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# Quantum Tunneling and Magnetization Dynamics in Low Dimensional Systems

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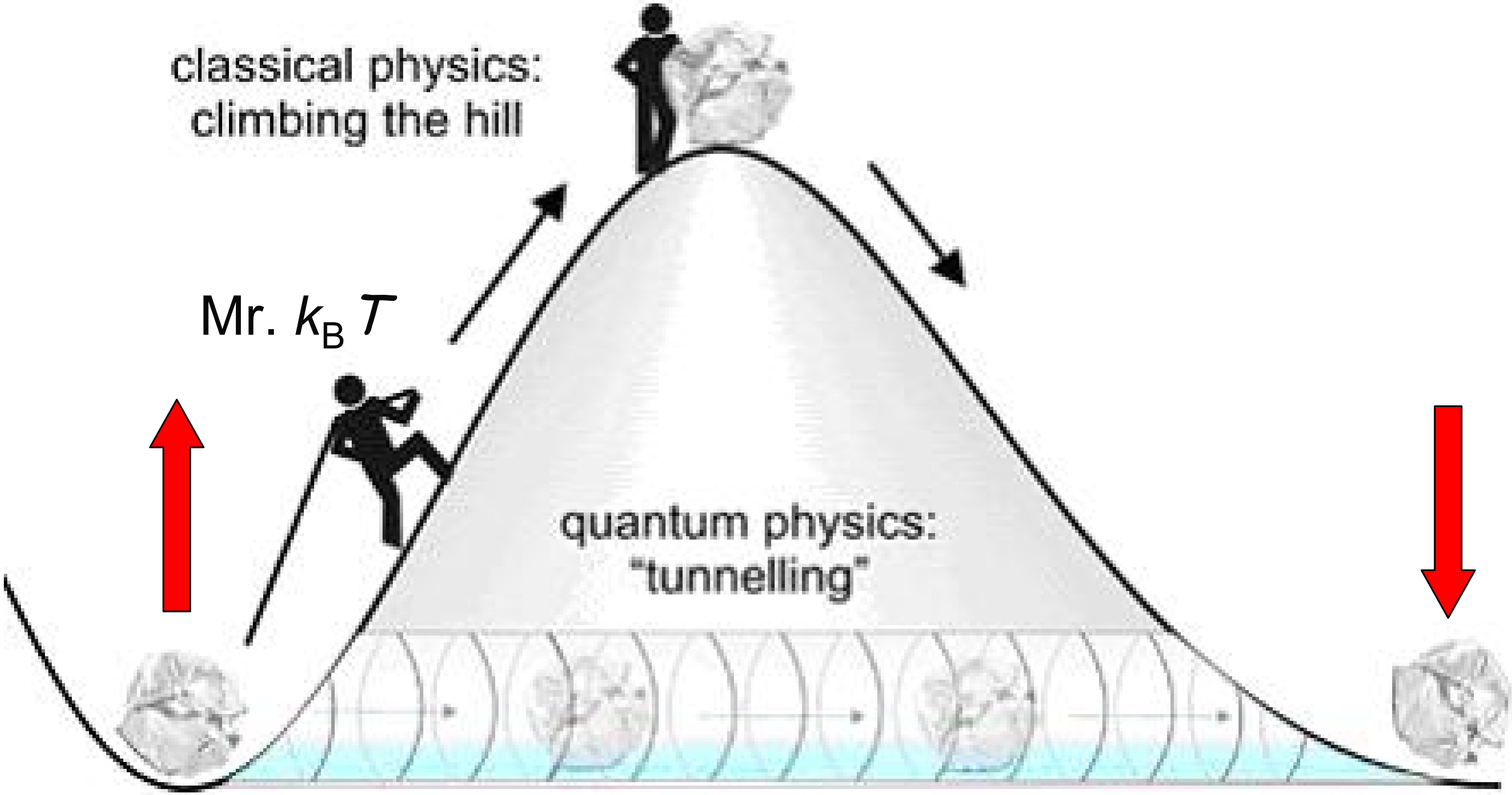

classical physics:
climbing the hill
Mr. $k_B T$
quantum physics:
"tunnelling"

# Outline

- **Quantum spins and magnetic anisotropy**
- **Boosting up molecular spin: from individual ions to high-spin clusters**
- **Slow magnetic relaxation in high-spin clusters: thermal activation *vs.* quantum tunneling effects**
- **Back to single ions: rare-earth complexes**
- **Glauber dynamics: a glance at Single-Chain Magnets**
- **Summary**

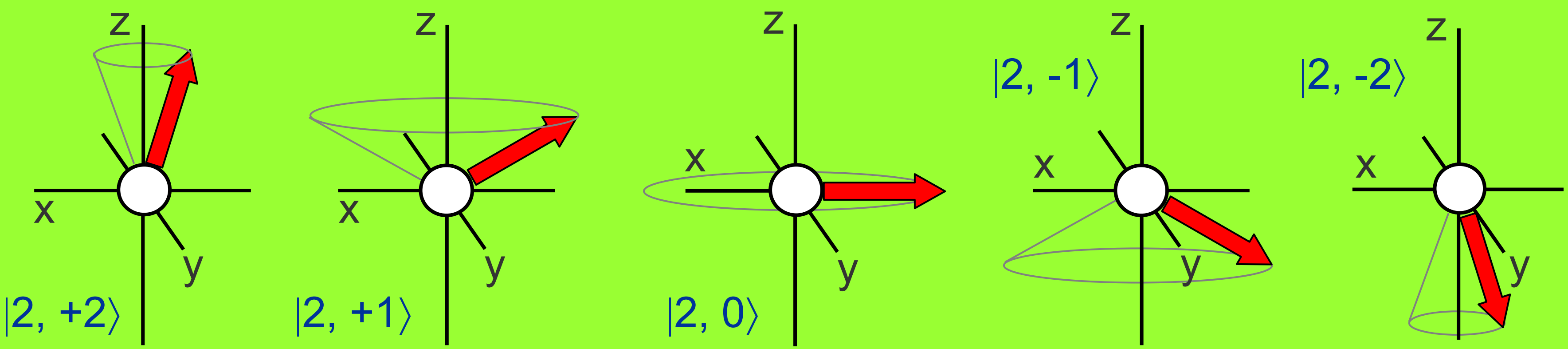
# The essence of quantum spins

- The spin vector and its components: $\mathbf{S} = (S_x, S_y, S_z)$
- Commutation relations:

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z \qquad [\hat{S}^2, \hat{S}_x] = 0$$
$$[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x \qquad [\hat{S}^2, \hat{S}_y] = 0$$
$$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y \qquad [\hat{S}^2, \hat{S}_z] = 0$$

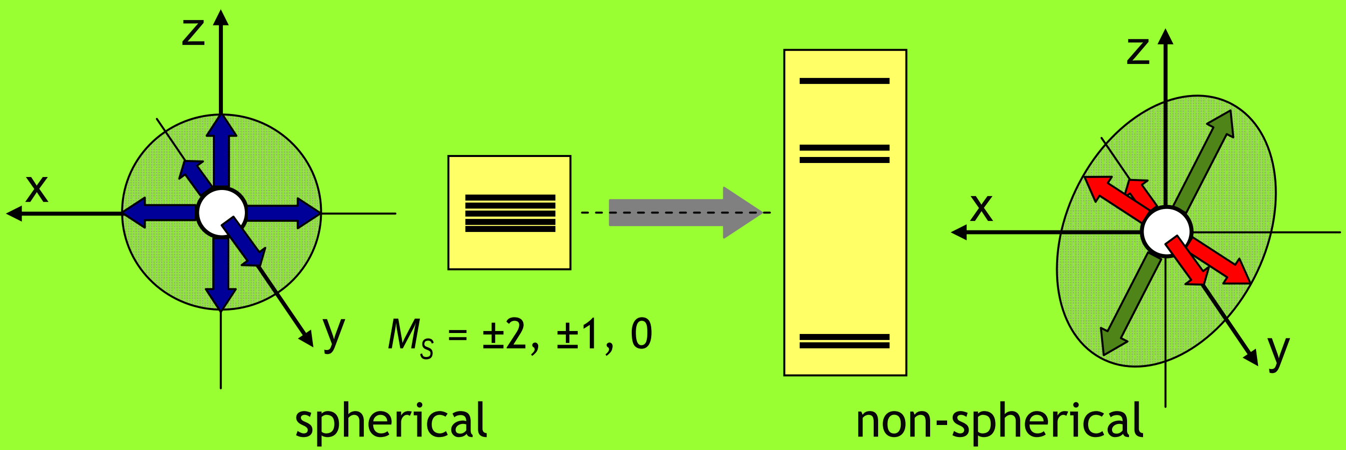
- Only $S^2$ and one of the components of **S** (e.g. $S_z$) can be exactly known at the same time
- Simultaneous EFs of $\hat{S}^2$ and $\hat{S}_z$ exist, with EVs $\hbar^2 S(S+1)$ and $\hbar M_S$ $(-S \leq M_S \leq S)$, respectively; the EFs are $2S + 1$ in number and are indicated as $|S, M_S\rangle$

$$\hat{S}^2\,|S, M_S\rangle = \hbar^2 S(S+1)\,|S, M_S\rangle \qquad \hat{S}_z\,|S, M_S\rangle = \hbar M_S\,|S, M_S\rangle$$



# A key ingredient: magnetic anisotropy

- A perfectly isolated electronic spin would show no preference for specific directions is space and its response to external perturbations would be perfectly isotropic*
- **SPIN ORBIT COUPLING (SOC)** makes the spin sensitive to the environment and to molecular structure
- In a spherical environment, even in the presence of SOC the spin remains isotropic and the $|S, M_S\rangle$ states are exactly isoenergetic
- A non-spherical environment lifts (partially or totally) the degeneracy of the $|S, M_S\rangle$ states **(ZERO FIELD SPLITTING, ZFS)**

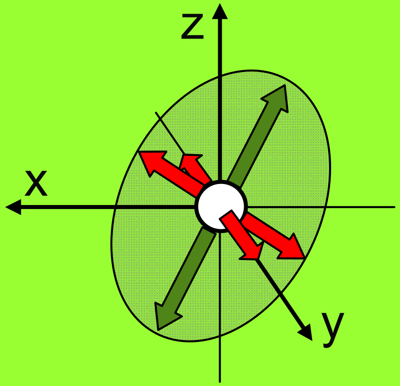


# The D tensor

- Being **S** an angular momentum, its components change sign upon time reversal
- **The Hamiltonian must be invariant upon time reversal: terms describing ZFS can contain only <u>even powers</u> of spin components ($S_z^2$, $S_xS_y$, $S_z^4$, etc.)**
- Usually, the leading terms are 2° powers of spin components ("second-order" terms); they are described by the **<u>D tensor</u>**, which is a **real symmetric traceless** 3x3 matrix

$$\hat{\mathbf{H}}_{ZFS} = D_{xx}\hat{S}_x^2 + D_{xy}\hat{S}_x\hat{S}_y + D_{xz}\hat{S}_x\hat{S}_z + D_{yx}\hat{S}_y\hat{S}_x + D_{yy}\hat{S}_y^2 + \ldots$$

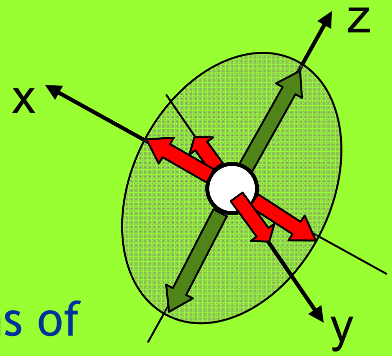
$$= (\hat{S}_x \ \ \hat{S}_y \ \ \hat{S}_z)\begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}\begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix} = \hat{\mathbf{S}}\cdot\mathbf{D}\cdot\hat{\mathbf{S}}$$




- $\boldsymbol{D_{xx}}x^2 + \boldsymbol{D_{xy}}xy + \boldsymbol{D_{xz}}xz + \boldsymbol{D_{yx}}yx + \boldsymbol{D_{yy}}y^2 + \ldots = 1$ is the equation of a general ellipsoid, which has three orthogonal principal axes

# *D* and *E* parameters

- If the reference frame is chosen along the principal axes, the new tensor **D'** is diagonal




$$\hat{\mathbf{H}}_{ZFS} = \hat{\mathbf{S}} \cdot \mathbf{D}' \cdot \hat{\mathbf{S}} = D'_{xx}\hat{S}_x^2 + D'_{yy}\hat{S}_y^2 + D'_{zz}\hat{S}_z^2$$

- By convention, the diagonal elements are re-defined in terms of the so-called axial (*D*) and rhombic (*E*) ZFS parameters

$$\mathbf{D}' = \begin{pmatrix} D'_{xx} & 0 & 0 \\ 0 & D'_{yy} & 0 \\ 0 & 0 & D'_{zz} \end{pmatrix} \equiv \begin{pmatrix} -D/3+E & 0 & 0 \\ 0 & -D/3-E & 0 \\ 0 & 0 & 2D/3 \end{pmatrix}$$

to give

axial ZFS parameter

rhombic ZFS parameter

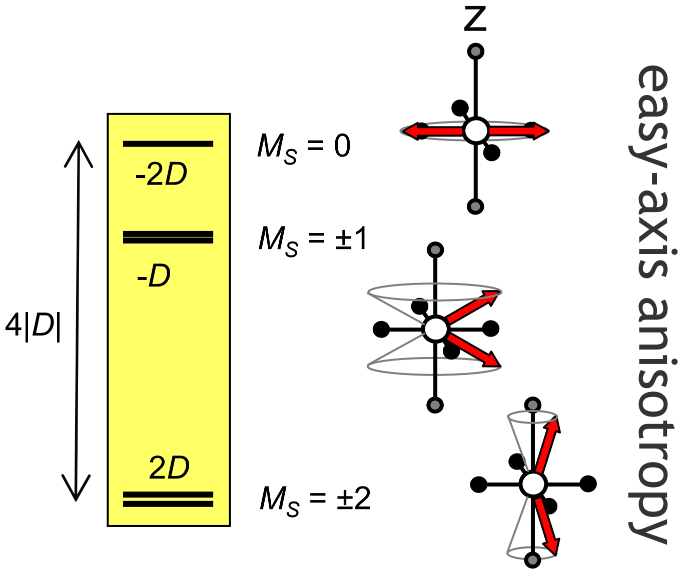
$$\hat{\mathbf{H}}_{ZFS} = (-D/3+E)\hat{S}_x^2 + (-D/3-E)\hat{S}_y^2 + (2D/3)\hat{S}_z^2 = D[\hat{S}_z^2 - \tfrac{1}{3}S(S+1)] + E(\hat{S}_x^2 - \hat{S}_y^2)$$

- For *E* = 0 only, the $|S, M_S\rangle$ are EFs of the ZFS hamiltonian, with the following EVs

