Adsorption-induced distortion of \( \text{F}_{16}\text{CuPc} \) on \( \text{Cu}(111) \) and \( \text{Ag}(111) \): An x-ray standing wave study

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(Received 20 December 2004; published 31 May 2005; corrected 6 June 2005)

The adsorption geometry of perfluorinated copper-phthalocyanine molecules (\( \text{F}_{16}\text{CuPc} \)) on \( \text{Cu}(111) \) and \( \text{Ag}(111) \) is studied using x-ray standing waves. A detailed, element-specific analysis taking into account nondipolar corrections to the photoelectron yield shows that on both surfaces the molecules adsorb in a lying down, but significantly distorted configuration. While on copper (silver) the central carbon rings reside 2.61 Å (3.25 Å) above the substrate, the outer fluorine atoms are located 0.27 Å (0.20 Å) further away from the surface. This nonplanar adsorption structure is discussed in terms of the outer carbon atoms in \( \text{F}_{16}\text{CuPc} \) undergoing a partial rehybridization (\( sp^2 \to sp^3 \)).

DOI: 10.1103/PhysRevB.71.205425

PACS number(s): 68.49.Uv, 68.43.Fg, 79.60.Fr

I. INTRODUCTION

The adsorption of organic molecules on various surfaces has become a subject of wide interest. With the realization of organic based semiconductor devices¹,² it has been recognized that the first molecular layer of organic thin films strongly influences their structural and electronic properties. Hence increasing efforts are being made to improve our still fragmentary understanding of the complex interaction of aromatic molecules with metal substrates. A variety of surface sensitive techniques are being used to explore organic thin films in the monolayer regime. Low energy electron diffraction (LEED),³,⁴ photoelectron diffraction (PED),⁵,⁶ and scanning tunneling microscopy (STM),⁷–¹⁰ for example, have been successfully employed in this area.

When studied in more detail, aromatic molecules exhibit a nontrivial adsorption behavior, benzene on various substrates being the simplest and best-studied example.³–⁶ Because of the relatively strong adsorbate-substrate interaction on metals organic compounds may undergo structural changes upon adsorption.⁵,⁶ In this context we chose to study perfluorinated copper-phthalocyanine (\( \text{F}_{16}\text{CuPc} \), see Fig. 1(a)) on \( \text{Cu}(111) \) and \( \text{Ag}(111) \) using the x-ray standing-wave (XSW) technique.¹¹–¹⁵

As one of the best air-stable organic \( n \)-type semiconductors \( \text{F}_{16}\text{CuPc} \) is a very promising material for future applications.¹,² The adsorption of \( \text{F}_{16}\text{CuPc} \), i.e., the bonding distances and possible distortions resulting from the interaction with the metal electrons, is very relevant as the charge transfer from and into the metal strongly depends on the structure of the first molecular layer.

This paper is organized as follows: In Sec. II we describe the experimental setup and procedures. Section III presents our XSW results on \( \text{F}_{16}\text{CuPc} \) with particular emphasis on the data analysis and nondipolar contributions. In Sec. IV we discuss several aspects and implications of the results. Section V concludes this work with a brief summary.

II. EXPERIMENTAL DETAILS

A. General

The experiments were carried out at beamline ID32 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, see Fig. 1(b) for details of the experimental setup. The molecular films of \( \text{F}_{16}\text{CuPc} \) were prepared and studied in situ using a multipurpose ultra-high vacuum chamber with several analytical components (base pressure \( 2 \times 10^{-10} \) mbar).

B. Sample preparation

The \( \text{Cu}(111) \) and \( \text{Ag}(111) \) single crystals were mounted on a variable-temperature, high-precision manipulator. Repeated cycles of argon ion bombardment and annealing at 600–700 K resulted in clean and largely defect-free surfaces as has been verified by x-ray photoemission spectroscopy (XPS) and LEED measurements. The \( \text{F}_{16}\text{CuPc} \) material supplied by Aldrich Chemical Co. (Germany) was purified by gradient sublimation. Using a thoroughly outgassed Knudsen cell the molecules were evaporated at typical rates of less than 1 ML/min with the substrate at 300 K. Each evapora-

FIG. 1. (Color online) (a) Perfluorinated copper-phthalocyanine (\( \text{F}_{16}\text{CuPc} \)). (b) Experimental setup at the x-ray standing wave beamline ID32 (ESRF).
tion process was controlled with a calibrated quartz crystal microbalance close to the substrate.

