ANGLE-SWEPT HIGH-FIELD EPR: APPLICATION TO LOW SYMMETRY SINGLE-MOLECULE MAGNETS

Stephen Hill,¹ Muralee Murugesu² and George Christou²

¹NHMFL and FSU Physics; ²UF Chemistry

Quantum World

Mn₄, Mn₁₂, Mn₃₀

Mn₈₄

-4.2 nm

1.9 nm

M/M s

μ₀H (mT)

1000 N

Magnetron Lab

National High Magnetic Field Laboratory

Florida State University - Los Alamos National Laboratory - University of Florida
The king of single-molecule magnets – \( \text{Mn}_{12} \)

**Crystals (3D arrays)**

- High symmetry - \( S_4 \)
- Monodisperse

\[ \text{Mn}_{12} \text{O}_{12} (\text{O}_2\text{CCH}_2\text{BuAc})_{16} (\text{MeOH})_4 \cdot \text{MeOH} \]

- \( \text{Mn}_{12} \)-acetate (Lis - 1980); \( \text{Mn}_{12}\)-tBuAc (Murugesu – 2005, unpublished)

**Organic ligands (insulation)**

**Anisotropy from Jahn-Teller elongation due to axial ligands**

\[ S = (8 \times 2) - (4 \times 3/2) \]

\[ S = 10 \]
The giant spin approximation

Simplest effective model: uniaxial anisotropy

\[ \mathcal{E}(m_s) = -|D|m_s^2 \]

Spin projection - \( m_s \)

Energy

-10 -8 -6 -4 -2 0 2 4 6 8 10

"up" "down"

Magnetic anisotropy \rightarrow\text{bistability, hysteresis}
Magnetic anisotropy $\rightarrow$ bistability, hysteresis

Simplest effective model: uniaxial anisotropy

$$\mathcal{E}(m_s) = -|D|m_s^2$$

\[ \Delta E \sim DS^2 \]

10-100 K

"up"

Thermal activation

("down"

\[ |D| \sim 0.1 - 1 \text{ K} \]

for a typical single molecule magnet)
AC $\chi$ data for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Br})_{16}(\text{H}_2\text{O})_4]\cdot\text{Solvent}$

$U_{\text{eff}} = 72.5(5)$ K
$\tau_0 = 2.0 \times 10^{-9}$ s

Dry crystals

Wet crystals

$\chi''$

$\chi''$

Temperature (K)

$1/T$ (K$^{-1}$)

$M/N_H_0$

$H/T$ (kG/K)

Fast and slow relaxing forms of $\text{Mn}_{12}\text{-Bu}^{'\text{Ac}}$

$[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^{'})_{16}(\text{MeOH})_4]\cdot\text{Solvent}$

Solvent = $\text{CH}_2\text{Cl}_2$, MeNO$_2$

$U_{\text{eff}} = 43(2)$ K

Low Symmetry

$U_{\text{eff}} = 66(1)$ K

High Symmetry

Solvent = $\text{CH}_2\text{Cl}_2$, MeCN

Note: no shifts in the peak positions

The Punch Line: Quantum Tunneling

Break axial symmetry:

\[ \hat{H} = D \hat{S}_z^2 + \hat{H}_T \]

\([\hat{H}_T, \hat{S}_z] \neq 0\]

Contains \(\hat{S}_x\) and \(\hat{S}_y\).

- \(m_s\) not good quantum #
- Mixing of \(m_s\) states
  \(\Rightarrow\) resonant tunneling (of \(m_s\) through barrier)
- Effective barrier reduction

\[300 \text{ GHz}\]

"up"

"down"

We are forced to do single-crystal HF-EPR

Rotate field in $xy$-plane and look for symmetry effects

$$E(m_s) \approx \left\{- \frac{1}{2} D \pm |\mathcal{H}_T| \right\} m_s^2 + g \mu_B B m_s$$

In high-field limit ($g \mu_B B > DS$), $m_s$ represents spin-projection along the applied field-axis
Two-axis: split-coil magnet + rotating cavity

