

Experimental evidence of the vibrational coupling of nearest neighbours in 1D spin crossover polymers of rigid bridging ligands

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Abstract The nuclear inelastic scattering signatures of the low spin centres of the methanesulphonate, tosylate and perchlorate salts of the spin crossover polymer $([\text{Fe}(\text{II})(4\text{-amino-1,2,4-triazole})_3]^{+2})_n$ have been compared for the pure low-spin phase, for the mixed high-spin and low-spin phases, as well as for Zn(II) diluted samples. Within this series a change in the spectral pattern in the 320–500 cm^{-1} region is observed involving the decrease of the intensities of a band at $\sim 320 \text{ cm}^{-1}$ and those over 400 cm^{-1} as the molar fraction of the low-spin centres decreases. On the basis of the DFT calculations (B3LYP/CEP-31G) this effect is interpreted in terms of vibrational coupling of the iron centres of the same spin.

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

1 Introduction

The cooperativity of the spin transition in spin crossover (SCO) materials which determines the strength of hysteresis during SCO [1–3] is a key property required for their application

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in future electronics [4]. The established theoretical models of the SCO phenomenon [5, 6] underline the importance of the elastic properties and imply different interactions between centres of the same and between centres of different spin. Particularly, for the iron(II) containing polymeric complexes involving rigid bridging ligands like aminotriazoles the short-range interactions between the nearest neighbours seem to be crucial for the observed cooperative hysteresis effects [7, 8]. The influence of different spin states between neighbours in such systems should result in a change of their iron-ligand bond distances, which is in principle, observable by means of vibrational spectroscopies. Nevertheless, to the best of our knowledge, probably due to paucity of the far-IR data and limitations of the Raman spectroscopy as applied for SCO systems [9] no experimental evidence of such effect has been reported yet. As we have shown recently the nuclear inelastic scattering (NIS) signature of a SCO polymer, based on 4-amino-1,2,4-triazole (ATZ) complexes, displays a significantly larger number of bands as compared to those obtained by Raman spectroscopy [10, 11]. It has been shown that the NIS signature of the above mentioned SCO polymer is independent on the nature of anion and could be reproduced well by DFT calculations. Here we present a NIS investigation of a series of three $[\text{Fe}(\text{ATZ})_3]\text{X}_2$ compounds with $\text{X} =$ methanesulphonate, tosylate, perchlorate in order to explore selectively the influence of neighboring HS sites on a given LS site and its vibrational properties. The observed spectral effects are interpreted by means of density functional theory calculations.

2 Materials and methods

The complexes under study were the methanesulphonate (**1**), tosylate (**2**), and metal—diluted methanesulphonate (10 % of iron and 90 % of zinc) (**3**) salts of the $[\text{}^{57}\text{Fe}(\text{ATZ})_3]^{+2}$ complex. Sample (**1**) and (**2**) were prepared as described in [10, 11], respectively. (**3**) was prepared analogously to (**1**), using a 1:9 mixture of $^{57}\text{Fe}/\text{Zn}$ metanosulphonates. NIS was performed at the Nuclear Resonance Beamline ID 18 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (see [11] for details) and at P01, PETRA III, DESY in Hamburg, Germany. The storage ring PETRA III was operated in 40 bunch mode with a bunch separation of 192 ns. DFT calculations were performed as described in [11], using a pentanuclear model system with full charge compensation.

3 Results and discussion

The partial density of states (PDOS) has been obtained for (**1**) at 80 K (Fig. 1a), for (**2**) at 273 K (Fig. 1b) and for (**3**) at 80 K (Fig. 1c). Since the SCO for (**1**) and (**2**) occurs at ca. 293 K (with hysteresis), the PDOS shown in Fig. 1a is characteristic for a $[\text{Fe}(\text{ATZ})_3]^{+2}$ polymer with all iron sites being in the LS state and the PDOS shown in Fig. 1b reflects a $[\text{Fe}(\text{ATZ})_3]^{+2}$ polymer with $\sim 50\%$ HS iron sites and $\sim 50\%$ LS iron sites. The PDOS of (**3**) shown in Fig. 1c is characteristic for a situation where $\sim 50\%$ of the NIS visible ^{57}Fe sites are in the LS state and $\sim 50\%$ in the HS state, but these sites are separated from each other by the diamagnetic Zn(II) ions which act as NIS silent models of HS sites [1–3]. The conventional Mössbauer spectrum of (**1**) is shown in Fig. 2 and confirms its LS state at 80 K. For complex (**2**) at 273 K (Fig. 2b) and for complex (**3**) at 80 K (Fig. 2c) a relative area of ~ 1 is obtained from simulation using Lorentzian line shape. We note that for a more exact determination of the LS/HS ratio an analysis using the transmission integral formalism is required. But this is beyond the scope of this communication.

