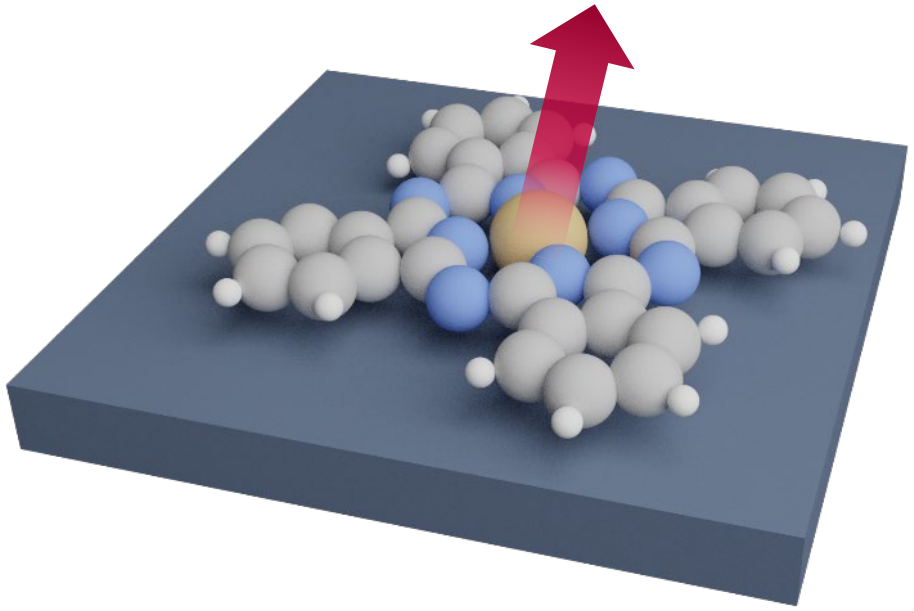


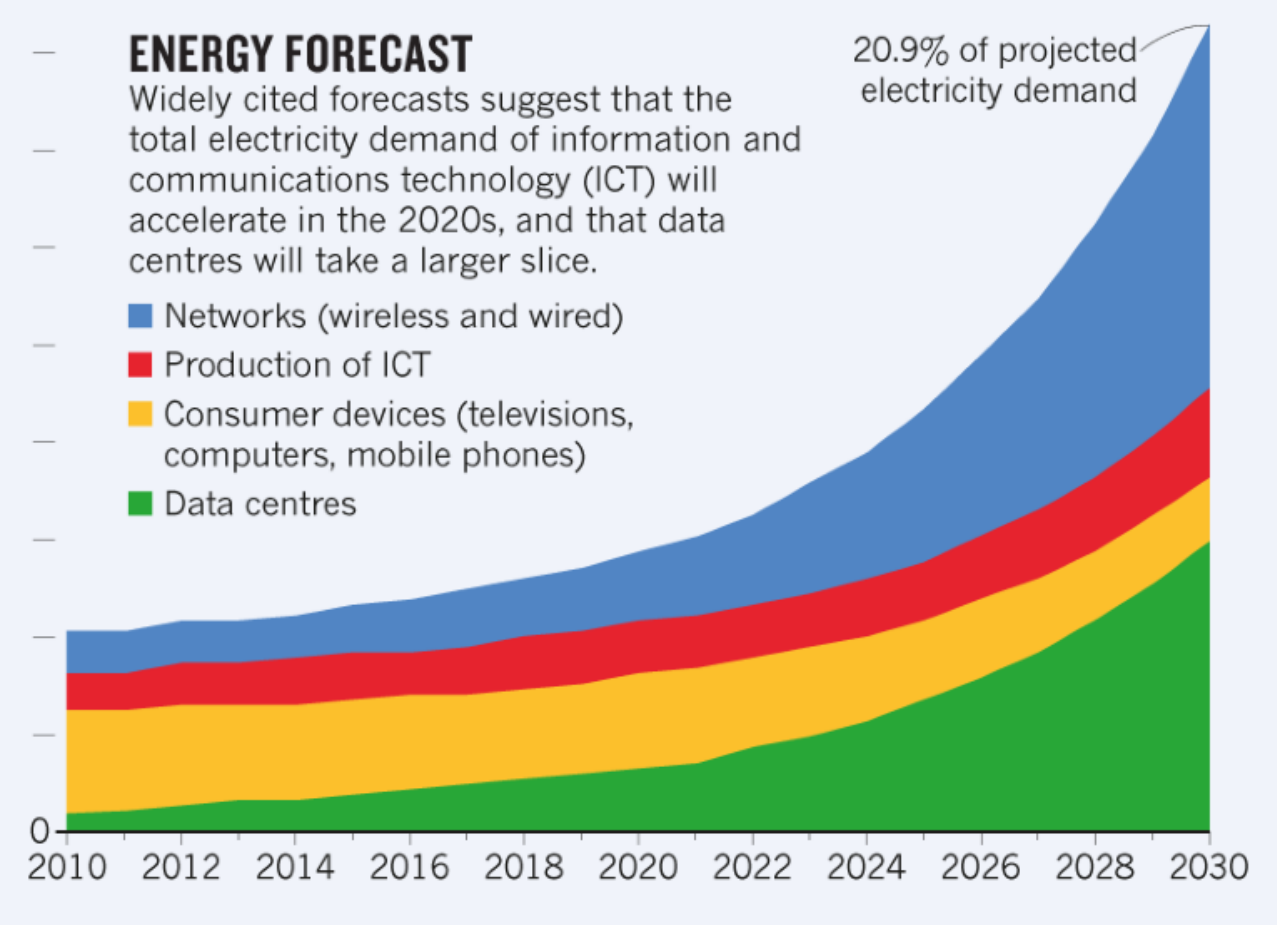
From wavefunctions to molecular magnetism

ANGELA WITTMANN

MPA RETREAT

JOHANNES GUTENBERG UNIVERSITÄT MAINZ

Energy challenge

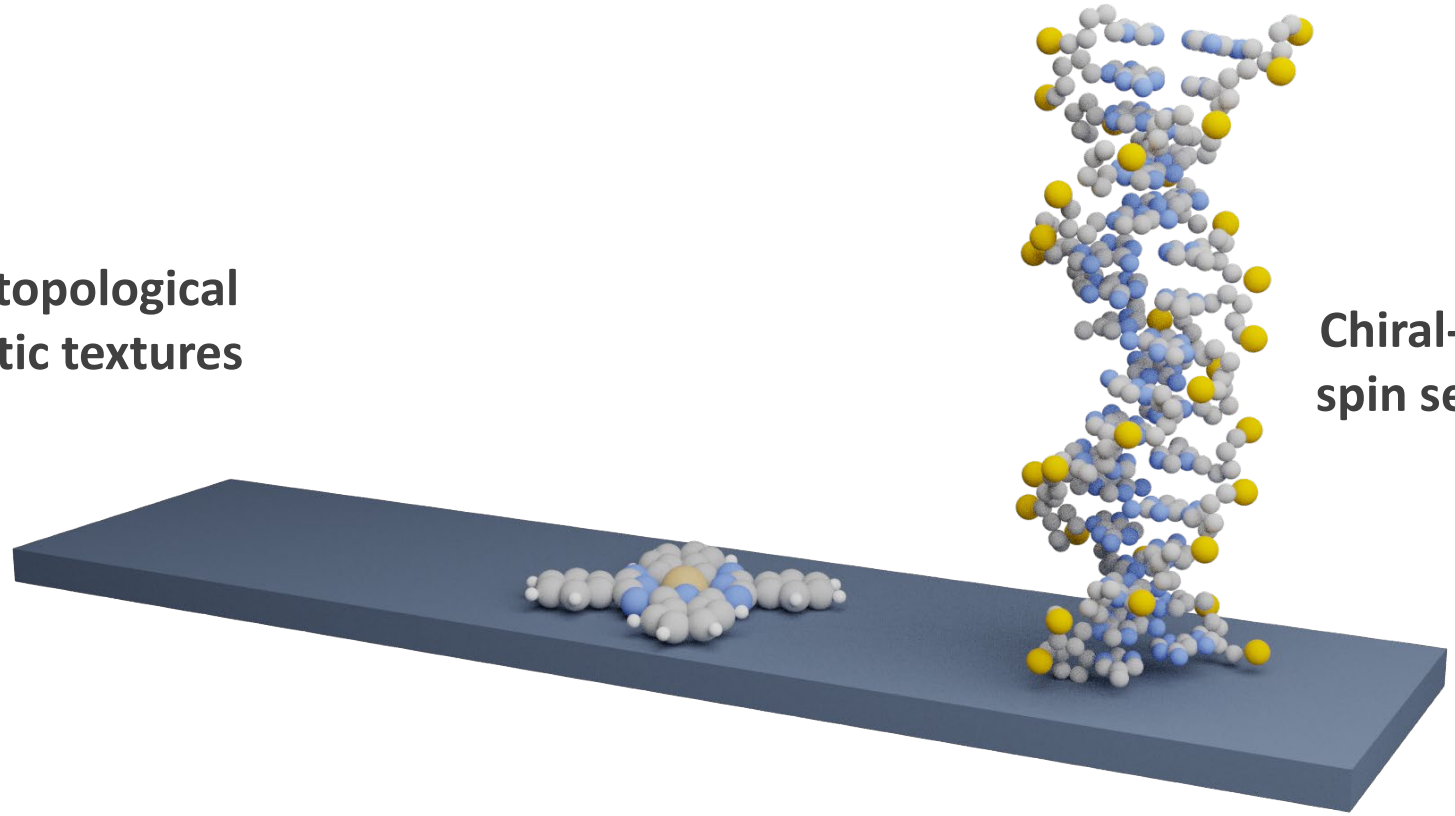


N. Jones, Nature 561, 163 (2018)

- CMOS+X: Need for innovation to transform technology fundamentally

Overview

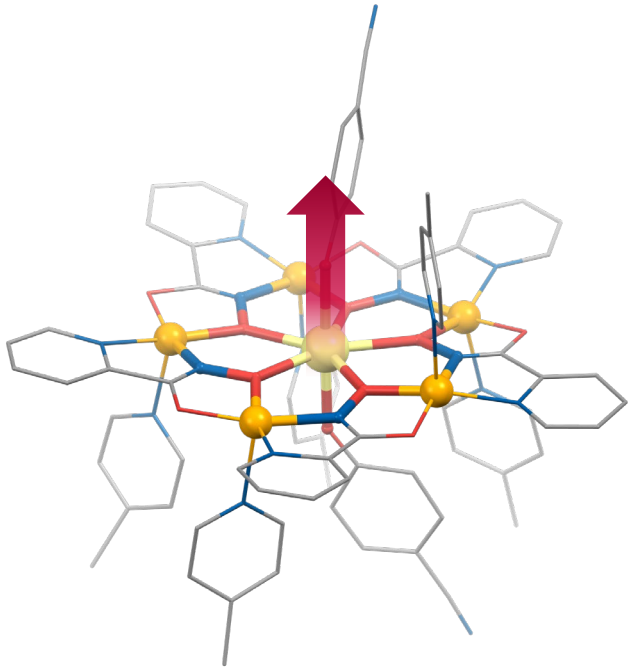
Exotic topological magnetic textures



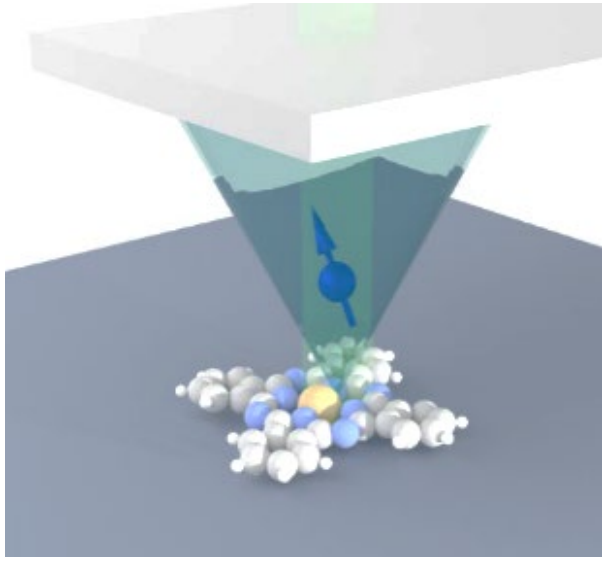
Chiral-induced spin selectivity

Tuning hybrid interfaces by molecular design

Overview

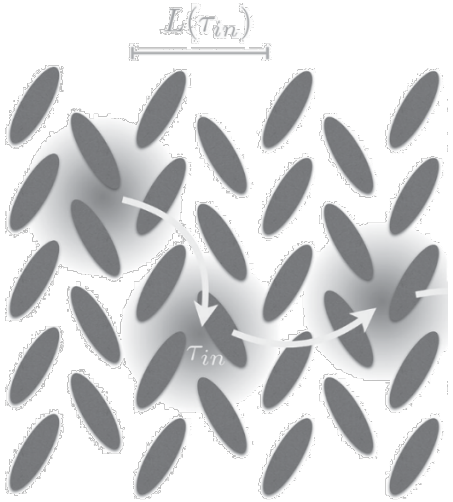


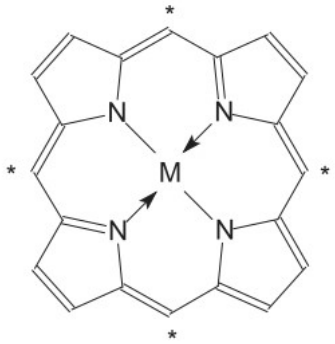
- Basics of (molecular) magnetism
- Single-molecule magnets
- Nitrogen-vacancy center magnetometry
- Probing magnetic fluctuations with spin relaxometry



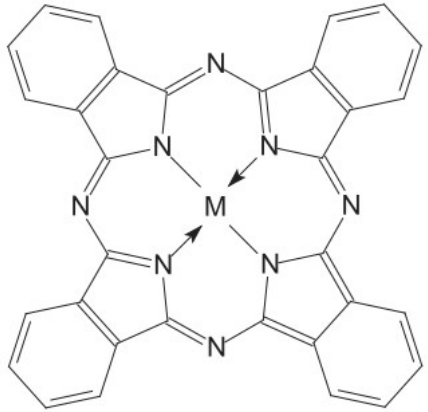
Spintronics in molecular systems

- Unique charge transport mechanisms
- Low spin-orbit coupling
- Plethora of possibilities for molecular design

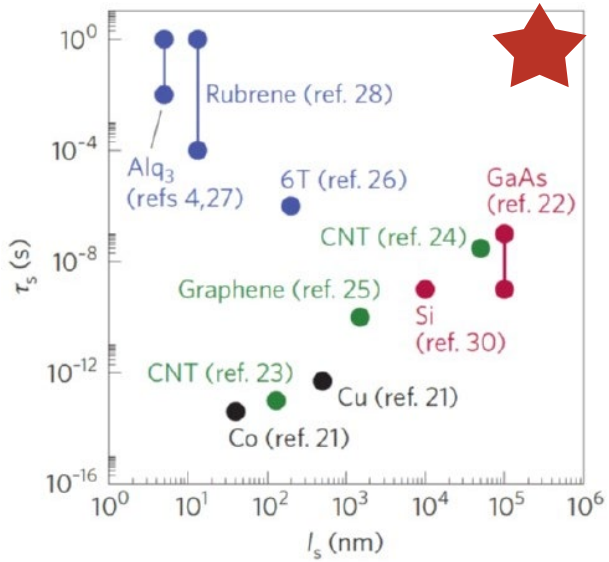




metalloporphyrin



metallophthalocyanine



S. Fratini et al. Adv. Funct. Mater. 26, 2292 (2016)
G. Szulczewski et al., Nat. Mater. 8, 693 (2009)
T. L. Francis et al., New J. Phys. 6, 185 (2004)
V. Dediu et al., Solid State Commun. 122, 181 (2002)
M. Grünewald et al., Phys. Rev. B 84, 125208 (2011)

Recap: Exchange coupling

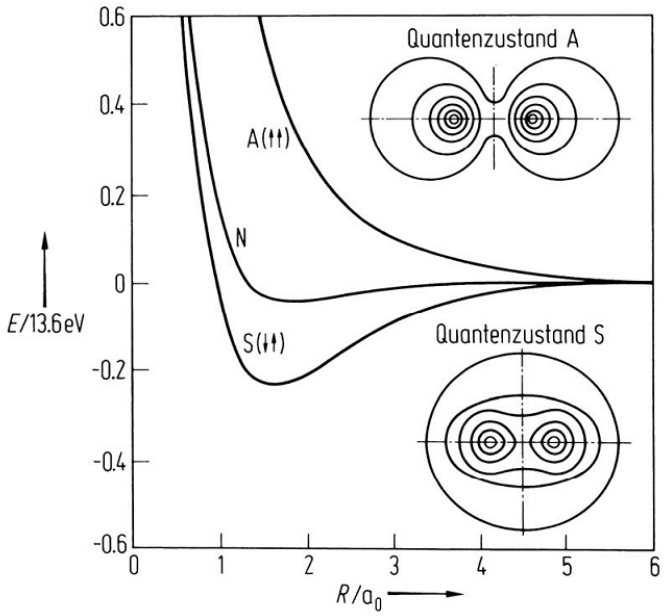
- Only considering nearest neighbors: Heisenberg model

$$\widehat{\mathcal{H}}_{\text{exch}} = -\sum_{i,j} J_{ij}\, \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

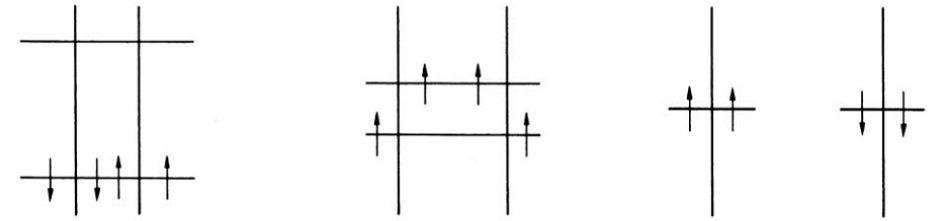
- If electrons on the same atom: spatial wavefunction is antisymmetric to minimize Coulomb energy → J>0, triplet spin state
- If electrons are located on neighboring atoms, total wave function is combination of two single-state wave functions

