Magnetic Interactions of Vanadyl Phthalocyanine with Ferromagnetic Iron, Cobalt, and Nickel Surfaces

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S *Supporting Information*

ABSTRACT: We have investigated the molecular orientation and magnetic properties of vanadyl phthalocyanine (VOPc) deposited on ferromagnetic Fe, Co, and Ni films, which were epitaxially grown on Cu(001) using X-ray absorption spectroscopy and X-ray magnetic circular dichroism. The results reveal that the VOPc framework lies flat on the surfaces with oxygen-up configurations. The spin of the central V atoms in VOPc is antiferromagnetically coupled with those of Fe or Co atoms in the ferromagnetic surface. In contrast, the magnetic coupling between V and Ni is not effective, exhibiting simple paramagnetism of VOPc.
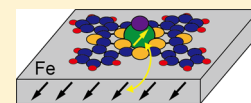
1. INTRODUCTION

Magnetic interactions of the central metal ions in metal phthalocyanines (MPcs) and metal porphyrins (MPs) with ferromagnetic surfaces have attracted significant attention from the viewpoint of scientific interests at the interfaces and also for technological applications, such as chemical switches[1,2] and giant magnetoresistance.[3] The ferromagnetic coupling between the central Mn ion in Mn porphyrin and the ferromagnetic Co film at the interface has been shown specifically using X-ray magnetic circular dichroism (XMCD) by Scheybal and co-workers.[4] The study revealed that the coupling is effective at the interface between the adsorbed molecule and ferromagnetic film. Similar ferromagnetic couplings have been reported in several systems, including Fe porphyrin on Co and Ni,[5,6] MnPc on Co(001),[7] Co porphyrin on Ni,[1] and Cu porphyrin on $Fe_3O_4(100)$.[8] On the other hand, Ni porphyrin deposited directly on Co does not show any magnetic coupling due to the absence of the net spin in the central Ni ion.[9] Based on theoretical calculations, Wende et al. ascribed the mechanism of ferromagnetic coupling to the superexchange interaction between the central ion and ferromagnetic surfaces via nitrogen in the ligand.[5] Furthermore, Chylarecka et al. experimentally substantiated the mechanism of the superexchange coupling using rough and smooth Co surfaces in combination with the theoretical calculation.[10]

Antiferromagnetic coupling of the central metal ions with the ferromagnetic surfaces has been realized in Fe porphyrin[11,12] and Mn porphyrin[13] deposited on oxygen-covered ferromagnetic films. In these systems, the central metal ions are coupled antiferromagnetically to the ferromagnetic surfaces, which is similar to the superexchange interaction via oxygen atoms in the antiferromagnetic metal oxides. Another kind of antiferromagnetic coupling was observed in $TbPc_2$ adsorbed on the ferromagnetic Ni substrate.[14] In this system, the Tb spin is coupled antiferromagnetically with that of the Ni surface atom via the phthalocyanine ligand. Furthermore, exchange bias was

demonstrated in $TbPc_2$ deposited on the antiferromagnetic Mn film.[15]

The magnetic interaction of the 3d-transition metal series in the MPcs and MPs adsorbed on bare (oxygen-covered) ferromagnetic surfaces has always been ferromagnetic (antiferromagnetic). However, the experimental observations of these magnetic interactions are limited in the cases of MPcs and MPs (M = Mn, Fe, Co, Cu). For early transition elements, such as V and Cr, the magnetic interactions with the ferromagnetic surfaces have been veiled. Therefore, in the present study, to reveal the underlying magnetic interactions, we have considered vanadyl phthalocyanine (VOPc) that has a spin ($S = 1/2$) in the central V ion.[16,17]

In this study, we have investigated the molecular orientation and magnetic properties of VOPc deposited on ferromagnetic Fe, Co, and Ni surfaces using element specific X-ray absorption spectroscopy (XAS) and XMCD measurements. VOPc is found to lie flat on the ferromagnetic surfaces with an oxygen-up configuration. The results indicate effective antiferromagnetic coupling of the central V ions with the ferromagnetic Fe and Co surfaces. On the contrary, VOPc deposited on the Ni surface exhibits almost no effective magnetic interaction at the measurement temperature of 5 K.