C. Data acquisition

While the photon energy was scanned through the first-order back-reflection condition for Cu(111) and Ag(111) around 2980 and 2630 eV, respectively, x-ray standing wave signals were recorded. For this purpose a vertically mounted hemispherical electron analyzer (Physical Electronics) at an angle of 45° relative to the incoming x-ray beam acquired a series of energy resolved photoemission spectra.

After positioning the sample the x-ray reflectivity was measured with a photodiode mounted at a small angle relative to the incoming beam. As illustrated for Cu(111) in Fig. 2 we observed the first-order Bragg peaks whose position and shape can be described very well within the framework of dynamical diffraction theory. Since noble metal crystals are known to exhibit a certain mosaic spread that broadens the Bragg peak, we always monitored the reflectivity signal to identify a suitable position on the substrate before doing the XSW experiment. Given an intrinsic width of 0.84 eV derived from dynamical diffraction theory for a defect free crystal we regard the observed value of 0.95 eV as an indication of sufficient crystal perfection.

III. RESULTS AND ANALYSIS

A. Photoemission analysis

In order to extract the XSW signal a thorough analysis of all photoemission spectra is required. As shown in Fig. 3 a Voigt-like asymmetric line shape and an independently scaled Shirley-type background describe the experimental C(1s), N(1s), and F(1s) core-level spectra very well. In particular, we found the careful subtraction of the strongly photon energy-dependent inelastic background essential. By taking integrated peak intensities and normalizing to the incoming photon flux we obtained the photoelectron yield datasets which are suitable for the XSW analysis.

Further insight can be gained from spectroscopic observations on the monolayer system of F_{16}CuPc. Importantly, no significant changes in the peak position or line shapes were observed during the XSW experiment, indicating that the molecules do not fragment due to radiation damage. Moreover, the stoichiometry of the adsorbed molecules can be determined by comparing relative photoemission intensities. After normalizing the integrated off-Bragg intensity by the photoionization cross sections, the core-level lines shown in Fig. 3 give a stoichiometric ratio which corresponds within

FIG. 2. (Color online) Normal incidence reflectivity curve around the [111] Bragg reflection of the copper substrate. The solid line represents the reflectivity calculated by dynamical diffraction theory with additional broadening due to the mosaicity of the sample and the finite monochromator resolution. The origin of the relative energy scale used throughout this paper refers to the Bragg peak position as it would be observed without refraction inside the crystal.

FIG. 3. (Color online) Photoemission core-level lines of fluorine, nitrogen, and carbon taken on a submonolayer of F_{16}CuPc on Cu(111). The complete XSW series are analyzed by fitting a Voigt-like asymmetric line shape (solid line) and a suitable background (dashed line) to the spectra. Closed symbols refer to a photon energy on the Bragg condition, whereas open symbols correspond to an energy 1 eV below. With improved energy resolution we are able to distinguish two components in the C(1s) region corresponding to different chemical environments of the carbon atom.
TABLE I. Stoichiometry of the adsorbate derived from photoemission intensities. When normalizing the raw intensity \( I \) obtained from the datasets shown in Fig. 3 by the photoionization cross-section \( \sigma \) a composition close to the sum formula \( F_{16}C_{32}N_8 \) is derived.

<table>
<thead>
<tr>
<th></th>
<th>( I/\sigma (\text{MB}^3) )</th>
<th>( I/\sigma | \text{(norm.)} )</th>
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<tbody>
<tr>
<td>C(1s)</td>
<td>100.0</td>
<td>1.23 \times 10^{-3}</td>
</tr>
<tr>
<td>N(1s)</td>
<td>44.6</td>
<td>2.03 \times 10^{-3}</td>
</tr>
<tr>
<td>F(1s)</td>
<td>198.4</td>
<td>4.96 \times 10^{-3}</td>
</tr>
</tbody>
</table>

\( ^{\text{a}} \)Taken from Reference 17.

the error bars to the \( F_{16}CuPc \) composition, see Table I. Similarly, the surface coverage in the monolayer regime was calibrated by evaluating intensities of a substrate and adsorbate signal.

