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CuPc/Au(1 1 0): Determination of the azimuthal alignment by a combination of angle-resolved photoemission and density functional theory

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ABSTRACT

Here we report on a combined experimental and theoretical study on the structural and electronic properties of a monolayer of Copper-Phthalocyanine (CuPc) on the Au(1 1 0) surface. Low-energy electron diffraction reveals a commensurate overlayer unit cell containing one adsorbate species. The azimuthal alignment of the CuPc molecule is revealed by comparing experimental constant binding energy ($k_x k_y$)-maps using angle-resolved photoelectron spectroscopy with theoretical momentum maps of the free molecule's highest occupied molecular orbital (HOMO). This structural information is confirmed by total energy calculations within the framework of van-der-Waals corrected density functional theory. The electronic structure is further analyzed by computing the molecule-projected density of states, using both a semi-local and a hybrid exchange-correlation functional. In agreement with experiment, the HOMO is located about 1.2 eV below the Fermi-level, while there is no significant charge transfer into the molecule and the CuPc LUMO remains unoccupied on the Au(1 1 0) surface.

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1. Introduction

The interface of organic thin films with noble metal surfaces has attracted considerable attention in the past years [1–4]. On the one hand, this interest is driven by the application in organic electronic devices such as light emitting diodes, field effect transistors, or solar cells. On the other hand, the desire to understand the basic physical properties at metal–organic interfaces represents a more fundamental motivation. Here, a surface science approach combined with theoretical investigations is particularly useful when studying the adsorption of organic monolayers adsorbed on metallic surfaces. While various surface science techniques are capable of measuring the overlayer periodicities, adsorption sites, heights and orientations and are able to reveal the electronic structure of the interface, often only a combination of experiment and theory allows for creating a coherent picture of the system under study. One example are images from scanning tunneling microscopy (STM) where *ab-initio* electronic structure calculations are often necessary to overcome ambiguities in interpreting STM images. Another example is the interpretation of ultra-violet photoelectron spectroscopy experiments, in particular its angle-resolved variant. This will be theme of this contribution.

Angle-resolved photoelectron spectroscopy (ARPES) is *the* technique to study the occupied electronic band structure of solids by measuring the kinetic energy of the photoemitted electrons versus their angular distribution [5]. Particularly, many questions in nanophysics and interface engineering are often addressed by this experimental technique which, in combination with density-functional-theory calculations, leads to important physical insights. In recent years it has been shown that for highly-ordered layers of organic molecules, ARPES also provides a route to obtain information about the spatial structure of individual molecular orbitals [6–10]. By comparing measured ARPES data with simulations of the photoemission intensity based on density-functional theory (DFT) and approximating the final state of the photoemission process by a plane wave, molecular orbitals can be identified and molecular orientations can be determined [11–14]. To date

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this approach, which has been termed *orbital tomography* [9], has allowed the orbital density reconstruction of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in highly-oriented monolayer films of sexiphenyl on Cu(1 1 0) [7] and pentacene and PTCDA on Ag(1 1 0) [15], respectively, and has enabled the analysis of the molecule-substrate hybridization in PTCDA and NTCDA layers on Ag(1 1 0) [9,11,16,17]. It has also been used to unambiguously assign molecular emissions in coronene and hexa-benzo-coronene films on Ag(1 1 1) [13] and to analyze monolayers and bilayers of PTCDA on Ag(1 1 0) [12,18–20]. In terms of determining molecular orientations, the orbital tomography method has led to the tilt angle of pentacene multilayer film [7] and azimuthal orientation of tetra-phenyl-porphyrine in a monolayer film on Cu(1 1 0) [14].

In this work, we focus on a monolayer film of copper-phthalocyanine (CuPc) on Au(1 1 0) surface. Phthalocyanines are among the most studied functional molecular materials due to their interesting optical and electronic properties and their potential in nonlinear optics, optical data storage, electronic sensors, xerography, solar energy conversion, nuclear chemistry, molecular magnetism, electrochromic displays and heterogeneous catalysis [21]. Their sub-monolayer to monolayer growth on various noble metal surfaces and the structural and electronic properties of the resulting interface has been studied intensively [22–30]. In terms of DFT calculations, both, various metal-Pc's [31] as well as the metal-free Pc [32] have been investigated on Au(1 1 1) and Au(1 1 0) surfaces, respectively, and the spin and orbital configuration of MePc chains assembled on the Au(1 1 0) have recently been investigated [33].