Recap: Exchange coupling

- J depends on electronic properties as well as distance due to balance of the Coulomb energy and the kinetic energy
- Atoms very close:
  Kinetic energy is minimal if both electrons are in between the atoms and hence antiparallel spins
  → Negative J, antiferromagnetism
- Atoms more distant:
  Parallel spins can be favored
  → Positive J, ferromagnetism



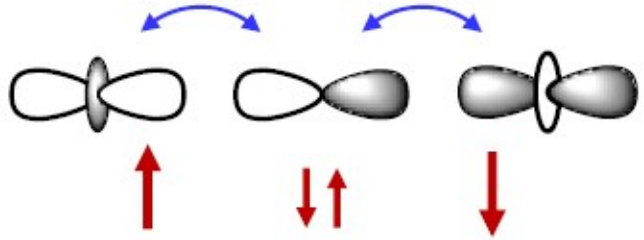
Binding energy as a function of the distance; binding singlet state (S) and antibinding triplet state (A)



geringer Atomabstand, starke Niveauaufspaltung, hoher Energieaufwand zur Neuverteilung der Elektronen: Antiferromagnetismus

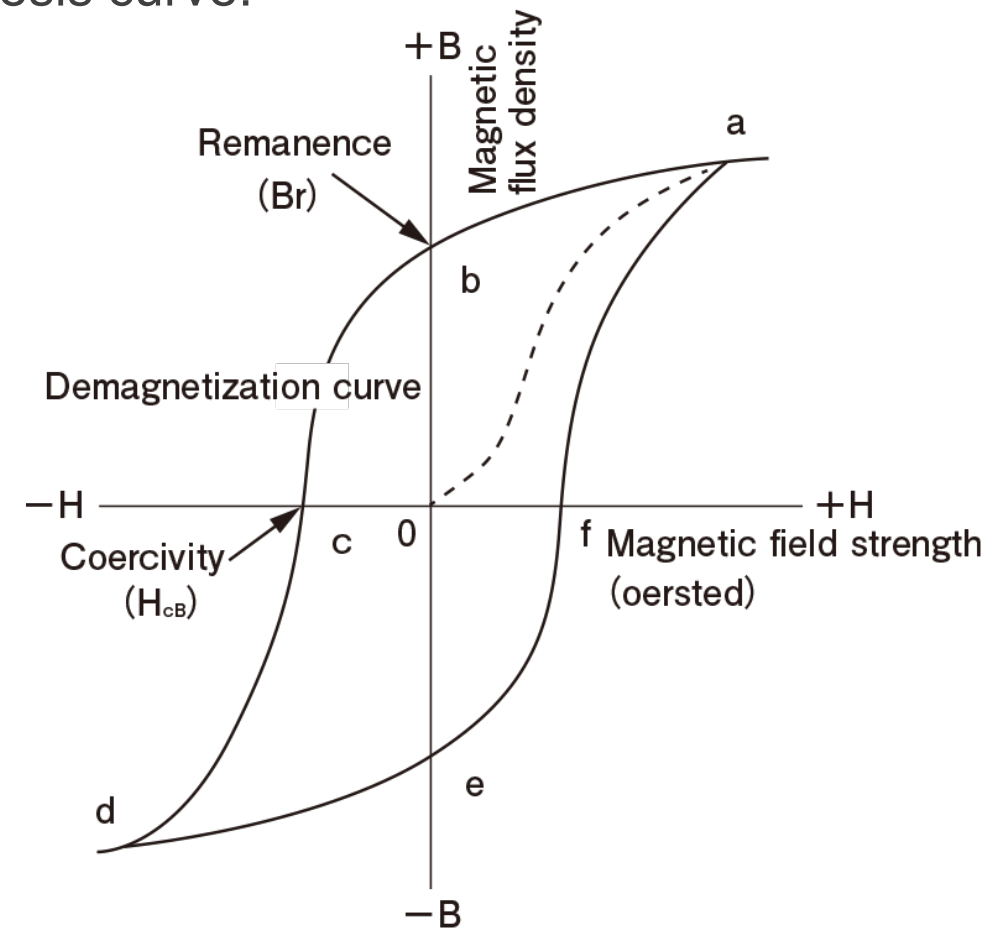
mittlerer Atomabstand, geringe Niveauaufspaltung, wenig Energieaufwand zur Neuverteilung der Elektronen: Ferromagnetismus

großer Atomabstand, keine Kopplung: Paramagnetismus



Recap: Magnetization curve

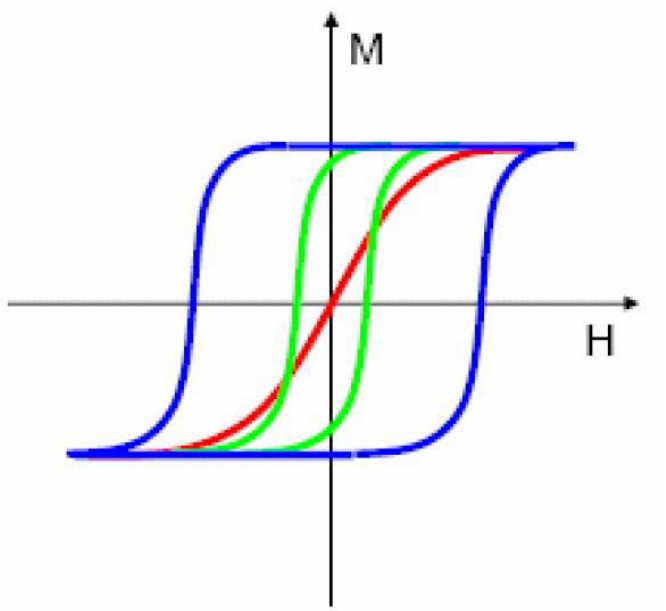
Typical magnetic hysteresis curve:

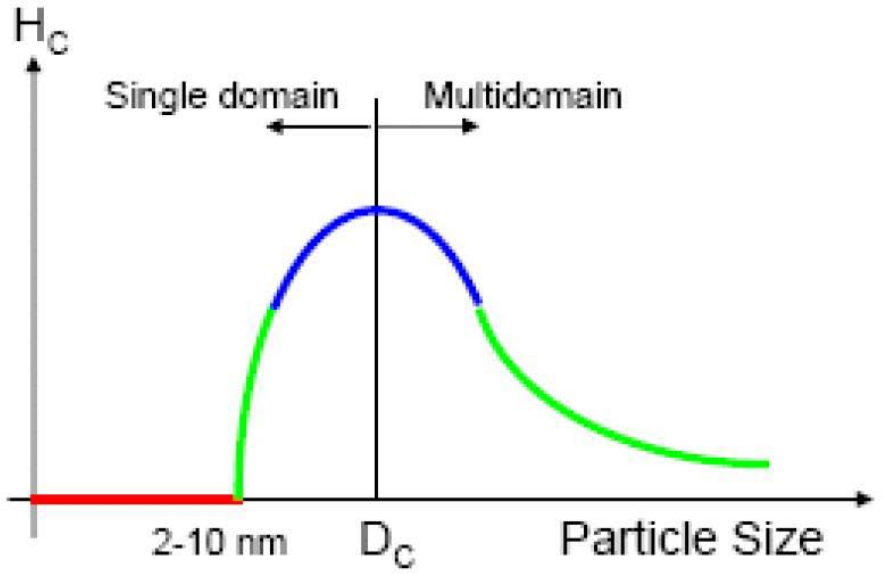


Magnetic hysteresis loop

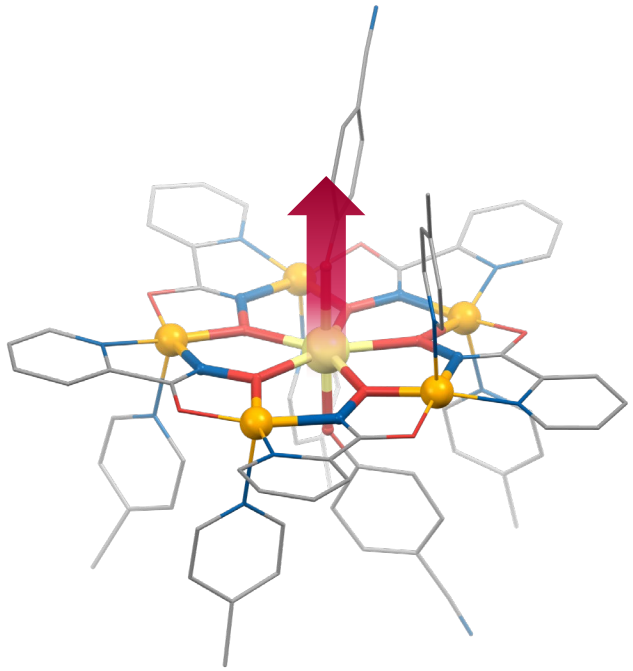
Recap: Superparamagnetic limit

- For large size: domain formation minimizes stray fields
- Below critical size: single domain state is favorable
- For very small size: coercivity vanishes below the superparamagnetic limit





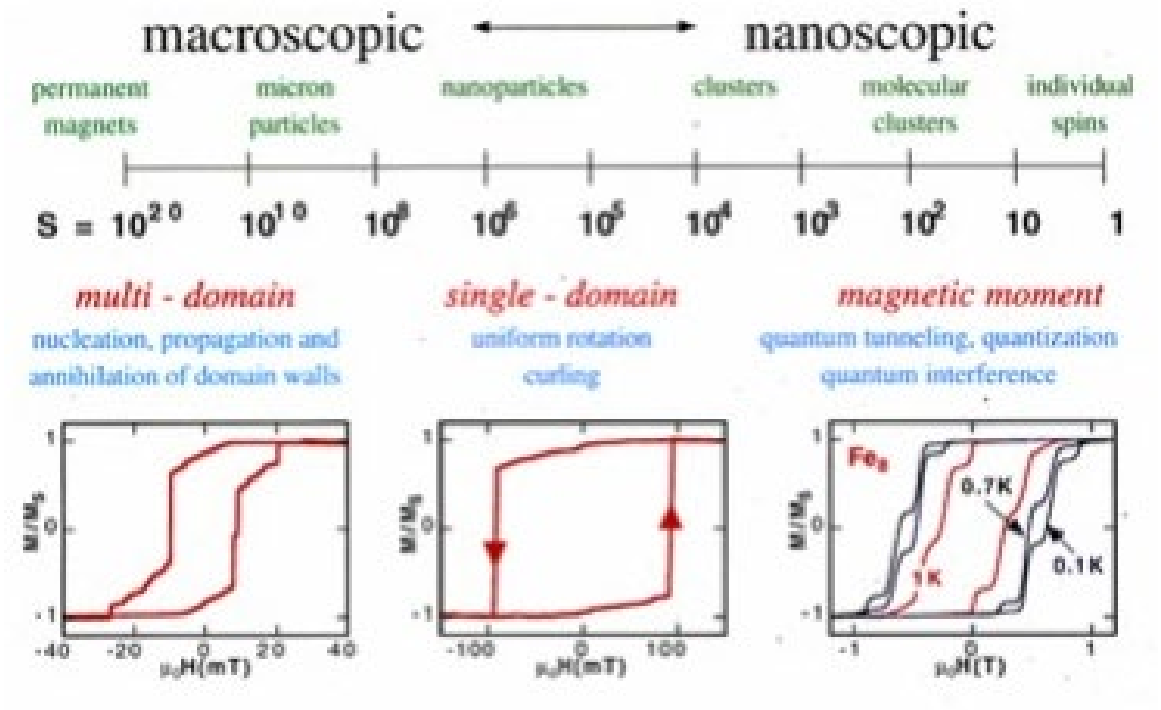
How can we get finite spontaneous magnetization at zero field on the atomic scale?



Single-molecule magnets (SMMs)

Single-molecule magnets (SMMs)

- Molecules with slow magnetic relaxation of purely molecular origin
- Long-range interactions with other molecules are not necessary
- Finite remanence, spontaneous magnetization
- Multilevel quantum systems showing distinct quantum properties



Polymetallic Mn complex

- First widely studied SMM

$$[Mn_4^{IV}Mn_8^{III}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$$

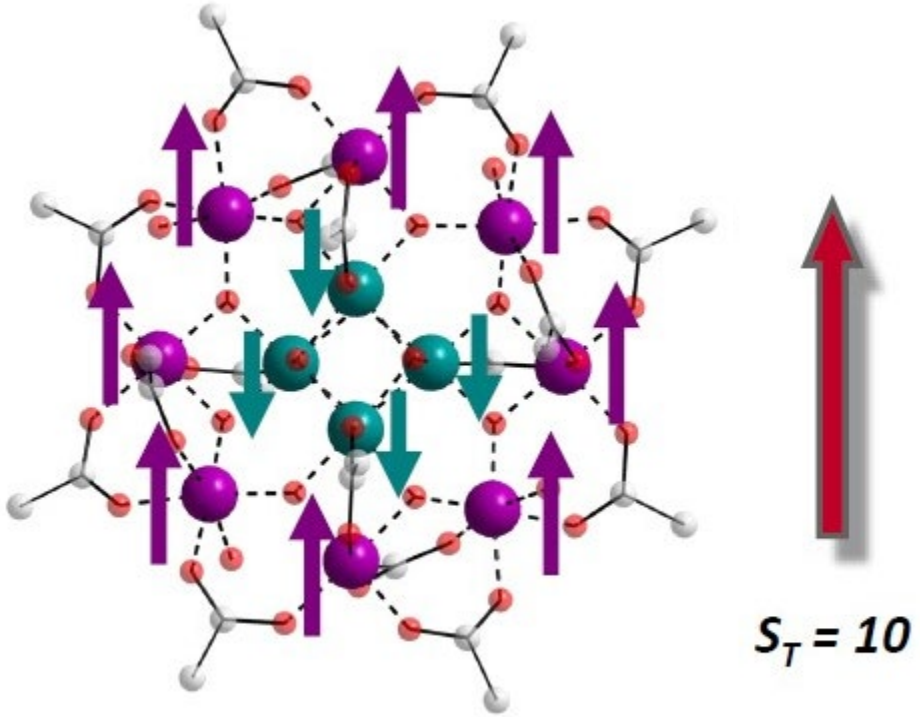
- Two different Mn states:

$$Mn^{IV}\ d^3 \Rightarrow S = {}^3/_2$$

$$Mn^{III}\ d^4 \Rightarrow S = 2$$

- Total spin:

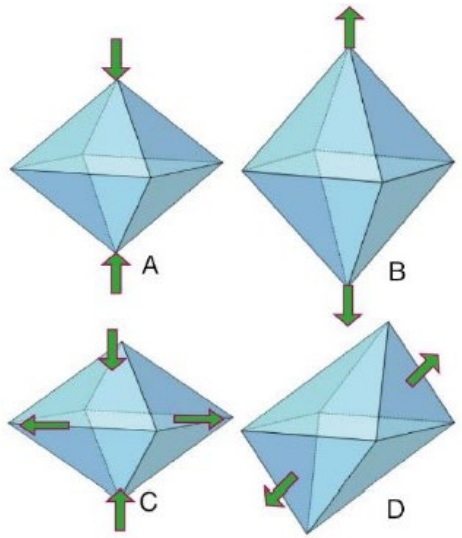
$$S_T = 8 \cdot S_{Mn^{III}} - 4 \cdot S_{Mn^{IV}} = 8 \cdot 2 - 4 \cdot {}^3/_2 = 10$$



$$[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$$

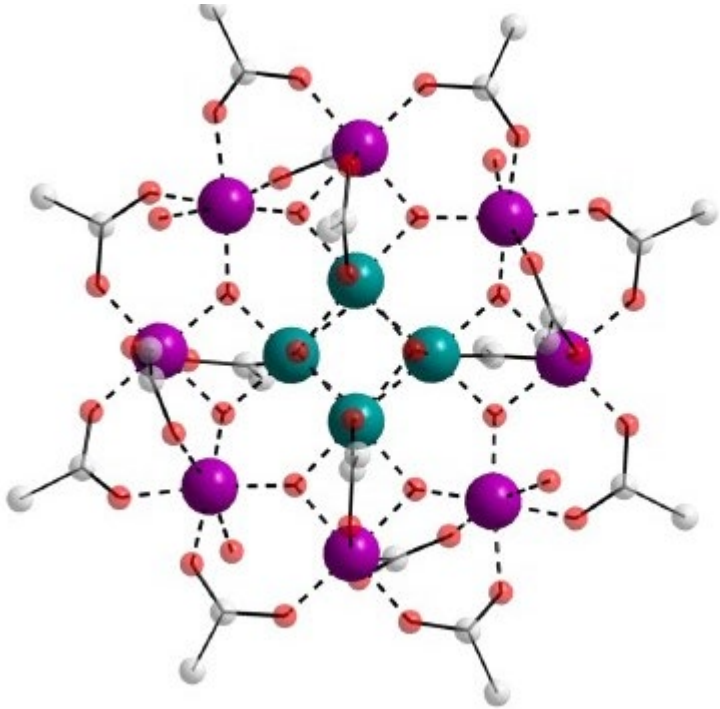
Zero field splitting

- Jahn-Teller-distortion



lower symmetry

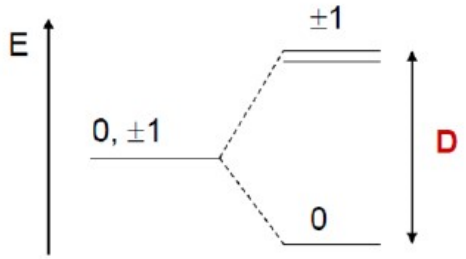
$[Mn_4^{IV}Mn_8^{III}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$