2. EXPERIMENTAL SECTION

The sample preparation was performed under ultrahigh vacuum conditions ($P \approx 4 \times 10^{-8}$ Pa). A Cu(001) substrate was cleaned by repeating a cycle of Ar ion sputtering and annealing at 800 K. Low-energy electron diffraction (LEED) of the Cu substrate exhibited a sharp (1×1) pattern which is shown in the Supporting Information. The amount of carbon contamination, estimated using Auger electron spectroscopy, was found to be less than 2% (see the Supporting Information). Subsequently, a

ferromagnetic Fe film was prepared on the Cu(001) by electron bombardment evaporation. During this process, the substrate was maintained at a relatively low temperature ($T \approx 110$ K) to avoid the formation of an Fe−Cu alloy. The Fe film was epitaxially grown on the substrate for up to 3 ML (monolayer) thickness, as confirmed from the reflection high-energy electron diffraction oscillations (see Supporting Information). Co and Ni films were also prepared using the above-mentioned procedure, but the substrate temperature was kept at room temperature during the evaporation. The thickness of the Co and Ni films thus obtained was estimated to be 3 and 4 ML, respectively.

Subsequently, sublimation-purified VOPc was deposited on the ferromagnetic films at room temperature using a home-made Knudsen cell evaporator fitted with an alumel−chromel (K-type) thermocouple. The deposition rate of VOPc was controlled at ~0.1 ML/min by adjusting the cell temperature to 530 K. LEED images of the samples were taken and LEED spots originating from VOPc were observed for VOPc on Co and Ni, while those of VOPc on Fe were unclear (see the Supporting Information). Details of the sample preparation procedure have been reported in the literature[16] and is also given in the Supporting Information.

The in situ XAS and XMCD measurements were performed using an XMCD system ($P < 1 \times 10^{-8}$ Pa, $\mu_0 H = 7$ T, $T = 3.8$ K) at the end station of the bending magnet Beamline 4B of UVSOR−III of Institute for Molecular Science (IMS), Okazaki, Japan. Details of the XMCD measurement system have been reported elsewhere.[18,19] Angle-dependent N K-edge XAS measurements were performed using linearly polarized X-rays, incident at an angle θ of 0°, 30°, and 55° with respect to the surface normal. The samples were rotated around the [110] axis, ensuring that the X-ray electric field vector was always in the (110) plane. Furthermore, circularly polarized XAS and XMCD spectra were obtained by the total electron yield detection mode in a magnetic field of 0 or ±5 T, at the temperature of 5 K and X-ray incidence angles of 0° and 55°. The circular polarization degree of the X-rays was estimated to be ~0.6 from the beamline parameters. The magnetic field was applied to the sample in parallel or antiparallel geometries with respect to the X-ray beam. The X-ray energy was calibrated using L-edge XAS of metallic V, Fe, Co, and Ni films. The nominal energy resolution (ΔE) was estimated to be 0.8 eV at the V L edge and 1.0 eV at the Fe, Co, and Ni L edges. The reproducibility of XAS and XMCD spectra was confirmed by their repeated measurements.

3. RESULTS AND DISCUSSION

Figure 1 shows the angle-dependent N K-edge XAS of VOPc. All the samples exhibit peaks A, B, and C attributed mainly to the transition from N 1s to π^* molecular orbitals.[20,21] On the other hand, peak S is detected only in the XAS of VOPc deposited on the Fe surface. The intensity of the π^* peaks increases gradually with the tilting of the X-ray electric field vector from the surfaces. This indicates that the phthalocyanine framework in the samples lies almost flat with respect to the surfaces. Satellite peaks such as peak S in VOPc on Fe have been observed in the system of adsorbed molecules on interactive surfaces[7,22,23] and peak S resembles the spectrum of MnPc on Co(001).[7] In the MnPc/Co system, the satellite peak has been ascribed to the transition from the N 1s orbital to the σ^* orbital of Mn−N by the theoretical calculation.[7] This peak appears at almost the same energy of the lowest π^* peak
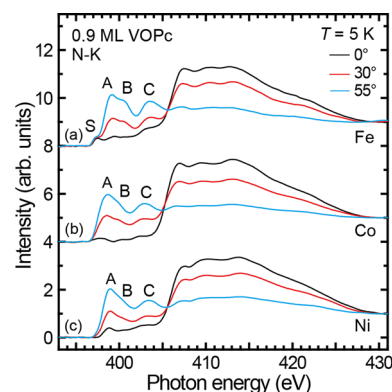

Figure 1. Angle-dependent linearly polarized N K-edge XAS of 0.9 ML VOPc on (a) 3 ML Fe, (b) 3 ML Co, and (c) 4 ML Ni films grown epitaxially on Cu(001). The measurement temperature was 5 K. The energy resolution (ΔE) was 0.3 eV at the photon energy of 400 eV.

