

STUDY ON $[\text{FeN}_6]$ CORE OF $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\cdot\text{EtOH}$ IN PHOTO-INDUCED HIGH-SPIN STATE BY NUCLEAR RESONANT INELASTIC SCATTERING

As a consequence of the splitting of d orbitals into t_{2g} and e_g orbitals, octahedral transition metal compounds with d^4 to d^7 electronic configurations may exist either in the low-spin (LS) or high-spin (HS) state. Compounds that show a transition between different spin states upon external perturbation, e.g., variation in temperature and light-irradiation, are of great importance due to their possible industrial uses such as in photo-switches, memories and display devices.

$[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\cdot\text{EtOH}$ (**1**) is one of the most well known among these compounds. The lattice of compound **1** is built from $[\text{Fe}(\text{2-pic})_3]^{2+}$ units (Fig. 1), in which each iron(II) ion is surrounded by six nitrogen atoms belonging to three 2-pic ligands (2-pic: 2-picolylamine). Recently, Tayagaki *et al.* reported that for compound **1**, the Raman and IR spectra of the photo-induced HS state are remarkably different from the spectra of the thermally induced HS state [1]. The observed differences suggest a distortion of molecules in the photo-induced phase, which according to the authors is most probably due to a cooperative Jahn-Teller effect. In order to confirm these conclusions, we performed ^{57}Fe nuclear resonant inelastic scattering (NRIS) measurements on the light-induced and thermally induced spin transition of compound **1** [2]. The NRIS is a novel technique for monitoring the vibration states isotope-selectively, and yields only the vibration modes that are associated with a significant

displacement of the resonant isotope, in this case ^{57}Fe . This selectivity simplifies data analysis, and is especially effective for the direct investigation of the vibrational states of $[\text{FeN}_6]$ in compound **1**. These vibration modes were not in the energy range of the IR and Raman measurements of Tayagaki *et al.*; therefore, the result of the NRIS measurement complements their previous findings.

The measurements were carried out at **BL09XU** beamline, on a ^{57}Fe -enriched sample of compound **1** placed in a cryostat. For the light-irradiation experiment, a Hg-arc lamp was used as a light source, and its light was directed through the cryostat window using a glass fiber. Figure 2 shows the spectra of compound **1** under various conditions. Upon irradiation at 35 K, the sample exhibits an almost complete photoinduced phase transition from the LS (t_{2g}^6) state (Fig. 2(a)) to a light-induced HS, LHS ($t_{2g}^4 e_g^2$) state (Fig. 2(b)), and the most intense peaks of the spectra move from 320-360 cm^{-1} (LS state) to 200-270 cm^{-1} (LHS state). The reason for this shift is that the spin-transition is associated with the transfer of two electrons from the nonbonding t_{2g} to the antibonding e_g orbital. The observed LS-HS conversion is reversible by switching off the light source; after a short annealing of the sample at 100 K, the peaks attributed to HS disappear from the spectrum remeasured at 35 K.

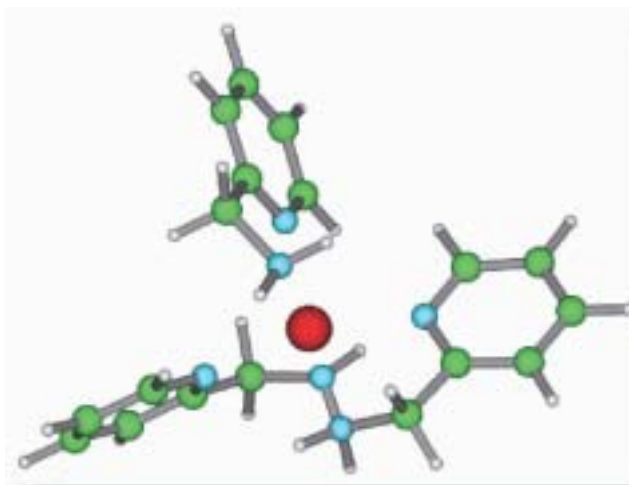


Fig. 1. Structure of $[\text{Fe}(\text{2-pic})_3]^{2+}$. Red: iron atoms; blue: nitrogens atoms; green: carbons atoms; gray: hydrogens atoms.