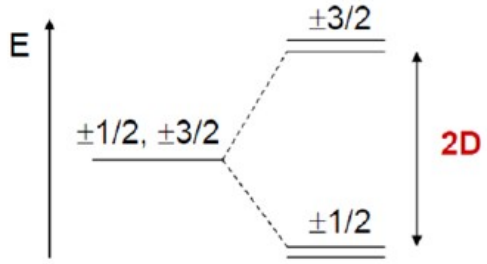


$S_T = 10$

- Zero field splitting

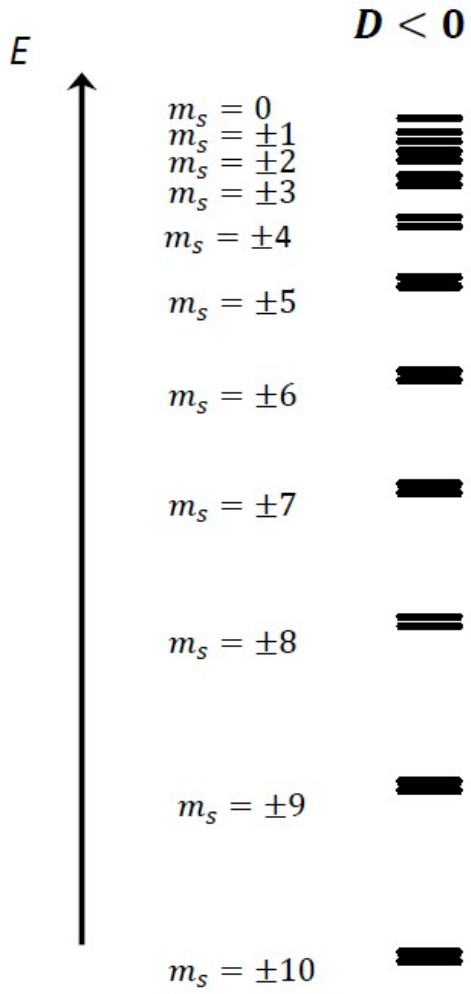
D = ZFS parameter $D > 0$



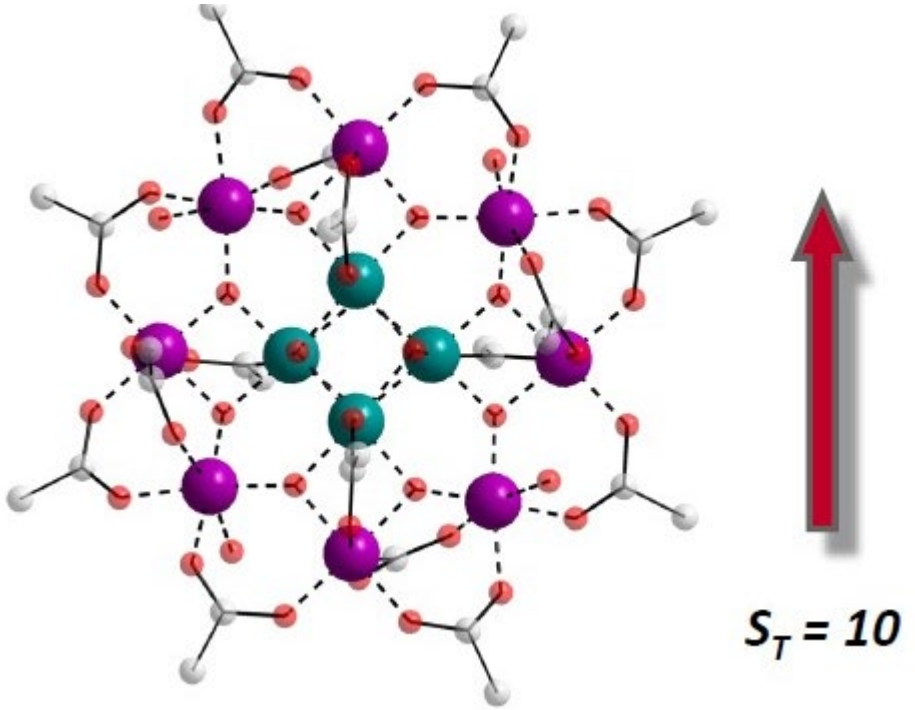


Multilevel system

- Multilevel quantum system

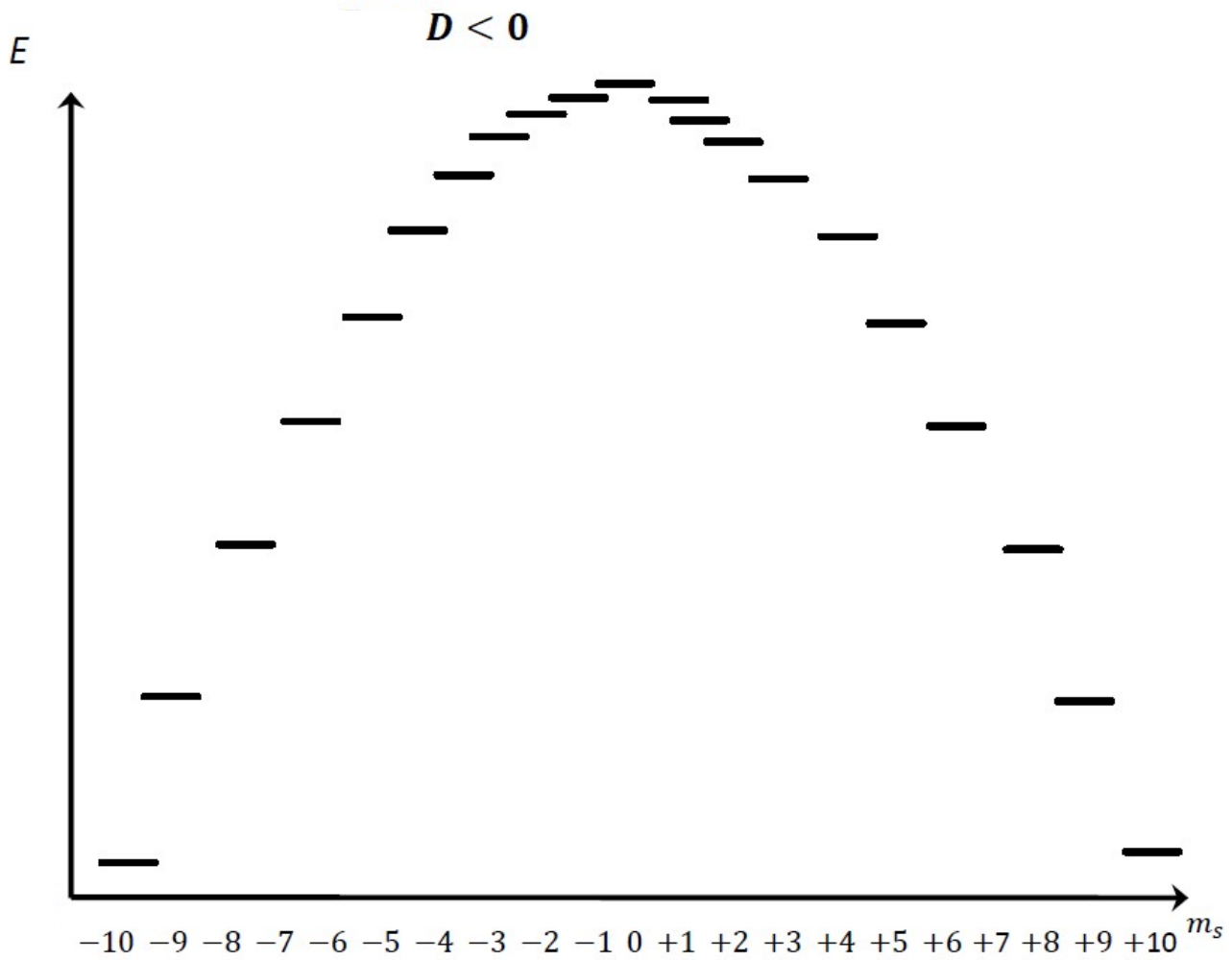


$[Mn_4^{IV}Mn_8^{III}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$

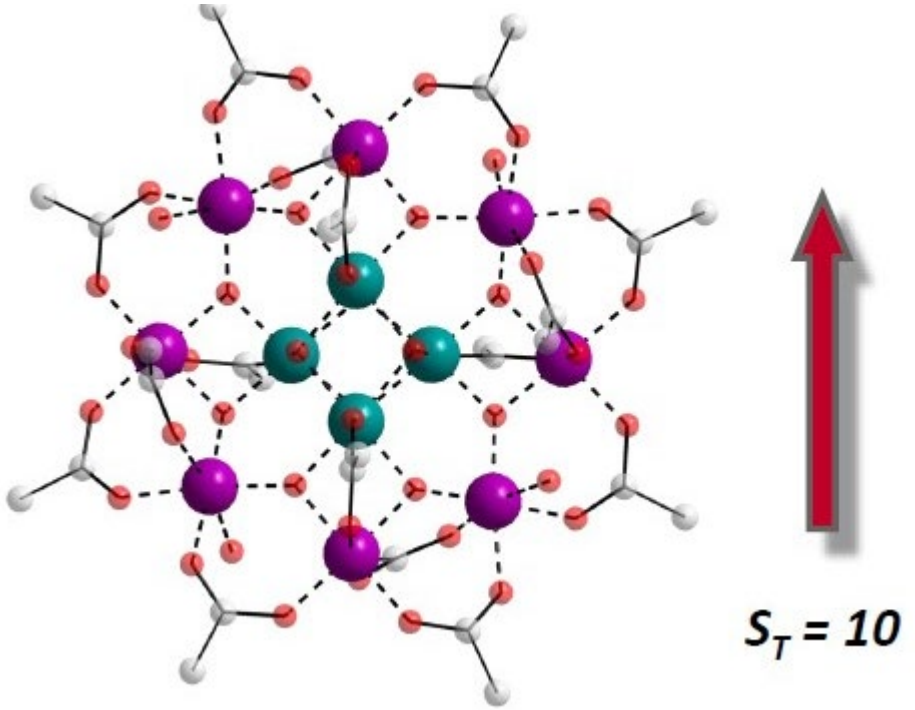


Multilevel system

- Multilevel quantum system

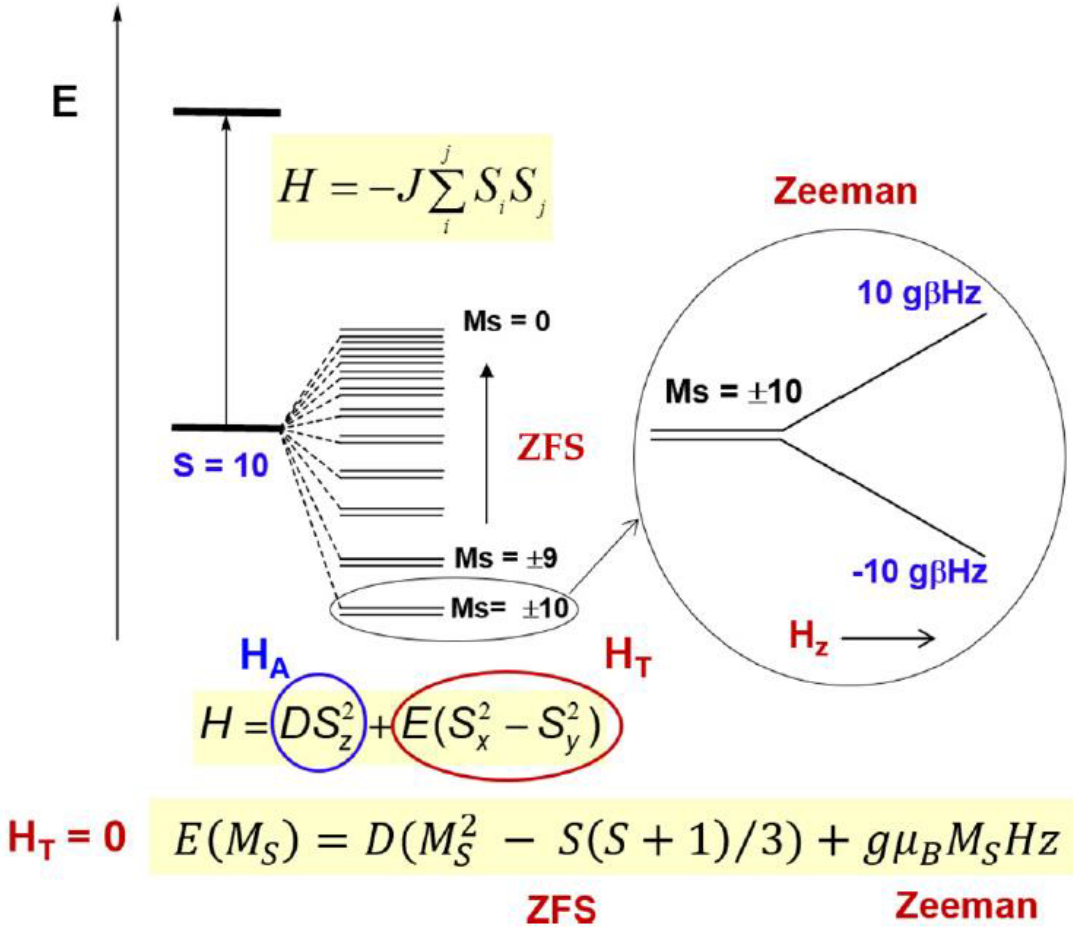


$[Mn_4^{IV}Mn_8^{III}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$

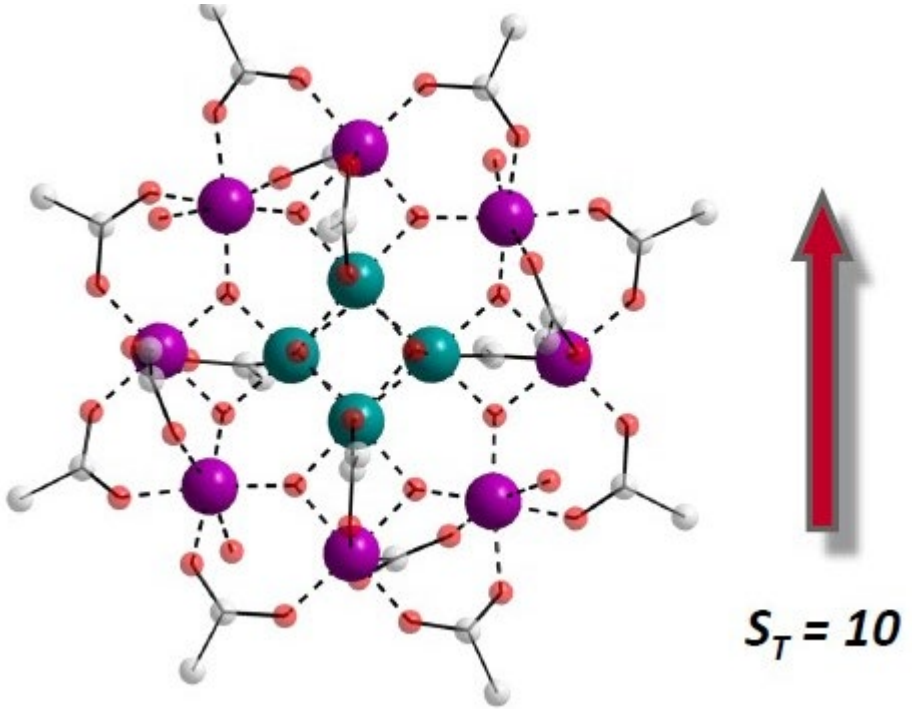


Multilevel system

- Multilevel quantum system

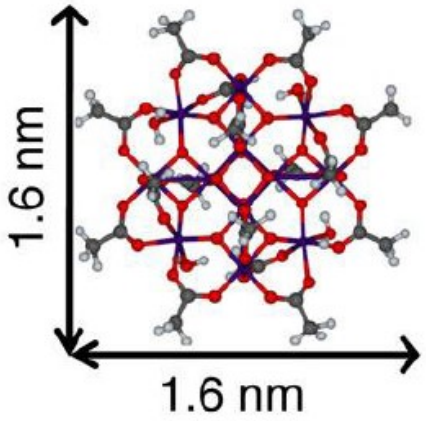


$[Mn_4^{IV}Mn_8^{III}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$

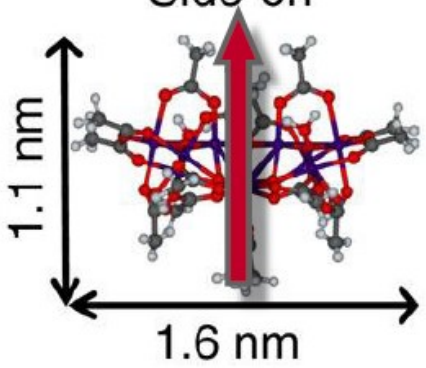


Anisotropy

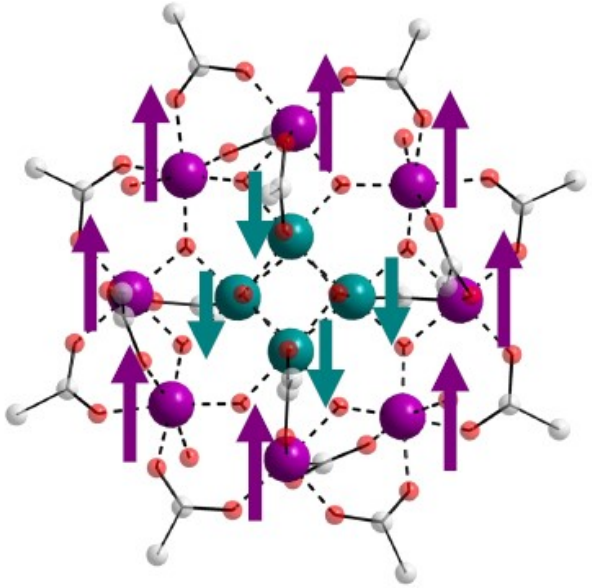
Top-down



Side-on



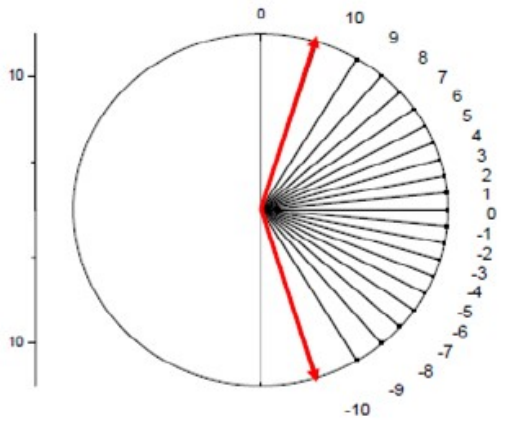
$[Mn_4^{IV}Mn_8^{III}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$

