

Nuclear inelastic scattering study of a dinuclear iron(II) complex showing a direct spin transition

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Abstract The results of the nuclear inelastic scattering (NIS)/nuclear resonance vibrational spectroscopy (NRVS) for the powder spectra of dimeric $[\text{Fe}_2\text{L}_5(\text{NCS})_4]$ (L= N-salicylidene-4-amino-1,2,4-triazole) complex are presented. This system is spin crossover (SCO) material tagged with a fluorophore that can sense or “feel” the SCO signal ripping through the molecular network and thereby providing an opportunity to register the SCO transition. The spectra have been measured for the low-spin and high-spin phases of the complex. The high-spin isomer reveals one broad band above 200 cm^{-1} , while the low-spin one displays two intense bands in the range from 390 to 430 cm^{-1} , accompanied by a number of weaker bands below this area and one at ca. 490 cm^{-1} . A normal coordinate analysis based on density functional calculations yields the assignment of the spin marker bands to particular molecular modes. In addition the vibrational contribution to the spin transition has been estimated

Keywords Nuclear inelastic scattering · Spin crossover · Molecular magnetism · Density functional theory · Fluorophore · Nuclear resonance vibrational spectroscopy

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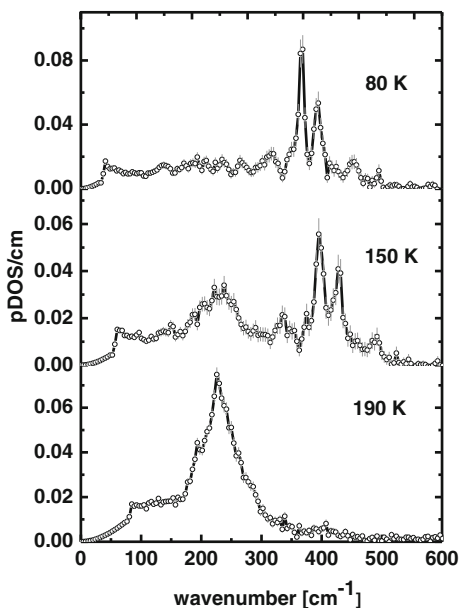
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Fig. 1 Experimental pDOS as obtained from the NIS data of **1** in the LS state (80 K), in the HS state (190 K) and at the transition temperature (150 K)



1 Introduction

Spin crossover (SCO) complexes are one of the most promising materials for the future electronics, particularly in the areas of data storage, information processing and sensors [1–6]. Recently one of us discovered a SCO material tagged with a fluorophore that can sense or “feel” the SCO signal ripping through the molecular network and thereby providing an opportunity to register the SCO transition [9]. The complex $[\text{Fe}_2(\text{L}1)_5(\text{NCS})_4] \cdot 4\text{MeOH}$ (**1**) is an Fe(II) dimer, bridged with three 1,2,4-triazole derivative, substituted with a thermochromic and photochromic Schiff base substituent (L1). The coordination sphere is completed by a mono-coordinating L1 ligand and two thiocyanate anions (see also ref. [8]). The system reveals a relatively abrupt spin transition with $T_c = 150$ K. In this study we present investigations of the complex by nuclear inelastic scattering (NIS) in its low-spin (LS) and high-spin (HS) states, as well as around the transition temperature. In addition density functional theory (DFT) calculations have been performed in order to assign the normal vibrational modes of complex **1** and to estimate the vibrational contribution to the spin transition entropy.

2 Materials and methods

The ^{57}Fe enriched (99 %) complex under study was prepared as described in ref. [9]. NIS was performed at P01, PETRA III, DESY in Hamburg, Germany, under Experiment I-20120310. The 6 GeV storage ring PETRA III was operated in 60 bunch mode with a bunch separation of 123 ns. The beam was monochromatized to an energetic width of 0.4 eV by a pair of Si(3 1 1) crystals and further down to 1 meV by a high resolution monochromator using two pairs of asymmetrically cut silicon crystals. The used reflections are twice Si(4 0 0) and twice Si(10 6 4). DFT calculations were performed as described in ref. [11], using a