$$E_{ZFS}(M_S) = D[M_S^2 - \tfrac{1}{3}S(S+1)]$$

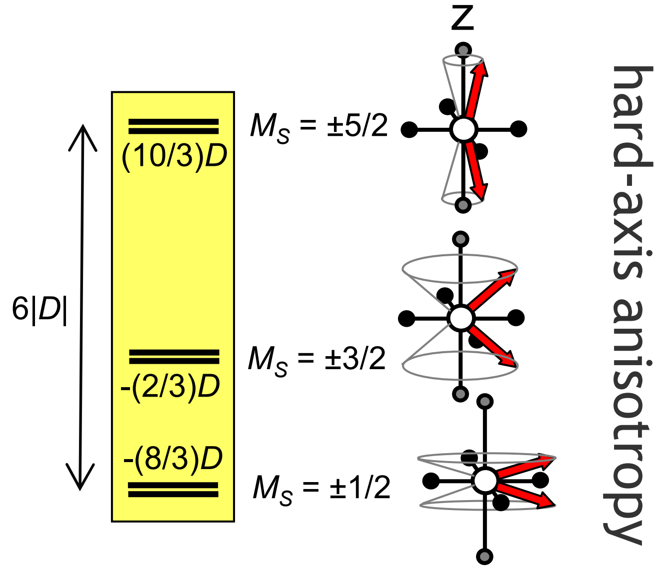
# Easy-axis and hard-axis anisotropies

## High-spin $Mn^{3+}$ ($S = 2$) with $D < 0$




$$E_{ZFS}(M_S) = D[M_S^2 - 2]$$

## High-spin $Fe^{3+}$ ($S = 5/2$) with $D > 0$




$$E_{ZFS}(M_S) = D[M_S^2 - 35/12]$$

## TOTAL SPLITTING

for integer $S$

$$|E_{ZFS}(0) - E_{ZFS}(\pm S)| = |D|S^2$$

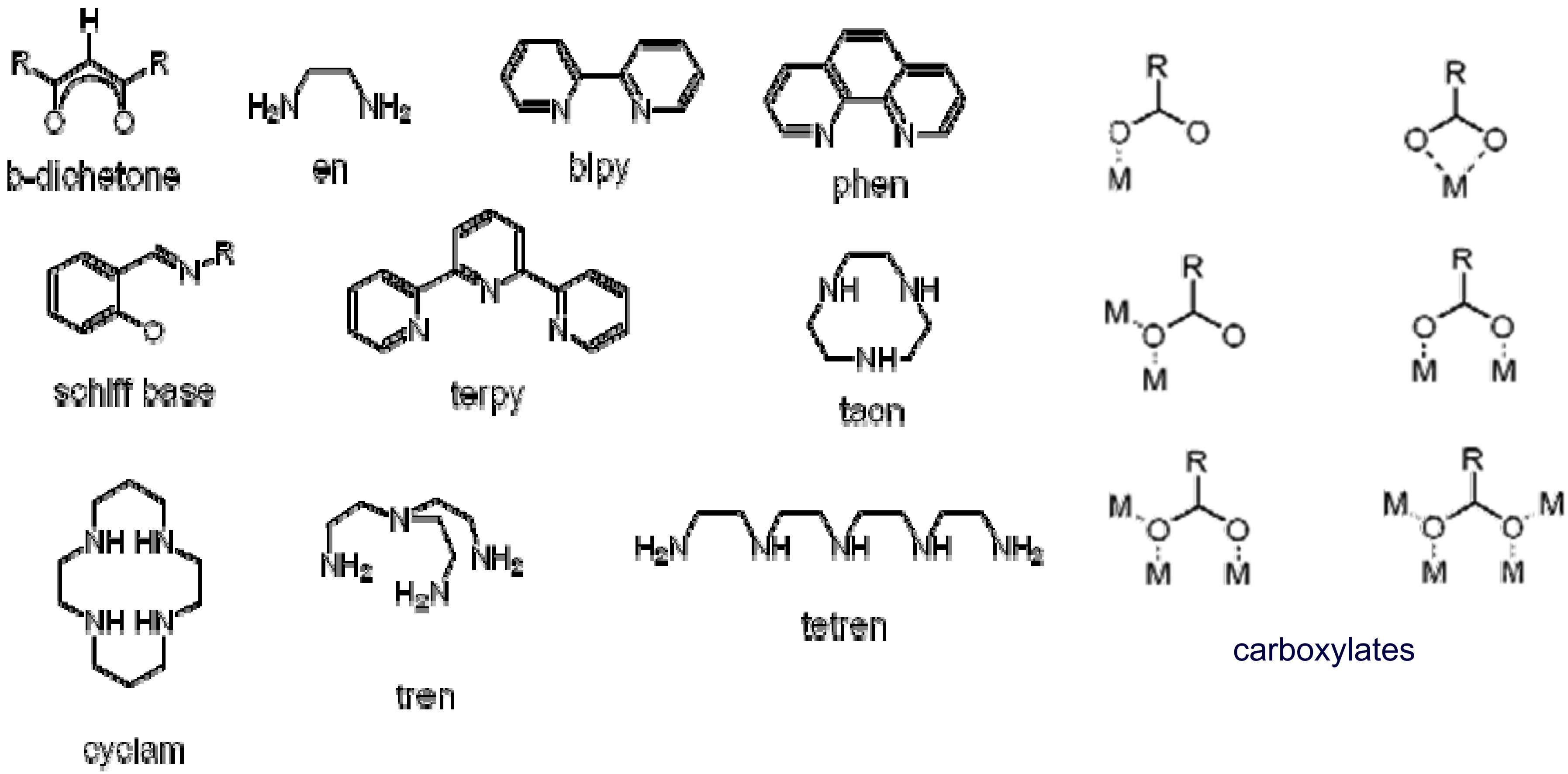
for half-integer $S$

$$|E_{ZFS}(\pm \tfrac{1}{2}) - E_{ZFS}(\pm S)| = |D|(S^2 - \tfrac{1}{4})$$

# Large metal ion clusters

low pH $H_2O$ high pH

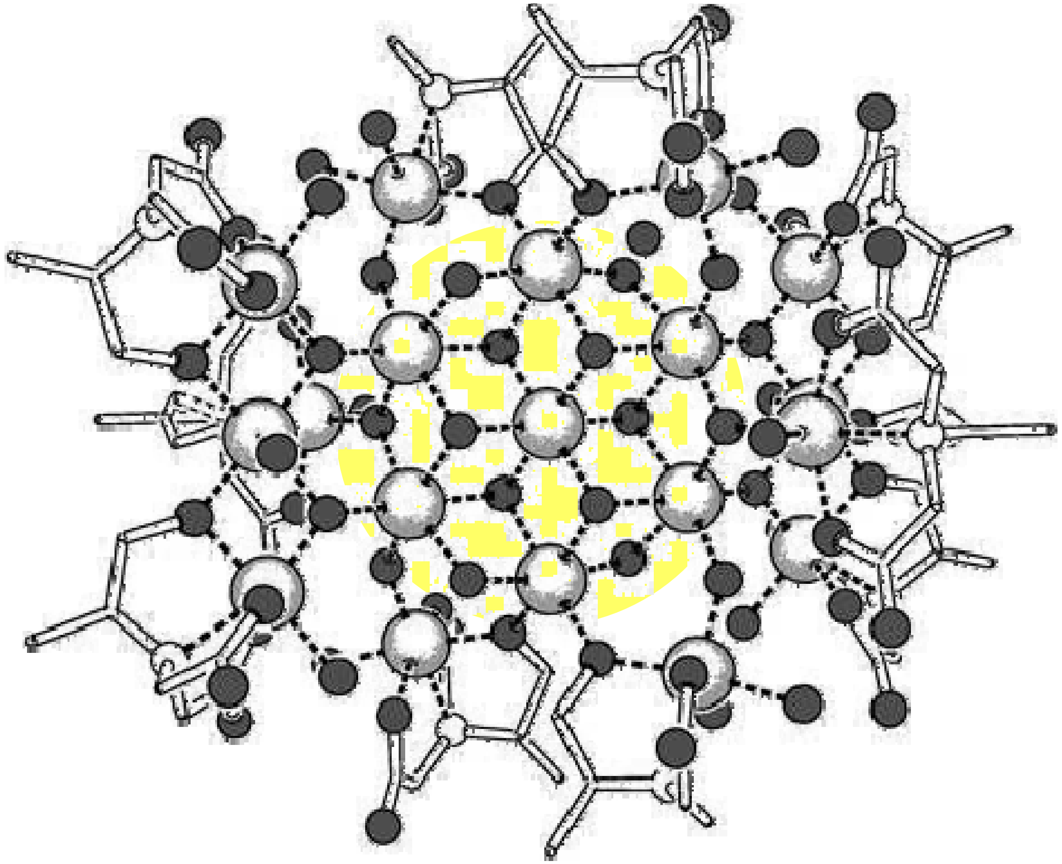
$[Fe(H_2O)_6]^{3+}$ → $[Fe_n(OH)_x(O)_y(H_2O)_z]^{3n-x-2y}$ → $Fe(OH)_3\downarrow$

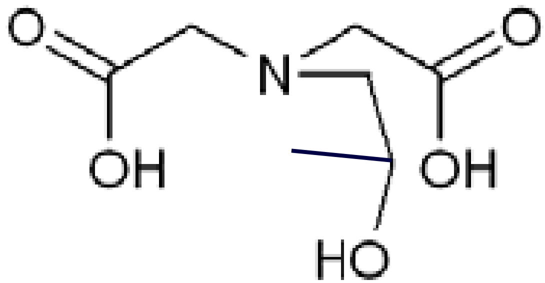


# Large metal ion clusters

$[Fe_{19}(OH)_{14}(O)_6(H_2O)_{12}(\textit{metheidi})_{10}]$

connecting ligands — terminal ligands

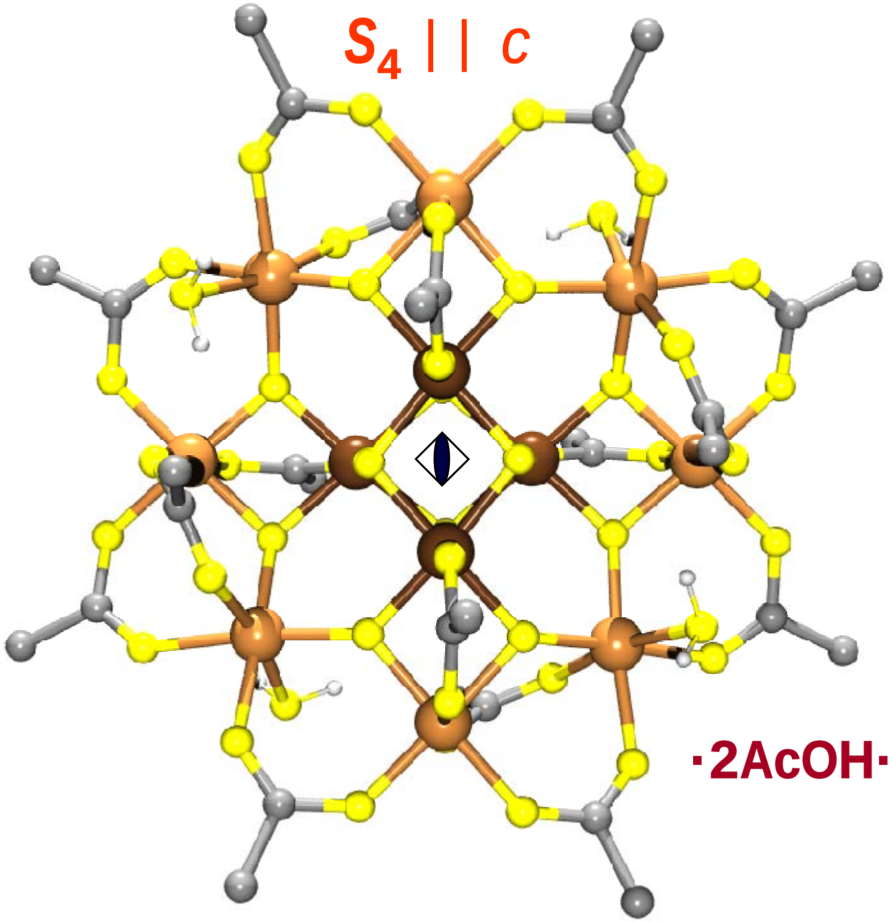





metheidi

Iron "crusts"

# $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 2AcOH\cdot 4H_2O$




$\cdot 2AcOH\cdot 4H_2O$

$Mn^{II}(OAc)_2\bullet 4H_2O + KMn^{VII}O_4$

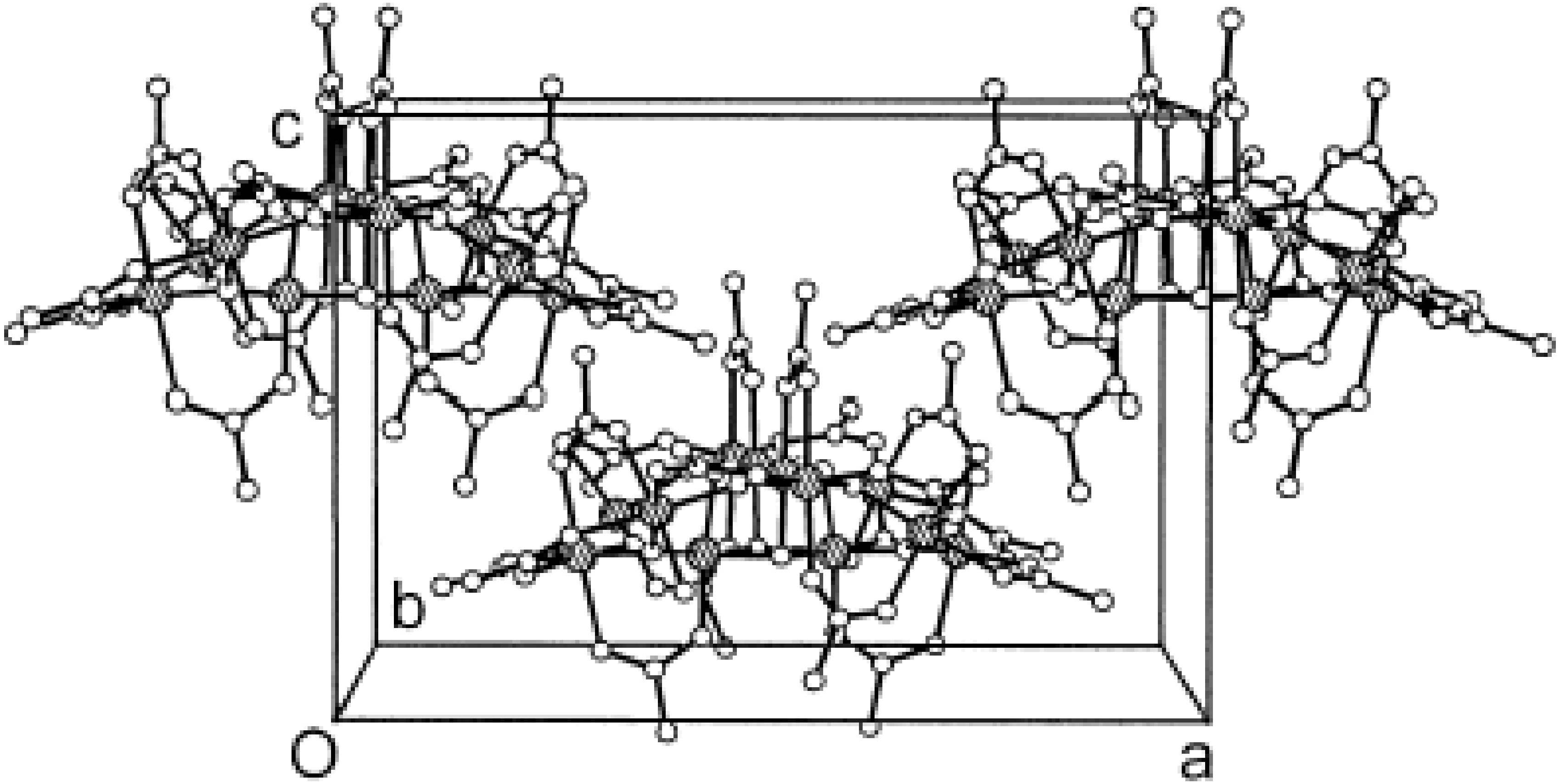
↓ 60% v/v $AcOH/H_2O$

$[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$
$\cdot 2AcOH\cdot 4H_2O$ (80%)
($8Mn^{III} + 4Mn^{IV}$)

**$Mn_{12}$*acetate***

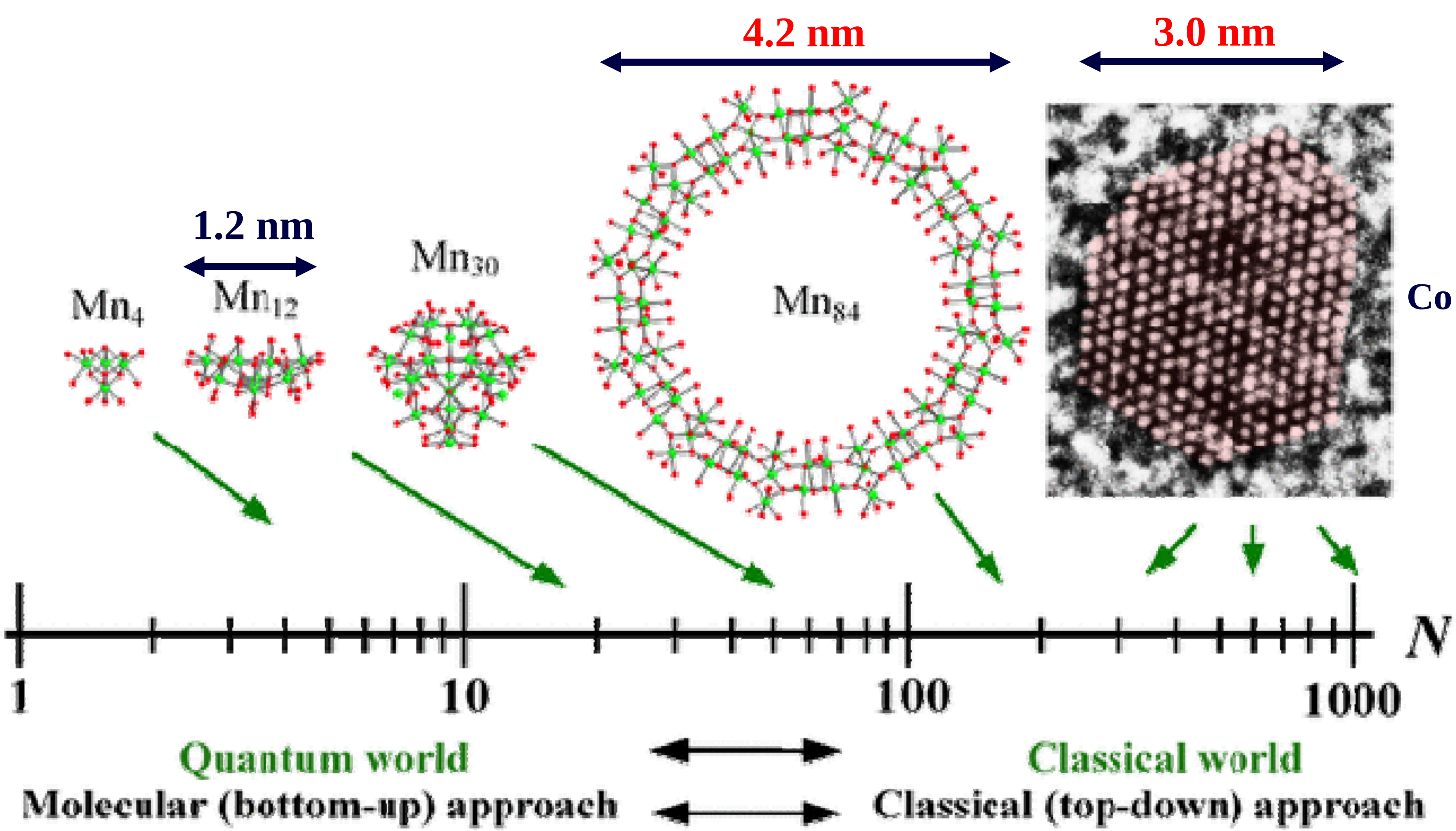
- Manganese(IV) ($s$ = 3/2)
- Manganese(III) ($s$ = 2)
- Oxygen
- Carbon
- Hydrogen

# $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]\cdot 2AcOH\cdot 4H_2O$



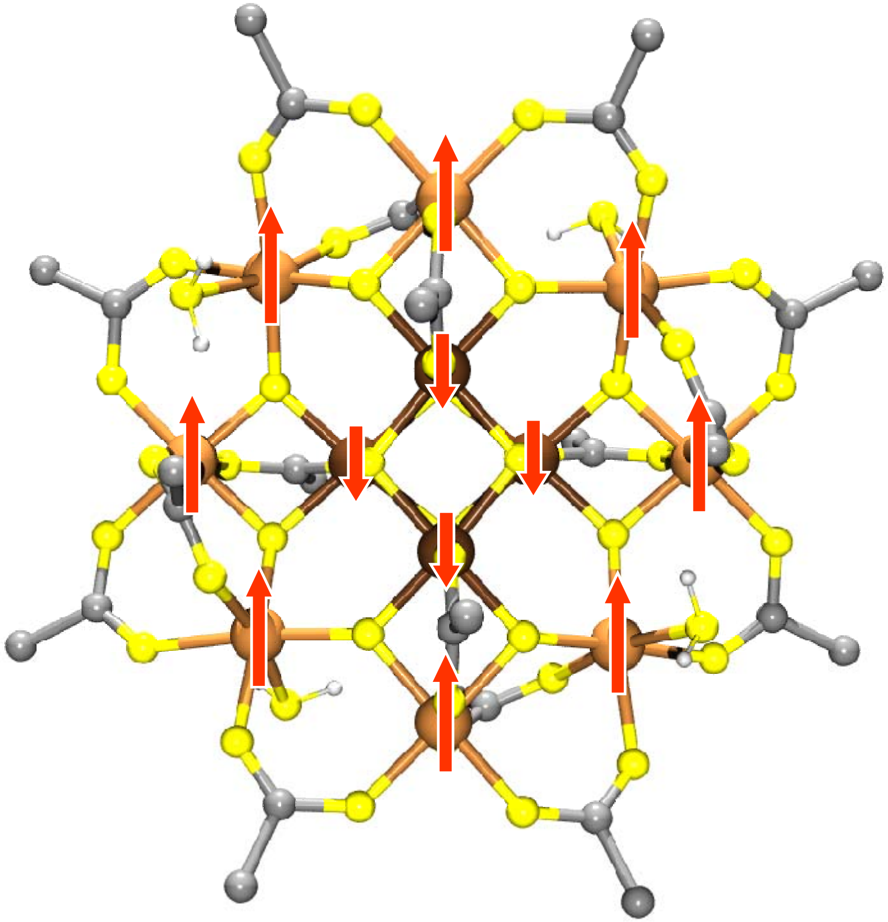

**Tetragonal Space Group $I\bar{4}$**

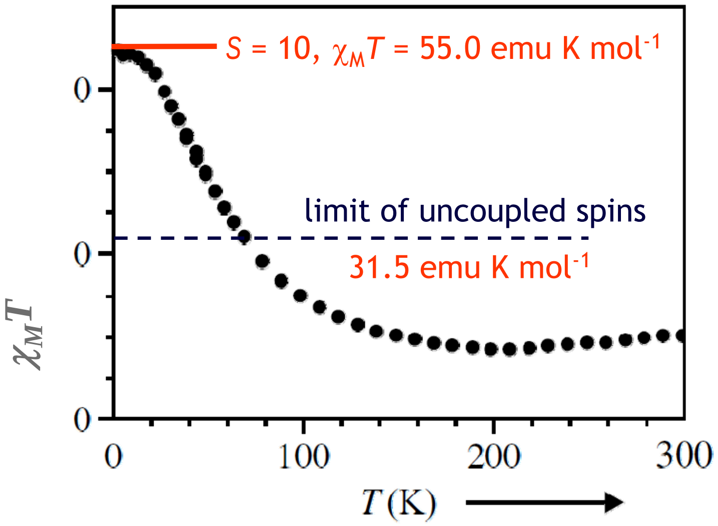
# How large? $Mn_{84}$ vs. a Co nanoparticle