in MnPc physisorbed on Cu(001) and is further shifted to a lower energy side in MnPc chemisorbed on Co(001) due to charge transfer from Co to ligand N.[7] On the other hand, in the cases of FePc[22] and ZnPc[23] on TiO_2(110), such satellite peaks appear at a higher photon energy side of the main π^* peaks due to charge transfer from the molecules to the substrates. In the present study, peak S can thus be attributed at least partially to the transition to the σ^* orbital of V−N, which is shifted toward a lower energy side than peak A due to chemical interaction, probably a charge transfer effect, between the N atoms in VOPc and Fe surface. Polarization dependence of peak S is however found to be quite weak in Figure 1, indicating some complicated nature of the origin of peak S. We can suppose that the peak originates from the V−N σ^* resonance and also some π^* transition.

The XAS results indicate that VOPc adsorbs with an oxygen-up configuration. This is confirmed by the V L- and O K-edge XAS of VOPc on Fe because the spectral shape and the peak position in the XAS of VOPc on Fe (Figure 2a) is similar to that of VOPc on Ag, where the oxygen atom is known to be directed upward.[16] In the cases of the Co and Ni surfaces, the spectral shape and the peak position in the XAS of VOPc (see Figures 3a and 4a) are almost similar to those of VOPc on Fe,
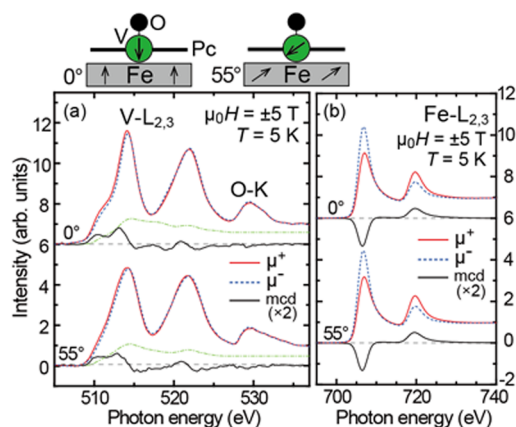
Figure 2. (a) V L-, O K-, and (b) Fe L-edge XAS and the XMCD spectra of 0.9 ML VOPc on 3 ML Fe/Cu(001) at a temperature of 5 K, magnetic field of ±5 T, and X-ray incidence angles of 0° (normal incidence) and 55° (grazing incidence). The green dashed line represents the integral of $\mu^+ - \mu^-$ from 507 to 527 eV.
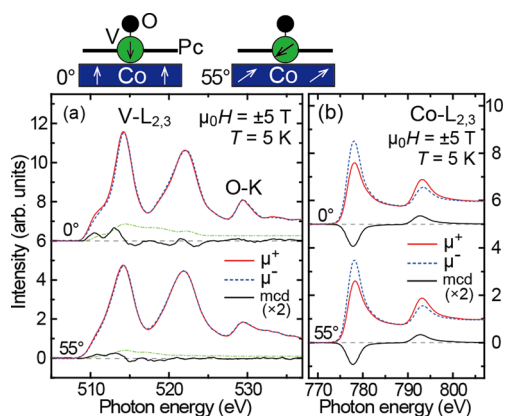
Figure 3. (a) V L-, O K-, and (b) Co L-edge XAS and the XMCD spectra of 0.9 ML VOPc on 3 ML Co/Cu(001) at a temperature of 5 K, magnetic field of ±5 T, and X-ray incidence angles of 0° and 55°. The green dashed line represents the integral of $\mu^+ - \mu^-$ from 507 to 527 eV.
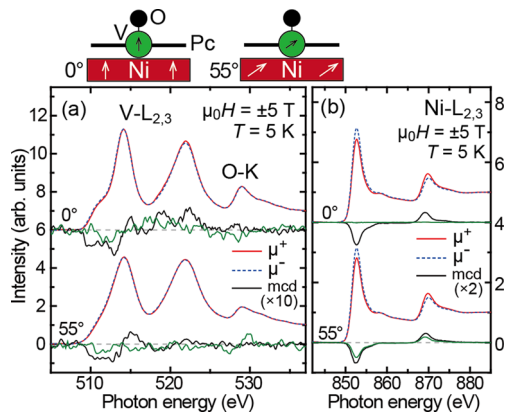
Figure 4. (a) V L-, O K-, and (b) Ni L-edge XAS and the XMCD spectra of 0.9 ML VOPc on 4 ML Ni/Cu(001) at a temperature of 5 K, magnetic field of ±5 T, and X-ray incidence angles of 0° and 55°. The XMCD spectra taken at remanent magnetization are depicted as green solid lines.

despite the absence of satellite peak S in N K-edge XAS. Comparing the N K-edge XAS of VOPc on Co with that of VOPc on Ni, we notice that the spectrum in the π* region on Co is broader than that on Ni and the π* peak on Co starts at the lower energy side than that on Ni, implying stronger interaction of VOPc with Co than that of VOPc with Ni.

