



Experiment title: Detection of iron-ligand vibrations in the thermally induced high-spin to low-spin transition of single crystalline $[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$		Experiment number: CH-738
Beamline: ID 18	Date of experiment: from: 1.12.1999 to: 5.12.1999	Date of report: 22.02.2000
Shifts: 12	Local contact(s): Dr. Aleksandr Chumakov	<i>Received at ESRF:</i>
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Report:

Nuclear inelastic scattering (NIS) spectra have been recorded from single-crystalline $[\text{Fe}(\text{tptMetame})](\text{ClO}_4)_2$ ($\text{tptMetame} = 1,1,1\text{-tris}((\text{N-(2-pyridylmethyl)-N-methylamino)methyl)ethane)$ which belongs to a class of iron(II) complexes that exhibit a low-spin (LS) \leftrightarrow high-spin (HS) crossover (Fig. 1). Since this spin crossover can be induced thermally or by irradiation with light these complexes are very promising materials for optical information storage. The spin transition is suggested to be entropically driven due to a softening of the iron-ligand bond stretching and bending modes in the HS state. NIS is the method of choice for testing this hypothesis because in the NIS spectra only those vibrational modes appear that contribute significantly to the mean-square displacement of the ^{57}Fe nucleus.

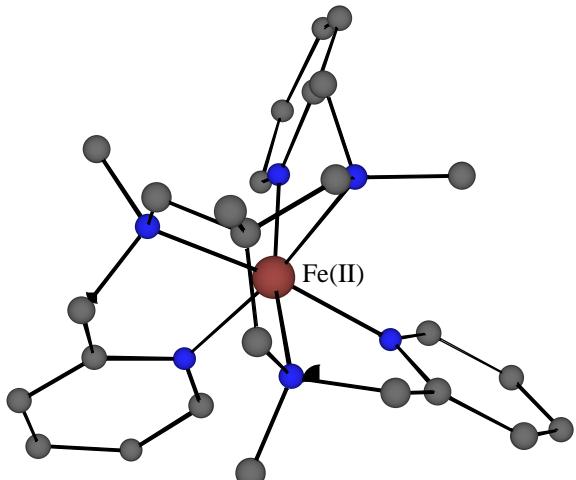


Figure 1. $[\text{Fe}(\text{tptMetame})]^{2+}$ cation.

First evidence for this hypothesis has been gained by a former NIS experiment at ESRF (CH-308) [1,2,3]. A new high resolution monochromator [4] at the beamline ID-18 with an energy resolution (0.65 meV), that has been increased by almost one order of magnitude, allows for the first time to detect individual intra-molecular vibrational modes of a single-crystalline spin-crossover complex.

The measurements were performed with single crystals of the monoclinic space group $P2_1/n$. All four complexes in the unit cell have the same orientation of their threefold symmetry axis (C_3), which makes this compound very suitable for recording angular resolved spectra. The single crystals had the form of 2 mm long needles with ca. 0.2 mm thickness. EPR spectra of Mn(II) traces in the sample suggest that the C_3 axis should be parallel to the needle axis \mathbf{n} . Currently the X-ray diffraction of the single crystal is measured in order to determine the exact orientation of the C_3 axis with respect to the crystal faces. The sample was mounted in a closed-cycle cryostat and cooled down to 30 K to reach the LS state. The first spectrum was recorded with \mathbf{n} parallel to the polarization vector \mathbf{e} of the γ -beam, two more spectra were recorded after rotating the crystal about \mathbf{n} by 45° each time. These three orientations yield identical spectra, the summation of which is shown in Figure 2 a. This has been expected due to the symmetry of the molecule. Before recording the fourth spectrum the needle axis \mathbf{n} was mounted parallel to the wavevector \mathbf{k} of the γ -beam. The resulting spectrum (Fig. 2 b) is clearly different from the previous spectra where \mathbf{n} was parallel to \mathbf{e} . A significant shift of the peaks to lower energy is observed in the spectrum of the HS isomer that was recorded at room temperature (Fig. 3).

By comparison with simulated NIS spectra (Fig. 2 a and b), calculated by density functional methods [3], individual normal modes of molecular vibration can be identified in the measured spectra. In summary, the recorded NIS spectra of $[\text{Fe}(\text{tpfMetame})]$ support the shift of the iron-ligand bond stretching and bending modes upon spin crossover and their attribution as driving force for the crossover.

References

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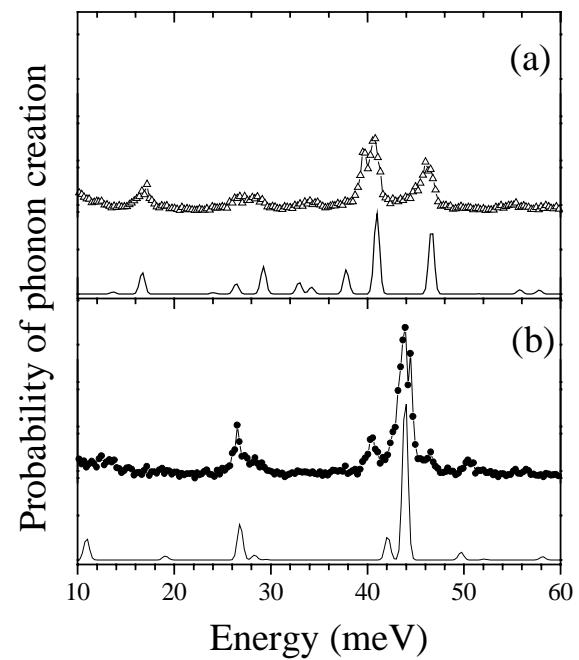


Figure 2. Experimental (Δ, ∇) and theoretical (solid lines) NIS spectra for the LS isomer ($T=30$ K) with $\mathbf{n} \parallel \mathbf{e}$ (a) and $\mathbf{n} \parallel \mathbf{k}$. (b).

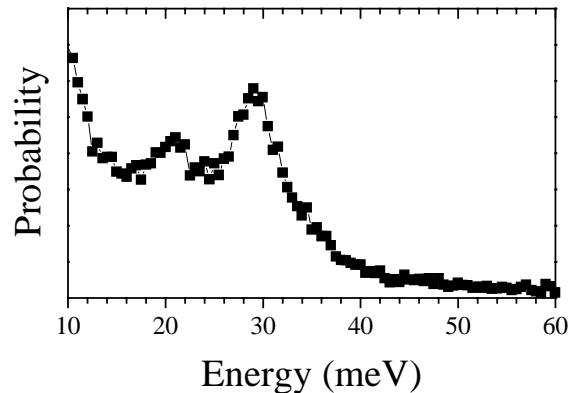


Figure 3. Experimental NIS spectra for the HS isomer ($T=300$ K) with $\mathbf{n} \parallel \mathbf{e}$.