Pressure tuning Raman spectroscopy of the spin crossover coordination polymer

Fe(C$_5$H$_5$N)$_2$[Ni(CN)$_4$]

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Gábor Molnár[1], **Takafumi Kitazawa**[2], **Leonid Dubrovinsky**[3],
John J McGarvey[4] **and Azzedine Bousseksou**[1,5]

[1] Laboratoire de Chimie de Coordination, CNRS UPR-8241, 205 route de Narbonne,
F-31077 Toulouse, France
[2] Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi,
Chiba 274-8510, Japan
[3] Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany
[4] School of Chemistry, Queen's University Belfast, Belfast BT9 5AG, UK

E-mail: boussek@lcc-toulouse.fr

Abstract
We have observed a reversible high-spin to low-spin transition around 11 kbar at room temperature for the polymeric spin crossover complex $Fe(pyridine)_2[Ni(CN)_4]$ using high pressure Raman spectroscopy. The pressure dependence of vibrational frequencies in the two spin-states has been studied up to 50 kbar. The results suggest that the vibrational entropy change associated with the spin crossover is independent of pressure in this pressure range.

1. Introduction

Certain (pseudo)octahedral transition metal complexes are known to display a molecular bistability of high-spin (HS) and low-spin (LS) electron configurations, which are distinguished by different occupation of antibonding e_g and non-bonding t_{2g} d orbitals of the central metal ion [1]. The electronic ground state of these spin crossover complexes may be reversibly interchanged under external stimuli, such as temperature, pressure, magnetic field or light irradiation [1–4].

The thermally induced spin crossover takes place because the HS form has lower vibrational frequencies as well as higher electronic degeneracy than the lower energy LS form. This mechanism produces higher entropy (vibrational as well as electronic) in the HS state and therefore drives the thermal spin-state change [5]. The coupling of the electronic configuration to the vibrational modes arises due to the different volume of e_g and t_{2g} orbitals
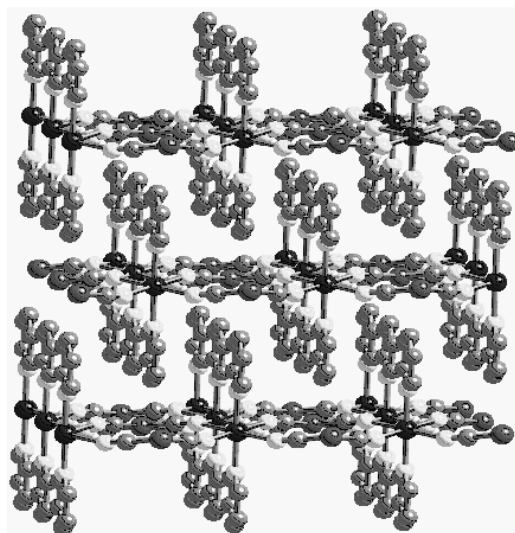
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[5] Author to whom any correspondence should be addressed.

Figure 1. Schematic structure of the compound Fe(pyridine)$_2$[Ni(CN)$_4$] in the HS phase.

of the central metal ion. Therefore, the vibrational modes most influenced by the spin-state change are the metal–ligand frequencies. This observation has been repeatedly confirmed by different experimental and theoretical methods [6–9].

The molecular spin crossover phenomenon is further influenced in the solid state by intermolecular interactions, which may give rise to a discontinuous, first-order phase transition accompanied by a hysteresis loop. Recently numerous efforts have been devoted to the design and study of such cooperative systems. One successful synthetic approach is based on the idea of replacing molecular crystals by polymers in which the active sites are linked to each other by chemical bridges allowing the propagation of strong interactions [10]. However, the number of such systems is still rather limited and the physics governing their properties is less explored than for molecular complexes.

In this context, we have recently started the study of a series of novel, isostructural iron(II) spin-crossover polymers of formulae Fe(pyrazine)[M(CN)$_4$]·2H$_2$O [11] and Fe(pyridine)$_2$[M(CN)$_4$] (M = Ni, Pd or Pt) [11, 12]. We recall briefly that the HS crystal structure[6] of the complexes consists of planar, polymeric sheets formed from square-planar M^{II}(CN)$_4$ ions bridged by six-coordinate Fe^{II} ions. The coordination of iron(II) is completed by two pyridine or pyrazine molecules in the trans position. In the 2D pyridine complexes (figure 1), the neighbouring layers are shifted by a symmetry operation of the monoclinic space group ($C2/m$), while the structure of the 3D pyrazine derivatives differs in that the bidentate pyrazine ligands bridge the iron atoms, thus no shift between the layers occurs and the space group is tetragonal ($P4/m$). The remarkable feature of these complexes is the high cooperativity of the spin transition induced by the network structure and associated with large thermal [11] and pressure [13] hysteresis loops. Moreover, the spin transition is accompanied by a marked colour change.