The goal of the present investigation is to fully characterize the CuPc/Au(1 1 0) interface of a fully developed monolayer in terms of its structural and electronic properties by means of a combined experimental and theoretical approach. In particular, the origin of the 1.2 eV binding energy peak in UPS data [25] needs to be clarified and the azimuthal alignment of the molecule to be determined. Moreover, it has been disputed whether the molecule adsorbs completely flat or exhibits a tilt angle with respect to the substrate surface [24,28]. In terms of electronic structure, the level alignment and orbital ordering of the adsorbed CuPc is of prime interest. While the electronic structure of isolated CuPc molecule has been computed by means of high-level theoretical approaches [34,35], it remains to be answered how issues arising from the self-interaction error of semi-local exchange-correlation functionals impact the electronic structure of such extended interfaces [36].

2. Method

2.1. Experimental details

The samples were prepared in an ultra-high vacuum chamber with a base pressure of 1×10^{-9} mbar attached to an analysis chamber for ARPES. A Au(1 1 0) single crystal was utilized applying a standard cleaning procedure of annealing and sputtering cycles. Surface cleanliness and order was checked by X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). The CuPc films were prepared by organic molecular beam epitaxy from a home made Knudsen cell with growth rates of about 0.03 monolayer per minute. The completion of the monolayer was identified by LEED by the well-known (5 × 3)-reconstruction [24,25] and verified by XPS and ARPES. The quality of the lateral order was improved by an additional annealing step of 10 min at 280 °C. The ARPES measurement were carried out at room temperature with a monochromatized Helium discharge lamp (SPECS UVS300) using the He I$_\alpha$-line at 21.22 eV. Photoelectrons were detected with a Scienta SES200 electron analyzer with an acceptance angle of ±7°. (k_x, k_y) momentum maps were derived by additional tilting the perpendicular polar angle in steps of 2° and azimuthal rotation by 10°. The intensity maps were corrected for the photoelectron emission characteristics by a cosine-function according to Lambert's law. In addition, the data was normalized to the channelplate function which was derived by measuring a polycrystalline Au-foil.

2.2. Computational details

All theoretical results presented here are obtained within the framework of density functional theory (DFT). Two types of calculations have been performed. First, orbital energies and corresponding wave functions of an isolated CuPc molecule are calculated by using either a generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof flavor [37] for exchange and correlations effects or by employing a hybrid functional according to Heyd et al. (HSE) [38,39]. These wave functions serve as input for the subsequent simulation of ARPES intensity maps within the one-step model of photoemission [40] and for which we approximate the final state by a plane wave [7]. Second, we have also performed calculations of an adsorbed monolayer on the Au(1 1 0) surface which we analyze in terms of molecule-projected density of states curves and charge density difference plots and for which we employ either a van-der-Waals-corrected GGA or HSE for exchange-correlation effects.

2.2.1. Simulation of ARPES maps

For the free CuPc molecule, we utilize the plane wave code ABINIT [41]. The all-electron potentials are replaced by extended norm-conserving, highly transferable Troullier-Martins pseudo potentials [42] using a plane wave cut-off of 50 Ryd. We employ a super cell approach with a box size of 50 × 50 × 22 Bohr^3 and Γ point sampling of the Brillouin zone. The geometry of the free molecule is optimized by using a generalized gradient approximation (GGA) [37] for exchange-correlation effects. Due to the odd number of valence electrons in one CuPc molecule, all calculation are performed in a spin-polarized manner.

The orbitals ψ_i of the optimized molecule are utilized to evaluate the intensities of the ARPES within the so called one-step model [40].

$$I(\theta, \phi; E_{kin}, \omega) \approx \sum_i |\langle \psi_f(\theta, \phi; E_{kin}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle|^2 \times \delta(E_i + \Phi + E_{kin} - \hbar\omega), \tag{1}$$

Here, θ and ϕ are the azimuthal and polar angle respectively, E_{kin} is the kinetic energy of the emitted electron and ω denotes the frequency of the incoming photon, Φ is the work function, and $\mathbf{p}$ and $\mathbf{A}$ are the momentum operator and the vector potential connected to the incoming radiation. We further approximate the final state ψ_f by a plane wave [43]. As outlined in more detail in a previous paper [7], and also noted earlier [44,45], these approximations lead to the simple result that the PE intensity from a given initial state i is proportional to the square modulus of the Fourier transform of the initial state wave function $\tilde{\psi}(\mathbf{k})$

$$I_i(\theta, \phi; E_{kin}) \approx |\tilde{\psi}(\mathbf{k})|^2 |\mathbf{A} \cdot \mathbf{k}|^2. \tag{2}$$

modulated by a weakly angle-dependent factor $|\mathbf{A} \cdot \mathbf{k}|^2$ which depends on the angle between the polarization vector $\mathbf{A}$ of the incoming photon and the direction of the emitted electron. Note that in the simulated momentum maps shown below, we have chosen to neglect this factor, thus the simulated results only show the first factor of Eq. (2), *i.e.*, the Fourier transform of the initial state.

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