Direct Observation of Zero-Field Splitting in Octahedral Co^{II} Molecule

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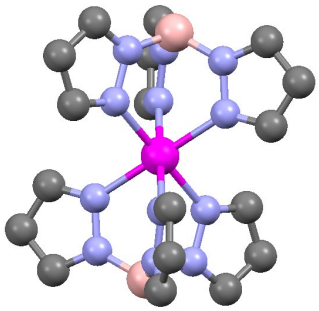

Fig.1 Ball-and stick representation of $CoTp_2$. Co: magenta, N: blue, B: pink, C: gray, H: omitted.

Introduction

Molecules which show slow relaxation of the magnetization at low temperatures continue to fascinate scientists. These so-called single-molecule magnets (SMMs) might allow performing data storage or quantum computing on the molecular scale. However, the blocking temperature T_B, roughly the temperature below which these molecules show SMM behavior, is far too low for practical applications. Hence, current research is focusing on highly anisotropic magnetic ions like lanthanides or cobalt.

One of the key ingredients for SMM behavior is the Zero Field Splitting (ZFS), i.e. the splitting of the spin energy levels at zero magnetic field. Most methods to determine the ZFS are indirect in nature and rely on a magnetic model, e.g. an effective spin Hamiltonian. However, for Co^{II} ions in a distorted octahedral ligand environment it is not obvious which Hamiltonian can be used. Therefore, a direct determination of the ZFS is even more important.

In this experiment, we studied an archetypal Co^{II} molecule, $[Co^{II}(Tp)_2]$ which is fairly symmetric (see **Fig. 1**) and several derivatives of it were synthesized. Its magnetic properties have been studied for decades,[1] and it was recently identified as an SMM.[2] However, its ZFS was up to now only estimated by indirect methods. Therefore, we performed Far-Infrared (FIR) transmission experiments in high magnetic fields.

Experimental

Far-infrared (FIR) transmission spectra were measured at the temperature of 4.6 K using a commercial FT-IR spectrometer (Bruker Vertex 80v) combined with a SC 17 T magnet (SCM3 at the DC Facility). A broadband multilayer beam splitter was used to obtain data in the spectral range between 25 and 900 cm^{-1} with 0.6 cm^{-1} resolution. HFEPR experiments were carried out at the EMR Facility using the 15/17 T SC magnet.

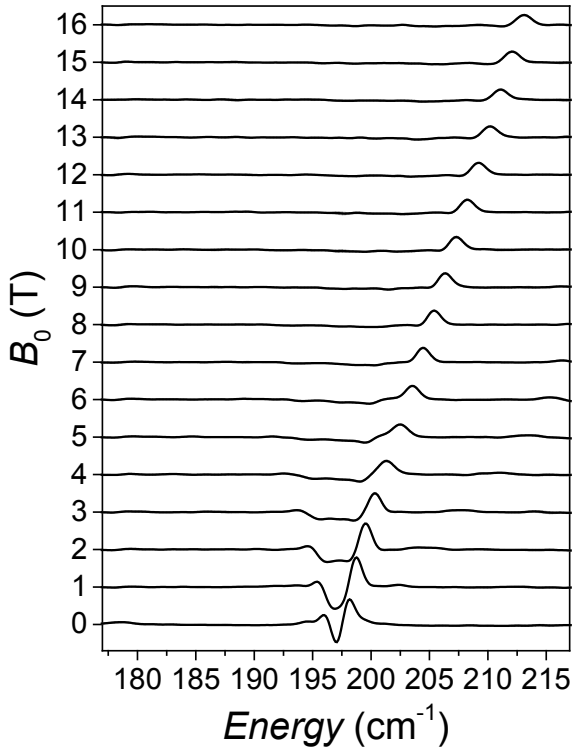

Fig.1 MDS of $CoTp_2$. Spectra are rescaled and offset according to the applied magnetic field B_0.

Results and Discussion

The FIR spectra are shown in **Fig. 2** as magnetic field division spectra (MDS). Spectra measured at a magnetic field B_0 are divided by a spectrum measured at a field of B_0 + 1 T. Such minima correspond to stronger absorption at B_0 and maxima to stronger absorption at B_0 + 1 T. At zero field a single line at 197 cm^{-1} was observed. Increasing the field leads to a broadening of the line. The high-energy branch of the transition could be observed up to the highest field of 16 T. Hence, we have directly observed the ZFS. The HFEPR experiments (not shown) suggest that the ZFS is highly axial and of easy-axis type.

Conclusions

We could directly, model-independently and unequivocally determine the ZFS of $[Co^{II}(Tp)_2]$. The data quality was exceptionally good, demonstrating that the FIR setup at NHMFL is an excellent instrument.

Acknowledgements

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References

[1] Jesson, J.P., J. Chem. Phys., **45**, 1049-1056 (1966).
[2] Zhang, J., *et al.,* Inorg. Chem., **57**, 3903-3912 (2018).