B. XSW analysis

1. Basic principles

The variation of the photoelectron yield observed from molecular adsorbates while scanning the photon energy through the Bragg condition holds structural information that can be analyzed quantitatively.\(^{11,12}\) However, it has been shown\(^{18-20}\) that depending on the experimental conditions the dipole approximation of photoemission is not generally applicable to the analysis of x-ray standing wave data. Higher-order terms contributing to the photoemission yield must not be neglected for low-\( Z \) elements and typical photon energies of several kilo electronvolts. Therefore the normalized photoelectron yield \( Y_p(\Omega) \) is not simply proportional to the standing wave intensity, as for the pure dipolar case. Instead, a generalized relation\(^{21}\)

\[
Y_p(\Omega) = 1 + S_R R + 2 |S_J| \sqrt{R} \exp(i\nu) \cos(\nu - 2 \pi P_H + \psi) \tag{1}
\]

that includes first-order corrections has to be used. Here the structural parameters \( f_H \) and \( P_H \) are the coherent fraction and position related to the \( H \)th Fourier component of the adsorbate atomic density. The photon energy-dependent reflectivity is described in terms of its absolute value \( \bar{R} \) and phase \( \nu \) between the incoming and outgoing waves. \( S_R \) and \( S_J = |S_J| \exp(i\psi) \) represent the higher-order contributions in the photoemission matrix element.\(^{20}\) Therefore they generally depend on the experimental geometry, the element number, the photon energy, and orbital symmetry of the initial state. Only within the dipole approximation with \( S_R = 1 \), \( |S_J| = 1 \), and \( \psi = 0 \) Eq. (1) reduces to the more familiar form.\(^{11,12}\)

In case of a back-scattering geometry as used throughout our experiments these three nondipolar parameters are not independent.\(^{20}\) Due to an additional constraint, i.e.,

\[
|S_J| = \frac{1}{2}(S_R + 1) \sqrt{1 + \tan^2 \psi} \tag{2}
\]

values for only two nondipole parameters have to be established to determine the structural XSW parameters \( f_H \) and \( P_H \). With \( 0 \leq P_H \leq 1 \) and \( d_0 \) as the distance of the substrate Bragg planes we derive the relative positions \( d_H \) of the adsorbate atoms to be \( d_H = d_0(1 + P_H) \).

As has been demonstrated before\(^{19,22}\) the nondipole parameter \( S_R \) can be determined by measuring the reflectivity and the XSW yield of the different atomic species. The relatively strong photoemission signals observed from multilayers of \( F_{16}CuPc \) provide datasets with almost negligible statistical noise that can be analyzed according to Eq. (3).\(^{23}\) On the basis of fits as the one shown in Fig. 4 we obtain \( S_R \) results on C(1s), N(1s), and F(1s) for first-order back-reflection energies of Cu(111) and Ag(111), see Fig. 4 and Table II. Our data are in good agreement with previous experimental results on Cu(111)\(^{18,22}\) and \( \text{ab initio} \) calculations.\(^{24,25}\) Given the experimental results, i.e., \( \approx 1.19 \approx S_R \approx 1.77 \) for the different elements, the nondipolar enhancement of the photoelectron yield is a key factor for the structural XSW analysis.

3. Coherent films

The photoelectron yield observed from a monolayer of \( F_{16}CuPc \) molecules is directly related to the the spatial phase of the XSW field at the atomic positions. Thus with \( f_H > 0 \) the coherent positions \( P_H \) can be determined, provided that
the nondipolar terms $|S|$ and $\psi$ are taken into account. By introducing effective quantities

$$f_{\text{eff}} = |S|/f_H \quad \text{and} \quad P_{\text{eff}} = P_H - \psi/2\pi$$

(4)

in Eq. (1) the photoemission yield may be written as

$$Y_p(\Omega) = 1 + S_R R + 2 \sqrt{f_{\text{eff}}} \cos(\nu - 2\pi P_{\text{eff}}).$$

(5)

Using the previously measured $S_R$ values the effective parameters defined in Eqs. (4) can now be derived directly from experimental photoelectron yield data. Therefore Eq. (5) has been the “working equation” for analyzing the XSW data.

The XSW scans on F(1s), N(1s), C(1s) presented in Fig. 5 (top) were taken on a submonolayer of F16CuPc on Cu(111). As a first, more qualitative result we note the similar overall shape of these XSW scans which indicate comparable coherent positions and thus a lying down configuration of the molecules. The low noise level achieved in these measurements, however, allows us to resolve small, but significant differences in the shape of the XSW signals; Compared to the carbon or nitrogen signal the fluorine yield shown in Fig. 5 (top) exhibits a more pronounced tail on the low-energy side. Accordingly, different coherent contributions are found by least-squares fits on the basis of Eq. (5) which yield a coherent position of $P_{\text{eff}}=0.395$ for fluorine and $P_{\text{eff}}=0.260$ for carbon.