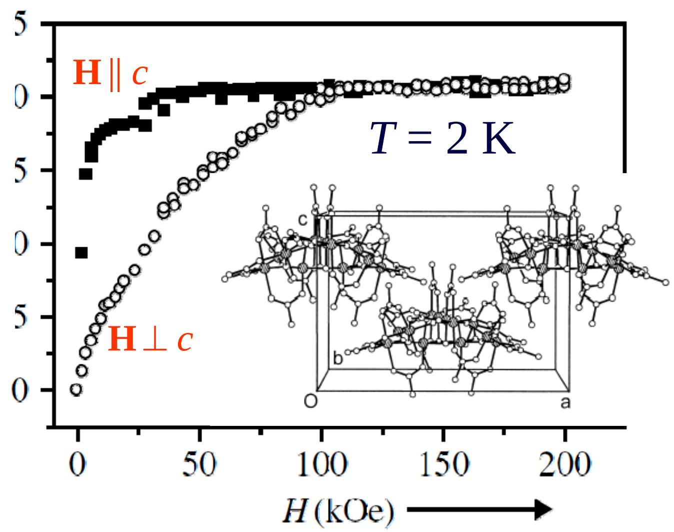



A. J. Tasiopoulos, et al., *Angew. Chem. Int. Ed.* 2004, *43*, 2117

# The physics of $Mn_{12}$*acetate* in a nutshell





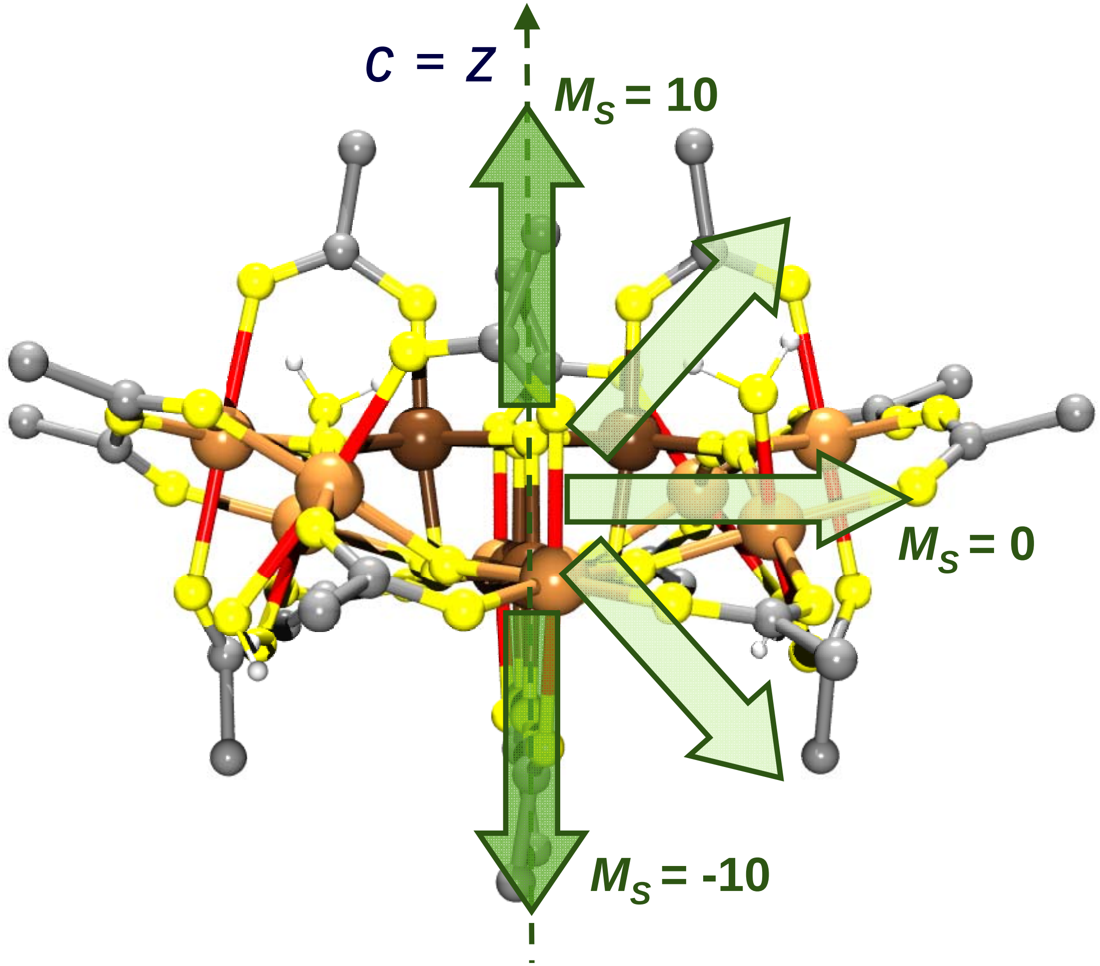



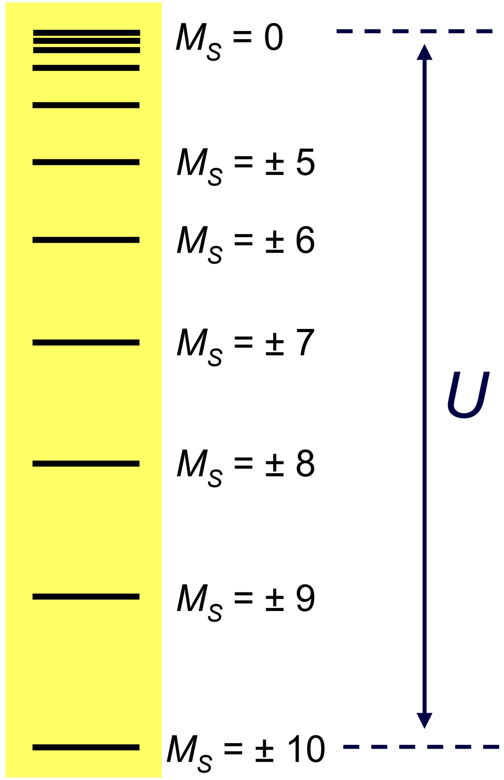

***S* = 10 (Giant Spin)** **(= 8×2-4×3/2)**

**$\mu \cong 20\ \mu_B$ (Giant Magnetic Moment)**

**Easy-axis Anisotropy**

# Magnetic anisotropy in $Mn_{12}$*acetate*



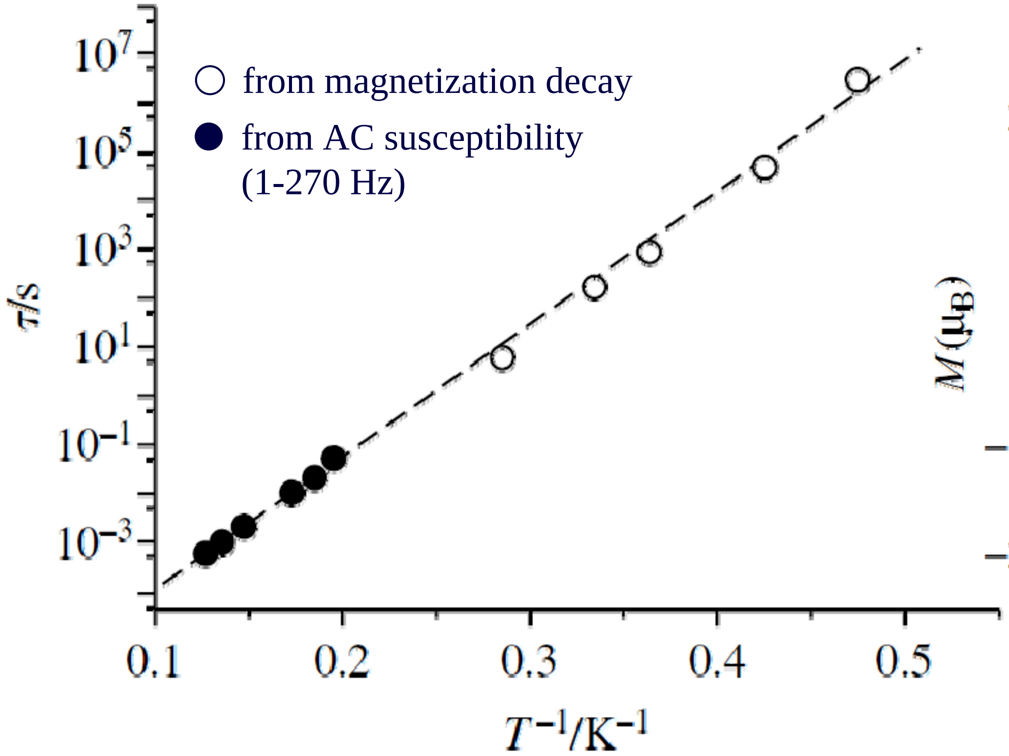

$$E_{ZFS}(M_S) = D[M_S^2 - 110/3]$$

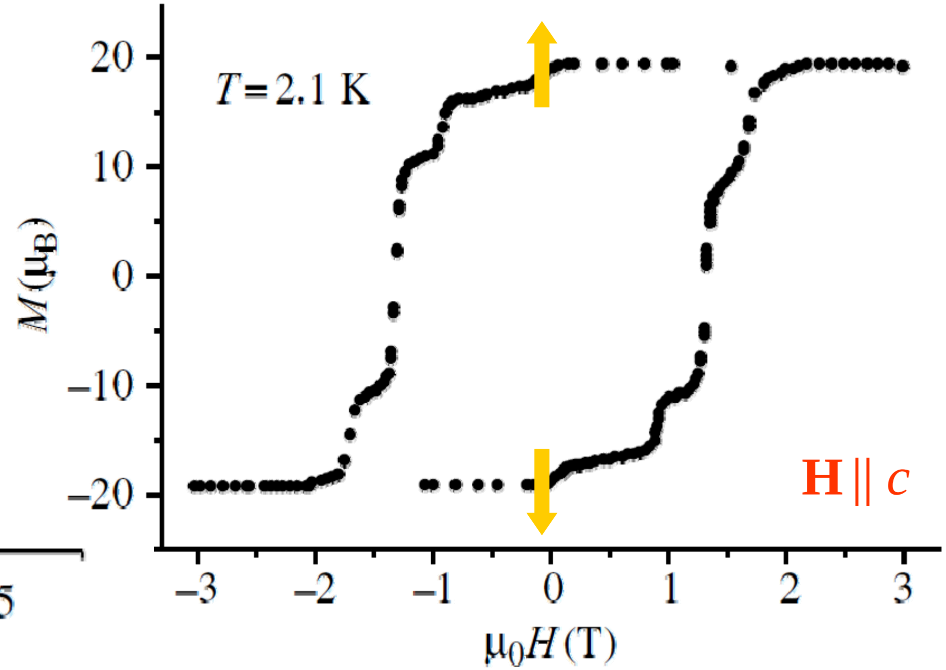
$D$ = -0.47 cm$^{-1}$
$E$ = 0
} from EPR

$U = |D|S^2 \sim 47$ cm$^{-1}$
$U/k_B \sim 68$ K

R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* 1993, *365*, 141

# Evidence for an energy barrier




$$\tau = \tau_0 \exp\left(\frac{U_{eff}}{k_B T}\right) \qquad \ln\tau = \ln\tau_0 + \frac{U_{eff}}{k_B T}$$

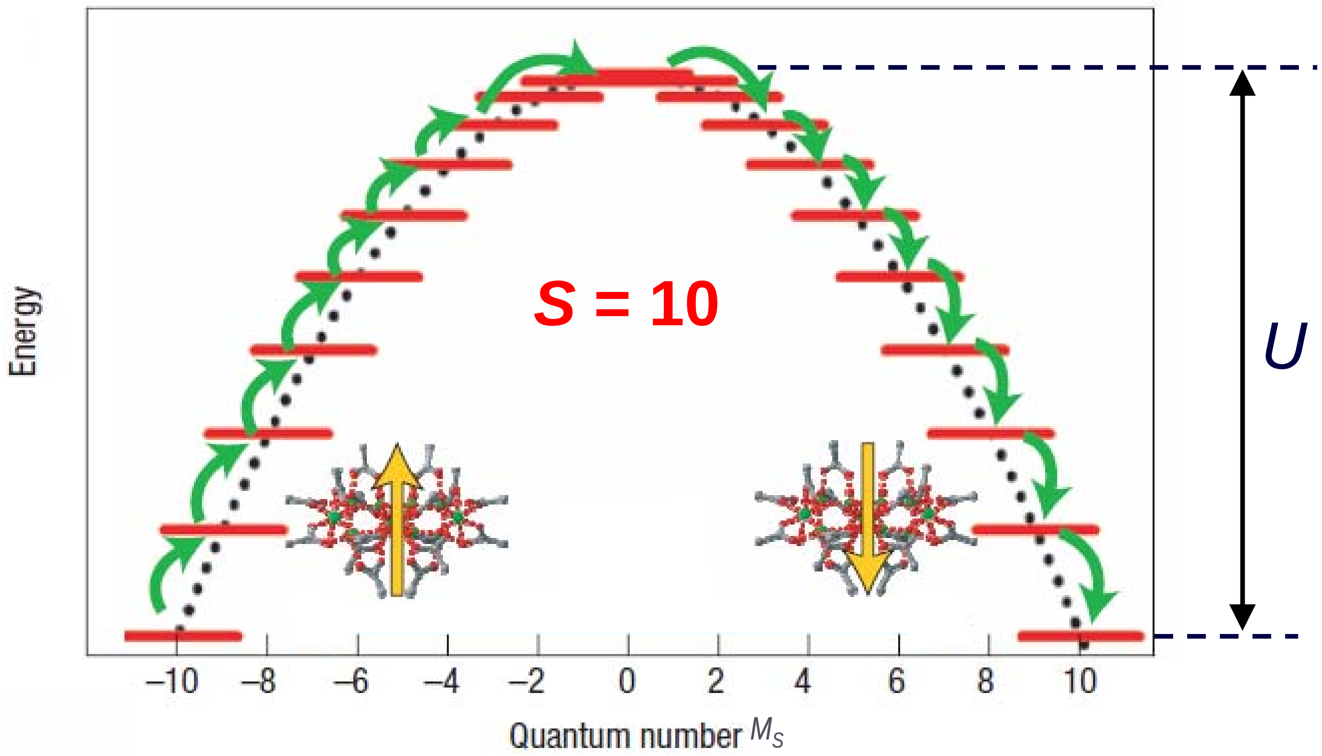
**$U_{eff}/k_B$ = 61 K**

**$\tau_0 = 2.1\times10^{-7}$ s**

## Arrhenius Law

**$\tau$(2.1 K) = 8.7 $\cdot 10^5$ s (10 d)**

# Single Molecule Magnets




for integer $S$

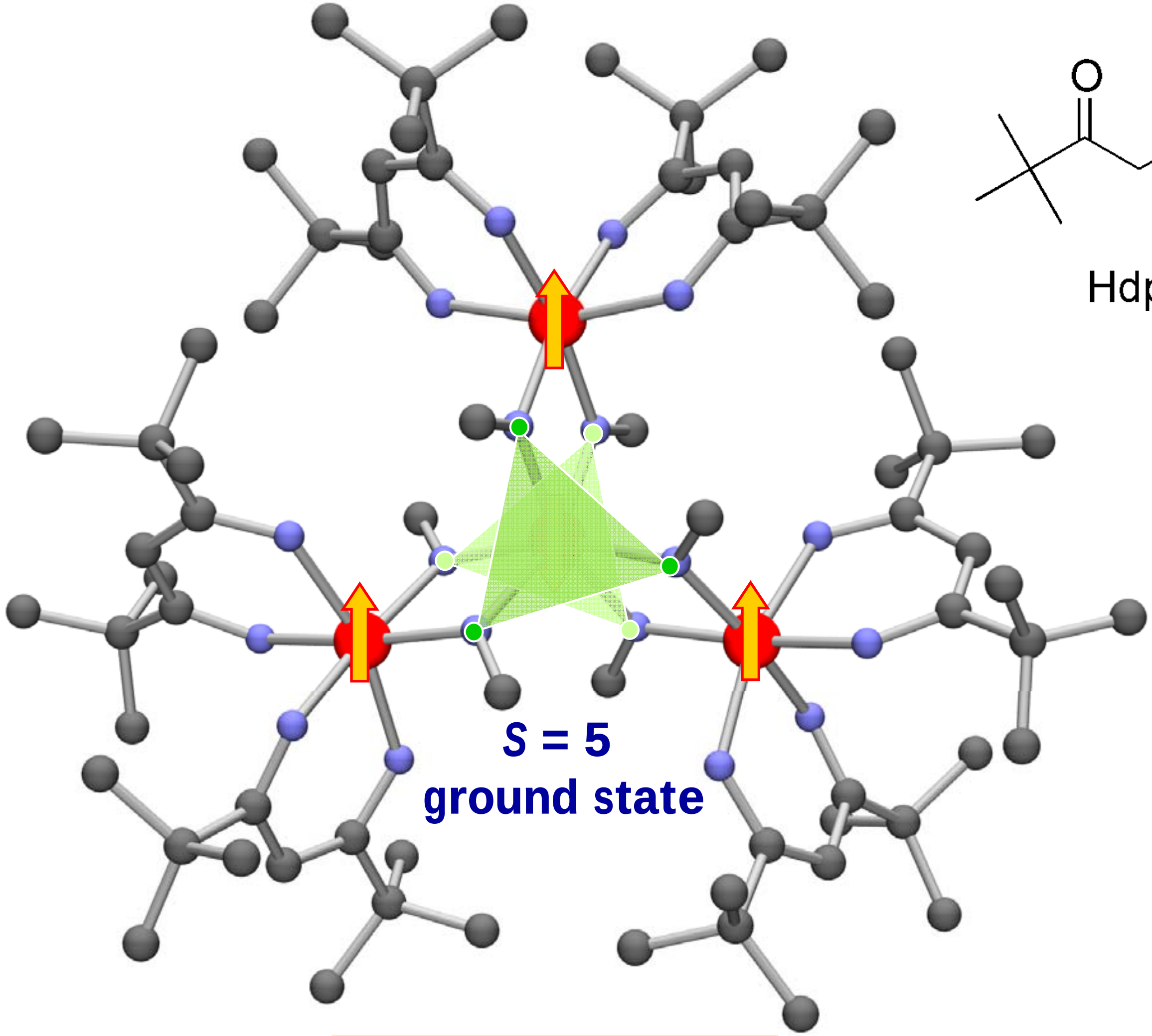
$$U = \left|E_{ZFS}(0) - E_{ZFS}(\pm S)\right| = |D|S^2$$

for half-integer $S$

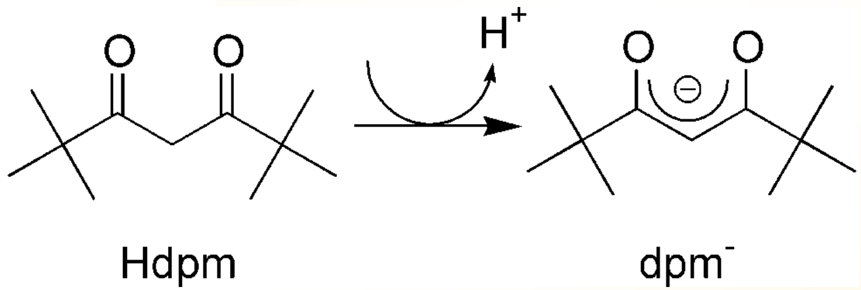
$$U = \left|E_{ZFS}(\pm \tfrac{1}{2}) - E_{ZFS}(\pm S)\right| = |D|(S^2 - \tfrac{1}{4})$$

$$\tau_0^{-1} \approx \frac{1}{\hbar^4 c_s^5 \rho} \left|\left\langle S, \pm 1 \middle| \hat{V}_{s-p} \middle| S, 0 \right\rangle\right|^2 [E_{ZFS}(0) - E_{ZFS}(\pm 1)]^3$$

