Hyperfine Interactions

Nuclear Inelastic Scattering Studies of a 1D- Polynuclear Spin Crossover Complex of Fe(II) Urea-Triazoles
--Manuscript Draft--

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Nuclear Inelastic Scattering Studies of a 1D-Polynuclear Spin Crossover Complex of Fe(II) Urea-Triazoles

J.A.Wolny[1], S. Sakshath[1], K. Jenni[1], L. Scherthan[1], H. Auerbach[1], H.-C. Wille[2], A.-M. Li[3], C. von Malotki[3], E. Rentschler[3], V. Schünemann[1]

[1]*Department of Physics, University of Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern, Germany*
[2]*DESY, Notkestraße 85, 22607 Hamburg, Germany*
[3]*Institute of Inorganic and Analytical of Chemistry, University of Mainz, D-55099 Mainz, Germany*

+49 631 205 40 50

+49 631 205 49 58

wolny@rhrk.uni-kl.de

Abstract The partial density of vibrational states (pDOS) of the low-spin isomer of the tosylate salt of [Fe{(N-Propyl)-N'-(1,2,4-triazole-4-yl-urea)}$_3$]$^{2+}$ was determined by nuclear inelastic scattering experiments performed at 8 K. The pDOS features a rich band structure from 320 to 500 cm^{-1} characteristic for the low spin state of the complex. Density functional theory calculations (B3LYP/CEP-31G) were used to assign molecular modes to experimentally observed bands in the pDOS.

Key words *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] is a key property required for their application in future electronics [2]. The established theoretical models of the SCO phenomenon [3] underline the importance of the elastic properties of the spin crossover materials, that themselves are related to the interactions between the spin centres, reflected in the vibrational pattern. Therefore, as first proposed by Kahn et al. [4] the polynuclear spin crossover systems in which the spin switching iron atoms are linked by a system of covalent bonds are of special interest. In this regard, the following question arises: How the vibrational and hence the elastic properties of a given spin crossover material depend on its dimensionality? A strategy to answer this question, is to study both one-

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dimensional (1D) and three-dimensional (3D) networks for the same coordination core of a SCO complex. This is a synthetic challenge, but nevertheless Rentschler and Malotki [5] reported that by using differently N-urea substituted triazoles it is possible to obtain not only the 1D chains, typical for the triazole Fe(II) systems, but also 3D networks. We here report first results of the study of the vibrational properties of the 1D complex [Fe{(N-Propyl)-N'-(1,2,4-triazole-4-yl-urea)}$_3$](tosylate)$_2$ (denoted as [Fe(n-Protrzu)$_3$(tos)$_2$, (**1**)) using nuclear inelastic scattering and accompanying density function theory calculations.

2 Materials and methods

The complex under study was prepared with 98% ^{57}Fe enrichment, following the method described in ref [5]. Nuclear inelastic scattering (NIS) and nuclear forward scattering (NFS) spectra were recorded at the Dynamics Beamline P01 at Petra III, DESY in Hamburg, Germany [6]. This beamline has a two-step monochromatisation. The first step is performed with a Si(111) double-crystal monochromator which renders a bandwidth of approximately 2 eV to the incident beam. The following high-resolution monochromator (HRM) decreases the bandwidth of the incident beam down to 1 meV. This beam is used to excite the 14.4125 keV level of the ^{57}Fe nuclei in the sample. The excited nuclear state with a lifetime of 141 ns decays to the ground state by emitting conversion electrons with a probability of 90 %. The subsequent 6.4 keV K-fluorescence radiation, which is delayed compared to electronic scattering, is measured with fast avalanche photodiodes (APD) with a time-resolution of 1 ns. NIS and NFS measurements of the sample were taken at 8 K using a helium closed-cycle-cryostat. Mössbauer spectra were measured in the 77-320 K area by means of an Oxford cryostat and a Wissel Electronics spectrometer. Density functional theory (DFT) calculations were performed with the Gaussian 09 software using the ONIOM method in which most of the atoms are calculated with the functional B3LYP and the basis set CEP-31G.. The n-propyl groups on urea fragments were modelled via MM2 molecular mechanics using the Universal Force Field method (see the ref [7] for more detailed discussion). Similar to our previous studies ([8] and references therein), the low-spin 1D chain was modelled with a heptanuclear molecule

