CHEM40111/CHEM40121

Molecular magnetism: tools and applications

6 Single-molecule magnets II

MANCHESTER 1824
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Course Overview

1 Fundamentals • Motivation • Origins of magnetism • Bulk magnetism	**5 Single-molecule magnets I** • Single-molecule magnets • Electrostatic model
2 Quantum mechanics of magnetism • Zeeman effect • Statistical mechanics • Magnetisation • Magnetic susceptibility	**6 Single-molecule magnets II** • Measuring magnetic relaxation • Relaxation mechanisms • Latest research
3 Magnetic coupling • Exchange Hamiltonian • Experimental measurements • Vector coupling	**7 Magnetic resonance imaging** • Paramagnetic NMR • Magnetic resonance imaging • Latest research
4 Magnetic anisotropy • Zero-field splitting • Impact on properties • Lanthanides • Spin-orbit coupling	**8 Quantum information processing** • Quantum information • DiVincenzo criteria • Latest research • ***Question time***

Intended learning outcomes

1. Explain the origin of magnetism arising from electrons in atoms and molecules using formal quantum-mechanical terms

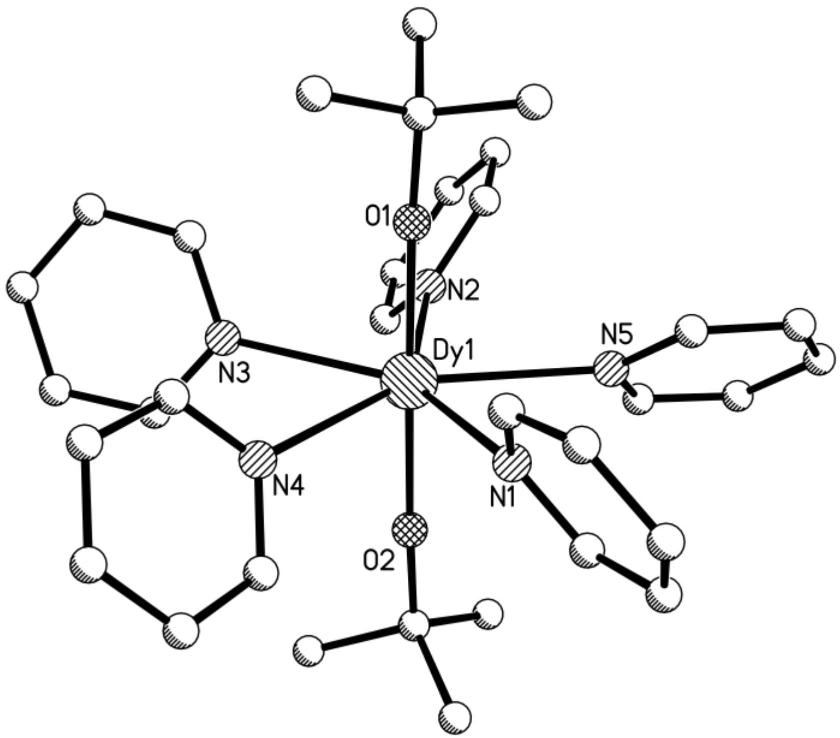
2. Compare and contrast the electronic structure of metal ions in molecules and their magnetic properties, for metals across the periodic table

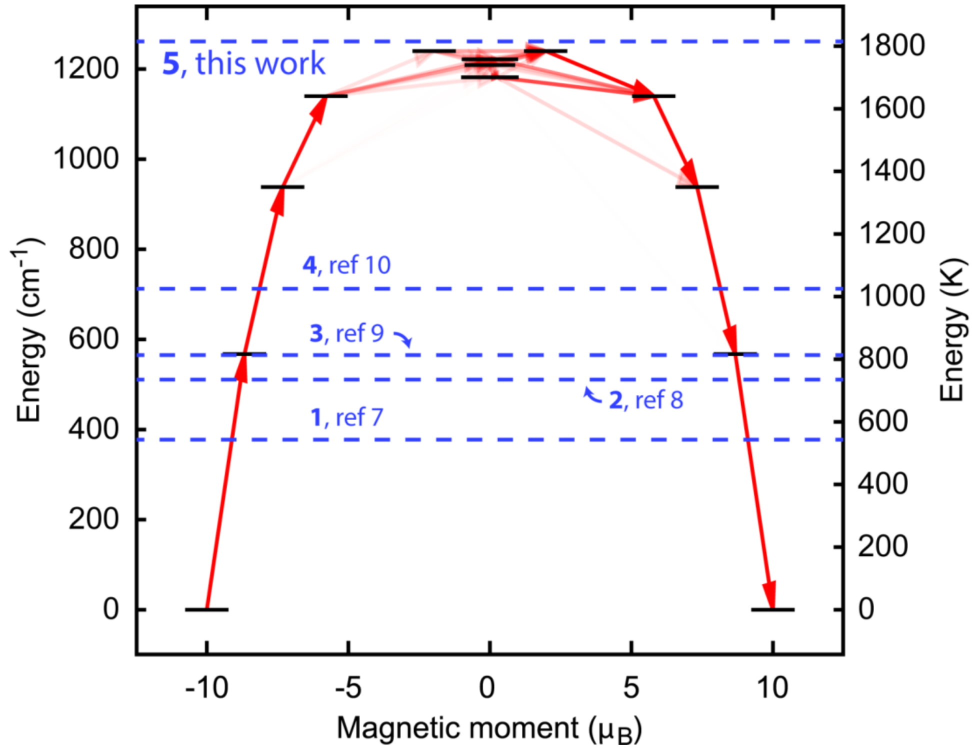
3. Select and apply appropriate models and methods to calculate molecular magnetic properties such as magnetisation, magnetic susceptibility and paramagnetic NMR shift

4. Deconstruct topical examples of molecular magnetism including single-molecule magnetism, molecular quantum information processing and MRI contrast agents

World record U_{eff} barrier

- Collaboration with Prof. Yanzhen Zheng (Xi'an, China): O^{-}–Dy–O^{-} = 178.9°



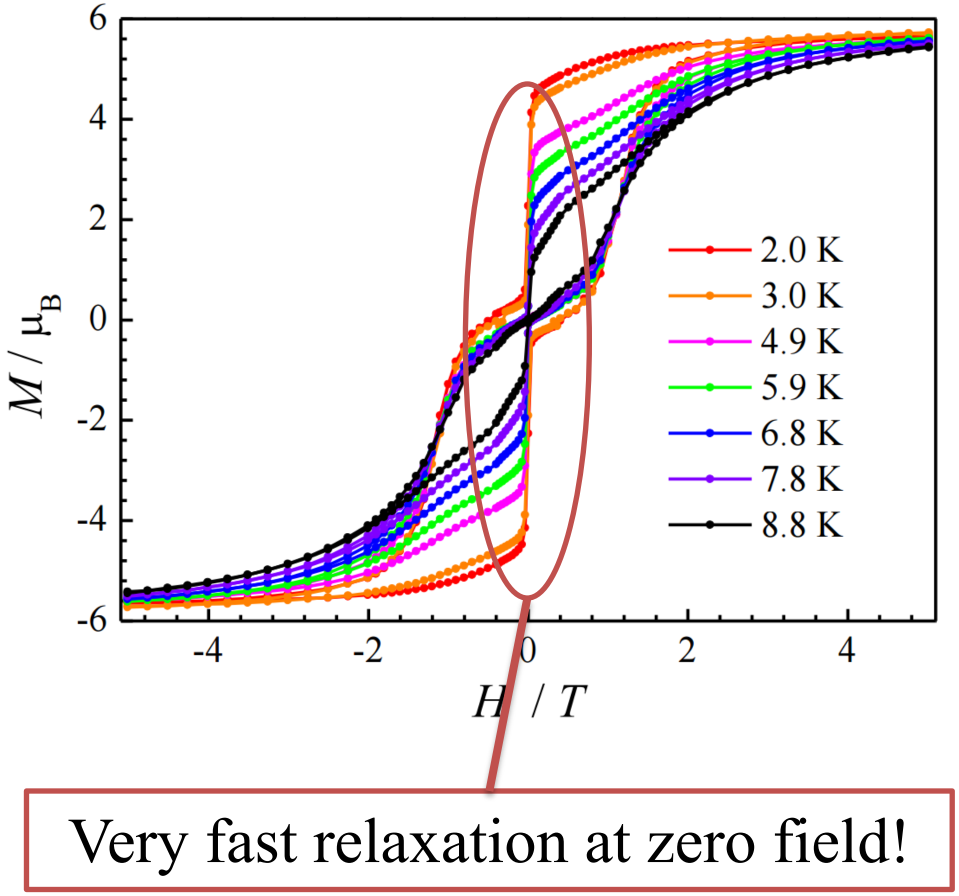


Two *trans*- O^{-} donors, neutral pyridine ligands!