The possibility of bilayer stacking structures of VOPc cannot be excluded completely from the XAS and other results. However, it is understood from the LEED images (see the Supporting Information) that deposited VOPc prefers to form monolayer structures rather than bilayer stacking structures. In the LEED images of VOPc on Co and Ni, diffused LEED spots originating from VOPc were clearly observed, which indicates the formation of relatively densely packed self-assembled states. In the case of VOPc on Fe, LEED spots were dim in comparison to the other samples due to stronger interaction of VOPc with Fe. Therefore, we conclude that most VOPc deposited on Fe, Co, and Ni favors the formation of monolayer, although small amounts of VOPc possibly form bilayer. However, the present conclusions concerning electronic and magnetic interaction of VOPc with the ferromagnetic films

would not be affected even if a small amount of bilayer stacking VOPc is formed.

Furthermore, we performed element specific XMCD measurements to gain deeper insights on the magnetic properties of VOPc deposited on the ferromagnetic surfaces. The XMCD spectra of VOPc on Fe are shown in Figure 2. Although the strong interaction of ligand N with the Fe film and satellite peak S was observed in N K-edge XAS, no significant change in Fe L-edge XAS/XMCD was detected between clean Fe and VOPc/Fe (see the Supporting Information). The V L-edge XMCD signals are clearly observed in both the 0° and 55° configurations, implying that the V spin is preserved at the interface without losing the spin against to the case of CoPc on the Fe film in which the spin of CoPc vanishes at the CoPc/Fe interface.[24] The Fe film is magnetized along the magnetic field, and the magnetization is saturated at 5 T in both the 0° and 55° configurations (magnetization curves of the ferromagnetic films are shown in the Supporting Information). In contrast to the Fe film, the V ions in the system are magnetized in the direction opposite to the magnetic field. This implies that the V spins are coupled antiferromagnetically with those of the Fe film. XAS and XMCD spectra of VOPc on Fe measured at remanence are given in the Supporting Information. The same result was observed in the VOPc/Co system, as shown in Figure 3 (XAS and XMCD spectra of VOPc on Co measured at remanence are also shown in the Supporting Information). The L_3 peak in the XMCD spectrum of Co shows a negative sign, while the L_3 peak of V exhibits a positive sign. These results are clearly different from the previous cases of MPcs and MPs (M = Mn, Fe, Co). In the cases of MPs, such as MnTPP (TPP = tetraphenylporphyrin)[10] and FeOEP (OEP = octaethylporphyrin),[5] on the ferromagnetic surfaces, the magnetic interaction between the central metal ions and ferromagnetic films was found to be ferromagnetic. The origin of the ferromagnetic interaction in these systems can be explained on the basis of the superexchange interaction via N atoms bonded to the central metal ion, given the fact that the distance between the metal ion and the surface is too large to show direct exchange interaction and that the theoretical calculations have predicted the chemical interactions of ligand N with the surfaces, although the possibility of direct exchange interaction cannot be completely eliminated for FeOEP.[6] On the other hand, in the MPcs systems, such as MnPc[7] and CoPc,[25] on Co, direct exchange couplings are probable because of the shorter distance between the metal ion and the surface, as compared to those in the above-mentioned MPs. In the present study, XMCD measurements indicate antiferromagnetic coupling of V with the Fe and Co surfaces. The coupling mechanism can be explained on the basis of the superexchange interaction via N atoms.[26,27] However, we cannot completely exclude the possibility of direct exchange interaction between the central V ions and the ferromagnetic Fe and Co surfaces.

Figure 4 shows the XMCD spectrum of VOPc on Ni surface. In contrast to that observed in the cases of Fe and Co, the central V ion in VOPc on Ni is magnetized at 5 T in the direction similar to that of the magnetic field and the Ni film. To identify the magnetic interaction, the XMCD spectra were also recorded at the remanent magnetization ($\mu_0 H = 0$ T). The corresponding results are indicated as green solid lines in Figure 4. The Ni L-edge XMCD was not observed at normal X-ray incidence, while the signal was observed at the grazing X-ray incidence, implying in-plane residual magnetization of the Ni

film. On the contrary, the V L-edge XMCD signals at 0 T was not observed clearly in either the 0° or 55° configurations. Besides, the shape of the XMCD spectrum at 0 T was obviously different from that at 5 T. These results suggest that the V L-edge XMCD signals at 5 T mainly originate from the simple Zeeman effect in the molecule itself, and not from the ferromagnetic interaction with the Ni film. In addition, the weak antiferromagnetic interaction of V with Ni film is expected due to the small V L-edge XMCD signal.