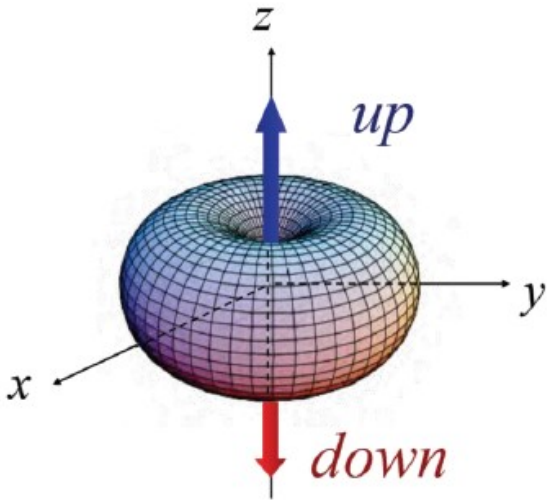


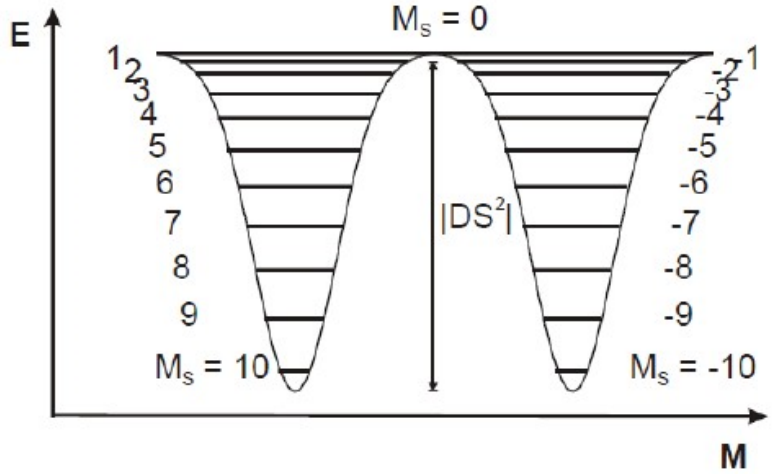
$S_T = 10$

$[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$

T_B = 4 K

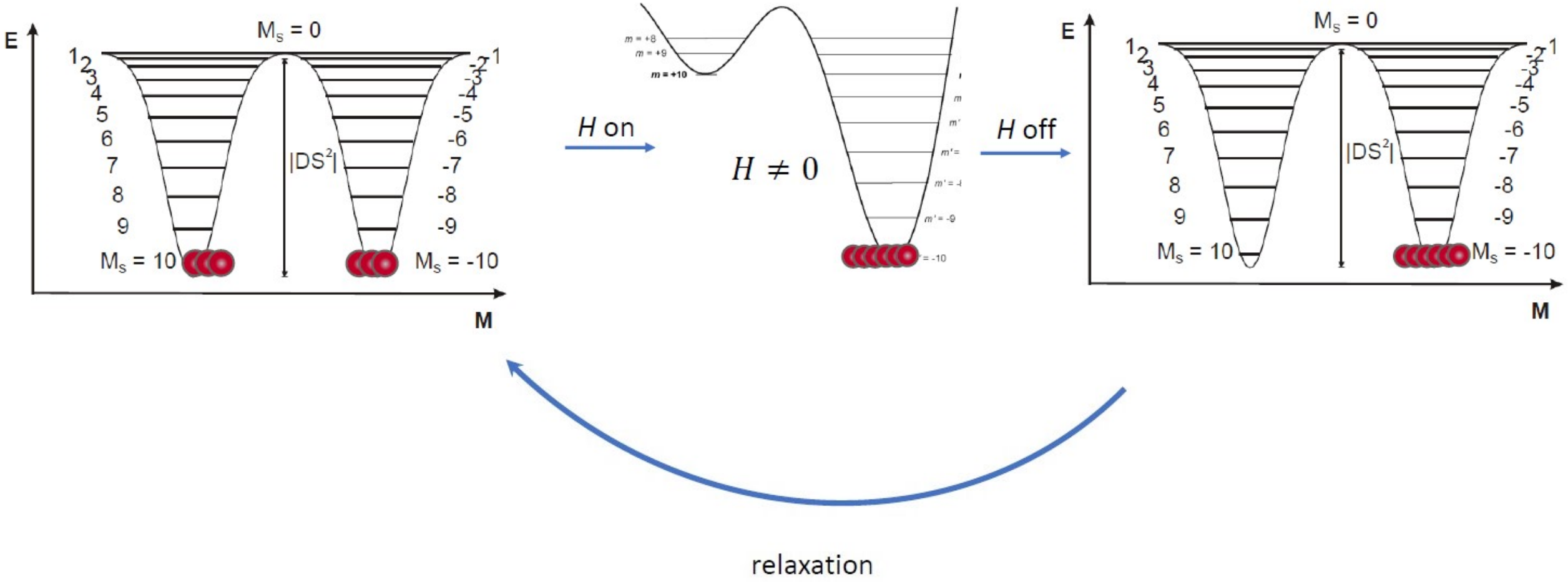






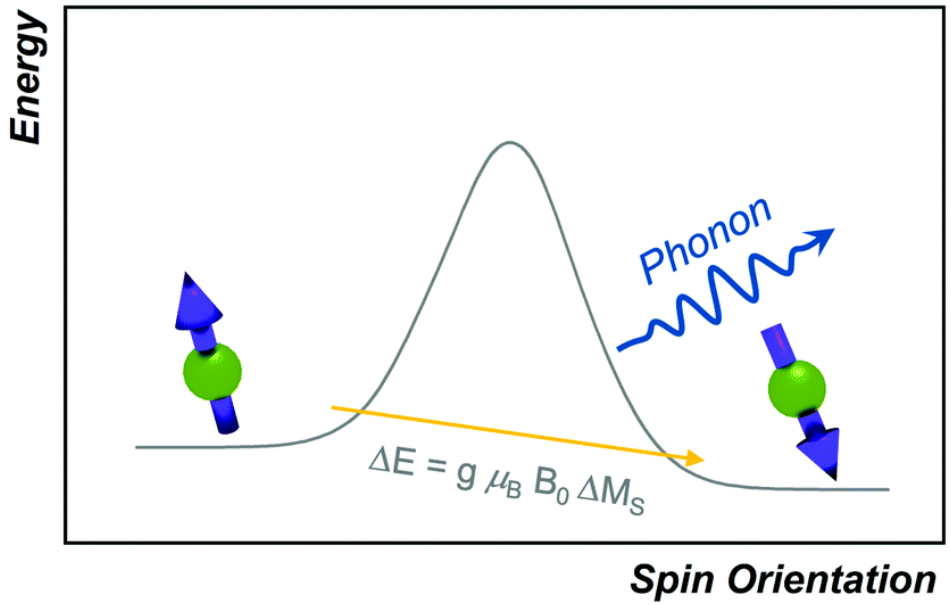
D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science* **1994**, *265*, 1054; D. Gatteschi, R. Sessoli, *Angew. Chem. I.E.* **2003**, *42*, 268; M. del Carmen Giménez-López, F. Moro, A. La Torre, C. J. Gómez-García, P. D. Brown, J. van Slageren & A. N. Khlobystov; *Nat. Commun.* **2011**, *2*, 407