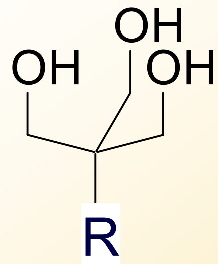
# Evidence for Quantum Tunneling




$Fe_4(OMe)_6(dpm)_6$



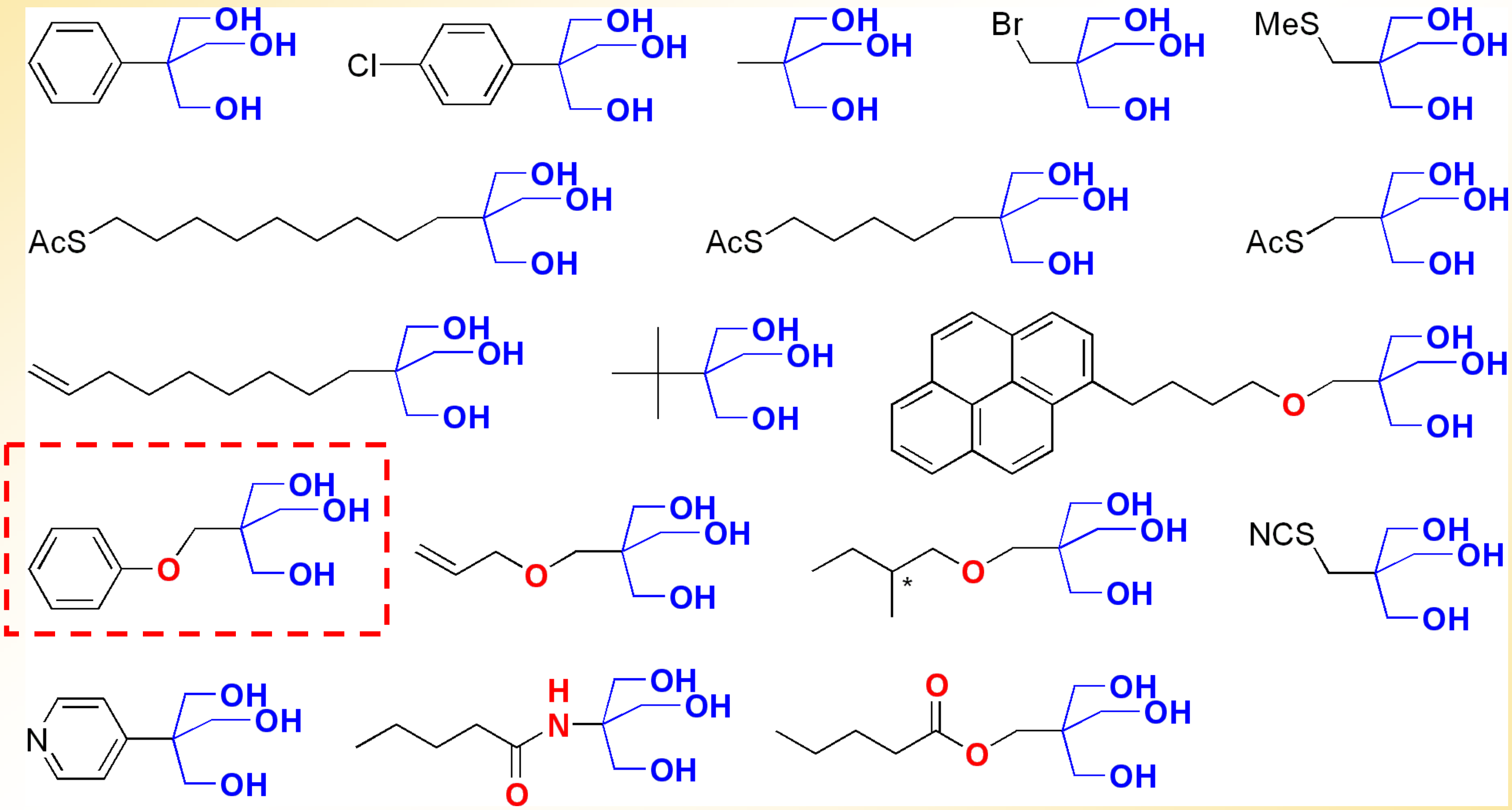

dipivaloylmethane



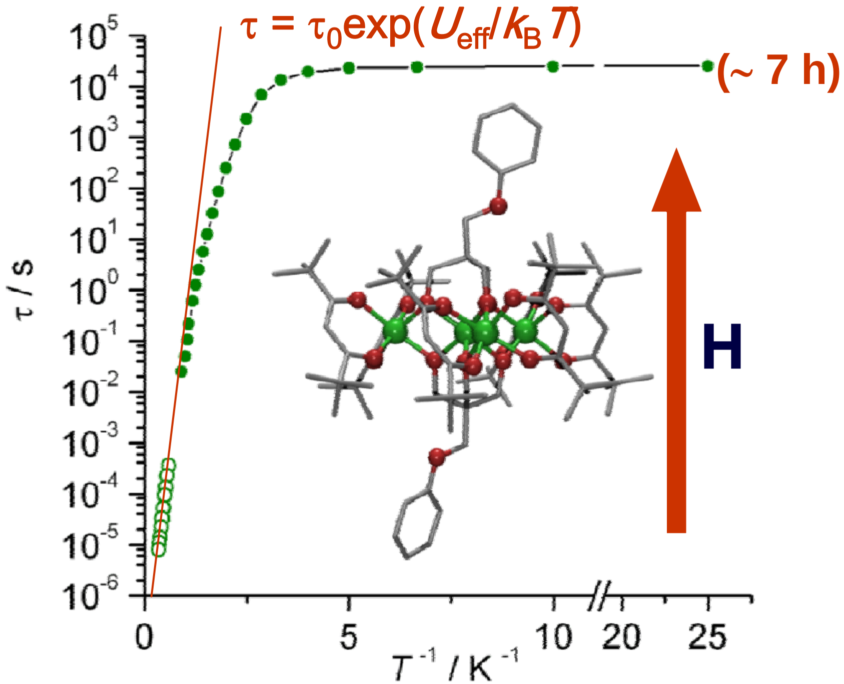

$H_3L$ = 2-R-2-hydroxymethyl--1,3-propanediol

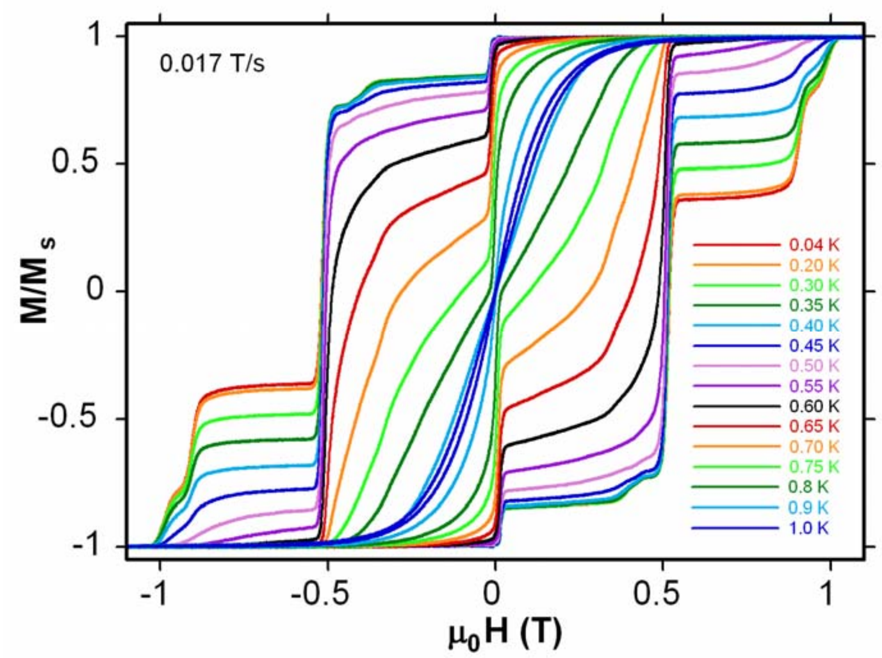
- **Iron(III) (*s* = 5/2)**
- **Oxygen**
- **Carbon**

# A library of ligands



# The breakdown of Arrhenius law




$U_{eff}/k_B$ = **15.7(2) K**

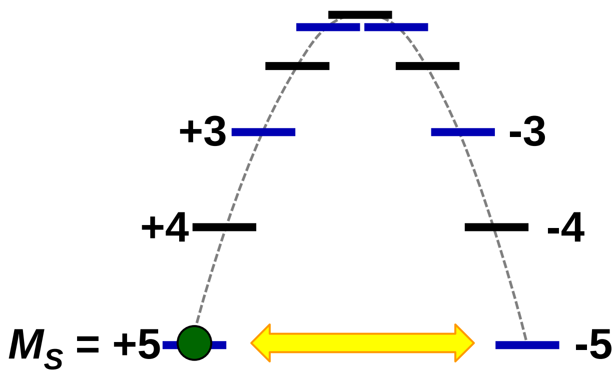
$\tau_0$ **= 3.5(5)×10$^{-8}$ s**

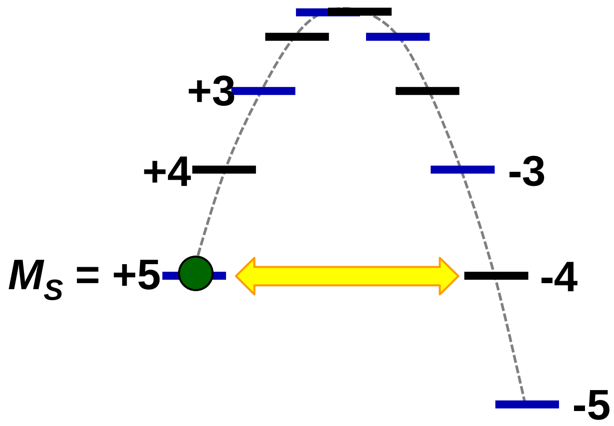
$D$ = -0.433(2) cm$^{-1}$

$E$ = 0.014(2) cm$^{-1}$

$U/k_B = (|D|/k_B)S^2$

**= 16.0 K**

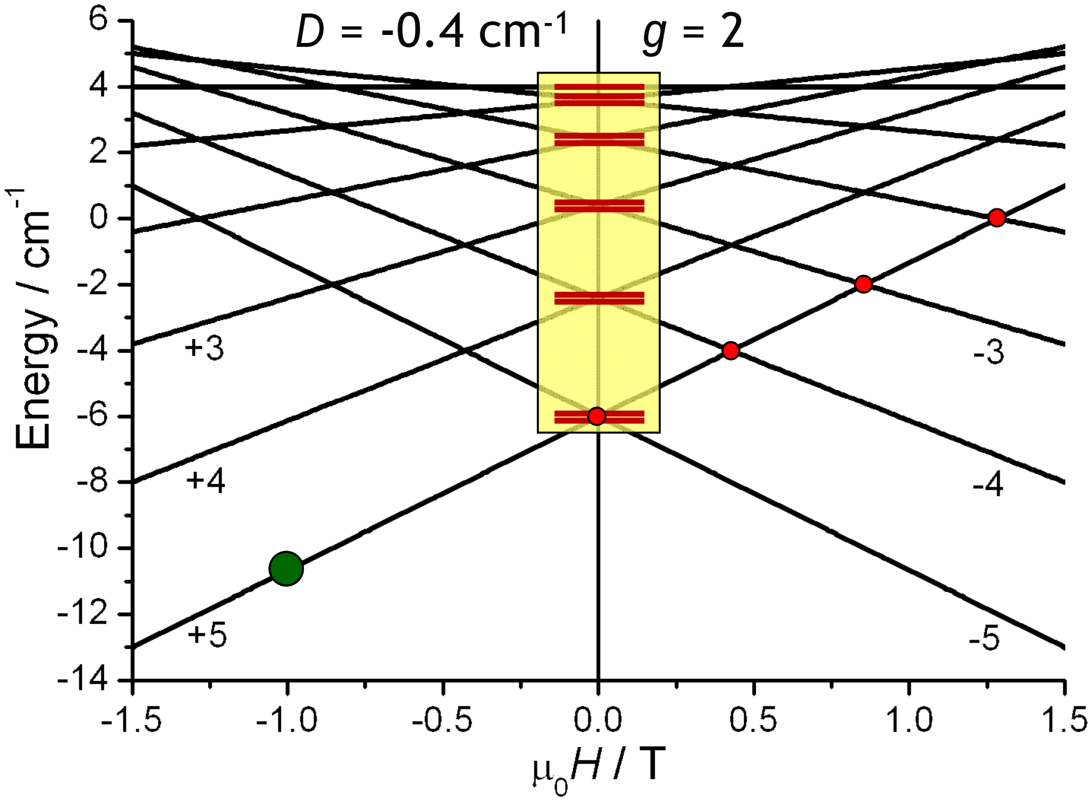


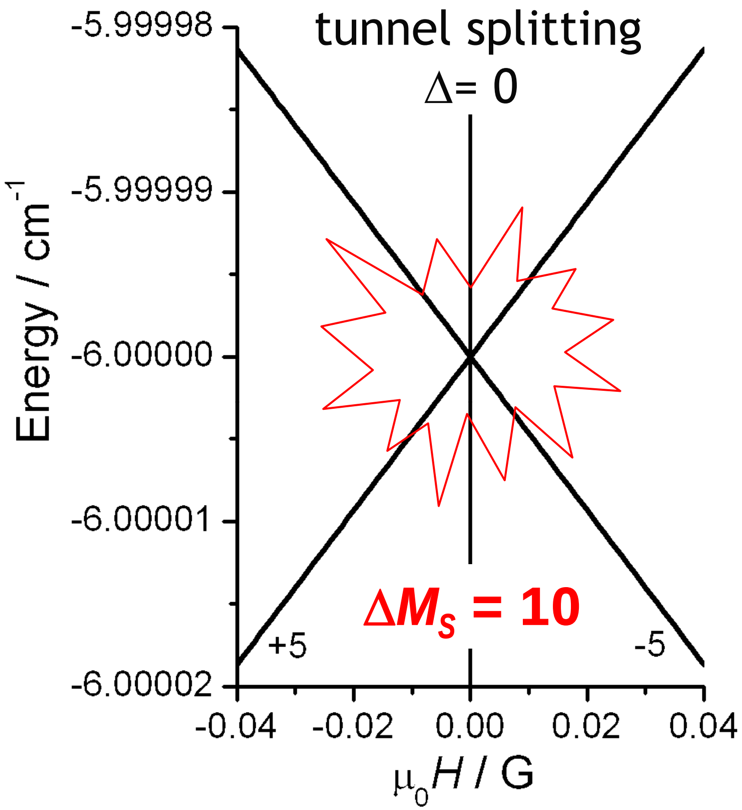



# Axial $S$ = 5 in a longitudinal field

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_{ZFS} + \hat{\mathbf{H}}_{Zee} = D[\hat{S}_z^2 - \tfrac{1}{3}S(S+1)] + \mu_0\mu_B g H \hat{S}_z$$

$$\text{Energy}(M_S) = D[M_S^2 - \tfrac{1}{3}S(S+1)] + \mu_0\mu_B g H M_S$$




$\mu_0 H_r = n|D|/(g\mu_B)$ = 0, ±0.43 T, ±0.86 T, ... **Resonant Quantum Tunnelling**

# What promotes quantum tunneling?

- The occurrence of tunneling requires the presence of spin Hamiltonian terms that DO NOT COMMUTE with $\hat{S}_z$ and mix $|S, M_S\rangle$ states with different values of $M_S$
- Such terms are, for instance, rhombic anisotropy terms permitted by the molecular structure, and transverse magnetic fields arising from dipolar or hyperfine interactions and from misalignement of crystal domains

$$\hat{\mathbf{H}} = D[\hat{S}_z^2 - \tfrac{1}{3}S(S+1)] + \mu_0\mu_B gH\hat{S}_z + \underbrace{E(\hat{S}_x^2 - \hat{S}_y^2)}_{\text{rhombic anisotropy}} + \underbrace{\mu_0\mu_B gH_x\hat{S}_x}_{\text{transverse Zeeman term}}$$

$$\hat{S}_x = (\hat{S}_+ + \hat{S}_-)/2 \qquad \hat{S}_y = (\hat{S}_+ - \hat{S}_-)/2i$$

$$\hat{S}_x^2 - \hat{S}_y^2 = \tfrac{1}{2}(\hat{S}_+^2 + \hat{S}_-^2)$$

$$\hat{S}_\pm |S, M_S\rangle = \sqrt{S(S+1) - M_S(M_S \pm 1)}\,|S, M_S \pm 1\rangle$$

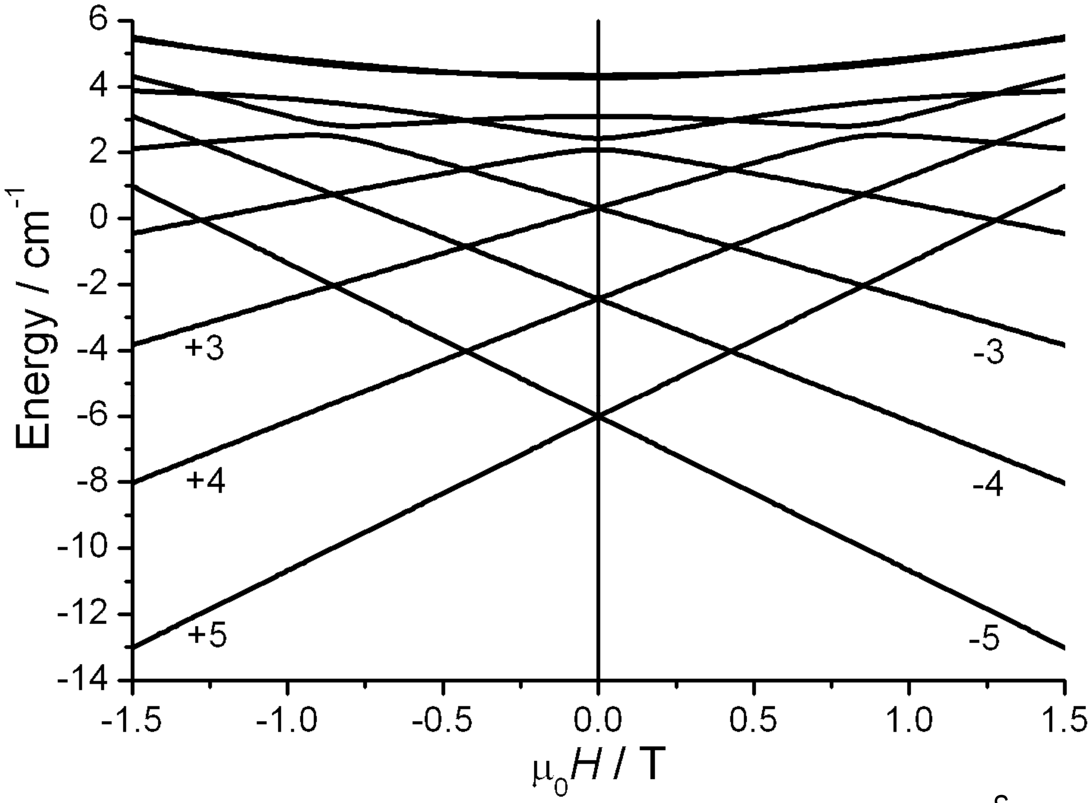
**rhombic anisotropy** $\Delta M_S = \pm 2$

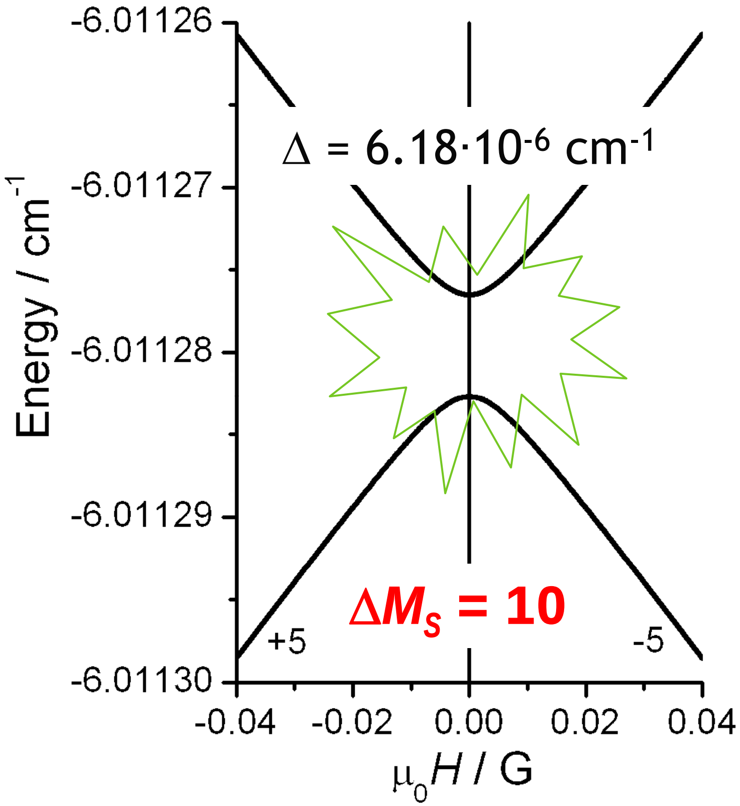
**transverse Zeeman term** $\Delta M_S = \pm 1$

- These terms may act in sinergy (see below)
- The EVs need to be calculated by numerical diagonalization of the representative of $\hat{\mathrm{H}}$ on the $|S, M_S\rangle$ basis.