Our calorimetric and vibrational spectroscopic study on this family of complexes revealed intriguing vibrational features [7]. One concerns the vibrational entropy change (ΔS_{vib}) associated with the spin transition, which is very high (50–70 J K^{-1} mol^{-1}). The contributions

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[6] At present no LS crystal structure is available for these materials.

of different vibrational modes to ΔS_{vib} were analysed within the harmonic approximation. It was shown that the spin state change in these compounds influences not only the vibrations that can be described as Fe$^{\mathrm{II}}$–ligand modes, *but all other low-frequency modes of the network* (below about 600 cm^{-1}). It was concluded that these latter modes make non-negligible contributions to the entropy change accompanying the spin crossover. The reason behind this involves either coupling with the Fe$^{\mathrm{II}}$–ligand vibrations or with the lattice contraction/expansion that accompanies the spin transition [7].

In order to better understand the vibrational properties of these compounds we have decided to study the influence of isotope substitution and high pressure on the vibrational spectra. Isotope substitution enables the extent of vibrational mode couplings to be explored. The results of isotope substitution (pyridine-D$_5$ and pyridine-^{15}N) effects have already been published [14]. Remarkably, in the HS state only certain modes (at 130, 140 and 165 cm^{-1}) displayed isotope shifts, while in the LS state the isotope substitution influenced apparently all vibrational modes assigned to the polymeric sheet. In other words, the isotope effect on the vibrations appears to be more extensive in the LS state compared to the HS state. Therefore, we inferred that *the range of vibrational couplings is significantly different in the two spin states*.

An externally applied pressure provides a direct means to test the effects of lattice contraction on the vibrational modes. In the present paper, we report the effects of high pressure (up to 50 kbar) on the vibrational frequencies of Fe(pyridine)$_2$[Ni(CN)$_4$]. This compound was selected for the following reasons:

(i) Among the complexes of this family it has the lowest spin transition temperature ($\sim$202 K). Therefore one can study both the HS and LS phases over a reasonably large pressure range without the necessity of heating the sample. (The pyrazine complexes are already converted to the LS form at the onset of the pressurization at room temperature [13].)

(ii) This sample is well crystallized with small ($\sim$1 μm) grain size, which is perfectly compatible with the diamond anvil cell (DAC) technique. The other pyridine complexes consist of large grains and we could not establish hydrostatic conditions with these samples in the DAC. The usual technique of grinding cannot be applied because we have found that it destroys the spin crossover properties of these compounds.

2. Experimental details

The synthesis of polycrystalline Fe(pyridine)$_2$[Ni(CN)$_4$] was carried out as described previously [12]. The sample was characterized by elemental analysis, powder x-ray diffraction, IR spectroscopy, calorimetry, variable temperature Raman and Mössbauer spectroscopy and magnetic susceptibility measurements [14].

Variable pressure Raman spectra were collected at room temperature in the 150–1150 and 1550–2350 cm^{-1} frequency ranges for total accumulation times of 2000 s. (Between 1150 and 1550 cm^{-1} the spectra were obscured by Raman scattering form the diamond anvils.) The micro-Raman spectrometer (LabRam Dilor) we used consists of an optical microscope, a holographic notch filter, a single (1800 grooves mm^{-1}) grating spectrograph and a CCD detector. The entrance slit was kept at 120 μm and a spectral resolution of about 2 cm^{-1} was obtained. The 632.8 nm line of a 30 mW He–Ne laser was used as the excitation source. The exciting radiation was directed through a neutral density filter (optical density 0.6) to avoid sample decomposition problems and was focused on the sample via a 50$\times$, long working-distance objective. The scattered light was collected in a backscattering configuration, using the same microscope objective. The spectrometer was regularly calibrated to the 520.7 cm^{-1}
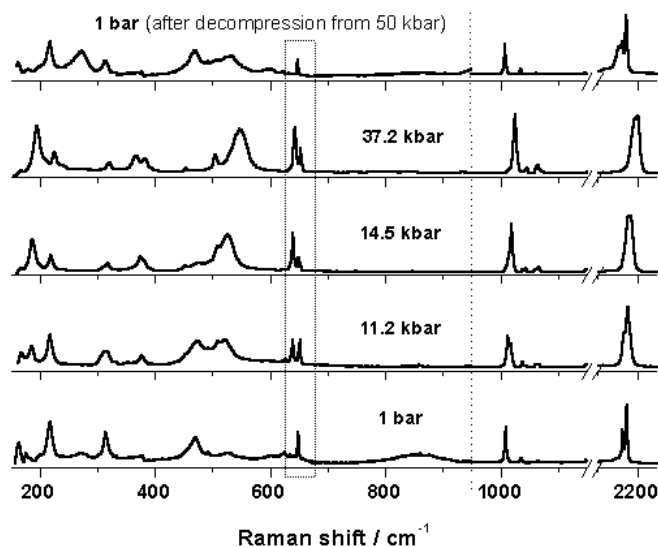
Figure 2. Selected Raman spectra of Fe(pyridine)$_2$[Ni(CN)$_4$] for different applied pressures at room temperature. Spectra below 950 cm^{-1} are expanded by a factor of five.

