Pressure Tuning of the Anisotropy Barrier in Fe_8 SMMs Probed Using High-Frequency EPR

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Introduction

Single-molecule magnets (SMMs) are molecular entities with a large spin ground state where quantum phenomena such as tunneling of magnetization through a large anisotropy barrier have been observed [1]. One such SMM that has been extensively studied is $[Fe_8O_2(OH)_{12}(tacn)_6]Br_8 \cdot 9H_2O$, also known as Fe_8, which has a giant spin S = 10 ground state. The eight S = 5/2 Fe^{III} atoms are bridged by oxygens, forming a butterfly structure where, in the simplest model, six Fe atoms have their spins up and two have their spins down [2]. This structure in fact gives rise to geometrical spin frustration [1]. By varying the interaction between the spins, manipulation of quantum tunneling in SMMs may be achieved. Typically, the manipulation of spin interactions is realized using chemical methods. Our aim was to employ high pressure as a cleaner alternative to tune the magnetic interactions within the core of the Fe_8 molecule. The pressure-induced changes were probed using multi-frequency EPR, which is an excellent tool for investigating magneto-structural correlations in SMMs.

Experimental

Multi-frequency EPR measurements based on a cavity perturbation technique were performed at high pressures up to 7.2 kbar. High pressures were generated using plastic turnbuckle diamond anvil cell (DAC) where samples of dimension ~200 μm × 200 μm were placed with a 1:1 mixture of fluorinert FC70 and FC77 as pressure transmitting medium. EPR measurements were performed at a temperature of 5 K.

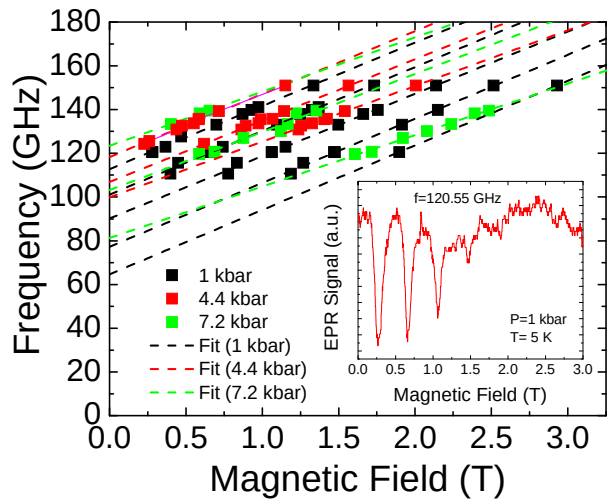

Figure 1. Frequency vs magnetic field plot of the EPR transitions in the Fe_8 SMM at three different pressures. The inset shows the easy axis EPR spectrum at a pressure of 1 kbar for a frequency of 120.55 GHz.

Results and Discussion

Multi-frequency EPR spectra of the Fe_8 SMM were recorded for pressures up to 7.2 kbar, with magnetic fields oriented close to the easy axis. A typical EPR spectrum consisting of a series of transitions corresponding to m_S = -10 to -9, -9 to -8, -8 to -7 etc., is shown in the inset to Fig. 1. A plot of the resonance frequencies for these transitions, as a function of magnetic field for the three measured pressures, is shown in the main panel of Fig. 1. It is obvious that the application of pressure leads to significant changes in the EPR data. The spacing between the resonance peaks, and the zero-field splitting increase as the applied pressure is increased. The changes are more dramatic for the pressure step from 4.4 kbar to 7.2 kbar.

Conclusions

Multi-frequency EPR studies on the Fe_8 SMM reveal significant changes in the magnetic interactions among the Fe atoms within the cluster upon the application of pressure. Further multi-frequency EPR and X-ray measurements at higher pressures will provide more information on the role of frustration within the Fe_8 molecule in determining the cluster anisotropy.

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References

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