[(OH$_2$)$_3$ Fe(n-Protrzu)$_3$[Fe(n-Protrzu)$_3$]$_5$(n-Protrzu)$_3$Fe(H$_2$O)$_3$](BF$_4$)$_{14}$(H$_2$O)$_3$], shown in Figure 1. The geometry of the molecule was optimized and the normal coordinate analysis was performed, which was used for calculation of the phonon density of states (pDOS).
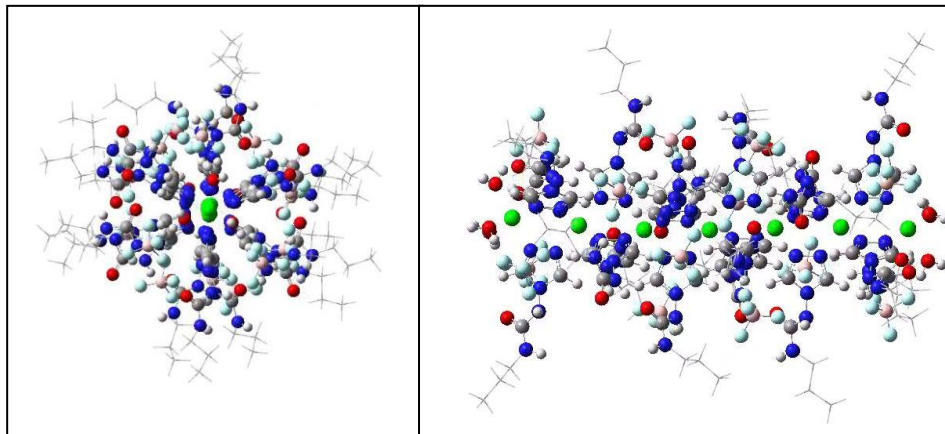

Figure 1 Model molecule of the complex **1** used in DFT calculations shown along the 1D axis (left) and perpendicular to it (right). For the simulations shown in Fig. 3 the atoms depicted as coloured balls were treated with DFT. The n-propyl group shown as framework were calculated with Molecular Mechanics. Fe atoms are shown in green, N atoms in dark blue, O in red, C in dark grey and H in pale grey.

3 Results and discussion

Mössbauer spectra of **1** are shown in Figure 2 indicating the presence of ca. 20 % of the high-spin (HS) isomer in the temperature range 78-270 K with a rapid increase above 270 K. Therefore, the NIS experiments were performed at 8 K in order to have the sample in a predominantly low-spin (LS) state. Indeed, the NFS spectrum shows also a beat pattern caused by the superposition of the contribution from LS and HS phases. However, the corresponding simulation reveals that only about 4.5% of the iron centers are in the HS state. The experimental pattern has been simulated by taking into account a variation of the effective thickness (varied from 20 to 120), caused by the powder sample. In this way quadrupole splittings of ΔE_Q^{HS}= 3.4 ± 0.05 mm/s and ΔE_Q^{LS}= 0.5 ± 0.05 mm/s were obtained.

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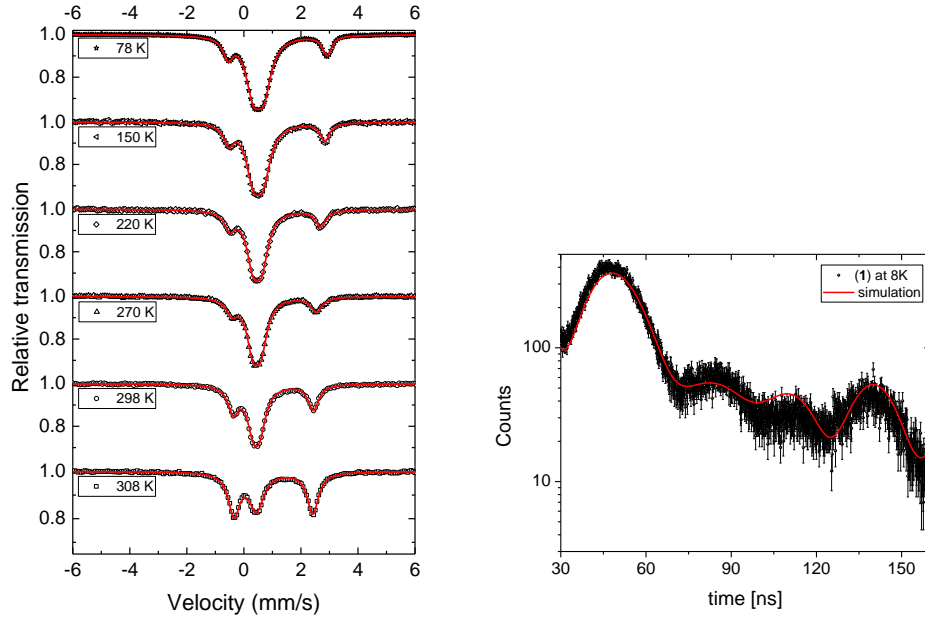
Figure 2. Left: Mössbauer spectra of **1** obtained at T = 78, 150, 220, 270, 298 and 308 K. The solid lines represent Lorentzian fits to the data with parameters listed in Table 1. Right: NFS spectra of the complex 1 at 8 K (black spheres) and simulation (red continuous line) performed using the CONUSS program, yielding a HS fraction of 4.5 ± 0.3% with parameters mentioned in the text.