Si mode. The samples were pressurized using a symmetric 4-pin DAC equipped with type IIa diamonds with 600 μm flat culets. The sample and ruby chips (3–5 μm diameter) were loaded into a steel gasket hole ($\sim$300 μm diameter, 250 μm thick, indented to a thickness of 150 μm). It is convenient that this very soft sample can be used alone as a reasonably hydrostatic pressure-transmitting medium in the applied pressure range. Pressure in the DAC was determined by the ruby fluorescence method. We also checked possible pressure gradients and found that the pressure differences, if any, were within the precision of the ruby scale (10–15%).

3. Results and discussion

Selected Raman spectra of Fe(pyridine)$_2$[Ni(CN)$_4$] at different pressures are shown in figure 2. In the frequency range investigated, two main groups of Raman frequencies occur. Following our earlier assignments [14], these can be attributed to internal modes of pyridine (600–1700 cm^{-1}) and vibrations associated with the 2D polymeric sheet around 2150 cm^{-1} and below 600 cm^{-1}. These latter involve various coupled metal–ligand stretches and bendings as well as lattice modes.

The Raman band maxima were located by deconvolution analysis of the observed spectra for assumed Lorentzian line shapes. Plots of wavenumber versus pressure reveal discontinuities in the slope of the graph in the pressure range between about 6 and 14 kbar (figure 3). We explain these discontinuities by a pressure induced HS $\leftrightharpoons$ LS spin-crossover since the changes in the Raman spectra are similar to those observed previously for the temperature induced spin transition [14], with pronounced frequency changes occurring below 600 cm^{-1} and much smaller shifts above 600 cm^{-1}. The high-spin fraction (γ_{HS}) can be approximated as $\gamma_{HS} = I_{649}/(I_{649} + I_{639})$, where I_{649} and I_{639} are the intensities of the selected HS and LS marker bands, respectively. (It should be noted that the behaviour of this mode is singular in that it shifts to lower frequencies upon HS to LS crossover. However, it represents an excellent, well-resolved marker for the whole pressure range.) Figure 4 shows the variation of γ_{HS} as a function of pressure. Upon pressurization about 80% of HS Fe^{II} species could be transformed
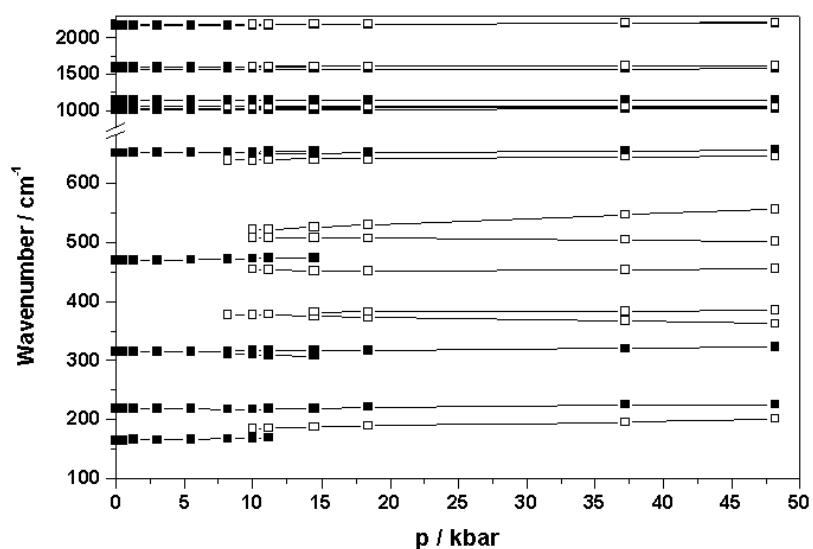
Figure 3. The pressure dependence of Raman frequencies in Fe(pyridine)$_2$[Ni(CN)$_4$]. Closed (open) symbols represent modes assigned to the HS (LS) phase. Lines are inserted to guide the eye.
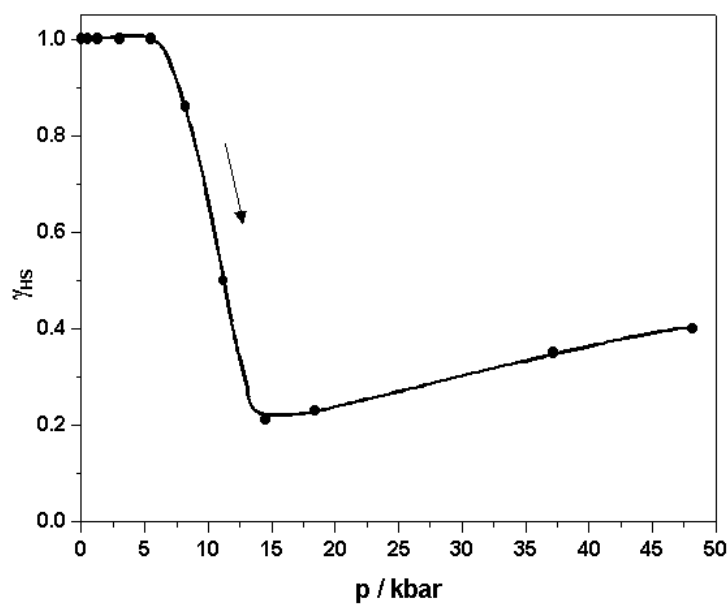

