Switching the electronic properties of Co-octaethylporphyrin molecules on oxygen-covered Ni films by NO adsorption

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Abstract.
Using X-ray absorption spectroscopy, we demonstrate that the electronic properties of Co-octaethylporphyrin (CoOEP) molecules on oxygen-covered ultrathin Ni films can be reversibly manipulated by a chemical stimulus. This is achieved by adsorption of nitrogen monoxide (NO), leading to the formation of a NO-CoOEP nitrosyl complex, and subsequent thermal desorption of the NO from the Co ions. The integration of the absorption spectra of the Co $L_{2,3}$ edges reveals a partial oxidation of the Co ions after dosing NO compared to the pristine sample, for which a valency of $+2$ and a low spin state of the Co ions can be deduced from the Co $L_{2,3}$ XAS line shape. By means of X-ray magnetic circular dichroism the magnetic moments of the Co ions were found to be coupled parallel to the magnetization of the Ni films across the intermediate layer of atomic oxygen, before and after NO uptake.

1. Introduction

Metalloporphyrins have been, for many decades, a matter of particular interest within the scientific community due to their unique optical, electronic, and chemical properties, which give them a relevant position as components for photovoltaic devices [1], chemical sensors [2], or catalysts [3]. Besides, they play a key role in biological systems as for instance in haem or chlorophyll [4] and, lately, became promising building blocks for applications in information technology industry [5]. As such, using paramagnetic metalloporphyrins as part of a molecular spintronic device requires on the one hand their immobilization, e.g., by placing them on top of a solid surface, and on the other hand a reversible control of their electronic and magnetic properties by external means. It has been shown that the coordination of NO to metalorganic molecules adsorbed on nobel metal surfaces modifies their interaction with the substrate due a competition of their axial ligands (*trans* effect) and can also change their spin state [6], whereas even a reversible switching of the interaction with the substrate has been achieved by a subsequent thermal desorption of NO [7, 8]. The study of paramagnetic metalorganic molecules on ferromagnetic metal

surfaces is of special interest, as the spins of the central ions get stabilized against thermal fluctuations by an exchange coupling aligning them either parallel to the substrate magnetization [9, 10, 11, 12, 13] or antiparallel, by an intermediate layer of atomic oxygen [14, 15]. Clearly, a reversible tuning of such substrate-induced magnetic ordering is desirable. It has been demonstrated that the strength of the magnetic coupling between Fe-octaethylporphyrins and oxygen-covered Co films can be reversibly controlled by the attachment and detachment of NO [16], whereas such a process leads to a reversible off–on switching of the molecular spins for Co-tetraphenylporphyrins on Ni films, as demonstrated by means of X-ray magnetic circular dichroism (XMCD) [17]. However, within this investigation, the issue of NO-induced modifications on the Co $L_{2,3}$ X-ray absorption (XA) spectra as well as their reversibility has not been addressed unambiguously.

In this paper we present an angle-dependent X-ray absorption spectroscopy (XAS) study of a submonolayer of Co-octaethlyporphyrin (CoOEP) molecules adsorbed on a ferromagnetic Ni film covered with an ordered $c(2 \times 2)$ layer of oxygen atoms. The formation of NO-CoOEP nitrosyl complexes is concluded from the changes of the Co $L_{2,3}$ XA spectra after dosing nitrogen monoxide (NO), whereby the Co^{+2} ions get partially oxidized. The thermal desorption of NO restores the pristine state of the metal ion and proves the possibility to switch the electronic properties of CoOEP with such a chemical stimulus. Dosing NO once more induces again the same modifications of the electronic properties. By means of XMCD we show that the magnetic moments localized on the Co ions are aligned parallel to the Ni substrate magnetization, both before and after NO uptake. This is the first report about a ferromagnetic coupling between paramagnetic metalloporphyrins and a ferromagnetic substrate across an intermediate layer of atomic oxygen. Angle-dependent XAS measurements at the N K edge reveal a quasi flat adsorption of the CoOEP molecules on the surface. Furthermore, they provide clear fingerprints of NO after its adsorption, and prove its dissociation after warming up the system to 350 K.

2. Experimental details

Experiments were performed *in situ* at a base pressure of $p = 5 \times 10^{-10}$ mbar. A Cu(100) single crystal was cleaned by cycles of Ar^+ sputtering at 1.0 keV and annealing to 900 K. The surface quality was checked by low-energy electron diffraction. Epitaxial Ni films were prepared by electron-beam evaporation on a preoxidized Cu(100) single crystal at room temperature. The oxidized Cu(100) surface was prepared following Ref. [18]. Ni growth on the Cu surface covered by half a monolayer of atomic oxygen occurs in a surfactant-assisted mode [18, 19] with the oxygen atoms at $c(2\times2)$ positions.