T (K)	δ^{LS} (mm/s)	δ^{HS} (mm/s)	ΔE_Q^{LS} (mm/s)	ΔE_Q^{HS} (mm/s)	Relative HS area (%)
78	0.51	1.18	0.37	3.47	19.6
150	0.50	1.16	0.34	3.37	19.7
220	0.47	1.10	0.31	3.18	22.6
270	0.45	1.07	0.29	2.96	23
298	0.44	1.04	0.23	2.80	37.8
308	0.44	1.04	0.10	2.76	63.6

Table 1. Parameters obtained from the Lorentzian analysis shown as red solid lines in Figure 2 (left). The superscripts refer to the LS and HS phases.

The results of the NIS experiments are shown in Figure 3. The first inspection of the experimental pDOS of **1** (Fig. 3b) reveals a clear difference compared to the pDOS of the

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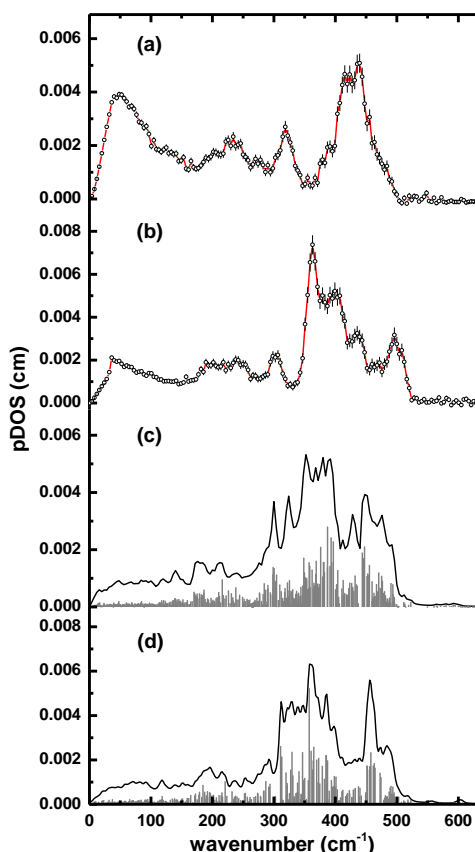
Figure 3. Experimental pDOS of **1** at 8 K (b) shown in comparison with the experimental pDOS of the related [Fe(trzH)$_2$(trz$^-$)](BF$_4$)$_2$ triazole complex (a) ([8], [9]).]). (c) DFT calculated pDOS for the model molecule using the ONIOM method. (d) pDOS calculated using a model molecule in which the n-propyl substituents on urea were replaced with hydrogen. It should be noted that for the simulations only the five inner iron centres were taken into account.

related [Fe(trzH)$_2$(trz$^-$)](BF$_4$)$_2$ complex (Fig. 3a). The spectra indicate that the substitution of triazole with N-substituted urea brings about the distribution of the normal vibrations involving Fe movement to a significantly broader area along with a concomitant shift of the maximum of the pDOS band structure towards lower frequencies. The influence of the n-propyl chains on the vibrational pattern is also seen in the results of the DFT modelling. The calculated pDOS (Fig. 3c) for the model shown in Figure 1 yields a much different pattern of the Fe-involving vibrations compared to the smaller model in which no n-propyl groups were modelled (Fig 3d). In the following, we discuss the experimentally obtained vibrational pattern with respect to DFT calculations for the model involving the n-propyl groups. The band in the experimental pDOS with maxima at ca. 360 and 405 cm^{-1} may be ascribed to the vibrational modes predicted to occur in the 350-395 cm^{-1} region. The predicted maxima around 380 and 395 cm^{-1} are due to

