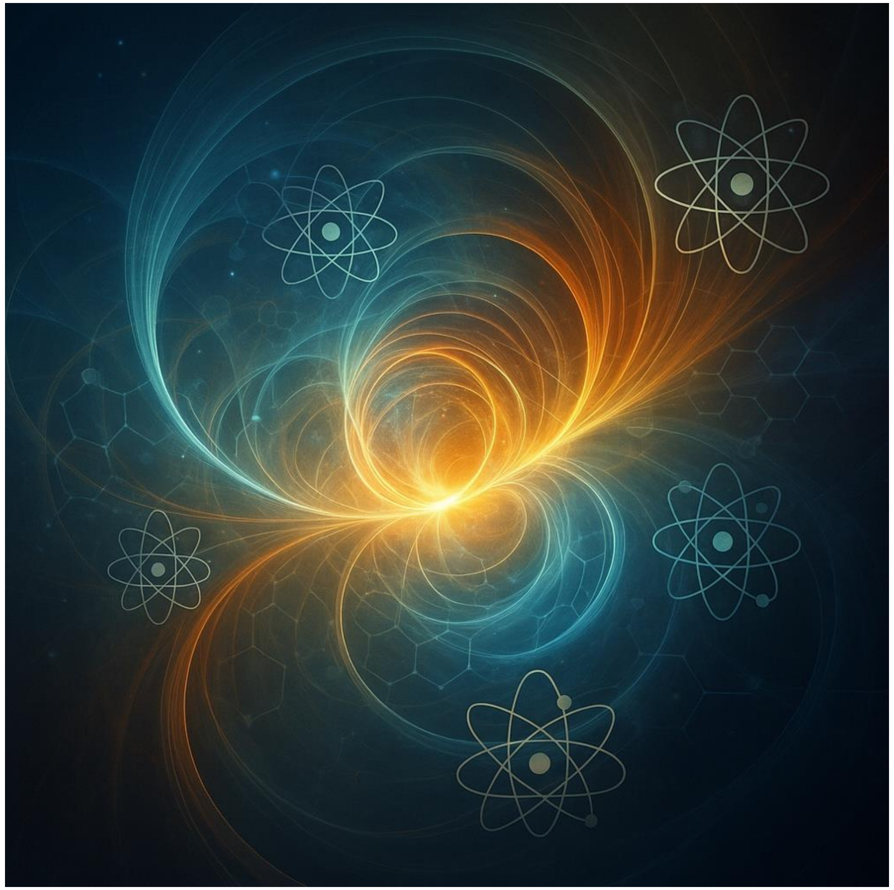
ΧΗΜΕΙΑ
ΠΑΝΕΠΙΣΤΗΜΙΟ ΠΑΤΡΩΝ
UNIVERSITY OF PATRAS
CHEMISTRY

Single Molecule Magnets



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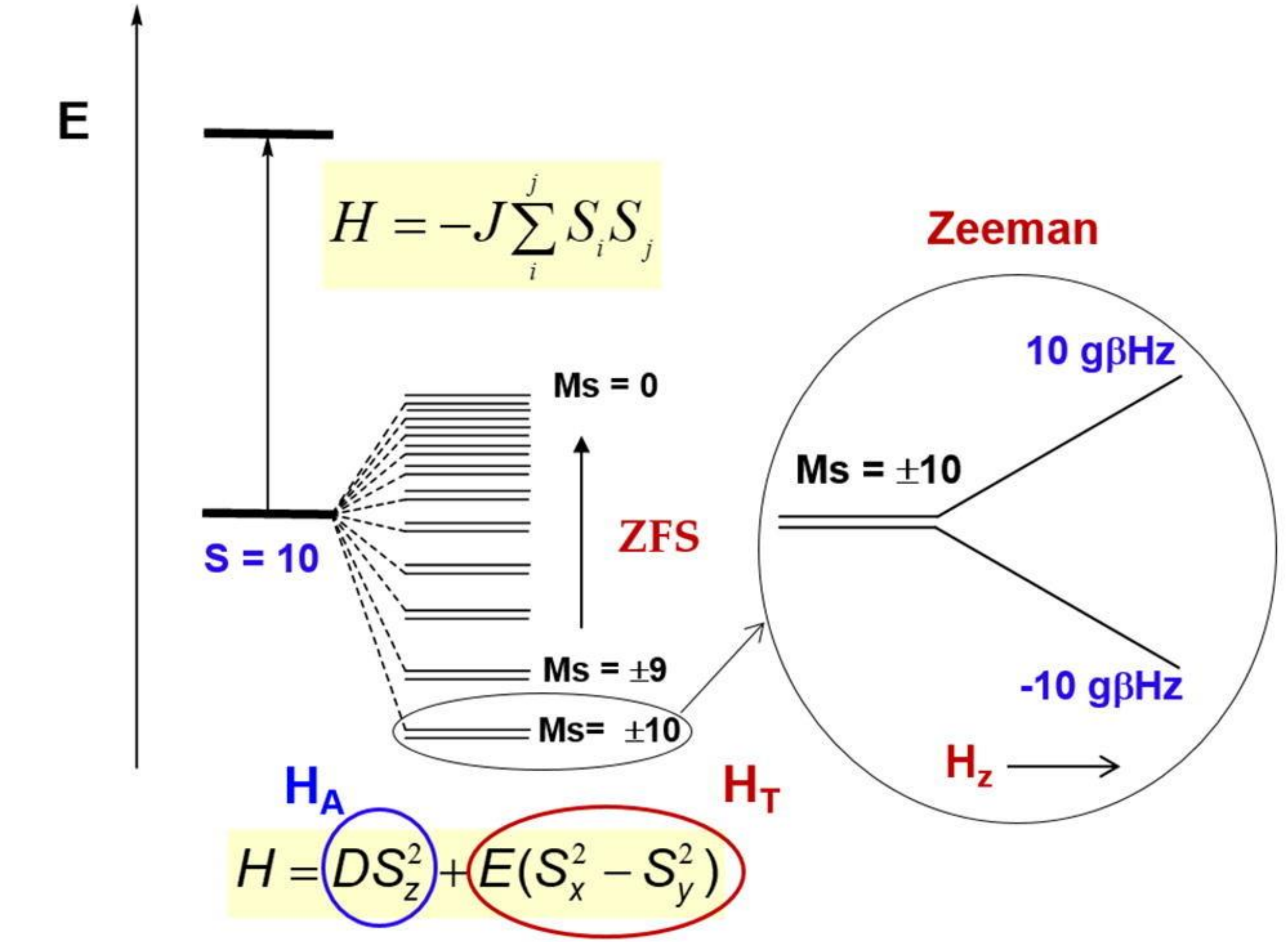
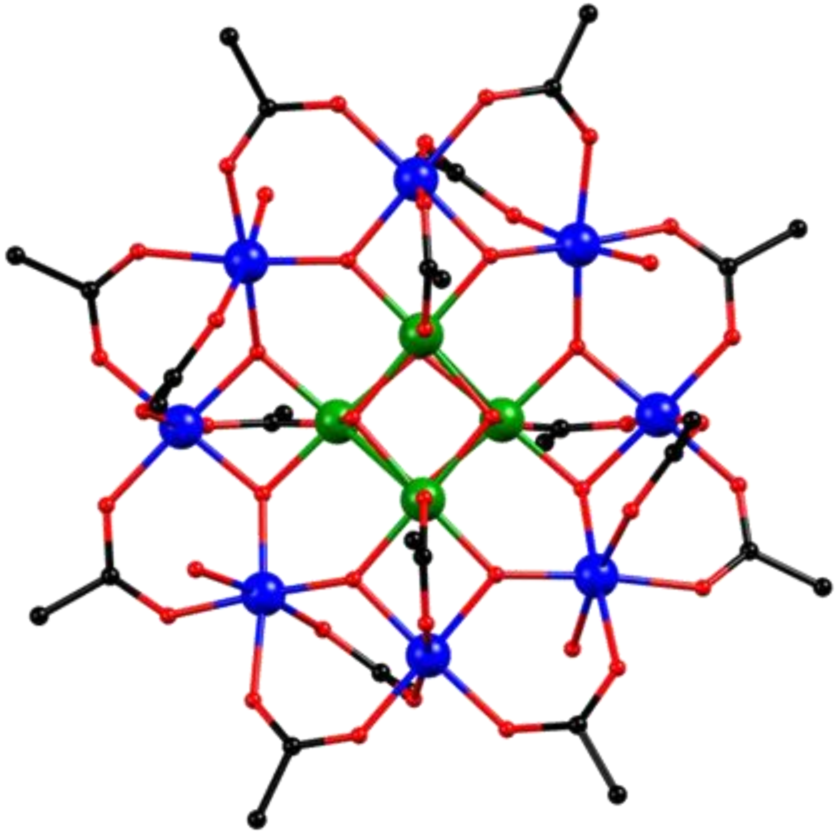
Single Molecule Magnets (SMMs)