Co(II)-2,3,7,8,12,13,17,18-octaethylporphyrin molecules were purchased from Porphyrin Systems, and evaporated by sublimating molecular powder from a crucible at around 485 K onto the sample held at room temperature. The thickness of the Ni film and the coverage with porphyrin molecules were determined by medium-energy electron diffraction intensity oscillations and a quartz microbalance, respectively, and were cross-checked by the signal-to-background ratio edge jump at the respective X-ray absorption edges. XAS and XMCD measurements were carried out at the bending magnet beamline PM3 at BESSY II in Berlin. Absorption spectra were aquired in total-electron-yield mode by recording the sample drain current as a function of the photon energy. The spectra were normalized to the total electron yield of a freshly
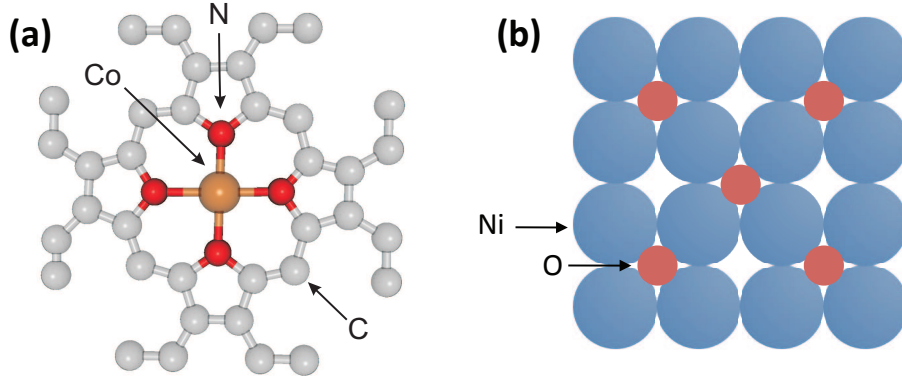
Figure 1. Schematic sketch of CoOEP molecule (a) and a top view of a $c(2\times2)$ O-Ni(100) surface (b) at the same scale

evaporated gold grid upstream to the experiment and the corresponding spectra of an oxygen-covered Ni film without adsorption of CoOEP. Data were collected with an energy resolution of 150 meV at the N K edge and 300 meV at the Co and Ni $L_{2,3}$ edges using p-linearly and circularly polarized light with 95% and 85% degree of polarization, respectively. Calibration of the photon energy is carried out by means of NEXAFS measurements of gaseous N_2 setting the position of the first N π^* resonance to 400.88 eV [20]. Typical photon flux densities at the sample of about 10^{12} s^{-1}cm^{-2} were used to prevent X ray induced damage of the molecules, which can be excluded here from the comparison of spectra taken immediately after sample preparation and at later times. Magnetic measurements were carried out in remanence of the Ni film with a thickness of 8 monolayers (ML) and an easy magnetization axis out-of-plane.

3. Results and discussions

3.1. Switching the electronic properties

Figure 2 shows Co $L_{2,3}$ XA spectra of 0.7 ML CoOEP on O/8 ML Ni/Cu(100) before dosing NO, after dosing 28 L of NO, after a subsequent thermal desorption of NO at 350 K, and after dosing once more 14 L of NO (1 L= 10^{-6} mbar s), measured with p-linearly polarized light and an angle of 20° (panel a), 55° (panel b), and 90° (panel c) between the incoming X-ray wavevector and the surface. The spectra of this measuring series, presented in fig.2, have been taken at a temperature of 130 K, at which also the NO was dosed in order to avoid its dissociation on the surface. Vertical arrows indicate the temporal sequence in which the spectra have been acquired. At all three detection angles significant changes occur in the spectra when NO is adsorbed to the molecules. Spectral weight is shifted to higher photon energies, both at the L_3 and the L_2 edge. This is most pronounced for 20° grazing incidence (panel a), but still significant for 90° normal incidence (panel c). In addition, the multiplet structure of the absorption peaks becomes less pronounced, and the linear dichroism, i.e., the difference between the absorption spectra for different incidence angles, is reduced after NO adsorption. To check for the reversibility of the NO-induced modifications, the sample was warmed up to 350 K in order to desorb the NO, and then cooled down again for recording angle-dependent Co $L_{2,3}$ XA spectra. As shown in figure 1, the

initial lineshape for measurements at all three different incident angles is recovered, proving the full reversibility of the process. It is even possible, by dosing once more 14 L of NO, to induce again the same spectral changes of the lineshape and thus to repeat the manipulation of the electronic properties, as shown by the topmost curves in figure 1 a–c.