[1] Y.-S. Ding *et. al.*, *Angew. Chem. Int. Ed.*, 2016, **55**, 16071

High-temperature SMMs?

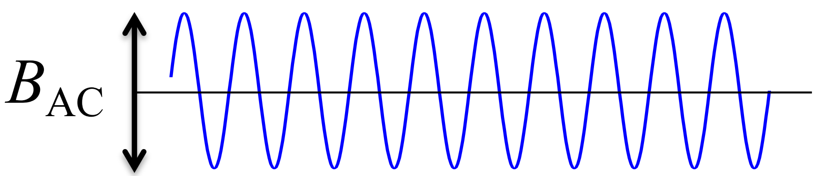
- So Dy^{III} SMMs can have HUGE barriers….are there any drawbacks?

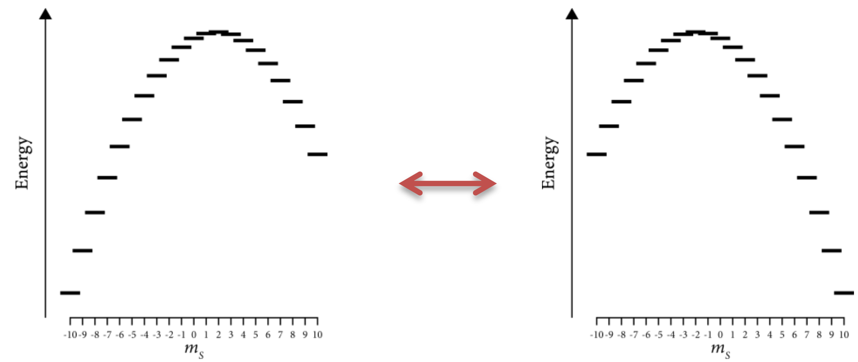


[1] Y.-S. Ding *et. al.*, *Angew. Chem. Int. Ed.*, 2016, **55**, 16071

Measuring magnetic relaxation

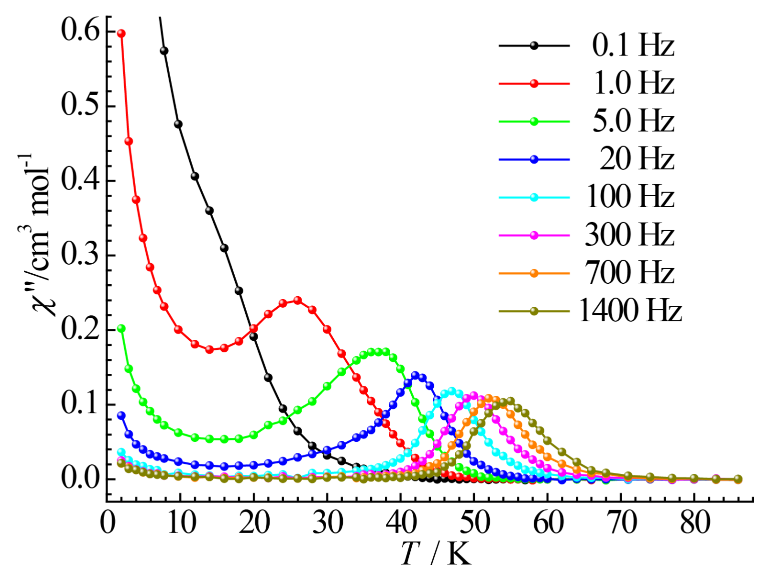
- The relaxation rate can be measured using alternating current (AC) susceptibility
  – Magnetic field oscillates positive and negative





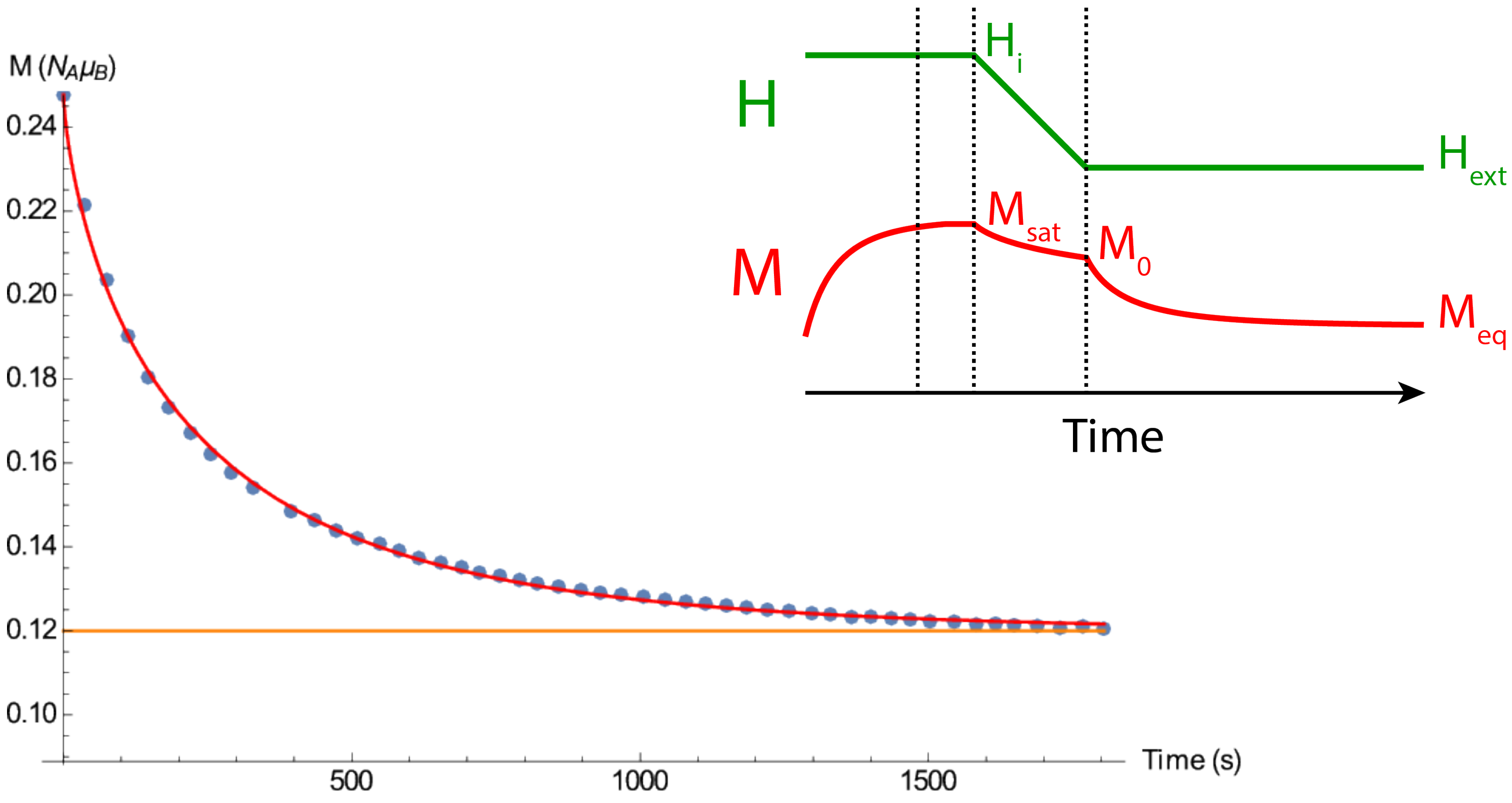
- At some temperature, the molecules can't jump the barrier fast enough to keep up with the AC frequency
  – We see an *out-of-phase* signal

$$\tau^{-1} = 2\pi\nu$$



Measuring magnetic relaxation

- We can also use direct current (DC) techniques
  - Apply a field to magnetise the same, switch it off and watch the magnetisation decay



