Orientational Ordering of Nonplanar Phthalocyanines on Cu(111): Strength and Orientation of the Electric Dipole Moment

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In order to investigate the orientational ordering of molecular dipoles and the associated electronic properties, we studied the adsorption of chlorogallium phthalocyanine molecules (GaClPc, Pc = $C_{32}N_8H_{16}{}^{-2}$) on Cu(111) by using the x-ray standing wave technique, photoelectron spectroscopy, and quantum mechanical calculations. We find that for submonolayer coverages on Cu(111) the majority of GaClPc molecules adsorb in a Cl-down configuration by forming a covalent bond to the substrate. For bilayer coverages the x-ray standing wave data indicate a coexistence of the Cl-down and Cl-up configurations on the substrate. The structural details established for both cases and supplementary calculations of the adsorbate system allow us to analyze the observed change of the work function.

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The adsorption of organic semiconductor molecules has been the focus of numerous experimental and theoretical investigations—many of them addressing the subtle interplay of electronic and structural properties. Early studies [1], which show that the energy levels of organic semiconductor-metal interfaces can exhibit large deviations from the Schottky-Mott relation, conveyed the significance of interface dipoles. Until today and despite the ubiquity of this concept in the field of organic materials, the origin of the interface dipole often remains vague.

To establish a better understanding of the energy level alignment at the interface, one should not neglect effects related to the molecular structure of organic adsorbates: Planar molecules such as F_{16}CuPc [2], PTCDA [3,4], or pentacene derivatives [5], for example, can distort upon adsorption due to the interaction with the substrate and therefore exhibit an induced molecular dipole. Nonplanar molecules such as TiOPc [6], SnPc [7–9], SubPc [10,11], and VOPc [12], which may adsorb in different orientations, form layers with at least partially aligned dipole moments. Hence, for this class of systems the orientational order on the surface is a quantity which strongly influences the interface dipole. In particular, it has been shown that, depending on the orientation, a layer of molecular dipoles p with an area density N_{dip} can shift the vacuum level (VL) in either direction and, therefore, increase or decrease the work function Φ of the sample according to [13]

$$\Delta\Phi_{\text{dip}} = \pm e p N_{\text{dip}}/\epsilon_0\epsilon, \tag{1}$$

where ϵ is the effective dielectric constant of the monolayer. An experimentally and theoretically challenging model system of nonplanar organic molecules with a significant dipole moment, for which these effects can be directly studied, is chlorogallium phthalocyanine (GaClPc, Fig. 1) [14].

In this Letter, we present a detailed study on the bonding and orientational ordering of GaClPc on Cu(111) surfaces by using the x-ray standing wave (XSW) technique [15], ultraviolet photoelectron spectroscopy (UPS), and density functional theory (DFT) based calculations. While XSW data are taken to determine the exact atomic positions along the surface normal and, thereby, also the orientation of the molecules, the UPS measurements reveal how the adsorbate affects the electronic energy levels. In particular, our results demonstrate that the observed VL shift can be modeled very well if one accounts for the adsorption geometry and the orientation of the molecules.

The XSW experiments were carried out at beam line ID32 of the European Synchrotron Radiation Source in

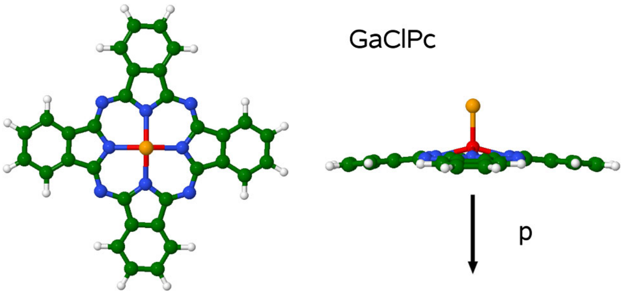

FIG. 1 (color online). Structure of the free GaClPc (Pc = $C_{32}N_8H_{16}{}^{-2}$) molecule as obtained by geometry optimization using the GAUSSIAN03 program package. The results show that the Ga (red) and Cl atoms (orange) are located above the molecular plane with a Ga-Cl bond length of 2.21 Å. The Pc group itself is nonplanar with the two inequivalent N species (blue) 0.50 and 0.58 Å below the Ga atom.