The spectra of the pristine sample show two prominent features, building up the fine structure of the Co L_3 edge. One is a narrow peak at 777.7 eV, being more prominent in the spectra taken at grazing incidence (panel a) and therefore originating from excitations into states with out-of-plane hole density. The other feature, a broader peak with a maximum at 779.5 eV and two shoulders at 780.3 eV and 781.6 eV, is more apparent in the spectra taken at normal incidence and for this reason originates from excitations into states with in-plane hole density. For spectra taken at the so-called magic angle of incidence for linearly polarized X rays (55°, panel b) the dependence on the orientations of the molecular orbitals cancels out, such that they can be directly compared to spectra of polycrystalline bulk samples. Our spectra of the pristine sample closely resemble those of a recently published paper on thin films of cobalt phthalocyanine (CoPc) and the corresponding multiplet calculations of the Co $L_{2,3}$ edges [21, 22]. Taking into account the similarity of Co $L_{2,3}$ XA spectra of bulk CoPc and bulk CoOEP samples [23], we conclude that the Co ions of the molecules preserve the physical properties which they have in isolated CoOEP, despite the interaction between the CoOEP molecules and the oxygen-covered Ni film. Density functional theory (DFT) calculations reveal a +2 valency and a low-spin state of the Co ions for free molecules [24]. Following this comparison and considering the angular dependence and the energetic position between the fine structure components of the Co L_3 edge, an assignment of the empty orbitals accessed by excitations of the $2p$ core-level electrons can be qualitatively done. According to ligand field theory, the $3d$ orbitals of the Co ions transform as a_{1g} (d_{z^2}), b_{1g} ($d_{x^2-y^2}$), b_{2g} (d_{xy}), and e_g ($d_{yz,xz}$) in a C$_{4v}$ symmetry, which is expected for flatly adsorbed CoOEP molecules. According to DFT calculations for isolated CoOEP [24], the b_{1g} ($d_{x^2-y^2}$) state is highest in energy and completely empty. It can therefore be related to the energetically higher-lying broad peak with a maximum at 779.5 eV, whereas the a_{1g} (d_{z^2}) state is half filled and can be related to the narrow peak at 777.7 eV. However, the e_g ($d_{yz,xz}$) and the a_{1g} (d_{z^2}) states could also together carry one hole according to the mentioned multiplet calculations. Assuming such a case, excitations into the e_g ($d_{yz,xz}$) state would also contribute to the spectra for 55° and 20° incidence angle. Co $L_{2,3}$ XA spectra of CoOEP adsorbed on an oxygen-covered Cu(100) surface show almost the same lineshape as the ones for CoOEP on the oxygen-covered Ni film, indicating a small electronic coupling between the Co ions and the substrate [25], whereas for CoOEP on Ag(110) [24] and on Ag(111) [26] a direct electronic interaction was reported, which partially reduces the Co^{+2} ions.

A reduced electron density at the Co site after the uptake of NO is found by applying the charge sum rule [27] to the isotropic Co $L_{2,3}$ XA spectra, before and after NO uptake. An increase of integrated intensity of the white line, and hence of the number of holes of the Co ions within the $3d$ shell, by $10\% \pm 2\%$ is observed. Performing the same integration for the angle-dependent XA spectra recorded at normal and grazing incidence yields a rise in white-line intensity of $8.5\% \pm 2\%$ and $12\% \pm 2\%$, respectively, which shows that the electron density withdrawn from the Co ion by the attachment of NO is higher for out-of-plane than for in-plane orbitals. The shift to higher photon energies of the Co $L_{2,3}$ absorption spectra after dosing NO is consistent with a reduction of electron density at the Co site.
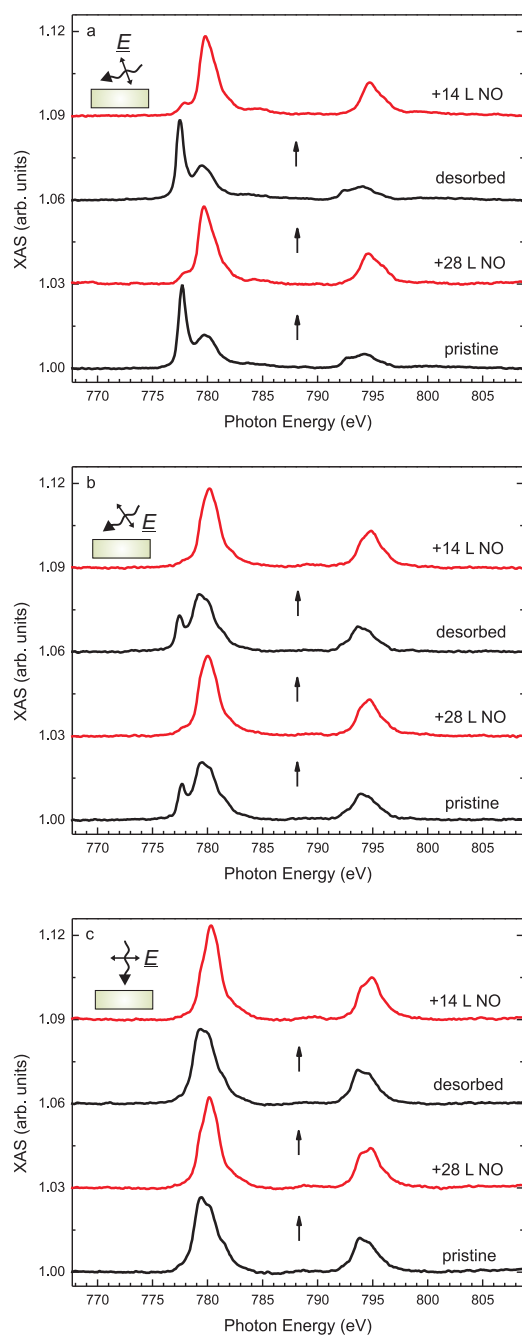
Figure 2. Co $L_{2,3}$ XA spectra of 0.7 ML CoOEP on O/Ni measured with p-linearly polarized light and an angle of 20° (a), 55° (b), and 90° (c) between the X-ray wavevector and the surface at 130 K for each NO dosage step. From the bottom to the top for each subfigure, the spectra are shown for the sample in the pristine state, after dosing with 28 L of NO, after ensuing desorption of NO by heating to 350 K, and after dosing again 14 L of NO. The spectra are shifted vertically for clarity.