$H_T = 0$ $$E(M_S) = D(M_S^2 - S(S+1)/3) + g\mu_B M_S Hz$$

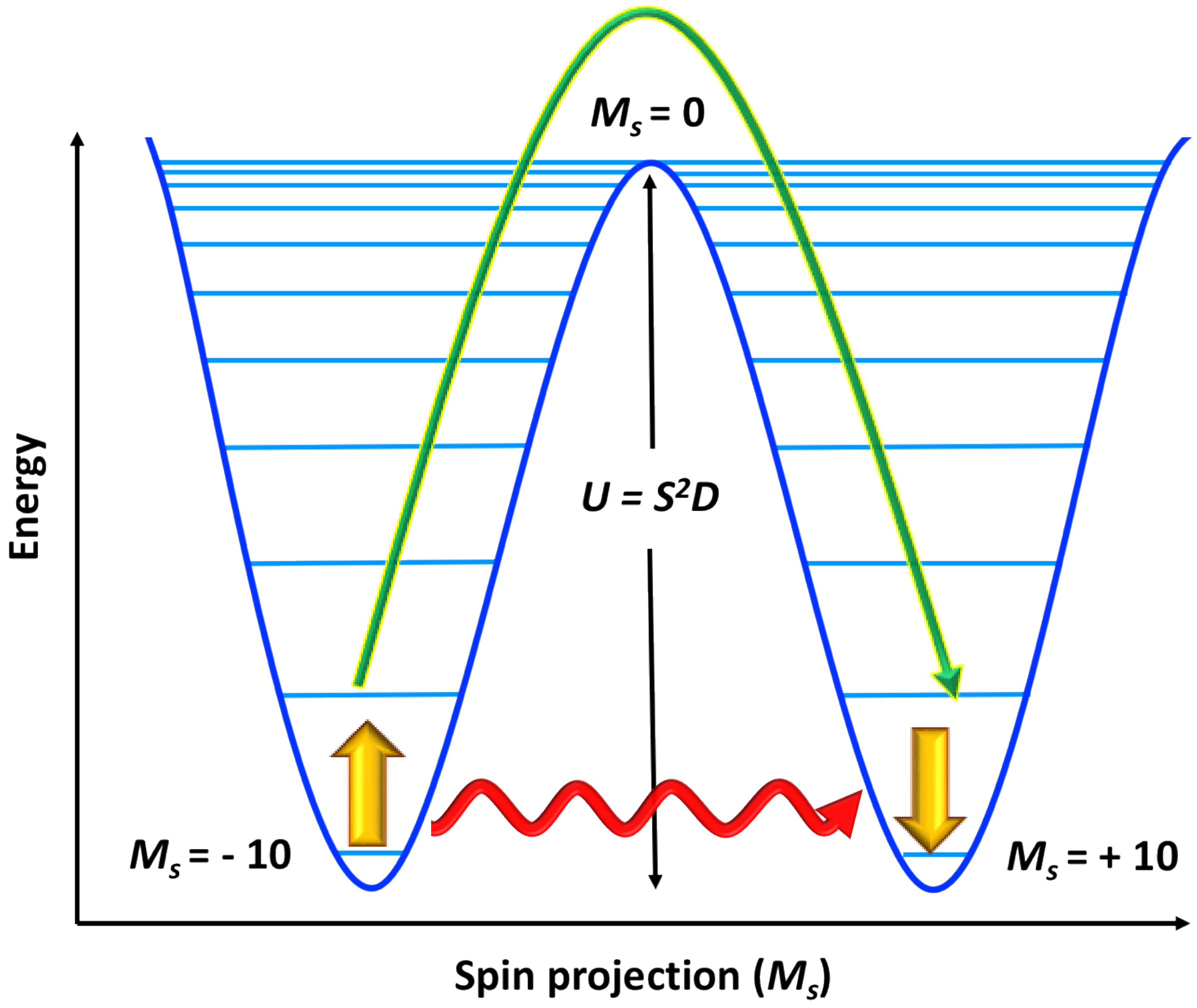
ZFS Zeeman

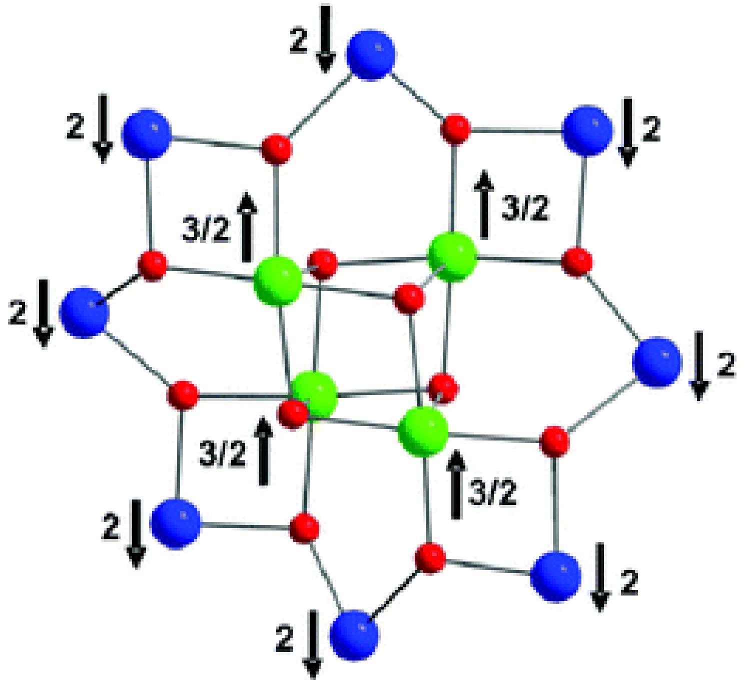


$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$

U_{eff} = 74 K

Single Molecule Magnets (SMMs)





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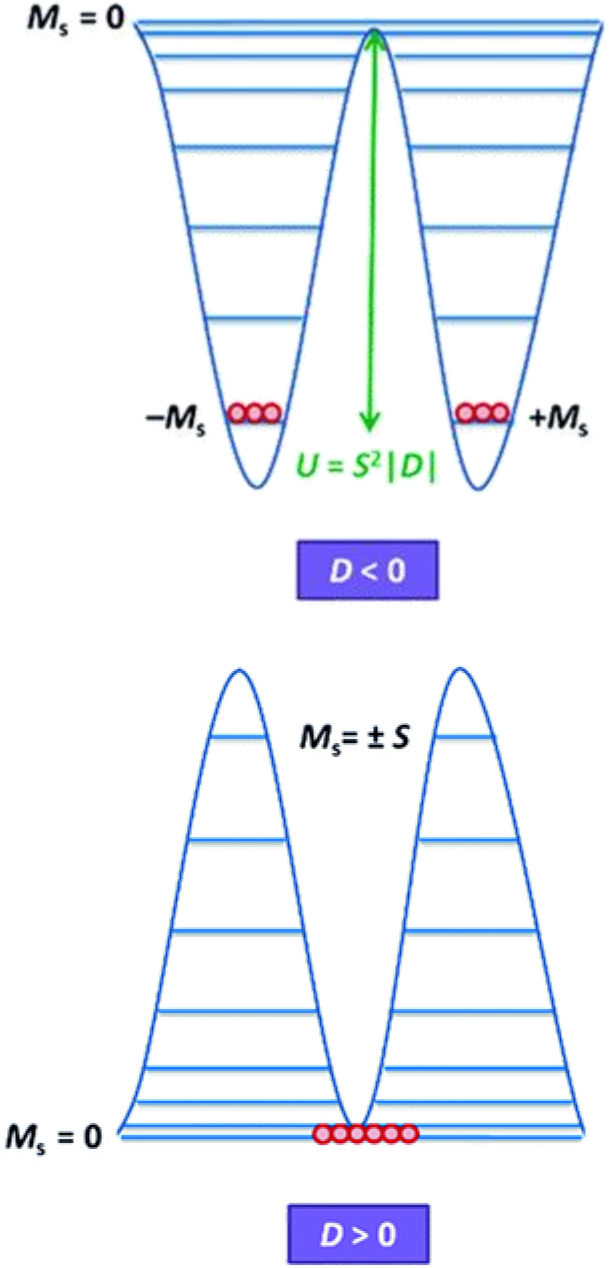
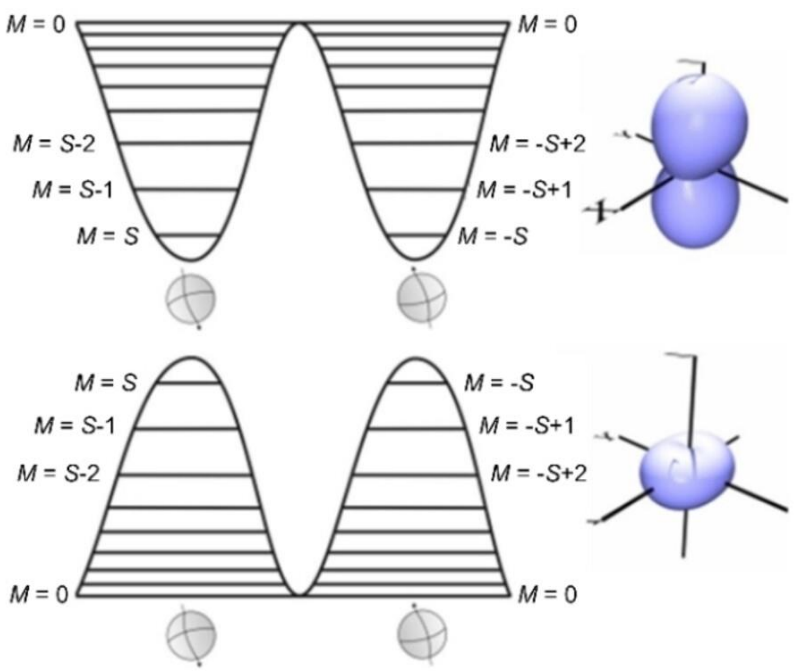
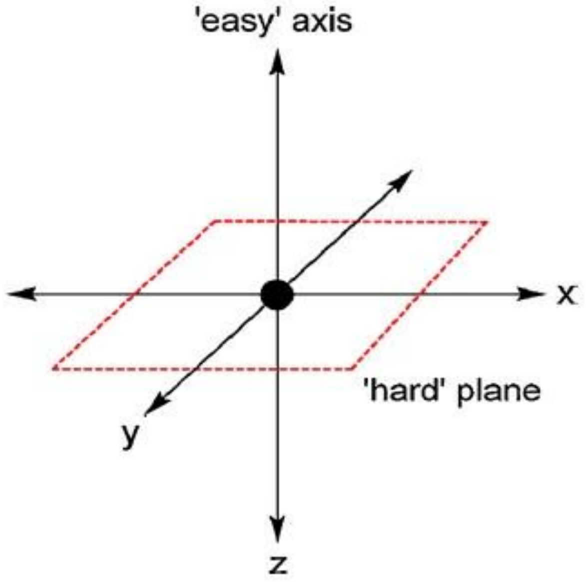
D. Gatteschi et al., *Nature*, ***1993***, *365*, 141

Single Molecule Magnets (SMMs)







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

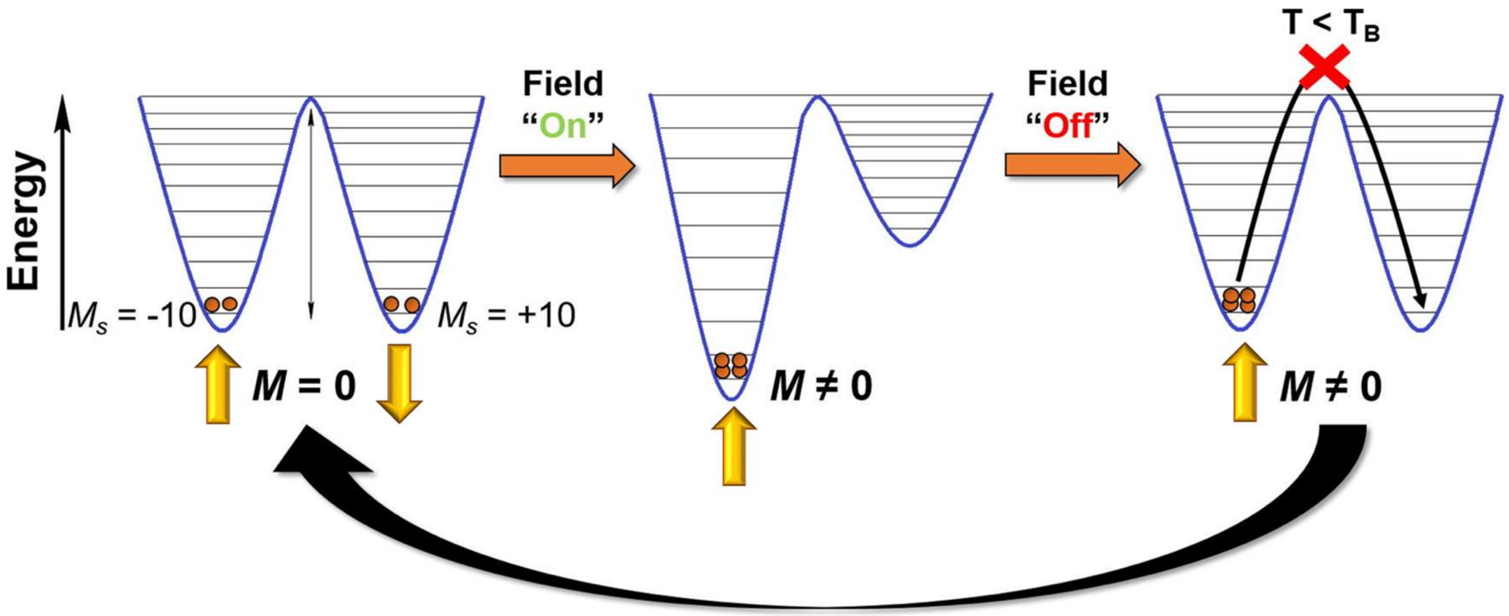
$\hat{S}_{xyz}$, Cartesian spin projection operators

