Investigating Molecular Magnetism by Magneto-Raman Spectroscopy

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Introduction

Single-molecule magnets (SMMs) are transition-metal or lanthanide compounds with large magnetic anisotropy, leading to a large barrier between ground states and slow relaxation. Raman spectroscopy has recently shown that it may be used in conjunction with both far-IR and inelastic neutron scattering (INS) to directly probe the height of these barriers in SMMs.[1-2] Magnetic peaks often overlap with phonon/vibrational peaks in SMMs, so together with far-IR spectroscopy, Raman experiments coupled with magnetic fields will help distinguish the two in addition to revealing spin-phonon coupling.

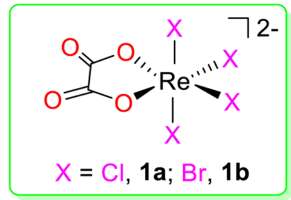

Fig.1 Anions in **1a-b**.

In the past few years, $(NBu^n{}_4)_2[ReBr_4(ox)]$ (**1b**; ox = oxalate and $NBu^n{}_4{}^+$ = tetra-n-butylammonium cation) has been studied as a rare Re-based SMM with large axial anisotropy value (*D* = -73 cm^{-1}). The Cl^- analog (**1a**) also has a large reported anisotropy (*D* = -57 cm^{-1}). Both were reported by Martínez-Lillo *et al.* to exhibit slow relaxation of the magnetization at very low temperatures in a dc field.[3]

Experimental

Raman spectra of **1b** were measured in the EMR facility and its 15/17 T SC magnet in a backscattering Faraday geometry using a 532 nm free beam laser excitation. The collected scattered light was guided via direct optics to a spectrometer equipped with a liquid-nitrogen-cooled CCD camera, at temperatures down to 5 K and fields up to 14 T. The Cl^- analog (**1a**) was also investigated, but the signal was not clear and no field-dependent transitions were detected.

Results and Discussion

The spectra of **1b** at 0-14 T are given in **Fig.2**. The peak at ~145 cm^{-1} displays a very distinct splitting with increasing magnetic fields, and is very similar to the reported 2*D* value of ~146 cm^{-1}. Additionally, another field-dependent peak appears to originate from 0 cm^{-1} and shifts to higher energies with field, indicating a transition between the split states of the ground Kramers doublet (KD). This is likely due to the high rhombic anisotropy (*E*/*D* = 0.22), which can cause the KDs to mix heavily. In addition, there is also a phonon at ~146 cm^{-1} that shifts with field, indicating that it may be coupled with the magnetic peak in some fashion.

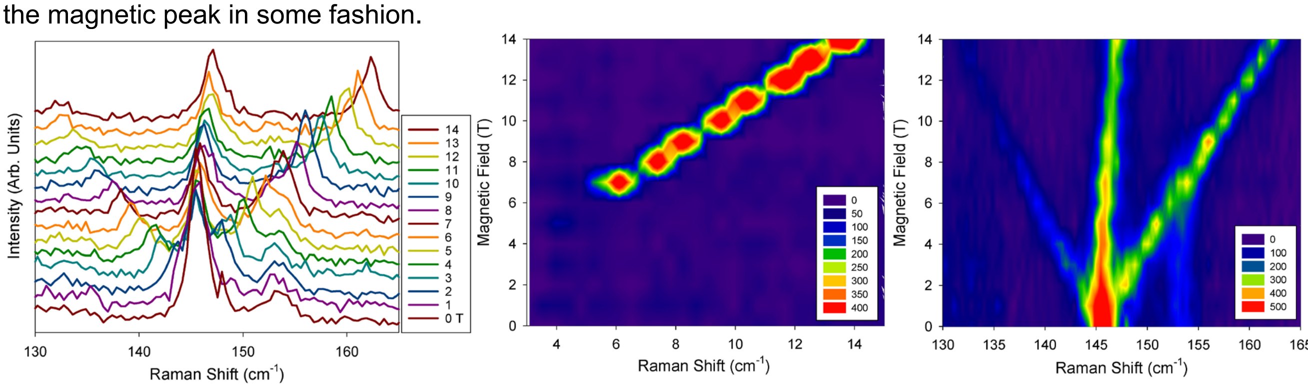

Fig.2 (Left) Raman spectra of **1b**; (Middle + Right) Contour maps of **1b** in 0-14 T magnetic fields.

Conclusions

Raman spectroscopy at variable magnetic fields was successfully performed on the SMM, proving it is a valuable direct method to probe magnetic transitions and spin-phonon coupling in SMMs.

Acknowledgements

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References

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[3] Martínez-Lillo, J., *et al.*, J. Am. Chem. Soc., **135**, 13737 (2013).