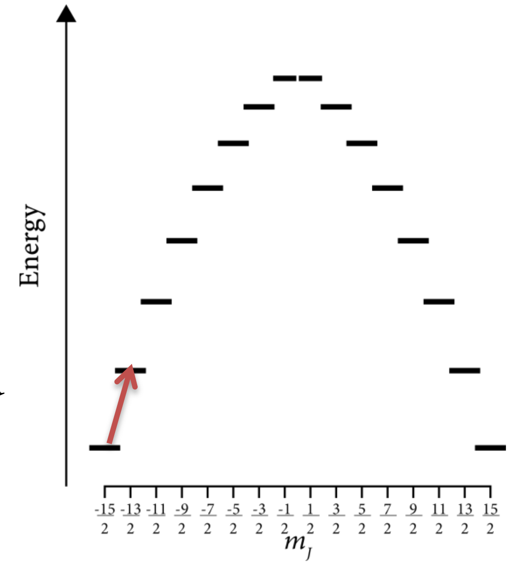
Relaxation mechanisms

- How do the molecules magically jump between these magnetic states?
- They are not isolated and interact with their environment
- They can absorb or emit *phonons* – quantised vibrational modes of the crystal lattice
- Recall – molecular vibrations/phonons are essentially the microscopic origin of temperature
- The exchange of phonons conserves the energy and angular momentum of the entire crystal

Relaxation mechanisms

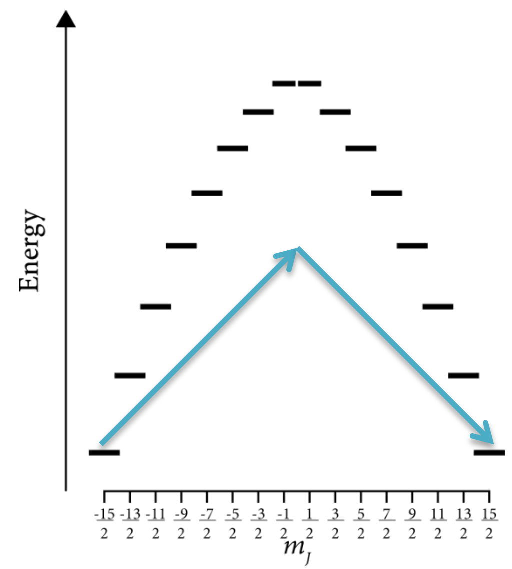
- Two different kinds of spin-phonon transitions:
  - Direct interaction
    - A single phonon absorbed or emitted

$$\gamma_{a,b} \propto \sum_i \left|\langle a|\widehat{H}_i|b\rangle\right|^2$$



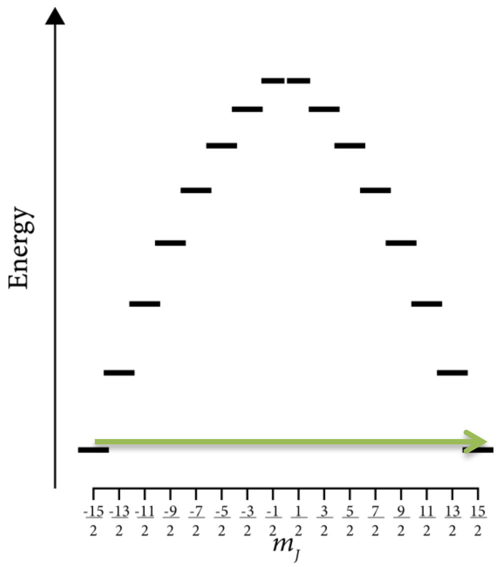
  - Raman interaction
    - Two phonons involved *via* ‘virtual state’

$$\gamma_{a,b} \propto \sum_c \sum_i \sum_j \frac{\left|\langle a|\widehat{H}_i|c\rangle\langle c|\widehat{H}_j|b\rangle\right|^2}{E_c}$$



Relaxation mechanisms

- A third type of transition is possible:
  - Quantum tunnelling of the magnetisation (QTM)
    - No energy cost, no phonons involved



Relaxation mechanisms

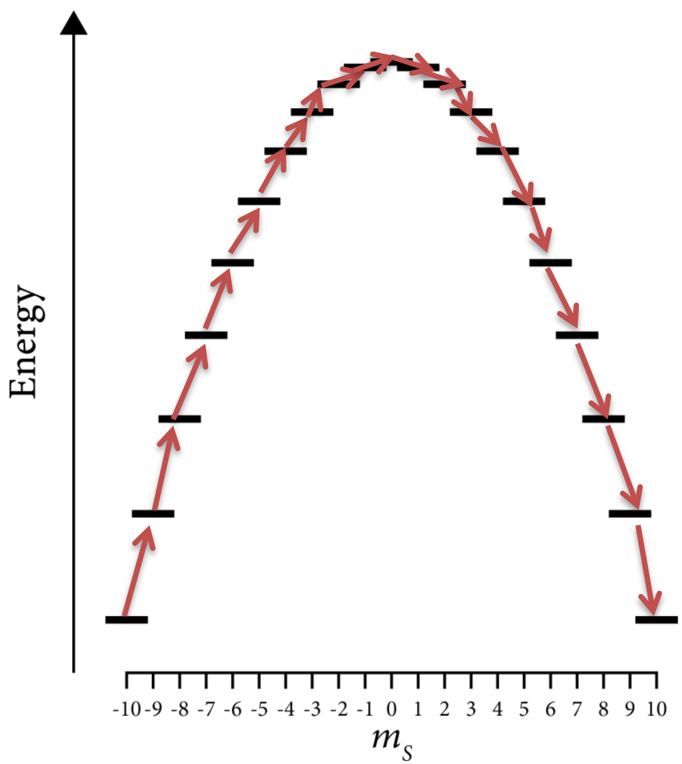
- Most commonly, we observe multiple sequential transitions

- For $Mn_{12}Ac$ we see sequential Direct spin-phonon transitions

- This is collectively known as the Orbach process and has an exponential temperature dependence

$$\tau^{-1} = \tau_0{}^{-1} \exp\left[\frac{-U_{eff}}{k_B T}\right]$$

- Note similarity to Arrhenius Law and first order reaction kinetics

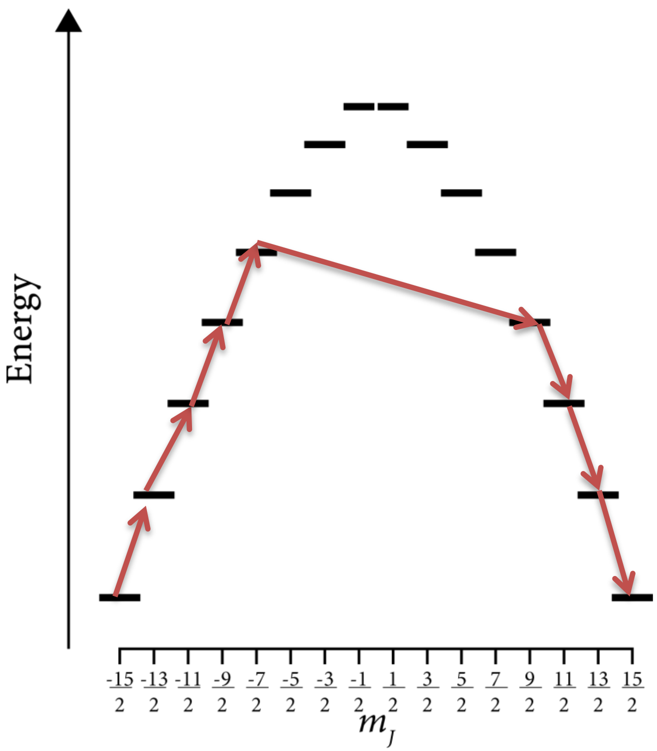


Relaxation mechanisms

- Most commonly, we observe multiple sequential transitions

- For Ln SMMs four sequences are common:
  1. The Orbach process. It is unusual to reach the most energetic states in Ln SMMs.