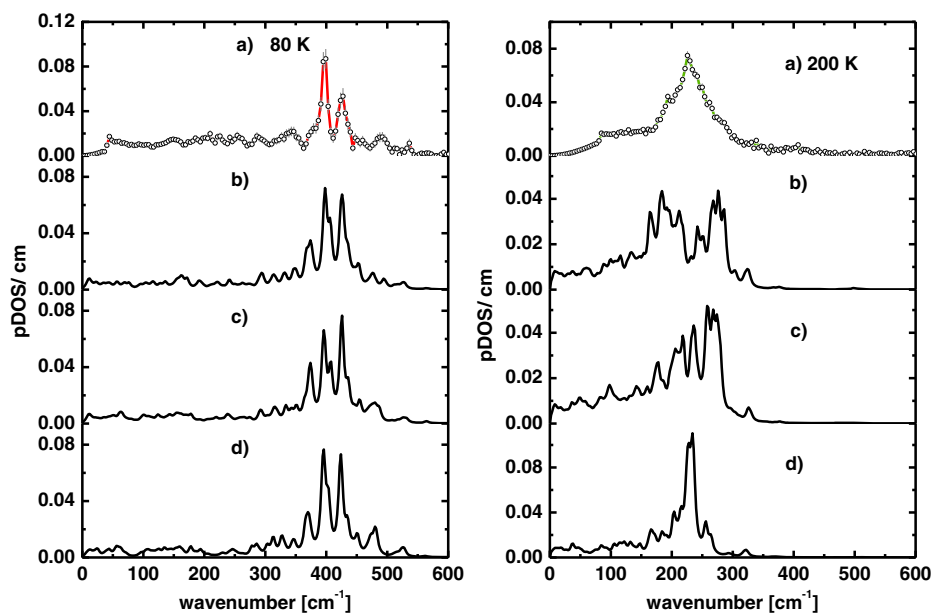


Fig. 2 Experimental **a** and calculated pDOS for LS-LS (*left*) and HS-HS (*right*) spin isomers of **1**, for the isolated molecule, model (i), (b); $1 \cdot (\text{CH}_3\text{OH})_4$, model (ii) **b** and polarisable continuum with methanol cavity, model (iii) (d)

pentanuclear model system with full charge compensation. The powder sample of the complex was mounted on the glass rod covered with some silicon grease and was immediately placed in a stream of a nitrogen gas cryostream cooler (Oxford Cryosystem Ltd.) that was used as cooling device. The sample showed to be stable under the experimental conditions. The DFT calculations were performed with Gaussian 09, using the TPSSh functional [10] and the TZVP basis set [11, 12], for the models discussed. The vibrational contribution to entropy was calculated as described in ref. [13].

3 Results and discussion

Figure 1 shows the phonon partial density of states (pDOS) of **1** obtained at 80 K (Fig. 1a), at 150 K (Fig. 1b) and 190 K (Fig. 1c). The pDOS obtained at 80 K displays bands in the spectral region typical for Fe(II) LS ions. The pDOS obtained at 190 K has bands which are characteristic for Fe(II) HS sites. The spectral patterns of the LS-LS and HS-HS isomers are characteristic for Fe(II) SCO systems, revealing a characteristic, $\sim 180 \text{ cm}^{-1}$ shift of the metal-ligand vibrations towards lower frequencies on going from LS-LS to the HS-HS state. The spectrum at 150 K reveals a sum of the spectra of the LS-LS and HS-HS isomers (see [Supplementary](#)), suggesting that no LS-HS pairs occur during the transition, as confirmed by ^{57}Fe Mössbauer spectroscopy [7].

We have found that in simulations of the obtained pDOS of **1** in its both spin states the best reproduction of the experimental data can be obtained with the TPSSh functional and the TZVP basis set. As the crystal structure of the complex under study reveals the presence of four non-coordinated methanol molecules in the unit cell, that interact with OH groups

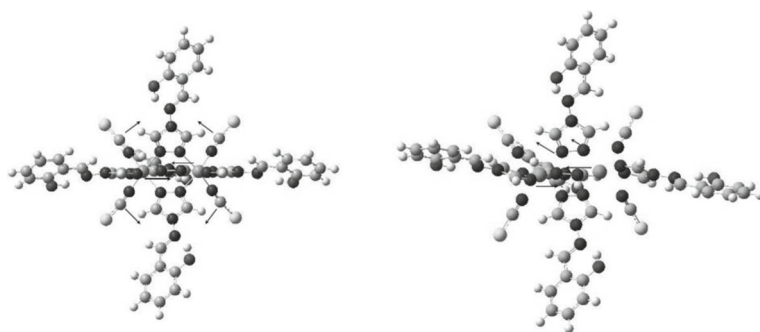


Fig. 3 Calculated normal modes of the LS-LS isomer of **1**, predicted at 394 cm^{-1} (*left*) and the corresponding mode of the HS-HS isomer, predicted at 216 cm^{-1} (*right*)