The transfer of a non-integer charge away from the Co ions can be understood within the charge transfer multiplet model, in which the ground state is built by combining different oxidation states of the Co ions and the corresponding electrons or holes in the ligands. In such a model, the contraction of the multiplet structures after the uptake of NO can be comprehended as the consequence of such charge transfer effects, which are provoked by charge fluctuations in the initial and final states involved in the absorption process [28]. For that reason an NO-induced reduction of charge at the site of the Co ion leads to a less pronounced multiplet structure. According to crystal field theory [29], the detected decrease of linear dichroism after the uptake of NO points towards an alteration of the crystal field acting on the Co ions, which possesses then a less tetragonally acentric distorted shape (C_{4v} symmetry), but rather approaches a more octahedral (O_h symmetry). The observed redistribution of the spectral weight, the shift to higher photon energies of the spectral height especially for measurements at grazing incidence compared to the ones at normal incidence, is consistent with such a change of the symmetry. A coordination of NO as an additional axial ligand to the Co ions pushes the $3d$ states with an out-of-plane charge distribution e_g and a_{1g} to higher energies, while having a minor influence on states with an in-plane charge distribution b_{1g} and b_{2g}.

In summary, NO-CoOEP nitrosyl complexes are formed after NO dosage, concluded from the strong NO-induced modifications of the Co $L_{2,3}$ XA spectra, which goes hand in hand with a partial oxidation of the Co 2+ ions of the CoOEP molecules and a reduction of the tetragonal distortion of the Co $3d$ electron distribution. The detailed electronic interaction between the Co ions and the NO molecules can be rather complex and literature about molecular orbital theory of NO-Co porphyrin nitrosyl complexes can be found somewhere else [30, 31].

3.2. Substrate-induced magnetic ordering

In figure 3, Co L_3 (panel a) and Co L_2 (panel b) XA spectra are presented, which were taken with circularly polarized light. They belong to the same preparation as the respective spectra in figure 2, and were measured at 30 K at normal incidence. For a magnetization of the sample being parallel and antiparallel to the direction of the photon angular momentum of the incomming X rays, Co L_3 and Co L_2 XA spectra with a different line shape are detected for the pristine sample (dark and dotted blue lines) as well as after dosing 28 L of NO (orange and dotted magenta lines). The corresponding raw data are shown in the supplementary information. In panel d of figure 3, the corresponding XMCD difference spectra are presented, in which the non-vanishing signal proves a magnetic moment on the cobalt ion and a magnetic coupling between this moment and the ferromagnetic substrate, for both the CoOEP molecules and the NO-CoOEP nitrosyl complexes. The energetic position of the Co $L_{2,3}$ XMCD signals before (black line) and after (red line) dosing NO is nearly the same, whereas the Co XMCD signal after dosing is about a factor two smaller than before dosing.