D, axial anisotropy

E, rhombic or transverse parameter

M. Murugesu et al., *Chem. Sci.* **2016**, *7*, 2470

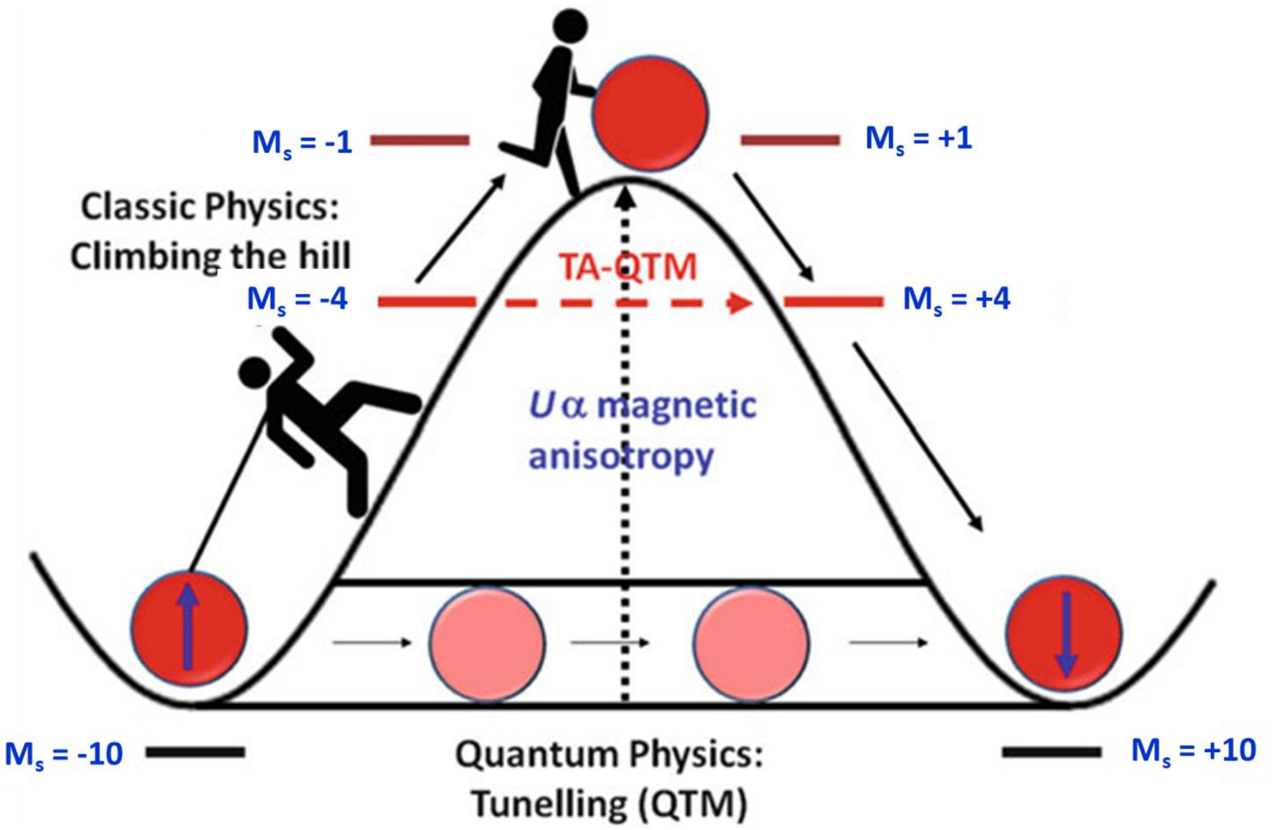
Relaxation Processes in SMMs

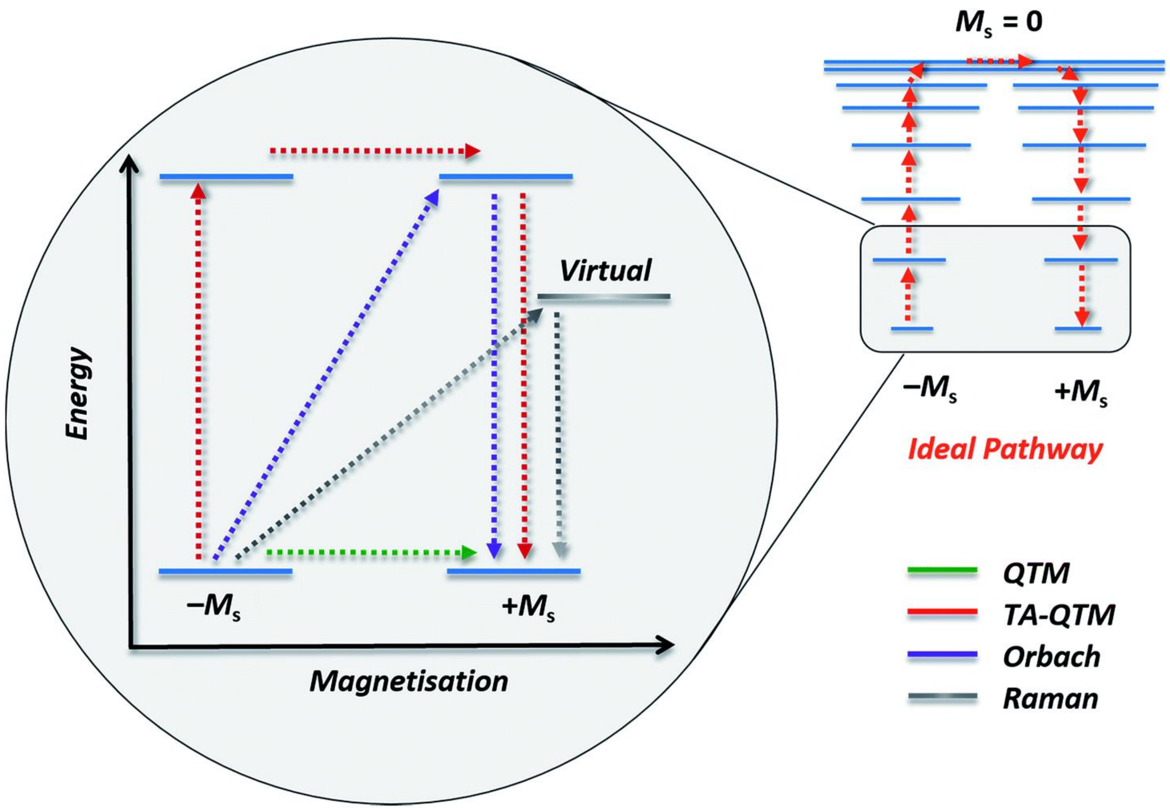


- External field OFF, M_S = ±10 sublevels own the same energy, are equally populated, the system does not present any magnetization
- External field ON, one of the M_S sublevels is stabilized, the material has magnetization, since the spin of all the molecules point out in the same direction
- External field OFF, if thermal energy, $E_T > U$, the material will tend to achieve the equilibrium between the two orientations losing magnetization
- if $E_T < U$, when $T < T_B$, the magnetization will be blocked and that is why SMMs are able to store information

Relaxation Processes in SMMs

spin-phonon coupling or due to **quantum nature** of materials



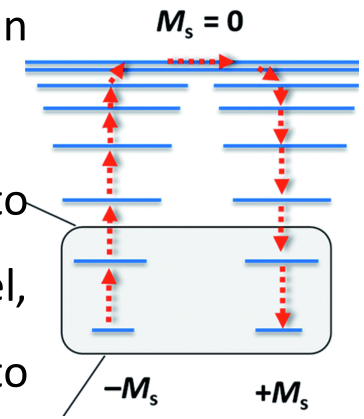


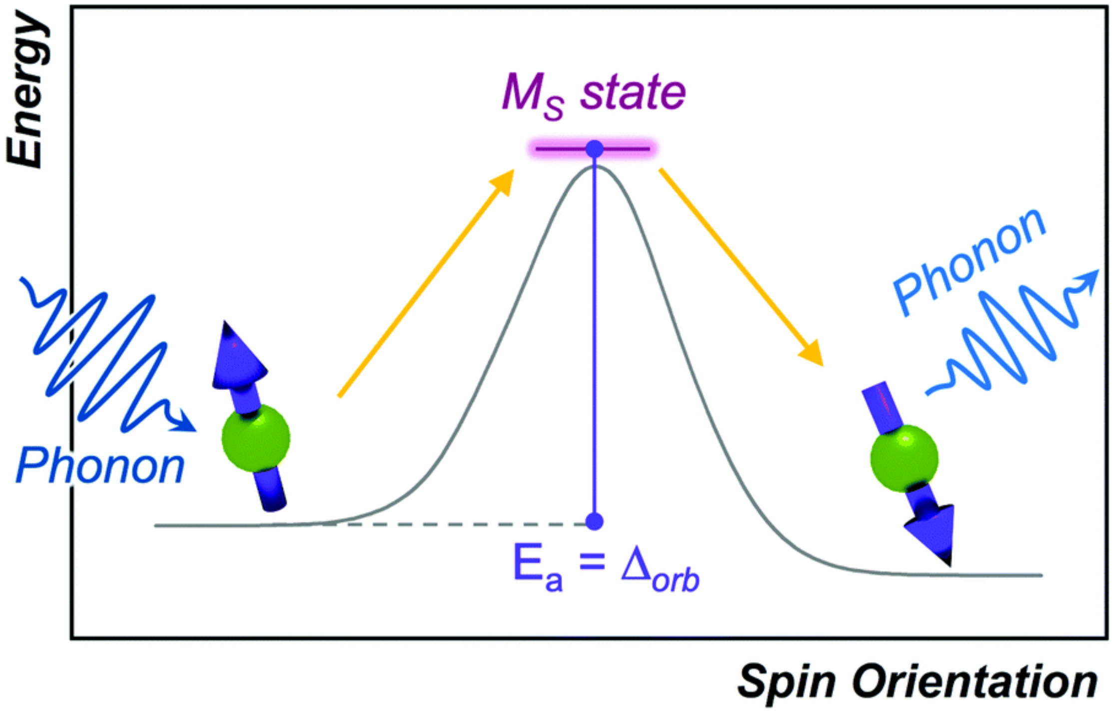
E. Colasio et al., *Coord. Chem. Rev.* **2021**, *441*, 213938.

Relaxation Processes in SMMs

Orbach Process

- **What it is:** A **thermally activated** relaxation mechanism via a **real excited state** (not virtual).
- **How it works:** The spin **absorbs phonons** to climb to an excited crystal-field/anisotropy level, then **relaxes back down** (emitting phonons) to the other side of the barrier, flipping the magnetization.
- **Energy scale:** Controlled by an effective barrier U_{eff} (energy gap to the relevant excited state/pathway).
- **When it matters:** Dominant at **higher temperatures**, when enough phonons exist to populate the excited state.





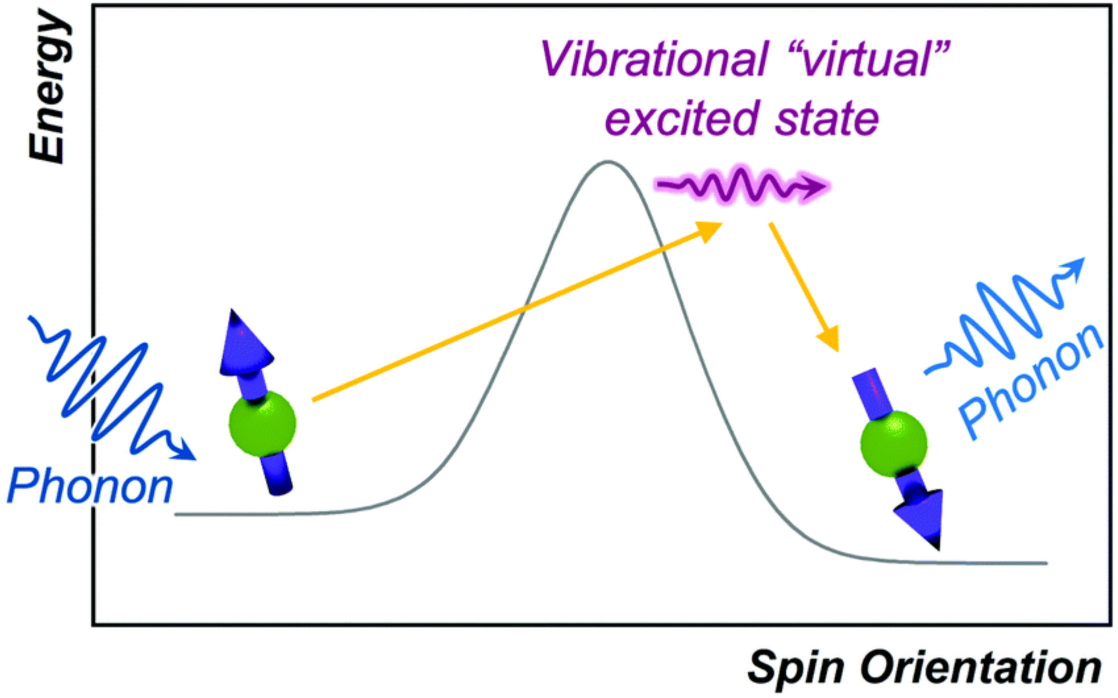
$$\tau = \tau_0 \exp\left(\frac{U_{\text{eff}}}{k_B T}\right) \qquad \ln \tau = \ln \tau_0 + \frac{U_{\text{eff}}}{k_B} \frac{1}{T}$$

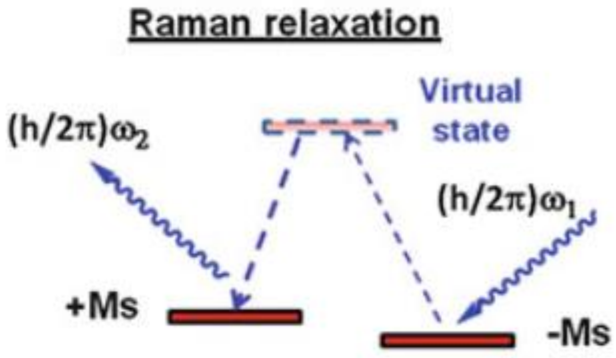
$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{U_{\text{eff}}}{k_B T}\right) \qquad \ln\left(\tau^{-1}\right) = \ln\left(\tau_0^{-1}\right) - \frac{U_{\text{eff}}}{k_B} \frac{1}{T}$$

Relaxation Processes in SMMs

Raman Process

- **What it is:** A **two-phonon** relaxation mechanism (spin relaxes by interacting with **two phonons** via a **virtual** intermediate state).
- **How it works:** The system **absorbs one phonon** to reach a *virtual* state and **emits another phonon** (or vice-versa), ending in the other magnetic sublevel-no real excited electronic level needs to be populated.
- **When it matters:** Typically dominates at **intermediate temperatures** (below Orbach, above pure QTM/very-low-T regimes).





