffracted through the $\mathbf{B}^{\star}_{\mathrm{ZnPc}}$ molecular reciprocal lattice vectors [red/gray line in Figs. 2(a) and 2(c)]. This excellent agreement directly provides evidence that the adsorbed molecular ML can change the escape conditions of substrate photoelectrons in a controlled way.

Interestingly, the effect of the surface umklapp is not the same for all molecular reciprocal vectors. This is readily seen by considering direct transitions diffracted by $2\mathbf{B}^{\star}_{\mathrm{ZnPc}}$ vectors [blue/dark gray lines in Figs. 2(a) and 2(c)]. Figure 2(c) shows a detail of the 2D photoelectron map with enhanced contrast: Bands diffracted by the $2\mathbf{B}^{\star}_{\mathrm{ZnPc}}$ vector are clearly distinguishable between 1.5 eV and the Fermi level but are much fainter than the main band. No other dispersing features were detected in the present experiment. For instance,

bands diffracted by the $A^\star_{ZnPc}$ molecular reciprocal lattice vectors do not show appreciable intensity in the measured spectrum.

In the one-step model of PE, the final state is indeed considered as a time-reversed LEED state,[19] and it has been argued that the diffracted intensities of the very-low energy LEED (VLEED) pattern reflect approximately the Fourier composition of the PE final state in the crystal.[20] There is thus a direct link between the diffracted VLEED intensity at a given 2D reciprocal lattice vector and the intensity of a particular structure folded back in the normal-emission PE spectra by final-state diffraction at the corresponding vector. In both the VLEED pattern and the Fourier-transformed scanning tunneling microscopy (STM) [Fig. 2(f)], the $B^\star_{ZnPc}$ spots appear much stronger than the $A^\star_{ZnPc}$.[21] The fact that the $B^\star_{ZnPc}$ diffracted bands dominate the spectrum follows then from the time-reversed LEED model for photoemission.[19]

Aside from the striking effectiveness of the surface-umklapp effect reported here, it is remarkable that the presence of the diffracting adsorbate allows probing a reciprocal space region otherwise barely accessible in a standard ARPES experiment (that is employing an analyzer in fixed geometry). For instance, by rotating the polar and azimuthal angles one can detect photoelectrons on the $B^\star_{ZnPc}$ rods. Nevertheless, the analyzer dispersion direction would probe a different line in the reciprocal space.

Final-state diffraction or the surface-umklapp process is known to be an important effect in photoemission from nanostructures[9] and thin films, including quantum well states scattering from buried interfaces.[22,23] The results reported in this Rapid Communication demonstrate that the surface umklapp is important also at organic-metal interfaces: The diffraction of substrate photoelectrons needs to be taken into account when trying to assign genuine interface states. Moreover, evidence is provided that substrate band mapping can be effectively performed through diffraction by an organic molecular adsorbate.

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