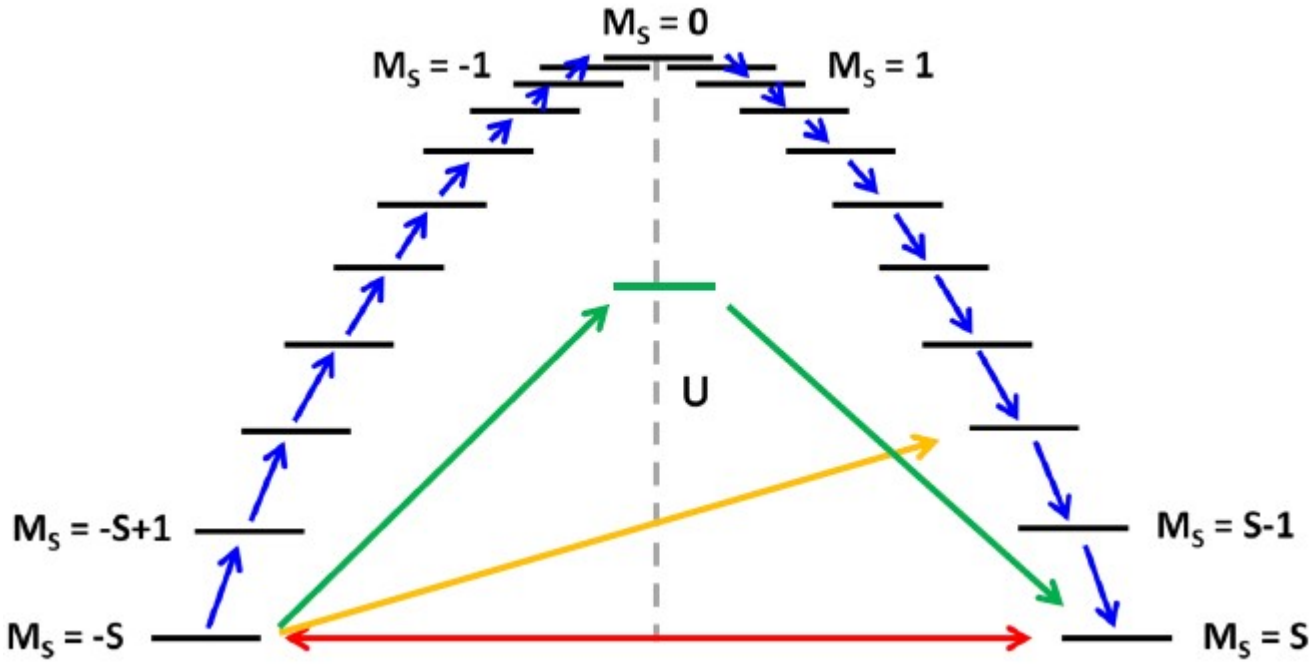
Energy barrier



Relaxation pathways

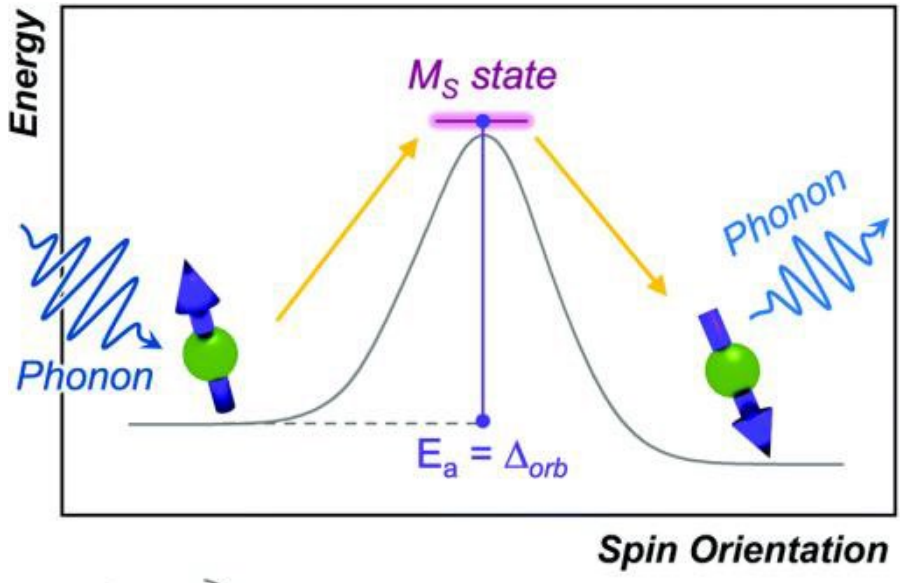
- Direct

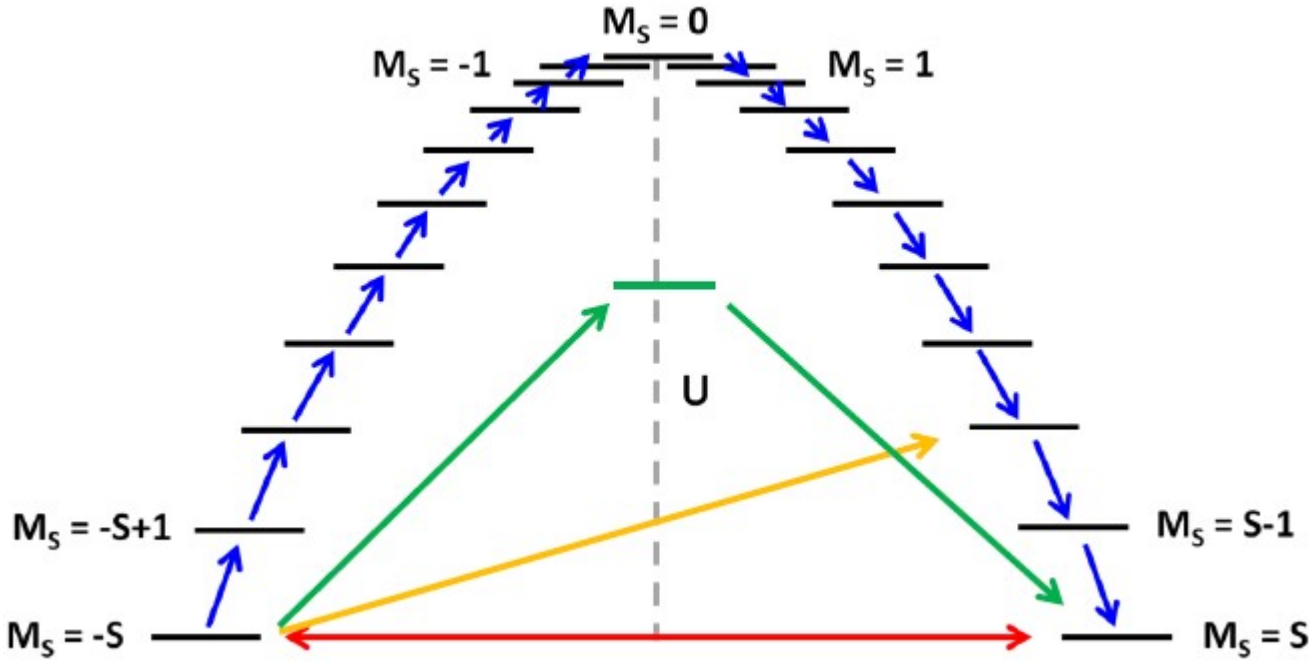




Relaxation pathways

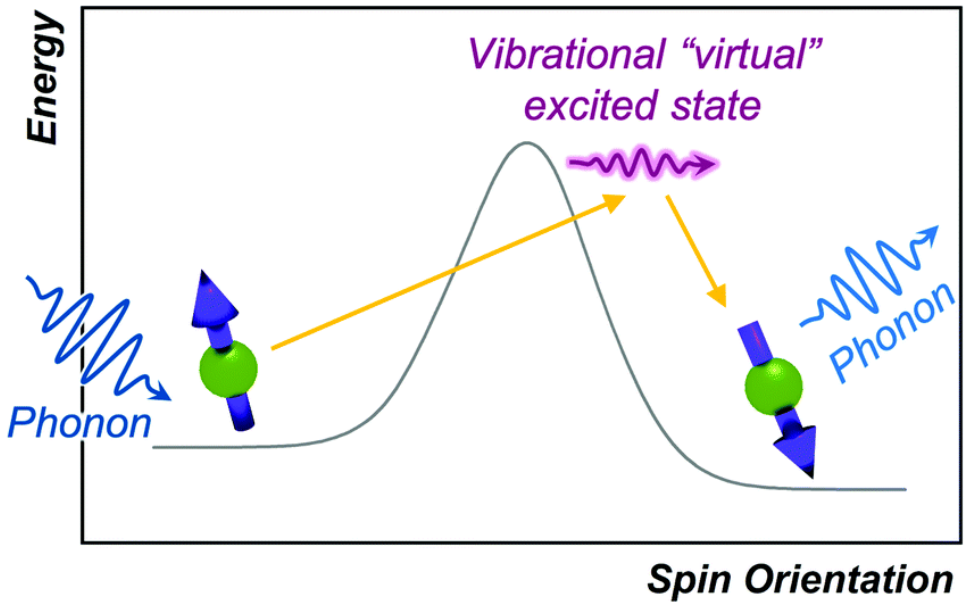
- Direct
- Orbach

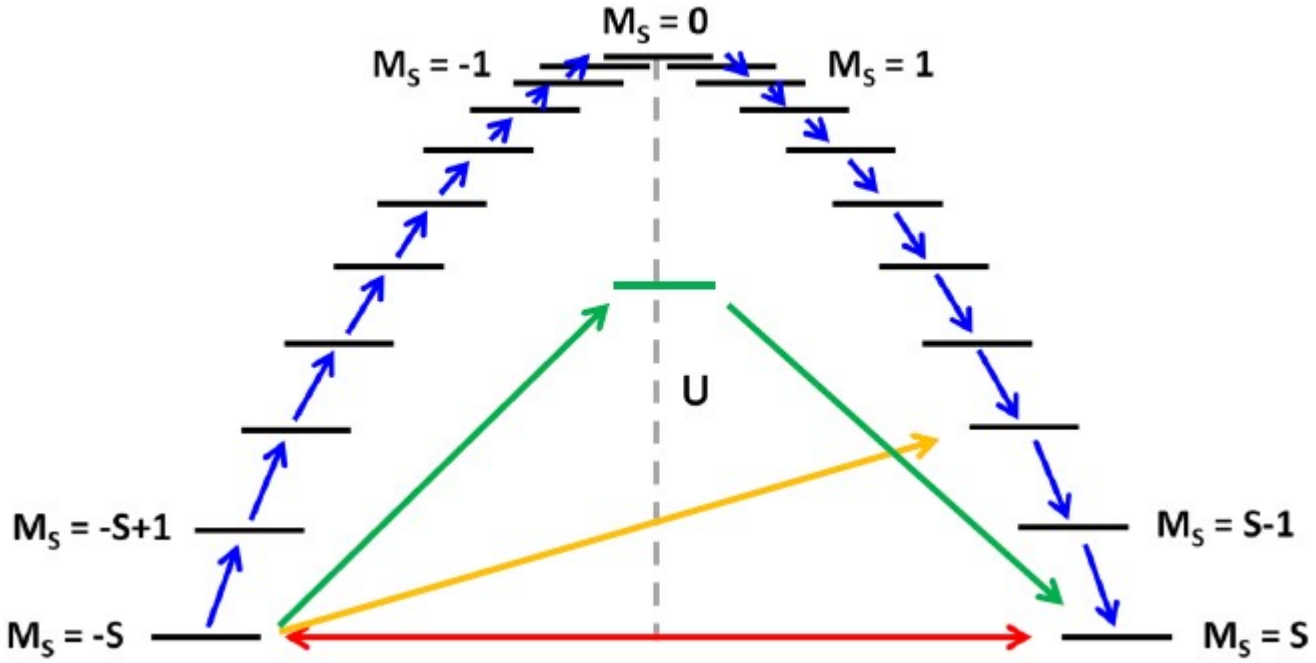




Relaxation pathways

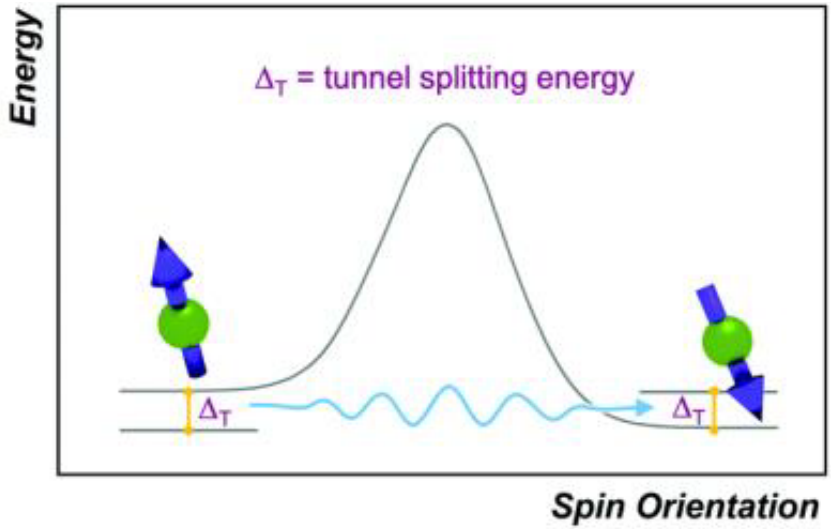
- Direct
- Orbach
- Raman

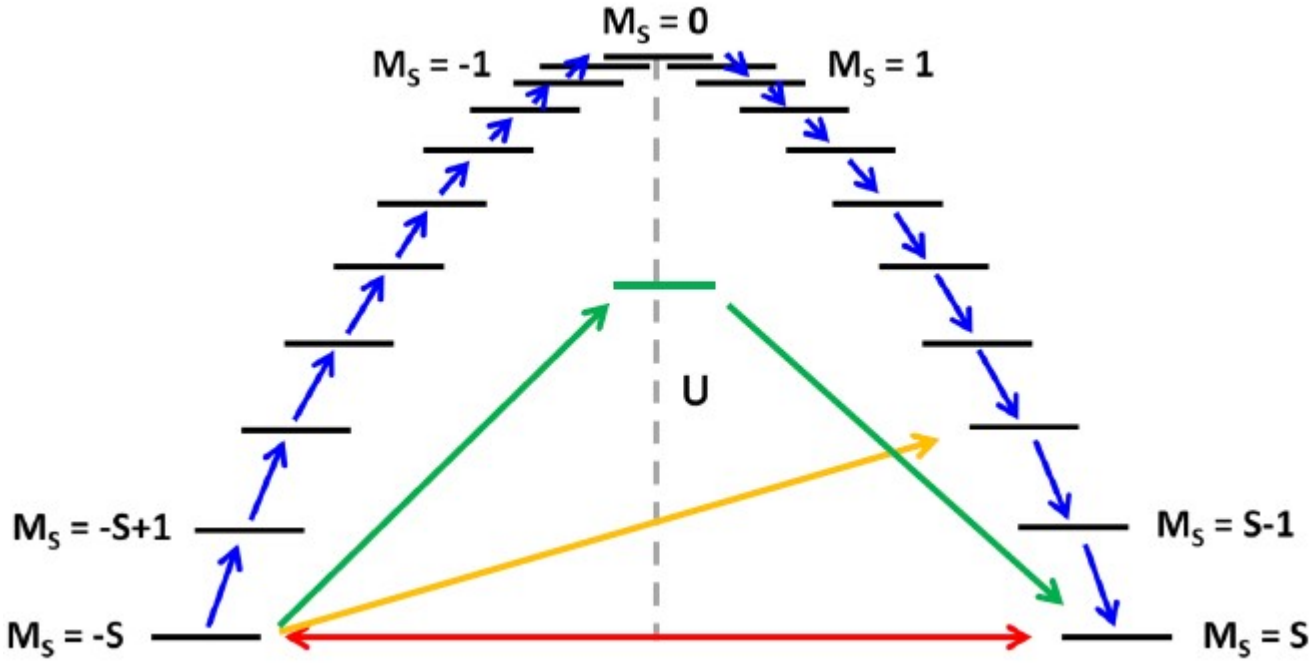




Relaxation pathways

- Direct
- Orbach
- Raman
- Quantum tunneling (QTM)



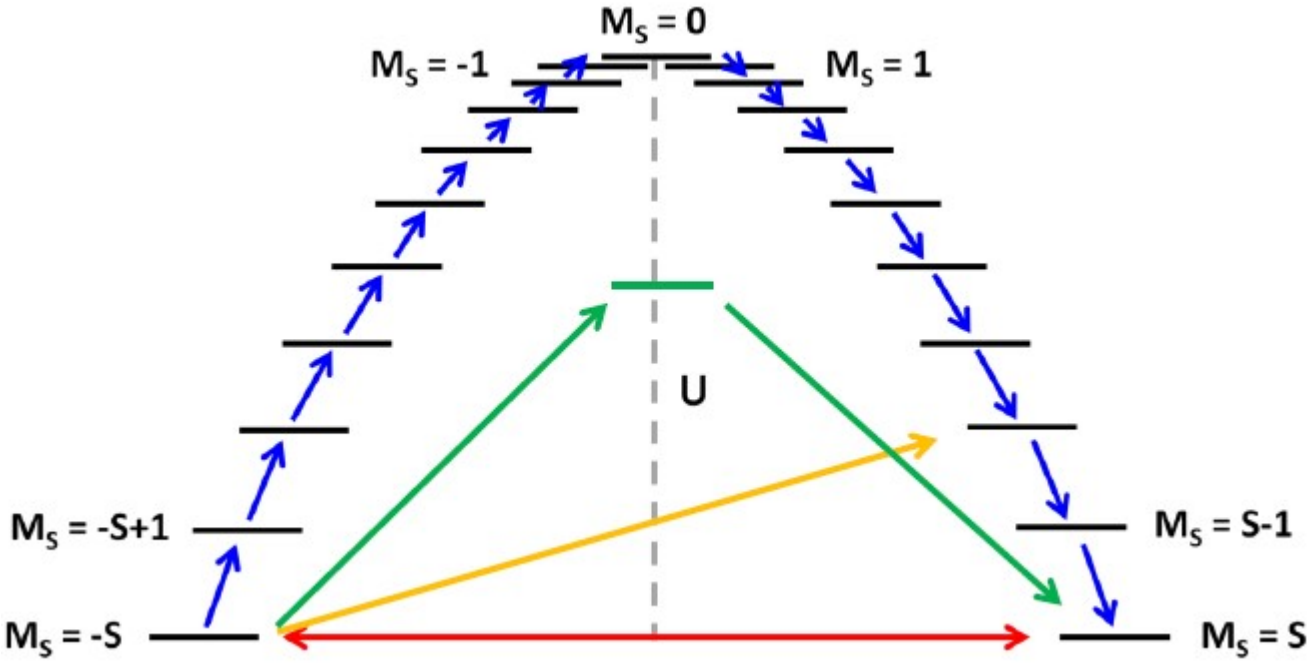


Relaxation pathways

- Direct
- Orbach
- Raman
- Quantum tunneling (QTM)

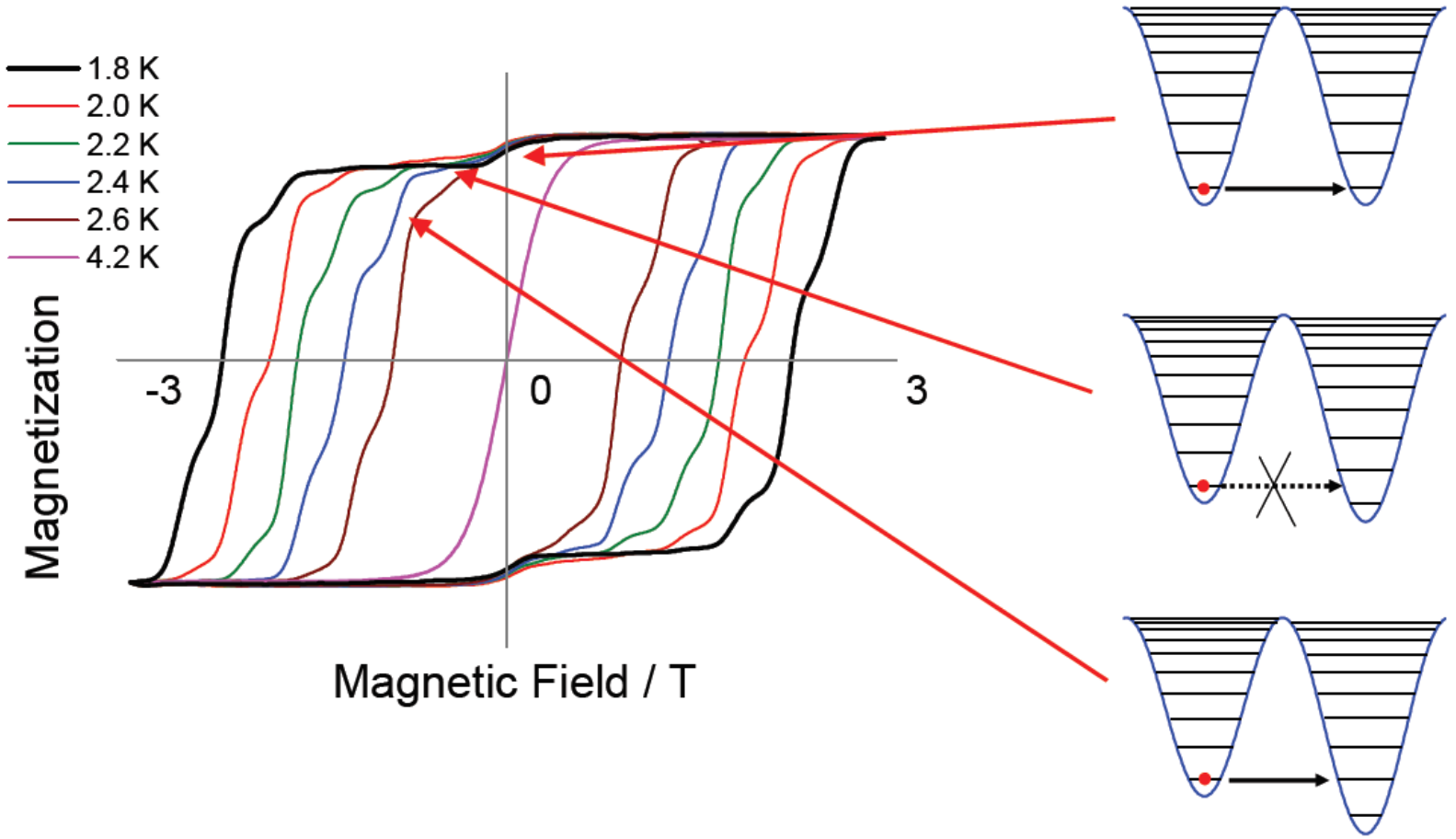
$$\tau^{-1} = \underbrace{\frac{B_1}{1 + B_2 H^2}}_{\text{QTM}} + \underbrace{A \cdot H^4 \cdot T}_{\text{Direct}} + \underbrace{C \cdot T^n}_{\text{Raman}} + \underbrace{\frac{1}{\tau_0} \cdot e^{-\frac{U_{eff}}{k_B T}}}_{\text{Orbach}}$$

field dependent | temperature dependent



Hysteresis in SMMs

- Finite hysteresis below blocking temperature

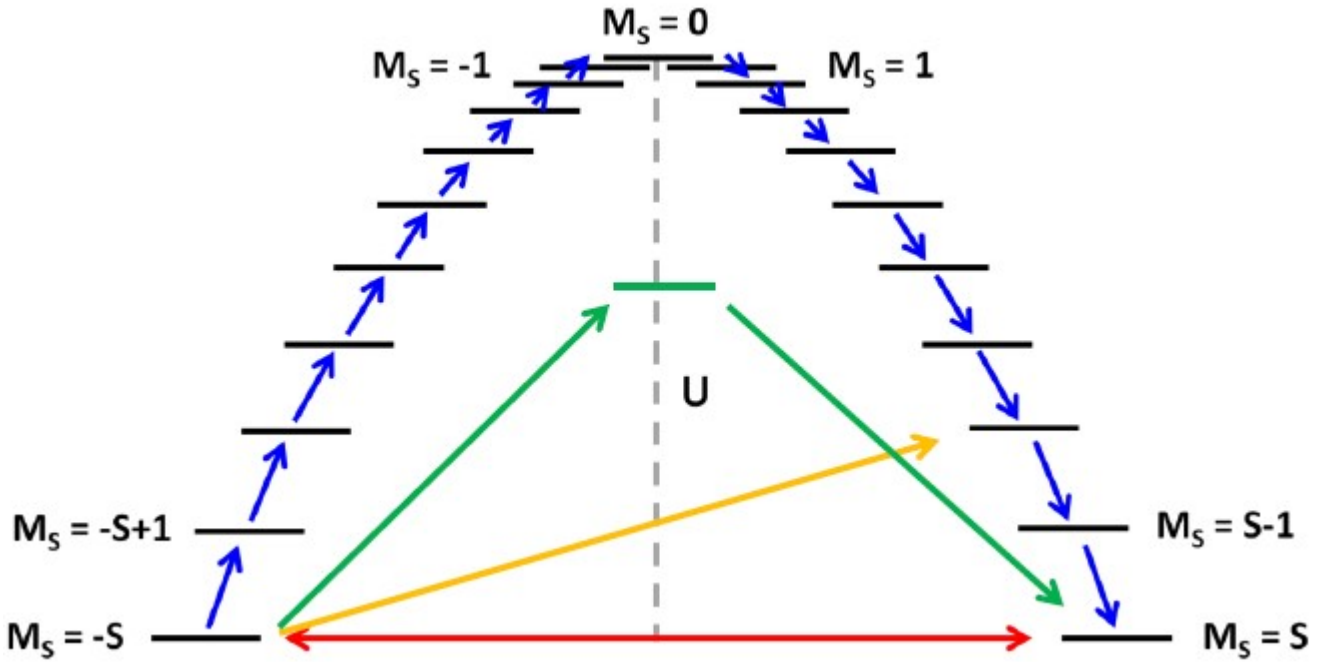


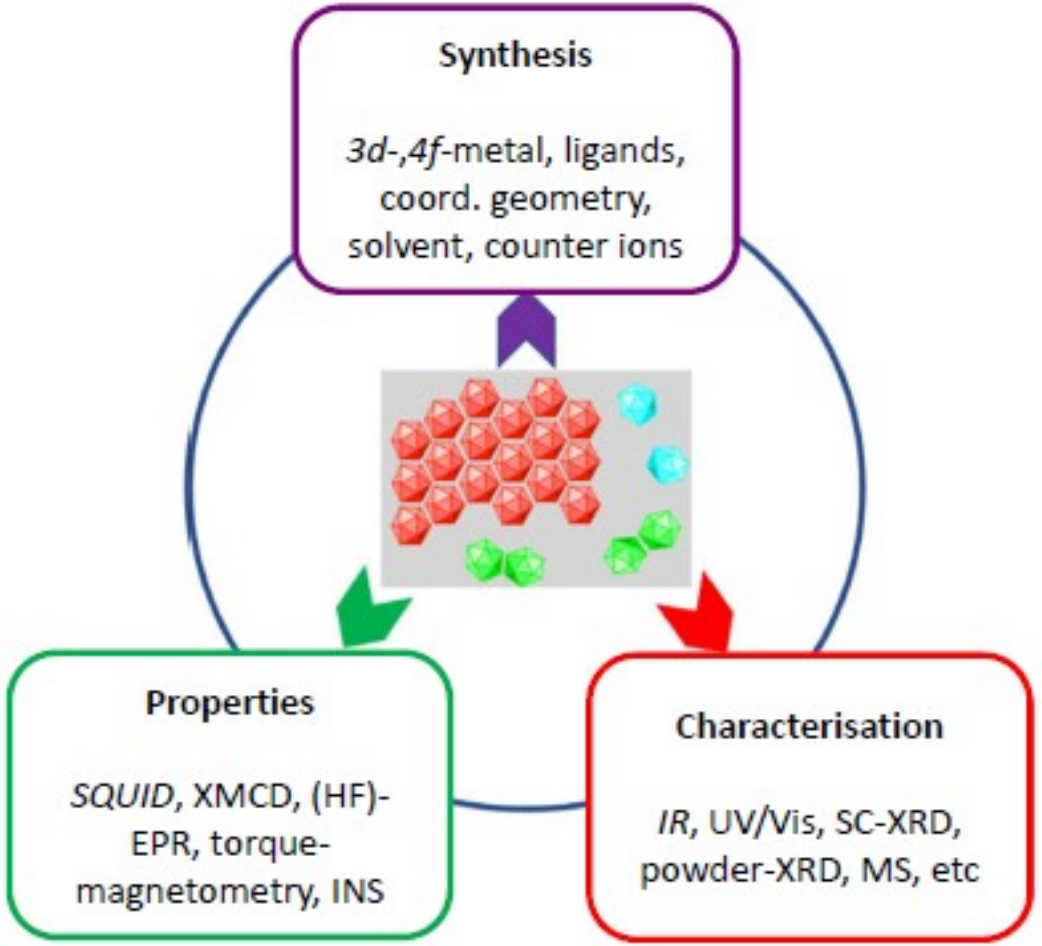
Relaxation pathways

$$\tau^{-1} = \frac{B_1}{1 + B_2 H^2} + A \cdot H^4 \cdot T + C \cdot T^n + \frac{1}{\tau_0} \cdot e^{-\frac{U_{eff}}{k_B T}}$$