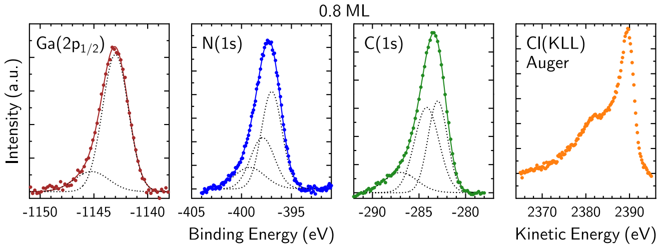

FIG. 2 (color online). Background-corrected core-level spectra measured with a hemispherical electron energy analyzer for a submonolayer of GaClPc on Cu(111). The intensity of the peaks relative to the substrate signal has been used to determine the surface coverage in monolayer equivalent units (ML).

Grenoble. Using the (111) reflection of the copper substrate, we have taken data in back-reflection geometry [2,4], corresponding to the lattice plane spacing $d = 2.08$ Å with photon energies around $E_{\mathrm{Bragg}} = 2.97$ keV. The UPS experiments for different coverages were performed with a photoelectron spectrometer equipped with a standard He I light source (photon energy 21.2 eV) in our home laboratory. The Cu(111) crystal with a small mosaicity was prepared under ultrahigh vacuum conditions by repeated cycles of argon sputtering and annealing (base pressure 4×10^{-10} mbar). The GaClPc material was purchased from Sigma-Aldrich, purified by gradient sublimation, and thoroughly degassed. With a quartz microbalance, typical deposition rates of 0.2 Å/ min were realized. For all experiments reported below, the substrate temperature was carefully monitored. To model the electronic structure of the molecules on the Cu(111) surface, we employed slab-type DFT-based band structure calculations using VASP [16]; more details on the theoretical methods and the chosen geometry are given in Ref. [17].

The core-level spectra of GaClPc on Cu(111) show several signals that are suitable for XSW experiments (Fig. 2). By measuring photoemission spectra related to all atomic species in the molecule, namely, C(1s), N(1s), Ga(2$p_{1/2}$), and Cl(2s)/Cl(KLL) Auger, we achieve a detailed electronic and structural characterization of the system.

The bonding distances and orientation of the molecule have been derived from the characteristic variation of the photoelectron yield Y_p around the Bragg condition. The XSW data, which can be analyzed according to a well-established procedure using the experimental reflectivity R of the sample, yield two structural parameters: the coherent position P_H and coherent fraction f_H, both of which can be determined by a least-squares fitting routine [17]. While P_H gives the average position of the atoms relative to the diffraction planes, f_H yields the spread of positions within the ensemble.

Figure 3 shows XSW results for two different coverages, which were derived from series of core-level spectra. Unlike planar organic molecules [2,4], the data corresponding to the different atoms exhibit pronounced differences. For submonolayer coverages [0.8 ML, Fig. 3(a)], our results indicate high orientational order within the molecular ensemble on the surface. To convert the coherent positions given in Fig. 3(a), i.e., $P_H(\mathrm{Ga}) = 0.03$, $P_H(\mathrm{C}) = 0.14$, $P_H(\mathrm{N}) = 0.27$, and $P_H(\mathrm{Cl}) = 0.90$, into the (average) bonding distances d_H, one must take into account the modulo-d ambiguity of the XSW technique

