

Nuclear inelastic scattering of 1D polymeric Fe(II) complexes of 1,2,4-aminotriazole in their high-spin and low-spin state

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Abstract The vibrational properties of Fe(II) 1D spin crossover polymers have been characterized by nuclear inelastic scattering (NIS). The complexes under study were the tosylate and perchlorate salts of $[\text{Fe}(\text{4-amino-1,2,4-triazole})_3]^{+2}_n$ complexes. The complexes have LS ($S = 0$) marker bands in the range of $300\text{--}500\text{ cm}^{-1}$, while the marker bands corresponding to the HS ($S = 2$) state are detected between 200 cm^{-1} and 300 cm^{-1} , in line with the decreasing Fe-N bond strengths during the transition from LS to HS. Accompanying DFT calculations using the functional B3LYP and the basis set CEP-31G confirm these assignments.

Keywords Nuclear inelastic scattering · Spin crossover · Molecular magnetism · Density functional theory

1 Introduction

The design of new spin crossover (SCO) materials [1, 2] requires a better understanding of the nature and origin of the co-operative behavior and resulting bistability of this class of compounds. Vibrational spectroscopy combined with quantum chemical calculations may provide a better understanding of the SCO effects by clarifying the

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relationships between microscopic effects of vibrations, energy and molecular strain and the terms derived from phenomenological models [3]. Among them, nuclear inelastic scattering (NIS), also called nuclear resonant vibrational spectroscopy (NRVS) is of special interest because it gives much more details on the vibrational properties of Mössbauer nuclei, as compared to Raman and IR spectroscopy [4]. We have previously reported the results of NIS studies for the linear trimeric SCO $[\text{Fe}_3(4-(2'\text{-hydroxy-ethyl})-1,2,4\text{-triazole})_6(\text{H}_2\text{O})_6]^{+6}$ system [5]. Here we report the first NIS study of a one-dimensional polymeric material, based on 4-amino-1,2,4-triazole (ATZ) complexes. This class of complexes has been widely studied by other methods [6] because of the strong dependence of transition temperature and hysteretic behavior on the nature of the anion. Therefore we performed NIS measurements for two systems with different counterions: the low-spin isomer of the tosylate salt of $([\text{Fe}(4\text{-amino-1,2,4-triazole})_3]^{+2})_n$ (**1**) and its perchlorate analogue (**2**). The tosylate salt (**1**) is low-spin at room temperature [7]. For the perchlorate salt (**2**) the transition temperatures of 210 K [8] and 130 K [9] were reported independently.

2 Materials and methods

The complexes were obtained by a slightly modified literature method [8], i.e. by mixing the ethanolic solution of the 4-amino-1,2,4-triazole ligand with a water solution of the corresponding salt containing 99% enriched ^{57}Fe . The latter were obtained from $^{57}\text{Fe}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$ and the corresponding barium salts. Nuclear inelastic scattering (NIS) was performed at the Nuclear Resonance Beamline ID 18 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, under experiment No. CH 2839. During the experiments the 6 GeV electron storage ring was operated in 16 bunch mode. The incident beam was monochromatized by a Si(111) double-crystal premonochromator to a bandwidth of 2.1 eV. A further decrease of bandwidth down to 1 meV was obtained with a refractive beryllium collimator and a high-resolution monochromator.

DFT calculations were performed as described in [5], using a pentanuclear model system with full charge compensation.