QTM | Direct | Raman | Orbach

field dependent | temperature dependent



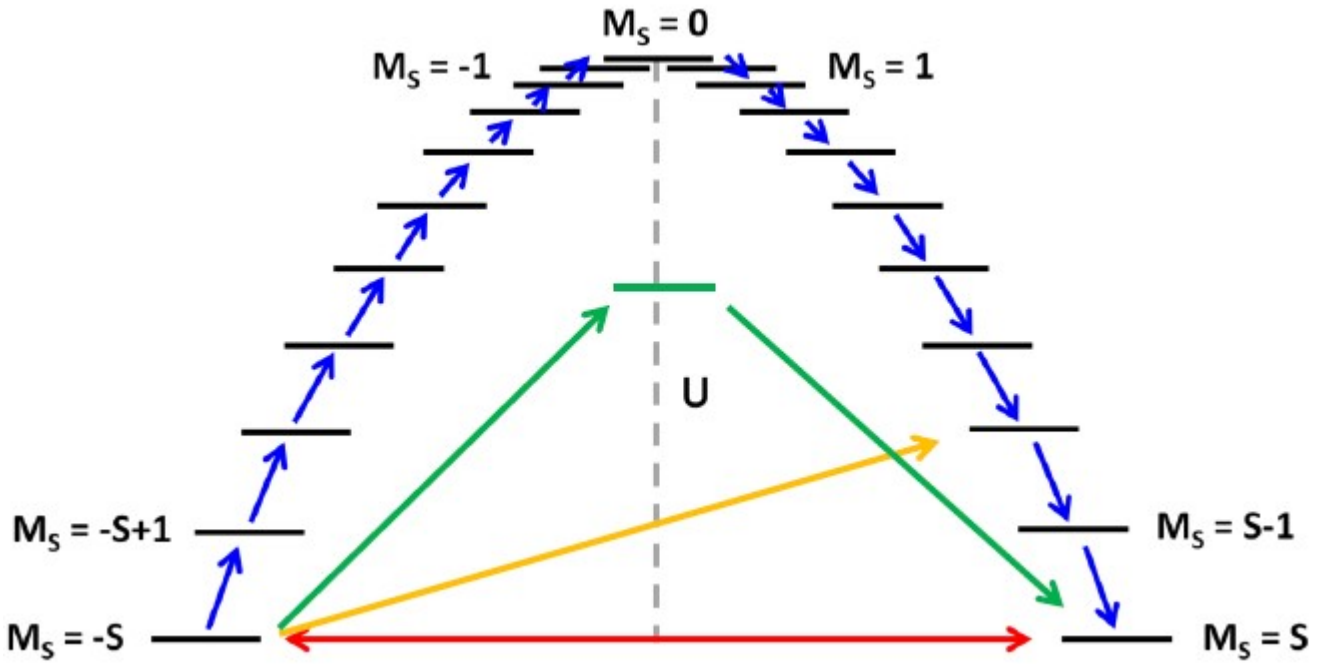


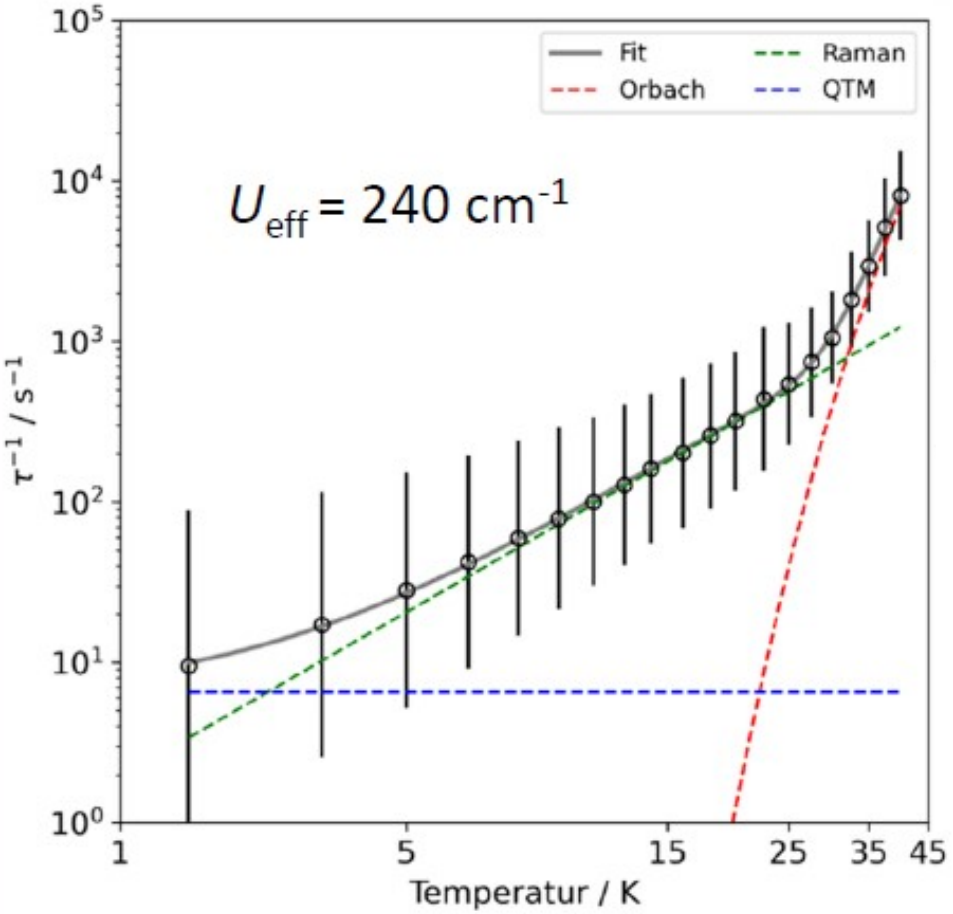
G. Gabarró-Riera, G. Aromí, E. . Sañudo, *Coord. Chem. Reviews*; 2023, *475*, 214858

Relaxation pathways

$$\tau^{-1} = \underbrace{\frac{B_1}{1+B_2H^2}}_{\text{QTM}} + \underbrace{A \cdot H^4 \cdot T}_{\text{Direct}} + \underbrace{C \cdot T^n}_{\text{Raman}} + \underbrace{\frac{1}{\tau_0} \cdot e^{-\frac{U_{eff}}{k_B T}}}_{\text{Orbach}}$$

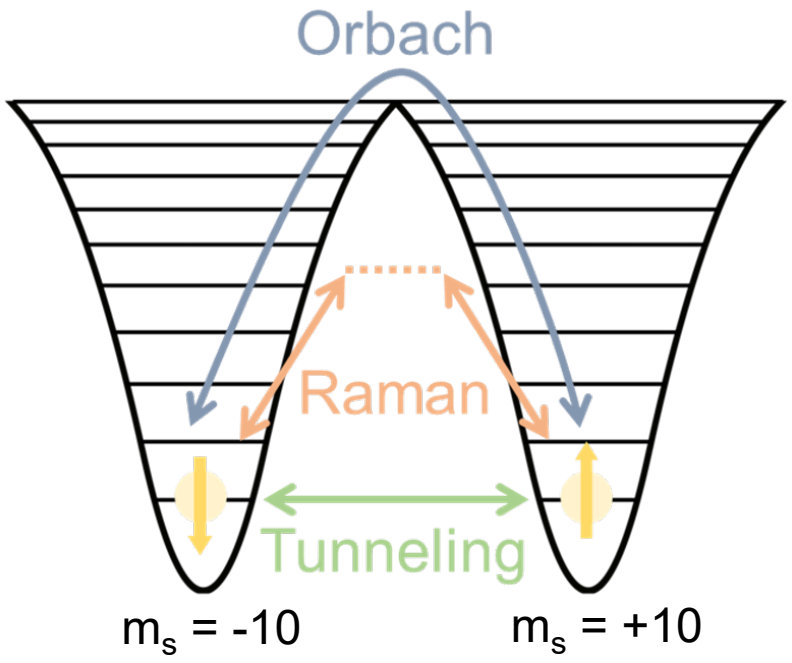
field dependent | temperature dependent



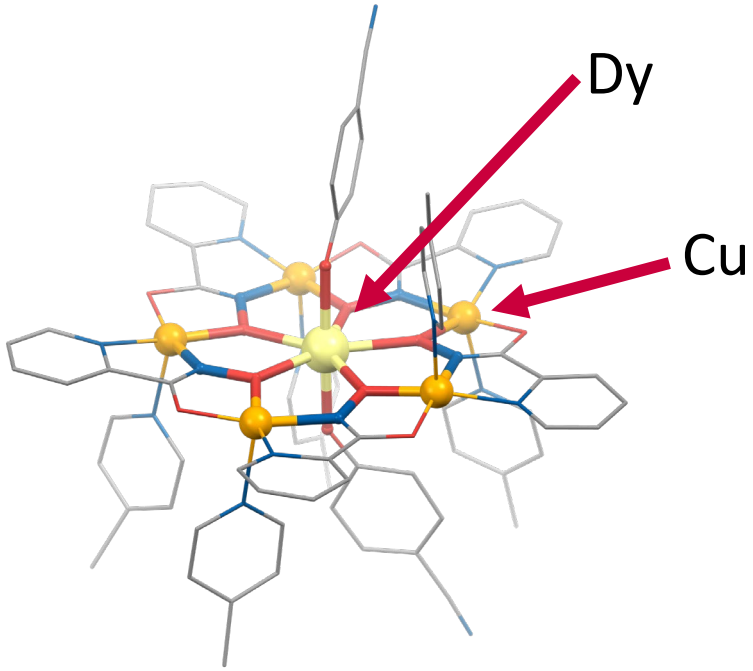


Metallacrown SMMs

- Magnetic core with a shell of ligands
- Magnetic hysteresis below blocking temperature
- No long-range magnetic ordering necessary
- Blocking temperature ~ 40 K



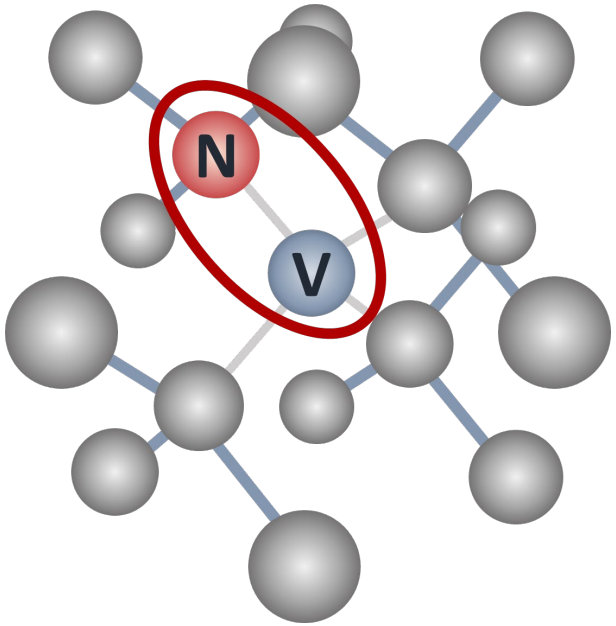
Shi-$DyCu_5$-CNP



[$Dy(4\text{-Picolin})_5$[15-$MC_{Cu(II)N(PicHA)}$-5](4-Cyanophenol)^2]OTf

Can we probe the (quantum) magnetic fluctuations in SMMs directly?

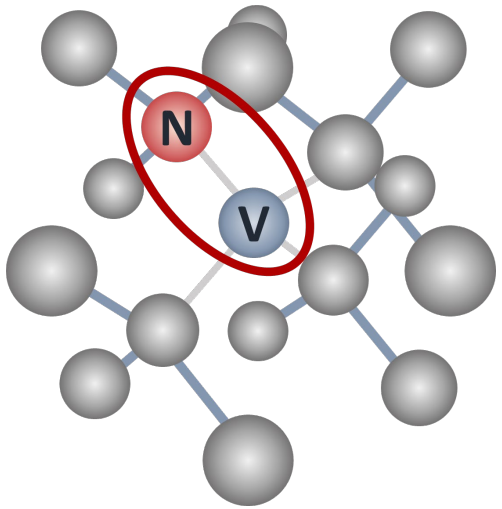
Chakraborty, A. *et al.*, Eur. J. Inorg. Chem., 1180-1200 (2019)

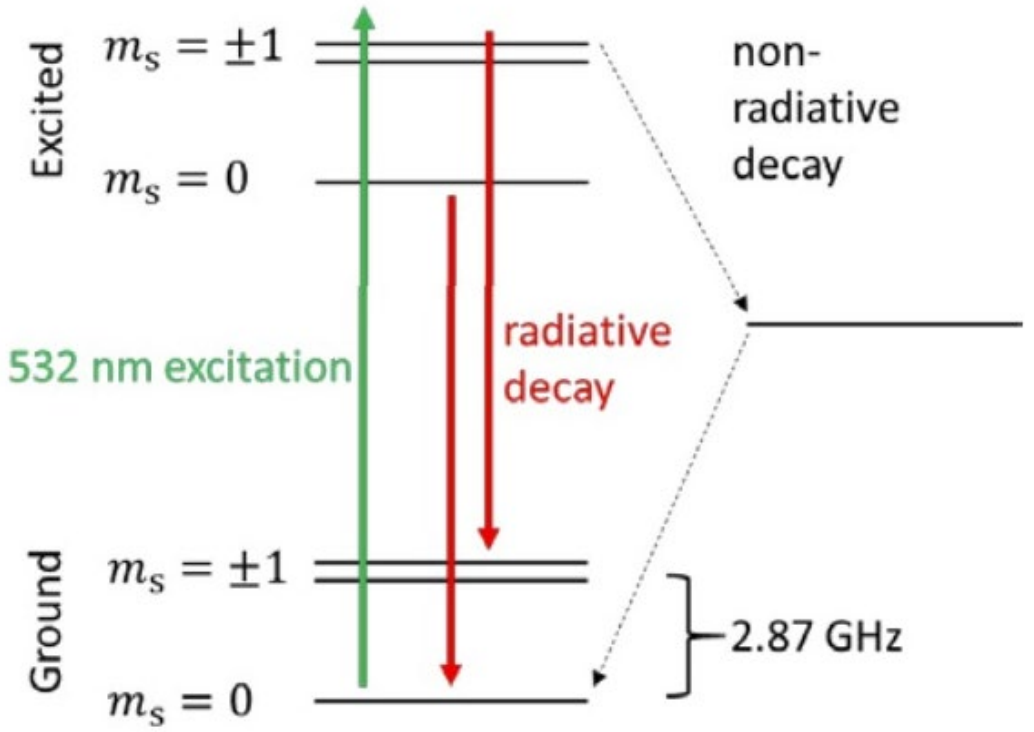


Nitrogen-vacancy center magnetometry

Nitrogen-vacancy centers

- Photoluminescent point defect/ color center in diamond (NV^-)
- Triplet ground state





Nitrogen-vacancy centers

- Photoluminescent point defect/ color center in diamond
- Triplet ground state
- Hamiltonian:

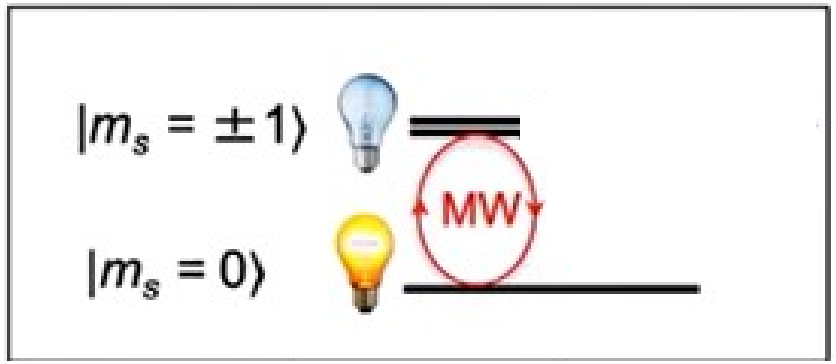
$$\hat{H} = \overbrace{\hbar D\left[\hat{S}_Z^2 - \frac{2}{3}\right] + \hbar E(\hat{S}_X^2 - \hat{S}_Y^2)}^{\text{zero-field term}} + \overbrace{\hbar\gamma_{nv}\vec{B}\cdot\hat{\vec{S}}}^{\text{magnetic interaction}} + \overbrace{\hbar\delta_{\parallel}\mathcal{E}_Z\left[\hat{S}_Z^2 - \frac{2}{3}\right] - \hbar\delta_{\perp}\left[\mathcal{E}_X(\hat{S}_X\hat{S}_Y + \hat{S}_Y\hat{S}_X) + \mathcal{E}_Y(\hat{S}_X^2 - \hat{S}_Y^2)\right]}^{\text{electric interaction}}$$