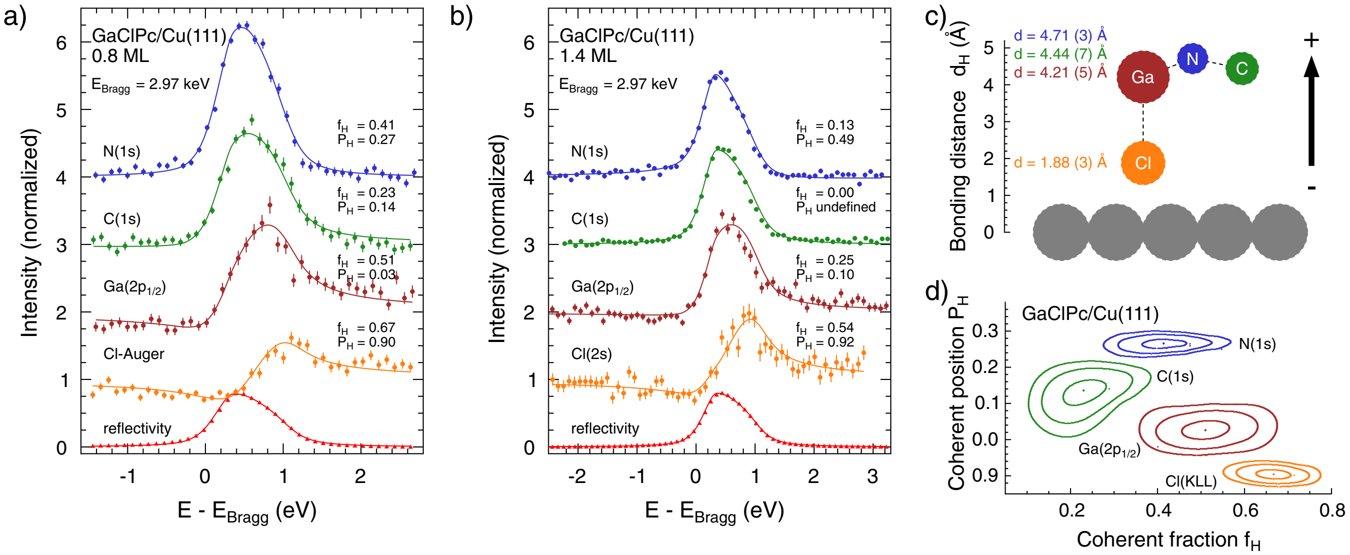

FIG. 3 (color online). (a),(b) XSW data for GaClPc on Cu(111) taken for two different coverages in back-reflection geometry at an elevated temperature. The photon energy has been scanned around $E_{\mathrm{Bragg}} = 2.97$ keV to measure the photoelectron yield (circles) and reflectivity (triangles). Least-squares fits to the data (solid lines) give the coherent fraction f_H and coherent position P_H that are related to the adsorption geometry. (c) Average bonding distances d_H for GaClPc as derived from the data in (a). (d) χ^2-confidence map for fits to the XSW data in (a). The 1σ-, 2σ-, and 3σ-contour levels show the statistical significance of the data analysis [4].

[15]. In principle, two different configurations can be considered for low GaClPc coverages: either a scenario Cl-up with interatomic distances which deviate strongly from the gas phase structure (e.g., a hypothetical Ga-Cl bond length of only 1.83 ± 0.07 Å compared to 2.21 Å in the gas phase) or a scenario Cl-down with a corresponding Ga-Cl bond length of 2.33 ± 0.07 Å and a vertical N-Ga distance of 0.50 Å, i.e., values that are close to the interatomic distances in the gas phase. DFT calculations for the isolated molecule, which show that large molecular distortions of GaClPc are energetically very unfavorable, can be used to rule out the Cl-up case. The obvious conclusion that the molecules adsorb—similar to other Pc derivatives [10,11]—predominantly in a Cl-down configuration implies that the molecular dipoles contribute with $\Delta\Phi_{\text{dip}} < 0$ to the overall VL shift. Having established the bonding distances for the low coverage [Fig. 3(c)] with the corresponding error bars [Fig. 3(d)], we see that the Cu-Cl layer spacing of 1.88 Å coincides with experimental results for chlorine adsorption on Cu(111) [18]. This agreement suggests a covalent bonding of the Cl atoms to the substrate and, moreover, a hollow adsorption site as reported in Ref. [18].