Likewise we obtained x-ray standing wave signals from a coherent layer of F16CuPc on Ag(111). The XSW scans on C(1s), F(1s), and Cu(2p$_{3/2}$) shown in Fig. 5 (bottom) again reveal a lying down configuration of the molecules. Despite slightly worse statistics in these data our analysis works well and the fitted parameters $f_{\text{eff}}$ and $P_{\text{eff}}$ can be determined precisely. As on Cu(111) we derive a markedly larger coherent position $P_{\text{eff}}=0.45$ for fluorine compared to $P_{\text{eff}}=0.37$ for carbon. Further details on the resulting effective parameters both on Cu(111) and Ag(111) can also be found in Table III. The exact atomic positions $d_{\mu}$ however, cannot be derived unless the nondipolar contributions are separated out.

### 4. Non-dipolar corrections

In order to retrieve the coherent position $P_H$ and the coherent fraction $f_H$ from the effective parameters either the additional phase $\psi$ or $|S|$ has to be known. Importantly, in case of initial $s$-state symmetry this problem can be overcome because $\psi$ is directly related to the partial phase shift $\Delta = \delta_{\text{P}} - \delta_{\text{p}}$ between the possible final $p$ and $d$ states of the photoexcitation process. Since it can be shown that

$$\tan \psi = \frac{S_R - 1}{S_R + 1} \tan \Delta,$$

(6)

the XSW phase $\psi$ is a simple and unique function of the partial phase shift $\Delta$. Using an averaged experimental value of $S_R=1.75$ as a first estimate we hence find $\psi=0.27\Delta$.  

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**Table II.** Non-dipolar parameters: The $S_R$ values are derived experimentally from incoherent films, whereas $\Delta$ is obtained from ab initio calculations (Ref. 24). For comparison, values taken from Ref. 21 are given. Evaluation of Eqs. (2) and (6) then gives $\psi$ and $|S|$, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Cu(111)</th>
<th>Ag(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(1s) N(1s) F(1s)</td>
<td>C(1s) N(1s) F(1s)</td>
</tr>
<tr>
<td>$S_R$</td>
<td>1.76(1) 1.77(1) 1.72(1)</td>
<td>1.74(1) 1.59(1)</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-0.199 -0.236 -0.321</td>
<td>-0.211 -0.346</td>
</tr>
<tr>
<td>$\Delta^a$</td>
<td>-0.20 -0.24 -0.33</td>
<td></td>
</tr>
<tr>
<td>$\psi$</td>
<td>-0.055 -0.067 -0.088</td>
<td>-0.058 -0.082</td>
</tr>
<tr>
<td>$</td>
<td>S</td>
<td>$</td>
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*a Taken from Reference 22.*
TABLE III. XSW results taken on a submonolayer of F16CuPc on Cu(111) and Ag(111): By taking into account the nondipolar effects we derive the atomic position \(d_H\) relative to the Bragg planes of the substrate. In parentheses we give the statistical uncertainties of the parameters. With systematic uncertainties included we estimate the error bar of \(d_H\) to be ±0.07 Å on copper and ±0.10 Å on silver.

<table>
<thead>
<tr>
<th></th>
<th>Cu(111)</th>
<th>Ag(111)</th>
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<tbody>
<tr>
<td></td>
<td>C(1s)</td>
<td>N(1s)</td>
</tr>
<tr>
<td>(f_{\text{eff}})</td>
<td>0.69(4)</td>
<td>0.41(4)</td>
</tr>
<tr>
<td>(P_{\text{eff}})</td>
<td>0.260(5)</td>
<td>0.308(8)</td>
</tr>
<tr>
<td>(f_H)</td>
<td>0.50(1)</td>
<td>0.30(1)</td>
</tr>
<tr>
<td>(P_H)</td>
<td>0.251(5)</td>
<td>0.297(8)</td>
</tr>
<tr>
<td>(d_H)</td>
<td>2.61 Å</td>
<td>2.70 Å</td>
</tr>
</tbody>
</table>

For each element and electron energy phase shifts \(\Delta\) are determined independently by means of relativistic \textit{ab initio} calculations. Our results as given in Table II are in excellent agreement with previous theoretical efforts (Ref. 24 and Fig. 7 in Ref. 21. The corresponding nondipolar XSW phases \(\psi\) for carbon, nitrogen, and fluorine turn out to be relatively small and similar, with only minor impact on the effective coherent positions. Therefore we find \(\vert S_1 \vert = \frac{1}{2} (S_R + 1)\) as a good approximation to Eq. (2) with \(S_R\) and \(S_I\) being the truly important nondipolar parameters in our experiment.

