Beyond the Giant Spin Approximation: The view from EPR

Simple is better

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Simple is better

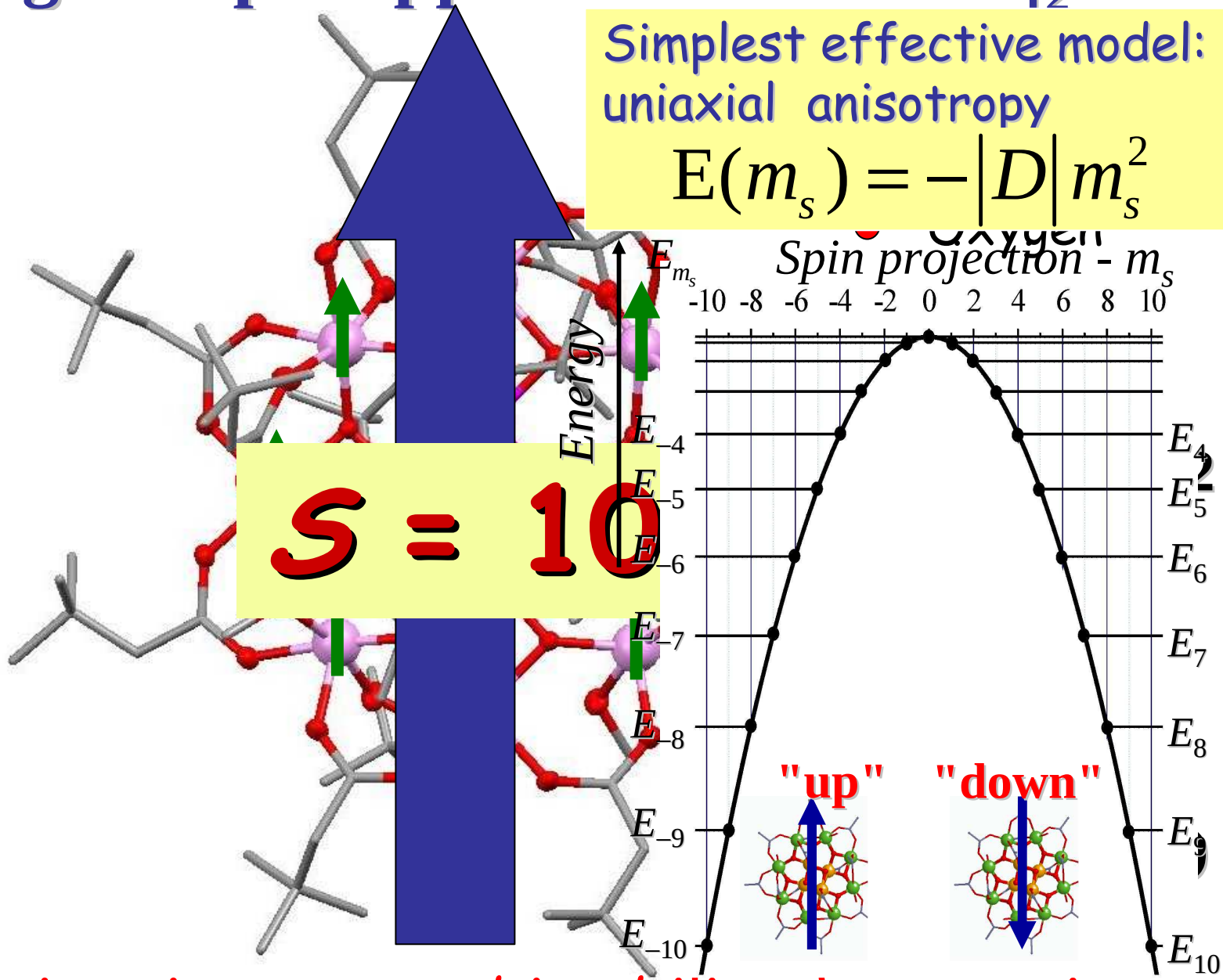
Outline

- The Giant Spin Approximation – why/why not use it?
- Simple molecules; consider single-ion physics
- The view from EPR, with some examples:
  - Interplay between exchange and anisotropy
  - Origin of fourth-order (+ higher) anisotropy
  - SMM properties as a result of anisotropic exchange
  - Spin control - raising the barrier in SMMs
  - Symmetry and QTM selection rules
- Summary and conclusions

The giant spin approximation – Mn_{12}

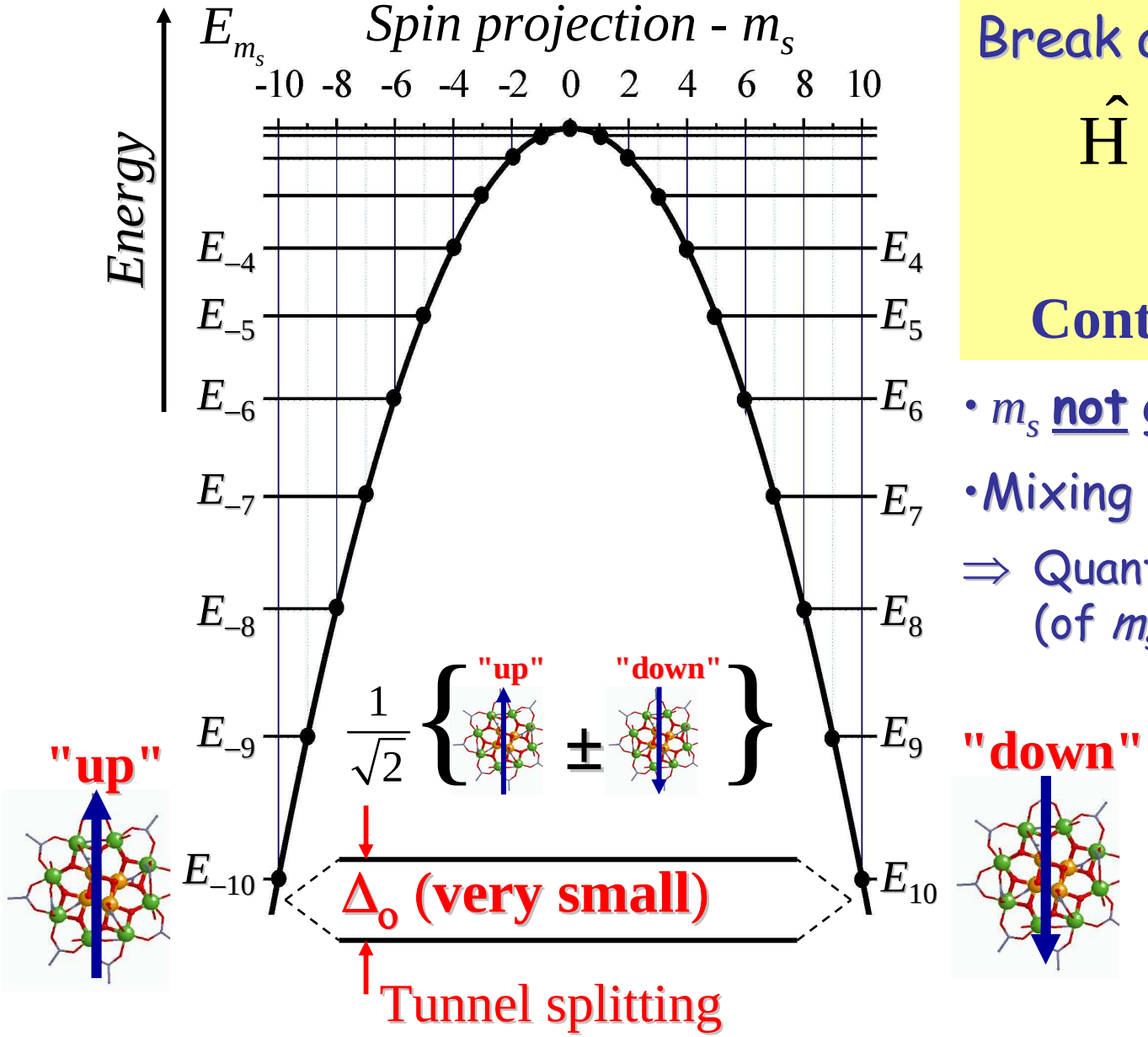
Simplest effective model: uniaxial anisotropy

$$E(m_s) = -|D| m_s^2$$



Magnetic anisotropy → bistability, hysteresis

Quantum effects at the nanoscale (S = 10)



Break axial symmetry:

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

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

Contains $\hat{S}_x$ and $\hat{S}_y$.

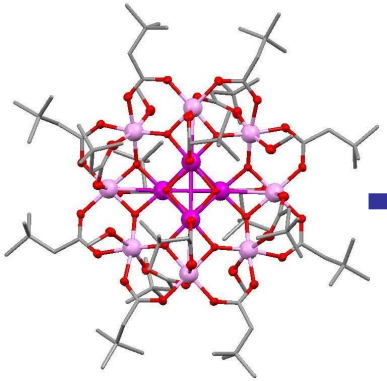
- m_s **not** good quantum #
- Mixing of m_s states

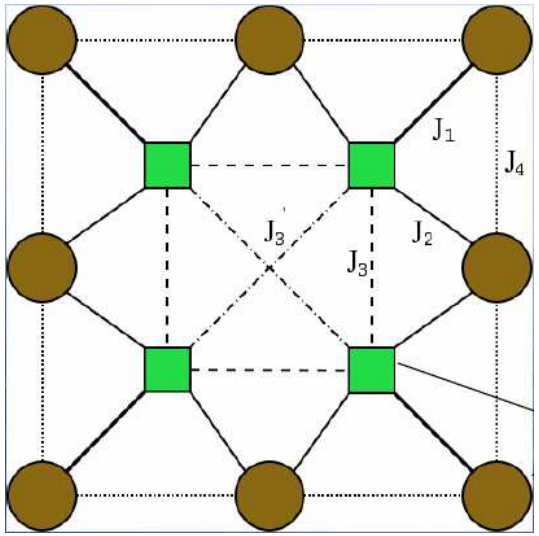
$\Rightarrow$ Quantum tunneling (of m_s) through barrier

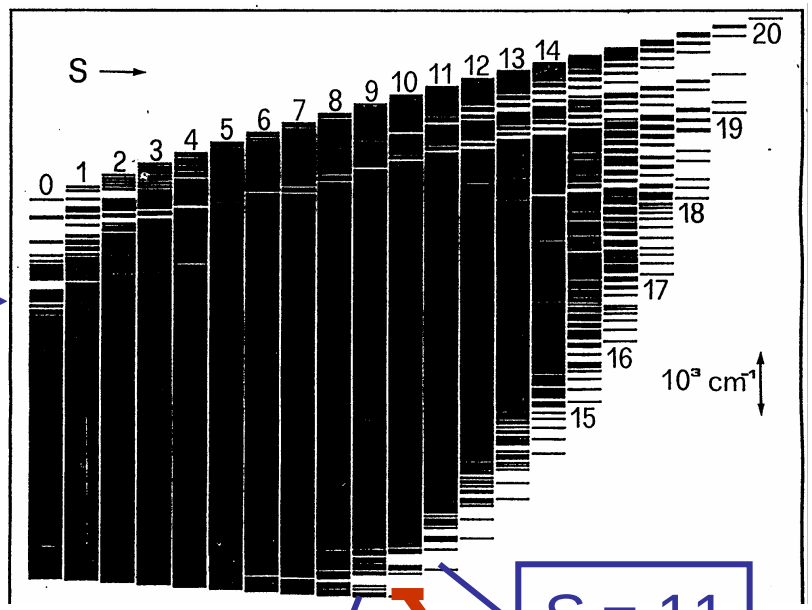
Tunnel splitting a measure of tunneling rate

Why use a giant spin approximation?