The XMCD spectrum of the pristine sample displays the typical line shape of a cobalt d^7 low-spin system in an environment with C_{4v} symmetry, recorded in normal incidence, which exhibits zero crossings of the XMCD signal at the L_3 edge as well as at the L_2 edge [22, 25]. Since the presented spectrum does not represent the isotropic XMCD, it also carries information about the distribution of the spin density, being correlated to the distribution of the unpaired electron density. Therefrom the characteristics of its line shape can be better comprehended by the fact that the
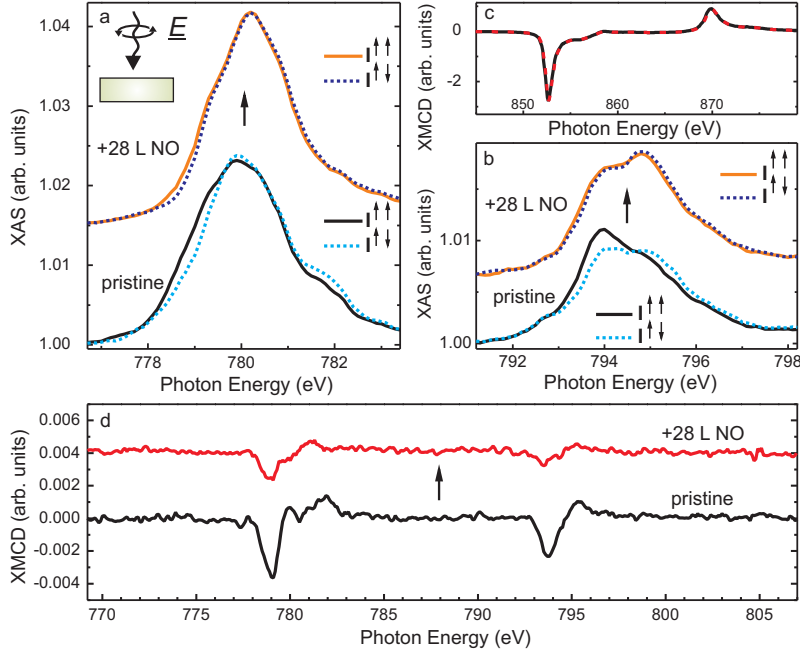
Figure 3. Co L_3 (a) and Co L_2 XA spectra (b), which are recorded at 30 K at normal incidence with circularly polarized light and a magnetization of the sample being parallel and antiparallel to the direction of the photon angular momentum of the incomming X-rays before (continuous dark and dotted blue lines) and after dosing 28 L of NO (continuous orange and dotted magenta lines), and corresponding XMCD spectra (d) before (red line) and after dosing 28 L of NO (red line) of 0.7 ML CoOEP on O/Ni. Spectra are shifted vertically for clarity. (c) XMCD spectra at the Ni $L_{2,3}$ before (full black line) and after (dashed red line) dosing NO.

XMCD signal originates from the density of unpaired $3d$ holes, which has mainly an out-of plane distribution, while on the other hand the in-plane unoccupied density of states is probed by the measurement under normal incidence.

In panel c of figure 3 the XMCD spectrum of the Ni substrate of the pristine sample (black line) is shown, which exhibits a negative sign of the XMCD signal at the L_3 edge. Interestingly, the cobalt XMCD signal predominantly presents a negative signal at the L_3 edge, too. This finding verifies a ferromagnetic coupling of the molecules to the Ni film through the intermediate layer of atomic oxygen, the strength of which must be comparatively small, since at temperatures higher than 30 K no significant XMCD signal could be measured, in contrast to, for instance, Fe octaethylporphyrin molecules (FeOEP) on ferromagnetic substrates [10, 11].

Pondering about the coupling mechanism, a direct magnetic interaction between the Co ions and the substrate is unlikely due to the intermediate layer of atomic oxygen. In contrast, an indirect coupling mechanism via the oxygen atoms seems to be very likely, and has been already reported for manganese tetraphenylporphyrin chloride (MnTPPCl) and FeOEP on oxygen-covered ferromagnetic metal surfaces. Along such an exchange path a 180° superexchange interaction can establish an antiferromagnetic coupling between the paramagnetic metalloporphyrins and the

magnetization of the substrate [14, 15], but also a ferromagnetic double exchange interaction across the oxygen layer has been theoretically predicted [32]. The latter could explain the ferromagnetic coupling between the magnetization of the Ni film and the paramagnetic CoOEP molecules. However, a magnetic exchange coupling of the Co ions to the magnetization of the substrate across the atomic oxygen, which is mediated by the π system of the porphyrins, can not be excluded.

In order to work out the impact of the adsorption of NO on the magnetic properties of the Co ions, the effect of the NO adsorption on the magnetization of the Ni film has to be considered, too. Panel c of figure 3 also shows the XMCD spectrum of the Ni substrate after dosing 28 L of NO (red dotted line). The virtually identical Ni XMCD spectra before and after dosing of NO validates that the NO has no significant impact on the magnetism of the Ni film, which appears to be protected by the oxygen adatoms. After the adsorption of NO to the sample, the Co XMCD signal, as already mentioned above, is reduced by about a factor of 2. This is different than for NO coordinated to CoTPP on Ni where the XMCD signal disappears completely at 300 K [17]. Here, the spin of the Co ions can not be zero because the XMCD signal is not vanishing. The reduction of the XMCD is in qualitative agreement with the partial oxidation of the Co ions. Since XMCD probes the local spin polarization at the site of the Co core, the net transfer of non-integer charge away from the Co ion caused by the adsorption of NO could result in a reduction of the XMCD signal, if the low-spin state is maintained, since then the a_{1g} (d_{z^2}) state would be less than half filled. The small change of the XMCD line shape at the high-energy flank of the L_3 peak that is visible after coordination of NO points towards an NO-induced electronic modification of the in-plane orbitals. Alternatively, the reduction in XMCD signal might be also explained by an influence on the strength of the magnetic coupling to the substrate. The coupling strength between the magnetic moments localized on the Co ions and the substrate magnetization might be lower after the formation of the nitrosyl complexes, which would also lead to a lower XMCD signal at finite temperatures.