Finally, we are now able to deduce the coherent fractions \(f_H\) and coherent positions \(P_H\) which yield the adsorbate bonding distances \(d_H\) relative to the Bragg planes of the substrate. On Cu(111) we find \(d_H = 2.61\) Å for carbon, whereas the fluorine atoms reside at \(d_H = 2.88\) Å, i.e., 0.27 Å above the central benzene rings of the F16CuPc molecule. With \(d_H = 2.70\) Å we locate nitrogen in an intermediate position somewhat closer to the carbons. The coherent fractions we derive on copper are nearly identical for fluorine and nitrogen, yet larger for fluorine. On Ag(111) we obtain \(d_H = 3.25\) Å for carbon, and \(d_H = 3.45\) Å for fluorine. Again this difference of 0.20 Å between both elements reveals a noticeable distortion of F16CuPc with the fluorine atoms above the plane defined by the inner carbon rings.

5. Error analysis

Showing the relevant fits to our XSW data on copper and silver, Fig. 6 demonstrates the obvious differences between these datasets. In order to assess our XSW results and decide whether the different bonding distances are significant a careful error analysis is necessary. We included Poisson-like errors as weighting factors in the fitting procedure of Eq. (5). As shown in Table III the obtained error bars for the coherent position \(P_{\text{eff}}\) are usually quite small. The corresponding uncertainties in the adsorbate positions \(d_H\) therefore amount to barely ±0.01...0.02 Å for datasets as those shown in Fig. 5.

Systematic errors of different origin, however, are much more difficult to quantify. Experimental insufficiencies and simplistic data analysis practices may inflict deviations from the “true” XSW signal. Because of the fixed focus of the electron analyzer, for example, a drifting x-ray beam on the sample can be precarious. Similarly, a wrong decomposition of the photoemission spectra causing erroneous XSW intensities can be misleading. Nevertheless, the pronounced tail on the low-energy side of the fluorine XSW signal as seen in Fig. 5 is consistently observed from monolayers F16CuPc on Cu(111) and Ag(111). Based on our experience with many different datasets we consider the systematic error of \(d_H\) to be dominant resulting in an accuracy of typically ±0.05...0.10 Å. We therefore conclude that the elevated positions of the fluorine atoms relative to the central benzene rings and the nitrogen atoms are significantly beyond the combined error bars.

![Comparison of XSW fits of F16CuPc on Cu(111) and Ag(111) for C(1s), N(1s), and F(1s) with different tails on the low and high energy side of the XSW signal. The inset shows the corrected values for \(f_H\) and \(P_H\) with realistic error bars in the Argand diagram corresponding to \(\Delta d_H = ±0.07\) Å(±0.10 Å) on copper (silver).](image-url)
TABLE IV. Atomic and van der Waals radii of the relevant atoms in F_{16}CuPc. These van der Waals radii $r_{vdW}$ are established from contact distances between nonbonding atoms and neglect the molecular structure of F_{16}CuPc.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>F</th>
<th>Cu</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{atomic}$ (Å)</td>
<td>0.70</td>
<td>0.65</td>
<td>0.50</td>
<td>1.35</td>
<td>1.60</td>
</tr>
<tr>
<td>$r_{vdW}$ (Å)</td>
<td>1.70</td>
<td>1.55</td>
<td>1.47</td>
<td>1.40</td>
<td>1.72</td>
</tr>
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</table>

IV. DISCUSSION OF RESULTS

Like many other molecules with extended π-electron systems F_{16}CuPc adsorbs in a lying down configuration on Cu(111) and Ag(111) forming a rather stable adsorbate complex. This behavior might be explained by the formation of interface states derived from the delocalized π-electrons in F_{16}CuPc. By aiming at a large orbital overlap with the electron cloud of the substrate, the molecules naturally adopt the lying down configuration as the energetically most favorable position. As we observe XSW signals with coherent fractions 0.3 ≤ $f_H^e$ ≤ 0.5, the corresponding disorder within the adlayer is significant. Given the size and symmetry of F_{16}CuPc, this appears to be the result of a statistical misalignment rather than a uniform tilt of all molecules. Since the lateral structure of F_{16}CuPc might be neither simple nor entirely static, the atomic positions reported here are element and time averaged results.