In order to compare the XMCD intensity, we calculated the integrated values of the V L-edge XMCD intensity for the three samples analyzed in this study, as summarized in Table 1. Here,

Table 1. Integrated V $L_{2,3}$-edge XMCD Intensities in 0.9 ML VOPc on the Fe, Co, and Ni Films[a]

incidence angle	VOPc/Fe	VOPc/Co	VOPc/Ni
0°	1.00	0.61	−0.38
55°	0.35	0.31	−0.23

[a]The values are normalized to that of VOPc/Fe at the 0° configuration. The sign corresponds to the direction of magnetization; a positive (negative) sign indicates that the direction of magnetization of the central V ion is antiparallel (parallel) with respect to magnetic field and magnetization of the ferromagnetic film.

the magnetizations of the ferromagnetic films were nearly saturated at 5 T in both the 0° and 55° configurations, which were confirmed from the XMCD intensities of Fe, Co, and Ni L_3-edges. In all the samples, the XMCD intensity of VOPc at 0° is found to be larger than that at the 55° configuration. The molecular magnetic anisotropy originates from the spin−orbit interaction of the 3d-electron in the $3d_{xy}$ orbital of the V ion. The integrated values of the V L-edge XMCD intensity show the reduction trend from Fe to Co and Ni, and the sign of the L_3 peak in the XMCD spectrum of VOPc/Ni is reversed when compared to the other two samples. These imply that the antiferromagnetic interaction of the central V ion with the ferromagnetic surfaces weakens in the order of Fe, Co, and Ni films. This tendency is consistent with the cases of FeOEP on Co and Ni,[6] which is related to the strength of the exchange interaction of the central V ions with the ferromagnetic surfaces. In addition, it is found that the order of the strength of the magnetic interaction of VOPc with the films is in accord with that of the electronic interaction between ligand N and the ferromagnetic surfaces. It is thus expected that the origin of the magnetic interaction is not only direct exchange interaction but also superexchange interaction via N in the systems of VOPc on the ferromagnetic films.

Finally, we will comment on the direction of the spin and orbital magnetic moments. In the half electron system such as V, total magnetic momentum J is usually as $J = L − S$ on the basis of Hund's third rule and this has been confirmed in many systems as not only atoms but also molecules, metal complexes, and bulk materials. In the present study, we cannot quantitatively evaluate the spin and orbital magnetic moments from the V L-edge XMCD due to the overlap between the V L_3 and L_2 edges and small intensity of the XMCD signal. However, the sign of these magnetic moments can be estimated by using sum rules related to the XMCD.[28,29] The sign of the spin and orbital magnetic moments in the VOPc/Fe and VOPc/Co systems are same, implying these systems show the coupling of $J = L + S$. Similar results obtained by XMCD have been also reported for VO complexes.[30] One interpretation that the

unusual LS coupling is attributed to the ligand field effect surrounding the V atom has been suggested by using a model of VAu_4 in the theoretical calculations.[31]

4. SUMMARY

We have investigated the magnetic properties of VOPc deposited on the ferromagnetic Fe, Co, and Ni surfaces using element specific XMCD measurements to demonstrate the magnetic coupling of V (with less than half 3d electron system) ions with the ferromagnetic atoms in the Fe, Co and Ni surfaces. In contrast to the previously reported cases of ferromagnetic interactions in MPcs and MPs (M = Mn, Fe, Co) deposited on oxygen-uncovered (bare) ferromagnetic surfaces, antiferromagnetic coupling was found to be dominant in VOPc/Fe and VOPc/Co systems. On the other hand, the magnetic interaction of V ions with the Ni surface was rather ineffective, with the Zeeman effect being dominant at the temperature of 5 K. Thus, the strength of magnetic interaction of VOPc with the ferromagnetic films was reduced in the order of Fe, Co, and Ni films. This trend was in the same order with the strength of the interaction of V with ferromagnetic surfaces as observed peak S in N K-edge XAS. It is suggested that the superexchange interaction via N coexists with the direct exchange interaction in a short distance between the central V and the ferromagnetic surfaces.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Sample preparation, LEED images, and other XAS/XMCD spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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