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The electronic structure of cobalt(II) phthalocyanine adsorbed on Ag(111)

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ABSTRACT

The electronic states of submonolayers and multilayers of cobalt(II) phthalocyanine (CoPc) adsorbed on Ag(111) were examined with photoelectron spectroscopy to obtain insight into the details of the substrate–adsorbate interaction. UV photoelectron spectroscopy (UPS) reveals the presence of two interaction-related valence states in the direct vicinity of the Fermi edge, in agreement with previous DFT calculations. X-ray photoelectron spectra indicate that the substrate–adsorbate interaction results in transfer of electron density from the substrate to the Co(II) ion. Substantial changes in the Co 2p multiplet structure, a spectral pattern induced by the open-shell character of the central Co(II) ion, indicate a complete quenching of the molecular spin. While pristine CoPc molecules are paramagnetic with $S=1/2$, molecules in direct contact to the Ag(111) substrate appear to be in a diamagnetic state.

1. Introduction

Metallotetrapyrrole complexes, in particular metalloporphyrins, are versatile functional units in many biological and biochemical processes [1]. These complexes and their synthetic analogs, the metallophthalocyanines, have also been utilized in technical applications, with the aim that their highly functional nature is retained after immobilization in an artificial (i.e., non-biological) framework. Well-investigated examples include gas sensors [2], solar cells [3] and catalysts [4,5]. In addition to these studies with focus on specific applications, there is the need for a fundamental understanding of the properties of metallotetrapyrroles embedded in non-biological environments. One possible approach to address this question is their adsorption on well defined metallic or semiconducting single-crystal surfaces under controlled conditions. Previous investigations [6–28], following this approach often showed substantial modification of the molecular electronic states by the substrate. In addition, it was demonstrated that adsorption can induce a change of the magnetic properties of the adsorbed metal complexes. In a study of the paramagnetic complex cobalt(II) phthalocyanine (CoPc) on Au(111), the complex was found to be diamagnetic in the adsorbed state, indicating a charge transfer mechanism combined with a compensation of the initially unpaired spin in the Co $3d_{z2}$ orbital [12]. Recent DFT calculations regarding the adsorption of CoPc on Ag(111) predict similar effects on this substrate [13].

In the present work, submonolayers and multilayers of CoPc on Ag(111) were examined with X-ray and UV photoelectron spectroscopy (XPS/UPS), in order to elucidate the existence and nature of the interaction between the metal complex and the substrate. Before presenting the results, we will briefly review the specific spectral features of transition metal compounds, in particular Co complexes, in XPS. Transition metal complexes show in general a rich multiplet structure in their most intense photoelectron signals. These multiplet patterns result from the interaction between the core-hole electron of the photo ion and unpaired electrons in the valence d shell. Therefore, the core-level spectra contain information about the state of the d shell, for example, about the spin state of the transition metal ion. In the case of cobalt complexes, it was demonstrated that each spin configuration has an individual spectral fingerprint, in particular in the 2p region [29–31]. Accordingly, Co(II) high-spin complexes ($S=3/2$) show a rich satellite structure and an apparent spin-orbit separation of ~16 eV, while diamagnetic Co(III) or Co(0) complexes do not feature strong satellites and show an apparent spin-orbit separation of only 15 eV combined with a more narrow peak shape. Co(II) low spin ($S=1/2$) compounds, such as CoPc, show an intermediate behavior, characterized by a slightly enhanced apparent spin-orbit separation of ~15.5 eV and a broader line shape due to the influence of one unpaired electron, but no enhanced satellite structure [29,30].