Mn_{12}







$S = 11$

$S = 9$

$S = 10$

$S = 10$

- Matrix dimension 21 × 21
- J^s irrelevant (apparently)!!
- Ignores (10^8 – 21) higher-lying states

But what is the physical origin of parameters obtained from EPR and other experiments – particularly those that cause MQT?

To answer this.... ..study simpler molecules

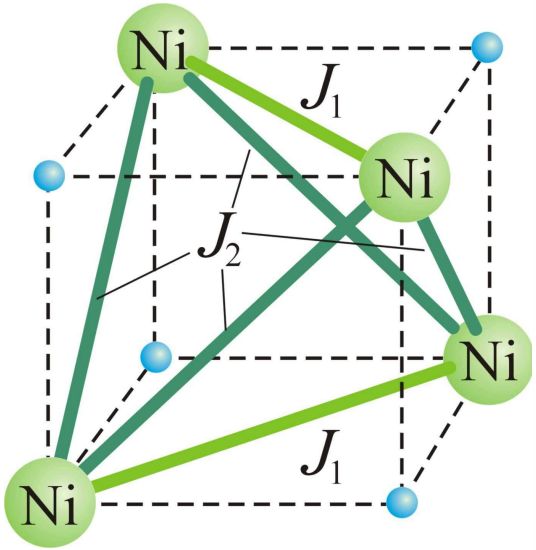
$$\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[d_i \hat{s}_{zi}^2 + e_i \left(\hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + \mu_B \vec{B} \cdot \overleftrightarrow{g}_i \cdot \hat{s}_i \right]$$

Ni_4^{II}

Mn_3^{III}

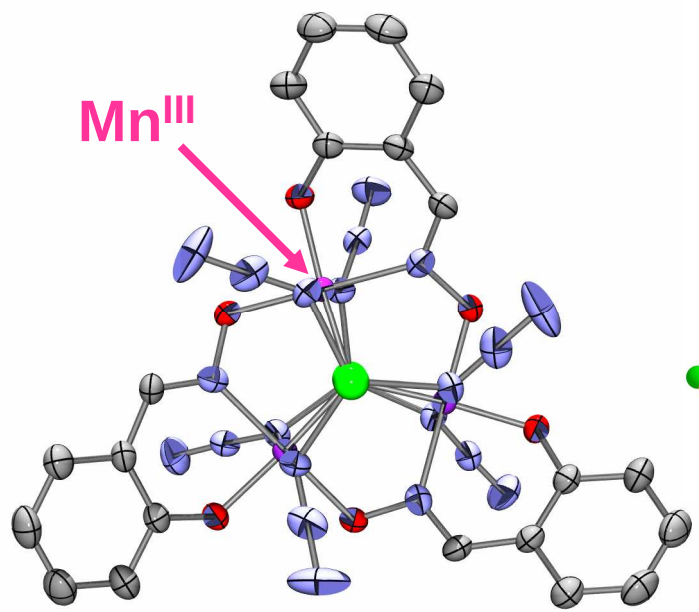
Mn_6^{III}

S_4 symmetry

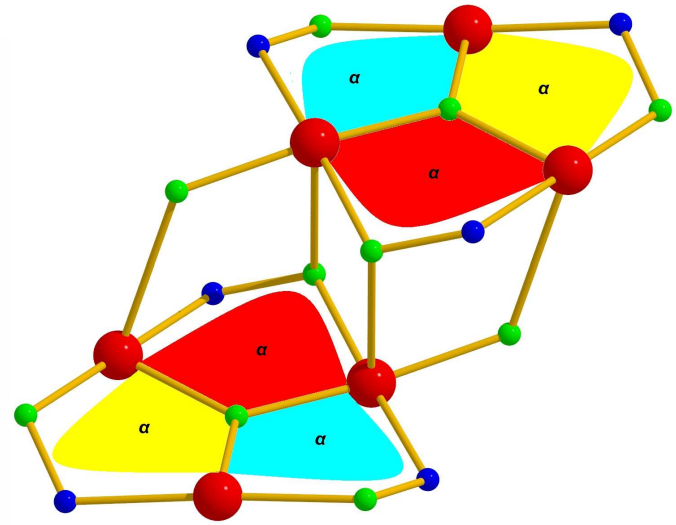


$(2S + 1)^4 = 81$

$R\bar{3}$



$(2S + 1)^3 = 125$



Centrosymmetric

$(2S + 1)^6 = 15625$

Ni_4: E.-C. Yang et al., Inorg. Chem. **44**, 3836 (2005); A. Wilson et al., PRB **74**, R140403 (2006).
Mn_3: P. Feng et al., Inorg. Chem. **46**, 8126 (2008); T. Stamatatos et al., JACS **129**, 9484 (2007).
Mn_6: C. Milios et al., JACS **129**, 12505 (2007); S. Datta et al., DOI: 10.1016/j.poly.2008.12.025.

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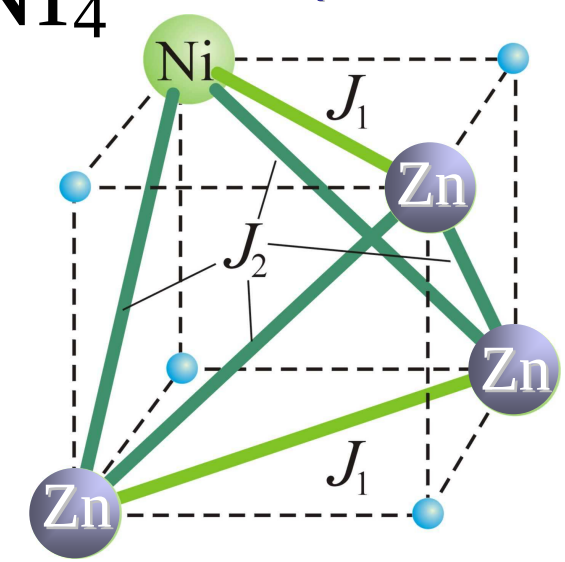
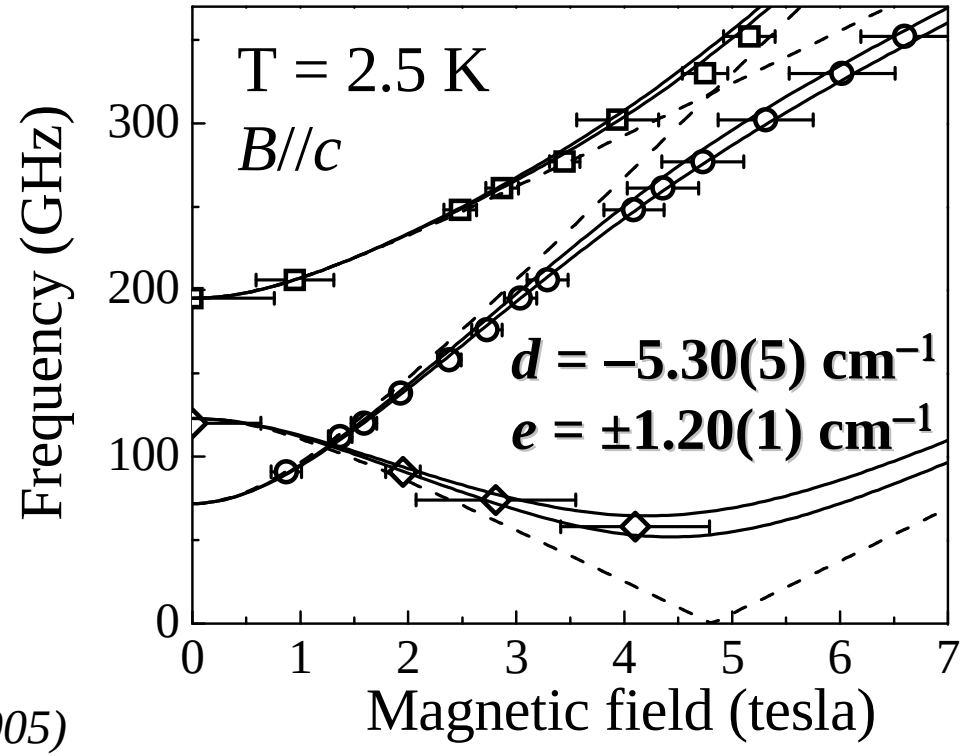
$S = 4$

Ni_4^{II}

S_4 symmetry

Can also study the Zn analog doped with Ni^{II} to obtain single-ion parameters





En-Che Yang et al., Inorg. Chem. ***44****, 3836 (2005)*

- Angle-dependent single-crystal HFEPR of 2% Ni-doped Zn complex
- Obtain 3×3 matrices and orientations for $S = 1$ Ni^{II}
- **Only 2nd order anisotropy for $S = 1$**

Wilson et al., PRB **74**, R140403 (2006); Datta et al., PRB **76**, 052407 (2007); Lawrence et al., Inorg. Chem. **47**, 1965 (2008); Cao et al., PRL **100**, 167206 (2008).

