



Vibrational properties of the mononuclear Fe[HBpz₃]₂ spin crossover complex

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Abstract

Within this work, we report the results of nuclear inelastic scattering experiments of the low-spin phase of the iron(II) mononuclear SCO complex Fe[HBpz₃]₂ and density functional theory based calculations performed on a model molecule of the complex. We show that the calculated partial density of vibrational states based on the structure of a single iron(II) center which is linked by three pyrazole rings to borat is in good accordance with the experimentally obtained ⁵⁷Fe-pDOS and assign the molecular vibrations to the prominent optical phonons.

Keywords Spin crossover · Nuclear inelastic scattering · Density functional theory

1 Introduction

The spin crossover (SCO) phenomenon refers to a reversible spin crossover (SCO) transition between the colored low-spin state (LS) and the typically colorless high-spin state (HS) in some materials based on 3d⁴ – 3d⁷ transition metal complexes. The spin transition can be triggered upon external stimuli like temperature, pressure or illumination with light. SCO materials display the properties for novel potential applications such as contrast agents [1], temperature/pressure threshold indicators [2, 3] and memory devices [4–6]. Iron(II) complexes with tris(pyrazolyl)methane or tris(pyrazole)borate ligands are promising classes of SCO compounds due to their relatively simple synthesis and almost endless possibility for modifications to tune the SCO properties [7, 8].

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This work focuses on the SCO compound $\text{Fe}[\text{HBpz}_3]_2$ which was studied at low temperature by nuclear inelastic scattering (NIS) experiments. In addition, simulations based on density functional theory (DFT) calculations on a model molecule are presented which permits the assignment of molecule vibrations to the vibrational modes observed by nuclear inelastic scattering.

2 Material and methods

The SCO compound $\text{Fe}[\text{HBpz}_3]_2$ (**1**) was synthesized as given in [9].

The ^{57}Fe NIS experiments were conducted in 40 bunch mode with a bunch separation of 192 ns at the Dynamics Beamline P01, DESY in Hamburg. The synchrotron beam was monochromatized to the 14.4125 keV nuclear resonance transition energy with a bandwidth of ca. 1.5 meV using a two-step monochromatization setup. Cooling of the powder samples to $T = 4.2$ K was performed by a dedicated cryostat from Janis Research. The NIS data were collected during several scans within the energy range of -20 to 80 meV with a 0.25 meV step size with an avalanche photodiode. The experimentally determined partial density of vibrational states (pDOS) was calculated with a binning of 0.5 meV. The evaluation of the NIS data was performed using the software *isdos2019*. The temperature of the sample was regulated with a dedicated cryostat (Janis Research).

The DFT calculations were conducted using the B3LYP [10] density functional and the cep-31G [11] basis set.

3 Results and discussion

Figure 1a displays the experimental ^{57}Fe -partial phonon density of states (pDOS) of the bulk powder of **1** recorded at $T = 4.2$ K. The pDOS depicts a broad vibrational multiband between 320 and 370 cm^{-1} . Two maxima with comparable intensity are located at 329 and 355 cm^{-1} . Furthermore, two multibands with high intensity are observed at 407 and

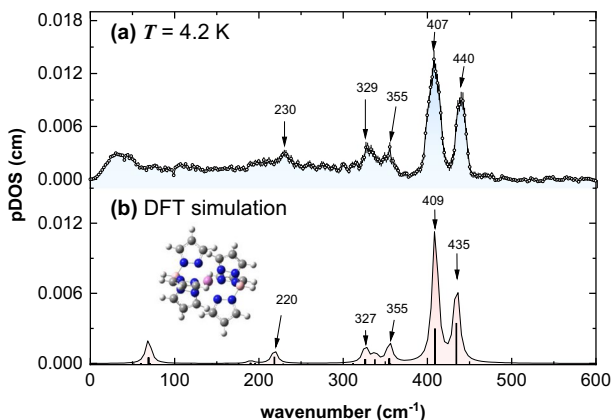


Fig. 1 **a** ^{57}Fe pDOS of bulk powder of **1** obtained at 4.2 K. **b** Calculated pDOS based on the depicted model molecule of **1** in the LS state ($S = 0$)

Table 1 Lamb-Mössbauer factor f_{LM} , thermodynamic parameters and mean force constant D extracted from the experimental ^{57}Fe -pDOS shown in Fig. 2

θ_D (K)	v_m (km·s $^{-1}$)	f_{LM}	D (N·m $^{-1}$)	c_v (k $_B$)	S (k $_B$)
63.46(1)	3.3(1)	0.89(1)	331(7)	0.01(1)	0.004(1)

440 cm^{-1} . The multiband at 407 cm^{-1} has the highest intensity in the pDOS. Moreover, a broad vibrational multiband with its maximum located at 230 cm^{-1} in the pDOS is identified between 200 and 240 cm^{-1} . Typically, vibrations above 300 cm^{-1} are reported to be characteristic of the LS configuration of a spin crossover complex [12]. Thus, the experimental pDOS suggests that the spin crossover is in the LS state due to the very intense vibrational multibands in this energy region.