The grouping of the different multiplet components around the $2p_{3/2}$ and $2p_{1/2}$ signal positions, as measured in the diamagnetic compounds, suggests a j–j coupling mechanism; the $j=1/2$ and $j=3/2$ states of the core hole couple with the total magnetic moment of the unpaired electrons in the d shell. This results in a perturbation of those states, associated with a splitting into several sub-states. The details of this coupling mechanism have been subject to several

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theoretical studies [32–34]. In the interpretation and assignment of individual multiplet components we will follow the work of Frost and Briggs [29–31]. Since both the $2p_{3/2}$ and $2p_{1/2}$ states show broad multiplet patterns, it is not clear a priori which signal positions are most appropriate to measure the spin-orbit separation. By convention [29–31,35,36], the positions of the most intense peaks in both multiplet signals were used to determine the apparent spin-orbit splitting.

Another characteristic of the 2p core level spectra of various transition metals is the larger full width at half maximum (fwhm) of the $2p_{1/2}$ signal, compared to the $2p_{3/2}$ signal. This effect can be clearly observed for Co metal, where multiplet effects are absent [36]. This phenomenon can be explained by a shorter lifetime of the $2p_{1/2}$ core hole due to an additional Auger electron decay channel, i.e., the decay via a $L_2L_3M_{4,5}$ Coster-Kronig process [37,38]. The higher decay rate causes a shorter lifetime and consequently a higher fwhm of the spectral line. According to Fuggle and Alvarado [37], the Co $2p_{1/2}$ state is broadened by a factor of ~1.2 compared to the Co $2p_{3/2}$ line.

In the following, we will apply the principles outlined above to CoPc adsorbed on Ag(111) and investigate how the electronic properties of the Co ion are influenced by the interaction with the substrate.

2. Experimental

The XPS experiments were performed with a monochromatized Al Kα X-ray source and a Scienta ESCA 200 photoelectron spectrometer. The base pressure was in the low 10^{-10} mbar range. Photoelectrons were detected under 70° relative to the surface normal, in order to achieve higher surface sensitivity. In the numerical analysis of the spectra, a Voigt-type peak shape was approximated by a weighted sum of Gaussian and Lorentzian functions.

CoPc submonolayers and multilayers were prepared by stepwise deposition of small amounts of CoPc from a Knudsen cell at 700 K. The Ag(111) crystal was kept at room temperature during deposition and measurements. In contrast to previous studies with other planar metal complexes [6–9], CoPc monolayers were not prepared by multilayer desorption here, since recent STM work shows the presence of a disordered adsorbate phase at room temperature if the sample was heated to ~600 K during deposition [13].

CoPc coverages were measured by Low Energy Ion Scattering (LEIS) and subsequently correlated with the respective C 1s/Ag 3d XPS intensity ratio. Since LEIS is exclusively sensitive to the topmost surface layer [39], the decrease of the substrate intensity is, in first approximation, directly proportional to the increase in coverage by adsorbed CoPc molecules. The coverage at which the substrate LEIS signal vanished was defined as a monolayer. Consequently, a coverage of, for example, 0.8 monolayers refers to a situation where 20% of the Ag(111) substrate is uncovered by the CoPc molecules, irrespective of the morphology of the CoPc phase.

The LEIS measurements were performed with He^+ ions at a kinetic energy of 1 keV. The ion beam conditions were chosen such that, after continuous irradiation of a phthalocyanine submonolayer (0.9 monolayers), first indications for beam damage became evident after ~20 min. In contrast, the accumulated sample irradiation time needed to correlate the XPS C 1s/Ag 3d intensity ratio to the sample coverage was only 70 s. The film thickness calculated for a monolayer was 2.6 Å, based on an estimation of the XPS attenuation length according to Lamont et al. [40] and atomic sensitivity factors by Wagner and co-workers [41]. This value is in reasonable agreement with the van der Waals diameter of carbon and nitrogen atoms. A comparison to the thickness obtained for well ordered CoPc monolayers on Au(100) of ~0.3 nm further corroborates the result [28]. These values suggest that the monolayer definition in the current study is equivalent to the presence of a single, closed layer of phthalocyanine molecules. However, it is not possible to comment on the presence of long-range order based on our experimental methods.

