


Experiment title:

Molecular spin transitions studied with X-ray emission spectroscopy

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Report:

The spin state of the so-called spin-transition molecules, which are compounds of transition metal ions having octahedral environment and electronic configuration between d^4 and d^7 , can be switched with external perturbations, such as temperature, pressure or light.[1,2] In a previous experiment, HE-1720, we studied thermally induced low spin (LS) to high spin (HS) transitions in molecular compounds with resonant and off-resonant X-ray emission spectroscopy (RXES and XES) spectroscopies. We demonstrated that spin transitions can be monitored via following the spectral evolution of a selected XES or partial fluorescence yield (PFY) XANES feature, and we provided reference spectra for some $3d^5...3d^7$ spin-transition molecules.[6]

We had two objectives for the present study. First, we wanted to exploit the element selectivity of X-ray spectroscopies to investigate the changes at the different (metal ion) sites of multinuclear spin-transition compounds. For this, our first candidate was a prussian-blue analogue material, $\text{Rb}^{\text{I}}\text{Mn}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, whose description at the spin transition was conflicting in different papers. In this compound Fe and Mn ions, linked by a CN group, alternate along the three axial directions of a cubic lattice. This material undergoes a magnetic transition with a huge hysteresis between 230K and 300K. First the magnetization measurements were interpreted as an evidence for an unusual $S = 3/2 \rightarrow S = 5/2$ spin transition of the Mn^{II} [3], but later structural work showed variations also at the Fe site, and suggested a $\text{Fe} \rightarrow \text{Mn}$ intermetallic electron transfer [4]. We studied both the Mn and Fe sites with XES and PFY XANES spectroscopy below and above the transition. While the $\text{K}\beta$ spectra of the iron showed that the ion remains low-spin, those of the manganese showed an increase of the intensity of low energy satellite to the main spectral line, which reflects an increase of the spin on Mn with temperature (see Fig. 1). The PFY XANES spectra (taken on the maximum of the $\text{K}\beta$ line) of Mn shows an edge-shift with elevating the temperature (Fig. 2), this indicates an increase of the valance. There is no large shift for the Fe edge (Fig. 3a), but this cannot exclude a valance change here, as in potassium ferro-

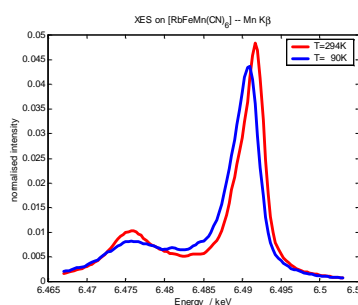


Figure 1

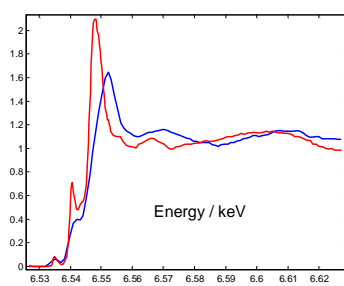


Figure 2

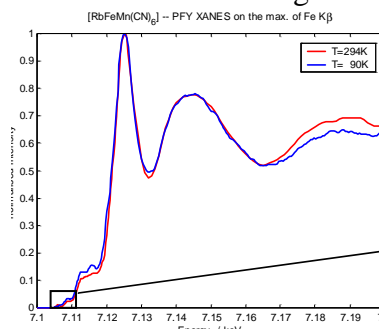


Figure 3a

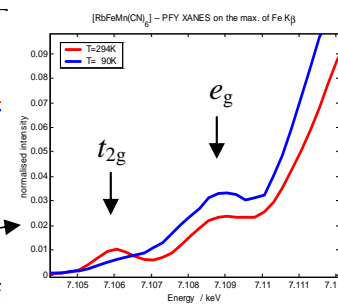


Figure 3b

and ferri-cyanides, despite the iron being Fe(II) and Fe(III), respectively, the edges hardly differ. The pre-edges of the PFY XANES spectra, however —where contributions from quadrupolar $1s \rightarrow 3d$ transitions are expected, and thus reflect the redistribution of the $3d$ electrons on the t_{2g} and e_g^* orbitals—, do show relevant changes (Fig. 3a): while at low temperature only the empty e_g^* levels are available, above the transition a peak at lower energy appears, which corresponds to the contribution of the t_{2g} . As we know from XES that the iron is low-spin, it is only the increase of the valance which can explain the appearance of an empty t_{2g} level. Thus, from these observations we can conclude that instead of a spin transition on the Mn site we have the following intermetallic electron transfer: $\text{Mn}^{\text{III}}(S=2)\text{Fe}^{\text{II}}(S=0) \rightarrow \text{Mn}^{\text{II}}(S=5/2)\text{Fe}^{\text{III}}(S=1/2)$.