3.3. Adsorption behaviour of NO

Angle-resolved N K edge XA spectra recorded with p-linearly polarized X rays were measured to gain insight into the adsorption character and geometry of both the CoOEP and the NO molecules. Spectra corresponding to the series of spectra displayed in figure 2, measured at angles of 55° and 90° between the incoming X-ray wavevector and the surface, are presented in figure 4 and figure 5, respectively. The data of the pristine sample, after dosing 28 L of NO, after subsequent warming up to 350 K, and after dosing again 14 L of NO are shown in panels a. For reasons of clarity, the spectra of the last three steps after subtraction of the spectra of the pristine sample are presented in panels b.

The isotropic spectrum of the CoOEP molecules (bottommost curve in figure 3 a) is characterized by two π^* resonances at energies of 399.1 and 402.0 eV and a broad σ^* resonance with a maximum at 406.8 eV, originating from the antibonding orbitals of the π and σ bonds to the adjacent atoms, respectively. At normal incidence (bottommost curve in figure 4 a) the σ^* resonance is more dominant, and features in the π^* region contribute much less. Such an angular dependence matches to a near-out-of-plane orientation of the N π^* orbitals and a pronounced in-plane orientation of the N σ^* orbital. The evaluation of the angular dependence of the intensities at 399.1 eV yields an averaged tilt angle [33] of 30° ± 3° between the N π^* orbitals and
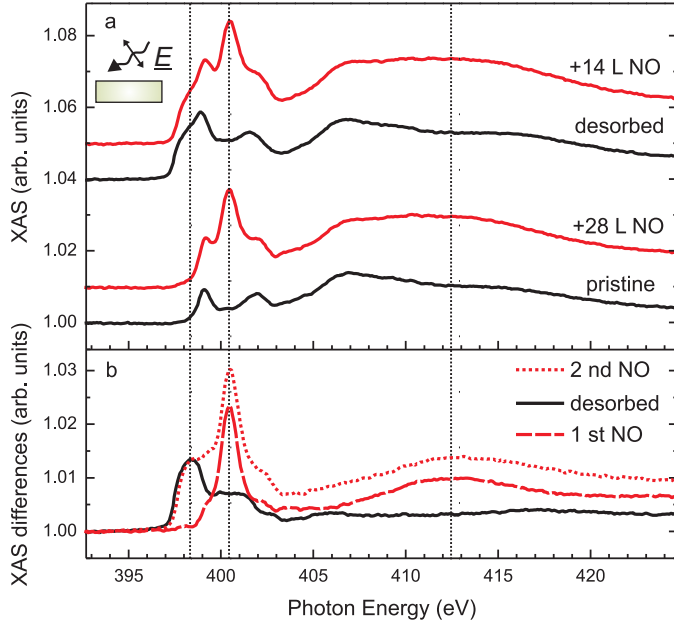
Figure 4. Panel a: N K XA spectra of 0.7 ML CoOEP on O/Ni measured at 130 K with p-linearly polarized light and an angle of 55° between the X-ray wavevector and the surface at each NO dosage step. Spectra are shifted vertically for clarity. Panel b: Difference spectra between the three spectra corresponding to the three dosage steps and the spectrum of the pristine sample in panel (a).

the surface normal. This result may be either interpreted as an average tilt angle of 30° between the surface and the porphyrin macrocycles, as reported for CoOEP on Ag(110) [24], or by a distortion of the macrocycles, which has been observed for Co-tetraphenylporphyrins on Ag(111) [34]. Moreover, a formation of new orbitals by a hybridization of the N π orbitals with electronic states of the substrate may also play a role [10], or a mixture of the above-mentioned explanations may be applicable.

After dosing 28 L of NO, a new π^* resonance at 400.5 eV and a new σ^* resonance with a maximum at 412.4 eV appear. This proves the presence of intact NO molecules on the sample, by comparison to XAS studies of gas phase NO [35]. It is known that NO chemisorbs on oxygen-covered Ni surfaces [36]. It is therefore reasonable to assume that there are NO molecules sitting on top of CoOEP molecules as well as NO molecules located between the porphyrins directly on the oxygen-covered surface, which both contribute to the N K XA spectra. However, just one peak in the π^* region is observed. This points to similar electronic properties of both these types of NO and therefore a chemisorption of the NO on the CoOEP molecules, being consistent with the partial oxidation of the Co^{+2} ions.

