Revelation of the crucial interactions in spin-hybrid systems by means of X-ray absorption spectroscopy

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ABSTRACT

Spin-hybrid systems consisting of magnetic molecules on surfaces are studied by means of X-ray absorption spectroscopy. The relevant magnetic interactions of paramagnetic molecules on ferromagnetic surfaces are analyzed utilizing the element specificity of the X-ray magnetic circular dichroism revealing the magnetic coupling for these systems. By the help of X-ray natural dichroism the orientation of the molecules on the surfaces and the electronic structure is probed. The structural properties are correlated with the magnetic characteristics to achieve a more complete understanding of the spin-hybrid systems. The possibility to tailor the magnetic coupling for these systems is demonstrated by modifying the interface of the molecules and the substrate by using an intermediate layer of atomic oxygen. As an outlook it will be discussed how a spin crossover behavior of the molecules might be achieved in specific spin-hybrid systems by employing graphene.

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1. Introduction

The creation of spin-hybrid systems by the combination of organic molecules with magnetic layers bears a great potential for new molecular spintronic devices [1,2]. Since the interface properties are crucial for the injection of spins into organic molecules, the term "spinterface science" was formed [3]. On the one hand single molecular magnets (SMMs) are discussed as possible building blocks for molecular spintronic devices [4]. However, because of the smallness of the magnetic coupling energies and the magnetic anisotropy constants, these systems exhibit their fascinating magnetic properties like quantum tunneling at very low temperatures (often below 4 K). Furthermore, the interaction of SMMs with surfaces often disturbs the molecules leading to a further decrease of the relevant (blocking) temperatures [5]. As an example, the opening of a hysteresis loop of Fe_4 complexes in direct contact with a gold surface was identified at 0.5 K [6]. However, the interaction with surfaces can also be used as an advantage: It has been shown that paramagnetic molecules as e.g. Mn-porphyrin molecules and Fe-porphyrin molecules can be ordered magnetically by adsorption on ferromagnetic surfaces [7–9]. The magnetic interaction is so strong that a magnetic hysteresis loop can even be identified at room temperature [7–9]. As discussed below a coupling strength of

about 70 meV was determined for Fe-porphyrin molecules to a Co substrate by means of temperature-dependent measurements [9]. Recent investigations indicate that the molecules are chemisorbed on the ferromagnetic substrates. This coupling can actually be tailored from a ferromagnetic coupling to an antiferromagnetic one by the help of an intermediate layer of atomic oxygen [10]. These magnetic coupling phenomena could also be relevant when studying the spin injection and transport in a ferromagnet/organic semiconductor heterojunction [11]. Because of the high sensitivity and the element specificity several of the investigations of the magnetic molecules on surfaces have been performed by utilizing X-ray absorption spectroscopy (XAS) and especially the X-ray magnetic circular dichroism (XMCD). As an example the XMCD spectroscopy was used recently to study paramagnetic molecules on surfaces [7–10,12], single molecular magnets [6,13–15] and molecular networks [16,17].

In this article it will be presented in which way the XAS, XMCD and X-ray natural linear dichroism (XNLD) spectroscopies can be utilized to reveal the relevant interactions for Fe-porphyrin systems on ferromagnetic surfaces. The element specificity of the spectroscopies allows for the separate study of the magnetism of the substrate and the molecules. Thereby, the crucial magnetic coupling strength and coupling range can be analyzed which determines the ferromagnetic or antiferromagnetic alignment of the magnetic moments of the molecules and the substrates. This article will be structured as follows: At first, the fundamental aspects and limitations of the X-ray absorption spectroscopies will

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be presented. The utilization of these techniques will be exemplified for the investigation of the spin-hybrid systems. Finally, an outlook and conclusions will be given addressing the possibility to modify the spin state of magnetic molecules.