Complementing this picture, we find increasing magnitudes of f_H for carbon (0.23), nitrogen (0.41), gallium (0.51), and chlorine (0.67), which indicate surprisingly different spatial spreads. Therefore, we studied the influence of thermally activated librational motions of the GaClPc molecules in the Cl-down configuration. Specific model calculations based on a statistical description of the ensemble (presented in Ref. [17]) were performed to refine the analysis. The time-averaged spread of positions resulting from our simulations gives XSW parameters f_H and P_H, which—by comparison with the experimental values—allow us to determine the libration amplitude. The analysis shows that the atomic species within the GaClPc molecule are affected very differently and that even for small amplitudes there are strong changes of the coherent fractions for C and N. The relative magnitude of the coherent fractions is consistent with a libration amplitude (rms) of $17 \pm 3°$ around the essentially fixed Cl atom.

For higher GaClPc coverages [1.4 ML, Fig. 3(b)], the situation becomes more complex. The relatively small coverage dependence found for the Cl (and Ga) data contrasts with significant changes for the N (and C) signal. In particular, the very different values $P_H(\text{N}) = 0.49$ and $f_H(\text{N}) = 0.13$ for nitrogen cannot be explained with only one molecular orientation. Model calculations, which take into account that the XSW parameters f_H and P_H refer to a coherent average over all inequivalent sites in the bilayer [15], i.e.,

$$f_H e^{2\pi i P_H} = \frac{1}{N} \sum_{k=1}^{N} (e^{2\pi i \Delta_k^{\text{down}}/d} + e^{2\pi i \Delta_k^{\text{up}}/d}) \qquad (2)$$

($\Delta_k^{\text{down/up}}$ denoting the position of the kth atom relative to the substrate lattice), indicate a coexistence of Cl-up and Cl-down configurations on the surface. The adsorption of GaClPc molecules with opposite orientation in the second layer—a phenomenon reported also for other Pc derivatives [6,9]—could be confirmed also by metastable atom electron spectroscopy measurements [19]. Within our coverage series, we verified that a deposition of more than 4 ML results in atomically disordered systems with incoherent XSW signals ($f_H = 0$) for all elements.

In order to study how the orientational order of the molecules affects the VL shift, we measured the work function of the system for increasing GaClPc coverage [Fig. 4(a)]. At first, the results obtained from the photoemission spectra reveal a rapid decrease below 0.2 ML as expected for the Cl-down configuration. The continuous, yet slightly retarded VL shift results in a minimum of $\Delta\Phi = -0.34$ eV at the monolayer coverage. To overcome possible kinetic limitations, we deposited more material (resulting in a gradual increase of Φ for coverages of more than 1 ML due to preferential Cl-up nucleation) and applied a short annealing of the multilayer at 300 °C. This procedure yields a coverage of slightly less than 1 ML and a shift of $\Delta\Phi = -0.60$ eV. Since DFT calculations, which we have performed by using the adsorption geometry shown in Fig. 3(c), predict a similar decrease of

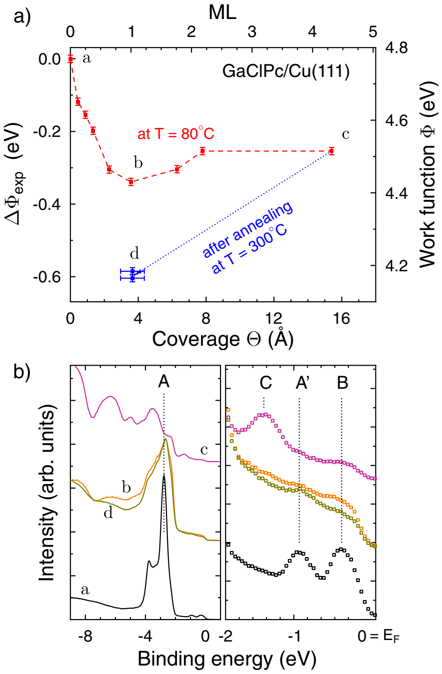

FIG. 4 (color online). (a) Coverage-dependent work function of GaClPc on Cu(111). (b) Valence band region measured by UPS for coverages labeled correspondingly in the top panel. In these spectra peak A belongs to the Cu 3d band, peak A' is a satellite of A due to excitation by parasitic He I_β radiation, peak B is the Shockley surface state of the clean Cu(111), and peak C is the HOMO-derived state of the multilayer film.