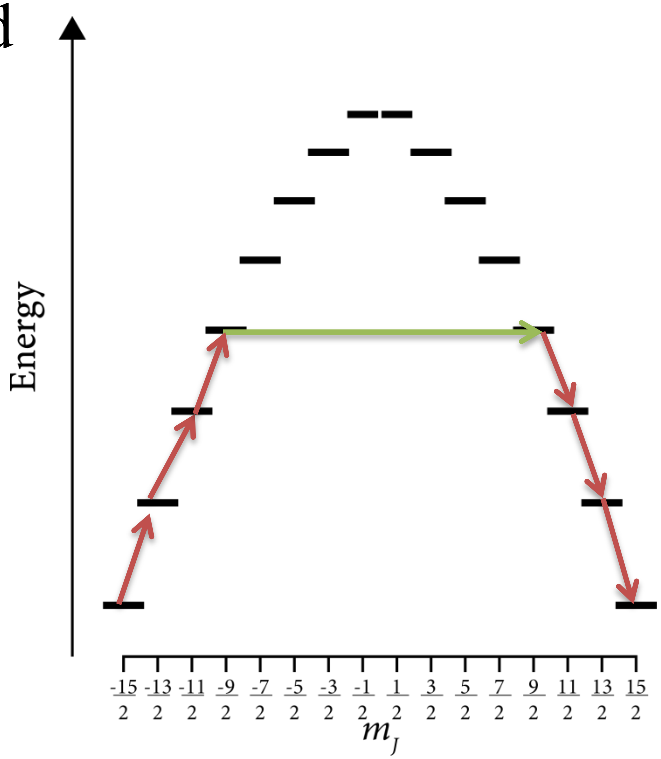
$$\tau^{-1} = \tau_0{}^{-1} \exp\left[\frac{-U_{eff}}{k_B T}\right]$$



Relaxation mechanisms

- Most commonly, we observe multiple sequential transitions

- For Ln SMMs four sequences are common:
  2. Direct transitions with a QTM step, thermally-assisted QTM (TA-QTM). Also has an exponential temperature dependence. ***Impossible to distinguish from the Orbach process!***

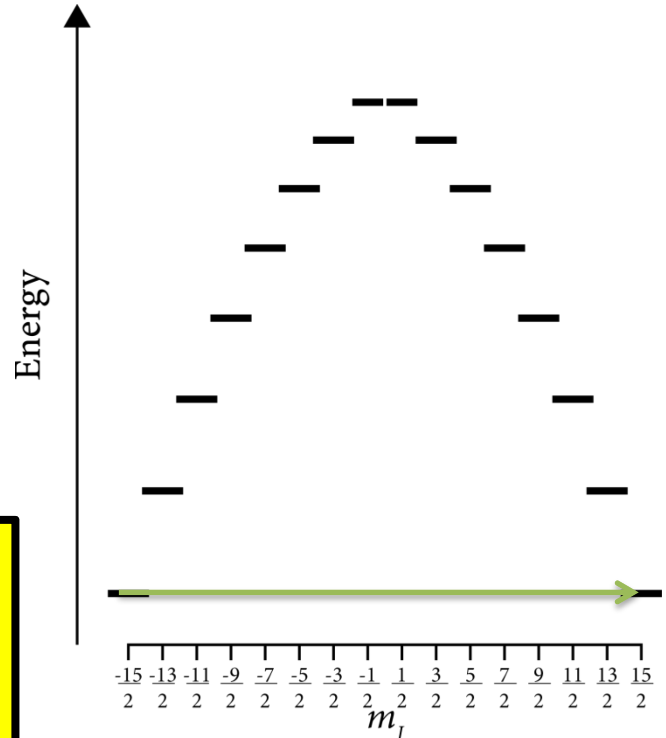


$$\tau^{-1} = \tau_0{}^{-1} \exp\left[\frac{-U_{eff}}{k_B T}\right]$$

Relaxation mechanisms

- Most commonly, we observe multiple sequential transitions

- For Ln SMMs four sequences are common:
  3. Ground state QTM. This is temperature independent.



$$\tau^{-1} = \tau_{QTM}^{-1}$$

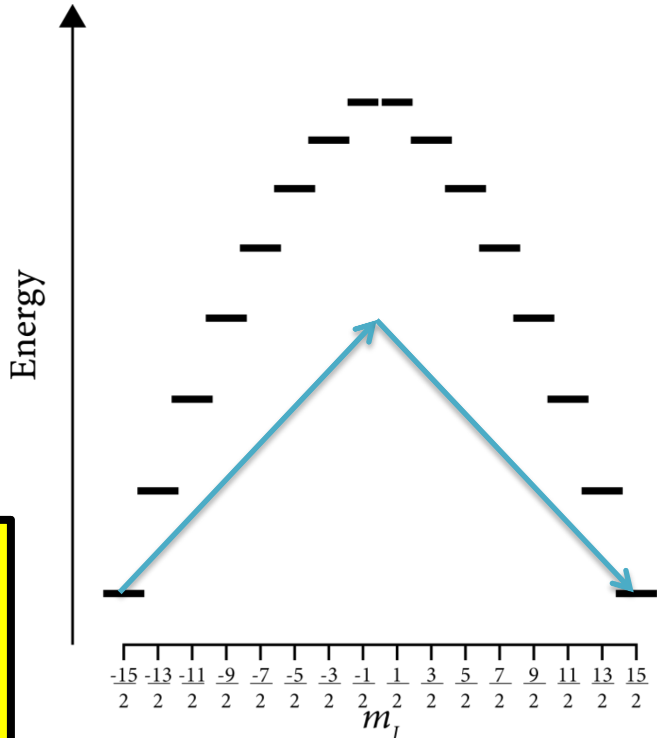
FEED FORWARD: ${\tau_{QTM}}^{-1}$ is the QTM *rate*, τ_{QTM} is the QTM *time*

Relaxation mechanisms

- Most commonly, we observe multiple sequential transitions

- For Ln SMMs four sequences are common:
  4. Raman mechanism.
     This has a power law temperature dependence. This form makes many assumptions about the phonons involved.

$$\tau^{-1} = CT^n$$



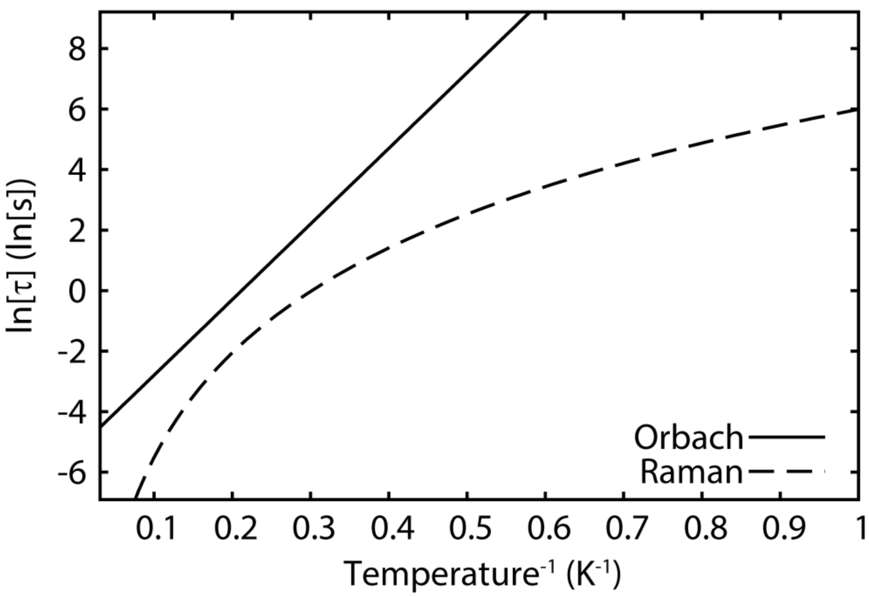
FEED FORWARD: CT^n describes the Raman *rate*, not the *time*! $\tau \neq CT^n$