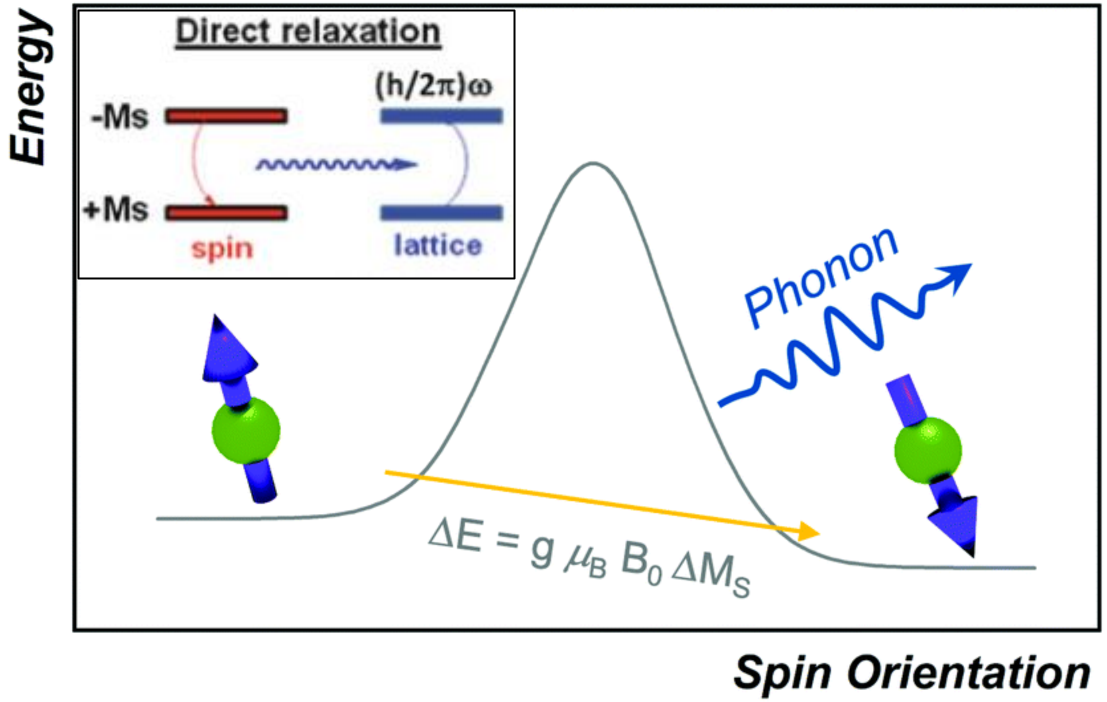
$$\tau = \frac{1}{C T^n} \qquad \ln \tau = -\ln C - n \ln T$$

$$\tau^{-1} = C T^n \qquad \ln\left(\tau^{-1}\right) = \ln C + n \ln T$$

Relaxation Processes in SMMs

Direct Relaxation

- **What it is:** A **one-phonon** relaxation mechanism (spin flips by exchanging energy with the lattice via a *single* phonon).
- **How it works:** The system makes a transition between two magnetic sublevels (often the ground doublet, e.g. +Ms ↔ −Ms by **absorbing or emitting one phonon** whose energy matches the level splitting $\hbar\omega$.
- **When it matters:** Most important at **low temperatures** (when Orbach is "frozen out") and when there is a **finite splitting** of the levels.
- **Field dependence:** Strongly **depends on magnetic field** because the field changes the splitting; the direct rate typically **increases with field**



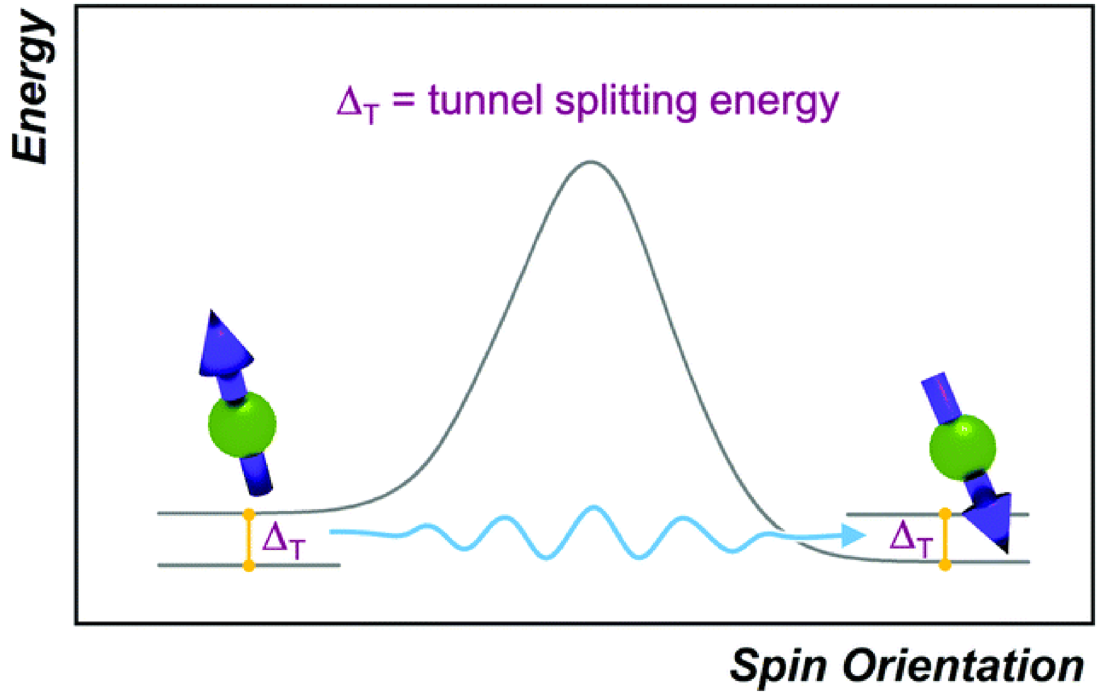
$$\tau = \frac{1}{A\,H^m\,T} \qquad \ln\tau = -\ln A - m\ln H - \ln T$$

$$\tau^{-1} = A\,H^m\,T \qquad \ln\left(\tau^{-1}\right) = \ln A + m\ln H + \ln T$$

Relaxation Processes in SMMs

Quantum Tunnelling

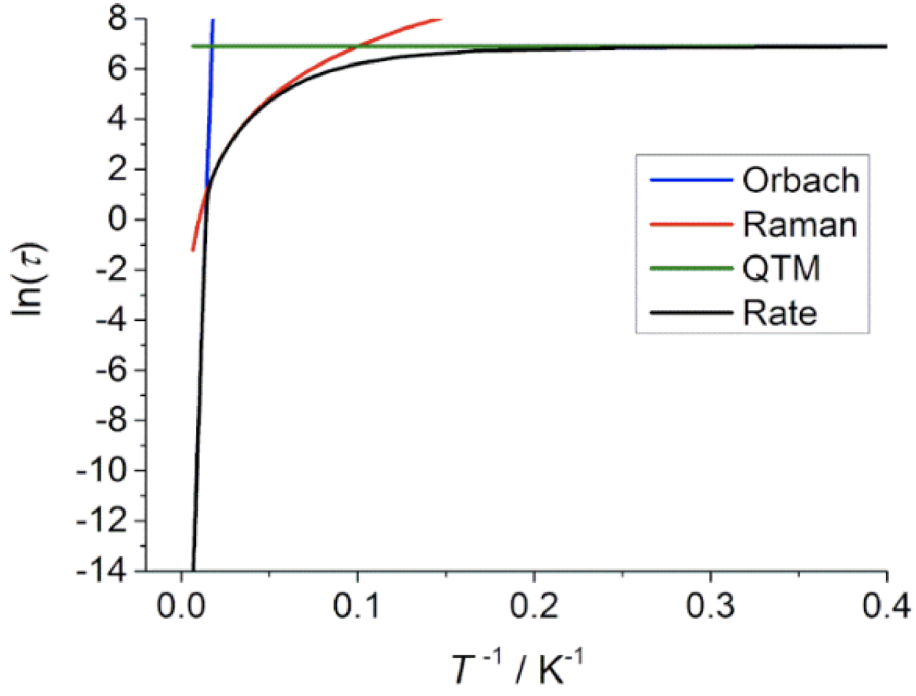
- **What it is: Quantum Tunneling of Magnetization (QTM),** relaxation by **tunneling** between the two opposite magnetization states (e.g. +Ms and −Ms) **without going over the barrier**.
- **How it works:** When the two states are (nearly) degenerate, transverse terms (transverse anisotropy, transverse field) mix them, giving an **avoided crossing** and allowing tunneling.
- **When it matters:** Usually dominant at **very low temperatures** (where thermal processes like Orbach/Raman are weak).