3 Results and discussion

The NIS spectrum of (**1**) obtained at 100 K reveals a number of bands in the 300–500 cm^{-1} region. On the other hand the system (**2**) displays two broad bands at 200–270 cm^{-1} . On cooling (**2**) to 100 K these are retained, but also new bands appear in the 300–500 cm^{-1} region (Fig. 1). The above results imply that the observed changes are due to a spin transition from HS to LS state on cooling. Consequently, the LS marker bands occur in the range of 300–500 cm^{-1} , while those corresponding to the HS state are seen between 200 cm^{-1} and 300 cm^{-1} , in line with the decreasing Fe–N bond strengths during the transition from LS to HS [1]. This assumption has been corroborated by the DFT calculations on a pentameric model molecule $[\text{Fe}_5(\text{ATZ})_{12}(\text{H}_2\text{O})_6]_2\text{Cl}_{10}$, using the B3LYP functional and the CEP-31G basis set (Fig. 2). The comparison of the experimental and theoretically derived spectra

Fig. 1 NIS spectra of (1) at 100 K (*bottom*) and of (2) at 300 K (*top*) and 100 K (*middle*)

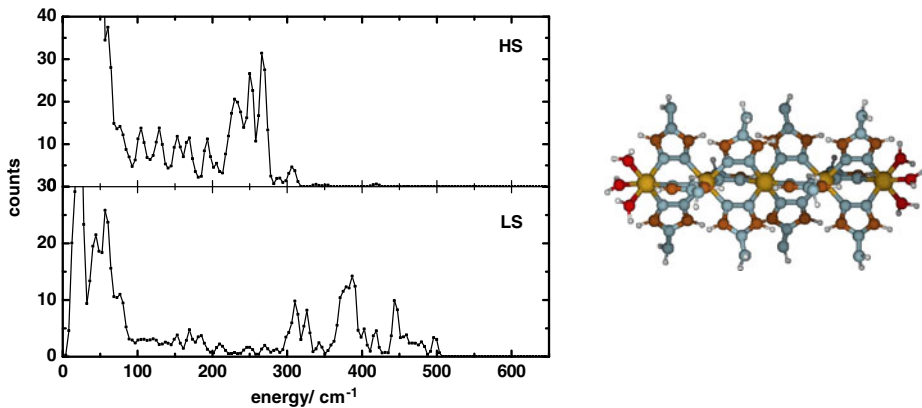
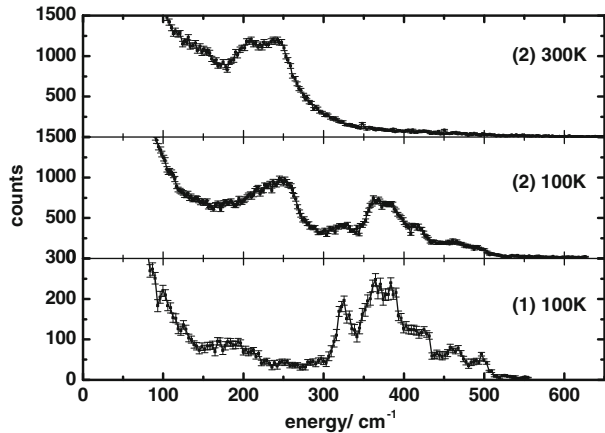


Fig. 2 Left simulated NIS spectra for the LS (*bottom*) and HS (*top*) based on DFT calculations for the pentameric model molecule $[\text{Fe}_5(\text{ATZ})_{12}(\text{H}_2\text{O})_6]_2\text{Cl}_{10}$. Right graphic representation of the model. Chlorine anions were removed for clarity. Movies of the representative HS marker bands (233 cm^{-1}) and of LS-marker bands (326 cm^{-1}) are given as [supplementary material](#)

shows that the NIS spectra of the Fe(II) polymers under study can be reliably reproduced using a pentameric model molecule. The calculations predict the iron-ligand stretching modes in the $320\text{--}500 \text{ cm}^{-1}$ and $200\text{--}300 \text{ cm}^{-1}$ regions, for LS and HS systems, respectively (Fig. 2). We previously reported that the only Raman LS marker bands for the polymers under study occur at ca. 260 cm^{-1} . According to the DFT calculations presented there this band corresponds to Fe-N bending, rather than stretching modes [10]. The comparison of the overall spectral pattern of the NIS spectra of both spin isomers of the systems point out to a negligible influence of the anion.

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