



## Probing Molecular Magnetism by Infrared & Raman Spectroscopies in Magnetic Fields

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### Introduction

Single-molecule magnets (SMMs) are metal compounds with large anisotropy and slow relaxation. SMMs have been actively studied for their fundamental magnetic properties and potential applications in, e.g., information storage and quantum computation [1]. One research goal is to design/prepare SMMs with large anisotropy and slow relaxation. Separations between magnetic ground and excited states and magnetic relaxation barriers in SMMs have been determined mainly by magnetic susceptibility measurements. Raman spectroscopy is one of the direct methods to determine the separations. However, magnetic peaks often overlap with phonon/vibrational peaks in SMMs. Thus, magneto-Raman experiments will help distinguishing magnetic peaks which change/shift positions or even split and phonon/vibrational peaks which do not usually show such changes.

Previously reported  $\text{Co}(\text{AsPh}_3)_2\text{I}_2$  (**1**, Fig.1) is part of a series of  $\text{Co}(\text{EPh}_3)_3\text{X}_2$  (E = P, As; X = Cl, Br, I) compounds in which the magnetic anisotropy increased with heavier atoms. Susceptibility studies of **1** gave the magnetic separation is  $2D \approx 149.7 \text{ cm}^{-1}$ . **1** and its analogues are attractive as they provide insight into the effect of molecular mass and the halide series on the magnetic anisotropy of SMMs. The magnetic separations of these materials have only been deduced by fitting susceptibility data, which may not be accurate. Our work aims to provide a definitive barrier for these compounds.

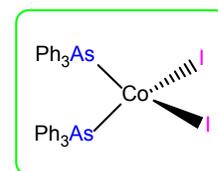


Fig. 1.  $\text{Co}(\text{AsPh}_3)_2\text{I}_2$  (**1**).

### Experimental

**1** was prepared at the U. of Tennessee, Knoxville, by previously reported procedures [2]. Raman spectra were measured in a backscattering Faraday geometry using a 532 nm laser excitation. The collected scattered light was guided via direct optics to a spectrometer equipped with a liquid-nitrogen-cooled CCD camera, at 5 K and up to 14 T fields in the EMR Facility. Calibration of the Raman spectrometer was conducted separately.

### Results and Discussion

The spectra of **1** at 0-15 T are given in Fig.2. The peak at  $\sim 55 \text{ cm}^{-1}$  at 0 T gradually shifts to higher energies with increasing magnetic fields. This value is corroborated by far-IR spectroscopy and INS conducted by our group. There is also a field-dependent peak at  $\sim 20 \text{ cm}^{-1}$  starting at 5 T. A spin phonon coupling analysis indicates that this peak originates at  $\sim 10 \text{ cm}^{-1}$  at zero field. The nature of this peak is unknown and the analysis of the data is ongoing.

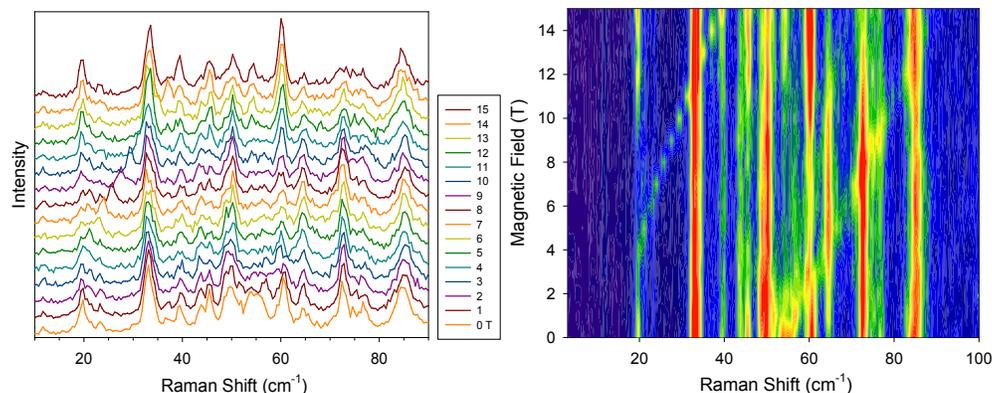


Fig.2 (Left) Raman spectra of **1**; (Right) Contour maps in 0-15 T magnetic fields.

### Conclusions

Raman spectroscopy at variable magnetic fields was successfully performed on the SMM. It is a direct method to probe magnetic transitions and magnetoelastic coupling in SMMs.

### Acknowledgements

A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida. The work was also conducted at the University of Tennessee with support from NSF (CHE-1362548 and CHE-1633870).

### References

- [1] Frost, J.M., *et al.*, Chem. Sci., **7**, 2470 (2016).
- [2] Saber, M.R., *et al.*, Chem. Comm., **50**, 12266 (2014).