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vibrations that involve the Fe-N stretching along and normal to the long axis of the molecule, coupled with the movement of triazole rings and stretching and bending of the urea fragment (see Fig 4a and 4b, respectively). A significant admixture of the movements of some n-propyl groups as a whole is also observed. The band at 438 cm^{-1} may be assigned to the modes predicted at 430-450 cm^{-1} that are similar to the described above with the iron atoms moving only normal to the long axis of the molecule (see Fig 4c). The band observed at 497 cm^{-1} may be due to vibrations predicted at 470-498 cm^{-1} which involve Fe-N stretching along the long axis of the chains, again coupled to the above-mentioned vibrations of the triazole and deformation of the urea fragments (see Fig 4d). Our results suggest that, contrary to the previously investigated triazolato- and aminotriazole 1D systems [8-9], complex **1** reveals a somewhat larger elasticity of the polymer chain towards deformations perpendicular to its 1D axis than along it.

In summary this study shows that in iron(II) azole containing SCO polymers the substitution of the N-4 triazole atom with a long n-propyl-urea chain has an effect on the vibrational bands involving iron ligand modes. This can be related to a different elasticity of the compound induced by a more bulky and flexible ligand environment like that of an n-propyl urea chain.
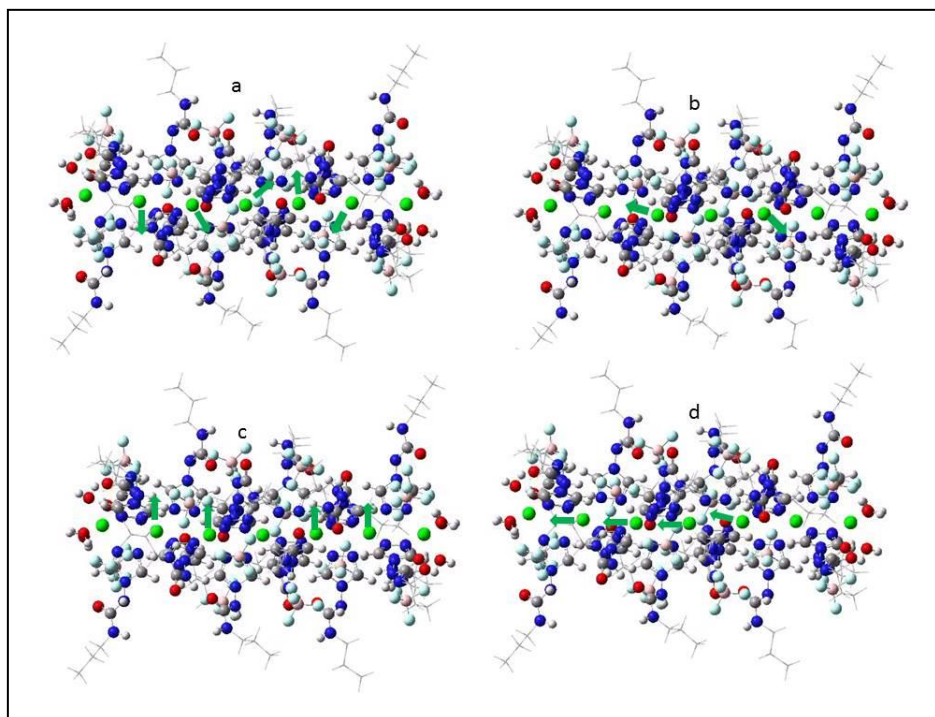
Figure 4. Calculated (ONIOM:B3LYP/CEP-31G/UFF) vibrations of the model molecule of **1**, predicted at 382 (a), 391 (b), 447 (c) and 493 (d) cm^{-1}, respectively. The green arrows depict the

mode of movement of iron atoms of significant amplitude. The GIF movies of the vibrations are given as Supplementary Materials.

