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Supplementary Information

Vibrational properties and cooperativity of the 3D spin crossover network [Fe(pyrazine)][Pt(CN)₄]

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DFT calculated normal modes in comparison to Raman and IR spectroscopy.

Far IR region

The Raman spectrum of the LS isomer of [Fe(pyrazine)][Pd(CN)₄]·2H₂O reveals five bands. The bands occurring between 300 and 320 cm⁻¹ was assigned by the authors as the stretching Fe-N(pyz) modes. Indeed, our DFT results predict two Raman active fully symmetric modes at 312 and 315 cm⁻¹ (see movies in ESI) corresponding to this stretching, one of them involving the movement of the terminal iron atoms on the symmetry axis. The second, rather broad band is observed below 275 cm⁻¹ and could be assigned to the vibrations predicted at 289 cm⁻¹ that involves the swinging of the pyrazine ligands and the correlated shifting of the cyanides along the symmetry axis. This second type of movement seems to be observed as a weak Raman band at ca. 230 cm⁻¹ and is predicted to occur at 238 cm⁻¹. The strong band at ca. 200 cm⁻¹ could be interpreted as the same type of Fe-N(C) bending (predicted at 215 cm⁻¹) coupled with the Fe-N(pyz) stretching (predicted at 214 cm⁻¹). The last band, occurring slightly below 100 cm⁻¹ was assigned by Molnár at al. to external modes. They could be identified as those NIS-active A vibrations predicted at 111 and 107 cm⁻¹ (vide infra).

The Raman spectrum of the HS isomer of $[Fe(pyrazine)][Pd(CN)_4]\cdot 2H_2O$ diplays three groups of bands centred at about 225, 175 and 60 cm⁻¹. Our DFT calculations for the $\{[Zn_{15}(pyrazine)_{20}][Pd(CN)_4]_{12}(CH_3CN)_{24}\}^{6+}$ model gives the three groups of the Raman-active bands, that correspond to the experimentally observed ones: Firstly, four bands are predicted at 239, 224, 220 and 215 cm⁻¹. The first and the third are the NIS-active ones (*vide infra*) and all of them involve the swinging of the pyrazine ring in its plane and the movement of cyanide perpendicular to the tetracyanometallate plane (see ESI). The second group of the predicted Raman-active vibrations span the range 195-158 cm⁻¹. The one predicted at 195 cm⁻¹ is similar to the previously mentioned NIS-active one at 192 cm⁻¹, i.e. it involves mainly the Fe-N(pyz) stretching with some admixture of the Fe-N(C) bending. With decreasing frequency, the relative amplitude of the Fe-N(C) bending increases. The mode at 158 cm⁻¹ is identical with the previously mentioned NIS-active one. Finally, at least five Raman-active bands are predicted at 77, 74, 73, 67 and 53 cm⁻¹. They involve the swinging of

the pyrazine ligand around the Fe-pyz-Fe axis (limited rotation) with additional Fe-N(C) bending. In the experimental spectra of the SCO complexes presented in ref. 1 a medium band at 492 cm⁻¹ is observed for the LS [Fe(pyrazine)][Pd(CN)₄]-2H₂O, while for the HS isomers of it and its Pt and Ni analogue this band shifts to ca. 466 cm⁻¹.

Molnár at al. assigned this bands to the pyrazine out-of-plane bending modes. Our DFT analysis supports this assignment predicting this bending mode at 512 and 515 cm⁻¹ for the LS isomer, and for 499 and 475 cm⁻¹ for the HS isomer.

Middle IR region

The LS complexes reveal strong to medium Raman bands at ca. 675 cm⁻¹ that shift to ca. 644 cm⁻¹ for the HS ones, where also very weak NIS bands could be seen. Furthermore, the DFT calculations for the LS system reveal one Raman active band at 681 cm⁻¹, a second one at 679 cm⁻¹ and a degenerated (E) one at 642 cm⁻¹ that could be also Raman active, while the calculated IR intensity is close (but not equal) to zero. All four modes involve the predicted in-plane C-H bending of the pyrazine rings coupled with ring stretching. Similar Raman-active modes were found for the HS model, namely two at 656 cm⁻¹ and one, fully symmetric at 657 cm⁻¹.

A strong band is observed in the IR spectra of the LS isomers at ca. 826 cm⁻¹ that shifts slightly to ca. 805 cm⁻¹ for the HS ones, that was assigned to the out-of-plane C-H bending. The DFT modelling predicts three such bands at 853, 857 and 873 cm⁻¹ for the LS isomer and at 847 and 841 cm⁻¹ for the HS one.