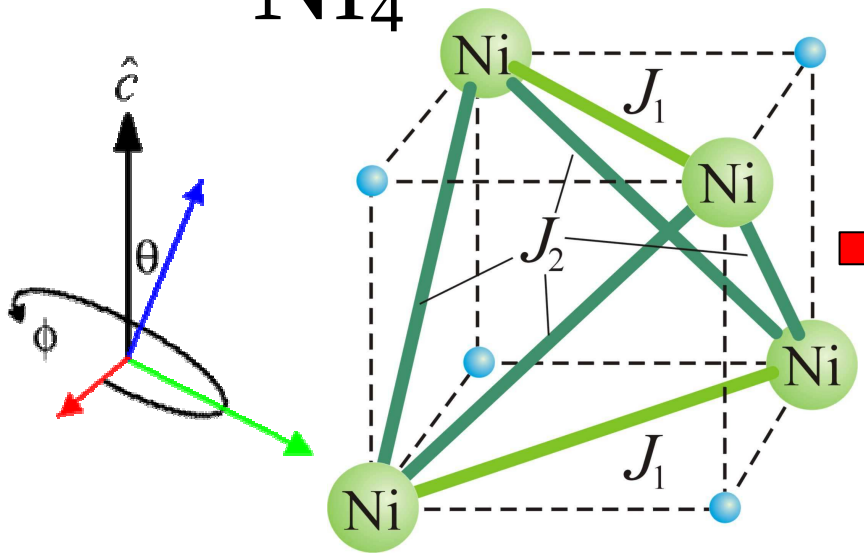
To answer this.... ..study simpler molecules

$$\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[d_i \hat{s}_{zi}^2 + e_i \left(\hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + \mu_B \vec{B} \cdot \vec{g}_i \cdot \hat{s}_i \right]$$

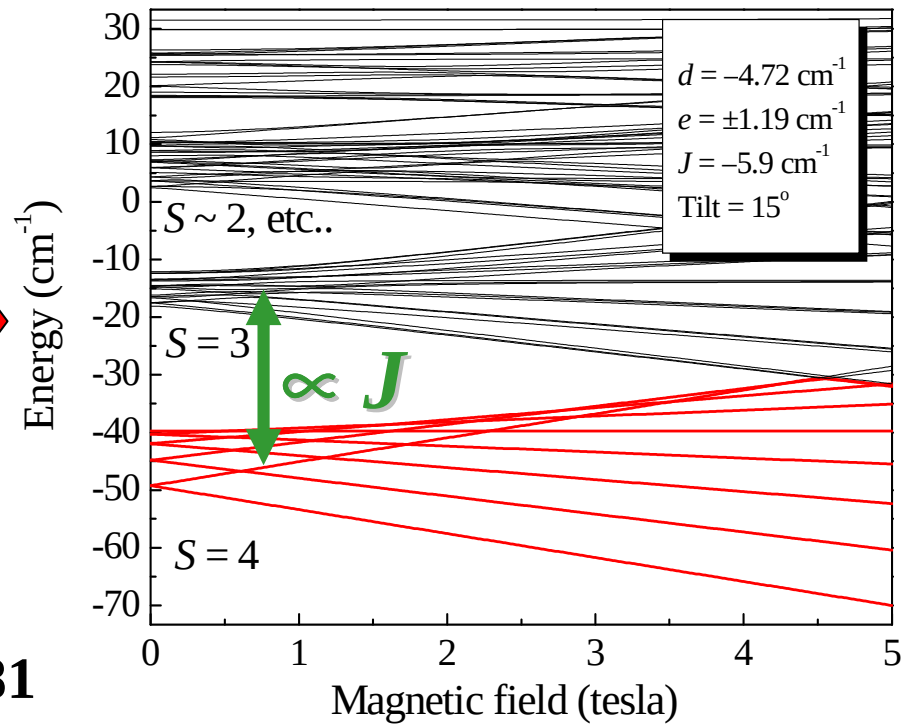
$S = 4$

Ni_4^{II}

S_4 symmetry



Matrix = $(2S + 1)^4$ = 81 × 81

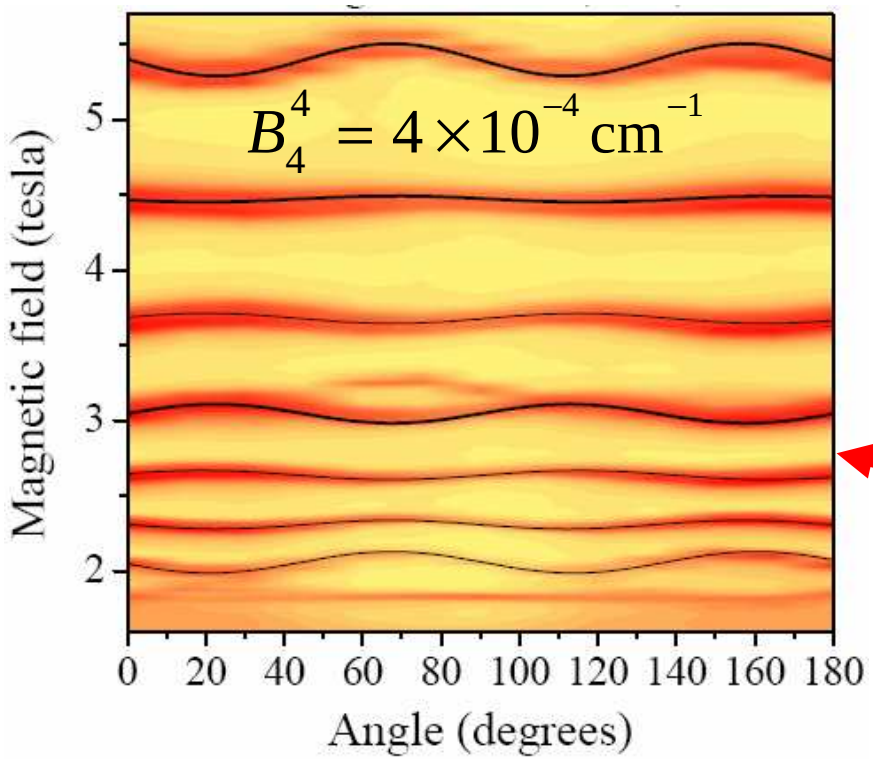


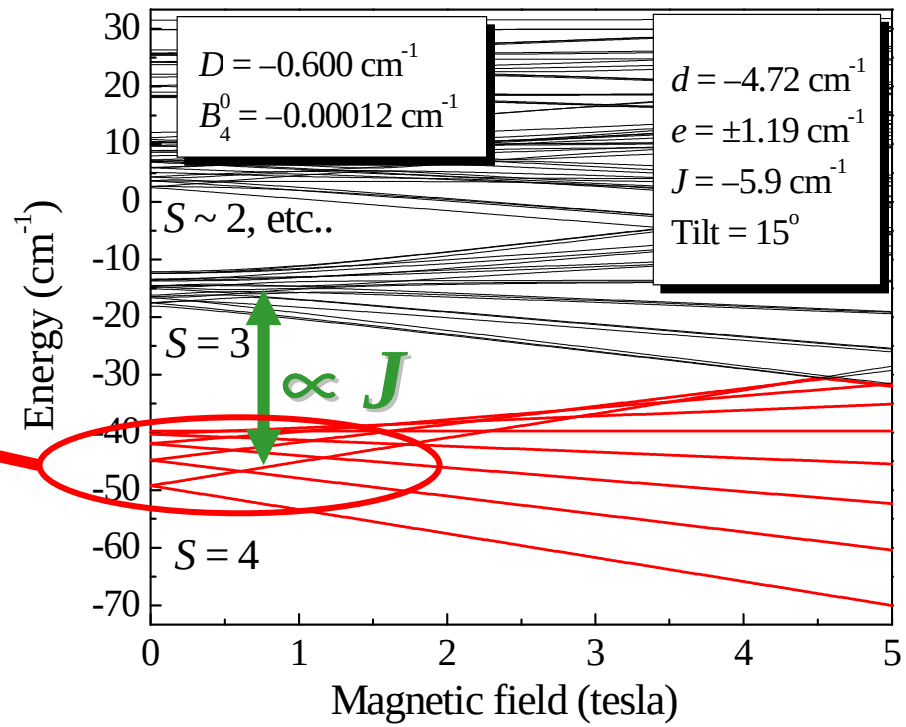
- Interplay between isotropic (exchange) and anisotropic (single-ion spin-orbit) admixes S = 3, 2, etc.. to the S = 4 state
- Causes S-mixing → corrections to zfs ~$(\hat{S}_z^2)^n$, i.e. 4th, **6th** order....

Wilson et al., PRB **74**, R140403 (2006); Datta et al., PRB **76**, 052407 (2007); Lawrence et al., Inorg. Chem. **47**, 1965 (2008); Cao et al., PRL **100**, 167206 (2008).

To answer this.... ..study simpler molecules

This physics is responsible for the QTM in Ni_4





- Interplay between isotropic (exchange) and anisotropic (single-ion spin-orbit) admixes $S = 3$, 2, etc. to the $S = 4$ state
- Causes S-mixing → corrections to zfs $\sim(\hat{S}_z^2)^n$, i.e. 4th, 6th order....

$$B_4^0 \text{ and } B_4^4 \propto 1/J$$

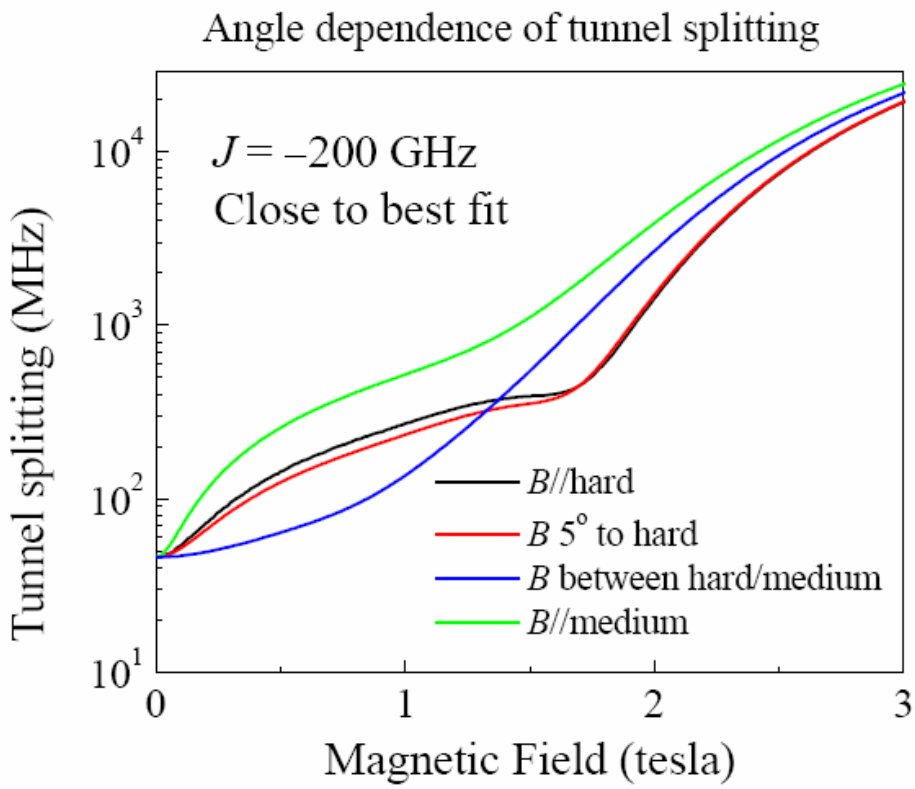
Wilson et al., PRB **74**, R140403 (2006); Datta et al., PRB **76**, 052407 (2007); Lawrence et al., Inorg. Chem. **47**, 1965 (2008); Cao et al., PRL **100**, 167206 (2008).