# Routes to Quantum Tunneling

$D$ = -0.4 cm$^{-1}$, **$|E/D|$ = 0.1**, $g$ = 2, $H_x$ = 0



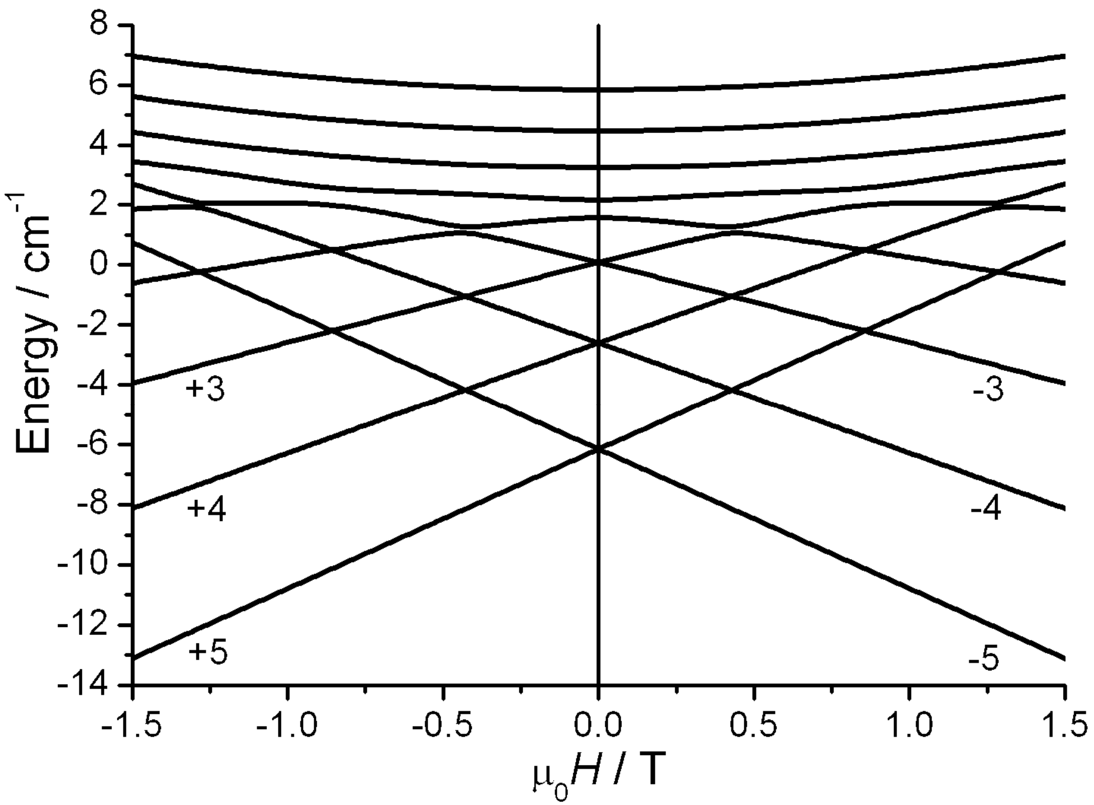

**prediction from perturbation theory***

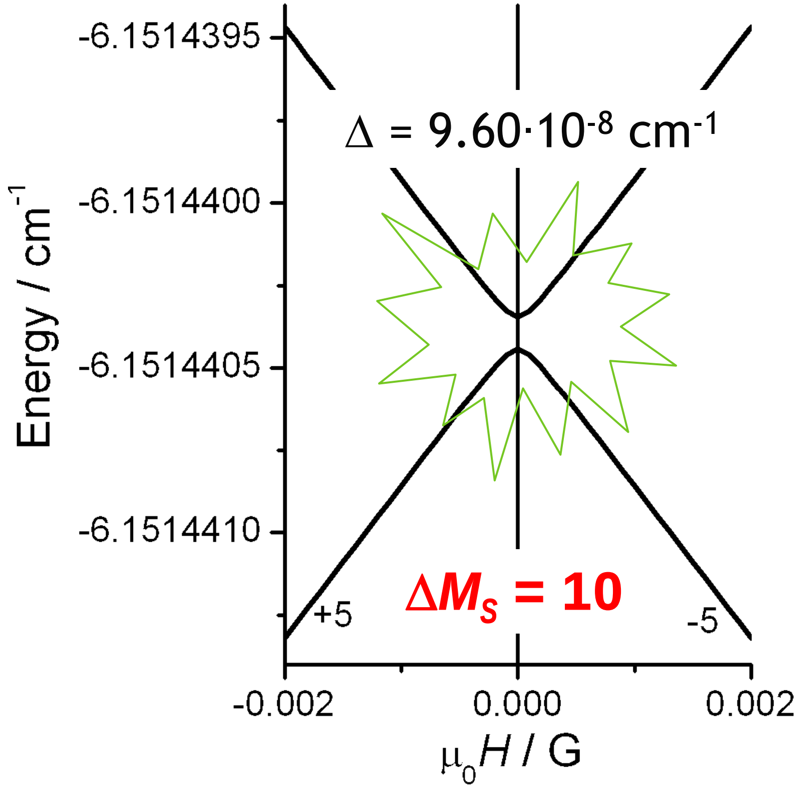
$$\Delta = 8|D|S^2\left(\frac{E}{8|D|}\right)^S \frac{(2S)!}{(S!)^2} = 6.15\cdot 10^{-6}\ \text{cm}^{-1}$$

*** for a single $Mn^{3+}$ ion with S = 2, $D$ = -4 cm$^{-1}$ and $|E/D|$ = 0.1: $\Delta$ = 0.12 cm$^{-1}$ !**

# Routes to Quantum Tunneling

$D$ = -0.4 cm$^{-1}$, $E$ = 0, $g$ = 2, **$H_x$ = 0.5 T** *




**prediction from perturbation theory**

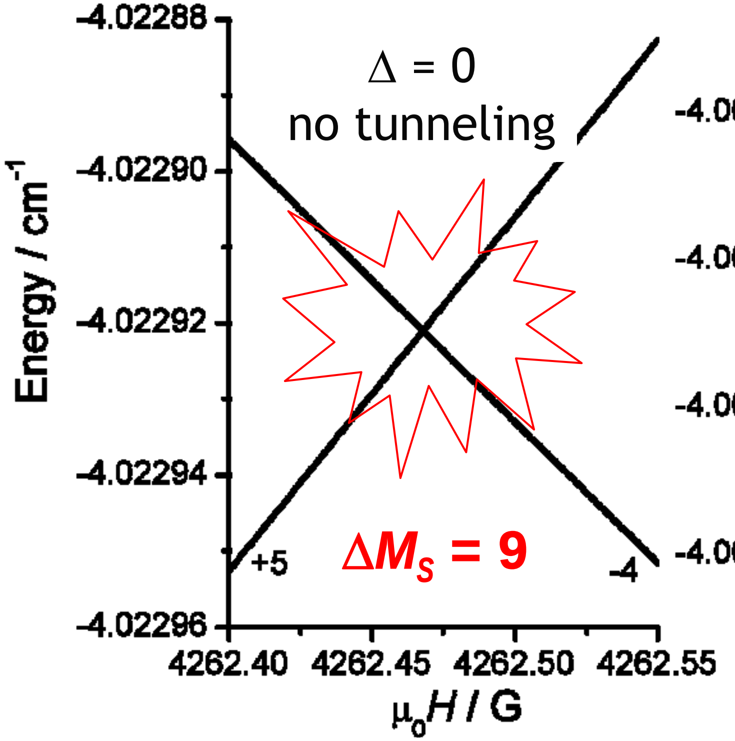
$$\Delta = 8|D|S^2\left(\frac{g\mu_B H_x}{2|D|}\right)^{2S}\frac{1}{(2S)!} = 1.01\cdot 10^{-7}\ \mathrm{cm^{-1}}$$

***for $H_x$ = 10 mT the splitting is of the order of 10$^{-24}$ cm$^{-1}$**

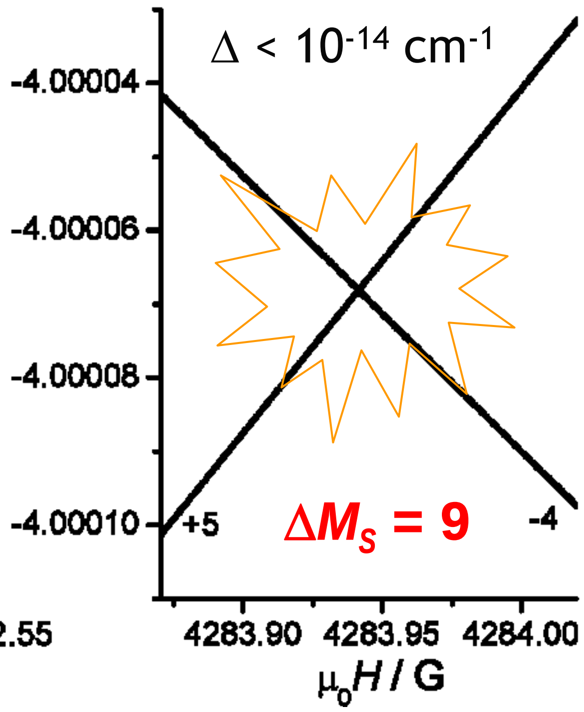
# Synergies in Quantum Tunneling

$D$ = -0.4 cm$^{-1}$, $g$ = 2

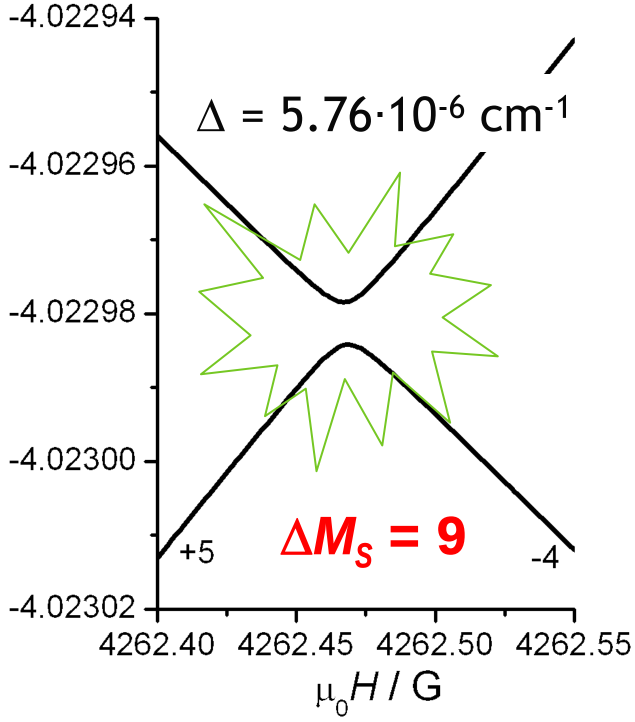
**|*E*/*D*| = 0.1**
$H_x$ = 0



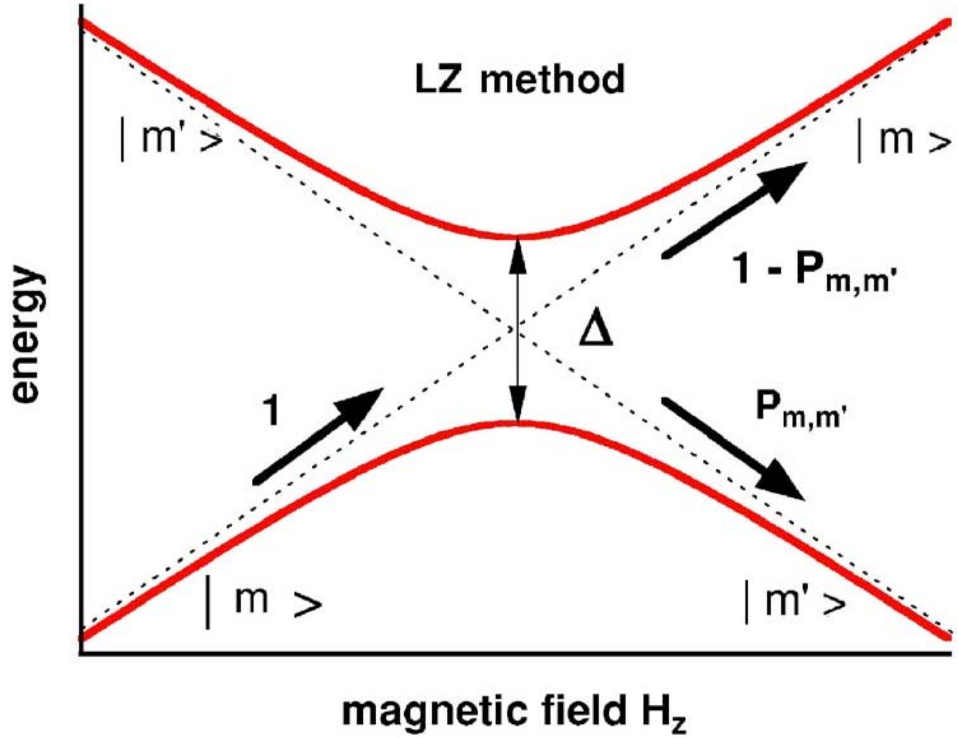

**|*E*/*D*| = 0**
**$H_x$ = 10 mT**



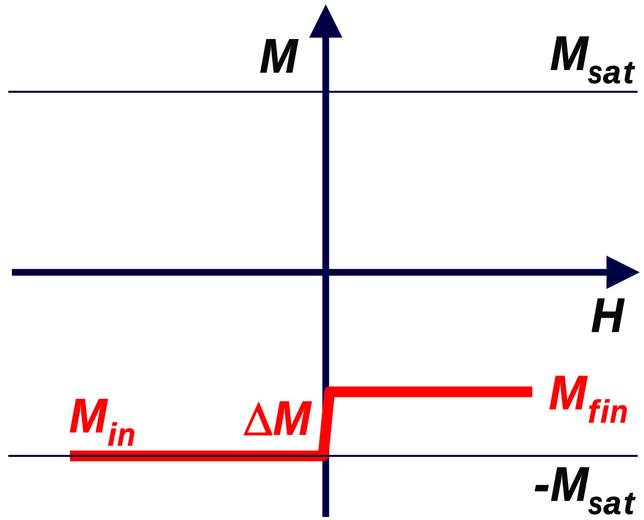

**|*E*/*D*| = 0.1**
**$H_x$ = 10 mT**



# Measuring Tunnel Splittings




**m = S, m' = -S**

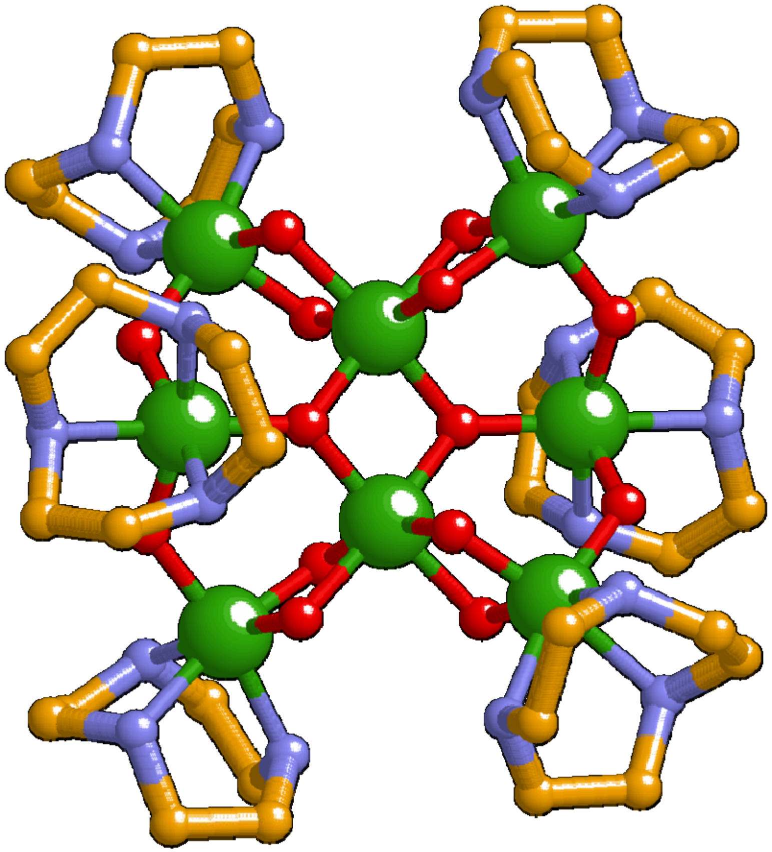



$$P_{S,-S} = \frac{M_{fin} - M_{in}}{2M_{sat}} = \frac{\Delta M}{2M_{sat}}$$

$$P_{m,m'} = 1 - \exp\left[ -\frac{\pi \Delta^2_{m,m'}}{2\hbar^2 g\mu_B |m - m'| \mu_0 \, dH_z/dt} \right]$$