The next strong bands are observed at ca. 1030 cm⁻¹ in the Raman spectra of both LS and HS isomers. The DFT modelling for the LS isomer displays a band at 1034 and two at 1035 cm⁻¹ corresponding to out-of-plane ring C-H bending and the bands at 1058 and 1059 cm⁻¹, corresponding, in line with the ref. 1 to the ring stretching, namely to breathing. For the HS isomer the DFT calculation reveals four bands for the out-of-plane C-H bending at 1017, 1021, 1023 and 1024 cm⁻¹, while the Raman active (not exactly zero intensity of the IR transition) ring breathing is found at 1047 and 1051 cm⁻¹ with additional ring stretching predicted at 1063 cm⁻¹.

Slightly higher in energy, at ca. 1053 cm⁻¹ the medium to strong no-spin state–sensitive IR bands were reported. The modelling exhibits two strong IR modes at 1068 cm⁻¹ for the low-spin and two for the high-spin state at 1063 and 1064 cm⁻¹, corresponding to ring stretching (as predicted in ref. 1). Interestingly, in line with the experiment, the combined IR intensity of both shall be higher for the HS state.

Weak (LS) to medium (HS) IR bands were observed at ca. 1085 cm⁻¹, that the authors assigned to C-H in-plane bending. Our calculations suggest another ring stretching mode, yielding vibration at 1087 cm⁻¹ for the LS state. The assignment of the HS band is more difficult, there is a ring stretching occurring at ca. 1064 cm⁻¹.

The IR bands showing a similar intensity pattern were detected at ca. 1126 cm⁻¹ and assigned to the in-plane C-H bending. Our calculations corroborating this assignment yield four modes of this type at 1149 (E) 1145 and 1146 and 1137 (E) cm⁻¹ for the LS model molecule. For the HS the corresponding bands modes were obtained at 1123 (E), 1125 (E), 1148 and 1149 cm⁻¹. A medium IR band is observed at 1177 cm⁻¹ for the LS state and 1157 cm⁻¹ for the HS state. The band was assigned to the ring in-plane bending. There are several IR-active modes of this type predicted for the LS state at 1215-1216, 1218, 1224 and 1231 cm⁻¹ and at 1213, 1214, 1216, 1222 cm⁻¹ for the HS one. Interestingly, at 1228-1132 cm⁻¹ a strong (for LS state) to medium (for the HS state) Raman band is observed, assigned by t Molnár at al. to the in-plane C-H bending. The DFT calculation for the LS state displays the Raman-active modes at 1216 and 1222 (two vibrations) cm⁻¹ that are identical as those predicted for the IR modes. The Raman active in-plane C-H bending, on the other hand is predicted at 1267 cm⁻¹. For the HS one, only the E band with clear Raman activity (the IR intensity of zero) that corresponds to the ring in-plane bending is predicted. The Raman-active in-plane C-H bending is predicted at 1270 cm⁻¹. Next, medium to strong IR bands are observed at ca. 1420 cm⁻¹, again assigned to a ring in-plane stretching. The DFT calculations for the LS state yield three doubly degenerate modes of this type at 1451, 1461 and 1465 cm⁻¹. The corresponding bands at 1446, 1447, 1453 and 1454 cm⁻¹ are found for the HS state. The weak Raman signals at ca. 1486 cm⁻¹ could be assigned to the same type of modes. Two such modes are predicted at 1462 and 1463 cm⁻¹ for the LS state and at 1453 and 1454 cm⁻¹ for the HS one.

Finally, a strong to medium Raman band was detected at ca. 1605 cm⁻¹ and assigned by Molnár at al. to fully symmetric ring stretching. The fully symmetric stretching mode is predicted at 1661 and 1671 cm⁻¹ for the HS and LS state, respectively. Apart from that the Raman active stretching is calculated at ca. 1570 cm⁻¹.

Summarizing, our DFT calculations confirm by and large the assignment given in ref. 1.

Synthesis of [Fe(pyrazine)][Pt(CN)₄]

The synthesis of the complex was performed according to the procedure by Real et al. (Ref. 2) starting from the 97% enriched ${}^{57}Fe(BF_4)_2 \cdot 6H_2O$ as microcrystalline material. Pictures of the synthesised sample are shown in Figure 1 and Figure 2. These picture were taken with a Raman spectrometer of the company *Bruker Optics* which uses a confocal microscope "BX51" of the company *Olympus*. The pictures were taken with objectives of different magnifications and display the microcrystallised material which varies in size.



Figure 1: Microscope image of the synthesised sample taken with a magnification of 10



Figure 2: Microscope image of the synthesised sample taken with a magnification of 50

Ref. 1: G. Molnár. V. Niel, A. B. Gaspar, J.-A. Real, A. Zwick, A. Bousseksou, J.J. McGarvey, J.Phys.Chem. B, 2002, **106**, 9701. Ref. 2: V. Niel, J.M. Martrinez-Agudo, C. M. Muñoz, A.B. Gaspar and J.-A. Real, Inorg. Chem. 2001, **40**, 3838.