The thermally induced spin-transition was observed at 115 K (Fig. 2(c)), and upon further elevating the temperature to 150 K, the spectra of thermally induced HS were also recorded (Fig. 2(d)). The spin-transition is manifested as a decrease in the intensity of the peaks at 320-360 cm^{-1} , characteristic to the LS state, and the occurrence of new peaks at 200-270 cm^{-1} . The spectra of the thermally induced HS phase show only minor differences compared with the light-induced HS phase (Fig. 2(b)).

The geometry and vibrational modes of an isolated $[\text{Fe}(\text{2-pic})_3]^{2+}$ in the LS and HS states were calculated by the BLYP DFT method, and the NRIS spectra were simulated using the results of DFT calculation (Fig. 3). The results of the simulation are in good qualitative agreement with the measurements, although the

calculation is less accurate for the LS state, most probably due to the neglected solid-state effects. We are currently trying to extend our studies by taking into account intermolecular interactions.

In summary, we found that the distortion in the light-induced HS phase of compound **1** reported by Tayagaki *et al.* [1] has only a minor effect on the dynamics of the $[\text{FeN}_6]$ core, as was also suggested by recent X-ray crystallographic reports on **1** [3].

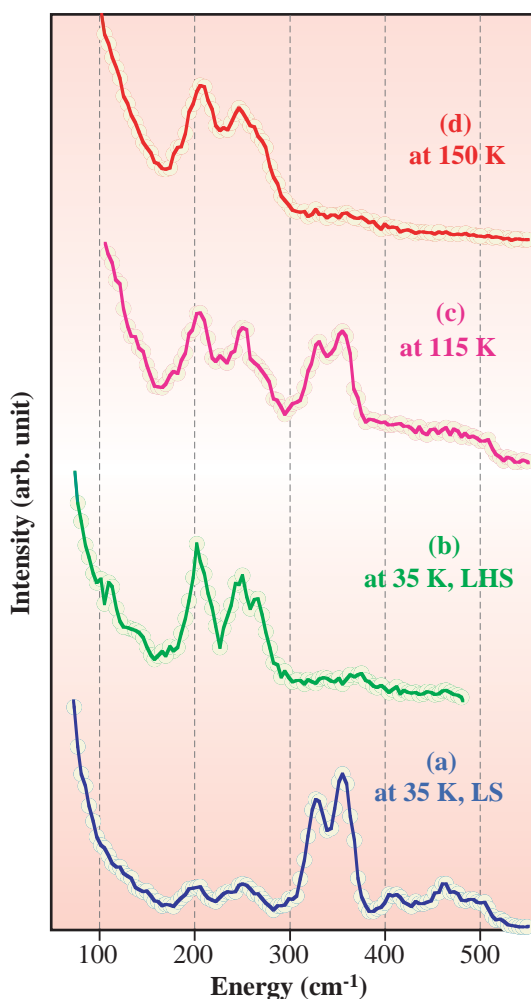


Fig. 2. NRIS spectra of $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (**1**) at 35 K before (a) and after light-irradiation (b); around the spin transition at 115 K (c); and in thermally induced HS state at 150 K (d).

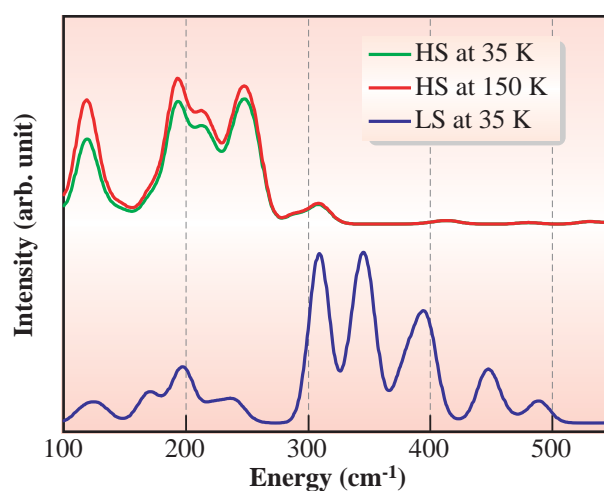


Fig. 3. Simulated NRIS spectra for LS state (at 35 K) and HS state (at 35 K and 150 K).

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