**Landau-Zener-Stückelberg formula**

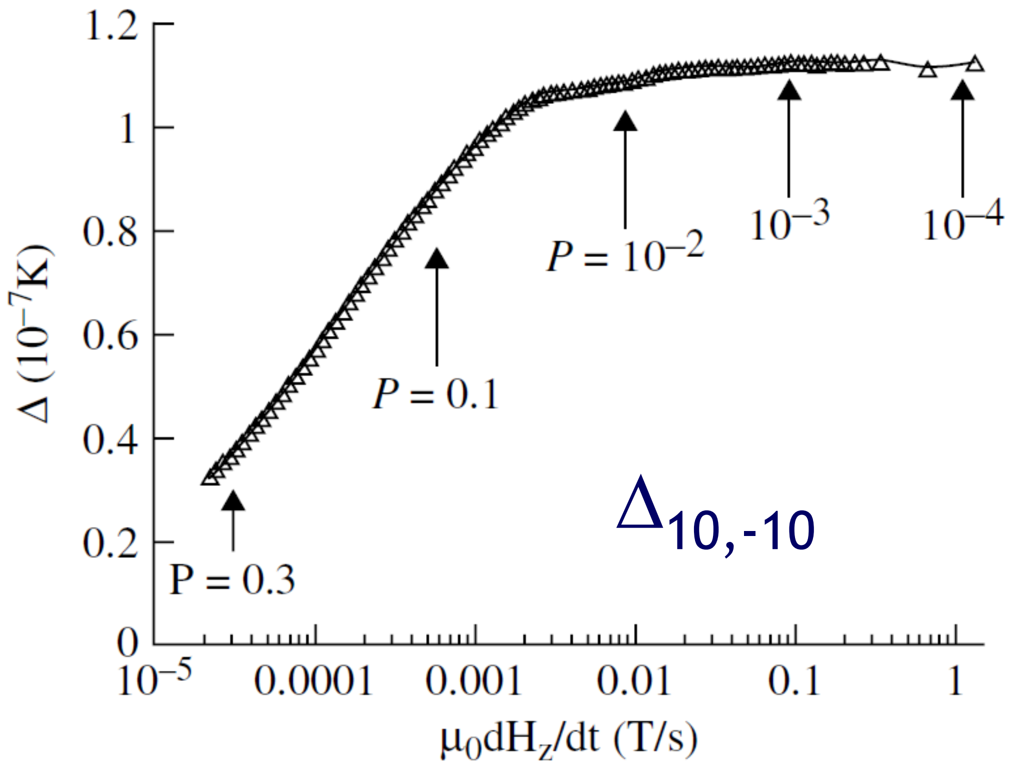
# Measuring Tunnel Splittings



$[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$

**$S$ = 10**

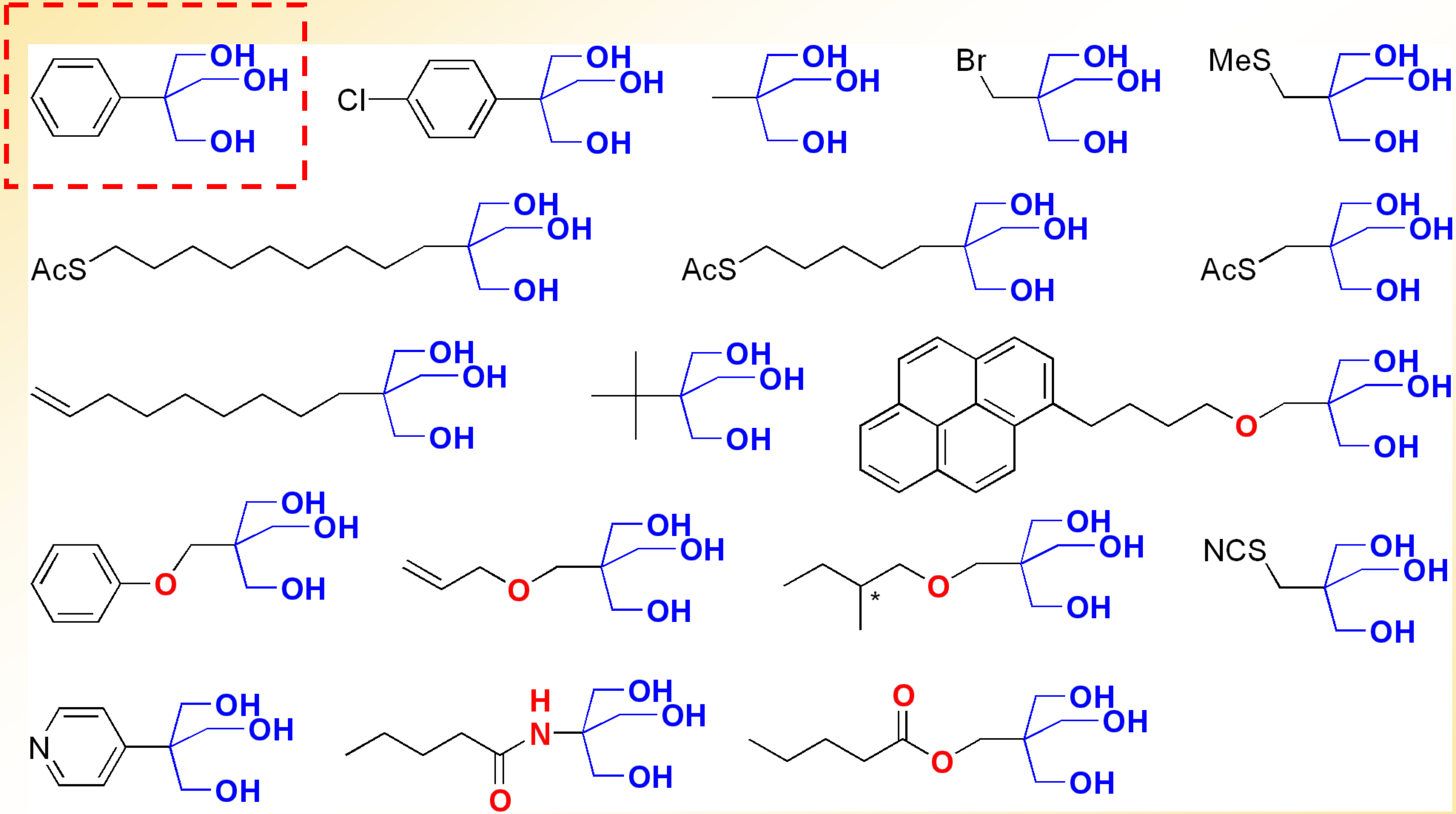
$D$ = -0.203 cm$^{-1}$ $|E/D|$ = 0.16



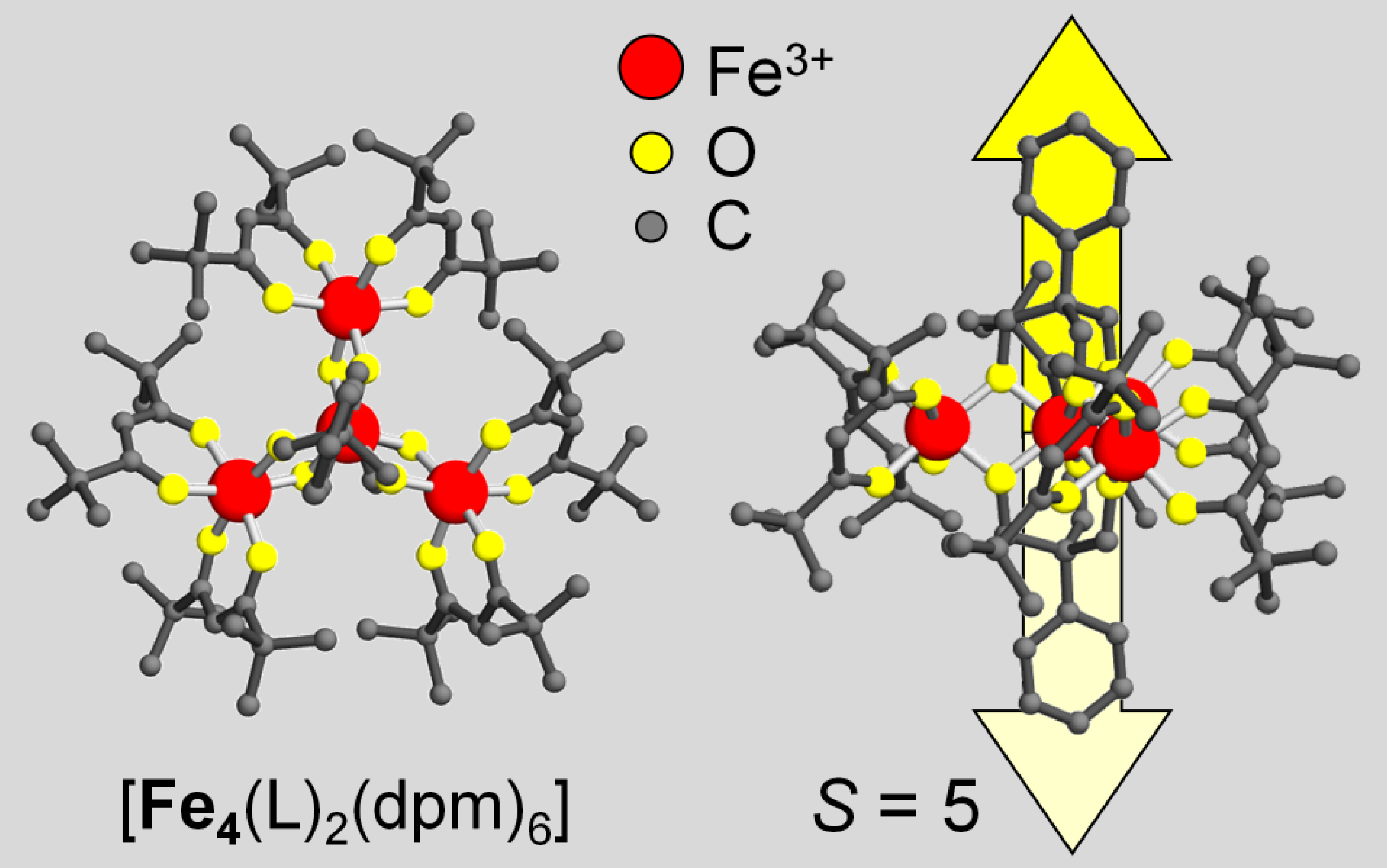

- **Iron(III) ($s$ = 5/2)**
- **Oxygen**
- **Carbon**
- **Nitrogen**

**How large is the tunnel splitting predicted by perturbation theory?**

# A library of ligands

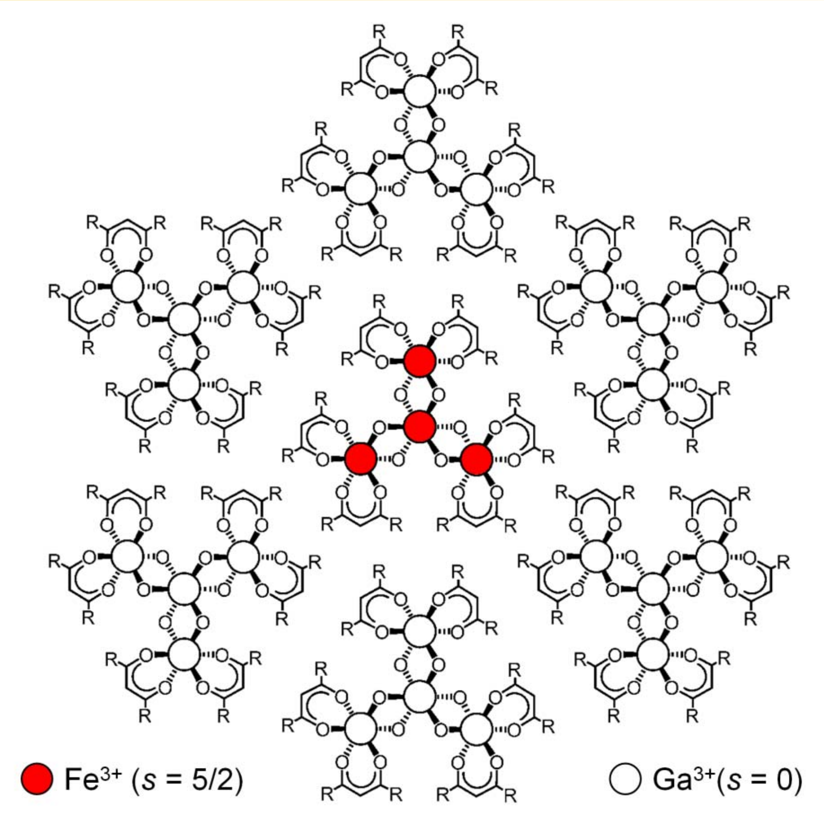


# Tunneling and Intermolecular Interactions

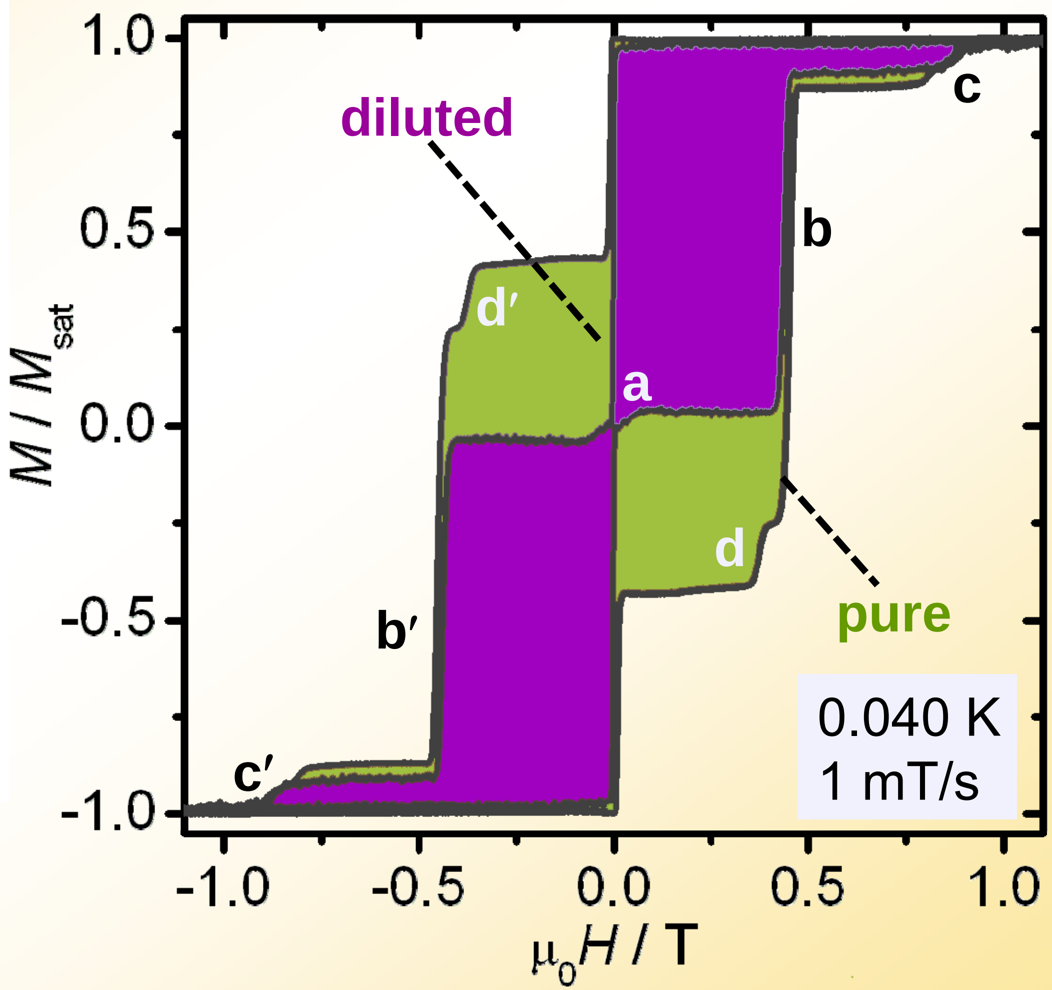



**$D$ = -0.416(2) cm$^{-1}$  $E$ = 0.016(1) cm$^{-1}$**

# One-body vs. Two-body Tunneling

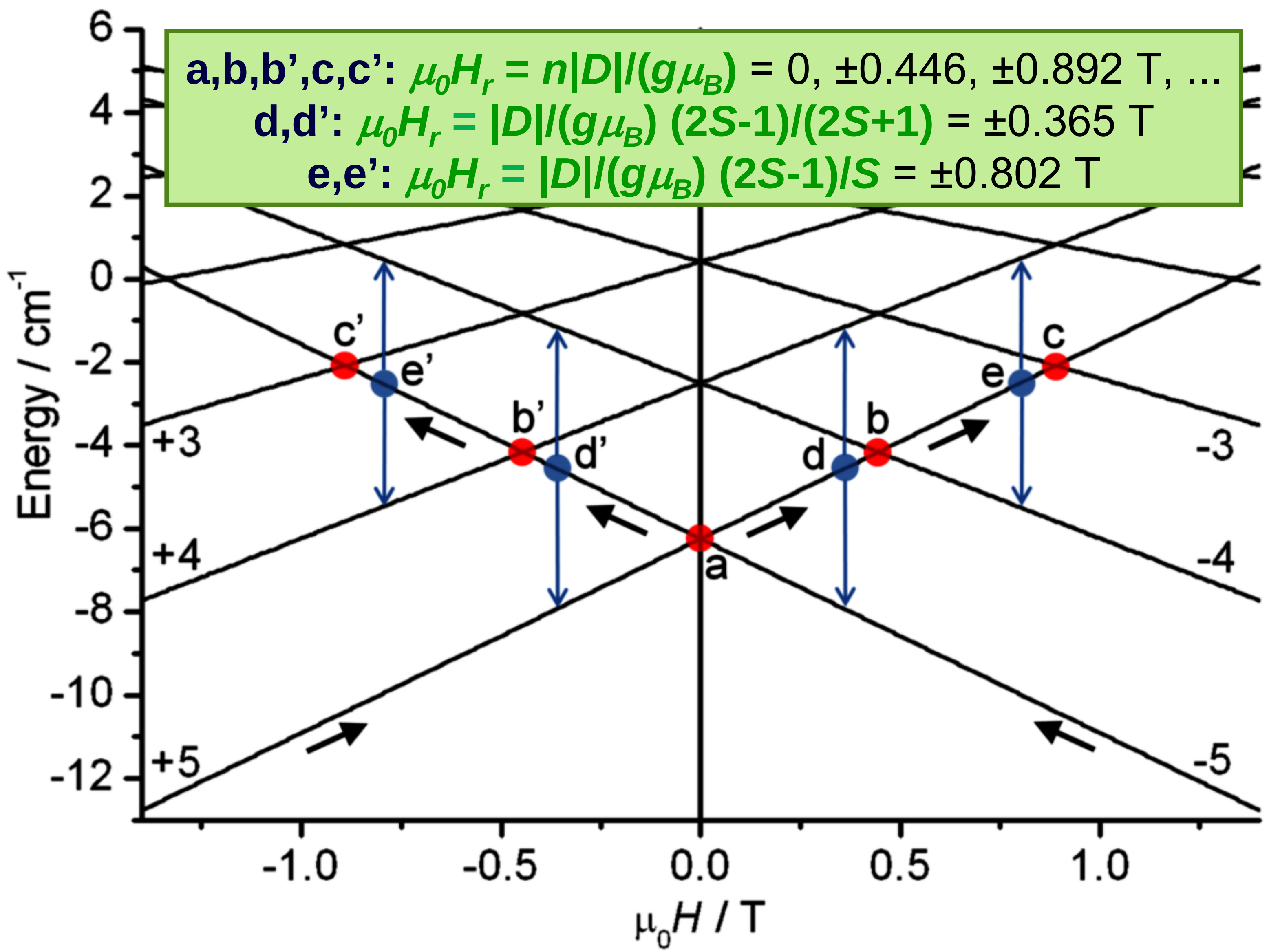



$[(\mathbf{Fe_4})_{0.01}(\mathbf{Ga_4})_{0.99}(L)_2(dpm)_6]$

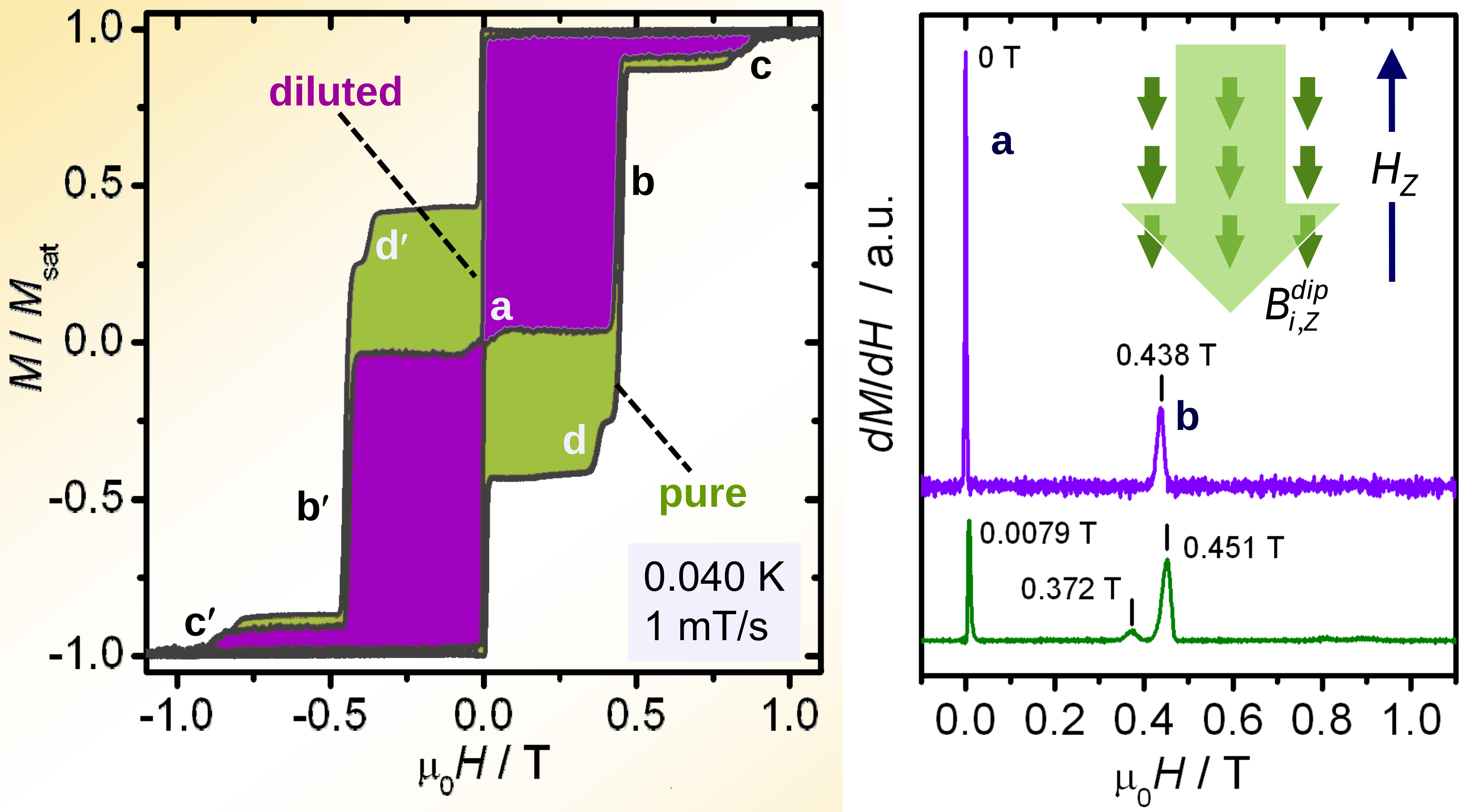


# One-body vs. Two-body Tunneling

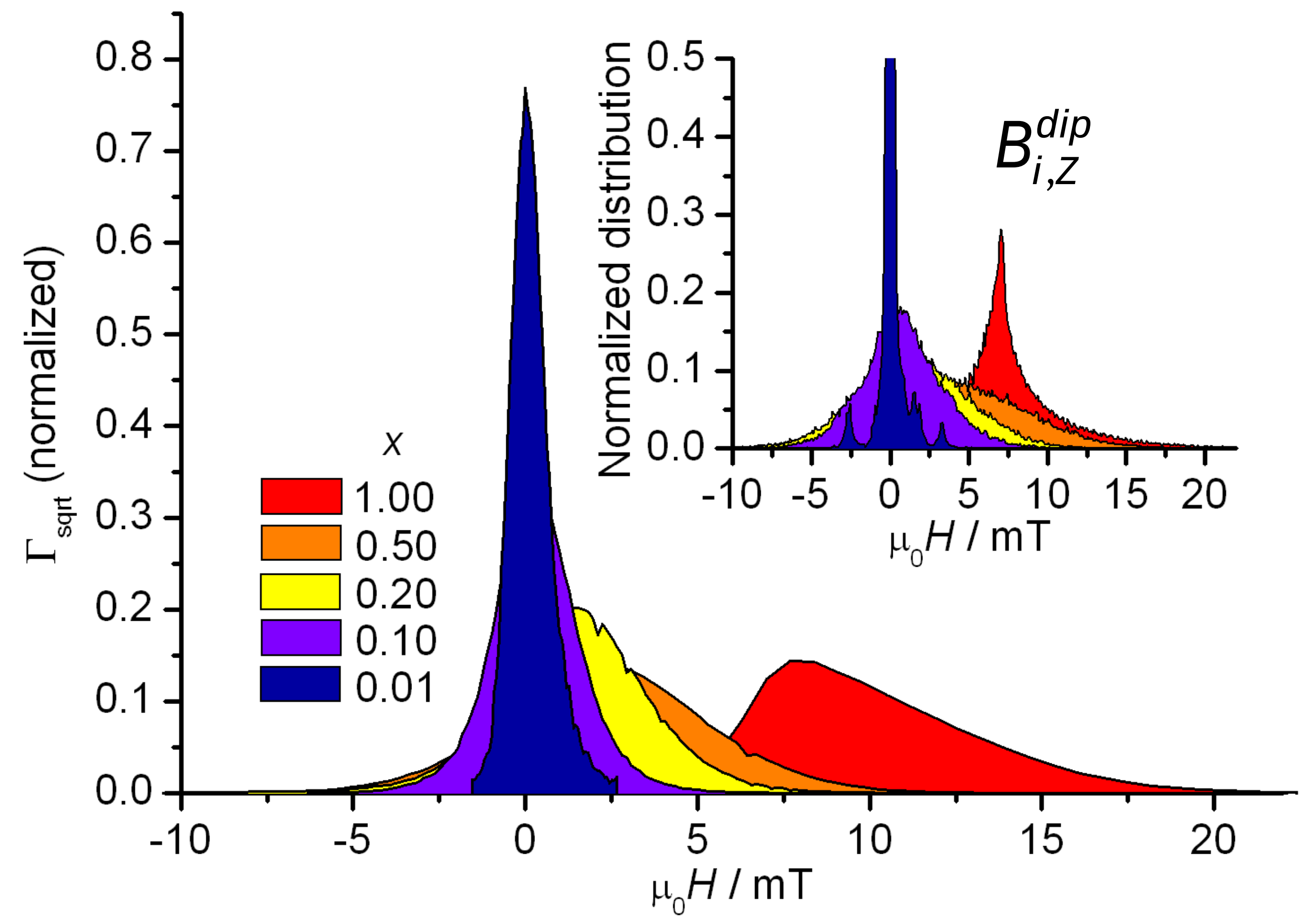
**a,b,b',c,c':** $\mu_0 H_r = n|D|/(g\mu_B)$ = 0, ±0.446, ±0.892 T, ...
**d,d':** $\mu_0 H_r = |D|/(g\mu_B)\ (2S-1)/(2S+1)$ = ±0.365 T
**e,e':** $\mu_0 H_r = |D|/(g\mu_B)\ (2S-1)/S$ = ±0.802 T



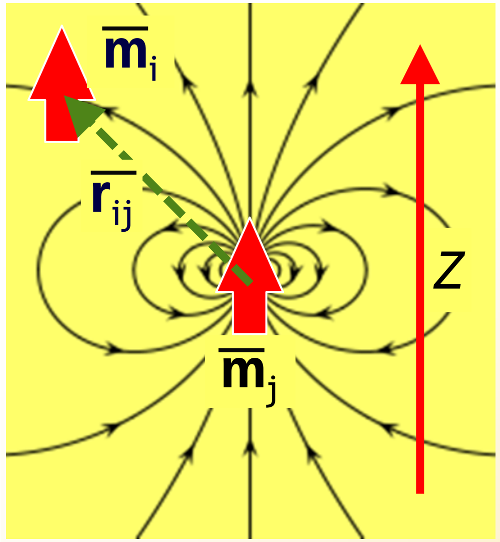
# Dipolar bias on magnetic relaxation



# Dipolar bias on magnetic relaxation



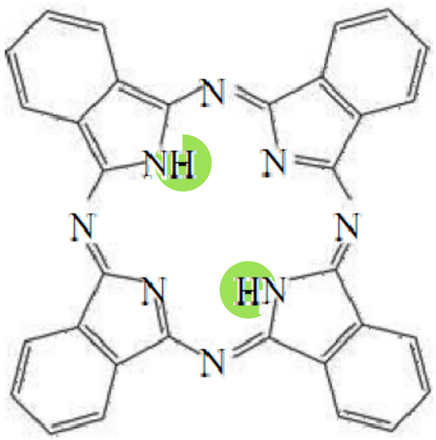

[$(\mathbf{Fe_4})_x(\mathbf{Ga_4})_{1-x}(L)_2(dpm)_6$]




$$\overline{B}_i^{dip} = \sum_j \frac{3\left(\overline{\mathbf{m}}_j \cdot \overline{\mathbf{r}}_{ij}\right)\overline{\mathbf{r}}_{ij} - \overline{\mathbf{m}}_j r_{ij}^2}{r_{ij}^5}$$

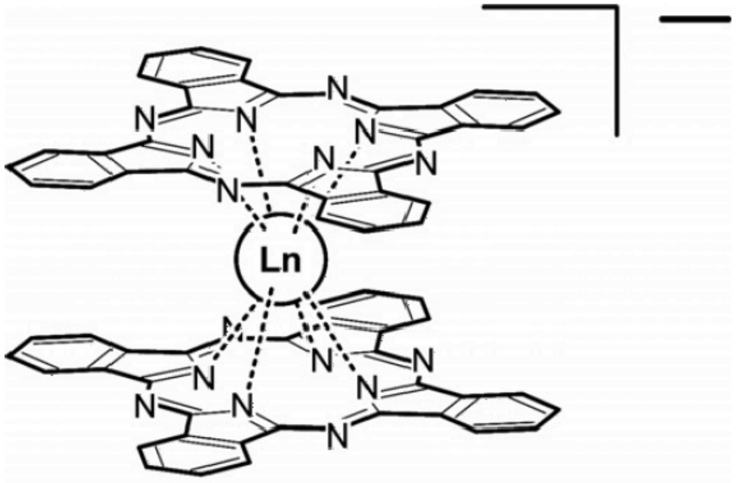
# Back to single ions

- $S$ = 7/2 is the largest spin for a single ion in $Gd^{3+}$ ([Xe]4$f^7$)
- $J$ = 8 can be reached in rare earth ions ($Ho^{3+}$)
- In rare-earth ions, crystal field effects can afford large easy-axis anisotropies




$H_2Pc$

Phthalocyanine



