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NRIS study on the [FeN_6] core in photo-induced high-spin state of [Fe(2-pic)$_3$]Cl_2·EtOH

Gergely Juhász,*[a] Makoto Seto,[b] Yoshitaka Yoda,[c] Shinya Hayami[a] and Yonezo Maeda[a]
[a] *Department of Chemistry, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan. E-mail: j.gerscc@mbox.nc.kyushu-u.ac.jp; Fax: 092-642-2607; Tel: 092-642-2588*
[b] *Research Reactor Institute, Kyoto University, Kumatori-cho, Osaka 590-0494, Japan*
[c] *Spring-8/JASRI, 1-1-1 Kouto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan*

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A comparison is reported for thermally and photo-induced high-spin phases of [Fe(2-pic)$_3$]Cl_2·EtOH (2-pic: 2-picolylamine) using the nuclear resonant inelastic scattering (NRIS) technique.

The spin-crossover compounds are well known for showing a thermally induced transition between high-spin (HS) and low-spin (LS) states. Other perturbations, *e.g.* light irradiation can also induce a spin transition from the LS to the HS state, and the metastable HS state can be trapped if the temperature is sufficiently low. This phenomenon is called the LIESST-effect (Light Induced Excited Spin-State Trapping). Due to possible industrial utilization and theoretical interest, the LIESST-effect and the characteristics of the light-induced high-spin state still attract great attention.[1]

[Fe(2-pic)$_3$]Cl_2·EtOH (**1**; 2-pic: 2-picolylamine or 2-aminomethyl pyridine) is one of the most extensively studied LIESST compounds.[2] In this coordination complex, six nitrogens form an approximately octahedral environment around the iron. Compound **1** has an abrupt two-step spin-transition at about 120 K, and LS–HS transition can be induced by light-irradiation below 40 K. Recently, Tayagaki and Tanaka reported that the resonance Raman spectrum of the light-induced HS state below 40 K is different from that of the HS state at high temperature.[3] In the Raman spectrum of the light-induced HS phase, a number of lines appear that are Raman-inactive in the thermally induced HS phase. In the light-induced HS state, significant mode softening (25–70 cm^{-1}) was observed for several lines, which were assigned as the vibrational modes of the ligand. A Jahn–Teller distortion that occurs only in the light-induced HS phase was proposed as an explanation. However, these IR–Raman measurements provided only information on the ligand vibrations. The Fe-ligand vibrations, *i.e.* the vibrational modes of [FeN_6] have not been investigated, though such data would be able to confirm the Jahn–Teller distortion.

Okamoto *et al.* carried out an XAFS study on **1**,[4] but similar Fe–N geometries were found for the light-induced and the high-temperature HS phases. An X-ray crystallography study of the light-induced phase was reported by Huby *et al.*[5] They have not observed symmetry breaking in the photoinduced phase, and the two HS states were found to be similar to each other. The IR and Raman spectroscopic measurements were repeated on single crystals with extremely homogenous light-excitation,[6] so the possibility that the observed distortion in the light-induced phase is a result of inhomogeneity of the metastable phase can be excluded.

The disagreement between these results may originate from the different nature of the measurement methods. The structural studies (XAFS and X-ray crystallography) and the investigations of the molecular dynamics (IR and Raman spectroscopy) have different viewpoints on the problem. However, none of the measurements could answer the question, whether the distortion observed in the light-induced phase can significantly influence the dynamics of the [FeN_6] core. To answer this question is crucial for the discussion of both the spin-crossover behaviour and the relaxation of the light-induced metastable HS state of the compound. The novel spectroscopic technique, nuclear resonant inelastic scattering (NRIS)[7] has a great potential to provide selective information about the vibrational states of a resonant atom (^{57}Fe in our case). NRIS was successfully used to study the dynamic behaviour of the iron core in coordination complexes and proteins.[8] With NRIS, we can only measure those normal modes that are connected with a mean-square displacement (msd) of the resonant ^{57}Fe atom, whereas the other vibrations remain silent. This isotope selectivity makes the NRIS method very useful to study the vibrational modes of the [FeN_6] in **1**, which were unexplored in the former IR/Raman studies.

The NRIS experiment was carried out at Spring-8, using the BL09XU beamline. A high-resolution nested monochromator with a resolution of 2.5 meV (20 cm^{-1}) was used for the measurement. **1** with 95% enrichment of ^{57}Fe was synthesized following the standard method.[2] The powder sample was mounted in a cryostat, and its temperature was monitored by a thermocouple attached to the sample holder. The spectra for the thermally induced HS phase were recorded at 150 K, those for the LS phase and the light-induced phase at 35 K. The irradiation of the sample was possible through a window of the cryostat with an Hg-arc lamp. In order to exclude the possibility of radiation damage or some other type of degradation (*e.g.* oxidation) during the experiment, the purity of the sample was checked by Mössbauer spectroscopy after the measurement. The recorded NRIS spectra were summed and normalized following the standard method.[9] The vibrational modes for the LS and HS isomers of an isolated [Fe(2-pic)$_3$]$^{2+}$ were calculated with the Gaussian'03 program[10] in order to interpret the spectra. We used the BLYP DFT method[11] with the Los Alamos effective core potential plus double-zeta valence for Fe[12] and the D95 basis set for H, C, and N.[13] The NRIS spectrum for the LS and HS phases was simulated[8] using the calculated vibrational modes.

