Magnetic Quantum Tunneling in a Mn₁₂ Single-Molecule Magnet Measured With High Frequency Electron Paramagnetic Resonance

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Abstract. The low temperature spin dynamics of the single-molecule magnet [Mn₁₂O₁₂(CH₃COOH)₁₆(H₂O)₄]·2CH₃COOH·4H₂O, hereafter Mn₁₂Ac, were studied using High Frequency Electron Paramagnetic Resonance (HFEP) in order to demonstrate magnetic quantum tunneling between resonant spin projection states. We prepare the spins such that they populate only one side of the axial potential energy barrier. Using a magnetic field we cause tunneling between resonant energy states. We then use HFEP to monitor the populations on each side of the potential energy barrier. We can estimate the tunneling relaxation time between spin projection states by plotting the area of an EPR peak as a function of wait time at a resonance field. This technique provides an alternative method to magnetometry experiments for measuring spin relaxation dynamics.

Keywords: single-molecule magnets, magnetic quantum tunneling

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INTRODUCTION

Mn₁₂Ac has been a widely studied single-molecule magnet (SMM) over the past decade. One particular area of interest has been to study the mechanisms that mediate the tunneling of the magnetic moment.¹⁻⁶,¹¹,¹² Magnetization relaxation studies involve techniques that can discern when (in time) and where (in field) the spins are tunneling. The EPR technique that we use allows us to estimate the relaxation time, providing an alternative method to direct magnetization measurements. It also provides information concerning which spins are tunneling during the relaxation process.

EXPERIMENT

We place the sample inside a resonant cavity at the end of a waveguide probe that sits in the bore of a superconducting magnet. The instrumentation and technique are described elsewhere.⁷,⁸ We align the sample such that its easy axis of magnetization (the c axis) is parallel to the applied magnetic field, and cool the sample from room temperature to 2 K in zero field. Then we apply a magnetic field of −6 T in order to bias the system such that all of the spins are in the ground (mᵢ = 10) state. For all sweeps, the frequency of radiation was 286 GHz. From −6 T we sweep to a magnetic field value of 0.9 T, where levels on either side of the barrier are in resonance, and hold the magnetic field at this value for different waiting times. This results in tunneling of spins between these states. Then we sweep back to −6 T and observe changes of the EPR intensities.

With the magnetic field applied parallel to the easy magnetization axis of the molecule, the dominant terms in the spin Hamiltonian will be:

\[
\hat{H}_s = D \hat{S}_z^2 + B \hat{S}_z^4 + g \mu_B B \cdot \hat{S}
\]  

(1)

where the terms have their usual meanings.¹⁰

DISCUSSION AND SUMMARY

Figure 1 shows EPR spectra for different waiting times at 0.9 T. Each trace involves sweeping from 0.9 T to −6 T after a different waiting time. The inset to Figure 1 shows the sweep from −6 T to 0.9 T, which was identical for all runs. As the figure shows, the area of the peak occurring on the positive field side decreases for longer wait times, while the area of the peak occurring on the negative field side increases.
accompanying the peak occurring at positive fields involves transitions on the metastable side of the potential energy barrier \((m_s = 10 \text{ to } m_s = 9)\). As the field is held at 0.9 T for longer times, more spins from the \(m_s = 10\) state tunnel through the anisotropy barrier to the \(m_s = -8\) state. After tunneling, they quickly decay back to the ground state, \(m_s = -10\). As the field is swept back to \(-6\) T, those spins that tunneled no longer contribute to the positive field peak, but will instead contribute to the negative field peak; i.e. the transition between the \(m_s = -10\) and \(m_s = -9\) states.

Figure 2 shows the area of the positive field peak as a function of wait time. This curve can not be satisfactorily fit to an exponential relaxation law, but can be fit to a stretched exponential of the form \(A_0 \exp[-(t/\tau)^\beta]\). This is in agreement with other work for magnetization relaxation in this temperature regime.\(^{15}\) We estimate an average relaxation time, \(\tau\), on the order of 500 s.

Previous studies on this compound have found significant distributions of the \(D\) and \(g\) parameters.\(^{9,10}\) All of the spins are subjected to a frequency of 286 GHz, but not all spins see the same microenvironment. Long range dipolar fields will also affect the tunneling,\(^{11}\) i.e. the local magnetic induction \(B\) will evolve due to the fluctuating dipolar fields of molecules that have tunneled. Careful inspection of the data reveals that different portions of the spectrum relax on different time scales. For example, the signal changes most rapidly at early times on the high-field sides of the peaks. Molecules contributing to these tails of the spectrum possess smaller than average \(D\) values. However, it also appears that a significant fraction of the molecules on the low-field (high \(D\)) sides of the peaks have already tunneled during the first 30 seconds, since one always observes weight in the spectrum at low negative fields. Once most of the molecules have tunneled, a small fraction of slower relaxing species remain, giving rise to the much narrower EPR peak at low positive fields. The fact that this remnant peak is quite narrow indicates that this population is probably rather pure. Thus, in addition to measuring the ensemble average of the relaxation, these EPR measurements demonstrate that one can separately monitor the relaxation from different parts of the inhomogeneous distribution of spin environments.

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REFERENCES