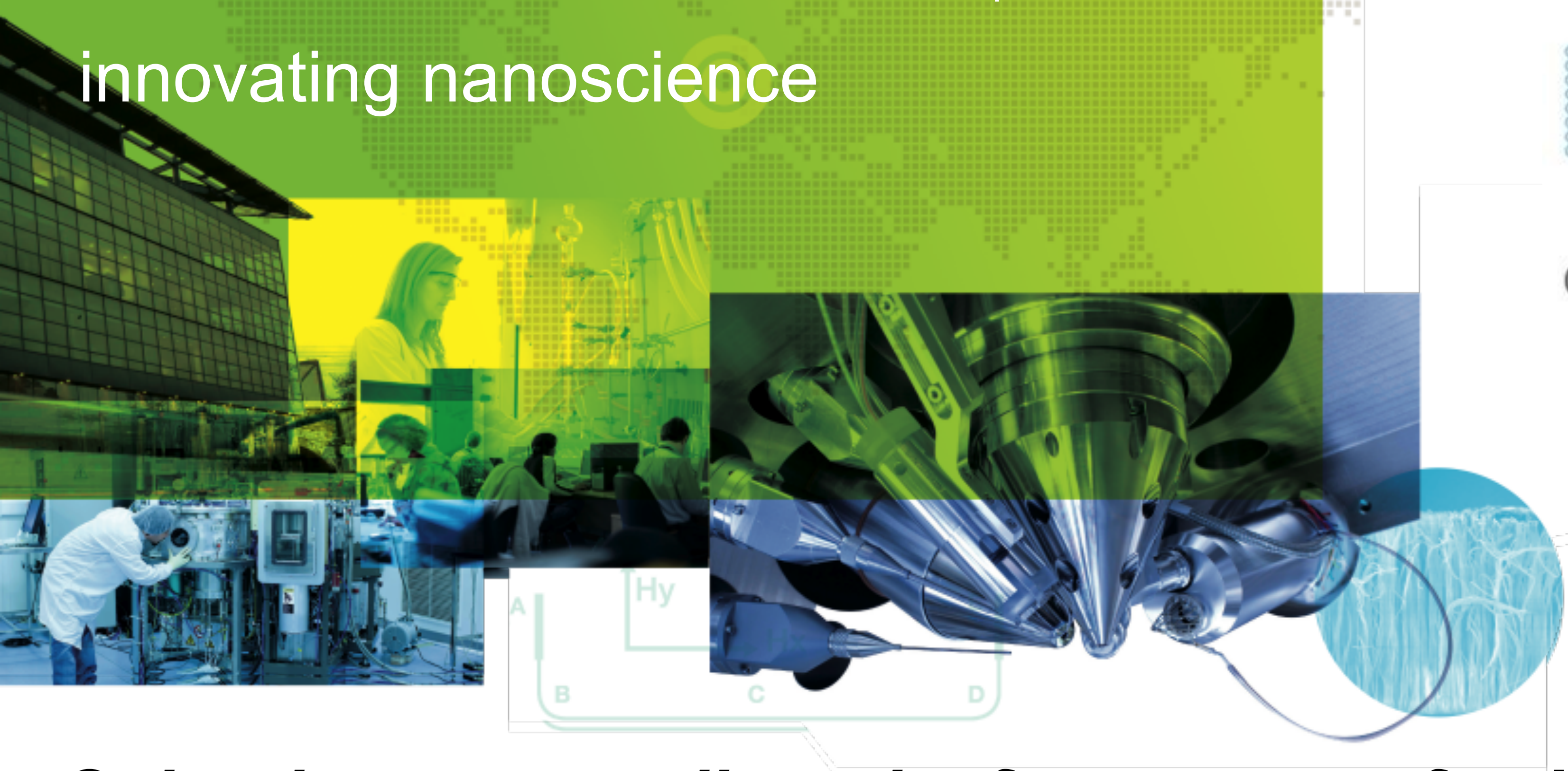
DFT 2019, Barcelona

September 2019



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Spin-phonon coupling: the funny case of spin relaxation in magnetic molecules

Alessandro Lunghi and Stefano Sanvito

School of Physics and CRANN, Trinity College Dublin, IRELAND

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The University of Dublin

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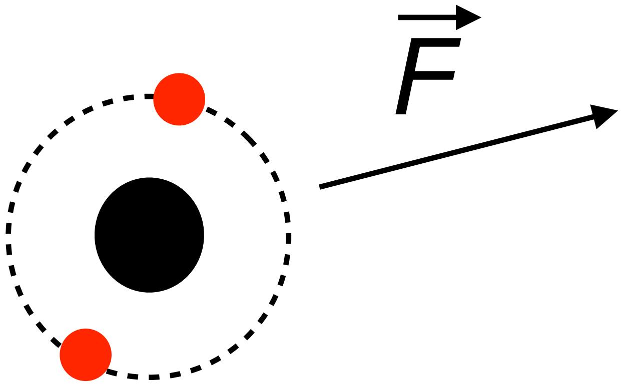
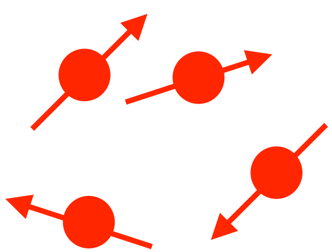
How can we model spin dynamics?