The exact bonding distances of F_{16}CuPc, to our knowledge determined for the first time here, are more difficult to interpret. As a first attempt one might compare our results with the van der Waals (vdW) radii $r_{vdW}$ of the different atoms, given in Table IV. These values, derived from contact distances between nonbonding atoms do not take chemical bonding or charge redistribution into account. In fact, in compounds of different atoms the radius strongly depends on the chemical bonding. In particular due to the presence of fluorine, the most electronegative element, one has to expect significant deviations from these numbers. Not too surprisingly, therefore, the bonding distances do not agree with added values of $r_{vdW}$. More instructive, however, is a comparison with experimental data available for similar systems. The simplest and probably best studied aromatic adsorbate system is benzene. On the transition metal surfaces Ni(111) and Ru(0001) generally smaller values for the carbon positions are found, i.e., 1.81 Å on nickel and 2.11 Å on ruthenium. Examples of more complex molecules are PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride, Ref. 30) with a bonding distance of 2.85±0.05 Å and NTCDA (1,4,5,8-naphthalene-tetracarboxylic acid-dianhydride, Ref. 31) with 3.02±0.02 Å both on Ag(111), i.e., values comparable to our results.

The different atomic positions within the molecule cannot be fully explained by means of a simple model which does not take the molecular structure of F_{16}CuPc and the presence of the substrate adequately into account. As discussed in a recent theoretical work, however, the distortion might be related to a partial rehybridization of the carbon atoms as they change from the $sp^2$ hybridization in the free molecule toward a more tetrahedral $sp^3$ symmetry upon adsorption. A convenient way to illustrate this concept is to consider the average angle $\delta$ between the C-F bond and the surface, see Fig. 7. Using a C-F bond length of 1.35 Å and our XSW results we can derive an angle of 90+ $\delta$=101.5±4.4° for Cu(111) and 90+ $\delta$=98.5±6.0° for Ag(111). Both values are considerably closer to the tetrahedral angle of 109.5 Å that would correspond to a full $sp^3$ symmetry. However, theoretical work is required to verify whether the surface interactions are large enough to promote the adsorbing molecule into a partially $sp^3$-hybridized state.

Further experiments using different ligands as “spacers” (e.g., replacing F with Cl, Br, or I) could test this hypothesis and reveal how the interaction between the central ring structure with the metallic electron cloud is mediated. We note that a distorted adsorption geometry of F_{16}CuPc has interesting and possibly important implications. Due to the high electron affinity of fluorine a permanent molecular dipole moment perpendicular to the substrate surface is created. This, however, results in an additional attractive force between the molecules and the metal as the induced image dipole stabilizes this configuration.

First-principles calculations of the adsorption of F_{16}CuPc could also shed more light on this phenomenon as they would include all important aspects of this system as, e.g., the character of the chemical bonding in the molecule, the partially filled d bands in noble metals, and the central copper atom in F_{16}CuPc. The molecular distortion could then be compared to theoretical results. These investigations would not only contribute to a better understanding of these adsorbate systems, but also provide clues for areas such as organic electronics, where the binding of the first molecular layer to a metal contact strongly influences the interface dipole and the charge carrier injection.

V. SUMMARY AND CONCLUSIONS

In this study we show that large π-conjugated F_{16}CuPc molecules adsorb in a lying down, but nonplanar configuration on the noble metal surfaces Cu(111) and Ag(111). A detailed, element-specific analysis of our XSW data reveals a
significant relaxation of the molecules upon adsorption. The coherent positions $P_H$ of the fluorine and carbon atoms differ beyond the experimental uncertainties: On copper (silver) the central carbon rings are located at $d_H=2.61 \, \text{Å}$ ($d_H=3.25 \, \text{Å}$) above the substrate, whereas the outer fluorine atoms are found at $d_H=2.88 \, \text{Å}$ ($d_H=3.45 \, \text{Å}$).

We hope that our results will stimulate further experimental and theoretical work in this area. Calculations on the adsorbate structure of large molecules would greatly promote our understanding of these systems and could also provide insight in the electronic properties of the organic-inorganic interface.

**ACKNOWLEDGMENTS**

The authors thank the ESRF for providing excellent facilities and N. Karl and J. Pflaum for purifying the F$_{16}$CuPc material. This work was financially supported by the EPSRC (UK).

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