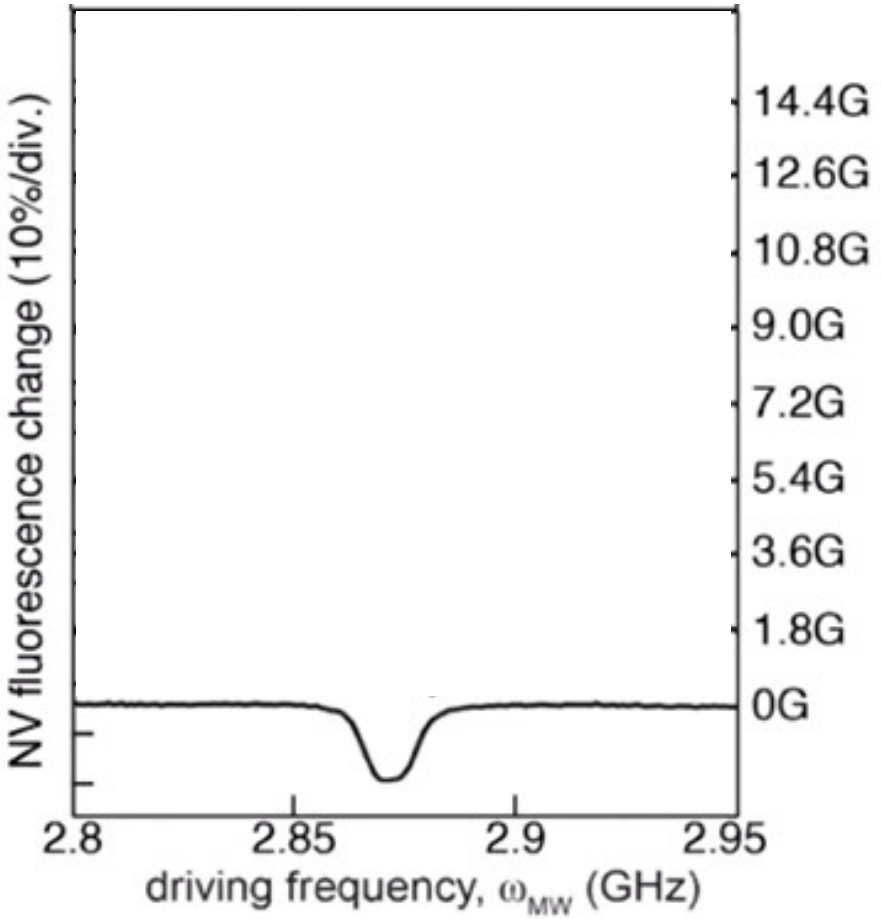
$$+\hbar\sum_{i=1}^{n}\left(\underbrace{\hat{\vec{S}}\mathcal{N}_i\hat{\vec{I}}_i}_{\text{hyperfine interaction}} + \underbrace{\gamma_i\vec{B}\cdot\hat{\vec{I}}_i}_{\text{nuclear Zeeman interaction}} + \underbrace{Q_i\hat{I}_{Z,i}^2}_{\text{nuclear quadrupole interaction}}\right)$$

NV magnetometry

- Optical initialization
- Continuous microwave drive
- Magnetometry via Zeeman splitting:

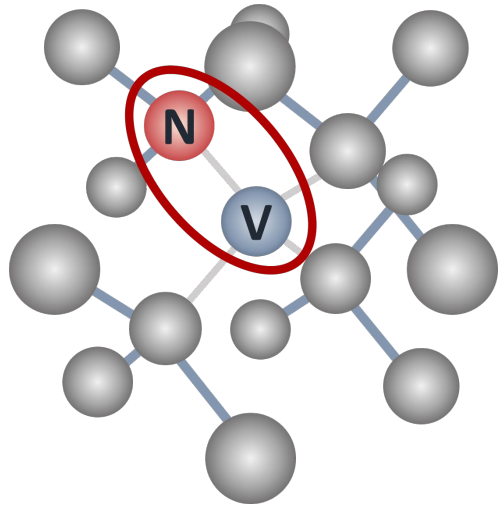
Rondin, Rep. Prog. Phys. (2014)





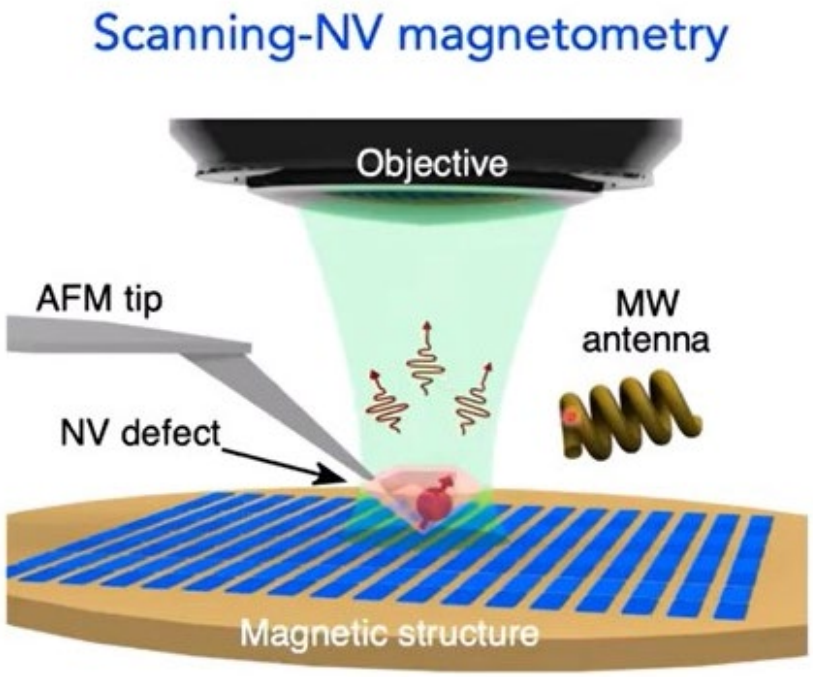
NV magnetometry

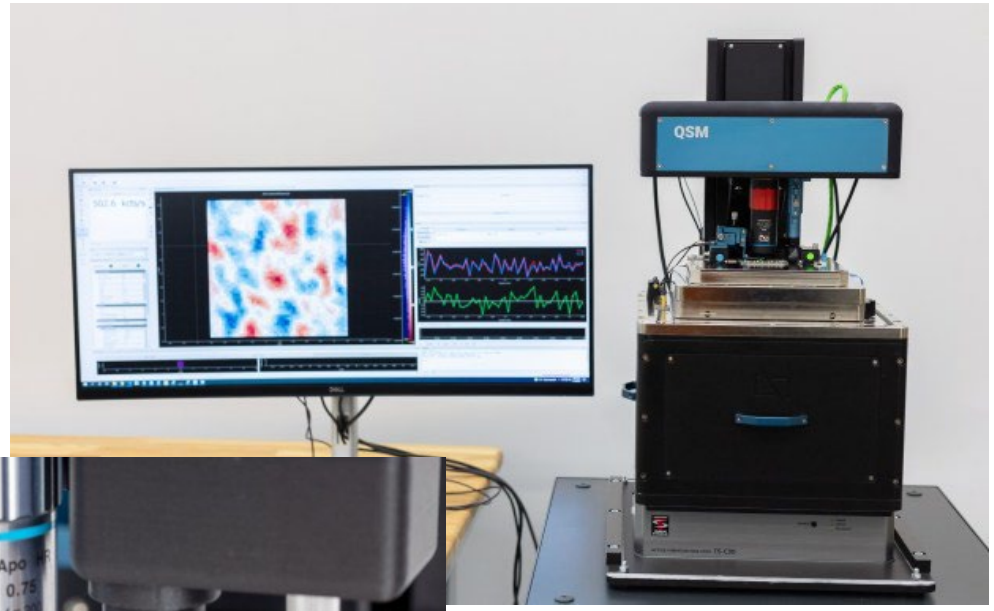
- Sensitive technique for quantitative measurement of magnetic fields along the NV axis
- Operational in a wide temperature and magnetic field range
- No magnetic backaction

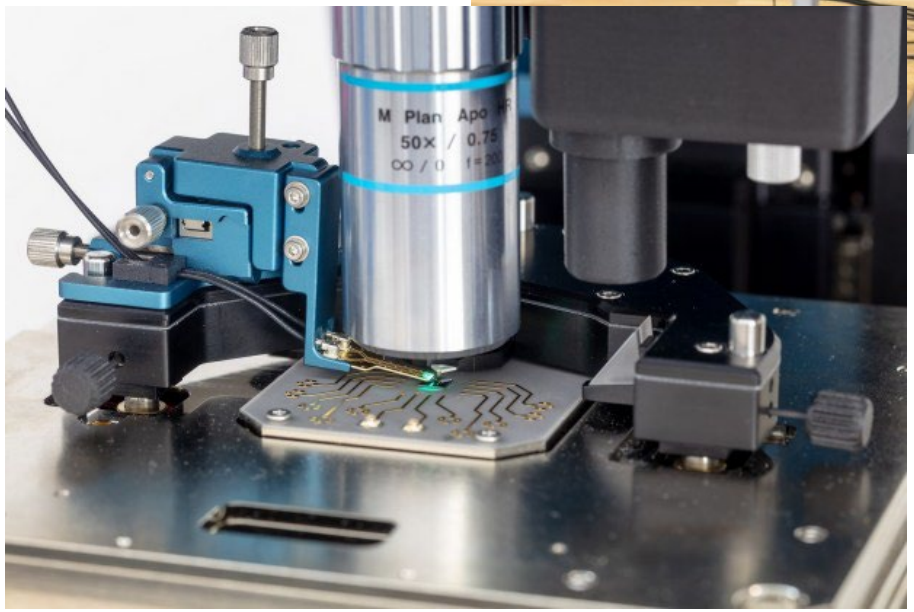


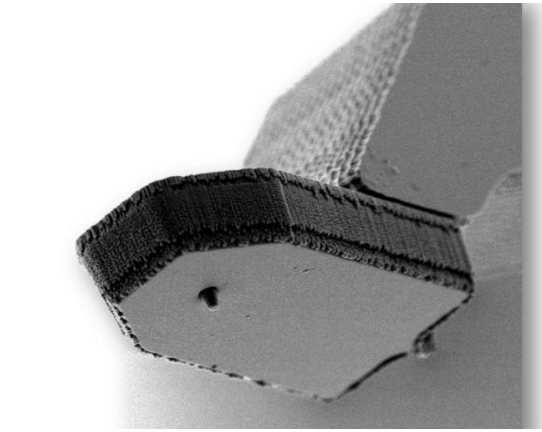
Scanning NV magnetometry

- Single NV center on tip of AFM cantilever
- Spatial resolution limited by implantation depth of the NV center





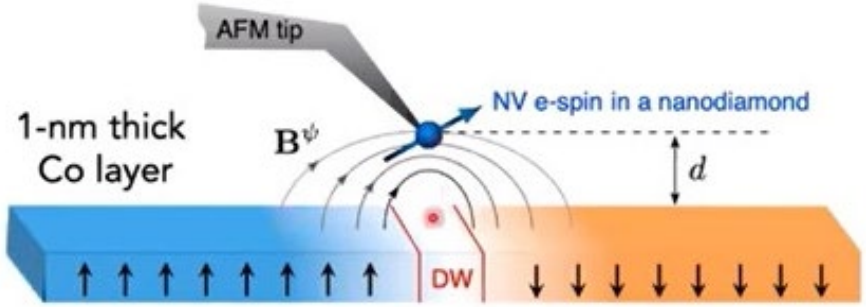


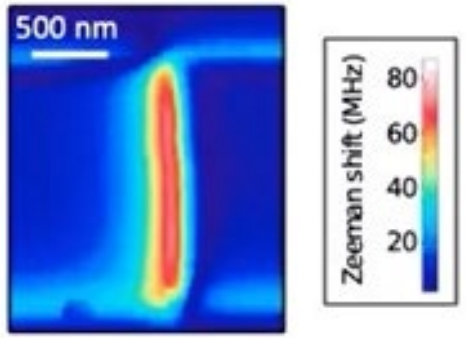


https://www.youtube.com/watch?v=KvENASIEnU4&ab_channel=petaspin

Scanning NV magnetometry

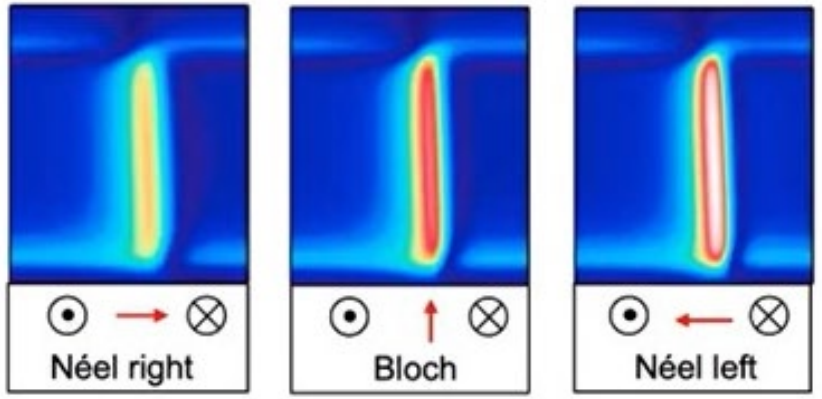
- Example: Imaging a domain wall





Tetienne, *Nat. Com.* (2015)
Gross, PRB (2016)

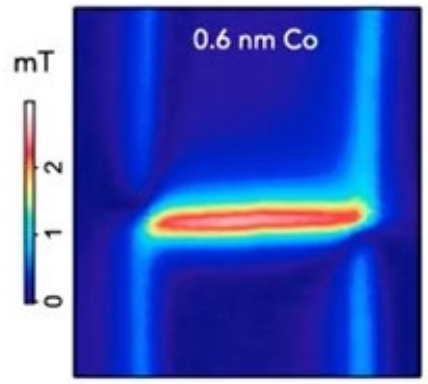
Comparison with theoretical predictions



Scanning NV magnetometry

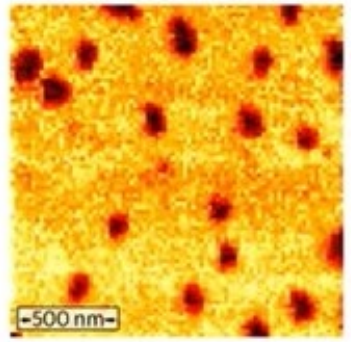
- More examples:

Chiral domain walls in thin ferromagnets



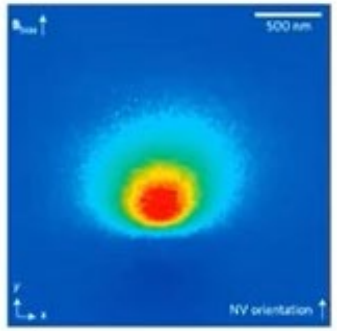
Tetienne *et al.*, *Science* (2014)
Tetienne *et al.*, *Nat. Commun.* (2015)

Magnetic skyrmions



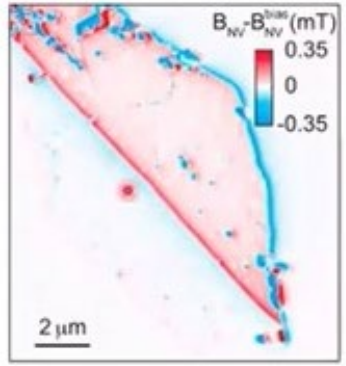
Akhtar *et al.*, *Phys. Rev. Appl.* (2019)
Rana *et al.*, *Phys. Rev. Appl.* (2020)

Superconducting vortices



Thiel *et al.*, *Nat. Nano* (2016)
Pelliccione *et al.*, *Nat. Nano* (2016)

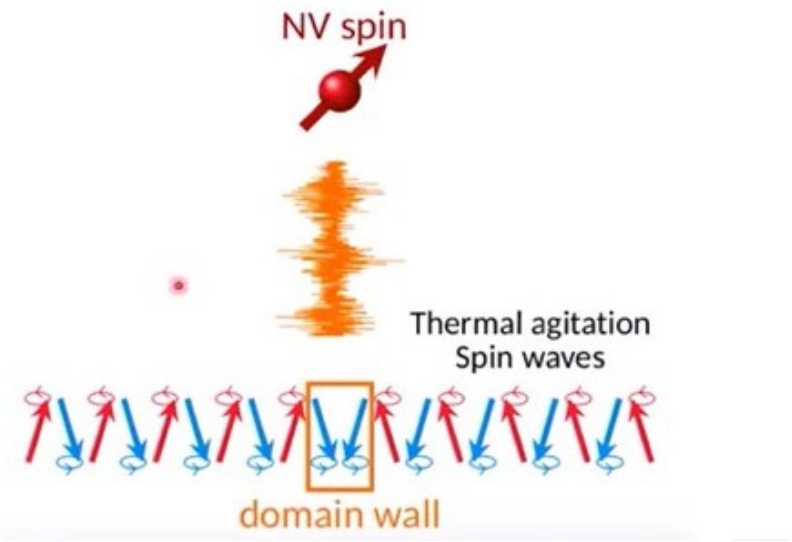
Magnetism in 2D-materials



Thiel *et al.*, *Science* (2019)

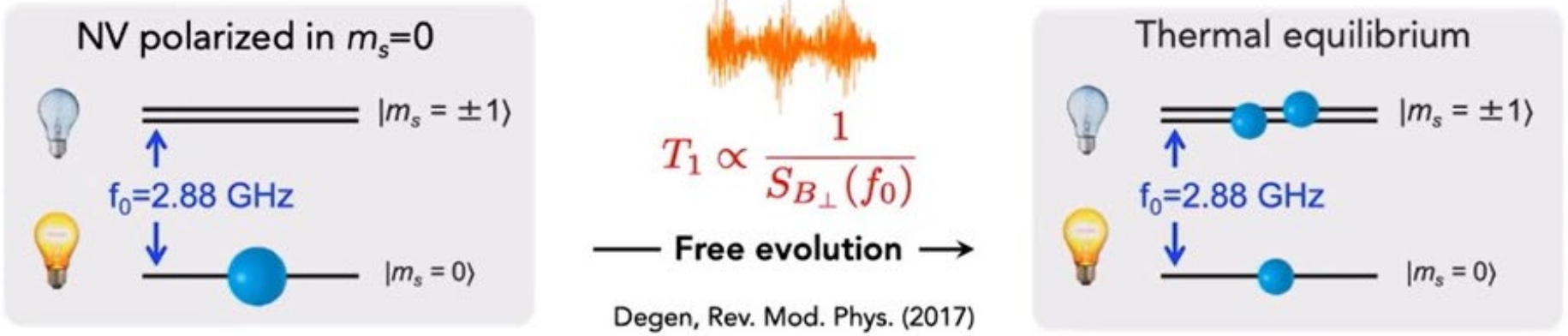
Spin relaxometry: probing noise

- NV centers can also probe AC magnetic fields via spin relaxometry
- Quantum sensor for probing magnetic noise