After annealing the sample to 350 K, the additional intensity at 400.5 eV disappears, consistent with the desorption of bonded NO molecules, while a new peak at 398.3 eV emerges. We suggest that the latter, as for NO on Fe octaethylporphyrin [16], may be ascribed to a chemisorbed atomic N species that could result from the dissociation of NO. The second dosage of NO leaves this peak unaffected, while the signals around 400.5 eV and 412.4 eV reappear. The detailed surface chemistry of nitric monoxide on transition metal surfaces can be rather complex, depending on
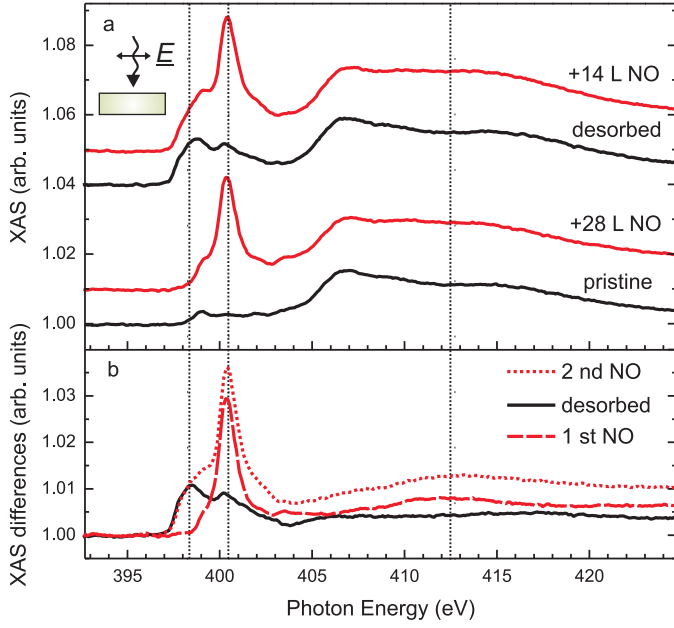
Figure 5. (a) N K X-ray absorption spectra of 0.7 ML CoOEP on O/Ni measured with p-linearly polarized light under normal incidence (angle of 90° between the X-ray wavevector and the surface) at 130 K at each NO dosage step. Spectra are shifted vertically for clarity. (b) Difference spectra between the three spectra corresponding to the three dosage steps and the spectrum of the pristine sample in panel (a).

surface reactivity, temperature or NO dosage, and can be found elsewhere [37, 38].

The additional NO-induced π^* peak at 400.5 eV photon energy is more intense at normal incidence (figure 5 b), while the additional σ^* intensity around 412.3 eV is stronger at more grazing detection angles (figure 4 b). This means that the NO molecules reside in a rather upright average orientation on the surface. The average zenithal angle between the surface normal and the NO bond axis, evaluated from the peak at 400.5 eV, is 24° ± 3°. This indicates a more upright adsorption of the NO molecules on CoOEP, as the observed angle for NO on oxygen-covered films was found to be about 50° with respect to the surface normal [39].

The additional feature at 400.5 eV and the NO-induced spectral changes of the Co $L_{2,3}$ absorption spectra in normal incidence have been used to monitor the amount of attached NO as a function of dosage. Saturation of NO-induced spectral changes of the Co $L_{2,3}$ absorption spectra in normal incidence is observed for dosages larger than 14 L, and no further change occurs for higher dosages. In order to make sure that all CoOEP molecules are coordinated by NO, a higher dosage of 28 L has been used for the first NO adsorption in the study presented here.

4. Conclusions

We have demonstrated that the electronic properties of Co-octaethylporphyrin molecules adsorbed on oxygen-covered Ni films can be reversibly controlled by adsorption and thermal desorption of NO molecules. This chemical stimulus allows to

fine-tune the amount of charge localized on the Co ions, as well as the energetic levels of their a_{1g} and e_g states. Before the uptake of NO, the porphyrin molecules adsorb quasi flat on the surface, and their Co ions have a valency of +2. A ferromagnetic coupling between the Co spins at the center of the porphyrin molecules and the magnetic Ni films is established across the intermediate layer of atomic oxygen. This is the first time that a ferromagnetic coupling between paramagnetic metalloporphyrins and a ferromagnetic substrate across adsorbed oxygen atoms is observed; so far only antiferromagnetic coupling has been reported. Future theoretical studies are desirable to investigate whether the proposed ferromagnetic double exchange could explain the phenomenon. The coordination of NO as an additional axial ligand to the Co ions leads to the formation of NO-CoOEP nitrosyl complexes, in which the original Co^{+2} ions get partially oxidized. The a_{1g} and e_g states of the Co ions are shifted up in energy, and the Co magnetization is about a factor 2 smaller at 30 K. A dosage of 14 L NO is sufficient to saturate these NO-induced modifications. This work clearly exemplifies the feasibility to gain control over the electronic and magnetic properties of Co-octaehylporphyrin molecules by the interaction of the metal center with specially designed axial ligands.