UV photoelectron spectra were acquired with 21.22 eV He–I radiation. A correct secondary electron cut-off was obtained by applying a bias voltage of −5 V to the sample.

All binding energies refer to the Fermi energy (E_F) of clean Ag(111). The substrate was cleaned prior to any deposition by extensive sputtering with Ar^+ ions ($E_{kin} = 1300$ eV) and subsequent annealing to 800 K. The purity and long range order were confirmed by XPS and LEED, respectively.

3. Results

3.1. X-ray photoelectron spectra

Fig. 1 displays a comparison between the C 1s and N 1s spectra of a CoPc multilayer and submonolayer. The multilayer had a thickness of >30 Å, resulting in a complete damping of any Ag related signals.

The N 1s signal of the multilayer can be deconvoluted into two components, originating from the nitrogen atoms which are in direct contact to the cobalt metal center (Nβ) and the nitrogen atoms interlinking the pyrrole units (Nα). The distance between the two subcomponents is, according to our least-squares fit, 0.48 eV, a value which is in excellent agreement with literature [42]. Prior to fitting, a simple Shirley type background was subtracted [43].

The N 1s submonolayer spectrum was background-corrected in a more complex way to compensate the strong overlap between the N 1s signal and underlying contributions from Ag 3d plasmon excitations [44]. The N 1s submonolayer spectrum as shown in Fig. 1 results from a two-step treatment of the raw data: first a least-squares fit of the N 1s signal together with the Ag 3d plasmons (constrained to the parameters of the clean Ag(111) surface) and, in a second step, the subtraction of the plasmon contribution from the raw signal (see Figure S1 in the supplementary data for further information). The N 1s signal positions in multilayer and submonolayer spectra are identical within the experimental error.

The C 1s multilayer and submonolayer spectra in Fig. 1 feature two main components, which are accompanied by satellite excitations. A least-squares fit reproduced the stoichiometric ratio between the different carbon species within the phthalocyanine ligand correctly, yielding a ratio of Cα:Cβ:Cγ of 2:1:1. In the multilayer spectrum, the signal that originates from the phenyl carbon atoms (Cα) is located at the lowest binding energy (284.0 eV), while the signal contribution of the carbon atoms at β position and the nitrogen-linked (N–C–N) carbon atoms (Cγ) are found at 284.5 eV and 285.5 eV, respectively. The satellite contributions at 286.1 and 287.5 eV can be attributed to π–π^* excitations [42]. The C 1s spectra of the submonolayer closely resemble the spectrum of bulk CoPc. While no significant shift of the Cγ-related signal component is detectable, the Cα and Cβ components shift to higher binding energies by ~0.2 eV.

Fig. 2 displays the Co 2p XP spectra of a CoPc multilayer (>20 monolayers) and submonolayer (~0.9 monolayers). The submonolayer spectrum was background corrected such that the ratio between the total $2p_{1/2}$ and $2p_{3/2}$ intensities fits the nominal value of 1:2. The multilayer spectrum represents a characteristic 2p signal pattern of a Co(II) ion in an $S = 1/2$ low-spin state [31]. Furthermore, the $2p_{3/2}$ component of the multilayer spectrum shows a minor contribution at 782.5 eV, whereas no obvious multiplet splitting or asymmetry is visible in the $2p_{1/2}$ component. The $2p_{3/2}$ component features a slight asymmetry, indicating the presence of further, experimentally not resolved multiplet components. The apparent spin-orbit separation, measured between the $2p_{3/2}$ and $2p_{1/2}$ signal maxima, is 15.7 eV for the multilayer, in close agreement with literature values for bulk CoPc [30]. The minor contribution to the Co $2p_{3/2}$ signal at 782.5 eV is in general associated with the multiplet structure, since an analogous feature in the $2p_{1/2}$ component is absent [31]. Thus, it cannot originate from a chemically different cobalt species on the sample, nor does it represent a regular shake-up or shake-off satellite. The key for the interpretation of this