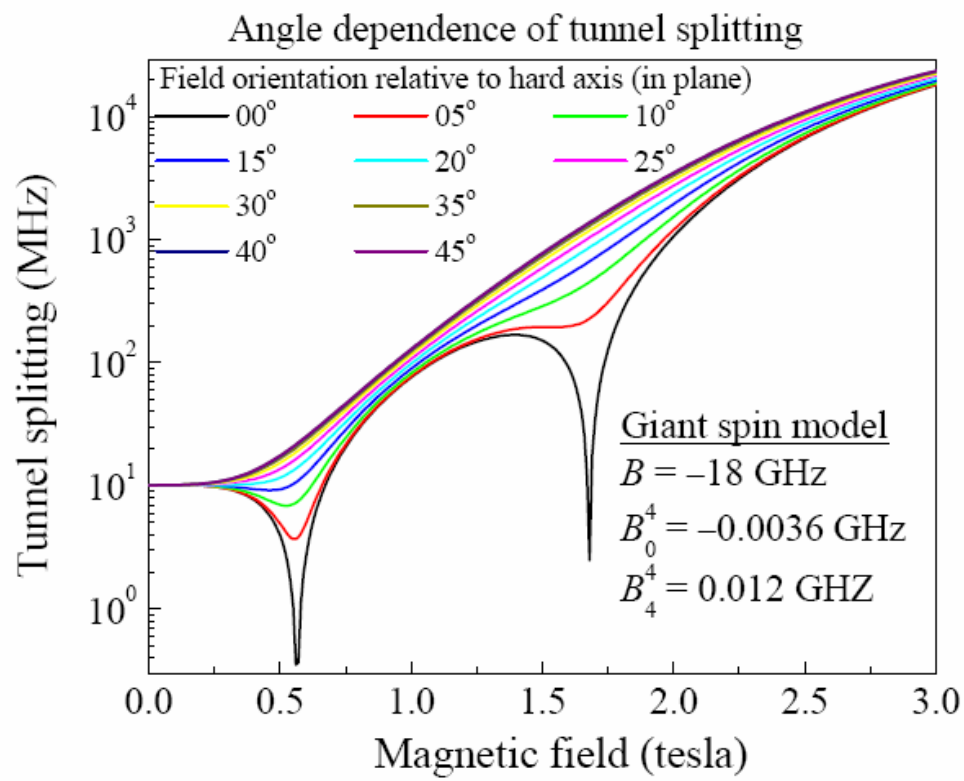
Be careful making predictions at vastly different energy scales

$$\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[d\hat{s}_{zi}^2 + \frac{e}{2}\left(\hat{s}_{+,i}^2 + \hat{s}_{-,i}^2 \right) + g\mu_B \vec{B} \cdot \hat{s}_i \right] \qquad B // \hat{z}$$

$$\text{Giant spin:} \quad \hat{\mathcal{H}} = \left(\frac{D'}{S^2} \right) \hat{S}_z^2 + \left(\frac{B'}{S^4} \right) \hat{S}_z^4 + \left(\frac{C'}{S^4} \right) \hat{O}_4^4$$

- Both of these models explain the HF EPR data extremely well, but.....