of the ligand and with sulphur atoms of the thiocyanate, we applied three structural models for the calculations: (i) isolated molecule of the dimer with no methanol molecules; (ii) molecule of the dimer with four methanol molecules, included in the starting geometries on the basis of the crystal structure [7]; (c) molecule of the dimer with no methanol molecules within a polarisable continuum model (IEFPCM keyword of Gaussian) but with a methanol cavity. The latter model introduces the environment with electric permeability corresponding to that of a methanol solution, rather than vacuum. The calculated pDOS for the HS and LS states of the three models in comparison to the experimental pDOS are shown in Fig. 2.

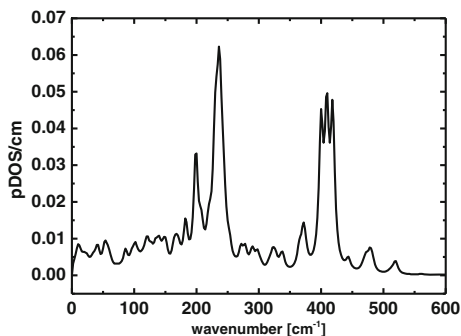
Inspection of Fig. 2 indicates that all three models yield a reasonable fit for the LS-LS state of the molecule under study. The allowing a higher dielectric constant of the environment in model (iii) leads to a good fit for the HS-HS state. Therefore we will further discuss only the calculated normal modes within model (iii).

The obtained normal coordinate modes show that the two main marker bands of the LS-LS state of **1**, occurring at 397 and 426 cm^{-1} are due to Fe-N stretching vibrations, all of them exhibiting the simultaneous stretching of Fe-N(triazole) bond and the Fe-N(NCS) stretching, with both nitrogens coordinated in *trans* position. We assigned them to two pair of modes predicted at $394/397\text{ cm}^{-1}$ and at $423/425\text{ cm}^{-1}$, respectively. The band observed at ca. 340 cm^{-1} corresponds to a similar mode, predicted at 344 cm^{-1} . The weaker band at ca. 490 cm^{-1} was assigned to two modes predicted at 482 cm^{-1} , involving mainly the thiocyanate bending with some Fe-N stretching. The spectrum of the HS-HS isomer that reveals a broad asymmetric band with maximum at ca. 226 cm^{-1} is a superposition of several stretching modes, of which particularly that predicted at 216 cm^{-1} seems to be due to a mode similar to that predicted at 394 cm^{-1} for the LS isomer (see Fig. 3), yielding a shift of nearly 180 cm^{-1} upon spin transition. Further representative calculated normal modes are shown as movies in [Supplementary Materials](#).

The model applying the polarization continuum model was further used to calculate the pDOS of the molecule containing one HS and one LS centre (HS-LS), (see Fig. 4). The obtained spectral pattern clearly does not correspond to the spectrum observed at 150 K, providing thus another indication that the complex under study reveals an abrupt transition involving both iron centres.

The theoretical estimation of the vibrational contribution to the entropy yields a value of $156\text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$ at 150 K for the complete switch from the LS-LS to the HS-HS isomer. The so obtained value is approximately twice as much as that calculated for polymeric 4-amino-1,2,4-triazole systems [14], which has been determined to $\sim 60\text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$ at

Fig. 4 Calculated pDOS for HSLs spin isomer of **1** with polarisable continuum model with methanol cavity



150 K for a LS to HS transition for one LS centre with LS neighbours. The calorimetrically determined vibrational contribution for the LS to HS transition entropy amounts to $42 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$ per Fe atom [7]. On the other hand our calculations yield corresponding contributions for the LS-LS to LS-HS and LS-HS to HS-HS transitions, of 55 and $101 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$ at 150 K, respectively. Taking into account, that the DFT calculated electronic energies of the LS-LS to LS-HS and LS-HS to HS-HS spin transition are 39 and $35 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, one may assume that the cooperative behavior of **1** may, on the molecular level, be assigned to entropic factors.

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