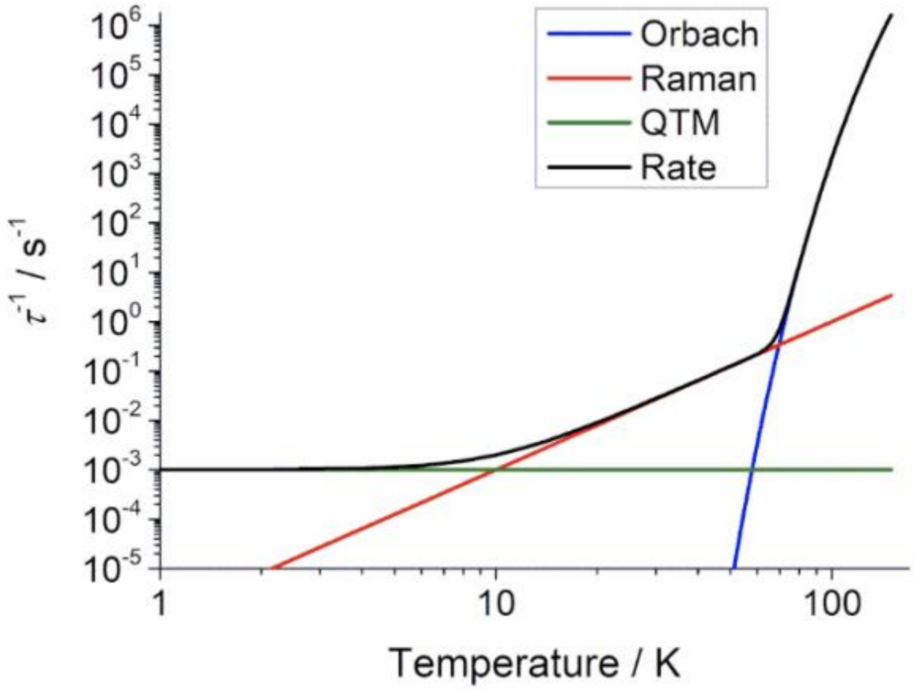


$$\tau = \frac{1}{\tau_{\mathrm{QTM}}} \qquad \ln\tau = -\ln\tau_{\mathrm{QTM}}$$

$$\tau^{-1} = \tau_{\mathrm{QTM}} \qquad \ln\left(\tau^{-1}\right) = \ln\tau_{\mathrm{QTM}}$$

Relaxation Processes in SMMs





$$\tau = \left[\tau_{\mathrm{QTM}} + A\,H^m T + C\,T^n + \tau_0^{-1}\exp\left(-\frac{U_{\mathrm{eff}}}{k_{\mathrm{B}}T}\right)\right]^{-1}$$

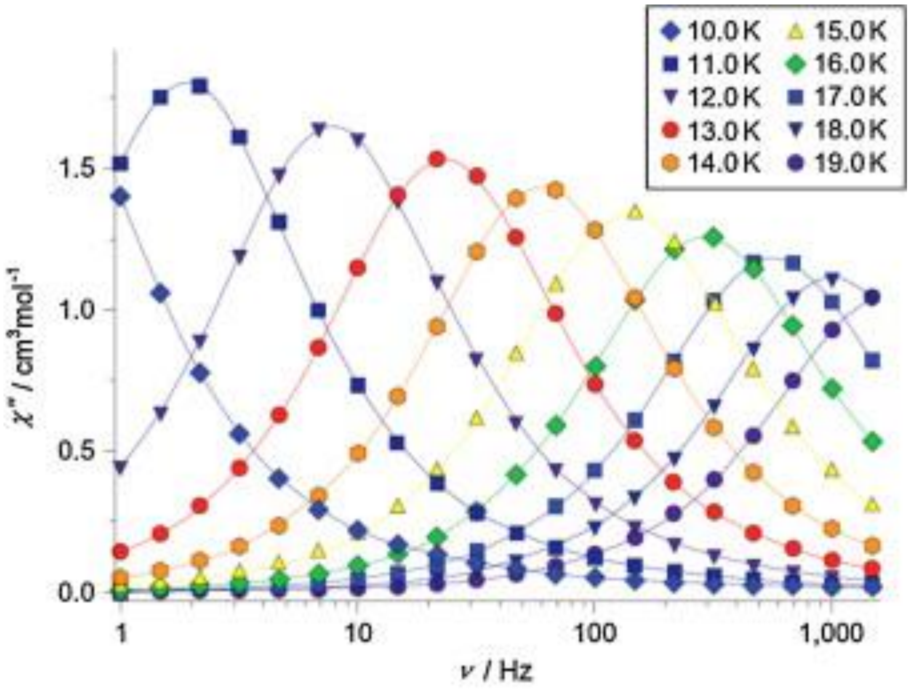
$$\tau^{-1} = \tau_{\mathrm{QTM}} + A\,H^m T + C\,T^n + \tau_0^{-1}\exp\left(-\frac{U_{\mathrm{eff}}}{k_{\mathrm{B}}T}\right)$$

$$\ln\tau = -\ln\left(\tau_{\mathrm{QTM}} + A\,H^m T + C\,T^n + \tau_0^{-1}\exp\left(-\frac{U_{\mathrm{eff}}}{k_{\mathrm{B}}T}\right)\right)$$

$$\ln\left(\tau^{-1}\right) = \ln\left(\tau_{\mathrm{QTM}} + A\,H^m T + C\,T^n + \tau_0^{-1}\exp\left(-\frac{U_{\mathrm{eff}}}{k_{\mathrm{B}}T}\right)\right)$$

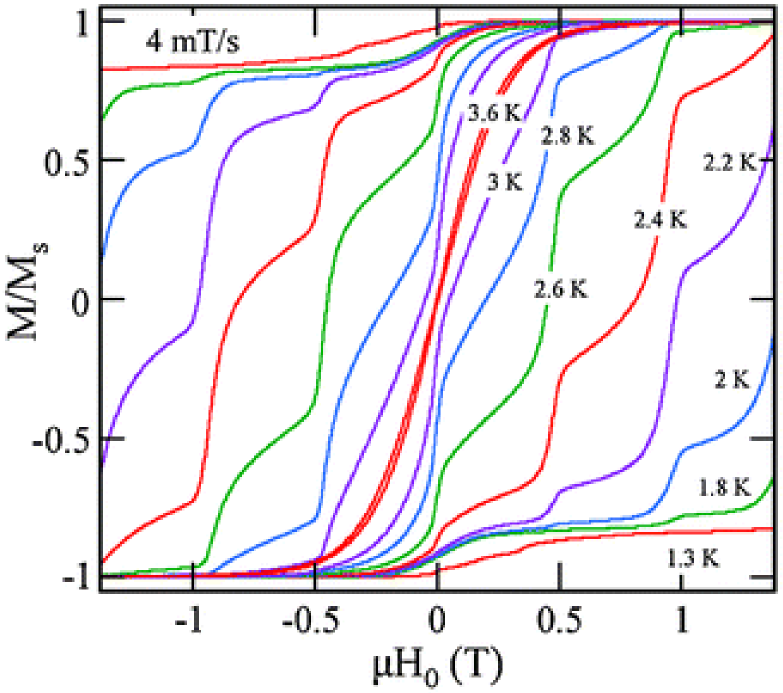
Single Molecule Magnets (SMMs)

Out-of-phase ac susceptibility



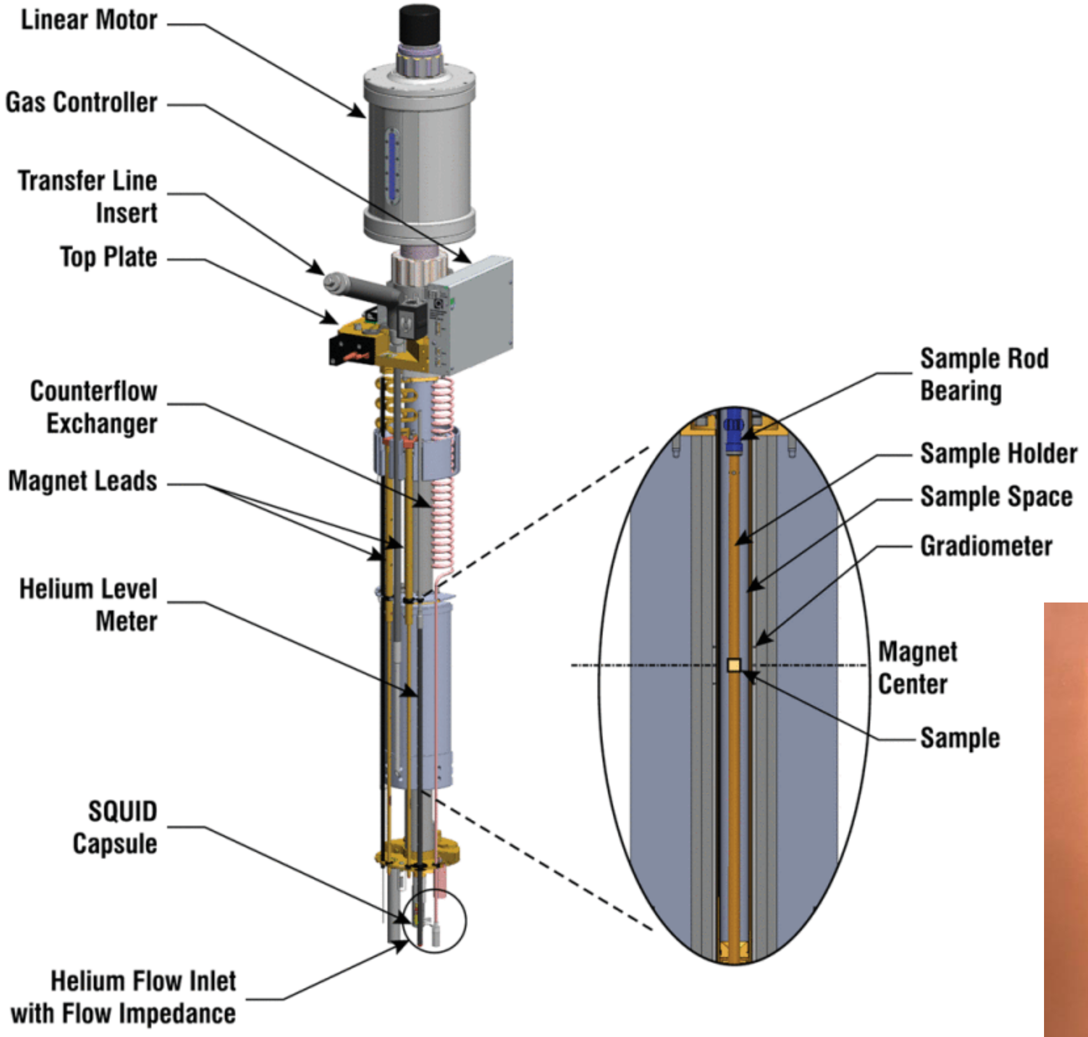
J. R. Long et al., *JACS* **2012**, *134*, 18564.

Magnetic hysteresis



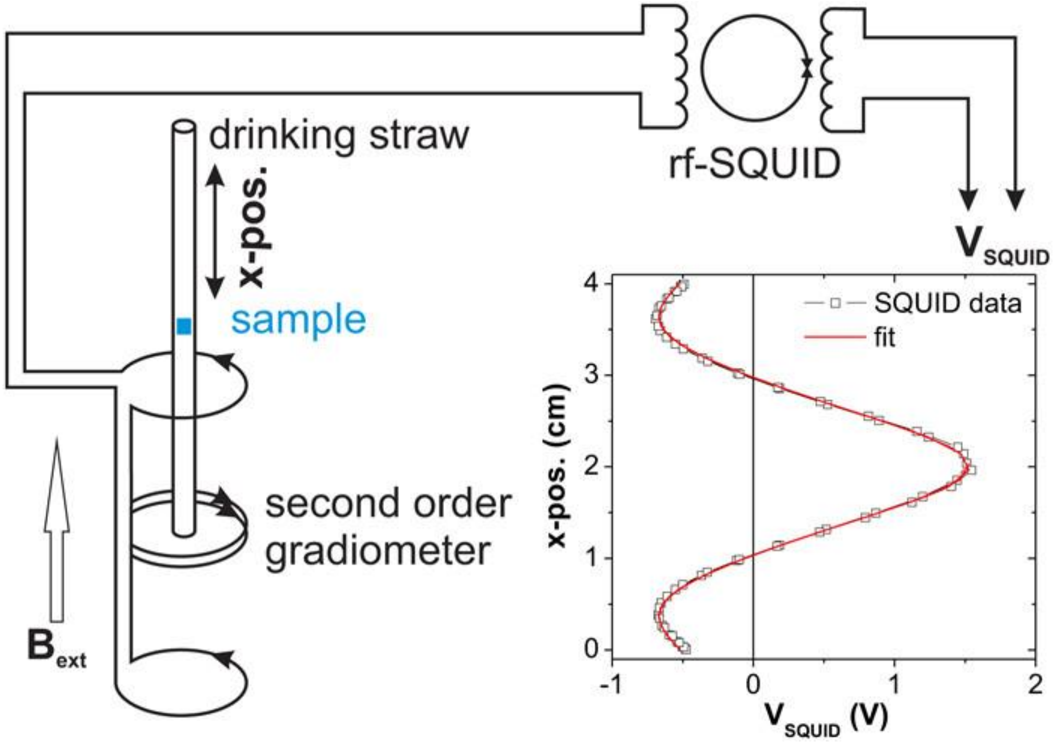
G. Christou et al., *Chem. Soc. Rev.* **2009**,*38*, 1011.