- TE011 = 52 GHz (up to 300+ GHz)  
  (Diameter × Height = 0.3'' × 0.3'')
- Q ~ 25,000 (TE011, 4.2 K)
- Sub-millimeter sized single-crystals
- Resolution < ±0.2° (< ±0.1° PPMS)
- Two-axis in fields up to 7T and T > 2K
- Single-axis in any NHMFL magnet & T > 0.6 K

1st Generation:  
25 tesla, 4He system

2nd Generation:  
45 tesla, 3He system

Nice example: the high-symmetry Mn_{12}Bu'-Ac

Rotation in plane orthogonal to hard plane – very long day of measurement

What if symmetry is low? Could take days/weeks by the above procedure.
**ANGLE-SWEPT HFEP**R: LOW SYMMETRY Mn$_{12}$Bu$^t$-Ac

$B = 4$ T, $f = 62$ GHz, smooth rotation of horizontal field at different cavity orientations

(a) $\phi = -8^\circ$

(b) $\phi = +9.8^\circ$

(c) $\phi = +27.3^\circ$

(d) $\phi = +44.9^\circ$

(e) $\phi = +62.5^\circ$

(f) $\phi = +80^\circ$
**Angle-Swept HF EPR: Low Symmetry Mn$_{12}$Bu$^t$-Ac**

- **Angle swept determinations**
- **Refinement: stepped field scans**

- **Locate principal magnetic axes**
- **Clear evidence for rhombic ($E$) anisotropy in the hard plane**
Refined Measurements: Mn$_{12}$Bu$^t$-Ac

A cut through hard-plane ($\phi = 62.5^\circ$)

Transmission (arb. units - offset)

PPMS angle - $\theta$ (degrees)

Hard plane

Hard-plane angle-dependence

Transmission (arb. units - offset)

Magnetic field (tesla)

Magnetic field (tesla)
PUTTING EVERYTHING TOGETHER...

Low-symmetry Mn_{12}-Bu'tAc

- \( S = 10, \ D = -0.42(1) \text{ cm}^{-1} \)
- \( B_4^0 = -2.2(3) \times 10^{-5} \text{ cm}^{-1} \)
- \( E = \pm 0.072(5) \text{ cm}^{-1} (D/E \sim 6) \)
- \( U_{\text{eff}} = 43(2) \text{ K} \)

- 40% reduction in \( U_{\text{eff}} \)
- Only 10% reduction in \( D \)

High-symmetry Mn_{12}-Bu'tAc

- \( D = -0.461(3) \text{ cm}^{-1} \)
- \( B_4^0 = -2.5(2) \times 10^{-5} \text{ cm}^{-1} \)
- \( E = 0 \text{ exactly} \)
- \( B_4^4 = \pm 4.3(2) \times 10^{-5} \text{ cm}^{-1} \)
- \( U_{\text{eff}} = 66(1) \text{ K} \)

Value of \( E \) and the reduction in \( D \) easily rationalized in terms of flipped JT-axis
**Low-symmetry Mn$_{12}$-Bu$^t$Ac**

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PUTTING EVERYTHING TOGETHER...

Classical – over the barrier

Disorder – quantum tunneling near top of barrier

Intrinsically low symmetry – leads to significant tunneling

http://arxiv.org/abs/0908.4434
• Faster relaxing Mn$_{12}$ crystallize in low-symmetry structures with one or more abnormally oriented Jahn-Teller axes.

• Problems due to solvent loss necessitate single-crystal EPR measurements.

• Angle-swept EPR enables efficient in-situ orientation of low-symmetry crystals.

• Low-symmetry causes enhanced tunneling, which is the dominant factor contributing to the effective barrier reduction and the faster relaxation in Jahn-Teller Mn$_{12}$ variants.

http://arxiv.org/abs/0908.4434
1. Tallahassee (NHMFL/FSU)
2. Gainesville (NHMFL/UF)

http://www.magnet.fsu.edu/

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$^1$The absolute sensitivity is the minimum number of detectable spins per mT linewidth and a 1 Hz bandwidth at room temperature.

$^2$In combination with a far-infrared laser, selected frequencies up to 2500 GHz are available.