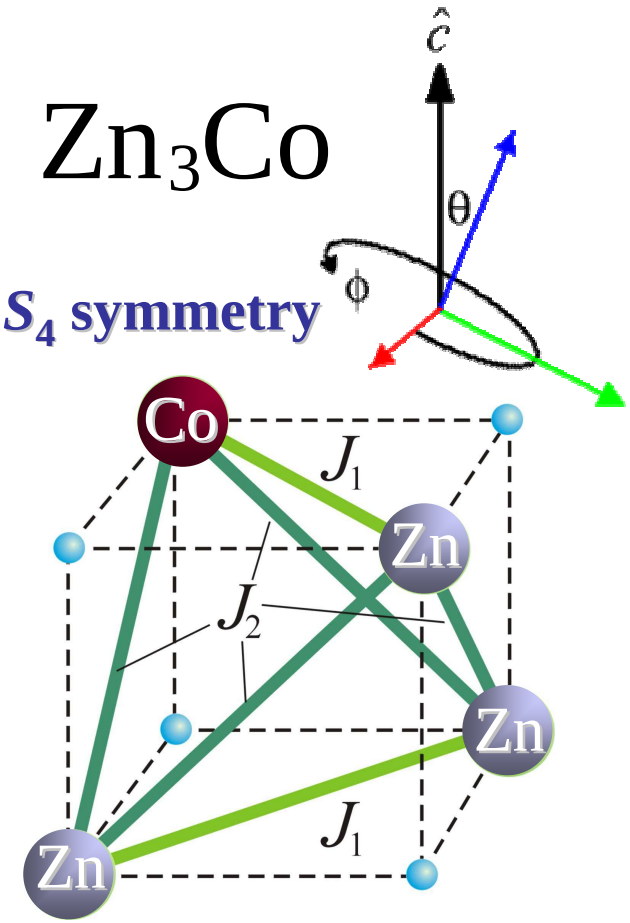


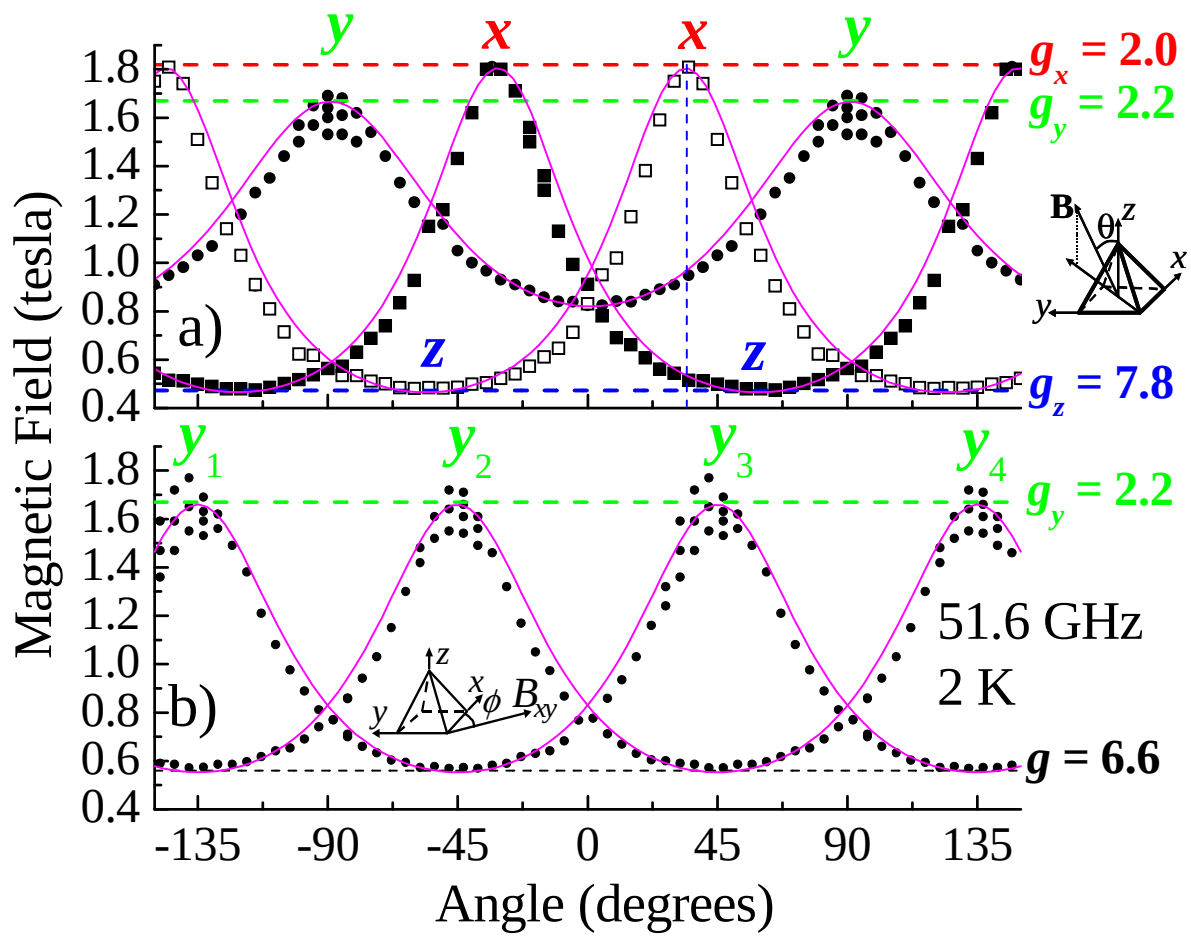


Same idea, different physics

Zn_3Co

S_4 symmetry

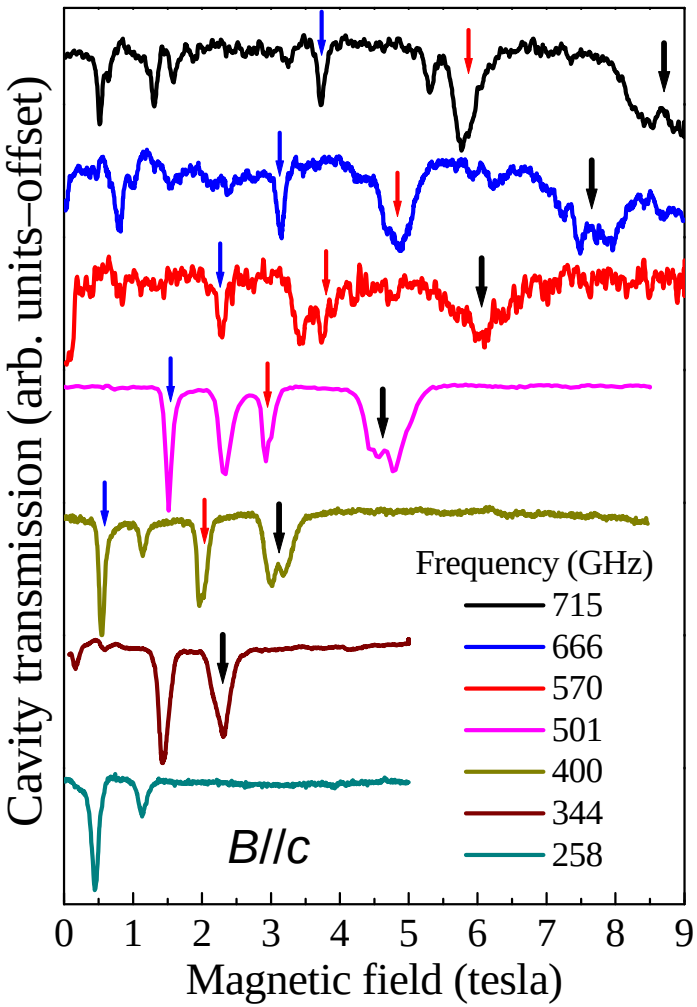


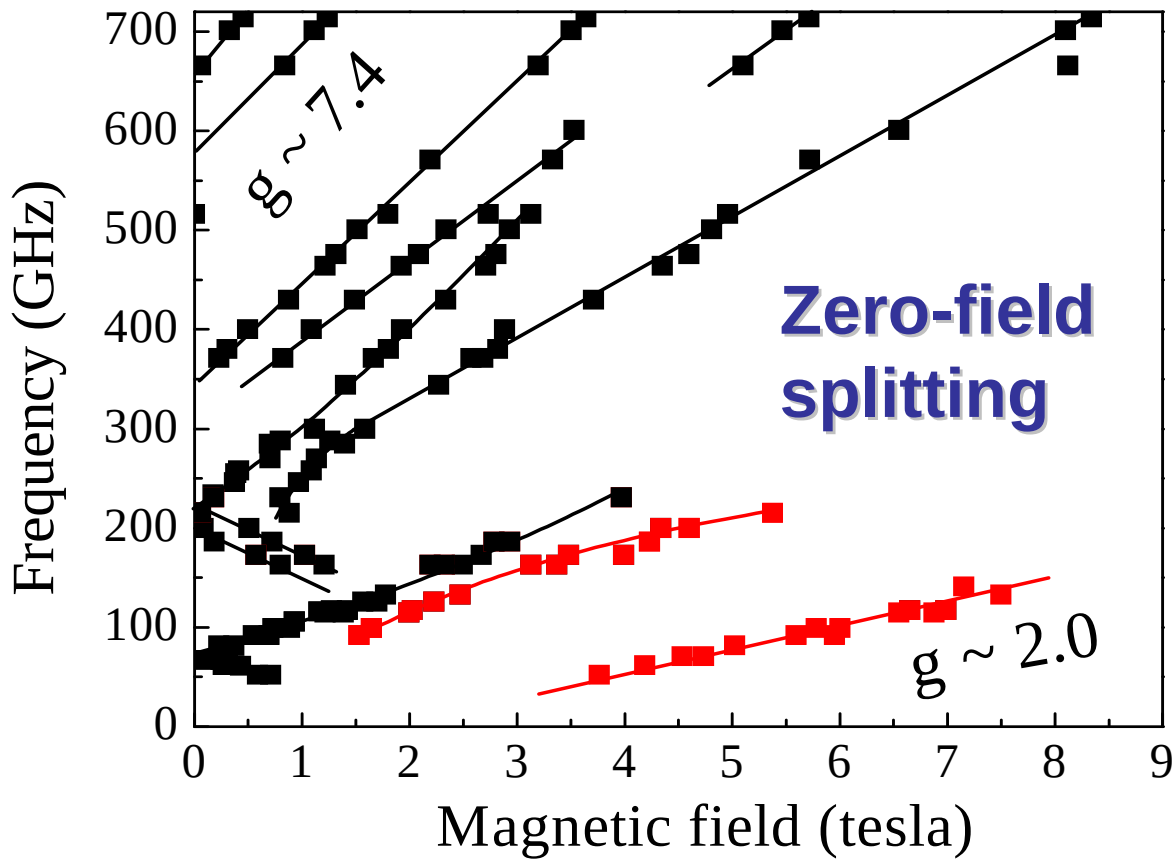


- **Effective *S′* = 1/2 ground state with highly anisotropic *g* – tensor**
- **Lower Kramers doublet of *S* = 3/2 state**
- **No single-ion zero-field-splitting (no zero-field anisotropy)**

Lawrence et al., Polyhedron **26**, 2299 (2007); Yang et al., J. Appl. Phys **91**, 7382 (2002).

Co_4 shows some characteristics of a SMM





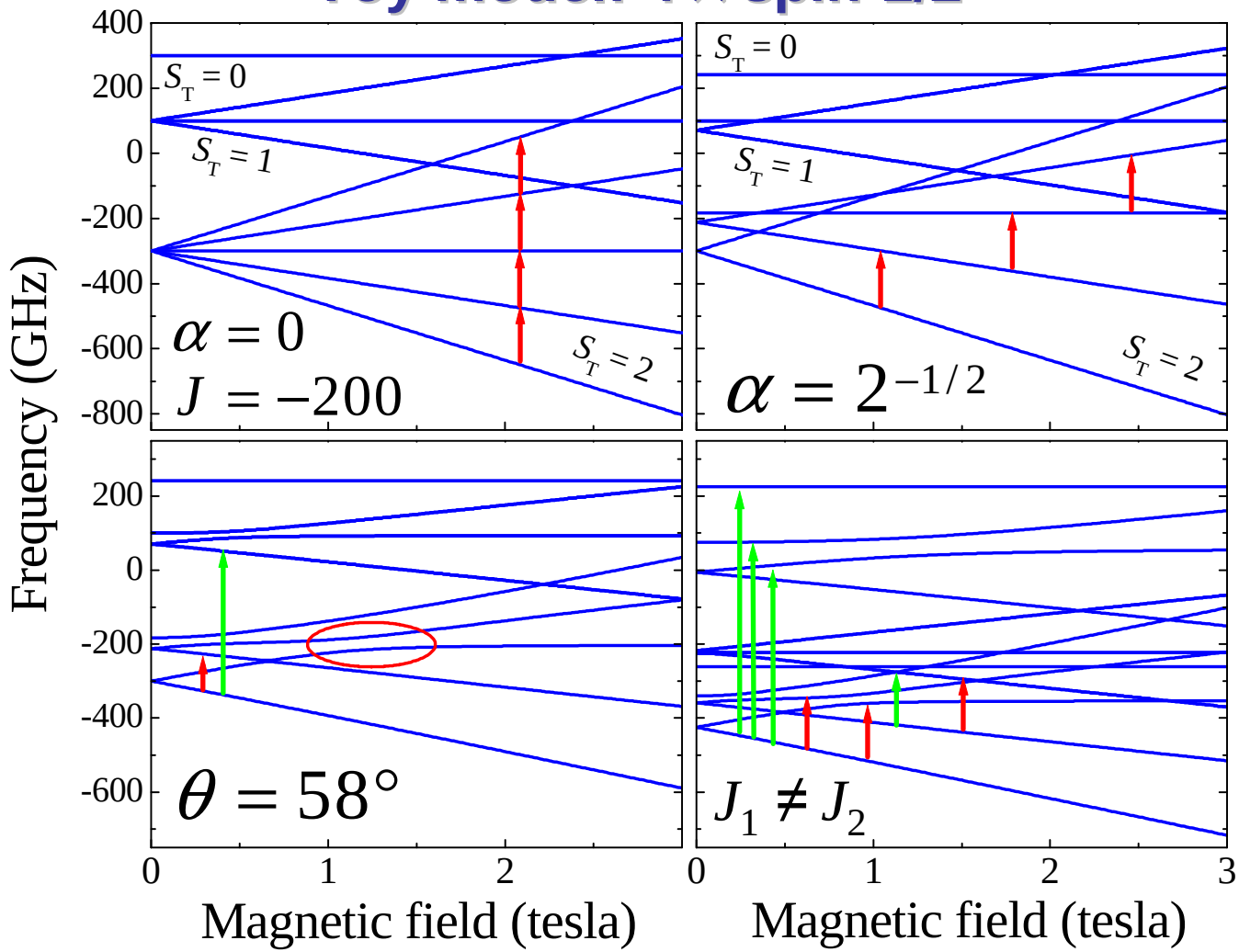
+ Magnetization hysteresis (below 1 K)

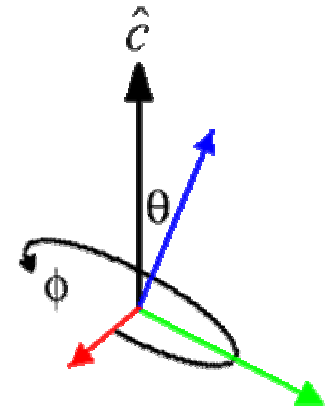
J. Liu et al., Polyhedron; DOI: 10.1016/j.poly.2008.10.064.
Lawrence et al., Polyhedron **26**, 2299 (2007); Yang et al., J. Appl. Phys **91**, 7382 (2002).

SMM properties from anisotropic exchange

$$H = J\sum_{i<j}\left[\hat{S}_{iz}\hat{S}_{jz} + \alpha\left(\hat{S}_{ix}\hat{S}_{jx} + \hat{S}_{iy}\hat{S}_{jy}\right)\right] + \sum_i \mu_B \vec{B}\cdot\vec{\vec{g}}_i\cdot\hat{S}_i$$

Toy model: 4 × spin-1/2





$g_z = 7.8$

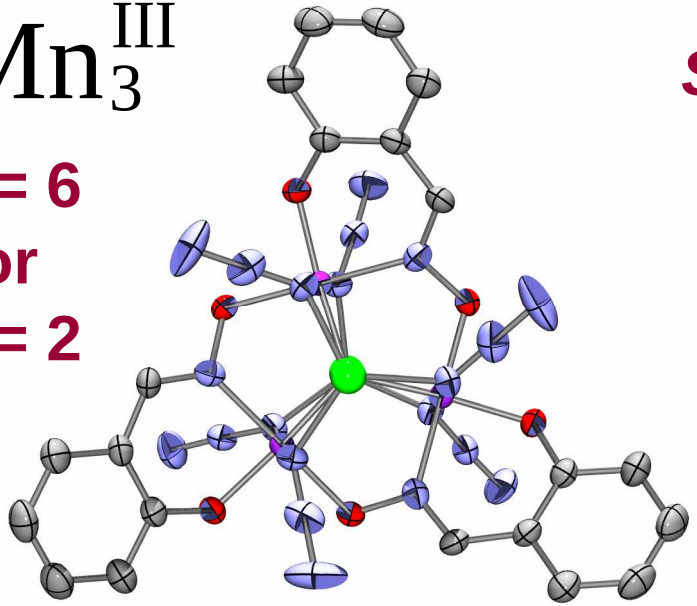
$g_{xy} = 2.0$

J. Liu et al., DOI: 10.1016/j.poly.2008.10.064; R. A. Klemm et al., PRB **77**, 184410 (2008).

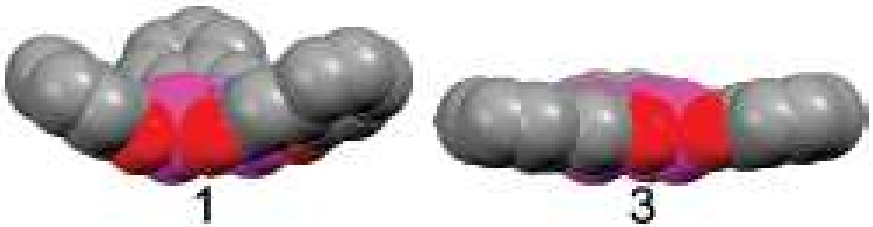
Spin control: targeted ligand-imposed distortion