SQUID Magnetometry



- SQUID: superconducting quantum interference device
- $\leq 10^{-8}$ emu sensitivity
- Temperature Range: 1.8 - 400 K
- 7 Tesla Magnet

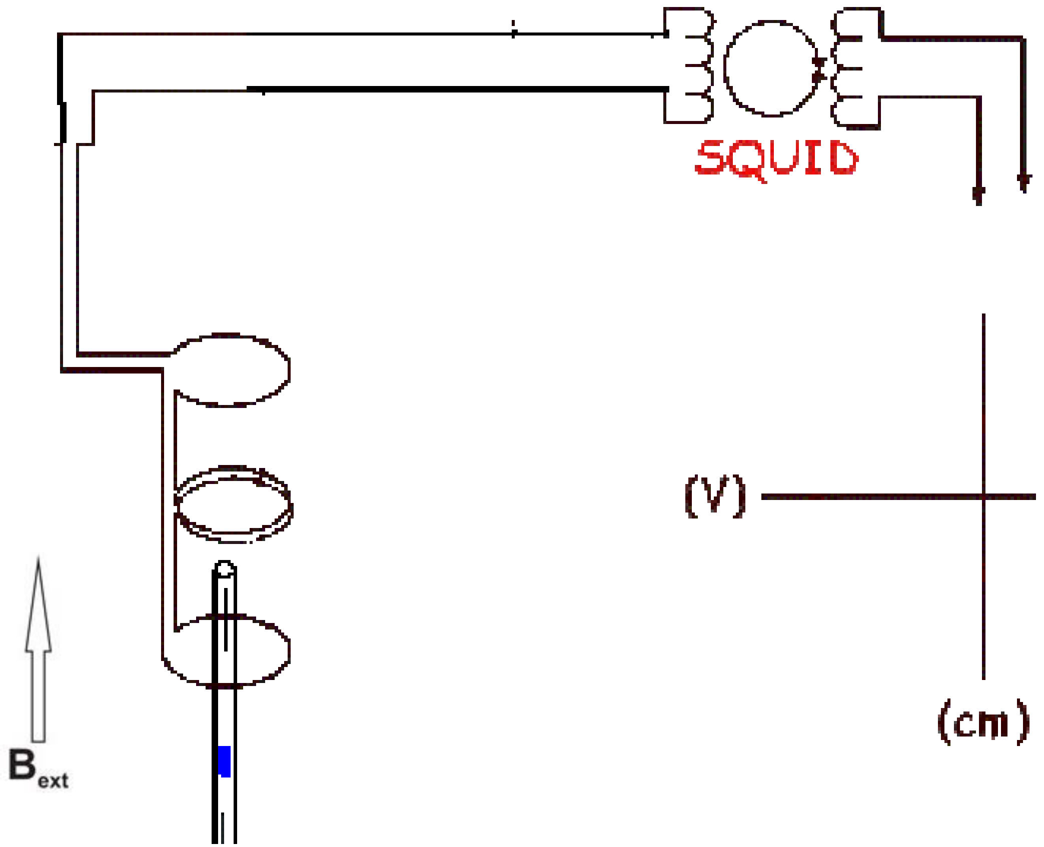
SQUID Magnetometry



A. Ney et al., *J. Appl. Phys.* **2018**, *124*, 161101.

- detects the change of **magnetic flux** created by **mechanically moving** the sample through a **superconducting pick-up coil** which is converted to a voltage V_{SQUID}
- the position is denoted as the x direction which is parallel to the external magnetic field B_{ext}
- to suppress all kinds of external magnetic fields, the pick-up coil is made as **second order gradiometer**
- SQUID scan is then **fitted automatically**, assuming that the sample is an ideal point dipole which is exactly positioned on the axis of the magnetometer, to get the **magnetic moment** of the assumed point dipole (**linear regression mode**)

SQUID Magnetometry



M. McElfresh, “Fundamentals of magnetism and magnetic measurements featuring Quantum Design’s Magnetic Property measurement System,” Tech. Rep. (Quantum Design, 1994).

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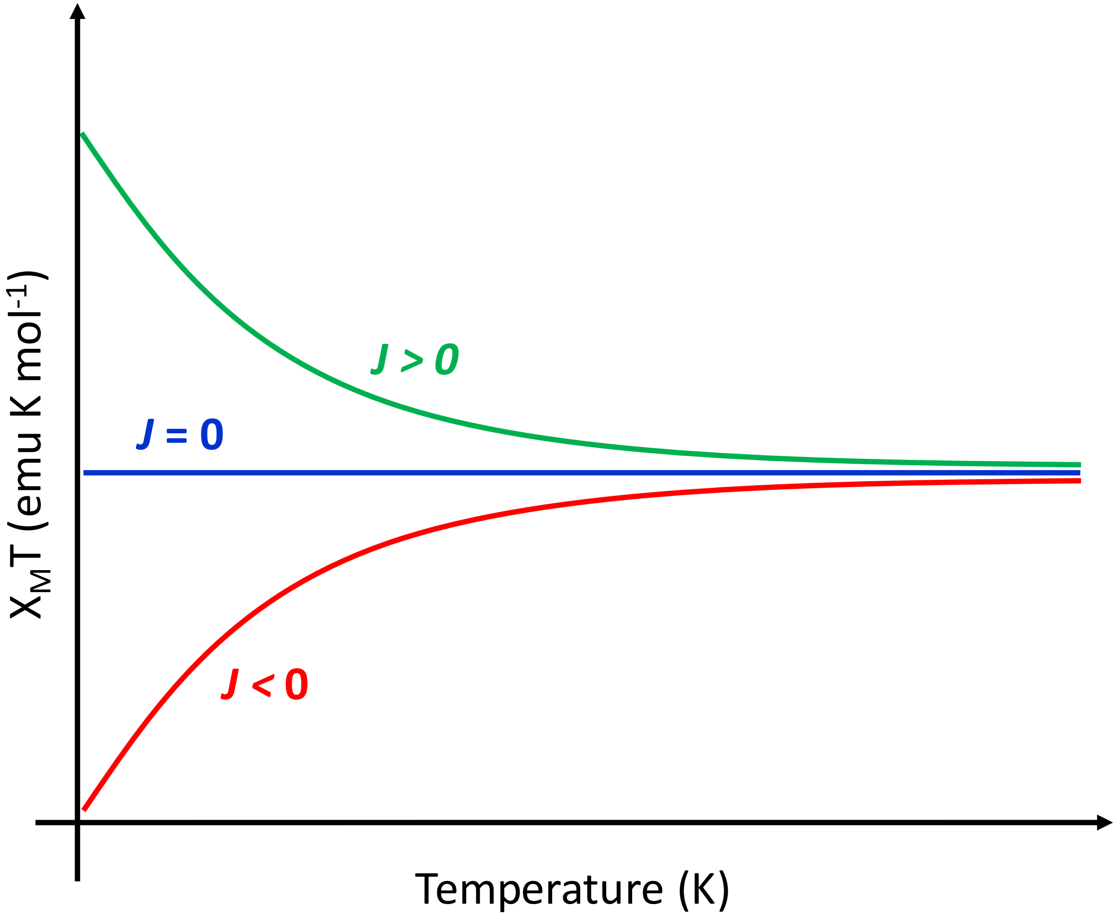
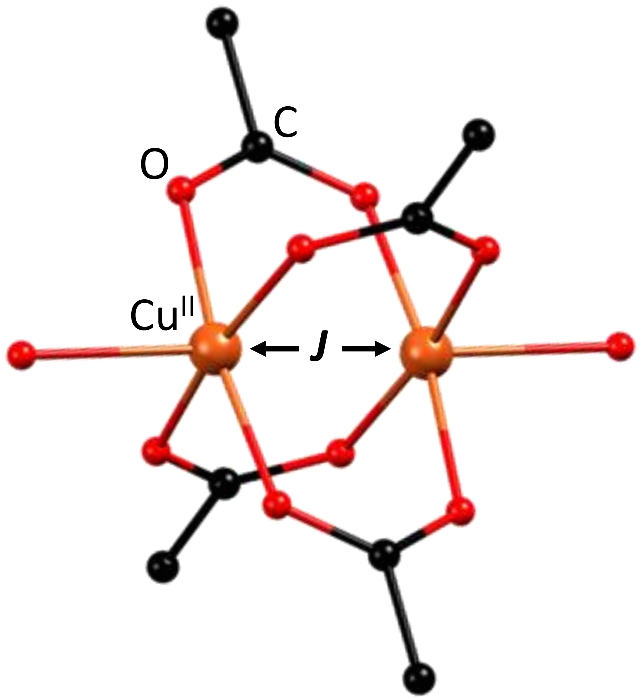
SQUID Magnetometry

Direct Current (DC) Measurements





$[Cu^{II}_2(O_2CMe)_4(H_2O)_2]$

$$\hat{H} = -2J(S_{Cu_1}S_{Cu_2})$$

$$H = \mu_B \boldsymbol{B} \cdot g \cdot \boldsymbol{S} + D\left(\boldsymbol{S}_z^2 - \frac{S(S+1)}{3}\right) + E(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2) - 2J(\boldsymbol{S}_1 \cdot \boldsymbol{S}_2)$$

$S_{Cu1} = S_{Cu2} = 1/2$

SQUID Magnetometry

Alternating Current (AC)
Measurements

- In *a.c.* magnetic susceptibility, a time varying, sinusoidal magnetic field is applied
- a static, *d.c.* magnetic field may also be applied
- field H inside the sample:

$$H = H_{\mathrm{d.c.}} + H_{\mathrm{a.c.}} \cos(\omega t)$$

- where ω ($\omega = 2\pi v$) is the frequency of the oscillating magnetic field
- v is typically in the range 0.1–10^4 Hz

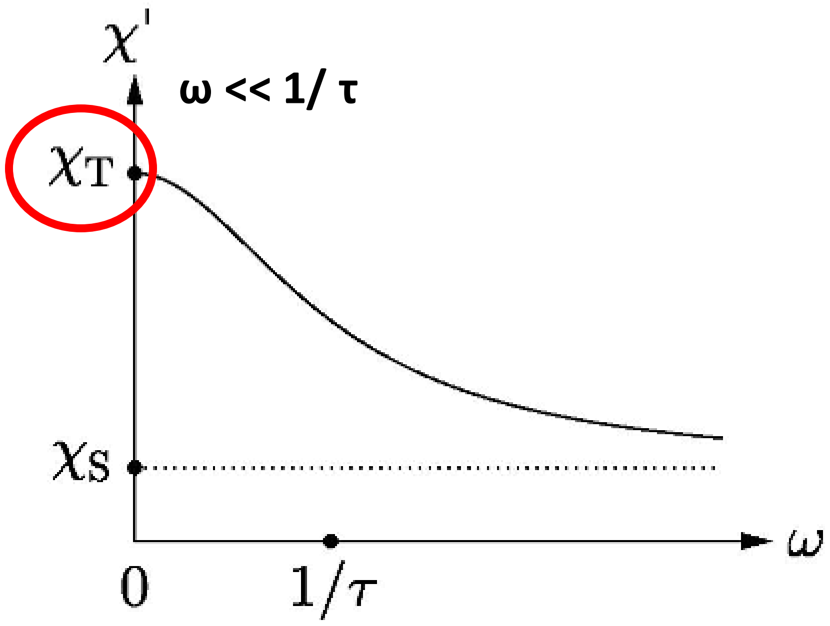
D. Gatteschi et al., *Molecular Nanomagnets,* Oxford University Press, March 2006, p. 69-75

C. V. Topping and S. J. Blundell, *J. Phys.: Condens. Matter* **2019**, *31,* 013001

SQUID Magnetometry

Alternating Current (AC) Measurements

Depending on the **relaxation time τ** of the magnetic moments of the system, **three** regimes can be defined



- **ω << 1/ τ**: corresponds to the *d.c.* limit in which the studied system responds essentially instantaneously to the a.c. field
- d.c. susceptibility is obtained ($\chi_{a.c.} \approx \chi_{d.c.}$)
- equilibrium response, the system can exchange energy with the lattice
- measurement of the isothermal susceptibility, χ_T