Fig. 1 **a** Experimental PDOS of (1) obtained at 80 K, of (2) at 273 K **b**) and of (3) at 80 K

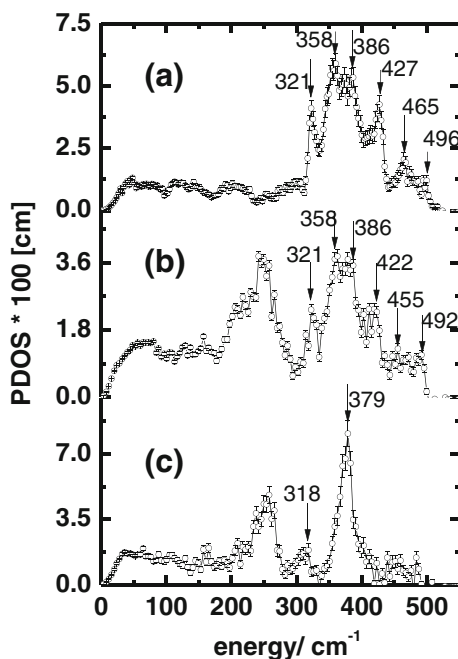
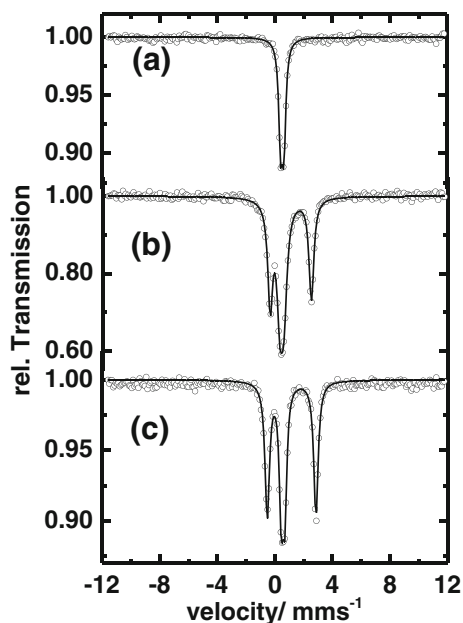


Fig. 2 Mössbauer spectra of (1) obtained at 80 K, of (2) at 273 K **(b)** and of (3) at 80 K. The *solid line* in **(a)** represents a Lorentzian fit yielding $\delta_{LS} = 0.52 \text{ mms}^{-1}$ and $\Delta E_{QLS} = 0.23 \text{ mms}^{-1}$ with $\Gamma_{LS} = 0.3 \text{ mms}^{-1}$. The *solid line* in **(b)** represents a Lorentzian fit yielding $\delta_{LS} = 0.45 \text{ mms}^{-1}$, $\Delta E_{QLS} = 0.28 \text{ mms}^{-1}$ with $\Gamma_{LS} = 0.5 \text{ mms}^{-1}$ (55 % rel. area) and $\delta_{HS} = 1.07 \text{ mms}^{-1}$, $\Delta E_{QHS} = 2.86 \text{ mms}^{-1}$ with $\Gamma_{HS} = 0.4 \text{ mms}^{-1}$ (45 % rel. area). The *solid line* in **(c)** represents a Lorentzian fit yielding $\delta_{LS} = 0.57 \text{ mms}^{-1}$, $\Delta E_{QLS} = 0.25 \text{ mms}^{-1}$ with $\Gamma_{LS} = 0.3 \text{ mm/s}$ (44 % rel. area) and $\delta_{HS} = 1.16 \text{ mms}^{-1}$, $\Delta E_{QHS} = 3.38 \text{ mms}^{-1}$ with $\Gamma_{HS} = 0.4 \text{ mms}^{-1}$ (56 % rel. area)



The inspection of Fig. 1 leads to the conclusion that the most prominent changes of the LS spectral pattern of the NIS data of (1), (2) and (3) concern a band at $\sim 320 \text{ cm}^{-1}$ which is well observable in the PDOS of (1) but loses intensity in the PDOS of (2) and almost diminishes in the Zn(II) diluted sample (3). The same trend is observed with respect to

Fig. 3 Calculated (DFT) summarized PDOS of three inner central iron atom in pentameric model molecules $[\text{Fe}_5(\text{ATZ})_{12}(\text{H}_2\text{O})_6]_2\text{Cl}_{10}$, revealing LS central Fe(II) atom with two LS (HLLH), one LS and one HS (HLLHH) and two HS (HHLHH) neighbours, respectively