$\Delta\Phi = -0.55$ eV for a comparable coverage, we may relate the electronic properties of annealed monolayer to the low-coverage XSW data. Because of the orientational order, we can separate the total change $\Delta\Phi$ into two contributions with

$$\Delta\Phi = \Delta\Phi_{\text{dip}} + \Delta\Phi_{\text{bond}}. \tag{3}$$

Thus, we distinguish $\Delta\Phi_{\text{dip}}$, which is related to the dipole moment of the molecules according to Eq. (1), and $\Delta\Phi_{\text{bond}}$, which contains the effect of the molecule-metal interaction. To quantify the dipole contribution we have calculated a monolayer of GaClPc without a metal substrate. Again using the adsorption geometry shown in Fig. 3(c), we obtain $\Delta\Phi_{\text{dip}} = -0.30$ eV. Because of the large substrate-Pc distance and the correspondingly small Pauli repulsion, the associated value $\Delta\Phi_{\text{bond}} = -0.25$ eV essentially reveals the effect of the charge rearrangement within the Ga-Cl group and between the Cl and Cu atoms [17].

These conclusions are corroborated by the interpretation of the valence band spectra shown in Fig. 4(b). The data obtained for different coverages show that neither before nor after the annealing procedure can prominent interface states—as they were reported for the adsorption of other planar [20] and nonplanar [21] Pc molecules directly below the Fermi energy—be observed. This absence of characteristic spectral features in the HOMO (highest occupied molecular orbital)-lowest unoccupied molecular orbital gap illustrates the weak interaction between the substrate and the Pc ring in the Cl-down orientation. We note that, due to the photoemission selection rules and the orientation of the molecules, no HOMO-derived states can be seen in the normal emission spectra of both monolayer films shown Fig. 4(b)—in contrast to the disordered multilayer film, which exhibits a pronounced HOMO-related peak centered at -1.42 eV. Moreover, the spectra illustrate the nonideal growth of GaClPc at 80 °C and the significant reordering caused by the annealing procedure. The strong quenching of the Shockley surface state, which we find for the annealed film, clearly indicates a more uniform substrate coverage.

In summary, the XSW data together with the UPS measurements and the DFT calculations give a conclusive picture of the molecules' orientation and bonding. For submonolayer coverages at a sufficiently high substrate temperature, the vast majority of GaClPc molecules adsorb in the Cl-down configuration with a Cl-Cu layer spacing of 1.88 Å that indicates covalent bonding of the chlorine atoms. The interaction with the substrate gives rise to subtle deviations from the gas phase structure: In agreement with the DFT calculations [17], the Ga-Cl bond length of 2.33 Å measured by XSW is slightly larger than in the gas phase, while the average position of the carbon atoms in the experiment and the calculations indicates a certain bending of the molecule [17]. Moreover, the coherent fractions observed in the experiment can be related to thermal librations of the molecules. Because of the orientational order, the molecular dipoles contribute significantly to the vacuum level shift and the resulting interface dipole. Detailed calculations for the annealed monolayer support this conclusion quantitatively with $\Delta\Phi_{\text{dip}} = -0.30$ eV. The influence of intermolecular interactions is demonstrated by the coexistence of Cl-down and Cl-up configurations found for deposition at 80 °C. Interestingly, a subsequent annealing allows a controlled reordering of the molecular dipoles and a change of the corresponding electronic properties. Furthermore, we believe that the adsorption behavior of GaClPc and its impact on the electronic structure represent important characteristics of nonplanar organic molecules.

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