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SQUID Magnetometry

Alternating Current (AC) Measurements

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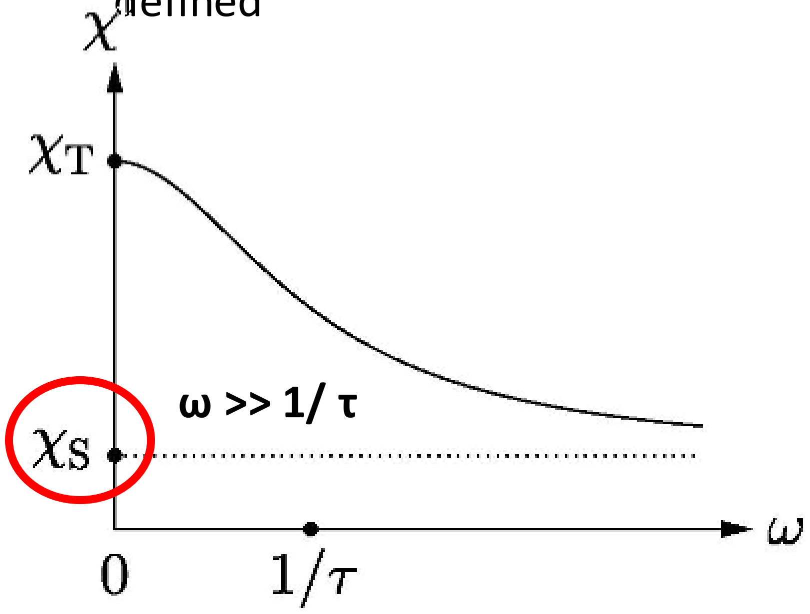

- **ω >> 1/τ** : field oscillates **too quickly** for the system to respond
- No time to equilibrate and exchange energy with the lattice
- Adiabatic susceptibility, χ_S

C. V. Topping and S. J. Blundell, *J. Phys.: Condens. Matter* **2019**, *31,* 013001

SQUID Magnetometry

Alternating Current (AC) Measurements

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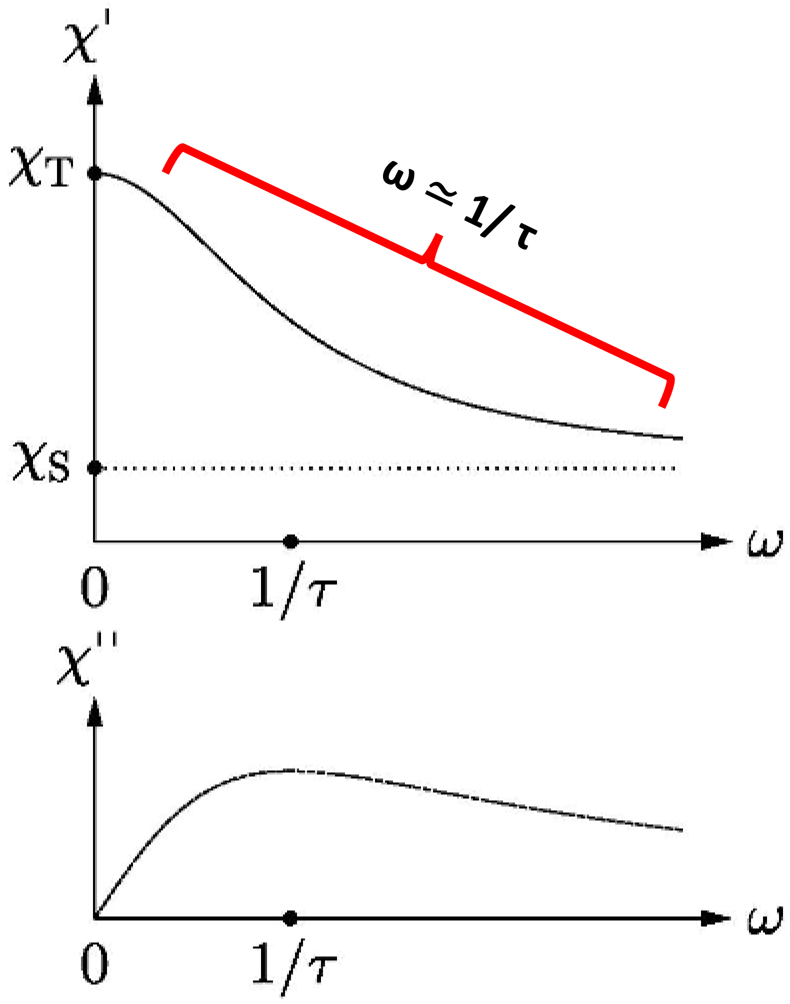


- **ω ≈ 1/τ** : frequency of the oscillating magnetic field is **comparable** to the timescale of the magnetic relaxation of the system
- may be some phase lag when the perturbation is slightly faster or slower than the natural frequency of the system
- the response is reported in two parts: **in-phase** and **out-of-phase** (or real and imaginary)
- a.c. susceptibility:

$$\chi_{\text{a.c.}} = \chi'_{\text{a.c.}} + i\chi''_{\text{a.c.}}$$

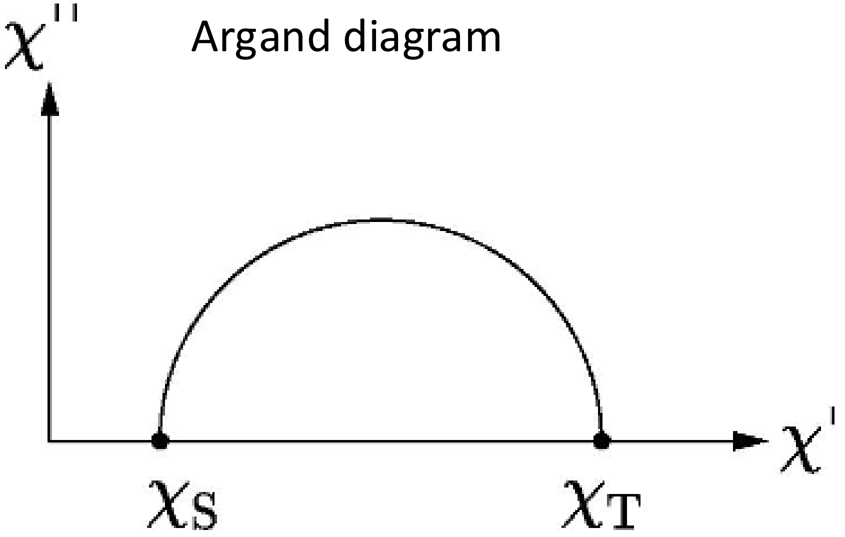
C. V. Topping and S. J. Blundell, *J. Phys.: Condens. Matter* **2019**, *31*, 013001

SQUID Magnetometry

Alternating Current (AC) Measurements

$$\chi(\omega) = \chi_S + \frac{\chi_T - \chi_S}{(1 + i\omega\tau)^{1-\alpha}}$$

Argand diagram

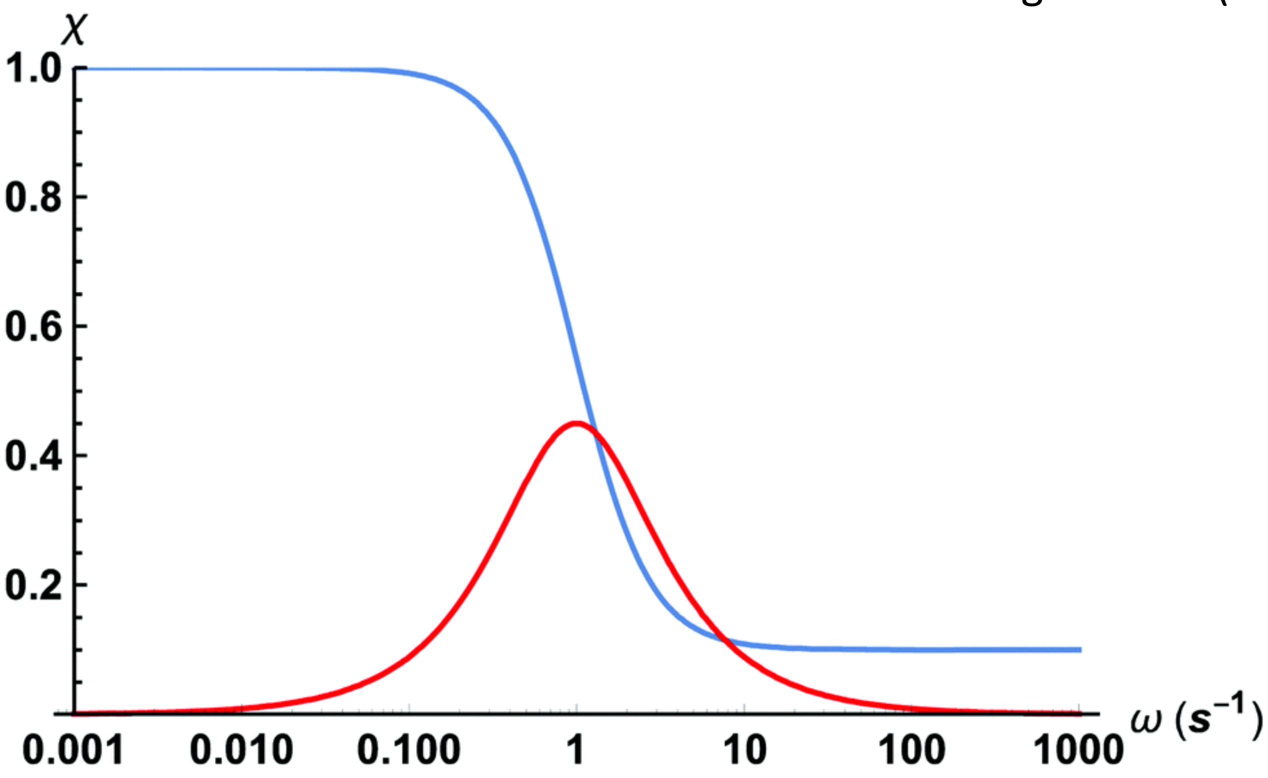


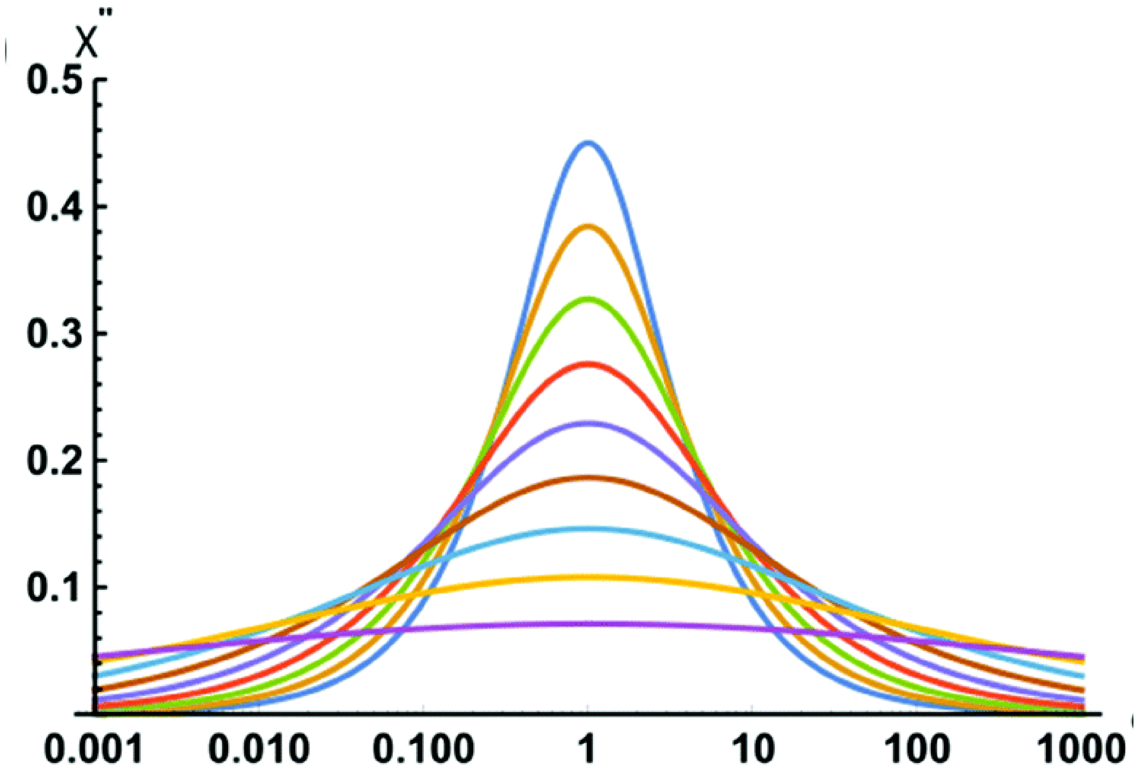
- the dynamic susceptibility is a complex function
- the relaxation is not characterised by a single process, but via a distribution of relaxation times
- Argand diagram, the imaginary susceptibility is plotted against its real counterpart
- each relaxation process appears as a half-circle
- the peak of a half-circle corresponds to the resonance frequency, from which one can identify the characteristic relaxation time via $\tau = \omega^{-1}$
- The extraction of the relaxation times is particular interesting in the studies of SMMs