The NRIS spectra between 50 and 500 cm^{-1} are shown in Fig. 1. Without light irradiation, at 35 K, the most intensive peaks are observed between 320 and 360 cm^{-1} (40–45 meV). Compound **1** has a complete spin-transition at this temperature, thus these peaks pertain to the LS phase. After 30 min of irradiation, the intensities of the peaks of the LS state significantly decrease and new, intense peaks appear at 200–270 cm^{-1} (25–32 meV) indicating the photo-induced phase transition. The lack of any intense peak at 320–360 cm^{-1} shows that the LS–HS conversion was approximately complete. Because of the relatively fast relaxation of the metastable HS state at this temperature, the irradiation was continuous during the measurement. The decrease of the vibrational energies in the light-induced HS state is expected,[14] and can be clearly observed. The antibonding character of e_g orbitals is stronger than that of the t_{2g} orbitals, that is why in the HS state ($t_{2g}{}^4e_g{}^2$), the iron–ligand bonds are weaker than those in the LS state ($t_{2g}{}^6$) and the frequencies of the related normal modes are lower. The observed LS–HS conversion is reversible: switching off the light-source, after a short annealing of the sample at 100 K, the peaks attributed to the HS disappear from the spectrum re-measured at 35 K (not shown in the figure).

Elevating the temperature well above the spin-transition temperature, at 150 K, the LS state is mainly converted to the

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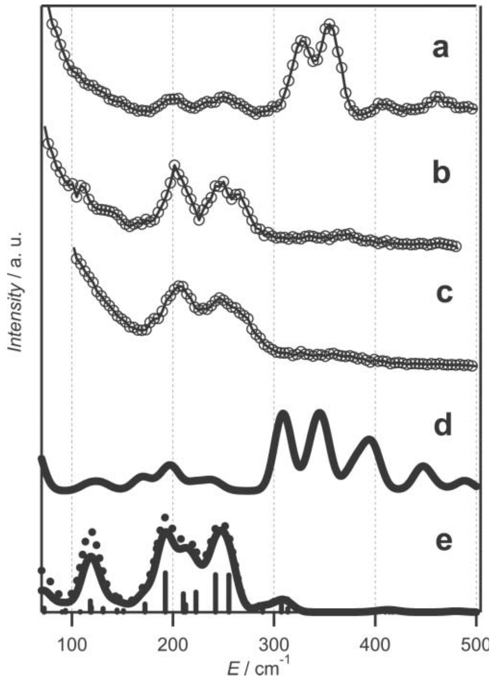

Fig. 1 The NRIS spectra of **1** at 35 K before (a) and after light-irradiation (b), at 150 K (c), and the calculated spectra for the LS state at 35 K (d), the HS state at 35 K (full line) and 150 K (dashed line) (e).

thermally induced HS state. The HS content is about 90%, estimated by magnetic susceptibility measurements. As can be seen in the figure, similarly to the light-irradiation experiment, the intensity of the peaks at 320–360 cm^{-1} significantly decreases and the intense peaks at 200–270 cm^{-1} appear. The spectra of the thermally induced HS phase show only minor differences compared to the light-induced HS phase. Although the resolution of our measurement (20 cm^{-1}) is poor compared to those of the IR and Raman measurements, there is no sign of such a huge frequency shift for the vibrational modes of the [FeN$_6$] as observed by Tayagaki[3,6] for that of the ligand. As a considerable distortion around the iron center of the complex would affect the intensities and the frequencies of these peaks, the result of the NRIS measurements suggests that the distortion of the molecule in the light-induced phase does not significantly affect the [FeN$_6$] core if compared to the 2-pic ligands.

The geometries calculated by DFT methods for an isolated [Fe(2-pic)$_3$]$^{2+}$ in LS and HS states are similar to the reported crystal structure.[15] Both the calculation and the measurement prove that the [FeN$_6$] core is strongly distorted in both spin-states and far from the ideal octahedral geometry. The calculated changes of the vibrational modes upon the spin-transition are similar to the measured ones. The intense peaks of the simulation have a good qualitative agreement with the measurements for the HS spin-states, the three intense peaks of the calculation are at 192 cm^{-1} (23.9 meV), 242 cm^{-1} (30.0 meV) and 255 cm^{-1} (31.6 meV). The calculation is less accurate for the LS state, however, such a difference between the measured and the calculated spectra is not exceptional.[8] We should not forget that the structure of **1** is strongly affected by intermolecular interactions, which we neglected during the calculation. Strong hydrogen bonds between the amine group and the Cl$^-$ anion have been reported.[15] A long-range ordered phase of mixed HS and LS states was also found recently, proving the uniqueness of the intermolecular interaction in this compound.[16] Above the spin transition, in the thermally induced HS state the ethanol molecule exhibits orientation disorder, which can also influence the dynamics of the [Fe(2-pic)$_3$]$^{2+}$. While the thermally induced spin-transition is accompanied by the order–disorder transition of the solvent molecule, the light-induced spin-transition is not necessarily. A possible explanation for the differences between the two HS states observed by Tayagaki *et al.*[3,6] can be the influence of the solvent on the vibrational modes of the amine group.

In conclusion, we found that the distortion in the light-induced HS phase of **1**, reported by Tayagaki *et al.*,[3] possibly has only a minor effect on the dynamics of the [FeN$_6$] core. The simulations based on DFT calculations for an isolated [Fe(2-pic)$_3$]$^{2+}$ can help in the interpretation of the measured data. However it is clear that the intermolecular forces have a strong role in this system, so further, more accurate calculations are needed.

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