Relaxation mechanisms

- Therefore, generally, we have the combined effect of all three

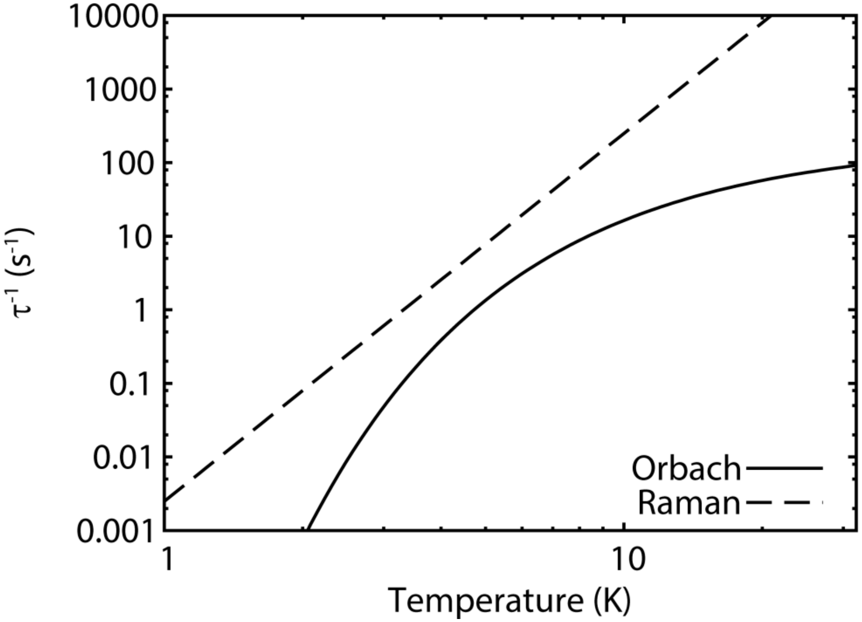
$$\tau^{-1} = \tau_0{}^{-1} \exp\left[\frac{-U_{eff}}{k_B T}\right] + \tau_{QTM}{}^{-1} + CT^n$$

- Measure the temperature dependence of the relaxation rate
- ln[τ] vs. 1/T



- Orbach linear

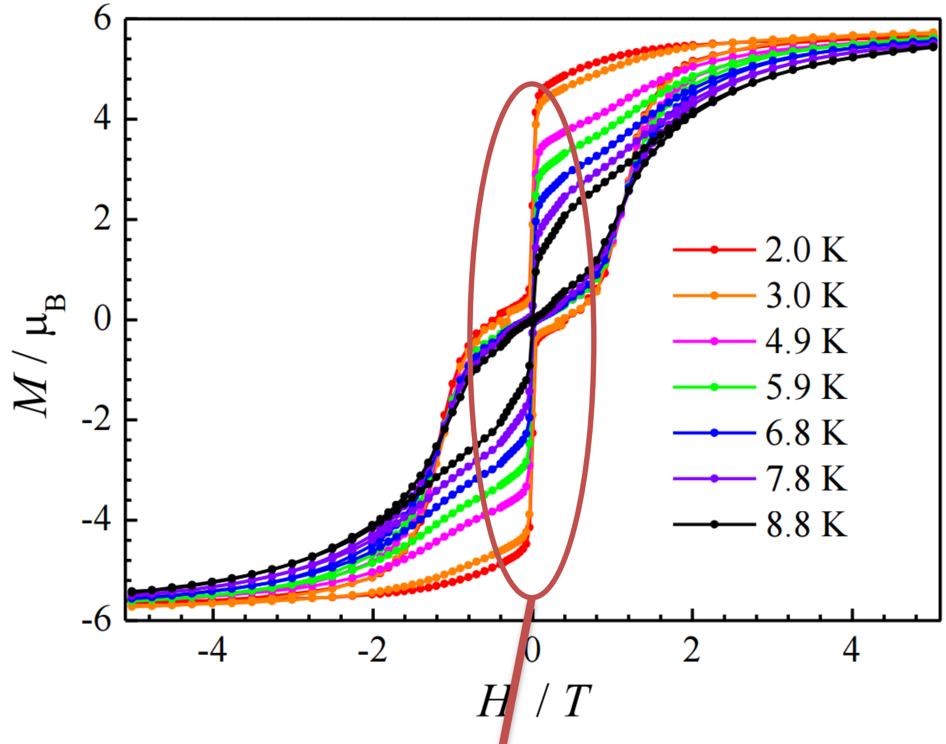
- τ^{-1} vs. T ($\log_{10}$ - $\log_{10}$)



- Raman linear

High-temperature SMMs?

- So Dy^{III} SMMs can have HUGE barriers….are there any drawbacks?

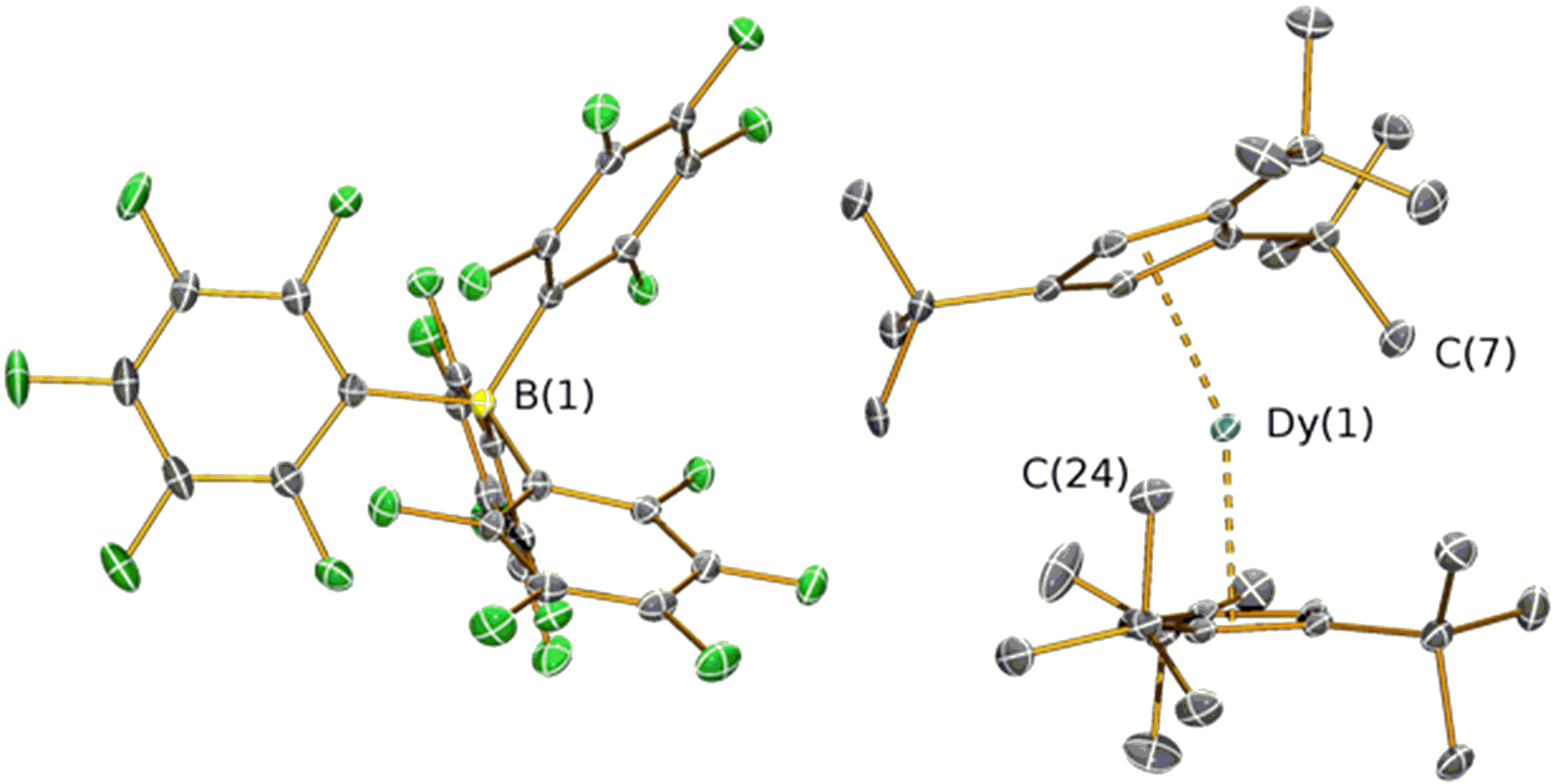


Very fast relaxation at zero field!

