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Spin- and phase transition in the spin crossover complex $[Fe(ptz)_6](BF_4)_2$ studied by nuclear inelastic scattering of synchrotron radiation and by DFT calculations

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Abstract

Nuclear inelastic scattering (NIS) spectra of $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-*n*-propyl-tetrazole) have been measured for five phases differing in spin state and crystallographic structure. Different spectral patterns have been found for the low-spin and high-spin phases and are described in terms of normal coordinate analysis of the complex molecule. For both low-spin and high-spin phases the conversion from ordered to disordered phase results in splitting of the observed NIS bands. Packing becomes visible in the NIS spectra via coupling of the Fe–N stretching vibrations with those of the terminal *n*-propyl groups. The DFT-based normal coordinate analysis also reveals the character of Raman markers.

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1. Introduction

The phenomenon of temperature dependent spin crossover (SCO) [1,2] in transition metal complexes has attracted increasing attention after the discovery of the light-induced spin-state trapping (LIESST) [3]. This makes SCO complexes promising materials for optical storage and display devices and for pressure sensors. The driving force for the temperature dependent SCO is the entropy difference between the high-spin (HS) and the low-spin (LS) isomers, which arises mainly from a shift of the vibrational frequencies when passing from the HS to the LS state. This frequency shift has been studied by IR and Raman spectroscopy and recently by nuclear inelastic scattering (NIS) of synchrotron radiation [1,4,5]. The NIS method [6–8] is isotope (^{57}Fe) selective, and therefore its focus is on iron–ligand bond stretching vibrations, which exhibit the most prominent frequency shift upon SCO [5].

The tetrazole compound $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-*n*-propyl-tetrazole) is a fascinating SCO system, not only from the photophysical point of view, but also regarding the five different phases which result from LIESST and reverse LIESST processes [9,10]: (a) the phase above 110 K consists of HS molecules and has a high-temperature ordered structure with $R\bar{3}$ symmetry; (b) the super-cooled high-temperature ordered $R\bar{3}$ phase after rapid cooling (30 K/min) to <100 K consists of LS molecules; c) the

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phase below 50 K after rapid cooling and LIESST consists of metastable HS molecules in an R$\bar{3}$ lattice; (d) the phase below 110 K after annealing the sample from (c) to 110 K and subsequent slow cooling (1 K/min) consists of LS molecules with disordered structure; (e) the disordered HS phase is obtained by LIESST from the disordered low-spin phase as described in [10]. Morimoto et al. reported a sixth HS phase forming between 50 and 110 K by irradiation with a laser power above some critical value [11]. Recently, Mousa et al. reported the Raman studies of some of these phases, showing distinct markers of spin transitions and crystallographic order–disorder transitions [12].

We have performed NIS measurements of the title compound to observe changes in molecular vibrations, especially those involving iron–nitrogen stretching modes. Density functional theory (DFT) calculations were carried out to quantitatively describe these vibrations and their changes upon SCO. With the NIS spectra revealing the partial density of vibrational states (PDVS) of iron centres we were able to compare the PDVS from four different phases (b)–(e) at the same temperature of 10 K, i.e. phases that differ in both spin state and structural properties. Finally, it was of interest to find out whether the NIS PDVS could reveal spectral markers for crystallographic order-disorder changes.

2. Experimental

[^{57}Fe(ptz)$_6$](BF$_4$)$_2$ was prepared as described by Franke et al. [13], enriched in ^{57}Fe. The isotope was accessible by dissolving (over 2 weeks) 0.33 mmol of enriched metallic iron in 2 mmol of aqueous HBF$_4$ solution. Subsequently, 3 mmol of the ligand ptz, dissolved in 2 ml of water, was added. Half of the solvent was evaporated in a nitrogen stream for one week. The product was filtered off and washed with water, ethanol and diethyl ether, yielding about 35% of white crystalline powder. Elemental analysis and a measurement of its magnetic properties confirmed the purity of the sample.