The redistribution of the $3d$ electrons at the spin transition in the case of Co(II) implies a configuration change from $(t_{2g})^6(e_g)^1$ to $(t_{2g})^5(e_g)^2$. This can be followed with XANES spectroscopy (as it was described above), since below the main $1s \rightarrow 4p$ dipolar features weak $1s \rightarrow 3d$ quadrupolar transitions appear in the pre-edge region. A RXES experiment, however, where the X-ray emission spectrum is measured for each (selected) incident energy, conveys more information on the electronic structure, as it makes accessible both the intermediate and final states of the scattering process, and one can hope to see features which are not resolved in the XANES spectra. Our second objective was to study a cobalt spin-transition compound with high resolution RXES, as having spectral details better resolved is a key to obtain a deeper insight into the

electronic structure of the close-lying levels of these systems. The selected compound, $[\text{Co}(\text{terpy})_2](\text{ClO}_4)_2$, is known for showing the smallest changes in bond length at the spin transition, which implies that the change of the electronic structure at the spin transition is predominantly affected by the redistribution of the $3d$ electrons. The PFY XANES spectra, taken on the maximum of the $\text{K}\alpha_1$ emission peak, is in accordance with the this: as one can see in Fig. 4., the change of the edge is relatively small, but there is relevant variation to the pre-edge. The interpretation of the pre-edge region is, however, debated, as signals of transitions to $4p$ - $3d$ hybrid levels and excitonic effects can also show up beside the quadrupolar transitions.[5] Fortunately, the spin-transition

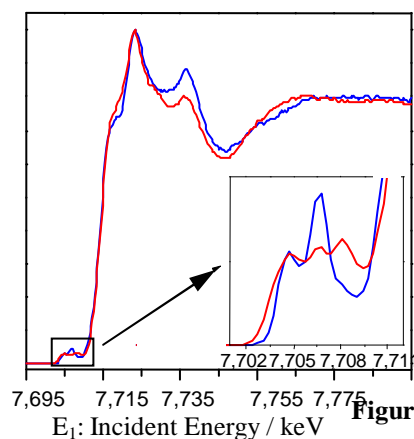


Figure 4

compounds provide an excellent testing ground for the study of the question of quadrupolar contributions, since here the changes take place on the $3d$ orbitals; this is especially valid for the case of the Co^{II} compound, where the structural variations and the accompanying changes in the chemical bonds are very small.

The $1s2p_{3/2}$ RXES spectra, taken with 0.2 eV resolution on the incident energy using a Si(440) channelcut post-monochromator, are shown in Fig. 5. The variations in the populations of the d -orbitals (in the HS state both the t_{2g} and e_g levels are available for excitations, while it is only the e_g for the LS state) are obvious from these spectra. With the ongoing theoretical analysis we hope to get a deeper insight not only into the electronic structure of the studied compound, but also into fundamental questions of the debated quadrupolar/dipolar nature of the pre-edge region of the X-ray absorption spectra.

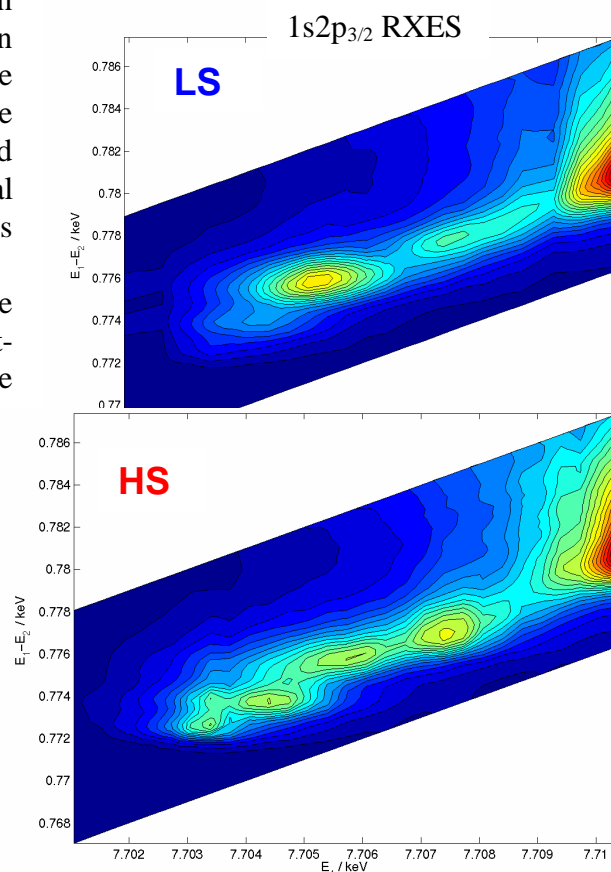


Figure 5

- [1] P. Gülich *et al.*, Angew. Chem. Int. Ed. Engl. 33 (1994) 2024.
- [2] O. Kahn *et al.*, Science 279 (1998) 44.
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- [4] Y. Morimoto *et al.*, J. Phys. Soc. Jpn. 9 (2002) 2978.
- [5] F. de Groot, Chem. Rev. 101 (2001) 1779.
- [6] see a) the experimental report on HE1270, and b) ESRF Highlights 2002, p. 59.