Figure 4. The pressure dependence of the HS fraction (γ_{HS}) in Fe(pyridine)$_2$[Ni(CN)$_4$]. The solid curve is drawn to guide the eye.

to the LS state with a characteristic spin crossover pressure of $p_{1/2} \cong 11(\pm 1)$ kbar, where $p_{1/2}$ is defined as the pressure for which $\gamma_{HS} = 1/2$. The pressure-induced spin crossover was found completely reversible, provided the samples were not compressed to pressures beyond about 25–30 kbar.

If pressure is increased further (up to 50 kbar), a reverse (LS $\rightarrow$ HS) transformation begins (figure 4). The formation of this new HS phase is irreversible, i.e. upon decompression the

Table 1. Zero-pressure frequencies, their tentative assignment (following [10]) and their pressure coefficients. Parameters were obtained from a linear fit to the experimental data.

Mode description	Phase	ω_0 (cm^{-1})	$d\omega/dp$ (cm^{-1} kbar^{-1})
ν_{FeN}	HS	163.8	0.39(5)
ν_{FeN}	LS	180.7	0.41(3)
ν_{FeN}	HS	217.2	Non-linear
δ_{NiCN}	HS	314.4	0.16(1)
δ_{NiCN}	HS	313.6	−0.43(5)
ν_{FeN}	LS	380.7	−0.38(2)
ν_{FeN}	LS	380.9	0.07(1)
δ_{NiCN}	LS	454	No reliable fit
ν_{CNi}	HS	469	0.31(2)
ν_{CNi}	LS	509.7	−0.15(1)
ν_{CNi}	LS	512.7	0.90(2)
δ_{ring}	LS	637.5	0.13(1)
δ_{ring}	HS	649.3	0.11(2)
ν_{ring}	HS	1009.1	0.34(2)
ν_{ring}	LS	1015.1	0.29(1)
ν_{ring}	HS	1036.6	0.15(1)
ν_{ring}	LS	1044.4	0.04(1)
δ_{CH}	HS	1064.3	−0.20(2)
δ_{CH}	LS	1067.2	−0.06(1)
δ_{CH}	HS/LS	1147.4	0.089(3)
ν_{ring}	HS/LS	1571.3	0.13(1)
ν_{ring}	HS	1600.5	0.31(2)
ν_{ring}	LS	1603.9	0.24(1)
ν_{CN}	HS	2162.8	No reliable fit
ν_{CN}	HS	2173.1	No reliable fit

original Raman spectra could not be restored. This finding is not unprecedented: several low-spin and spin crossover Fe(II) complexes have been converted to the HS state upon application of relatively high pressures [15]. Structural changes are considered to be the primary reason behind this, somewhat unexpected, phenomenon. In our case the Raman spectrum of this high-pressure HS phase is similar to that of the original HS phase, but some additional frequencies appear in the CN stretch region (around 2150 cm^{-1}) suggesting a symmetry lowering of the system (figure 2).