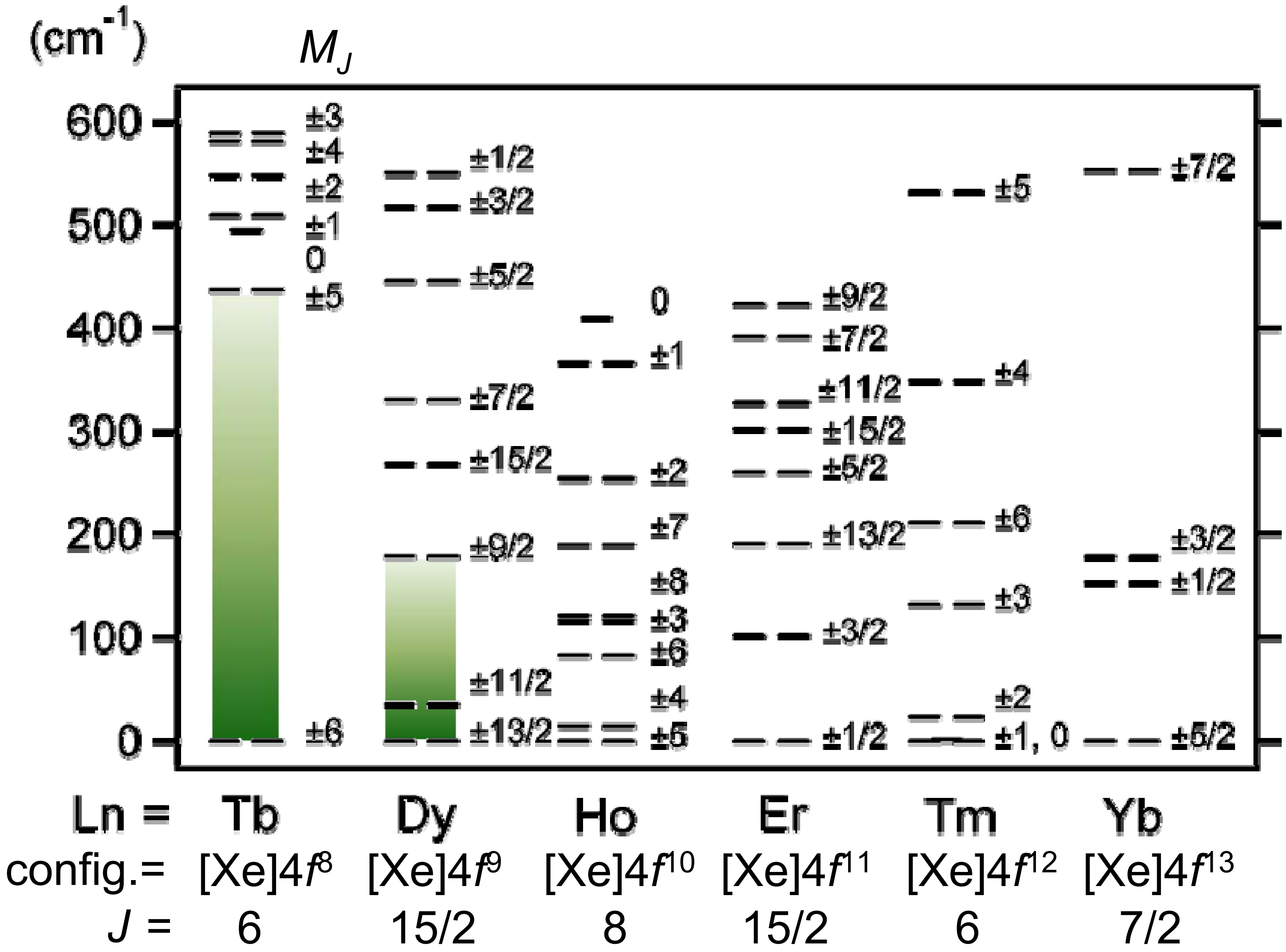

$[(Pc)_2Ln]^-$

Bis(phthalocyaninato)-lanthanide

''double-decker'' complexes

N. Ishikawa, *Polyhedron* 2007, *26*, 2147

# Single Ion Magnets

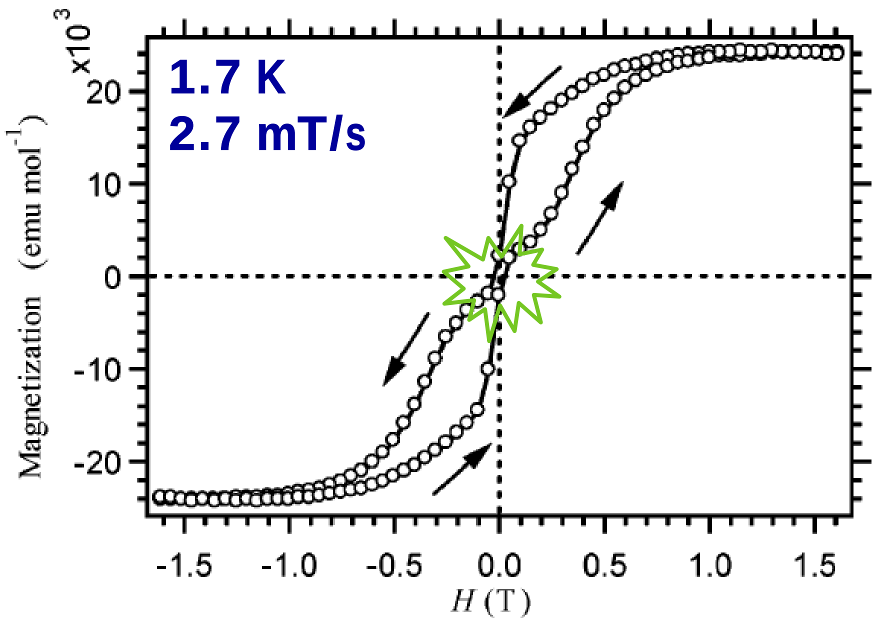


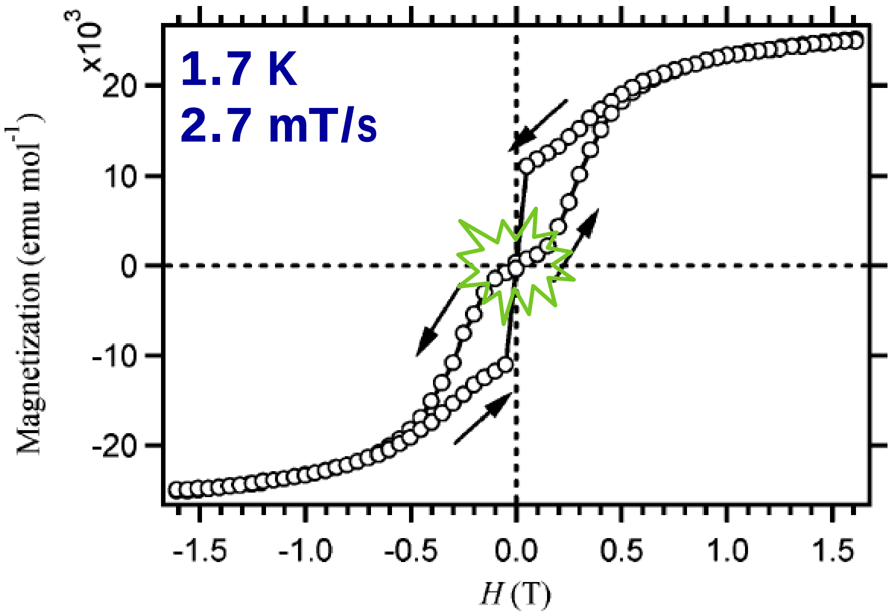
# Single Ion Magnets (SIMs)

**$[(Pc)_2Tb]^-$ $TBA^+$**
**$U_{eff}$ = 260 $cm^{-1}$, $\tau_0 = 2.0 \cdot 10^{-8}$ s**
**(25-40 K)**

**$[(Pc)_2Dy]^-$ $TBA^+$**
**$U_{eff}$ = 31 $cm^{-1}$, $\tau_0 = 3.3 \cdot 10^{-6}$ s**
**(3.5-12 K)**

**BUT**



# *J*-dependent slow relaxation

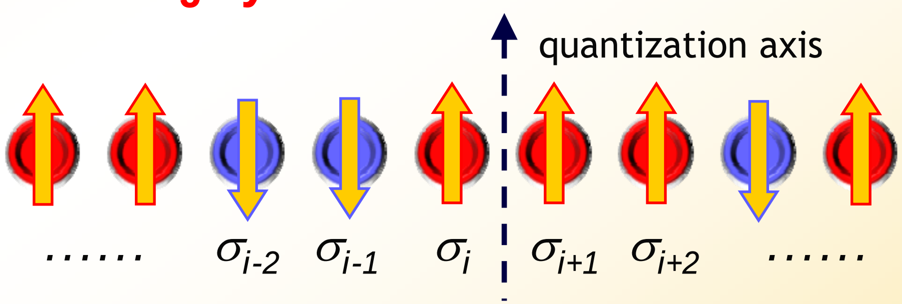
JOURNAL OF MATHEMATICAL PHYSICS VOLUME 4, NUMBER 2 FEBRUARY 1963

## Time-Dependent Statistics of the Ising Model*

ROY J. GLAUBER
*Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts*

The individual spins of the Ising model are assumed to interact with an external agency (e.g., a heat reservoir) which causes them to change their states randomly with time. Coupling between the spins is introduced through the assumption that the transition probabilities for any one spin depend on the values of the neighboring spins. This dependence is determined, in part, by the detailed balancing condition obeyed by the equilibrium state of the model. The Markoff process which describes the spin functions is analyzed in detail for the case of a closed $N$-member chain. The expectation values of the individual spins and of the products of pairs of spins, each of the pair evaluated at a different time, are found explicitly. The influence of a uniform, time-varying magnetic field upon the model is discussed, and the frequency-dependent magnetic susceptibility is found in the weak-field limit. Some fluctuation–dissipation theorems are derived which relate the susceptibility to the Fourier transform of the time-dependent correlation function of the magnetization at equilibrium.