Mn_3^{III}

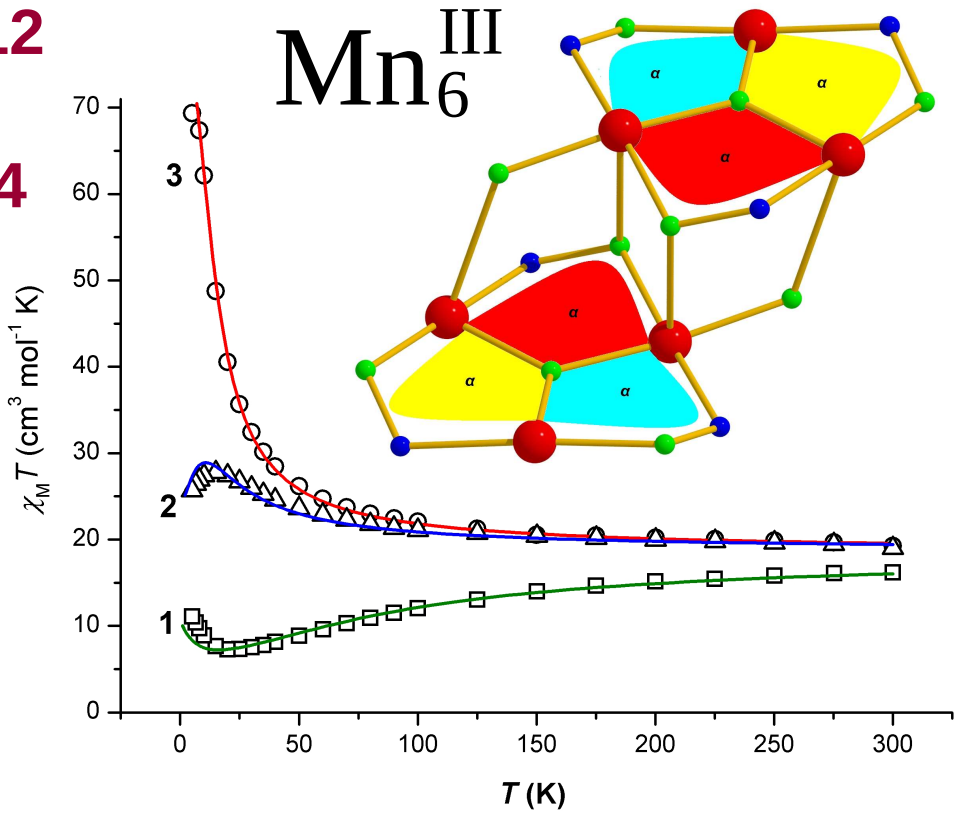
S = 6 or S = 2



S = 12 or S = 4



Mn_6^{III}



Molecule	Torsion angle α / °	J/cm^{-1}	S	Δ_{eff}/K	Δ_{EPR}/K
$[Mn_6O_2(Me\text{-}sao)_6(O_2CCPH_3)_2(EtOH)_4]$	25.5, 29.7, 42.4	1.2/-1.95	4	31.7	**29.2**
$[Mn_6O_2(Et\text{-}sao)_6(O_2CCMe_3)_2(EtOH)_4(H_2O)_2]$	23.3, 36.9, 42.1	-1.9/+1.4	7	30	
$[Mn_6O_2(Et\text{-}sao)_6(O_2CPh)_2(EtOH)_4(H_2O)_2]$	31.3, 38.2, 39.9	+0.93	12	53	
$[Mn_6O_2(Et\text{-}sao)_6(O_2CPhMe_2)_2(EtOH)_4(H_2O)_2]$	34.9, 39.1, 43.1	+1.6	12	86	**75**

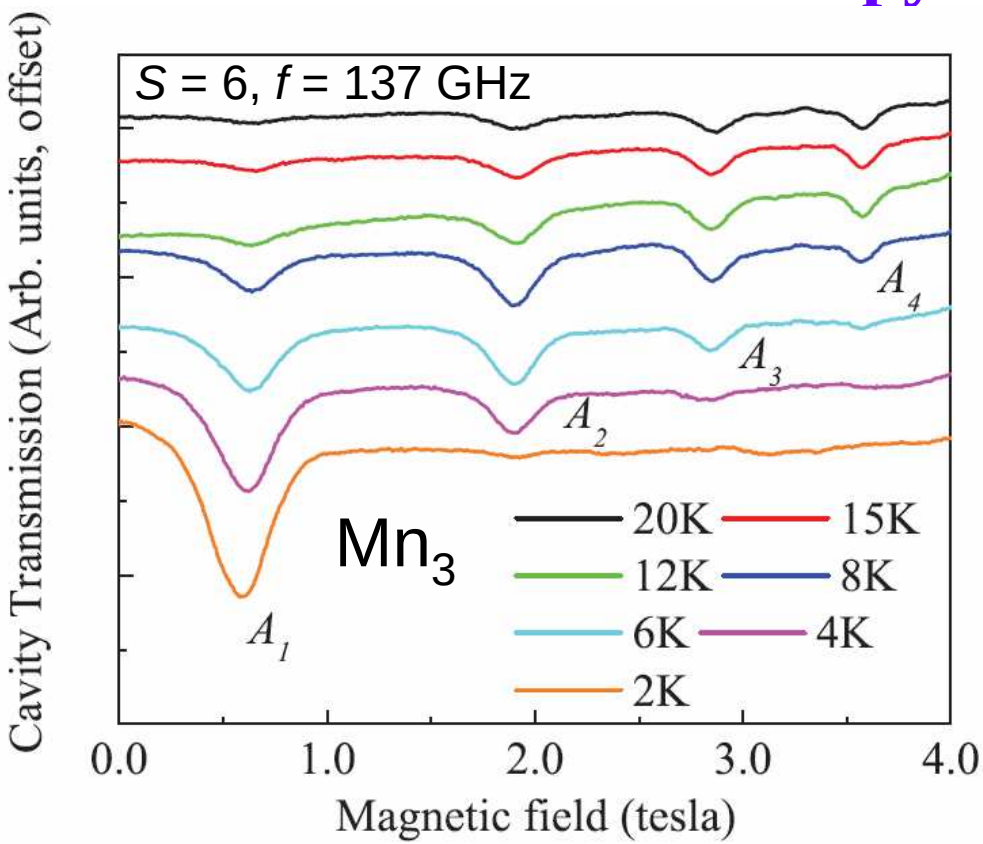
Mn_3: P. Feng et al., Inorg. Chem. **46**, 8126 (2008); T. Stamatatos et al., JACS **129**, 9484 (2007).
Mn_6: C. Milios et al., JACS **129**, 12505 (2007); S. Datta et al., DOI: 10.1016/j.poly.2008.12.025.

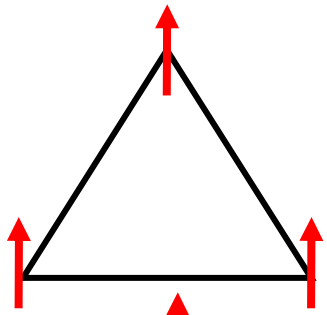
Spin control: raising the magnetic barrier

$$\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[d_i \hat{s}_{zi}^2 + \mu_B \vec{B} \cdot \vec{g}_i \cdot \hat{s}_i \right]$$

Projection technique (strong coupling, $J >> d_S$):

Total uniaxial anisotropy : $D_{tot} = \alpha_1 d_1 + \alpha_2 d_2 + \alpha_3 d_3$





$D_{S=6} = 3/11\ d_s$

SMM√

$9/49\ d_s$

SMM×

Barrier height:

[$\Delta_{S=6} / \Delta_{S=2}$] = 1.746

Ruiz *et al.* Chem. Commun., 52-54 (2008) O. Waldmann Inorg. Chem., 46, 10035-10037 (2007)

Spin control: raising the magnetic barrier

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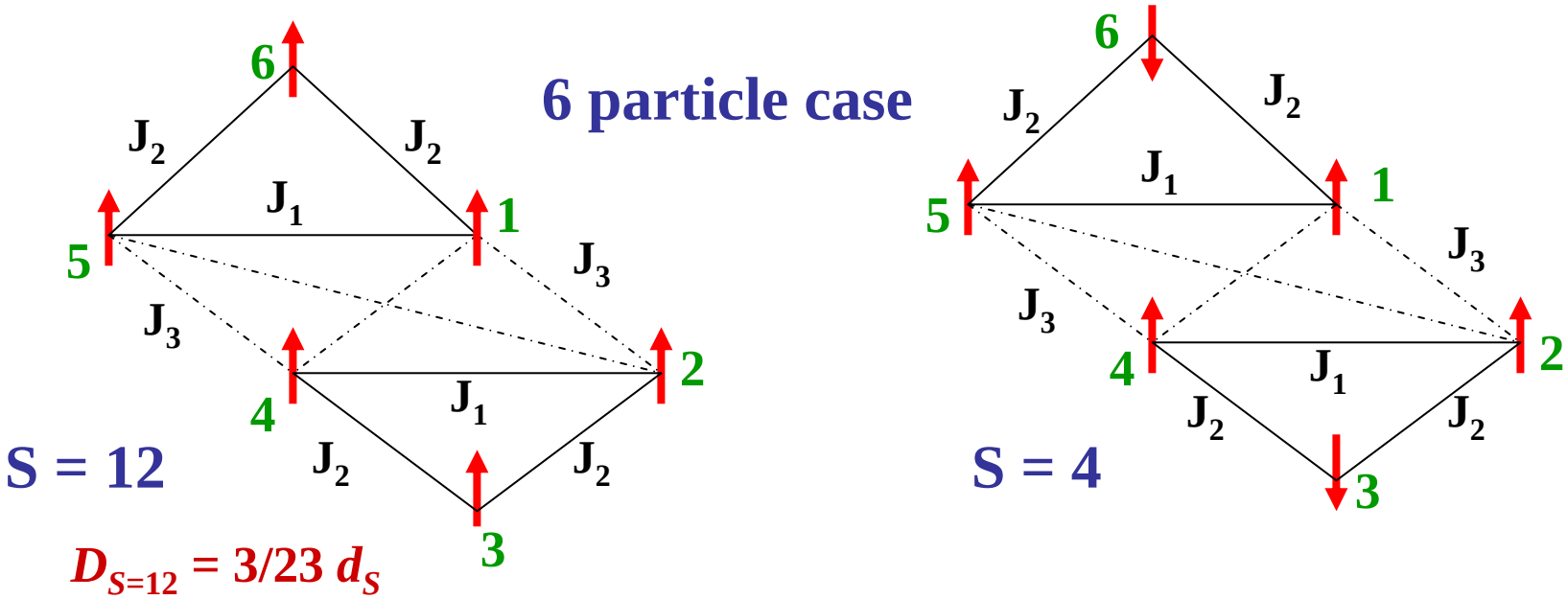
Projection technique (strong coupling, $J >> d_S$):