The above results also allow a rough estimation of the volume change associated with the spin transition (ΔV_{HL}) using the relation $dT_{1/2}/dp = \Delta V_{HL}/\Delta S_{HL}$ and the values of $T_{1/2}$ and ΔS_{HL} obtained at atmospheric pressure [14]. The calculated volume change ($\sim$10 Å^3) is reasonable though somewhat less than usually observed for Fe^{II} spin crossover complexes. A variable temperature and pressure study will be necessary to determine more precisely the (T, p) phase diagram.

The main motivation of the present work was to investigate the effect of externally applied pressure on the vibrational frequencies. This question has never been addressed experimentally although frequency shifts and the resulting entropy difference can be regarded as the driving force of the spin transition. In general the mode frequencies were found to change linearly with pressure except for the 217.7 cm^{-1} mode which is almost pressure independent up to $\sim$10 kbar but shows a frequency shift above this pressure. Table 1 reports the zero-pressure Raman mode frequencies (ω_0) for the HS and LS phases as well as their pressure coefficients

($\mathrm{d}\omega/\mathrm{d}p$), both obtained from linear fitting. Errors in the determination of the parameters in table 1 from the least-squares fits are typically around 0.2 cm^{-1} for ω_0, and 0.02 cm^{-1} kbar^{-1} for $\mathrm{d}\omega/\mathrm{d}p$. No reliable deconvolution could be obtained for the CN stretching modes under pressure; therefore pressure coefficients are not reported for these frequencies. In the HS phase below the onset of the phase transformation all Raman modes display normal positive pressure coefficients, except the 1064 cm^{-1} δ_{CH} mode. When the phase transition sets in, several low frequency modes show splittings in both phases (figure 3). The splitting of these modes has not been observed upon the temperature induced spin crossover and may be related to a symmetry lowering under externally applied pressure. Remarkably, one of these split modes shows in all cases a positive pressure coefficient while the other exhibits a negative coefficient. This behaviour, characteristic of soft modes, needs a detailed Landau description, which is beyond the scope of this paper.

Our interest is centred on the pressure effects on the vibrational entropy. The vibrational entropy change upon spin crossover can be estimated for an oscillator with frequency ω in the low-frequency approximation as: $\Delta S \cong R \ln(\omega^{\mathrm{LS}}/\omega^{\mathrm{HS}})$ [16]. The pressure shift of the Raman modes was found to be rather small (mostly between 0.1 and 0.4 cm^{-1} kbar^{-1}) up to 50 kbar (table 1). A clear separation between internal pyridine modes and low-frequency modes assigned to the polymeric sheet is not possible on the basis of the pressure coefficients. More importantly, no distinction between the HS and LS phases appear from the experimental pressure data. Then, taking into account the data of table 1 it appears that pressure effects on the entropy change are negligible and the usual assumption $\Delta S_{\mathrm{HL}}^{p} \cong \Delta S_{\mathrm{HL}}^{P\,\mathrm{atm}}$ is a good one at moderate applied pressures in this compound. It would be interesting, however, to extend this investigation to lower frequencies (<150 cm^{-1}) to get a more quantitative picture. Finally, we can note also that the internal pressure change that accompanies the spin transition [1] should not lead to a substantial variation in ΔS_{HL}, in so far as one can assume that internal and external pressure changes have a similar effect on the vibrational frequencies. Metal dilution experiments are in progress in order to gain further insight into the influence of internal pressure on the vibrational properties of these interesting spin crossover systems.

4. Conclusions

In conclusion, the results reported in this paper reveal a reversible pressure induced spin crossover in the compound Fe(pyridine)$_2$[Ni(CN)$_4$]. The high pressure Raman data suggest that the vibrational entropy change accompanying the spin crossover is not sensitive to an externally applied pressure up to 50 kbar ($\Delta S_{\mathrm{HL}}^{p} \cong \Delta S_{\mathrm{HL}}^{P\,\mathrm{atm}}$). It is likely therefore that influences other than internal pressure effects are responsible for the peculiar behaviour (i.e. frequency shifts, isotope effects) of low-frequency modes observed upon spin crossover in these compounds during previous experiments [7, 14].

Acknowledgment

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