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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] Although these materials have been extensively studied over decades, the final aim, *i.e.*, the production of photoswitchable devices has not been accomplished yet. Recent research work on such materials is concerned with systems containing two or more different metal sites and their behaviour under extreme conditions like high pressure; with such experiments new challenges are to be faced due to the possible presence of different metal ions and sample environments with limited access to standard techniques. Therefore, the field would certainly profit from element sensitive spectroscopic probes of the local (atomic) magnetism and the electronic state, which make use of penetrating radiation.

We decided to study such materials to demonstrate that off-resonant and resonant X-ray emission spectroscopy (XES and RXES) as well as (high resolution) partial fluorescence yield X-ray absorption near edge structure spectroscopy (PFY XANES)[2] are useful tools in studying spin crossover, and in general, (molecular) magnetism. It was also our intention to provide reference or benchmark data for these techniques at the different spin states, especially for XES, where the intensity of the satellite to the main $K\beta$ line is long known to be correlated with the local magnetic moment of the metal ion, but extracting precise quantitative information on this moment from the spectra is not obvious.[3] Finally, we intended to test the conclusion of a theoretical paper, which stated that $K\alpha$ emission spectra can also be used in spin polarised studies [4], and, as a consequence, in studying magnetism. Accordingly, we applied $K\beta$ and $K\alpha$ XES, PFY XANES taken on the maximum of the $K\beta$ and $K\alpha_1$ lines, as well as resonant $2p \rightarrow 1s$ XES to spin-transition molecules of certain Fe^{3+} , Fe^{2+} , and Co^{2+} compounds[5] at temperatures well below and above the transitions. These subject materials cover almost the entire $d^4 - d^7$ range, their spin states are unambiguous and they show diverse spin transitions ($S = 1/2 \Leftrightarrow 5/2$, $S = 0 \Leftrightarrow 2$, $S = 1/2 \Leftrightarrow 3/2$).

All of the selected methods were found to be sensitive to the spin state of the studied systems, which we illustrate below on Figure 1. with the $K\beta$, $K\alpha$ and PFY XANES (taken on the $K\alpha_1$ line) spectra of the Fe^{II} compound. Nevertheless, the largest differences were found in the lineshape of the $K\beta$ spectra, since, as mentioned above, the intensity of the low energy side satellite is correlated with the magnetic moment, due to the exchange interaction between the spin of the $3p$ orbitals (where a hole is created in the $K\beta$ emission process) and the $3d$ orbitals (which hosts the unpaired electrons responsible for the atomic magnetic moment). Furthermore, the pre-edge of the PFY XANES spectra, where contributions from quadrupolar $1s \rightarrow 3d$ transitions are expected, also varies substantially with the transition. Thus these two techniques provide efficient ways to follow such transitions, and, depending on the experimental conditions, they can be

advantageous or even second to none alternatives to conventional techniques.[6] It is also possible in principle to follow the transitions using the $K\alpha$ signal, although the spectral changes are less conspicuous than in the case of the $K\beta$ making it less attractive for experiments of high or at least reasonable count rates. Besides, the RXES spectra reflected the different availability of the t_{2g} and e_g^* orbitals for the $1s \rightarrow 3d$ excitation due to their different populations in the different spin states. However, to get a deeper insight into the electronic structure of these systems these should be re-measured with considerably better resolution of the incoming beam as the spectral details were not very well resolved in the current conditions.

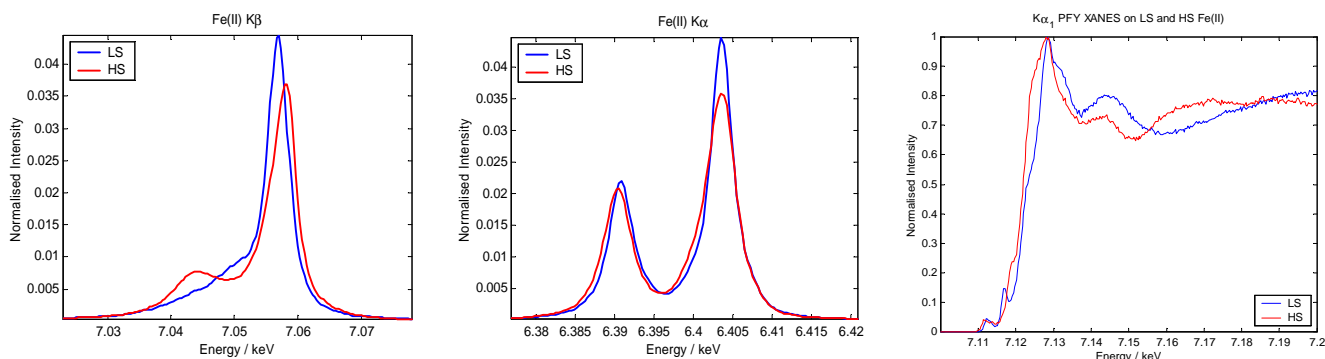


Figure 1. (from left to right:) The $K\beta$, $K\alpha$, and PFY XANES spectra of $[\text{Fe}(\text{phen})_2(\text{SCN})_2]$ at high and low spin state.

A remarkable effect was observed on the Fe^{II} system when the temperature was decreased below 50K: the majority of the sample has transformed to the HS state in the beam. Similar effect was observed on the same system upon irradiation with green light at such temperatures.[7] This effect, known as light induced excited spin state trapping (LIESST) emerges because the irradiation populates the excited HS state. The direct relaxation ($^5T \rightarrow ^1A$) is spin-forbidden; the path of intersystem crossings, which could move back the system to the LS ground state is blocked below 50K, as the necessary vibrational modes are inactive, and the tunnelling rate between the HS and LS state is very small in this compound [8], these all make the lifetime of the excited state practically infinite. In our case, as the means of excitations are different, the spin state trapping occurs very likely in the relaxation cascade that follows the electronic excitations made by Auger and secondary electrons. In accordance with this explanation, we have observed the disappearance of the HS signal when the temperature was increased above 50K (but was kept below the transition temperature.)

In summary, thermally induced $\text{LS} \leftrightarrow \text{HS}$ transition in molecular compounds was studied for the first time with XES, RXES and with PFY XANES spectroscopies. We demonstrated that spin transitions can be monitored via following the spectral evolution of a selected XES or PFY XANES feature.

Our results show that both $K\alpha$ and $K\beta$ XES reflects the variations of the $3d$ magnetic moment at the $\text{LS} \leftrightarrow \text{HS}$ transitions in the chosen $3d^5 \dots 3d^7$ compounds as predicted by theoretical calculations. Our systematic study of the variation of the spin states in transition metal ions with different $3d$ configurations could be regarded as benchmark measurements in studying magnetism with XES.

We have also observed that hard X-rays can cause an excited spin state trapping effect similar to LIESST.

References

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