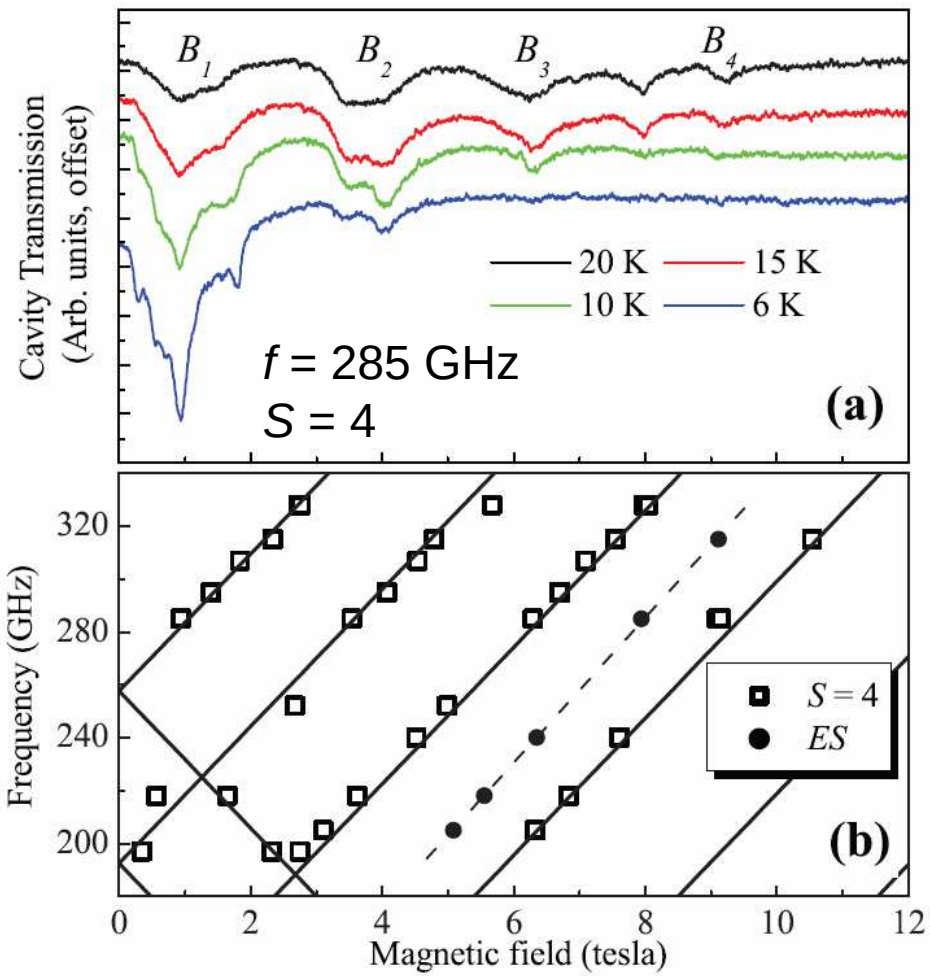
Case #1: $D_{S=4} = 21/25\ d_S$ **for the coupling scheme:** $(((((S_1+S_2)+S_4)+S_5)-S_3)-S_6)$

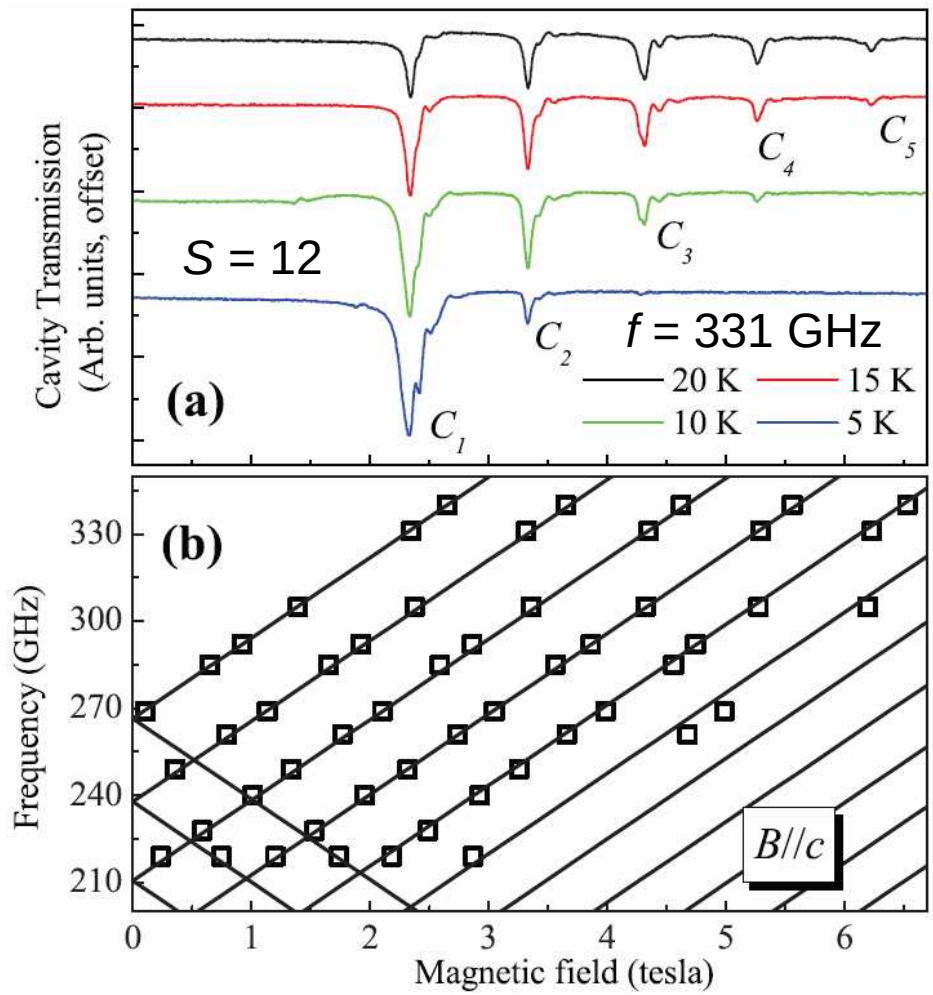
Case #2: $D_{S=4} = 2967/4235\ d_S$ **for the coupling scheme:** $(((((S_1+S_2)-S_3)+S_4)+S_5)-S_6)$

$$\boxed{D_{S=12}/D_{S=4} = 0.16 - 0.19; \quad \Delta_{12}/\Delta_4 = 1.44 - 1.71}$$

Ruiz *et al.* Chem. Commun., 52-54 (2008) O. Waldmann Inorg. Chem., 46, 10035-10037 (2007)

Spin control: raising the magnetic barrier





$D_{S=4} = -1.27(2)\ \mathrm{cm}^{-1}$

$B_4^0 = +1.3(3) \times 10^{-6}\ \mathrm{cm}^{-1}$

$D_{S=12} = -0.360(5)\ \mathrm{cm}^{-1}$

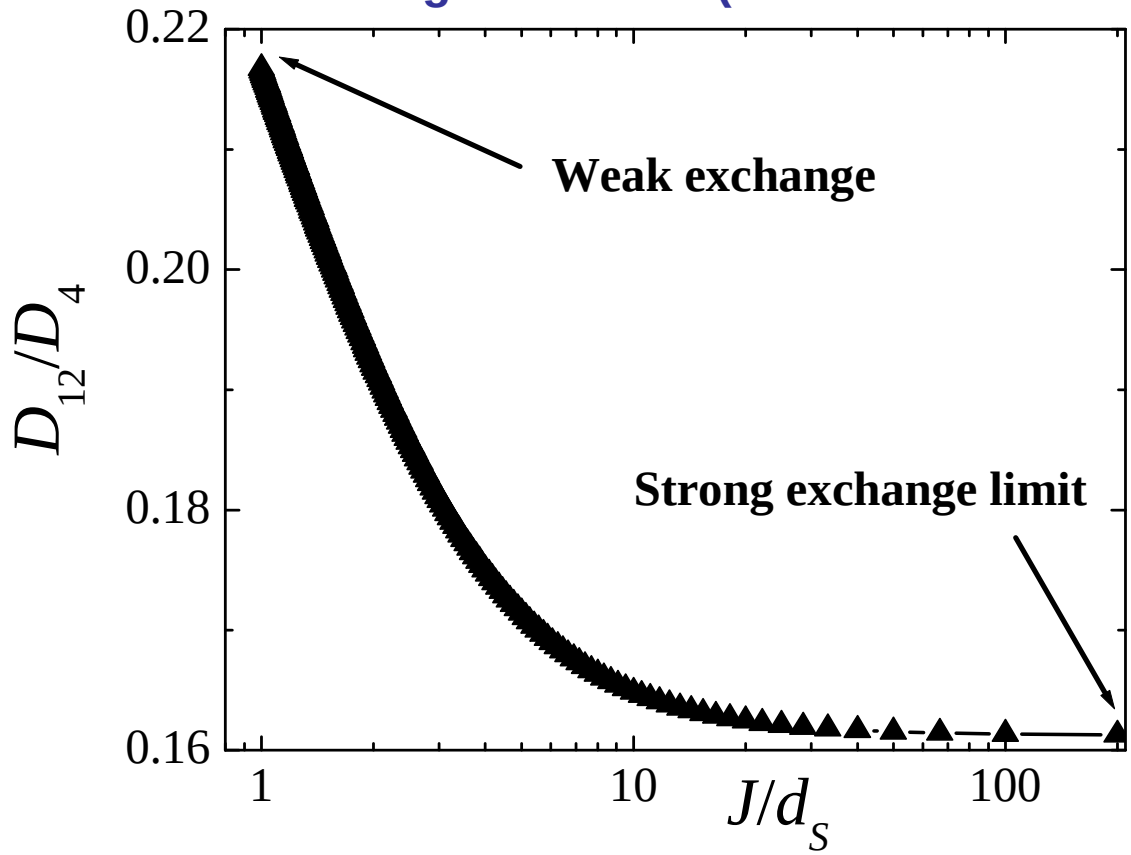
$B_4^0 = -5.7(5) \times 10^{-6}\ \mathrm{cm}^{-1}$

$$\boxed{D_{S=12}/D_{S=4} = 0.28;\ \ \Delta_{12}/\Delta_4 = 2.6}$$

Spin control: the barrier definitely increases

$$\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[d_i \hat{s}_{zi}^2 + \mu_B \vec{B} \cdot \overleftrightarrow{g}_i \cdot \hat{s}_i \right]$$

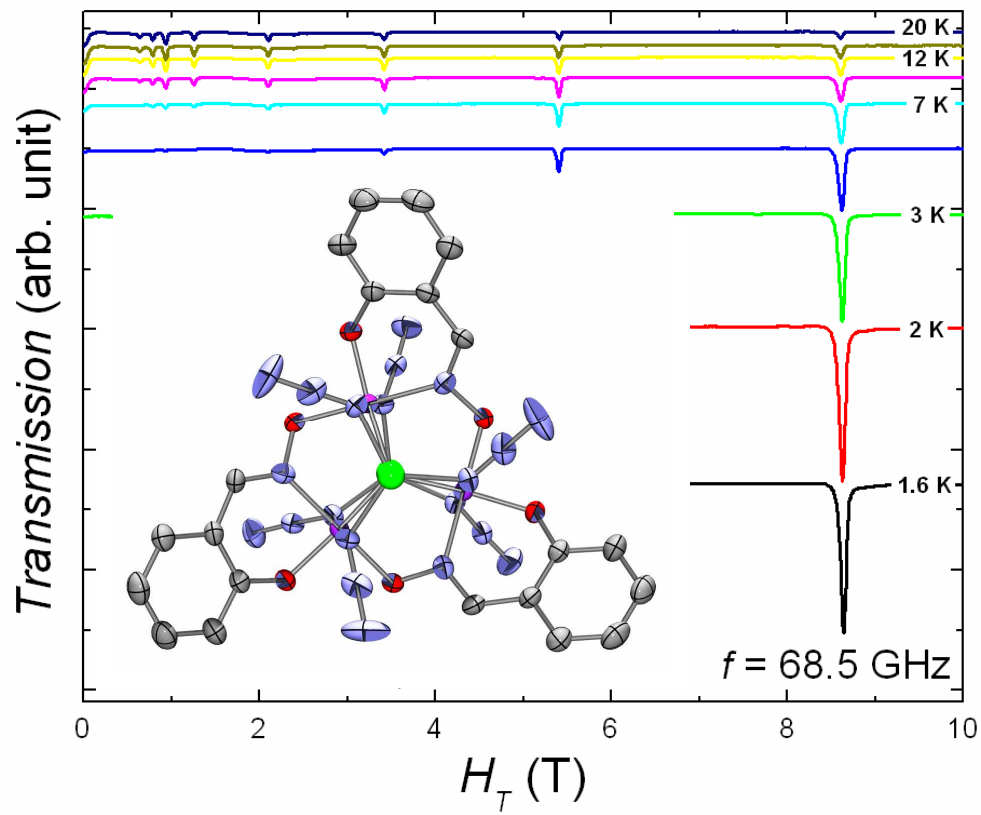
Exact diagonalization (dimension 15625^2)