[1] Y.-S. Ding *et. al.*, *Angew. Chem. Int. Ed.*, 2016, **55**, 16071

The magic molecule

- Dr David Mills' group (Manchester):



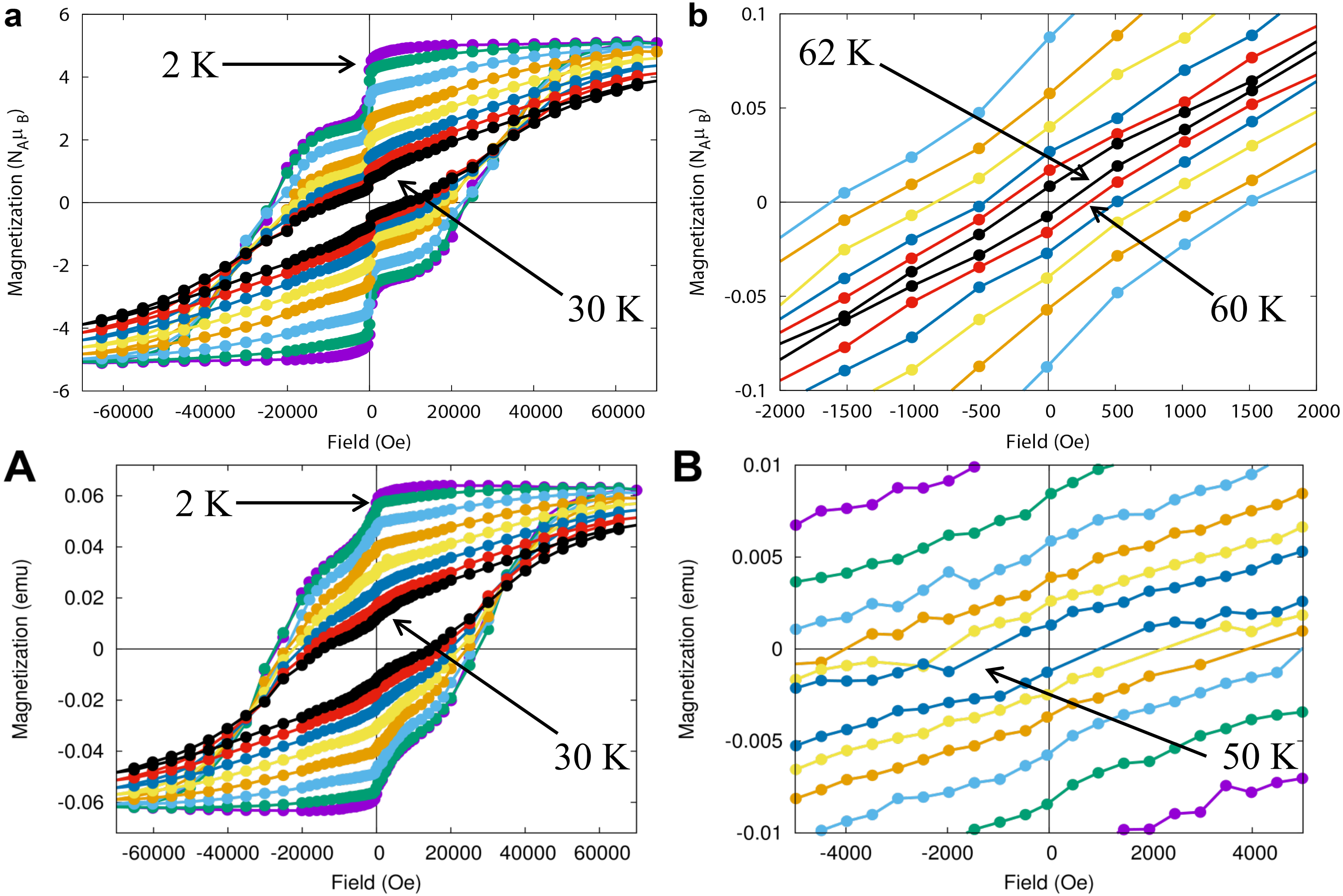
$[DyCp^{ttt}_2][B(C_6F_5)_4]$ Cp-Dy-Cp ~ 152°   Dy-Cp ~ 2.3 Å