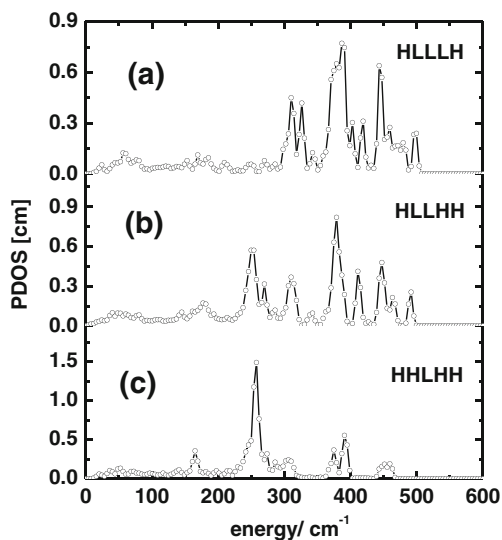
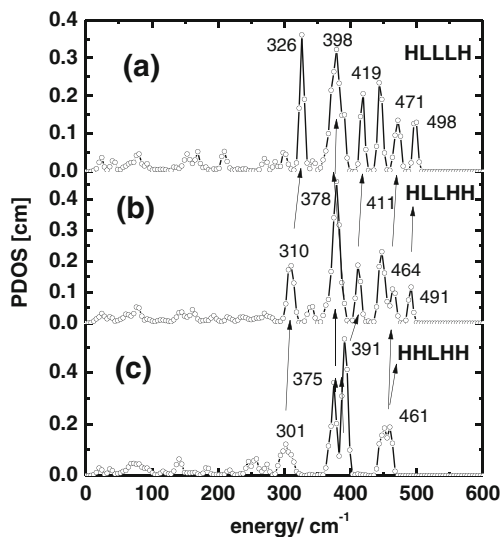


Fig. 4 Calculated (DFT) PDOS of the central LS iron atom in pentameric model molecules $[\text{Fe}_5(\text{ATZ})_{12}(\text{H}_2\text{O})_6]_2\text{Cl}_{10}$, revealing two LS (HLLH), one LS and one HS (HLLHH) and two HS (HHLHH) neighbours, respectively



bands in the region between 400 and 500 cm^{-1} . These changes are concomitant with the decreasing probability that a LS centre has LS neighbours on going from (1) to (3) in the 1D polymer series.

In order to verify this effect the PDOS of selected molecular units has been calculated via DFT and subsequent normal mode analysis. Figure 3 shows the calculated PDOS of the inner LS-LS-LS (Fig. 3a), LS-LS-HS (Fig. 3b) and HS-LS-HS units (Fig. 3c) of the pentameric model displayed in Fig. 4 with two outer centres always kept in the HS state, cf. [10, 11]. In order to explore the vibrational properties of a single LS centre as a function of neighbour spin states the corresponding calculated PDOS of a single LS unit for the configurations mentioned above have been obtained (see Fig. 4.)

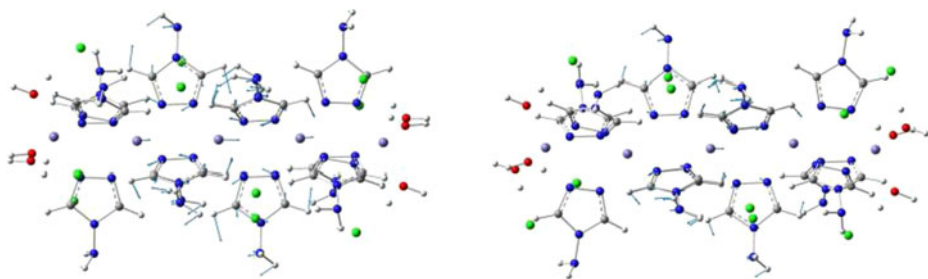


Fig. 5 *Left*: calculated vibrational mode (498 cm^{-1}) of the pentameric model molecule HLLLH. *Right*: calculated vibrational mode (465 cm^{-1}) of the pentameric model molecule HLLLH. Note the shift of the frequency, lack of movement of the HS neighbours and the decreases amplitude for the central LS iron. The same pattern is observed for the band predicted a 321 cm^{-1} (Movies of these calculated vibrations are given as Supplementary material)

The calculated PDOS of the central LS unit of HLLLH (Fig. 4a) shows a strong band at 326 cm^{-1} which loses intensity and shifts to 310 cm^{-1} for the central LS of a HLLHH configuration. This effect is even more pronounced for the HHLHH configuration (Fig. 4c) where this mode shifts to 301 cm^{-1} with again a decrease in intensity compared to the HLLHH configuration.

The analysis of all calculated modes shows that those modes which have significant Fe-N stretching character involve movement of all three iron centers in the LLL unit. If the neighbours of the LS center have different spin (e.g. in the LLH or HLH unit) these modes are localized and involve only the central Fe-center (see Fig. 5 and [Supplementary Materials](#)). Both, the experimental PDOS (Fig. 1) and the calculated PDOS of the central LS unit show that this decoupling of the iron movements has two consequences: (i) a slight down shift in the order of some wavenumbers of the corresponding mode as evident from Figs. 1 and 3, and (ii) a decrease of the band intensities in both the experimental and the calculated PDOS, which from the calculation can be attributed to a decrease of the movement of the iron atoms.

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