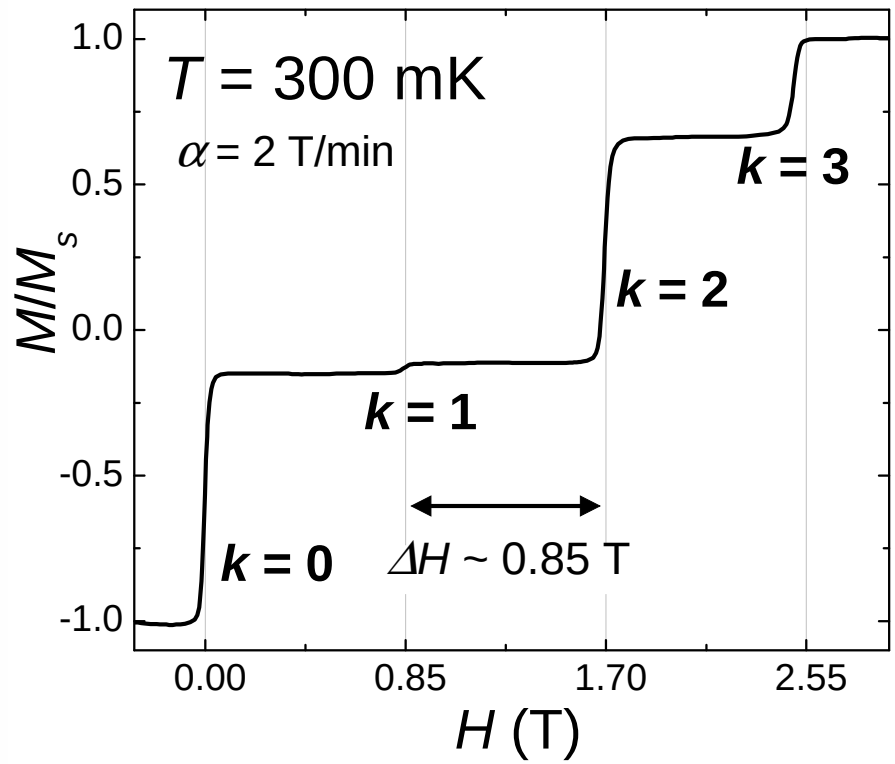


$$\boxed{D_{S=12}/D_{S=4} = 0.28; \quad \Delta_{12}/\Delta_4 = 2.6}$$

Mn_3, $R\bar{3}$, $S = 6$, no solvent→spectacular SMM

$$\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[d_i \hat{s}_{zi}^2 + e_i \left(\hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + \mu_B \vec{B} \cdot \vec{\vec{g}}_i \cdot \hat{s}_i \right]$$





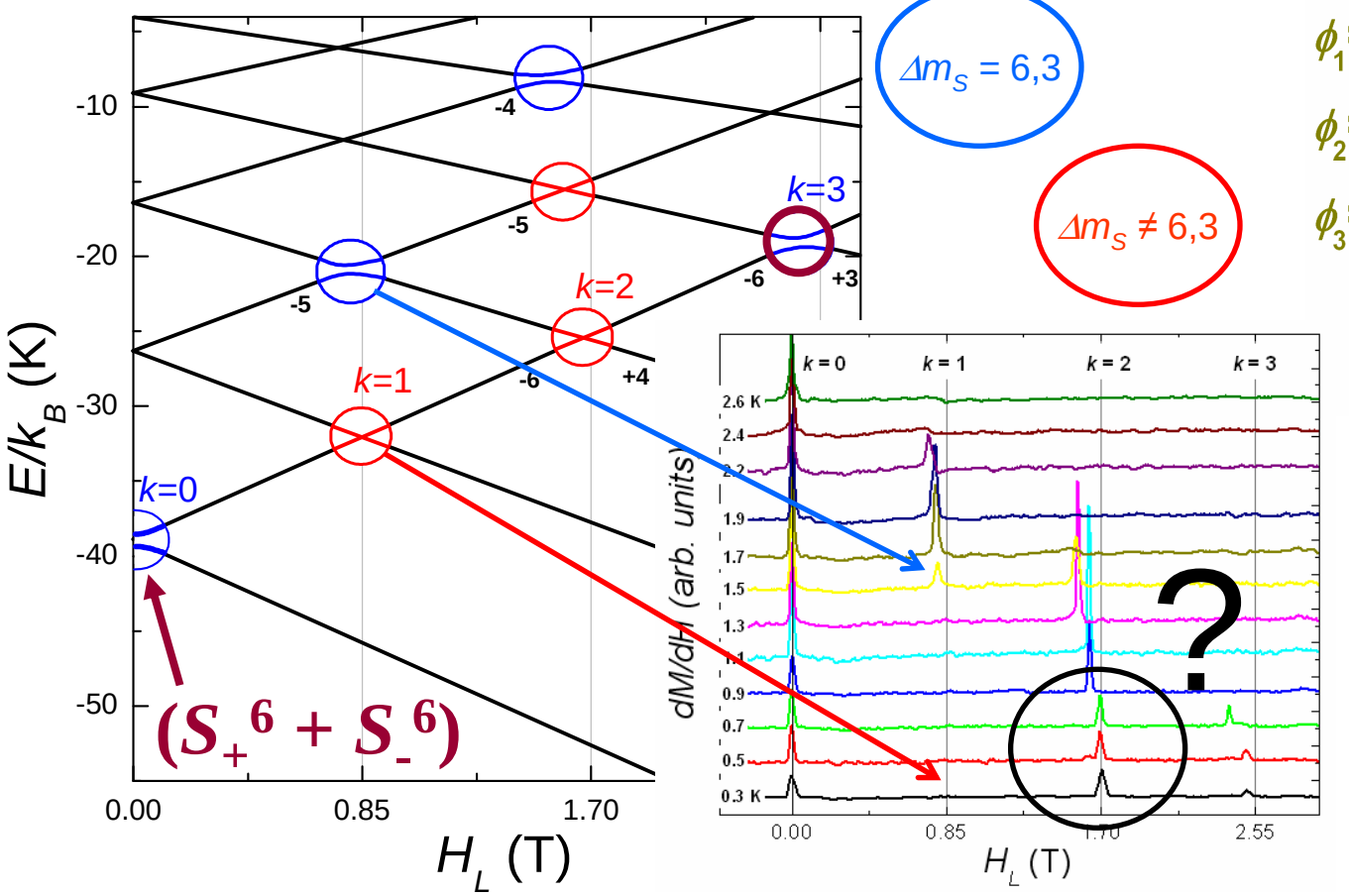
Chiral SMM: $[NEt_4]_3[Mn_3Zn_2(salox)_3O(N_3)X_2]$ with X = Cl/Br

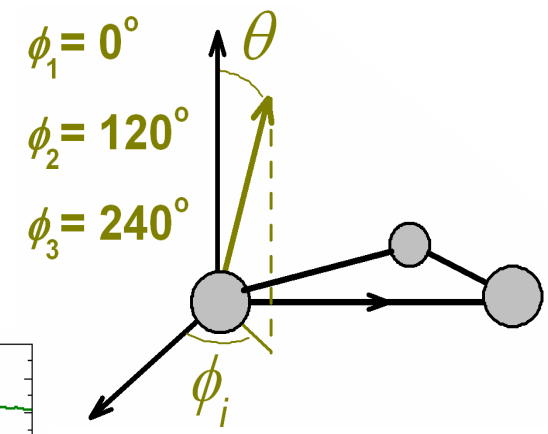
Clear observation of spin-selection rules;Likely due to lack of disorder

Feng *et al.*, *Inorg. Chem.* **47**, 8610 (2008); Feng *et al.*, *Inorg. Chem.* (in press) (2009).

Mn_3, $R\bar{3}$, $S = 6$, no solvent→spectacular SMM

$$\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[d_i \hat{s}_{zi}^2 + e_i \left(\hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + \mu_B \vec{B} \cdot \vec{g}_i \cdot \hat{s}_i \right]$$





$s = 2$
$d = 4.2$ K
$J = 4.88$ K
$g = 2$
$e = 0.9$ K
$\theta = 8.5°$

Tilting JT axes + dipolar fields explains all behavior

→ Chirality → $B_4^3 = S_z(S_+^3 + S_-^3)$

Summary and conclusions

Simple is better

- Simple low-nuclearity clusters provide remarkable insights into the physics of SMMs
- The interplay between exchange and anisotropy causes spin state mixing which, in turn, gives rise to terms in the Giant Spin Hamiltonian that do not otherwise arise naturally
- It is this physics that is behind much of the low-temperature quantum dynamics in SMMs

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Present/new/in development instrumentation

EMR Systems at the Magnet Lab in Tallahassee										
Spectrometer	Frequency (GHz)	Field range (T)	CW - EPR	Pulsed	Time Resolved	ENDOR	Rotation	Absolute Sensitivity[1] at 290 K (spins/mT)	Concentration Sensitivity at 290 K (spin/cm^3-mT)	Max. sample size (μl)
Transmission	23-660	0-17	■					10^{10}	5×10^{11}	200
Homodyne QO	190-670	0-17	■			■		5×10^{11}	2×10^{12}	10
Heterodyne QO & Transmission	120, 240, 336	0-12.5	■	■	■	■	■	10^{9} (in cavity) 2×10^{11}	5×10^{11} 2×10^{12}	0.1 100
DC-field[2] QO & Transmission	50-900	0-45	■		■		■	10^{9} (in cavity) 10^{10}	 5×10^{11}	200
Bruker X-band	9.7	0-1.5	■	■		■	■	10^{11}	10^{12}	70
Bruker W-band	95	0-6	■	■		■	■	5×10^{9}	10^{12}	0.4

[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

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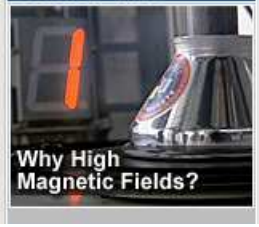

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The primary intent of this program is to provide greater access to our facilities and to seed research programs that help advance the laboratory. Funding is principally intended to support travel and local expenses. Requests for stipends are considered but given a lower priority.