Furthermore, Table 1 displays the thermodynamic parameters extracted from the NIS data of the bulk powder of **1** recorded at 4.2 K. According to the analysis, the Lamb-Mössbauer f_{LM} is 0.89, the mean force constant D is 331 Nm^{-1} and the Debye temperature θ_D is 63.46 K. Additionally, the specific heat c_v is calculated to be 0.01 k_B , the entropy S is 0.004 k_B and the sound velocity v_m is 3.3 kms^{-1} .

In addition to the experimental ^{57}Fe -pDOS, Fig. 1b contains the simulated Fe-pDOS obtained by performing normal mode analysis on the depicted model molecule in the LS state. The model molecule consists of a single iron(II) center which is linked by three pyrazole rings to borat on two sides. This iron(II) center in the LS state was used for the calculation of the theoretical pDOS. The simulated pDOS yields multibands at 220, 327, 355, 409 and 435 cm^{-1} . Generally, the simulation reproduced the experimental ^{57}Fe -pDOS very well with minor deviations of up to 10 cm^{-1} of the position of the multibands between

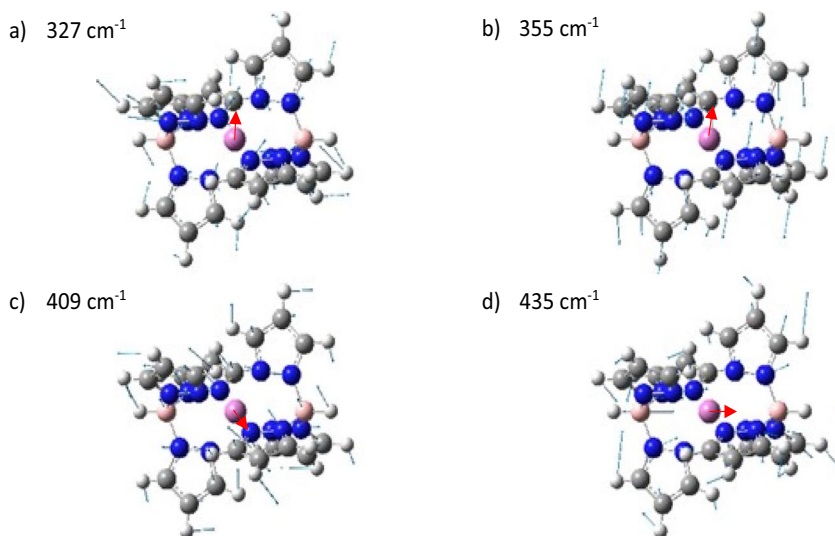


Fig. 2 Graphical representation of the vibrational bands at (a) 327 cm^{-1} , (b) 355 cm^{-1} , (c) 409 cm^{-1} and (d) 435 cm^{-1} . The Fe displacements are highlighted as red arrows. The color of atoms corresponds to the following elements: Fe = pink, B = light pink, N = blue, C = gray, H = white. For better visualization see movies in ESI

experiment and simulation. Both pDOS reveal the maximum with the highest intensity at ca. 407 cm^{-1} and a further maximum with high intensity at 435 cm^{-1} . Moreover, both pDOS show a broad vibrational multiband between ca. 320 and 370 cm^{-1} with two maxima at ca. 329 and 355 cm^{-1} and a vibrational mode at ca. 230 cm^{-1} . The shape of the experimental vibrational pattern is reproduced almost flawlessly by the simulated pDOS.

Due to the good match of the experimental and simulated pDOS, an assignment of the observed experimental modes to vibrations is possible. Figure 2 shows the vibrations assigned to the modes observed at 327 , 355 , 407 and 440 cm^{-1} in the simulated spectra. The four vibrations display a noticeable displacement of the central iron(II) center in different directions. The mode at 327 cm^{-1} mainly involves the rotation of the pyrazole rings without any expansion or shrinking of the molecule and the iron center moves perpendicular to the B-Fe-B chain. In contrast, the mode at 355 cm^{-1} is attributed to an antiphase movement of the opposite pyrazole rings in opposite direction and a movement of the iron center perpendicular to the B-Fe-B chain. Thus, the molecule continuously shrinks and expands. Furthermore, the mode at 409 cm^{-1} shows rotations of the pyrazole ligands perpendicular to the rings without expansion of the molecule. The central iron center oscillates perpendicular to the B-Fe-B chain. Lastly, the mode at 435 cm^{-1} displays rotations of the pyrazole ligands along with the pyrazole rings. Moreover, the iron center vibrates along the B-Fe-B chain.

4 Conclusion

In conclusion, we report the ^{57}Fe -pDOS of this SCO complex at 4.2 K as well as the thermodynamical parameters which were extracted from the experimental NIS data. Furthermore, we show that theoretical DFT simulations based on one molecule of this SCO complex reproduce the experimental data well and illustrate the vibrations assigned to the experimental vibrational modes.

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