**1-D Ising System**

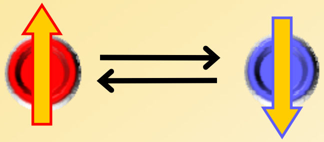



$$\hat{H} = -J\sum_i \sigma_i\sigma_{i+1}$$

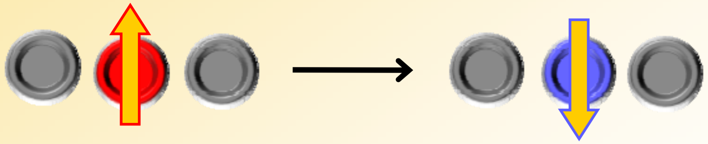
$\sigma_i = \pm 1$

stochastic functions of time

# A closer look at Glauber's model



isolated Ising spin
flipping rate = $\alpha/2$

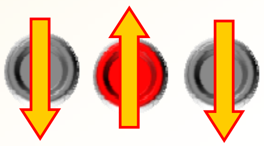



Ising spin within a chain
flipping rate = $w_i(\sigma_i)$

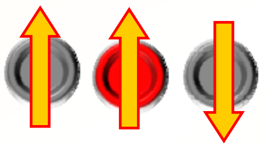
Interactions between spins are introduced by assuming that the flipping rate of spins depend on the orientation of the nearest-neighbouring spins

$|\gamma| \leq 1$

$w_i(\sigma_i) = \tfrac{1}{2}\alpha(1-\gamma)$



$w_i(\sigma_i) = \tfrac{1}{2}\alpha(1+\gamma)$



$w_i(\sigma_i) = \tfrac{1}{2}\alpha$

$$w_i(\sigma_i) = \tfrac{1}{2}\alpha[1-\tfrac{1}{2}\gamma\sigma_i(\sigma_{i-1}+\sigma_{i+1})]$$

**MASTER EQUATION**

$$\frac{d}{dt}p(\sigma_1,\cdots\sigma_N t) = -[\sum_i w_i(\sigma_i)]p(\sigma_1,\cdots\sigma_N t) + \sum_i w_i(-\sigma_i)p(\sigma_1,\cdots-\sigma_i,\cdots\sigma_N t)$$

# A closer look at Glauber's model

**Detailed balance condition at equilibrium at temperature *T***

**(for a given set of** $\sigma_1, \sigma_2, \ldots \sigma_{i-1}, \sigma_{i+1}, \ldots \sigma_N$)

$$\frac{p_j(-\sigma_j)}{p_j(\sigma_j)} = \frac{\exp\left[-(J/kT)\sigma_j(\sigma_{j-1}+\sigma_{j+1})\right]}{\exp\left[(J/kT)\sigma_j(\sigma_{j-1}+\sigma_{j+1})\right]}$$

$$\frac{p_j(-\sigma_j)}{p_j(\sigma_j)} = \frac{w_j(\sigma_j)}{w_j(-\sigma_j)}$$

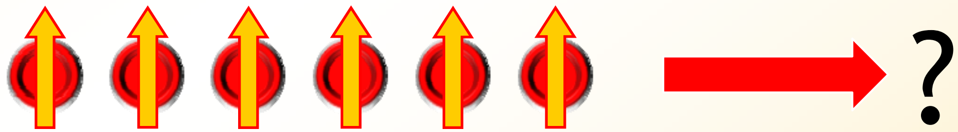
$$\gamma = \tanh(2J/kT)$$

$$= \frac{1-\frac{1}{2}\gamma\sigma_j(\sigma_{j-1}+\sigma_{j+1})}{1+\frac{1}{2}\gamma\sigma_j(\sigma_{j-1}+\sigma_{j+1})}$$

**Expectation value of** $\sigma_k(\mathrm{t})$

$$q_k(t) = \langle \sigma_k(t) \rangle = \sum_{\{\sigma\}} \sigma_k\, p(\sigma_1, \ldots, \sigma_N t) = e^{-\alpha t} \sum_{m=-\infty}^{\infty} q_m(0) I_{k-m}(\gamma \alpha t)$$

$t = 0$




$$q_k(0) = +1,\ k = -\infty \ldots. + \infty$$

$$q_k(t) = e^{-\alpha t} \sum_{m=-\infty}^{\infty} I_{k-m}(\gamma \alpha t) = e^{-\alpha t} e^{\gamma \alpha t} = e^{-\alpha(1-\gamma)t} = e^{-t/\tau}$$

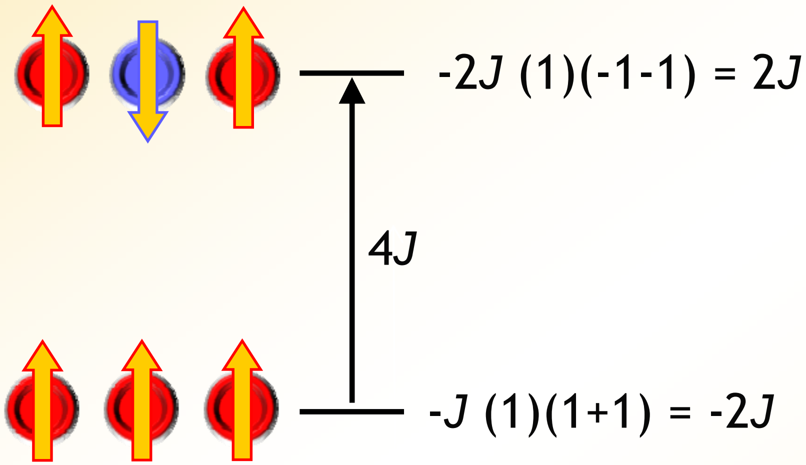
**! Exponential decay**

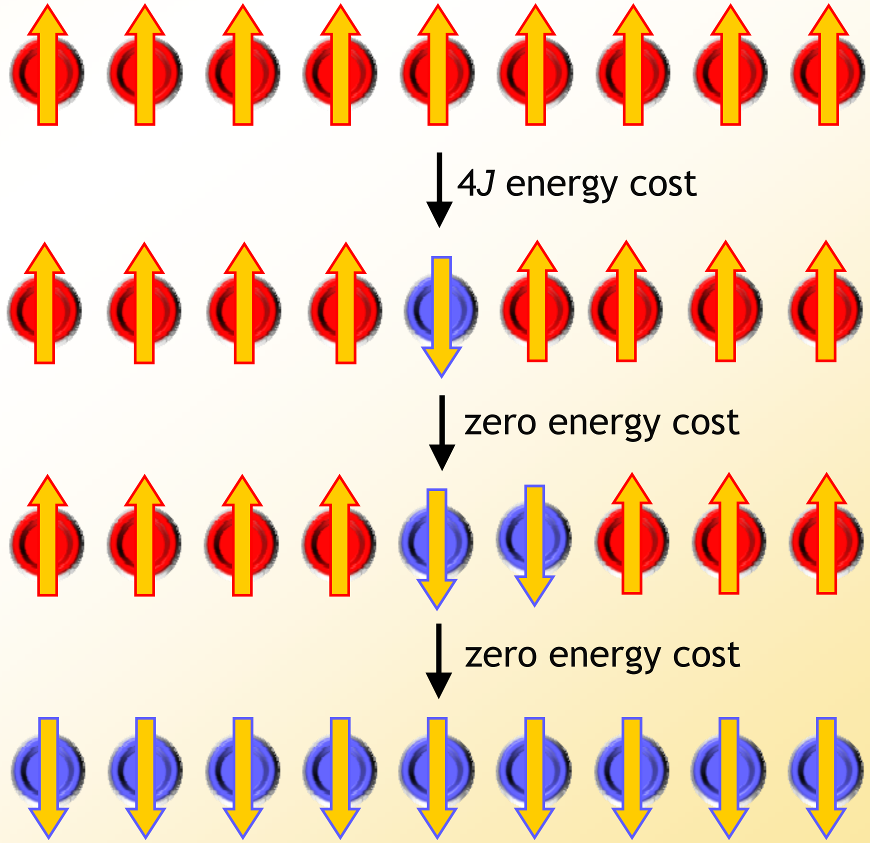
$$\tau^{-1} = \alpha(1-\gamma) = \alpha\,[1-\tanh(2J/k_B T)]$$

# A closer look at Glauber's model

for large $2J/k_BT$:* $\quad \tau^{-1} \approx 2\alpha e^{-4J/k_BT} \qquad \tau \approx \frac{1}{2\alpha} e^{4J/k_BT} = \tau_0 e^{U_{eff}/k_BT}$

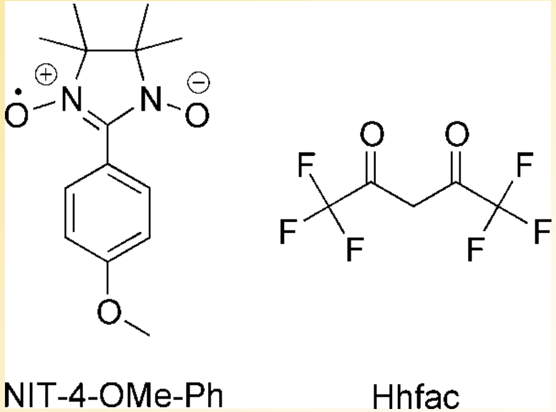
**Thermally-activated overbarrier process with $U_{eff}$ = 4*J***

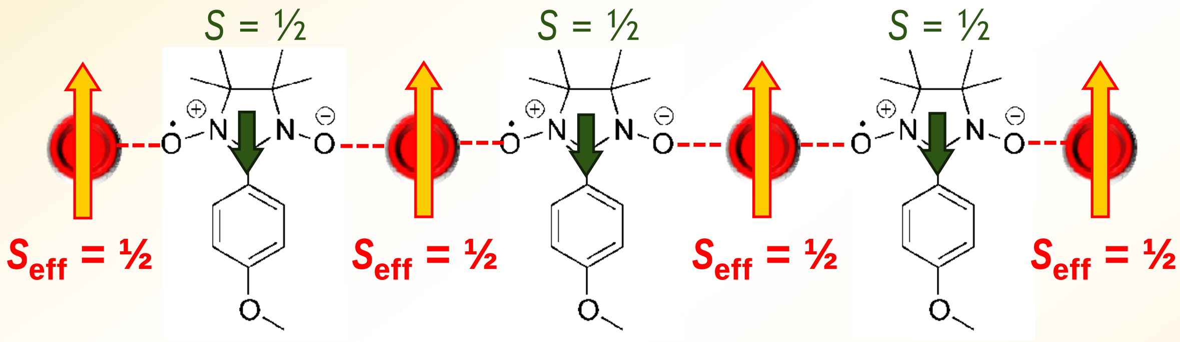


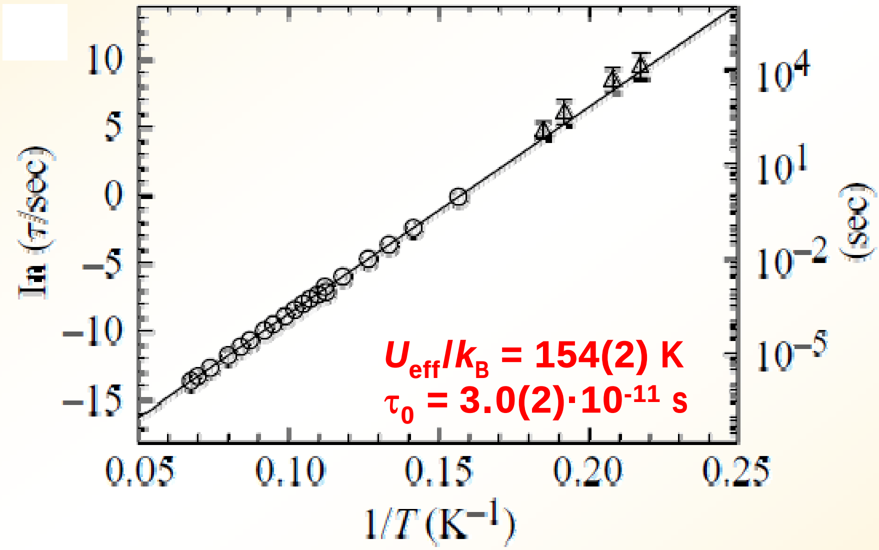

*for x >>1, 1-tanh($x$) ≈ $2e^{-2x}$

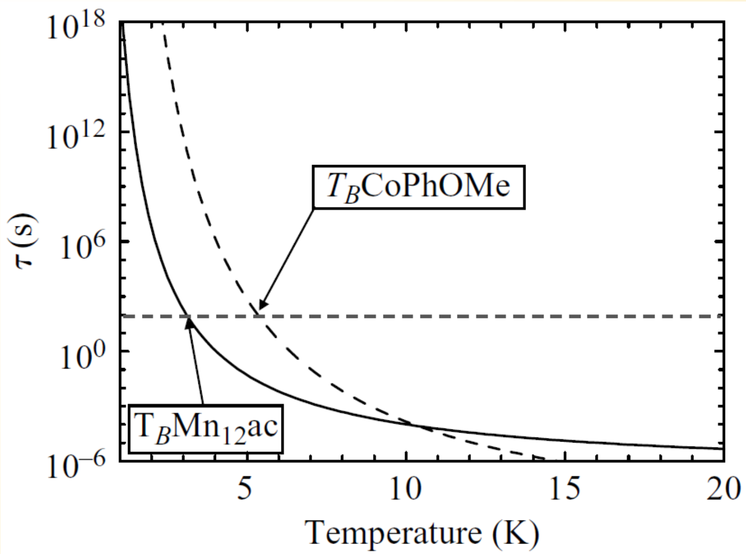
# $Co^{II}(hfac)_2(NIT\text{-}4\text{-}OMe\text{-}Ph)$




- **large easy-axis anisotropy of $Co^{II}$: $S_{eff}$ = ½, $g_{II}$ = 8-9, $g_{\perp}$ ~ 0**
- **strong intrachain magnetic interactions *(J)***
- **weak interchain magnetic interactions ($J' < 10^{-4}J$)**



# Single Chain Magnets

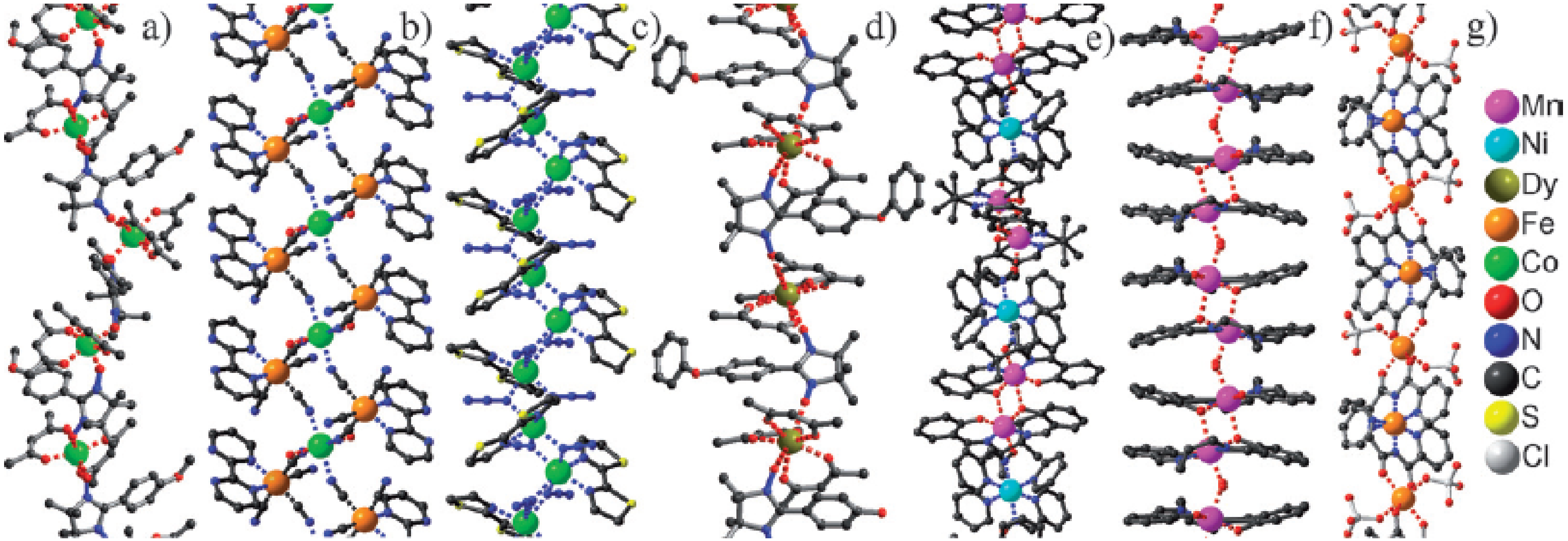



**Fig. 6** The crystal structures of selected examples of SCMs. The atomic colour code is the same for all structures, as reported on the right. (a) The archetypal SCM CoPhOMe.[10] The use of short linkers and peripheral shielding ligands is visible in: (b) the cyanide bridged heteronuclear $[Fe(bpy)(CN)_4]_2Co(H_2O)_2 \cdot 4H_2O$ chain[46,47] and (c) the homonuclear azide-bridged compound $[Co(2,2\text{-bithiazoline})(N_3)_2]$.[50] (d) The first rare-earth-based SCM $[Dy(hfac)_2NIT(C_6H_4p\text{-OPh})]$,[51] with bulky NIT radicals bridging the metals and shielding intrachain interactions. (e) The $Mn^{III}$-$Ni^{II}$ based $[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$ chain,[11] which uses the ligand field anisotropy of the $Mn^{III}$ centre with an elongated Jahn–Teller axis. (f) The $[Mn_2(salpn)_2(H_2O)_2](ClO_4)_2$ chain,[57] composed of a row of interacting SMMs based on $Mn^{III}$ ions, linked *via* H-bonds. (g) The $[Fe(ClO_4)_2\{Fe(bpca)_2\}](ClO_4)$ chain,[61] based on Fe centres with *XY* anisotropy.

L. Bogani, A. Vindigni, R. Sessoli, D. Gatteschi, *J. Mater. Chem.* 2008, *18*, 4750

# Summary

- **High-spin magnetic molecules can display slow relaxation of the magnetic moment (Single-Molecule Magnets);**
- **A key-ingredient for slow relaxation is the presence of an easy-axis anisotropy ($D < 0$), which produces an anisotropy barrier;**
- **The relaxation occurs via overbarrier thermal activation *plus* quantum tunneling (QT); such a coexistence of classical and quantum effects is typical of the nanoscale;**
- **QT effects convey to the system a residual ability to relax even at the lowest temperatures; they have a resonant character;**
- **Being extremely sensitive to molecular structure, QT effects are one of the most distinctive features of Single-Molecule Magnets*;**
- **Slow thermal relaxation and QT can be observed in complexes of individual rare-earth ions with a large total angular momentum, due to crystal field splitting of the ground level**
- **One-dimensional Ising systems display slow magnetic relaxation due to *J*-dependent barriers to spin flipping (Glauber dynamics).**

***M. Mannini, *et al. Nature* 2010, *468*, 417**

THANK YOU