5. Acknowledgments

References

[1] Yella A, Lee H-W, Tsao H N, Yi C, Chandiran A K, Nazeeruddin M K, Diau E W-G, Yeh C-Y, Zakeeruddin S M and Grätzel M 2011 *Science* **334** 629–34
[2] Rakow N A and Suslick K S 2000 *Nature* **406** 710–13
[3] Lu H and Zhang X P 2011 *Chem. Soc. Rev.* **40** 1899–909
[4] Fleming I 1967 *Nature* **216** 151–52
[5] Xiong Z H, Wu D, Vardeny Z V and Shi J 2004 *Nature* **427** 821–24
[6] Isvoranu C, Wang B, Schulte K, Ataman E, Knudsen J, Andersen J N, Bocquet M L and Schnadt J 2010 *J. Phys.: Condens. Matter.* **22** 472002
[7] Flechtner K, Kretschmann A, Steinrück H-P and Gottfried J M 2007 *J. Am. Chem. Soc.* **129** 12110–111
[8] Hieringer W, Flechtner K, Kretschmann A, Seufert K, Auwärter W, Barth J V, Gröling A, Steinrück H-P and Gottfried J M 2011 *J. Am. Chem. Soc.* **133** 6206–222
[9] Scheybal A, Ramsvik T, Bertschinger R, Putero M, Nolting F and Jung T A 2005 *Chem. Phys. Lett.* **411** 214–220
[10] Wende H *et al* 2007 *Nat. Mater.* **6** 516–20
[11] Bernien M *et al* 2007 *Phys. Rev. B.* **76** 214406(6)
[12] Iacovita C, Rastei M V, Heinrich B W, Brumme T, Kortus J, Limot L and Bucher J P 2008 *Phys. Rev. Lett.* **101**, 116602(4)
[13] Annese E, Fujii J, Vobornik I, Panaccione G and Rossi G 2011 *Phys. Rev. B.* **84** 174443(7)
[14] Bernien M *et al* 2009 *Phys. Rev. Lett.* **102**, 047202(4)
[15] Chylarecka D, Wäckerlin C, Kim T K, Müller K, Nolting F, Kleibert A, Ballav N and Jung T A 2010 *J. Phys. Chem. Lett.* **1** 1408–13
[16] Miguel J, Hermanns C F, Bernien M, Krüger A and Kuch W 2011 *J. Phys. Chem. Lett.* **2** 1455–1459
[17] Wäckerlin C, Chylarecka D, Kleibert A, Müller K, Iacovita C, Nolting F, Jung T A and Ballav N *Nat. Commun.* **1** 61
[18] Sorg C, Ponpandian N, Bernien M, Baberschke K, Wende H and Wu R Q 2006, *Phys. Rev. B* **73** 064409(7)
[19] Nünthel R *et al* 2003 *Surf. Sci.* **531** 53–67
[20] Sodhi R N S and Brion C E 1984 *J. Electron Spectrosc. Rel. Phenom.* **34** 363–72
[21] Kroll T, Aristov V Yu, Molodtsova O V, Ossipyan Yu A, Vyalikh D V, Büchner B and Knupfer M 2009 *J. Phys. Chem. A* **113** 8917–22
[22] Stepanow S, Mieddema P S, Mugarza A, Ceballos G, Moras P, Cezar J C, Carbone C, de Groot F M F and Gambardella P 2011 *Phys. Rev. B.* **83** 220401(R)
[23] Cook P L, Liu X, Yang W and Himpsel F J 2009 *J. Chem. Phys.* **131** 194701
[24] Fanetti M *et al* 2011 *J. Phys. Chem. C* **115** 11560–568
[25] Bernien M 2010, *X-Ray absorption spectroscopy of Fe complexes on surfaces*, PhD thesis, Freie Universität Berlin (http://www.diss.fu-berlin.de/diss/receive/FUDISS_thesis_000000019678)
[26] Bai Y, Buchner F, Kellner I, Schmid M, Vollnhals F, Steinrück H-P, Marbach H and Gottfried J M 2009 *New. J. Phys.* **11** 125004–644
[27] Stöhr J and König H 1995 *Phys. Rev. Lett.* **75** 3748–51
[28] de Groot F M F 2005 *Coord. Chem. Rev.* **249** 31–63
[29] Bethe H 1929 *Ann. Phys.* **395** 133–208
[30] Wayland B B, Minkiewicz J V and Abd-Elmageed M E 1974 *J. Am. Chem. Soc.* **96** 2795–2801
[31] Kozuka M and Nakamoto K 1981 *J. Am. Chem. Soc.* **103** 2162–2168
[32] van Veenendaal M 2008 *Phys. Rev. B.* **78** 165415(9)
[33] Stöhr J and Outka D A 1987 *Phys. Rev. B.* **36** 7891–905
[34] Auwärter W *et al* 2010 *Phys. Rev. B.* **81** 245403(14)
[35] Saito N and Suzuki I H 1991 *Phys. Rev. A* **43** 3662 –7
[36] Odörfer G, Jaeger R, Illing G, Kuhlenbeck H and Freund H-J 1990 *Surf. Sci.* **233** 44 –58
[37] Saito T, Imamura M, Matsubayashi N, Furuya K, Kikuchi T and Shimada H 2001 *J. Electron Spectrosc.* **119** 95–105
[38] Brown W A and King D A 2000 *J. Phys. Chem. B* **104** 2578–95
[39] Kuhlenbeck H *et al* 1991 *Phys. Rev. B.* **43** 1969–87