[1] C. Goodwin *et al.*, *Nature*, 2017, **548**, 349

Magnetic hysteresis

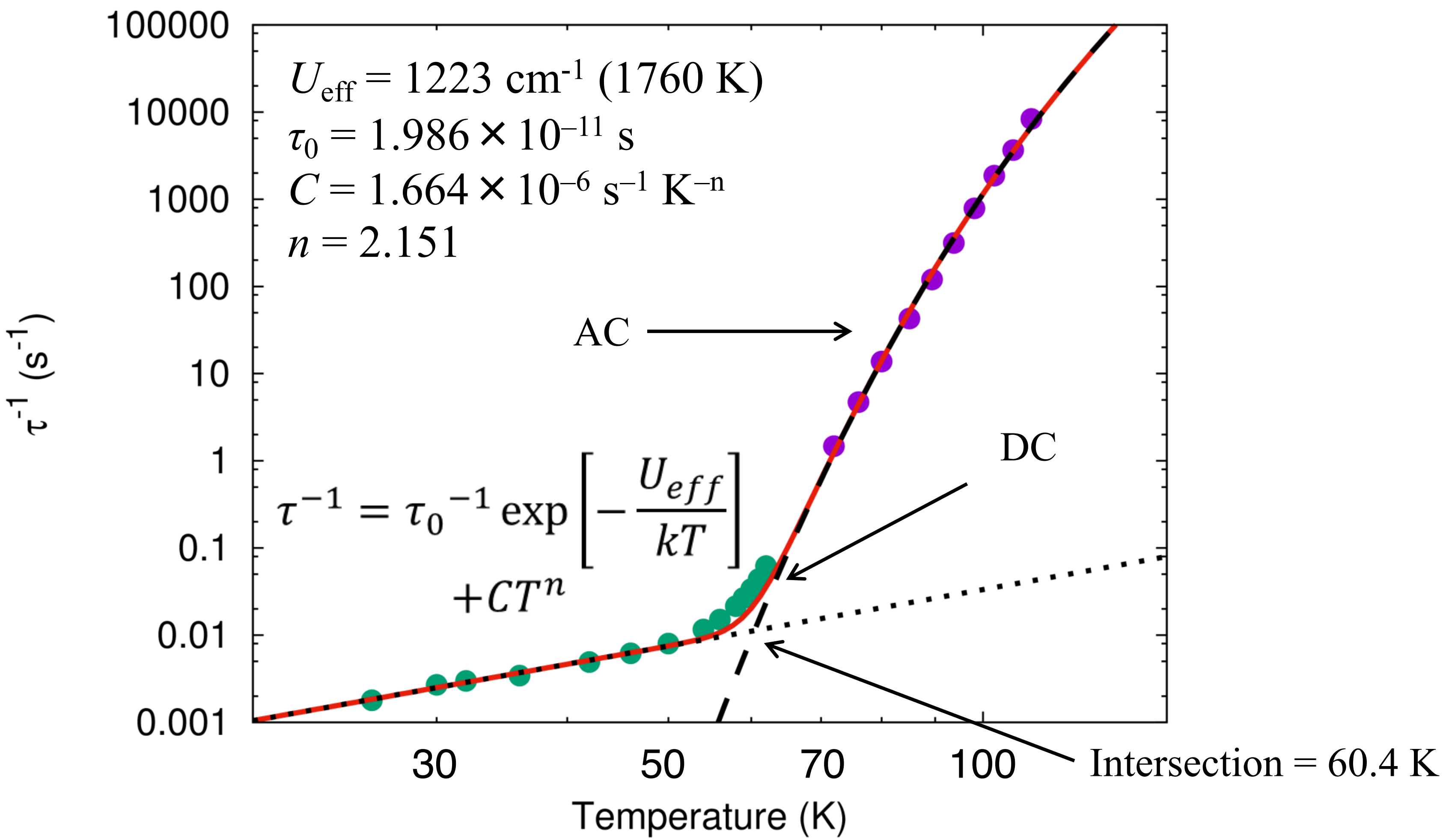
Pure

8 %
Dy@Y



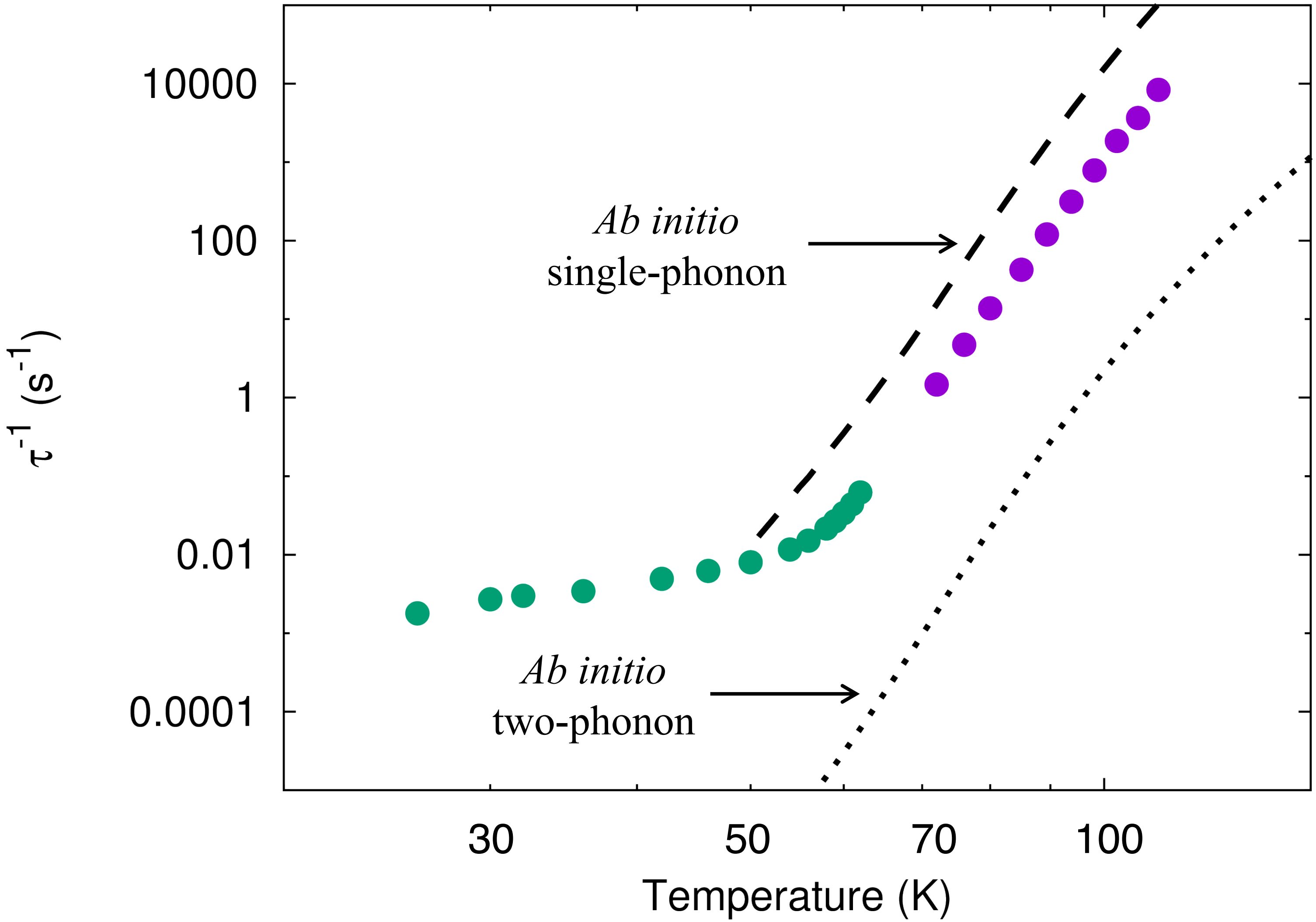
[1] C. Goodwin *et al.*, *Nature*, 2017, **548**, 349

Magnetic relaxation



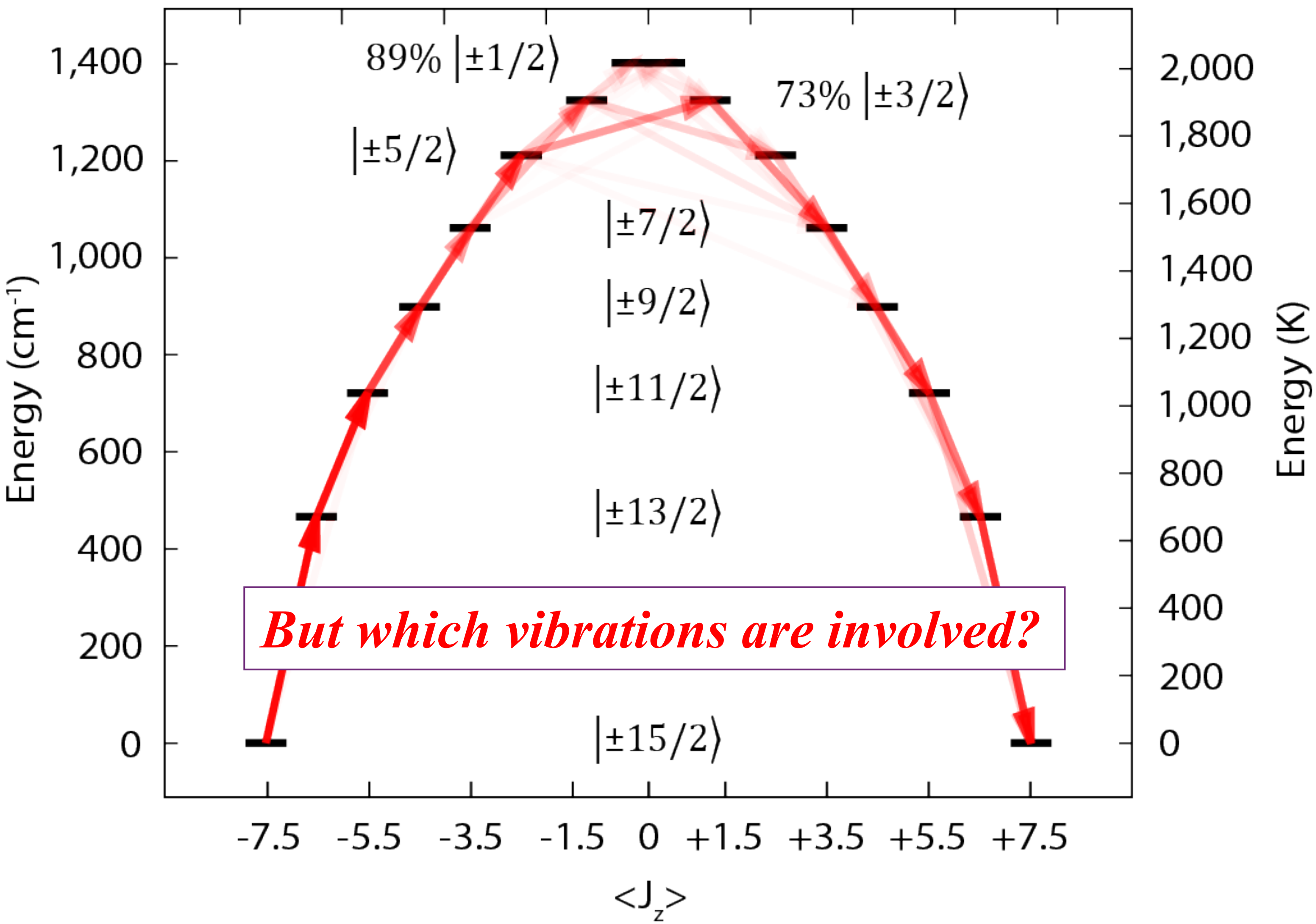
[1] C. Goodwin *et al.*, *Nature*, 2017, **548**, 349