2. Fundamental aspects

The crucial property to describe the attenuation of electromagnetic radiation is the attenuation coefficient $\tilde{\mu}(E)$ which depends on the photon energy $E = h\nu$. The absorption coefficient is given by Lambert-Beer's law

$$I(x) = I_o e^{-\tilde{\mu}(E)x} \tag{1}$$

Here, I_o is the intensity of electromagnetic radiation hitting the sample. For a sample with the thickness x, the intensity after transmission through the sample is $I(x)$. The strength of the attenuation of the radiation is described by $\tilde{\mu}(E)$. In the X-ray regime the photoelectric absorption, Raleigh scattering and Compton scattering contribute to absorption coefficient. However, in the soft X-ray regime discussed here, $\tilde{\mu}(E)$ is dominated by the photoelectric absorption coefficient $\mu(E)$. The characteristic features of this photoelectric absorption coefficient $\mu(E)$ are the X-ray absorption edges. If the photon energy is large enough to excite an electron of a core state to the continuum, a steep rise of the absorption coefficient $\mu(E)$ can be detected resulting in an edge-like spectroscopic feature, i.e. the X-ray absorption edges. The nomenclature for these absorption edges is as follows: edges origination from core electrons in the $1s_{1/2}, 2s_{1/2}, 2p_{1/2}, 2p_{3/2}, \ldots$ states are labeled as $K, L_1, L_2, L_3, \ldots$ edges. Since the electron binding energies are characteristic for the respective elements, the energetic position of the absorption edges in the X-ray absorption spectrum can be assigned to the different elements in the sample. This element specificity turns out to be one strength of the X-ray absorption spectroscopy (XAS) since the complex interaction of the elements e.g. in hybrid systems can be disentangled by this spectroscopy. A detailed description of the different theoretical models to calculate the X-ray absorption coefficient goes beyond the scope of this article. Extensive reviews can be found e.g. in Refs. [18,19]. As discussed for instance by Ebert [18], an extension of the non-relativistic spin-density-functional formalism in the form presented by MacDonald and Vosko [20] and by Ramana and Rajagopal [21] can be applied to described the crucial relativistic effects. The Dirac Hamiltonian has the form [18]:

$$H_D = \frac{c}{i}\boldsymbol{\alpha} \cdot \nabla + \frac{c^2}{2}(\beta - \boldsymbol{I}) + V_H(\boldsymbol{r}) + \bar{V}_{xc}(\boldsymbol{r}) + V_{spin}(\boldsymbol{r})$$

In this equation α_i and β are the usual Dirac matrices. Furthermore, $V_H(\boldsymbol{r})$ is the Hartree potential and the exchange correlation potential is described by a spin-averaged part $\bar{V}_{xc}(\boldsymbol{r})$ and a spin-dependent part $V_{spin}(\boldsymbol{r})$ with:

$$V_{spin}(\boldsymbol{r}) = \beta\boldsymbol{\sigma} \cdot \frac{\partial E_{xc}}{\partial \boldsymbol{m}}(\boldsymbol{r}) = \beta\boldsymbol{\sigma} \cdot \boldsymbol{B}(\boldsymbol{r})$$

Here, $\boldsymbol{m}$ is the spin magnetization density and $\boldsymbol{B}(\boldsymbol{r})$ is the (effective) magnetic field. The Dirac Hamiltonian given above defines the states, which are important for the calculation of the photoelectric absorption coefficient $\mu(h\nu)$. The energy dependence of $\mu(h\nu)$ in the vicinity of a specific absorption edge can be described by Fermi's golden rule in an one-electron approximation:

$$\mu(h\nu)\alpha \sum_{i\,occ} \sum_{f\,unocc} |\langle\psi_f|\boldsymbol{p} \cdot \boldsymbol{A}(\boldsymbol{r})|\psi_i\rangle|^2 \rho(E_f)\delta(E_f - E_i - h\nu) \tag{2}$$

