Investigating Molecular Magnetism by Magneto-Far-IR Spectroscopy

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Introduction

Far-IR spectroscopy, under variable magnetic fields, is a direct method to determine separations between magnetic ground and excited states in single molecular magnets (SMMs) and to probe spin-phonon coupling in SMMs. The determination will help measure magnetic anisotropy barriers and relaxations in SMMs. In SMMs, magnetic peaks often overlap with phonon/vibrational peaks. Far-IR inside magnetic fields will show that magnetic peaks change, including shifting the positions, or degenerate magnetic levels will split, while phonon/vibrational peaks do not, as our recent paper demonstrates.[1]

Metal compounds in Fig. 1 have been reported to be SMMs based on magnetic susceptibility measurements. $Co(PPh_3)_2X_2$ (**1a-c**) are part of a series SMMs indicating an increase in the *D* parameter with increased mass.[2] $(NBu^n_4)_2[ReX_4(ox)]$ (**2a-b**; ox = oxalate and $NBu^n_4{}^+$ = tetra-n-butylammonium cation) were reported by Martínez-Lillo *et al.* to exhibit slow relaxation of the magnetization at very low temperatures in a DC field.[3] $[Dy(O{=}PCy_3)_2(H_2O)_5]Cl_3(OPCy_3)\cdot H_2O\cdot EtOH$ (**3**) is an SMM with pentagonal bipyramidal symmetry to suppress fast quantum tunnelling of magnetization (QTM).[4]

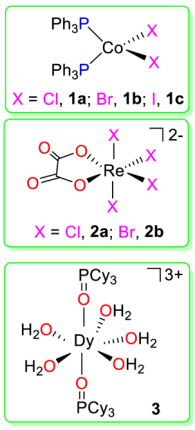

Fig. 1. 1a-c, anions in **2a-b** and cation in **3**.

Experimental

The far-IR spectra of the SMMs were measured at 5 K and magnetic fields up to 17 T using a Bruker Vertex 80v. The SMMs had been prepared by procedures similar to those in the literature.[1-3]

Results and Discussion

Far-IR spectra of **1c, 2a** and **3** are given in Fig. 2. Magnetic peaks in **1c** and **2a** were observed around 27 and 135 cm^{-1}, respectively, which undergo spin-phonon coupling. **3** shows a magnetic peak at 300-305 cm^{-1}.

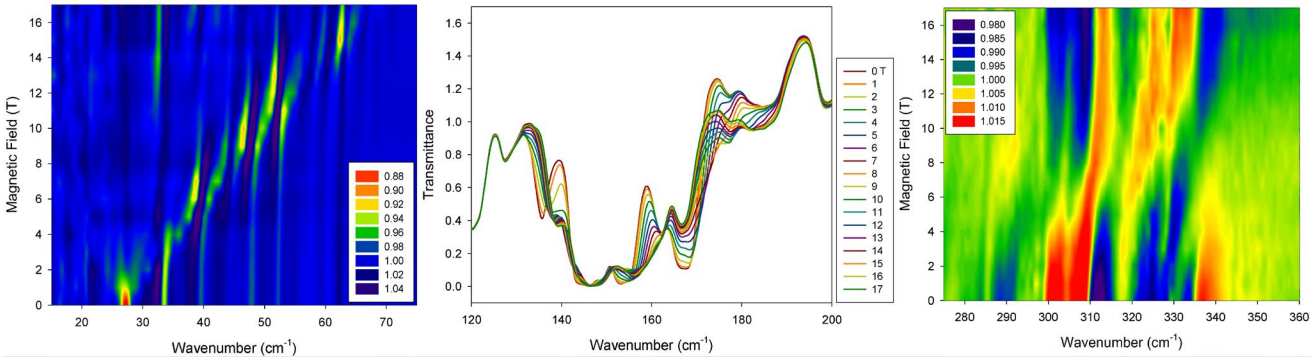

Fig. 2. Normalized far-IR transmittance spectra: (Left) **1c** as a contour map with magnetic fields; (Middle) **2a**; (Right) **3** measured at 5 K and at magnetic fields 0-17 T.

Conclusions

Far-IR, under variable magnetic fields, provides a direct spectroscopic means to probe magnetic separations in both transition metal and lanthanide based single molecular magnets (SMMs).

Acknowledgements

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References

[1] Moseley, D.H., *et al.*, Nature Communications, **9**, 2572 (2018).
[2] Saber, M.R., *et al.*, Chemical Communications, **50**, 12266 (2014).
[3] Martínez-Lillo, J., *et al.*, Journal of the American Chemical Society, **135**, 13737 (2013).
[4] Chen, Y.-C., *et al.*, Journal of the American Chemical Society, 138, 2829 (2016).