Ab initio relaxation rate



[1] C. Goodwin *et al.*, *Nature*, 2017, **548**, 349

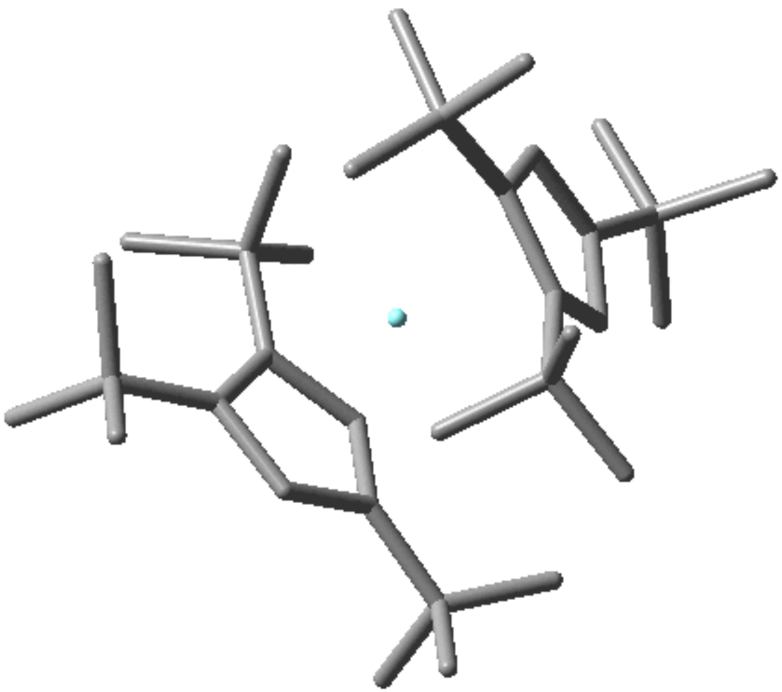
Ab initio relaxation pathway



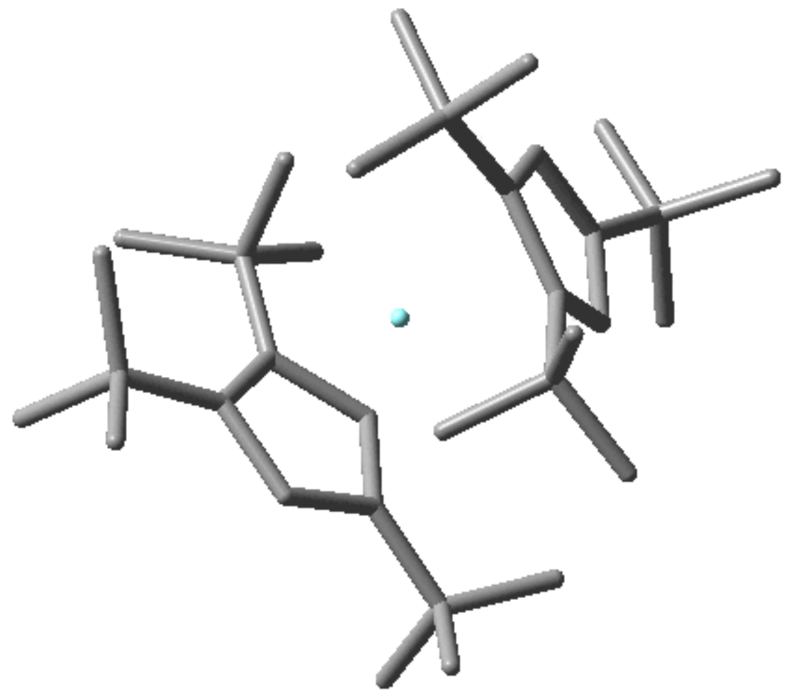
$|-15/2\rangle$
↓
$|-13/2\rangle$
↓
$|-11/2\rangle$
↓
$|-9/2\rangle$
↓
$|-5/2\rangle$
↓
$|+3/2\rangle$
↓
$|+7/2\rangle$
↓
$|+11/2\rangle$
↓
$|+13/2\rangle$
↓
$|+15/2\rangle$

C. Goodwin *et al.*, *Nature*, 2017, **548**, 349

Ab initio relaxation pathway



j = 64

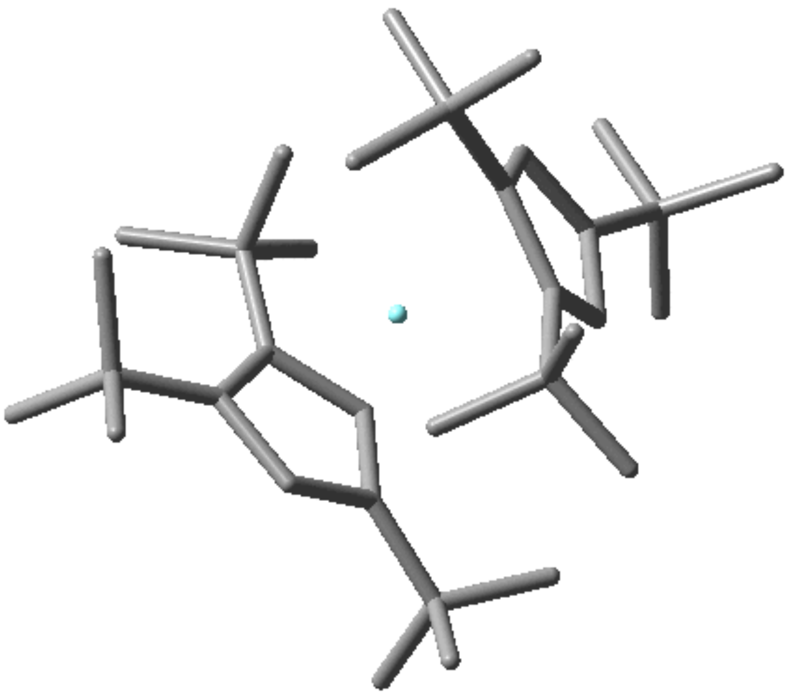


j = 65

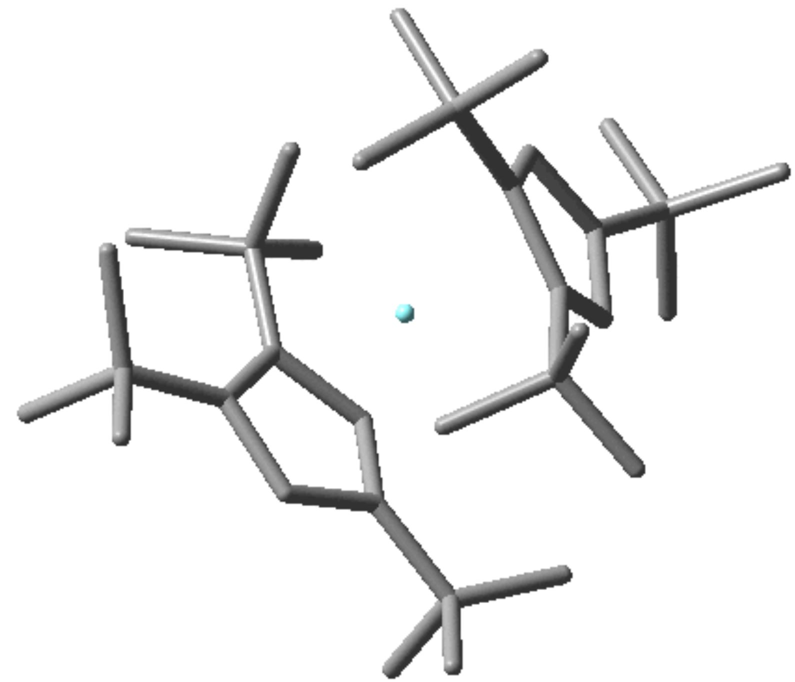
C-H groups of Cp^{ttt}

C. Goodwin *et al.*, *Nature*, 2017, **548**, 349

Ab initio relaxation pathway



$j = 66$



$j = 67$

C-H groups of Cp^{ttt}

C. Goodwin *et al.*, *Nature*, 2017, **548**, 349

Problem set:

1. Consider the plot of magnetic relaxation rates for a lanthanide SMM given below:
    a) How many different relaxation mechanisms are in operation?
    b) Identify which relaxation mechanisms give rise to the different sections.
    c) What mechanism dominates relaxation at 100 K?