The NIS experiments were performed at beamline ID 18 at the ESRF in Grenoble, France [14,15]. The beamline setup was optimized for NIS measurements on ^{57}Fe with an energy resolution of about 0.5 meV. The sample was placed in a variable temperature cryostat, which allows measurements in the temperature range between 5 K and room temperature, with a temperature stability of 0.1 K in the whole range. It also allows a temperature change of 30 K per minute in the cooling process. The powder-like sample was fixed (by vacuum grease) on a 24 mm^2 area of the sample holder (copper) with an angle of 85° between the normal of this area and the synchrotron beam. The green (514 nm) laser light, used for illumination of the sample, was passed through a glass fibre and a quartz optical window. The divergent light emitted from the glass fibre was directed to the sample area at an angle of 45° for 1 h at 10 mW. The detector was placed directly beneath (3 mm) the sample, separated by a beryllium window of 250 μm thickness and an effective area of 1 cm^2 [16]. Data acquisition was performed in energy steps of 0.2 meV (1.6 cm^{-1}) and in multiple scan mode. The scanned energy range was from -40 up to $+90$ meV (-320 to 720 cm^{-1}) relative to the nuclear resonance energy of ^{57}Fe. The DFT calculations were performed for the optimized structures of both spin isomers of the cationic molecule [Fe(ptz)$_6$]$^{2+}$, using the B3LYP functional [17] with the CEP-31 G basis [18–20], as implemented in the GAUSSIAN03 programme package [21].

3. Results and discussion

The experimental PDVS of the five different phases, (a)–(e), are shown in Fig. 1. At 160 K a broad line at approximately 230 cm^{-1} is observed for the ordered R$\bar{3}$ HS phase (Fig. 1a). Fast cooling leads to the corresponding ordered R$\bar{3}$ LS phase, displaying a number of lines of different intensity in the range of 290–510 cm^{-1} (Fig. 1b). Irradiation with green light at 10 K yields the ordered R$\bar{3}$ HS phase, revealing a broad line at approximately 240 cm^{-1} (Fig. 1c). The LS isomer has disappeared completely upon irradiation. The observed shift towards lower

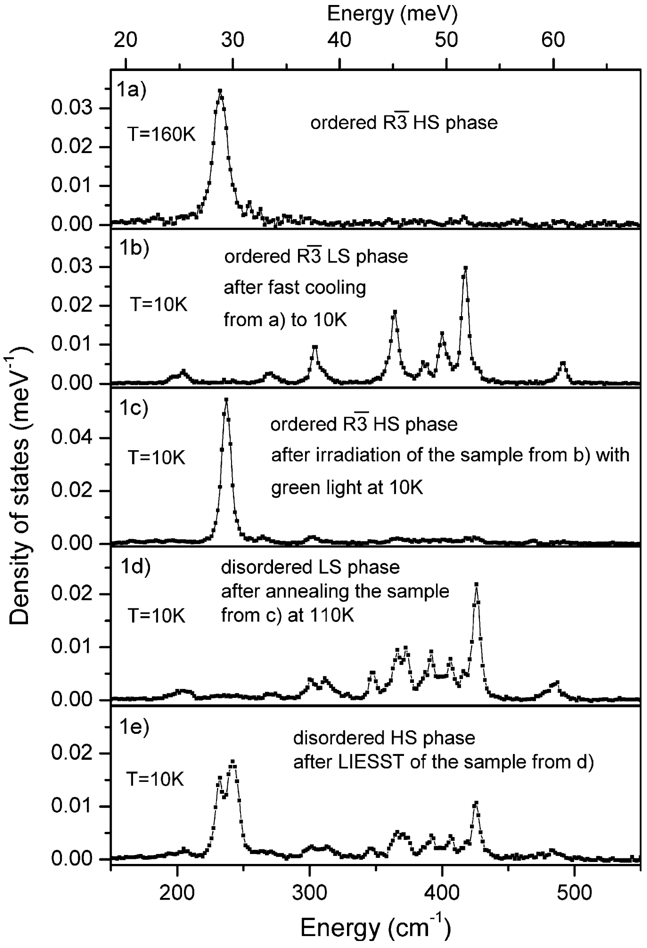

Fig. 1. Measured NIS PDVS for five different phases of [Fe(ptz)$_6$]$^{2+}$. Solid lines are a guide for the eye.