Supplementary materials. GIF movies showing the discussed predicted vibrations for **1, the numer in the name of GIF file denotes the calculated vibration energy in cm^{-1}**. Gaussian 09 reference.

Acknowledgment
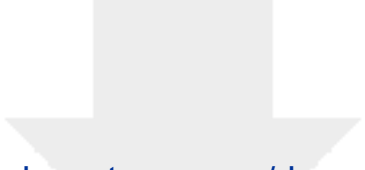
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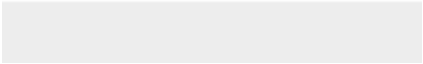
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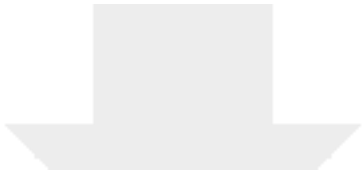
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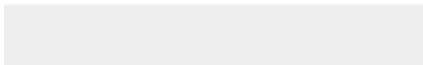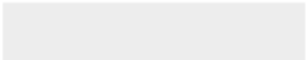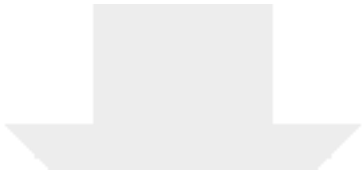
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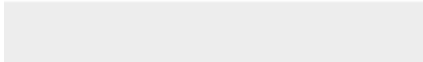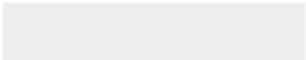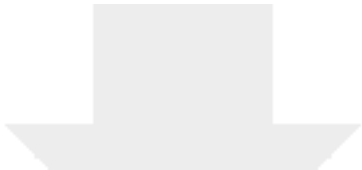
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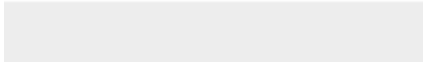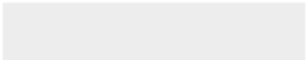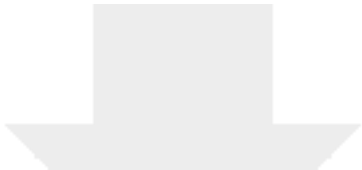**Supplementary Material**
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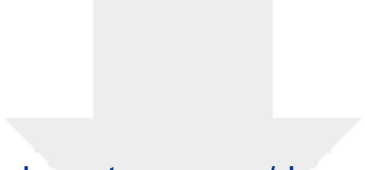Click here to access/download
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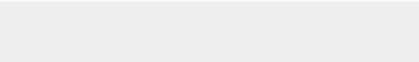
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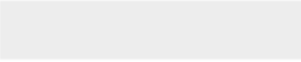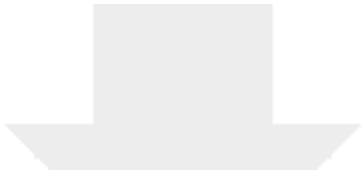**Supplementary Material**
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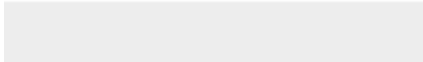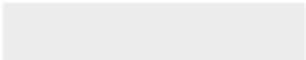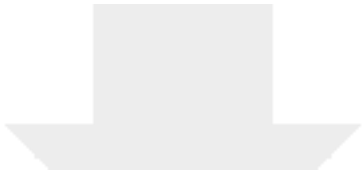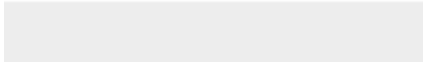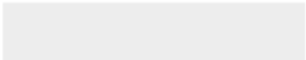
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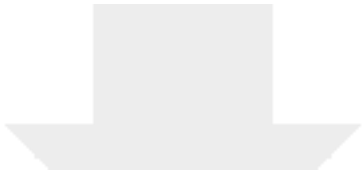Click here to access/download
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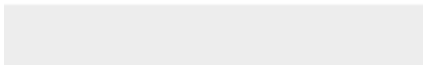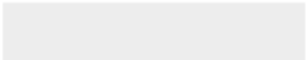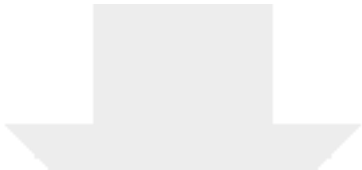**Supplementary Material**
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