C. V. Topping and S. J. Blundell, *J. Phys.: Condens. Matter* **2019**, *31,* 013001

SQUID Magnetometry

Alternating Current (AC)



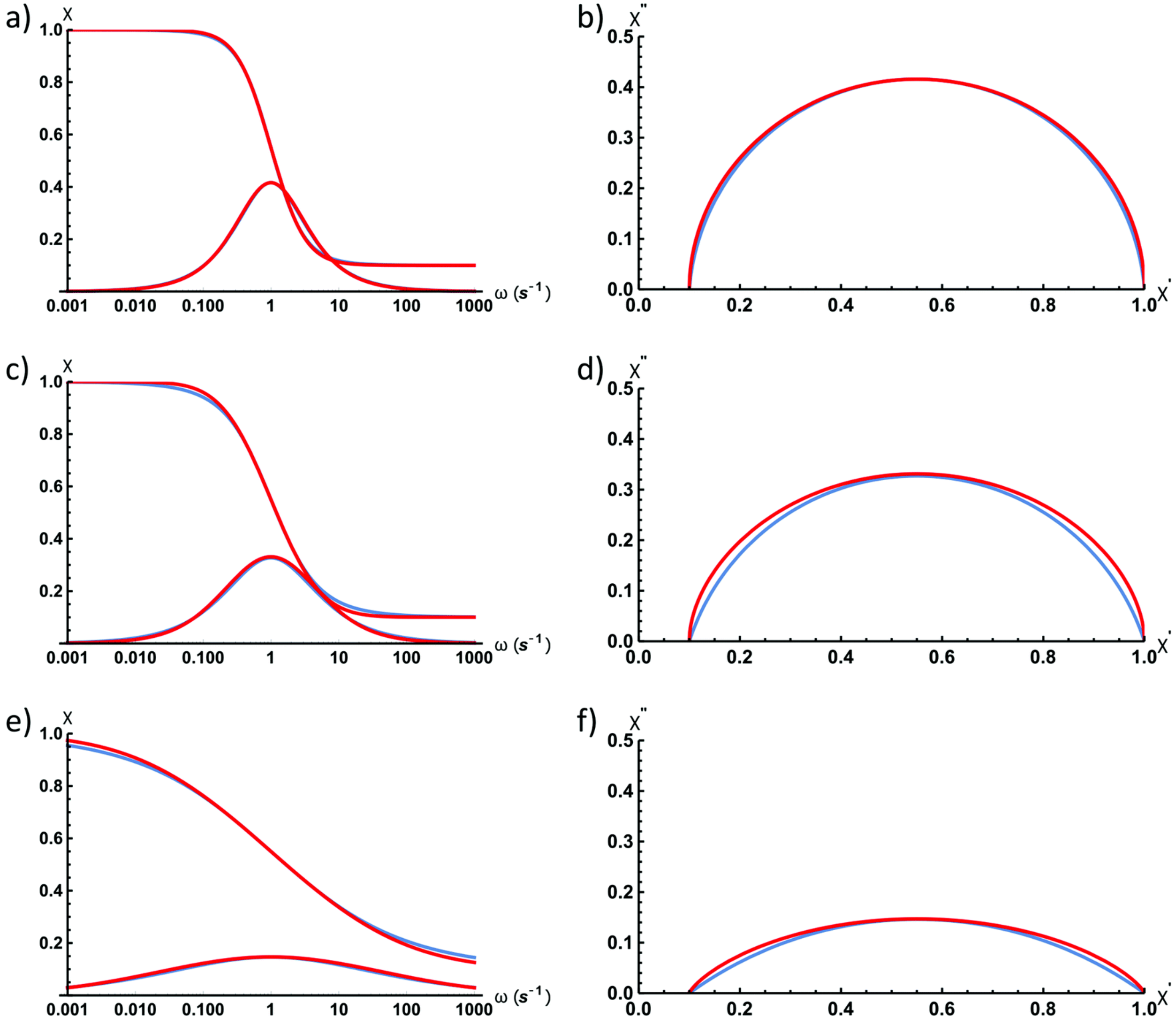


- **Cole–Cole parameter α** (0–1) quantifies the **distribution of relaxation times**.
- **α = 0**: **single** relaxation time (ideal Debye). The χ′′(ω) peak is **narrow and symmetric**.
- **Increasing α**: **broader** distribution of τ → the χ′′(ω) peak becomes **broader/flatter** and the χ′(ω) step becomes **more gradual**.
- Physically, larger α often indicates **multiple relaxation pathways**, **site/structural disorder**, or **intermolecular interactions**.

C. V. Topping and S. J. Blundell, *J. Phys.: Condens. Matter* **2019**, *31,* 013001

SQUID Magnetometry

Alternating Current (AC) Measurements



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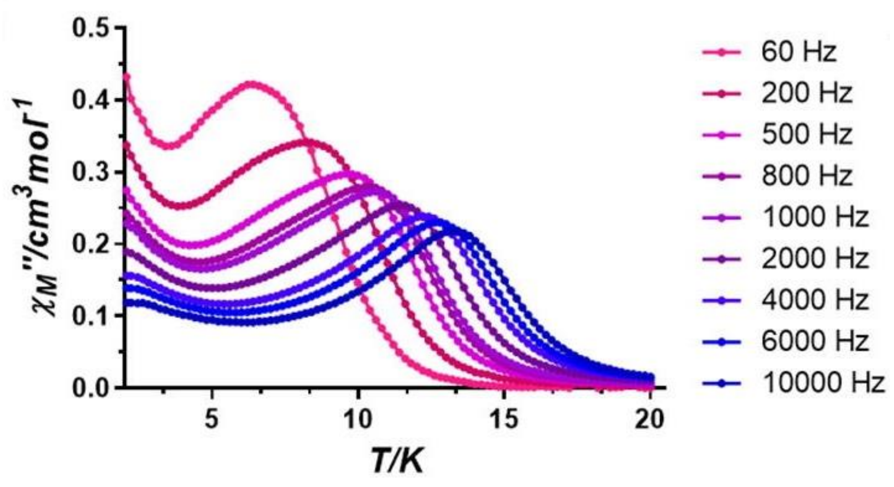
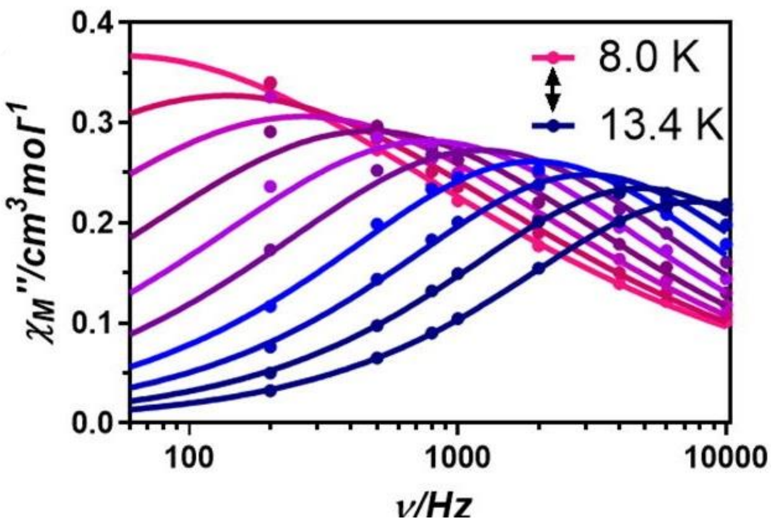
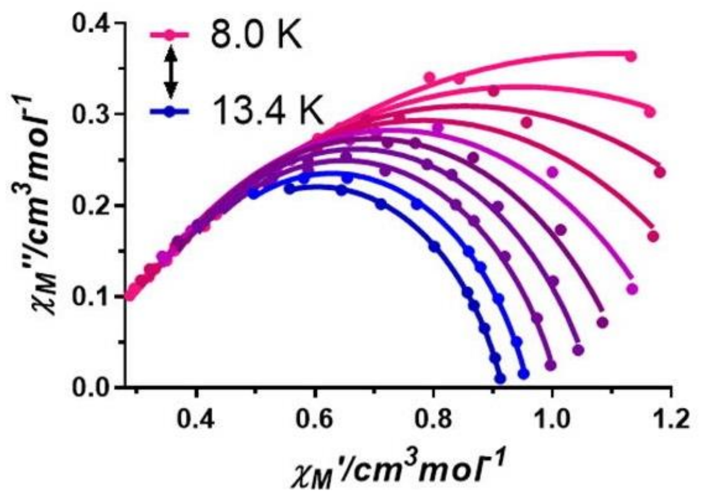
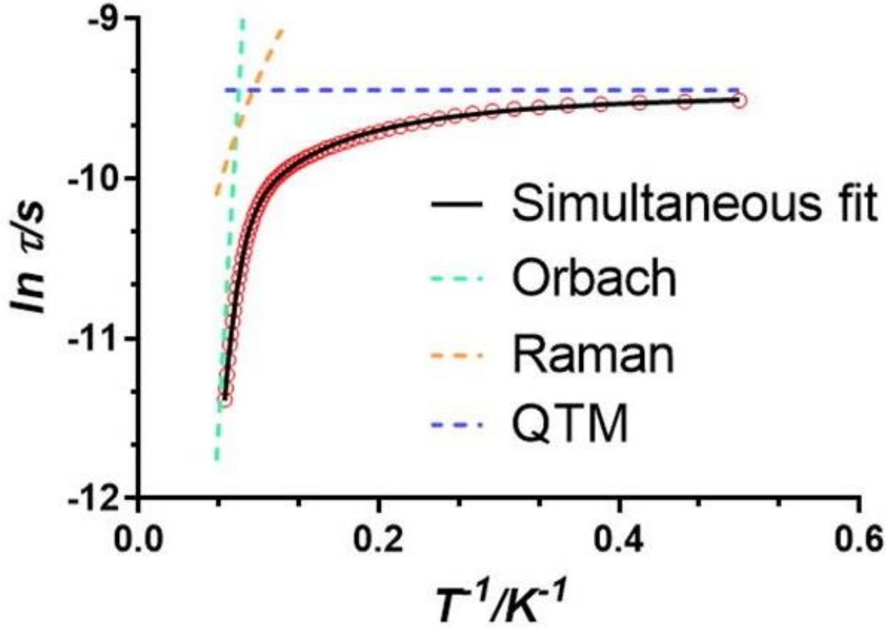
C. V. Topping and S. J. Blundell, *J. Phys.: Condens. Matter* **2019**, *31,* 013001

Relaxation Processes in Ln SMMs









$$\tau^{-1} = \tau_{QTM}^{-1} + CT^n + \tau_0^{-1}\exp\left(-\frac{U_{eff}}{k_BT}\right)$$

quantum tunneling *Raman process* *Orbach process*

E. Colasio et al., *Coord. Chem. Rev.* **2021**, *441*, 213938.