Here, $|\psi_i\rangle$ and $|\psi_f\rangle$ are the initial core states and the unoccupied final states of the electron, respectively. Since a single absorption edge is analyzed here, only the sum of the occupied final states $|\psi_i\rangle$

for this specific core shell (i.e. the relevant jm_j levels) enters in Eq. (2). Furthermore, $\boldsymbol{p} \cdot \boldsymbol{A}(\boldsymbol{r})$ is the interaction operator which describes the interaction of the electrons (momentum operator $\boldsymbol{p}$) with the electromagnetic field (vector potential $\boldsymbol{A}(\boldsymbol{r})$). The absorption coefficient is connected to the angular momentum projected density of unoccupied states (LDOS) which enters Eq. (2) by the density of the final states $\rho(E_f)$. The vector potential $\boldsymbol{A}(\boldsymbol{r})$ can be described by a classical wave with polarization $\boldsymbol{\epsilon}$:

$$\boldsymbol{A}(\boldsymbol{r}) \cong \boldsymbol{\epsilon} \cdot A_0 \cdot e^{i\boldsymbol{kr}} \tag{3}$$

In this article we will investigate the polarization dependence of the X-ray absorption spectra. Therefore, it is helpful to describe the polarization ϵ by right and left circularly polarized components $\epsilon_{R,L}$:

$$\boldsymbol{\epsilon} = a \cdot \boldsymbol{\epsilon}_R + b \cdot \boldsymbol{\epsilon}_L \tag{4}$$

with:

$$\boldsymbol{\epsilon}_R = \frac{1}{\sqrt{2}}(\boldsymbol{\epsilon}_x + i \cdot \boldsymbol{\epsilon}_y),$$

$$\boldsymbol{\epsilon}_L = \frac{1}{\sqrt{2}}(\boldsymbol{\epsilon}_x - i \cdot \boldsymbol{\epsilon}_y),$$

At modern synchrotron radiation facilities the use of helical undulators allows for the full control of the polarization of the X-rays. By shifting the magnetic rows relative to each other, right and left circularly polarized light as well as linearly horizontal and linearly vertical polarization can be achieved [22,23]. For the description of the degree of circular and linear polarization P_C and P_L the ratio r of the constants a and b in Eq. (5) is used:

$$r = \frac{|b|}{|a|}$$

With this ratio r the degree of circular and linear polarization is given by:

$$P_C = \frac{1 - r^2}{1 + r^2} \tag{5}$$

and

$$P_L = \frac{(1 + r)^2}{2(1 + r^2)} \tag{6}$$

This means that linear polarization is given by $P_L = 1$ and $P_C = 0$. Right (+) and left (−) circularly polarized X-ray are described by $P_C = \pm 1$ and $P_L = 0.5$.

A focus of this article is the analysis of the absorption of soft X-rays ($h\nu \approx 100$ eV–5 keV). In this regime the spatial dependence of the electromagnetic wave with respect to the charge distribution can usually be neglected and therefore the excitations can be described by electric dipole transitions (E1) by approximating in Eq. (3):

$$e^{i\boldsymbol{kr}} \cong 1 \tag{7}$$

The dipole selection rules for the one particle states $|\psi_i\rangle$ and $|\psi_f\rangle$ according to Eq. (2) are:

$$\Delta j = 0, \pm 1; \quad \Delta s = 0; \quad \Delta l = \pm 1; \quad \Delta m_j = \begin{cases} +1 & \text{left circular} \\ 0 & \text{linear} \\ -1 & \text{right circular} \end{cases}$$

Hence, at K-edges $s \to p$ transitions are probed whereas at the $L_{2,3}$-edge $p \to d$ and $p \to s$ transitions are possible. However, usually the spectral shape of the $L_{2,3}$-edge spectra of 3d transition metals studied here are dominated by the $2p \to 3d$ transitions. Therefore, the magnetism of 3d elements in hybrid systems can be probed by inspecting the transitions to the empty 3d states at the $L_{2,3}$ edges.