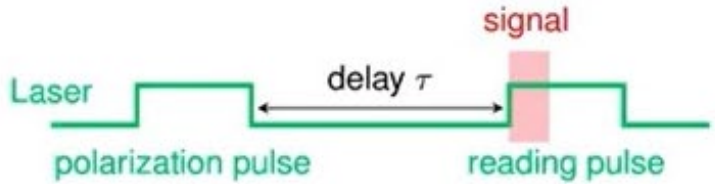


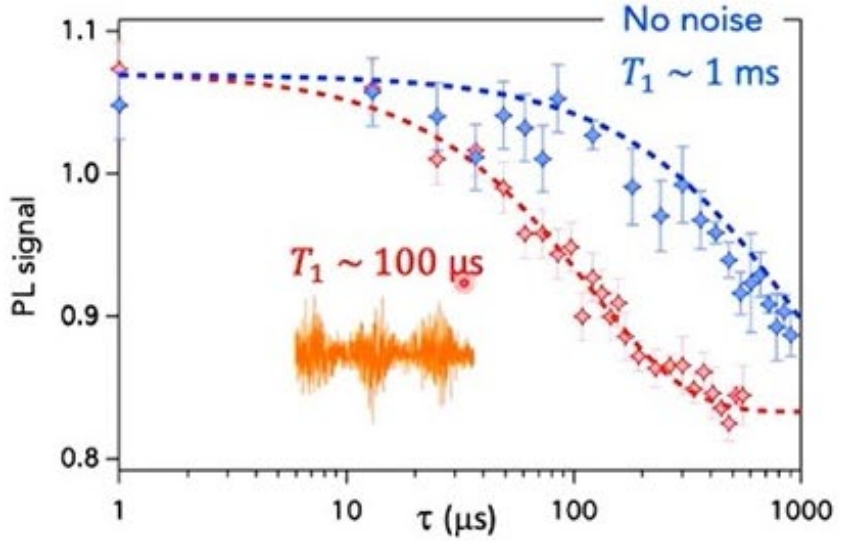
https://www.youtube.com/watch?v=KvENASIEnU4&ab_channel=petaspin

Spin relaxometry: probing noise



T_1 measurement



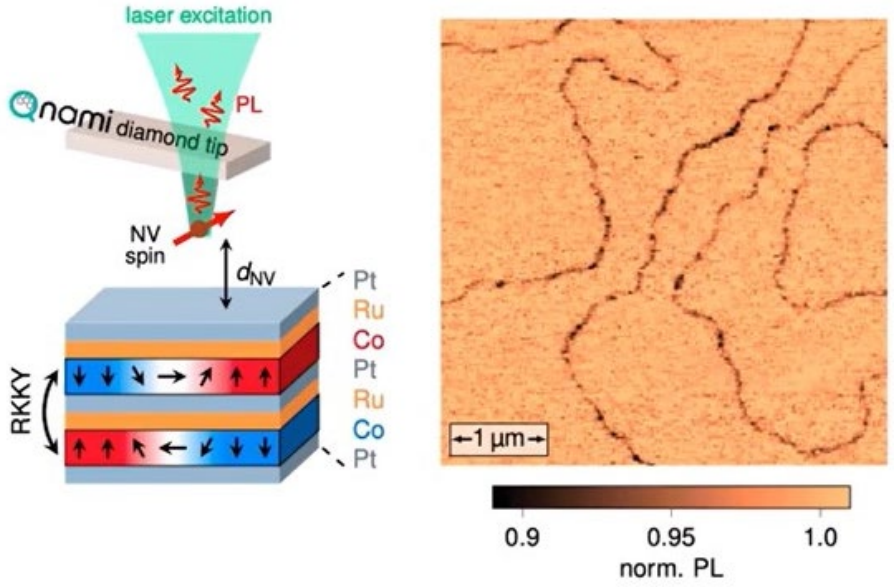


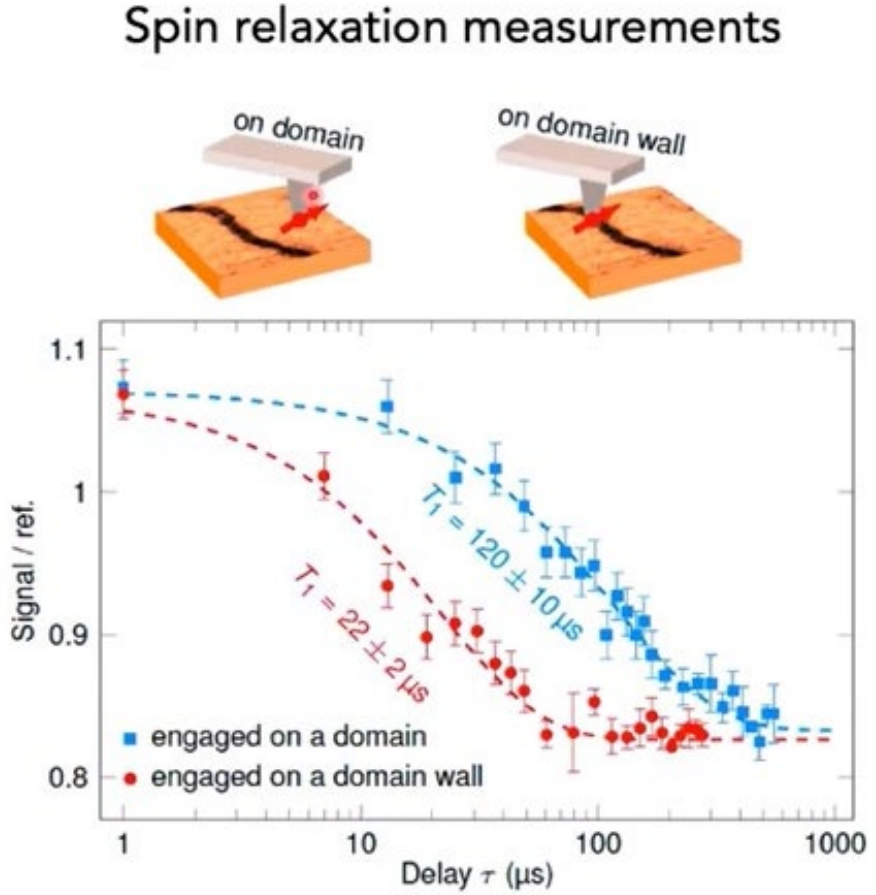
https://www.youtube.com/watch?v=KvENASIEnU4&ab_channel=petaspin

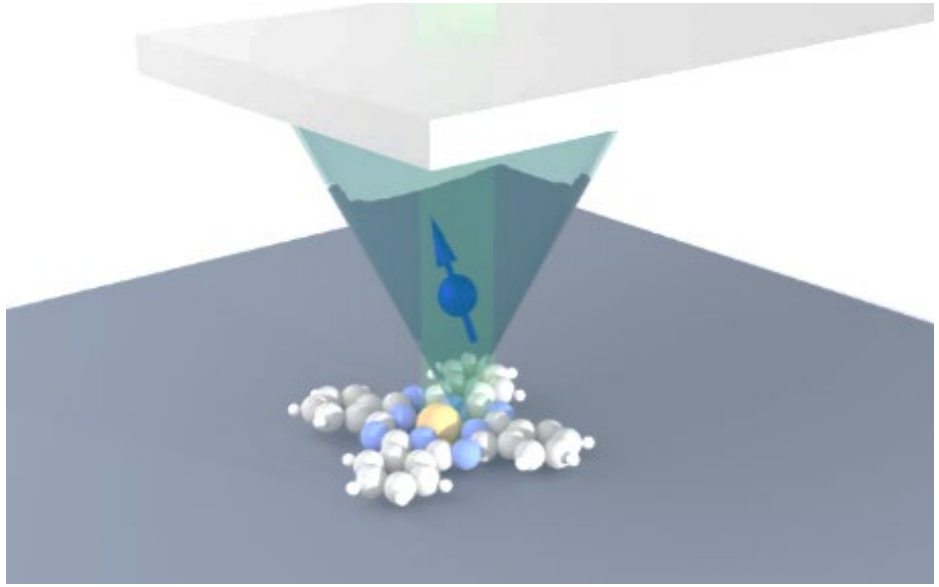
Spin relaxometry: probing noise

- Example:
  Magnetic noise at around a domain wall

Finco, Nat. Commun. **12**, 767 (2021)







Probing magnetic fluctuations in single-molecule magnets

Single Point T_1 Relaxometry

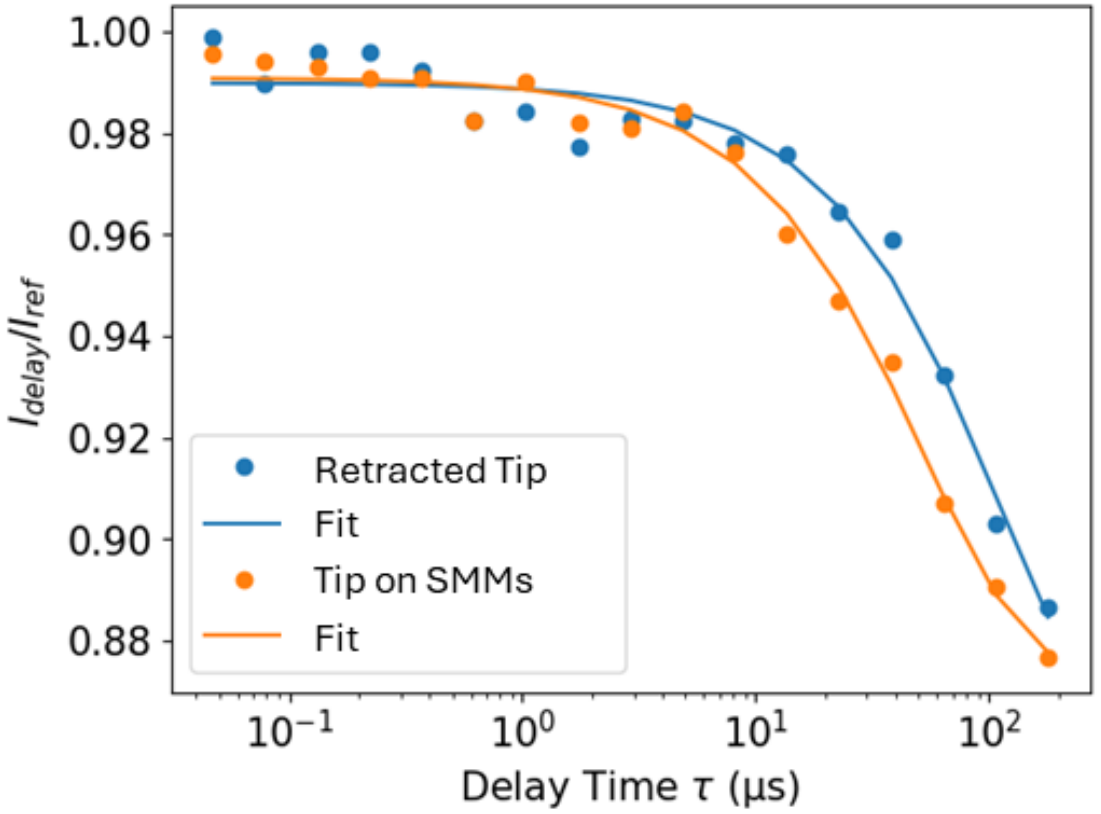
	T_1 on bare Au (µs)
Probe in contact	50.5 ± 12.2
Probe retracted	52.6 ± 13.5

- Unchanged T_1 in region with bare Au

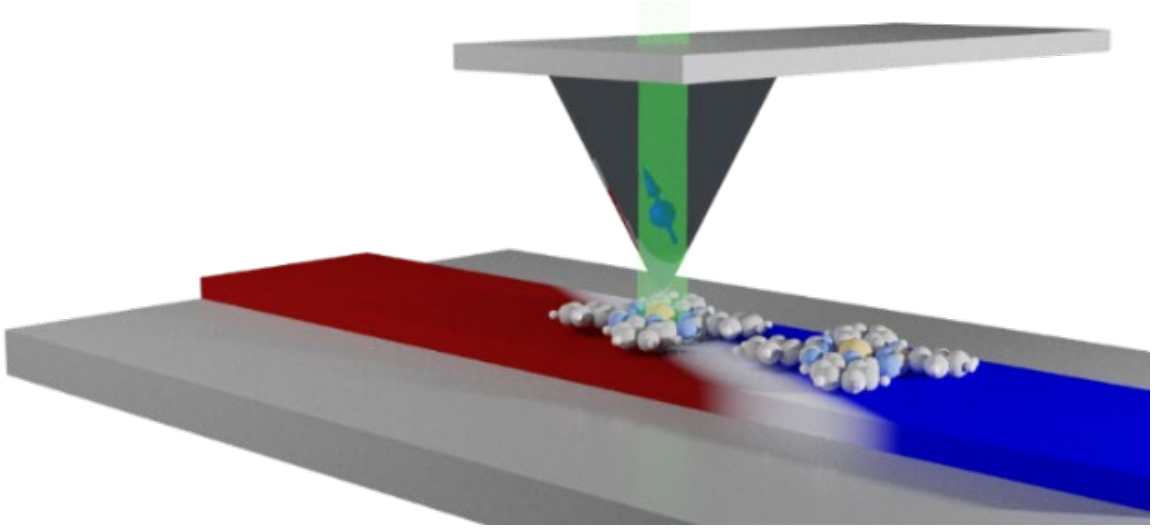
Single Point T_1 Relaxometry

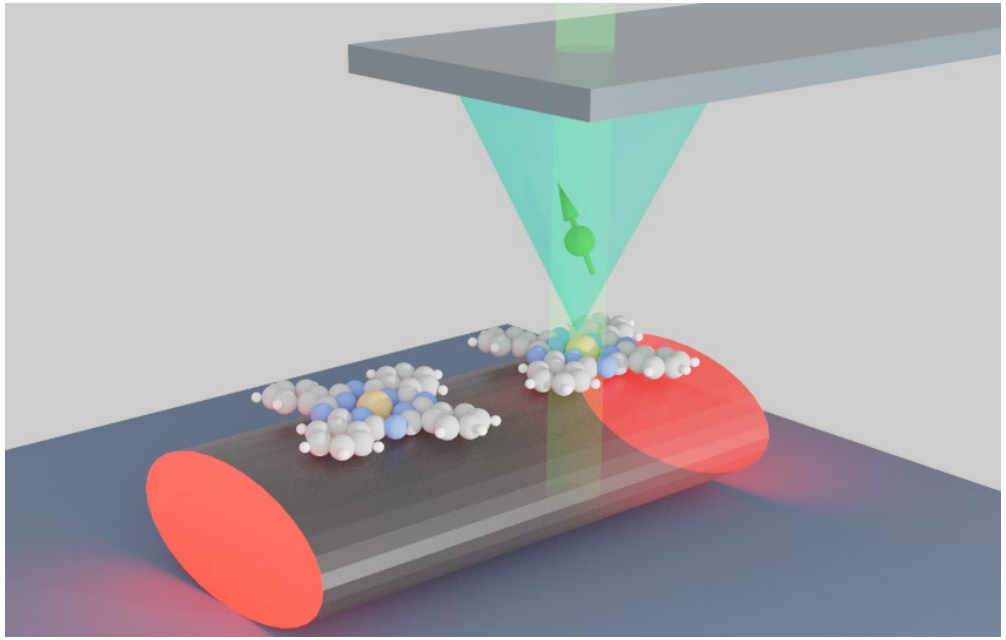
	T_1 on bare Au (µs)	T_1 on molecules (µs)
Probe in contact	50.5 ± 12.2	50.1 ± 5
Probe retracted	52.6 ± 13.5	104.5 ± 25.8

- Unchanged T_1 in region with bare Au
- Significantly reduced T_1 in region with molecules



Outlook

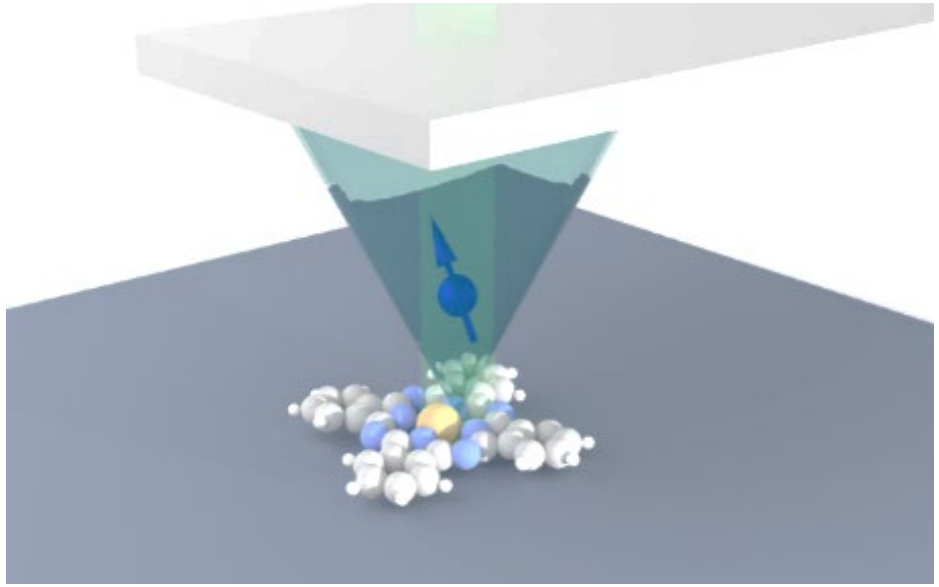




Toward quantum cooperativity in single-molecule magnets

Summary

- Molecules provide a platform for systematic studies of **structure property relations** of spin phenomena
- Single-molecule magnets are **mesoscopic systems** exhibiting both quantum and classical properties
- Nitrogen-vacancy center magnetometry is a powerful technique for **probing DC and AC magnetic fields**
- **Quantum fluctuations** in SMMs can be probed via **spin relaxometry** in NV centers



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DFG

Carl Zeiss Stiftung

Summary

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