Ions dynamics is conceptually easy



Forces may come from QM (eg DFT)

Spins are “attached” to electrons !!



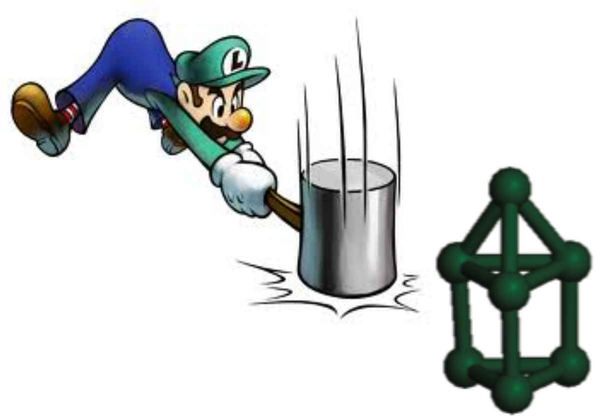
Spins dynamics is electrons dynamics

How can we model spin dynamics?

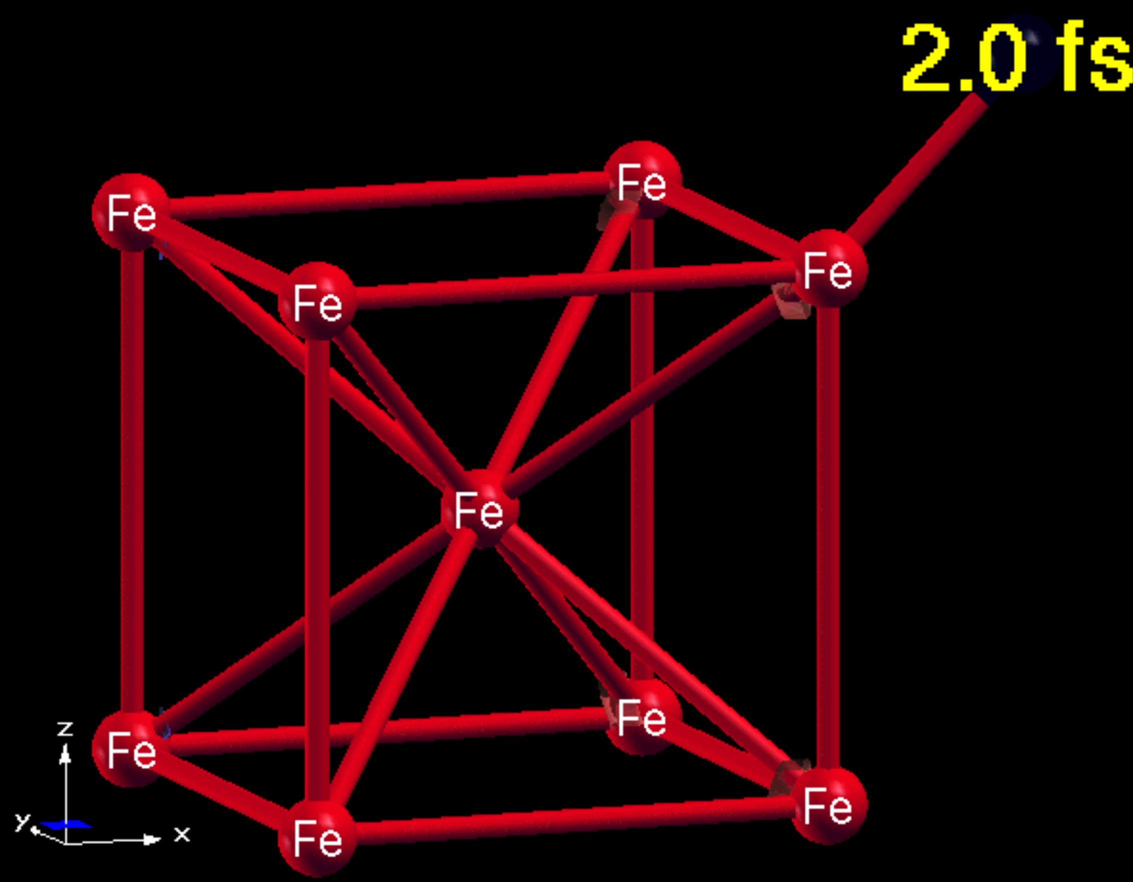
You can “*simply*” use time-dependent quantum mechanics

$$\left[i\mathrm{h}\frac{\partial}{\partial t} - \left(H_{KS}\right)_j^{\alpha\beta}(\boldsymbol{r},t)\right]\varphi_j^{\beta}(\boldsymbol{r},t) = 0$$

$$\left(H_{KS}\right)_i^{\alpha\beta} = \left(-\frac{\nabla_i^2}{2} + v_{H+SO+\mathrm{ext}}(\boldsymbol{r},t) + v_{xc}(\boldsymbol{r},t)\right)\delta^{\alpha\beta} + \left(\boldsymbol{B}_{\mathrm{ext}}(\boldsymbol{r},t) + \boldsymbol{B}_{xc}(\boldsymbol{r},t)\right)\cdot\hat{\boldsymbol{\sigma}}^{\alpha\beta}$$



How can we model spin dynamics?



$$s^z(\boldsymbol{r},t) - s^z_{GS}(\boldsymbol{r})$$

How can we model spin dynamics?

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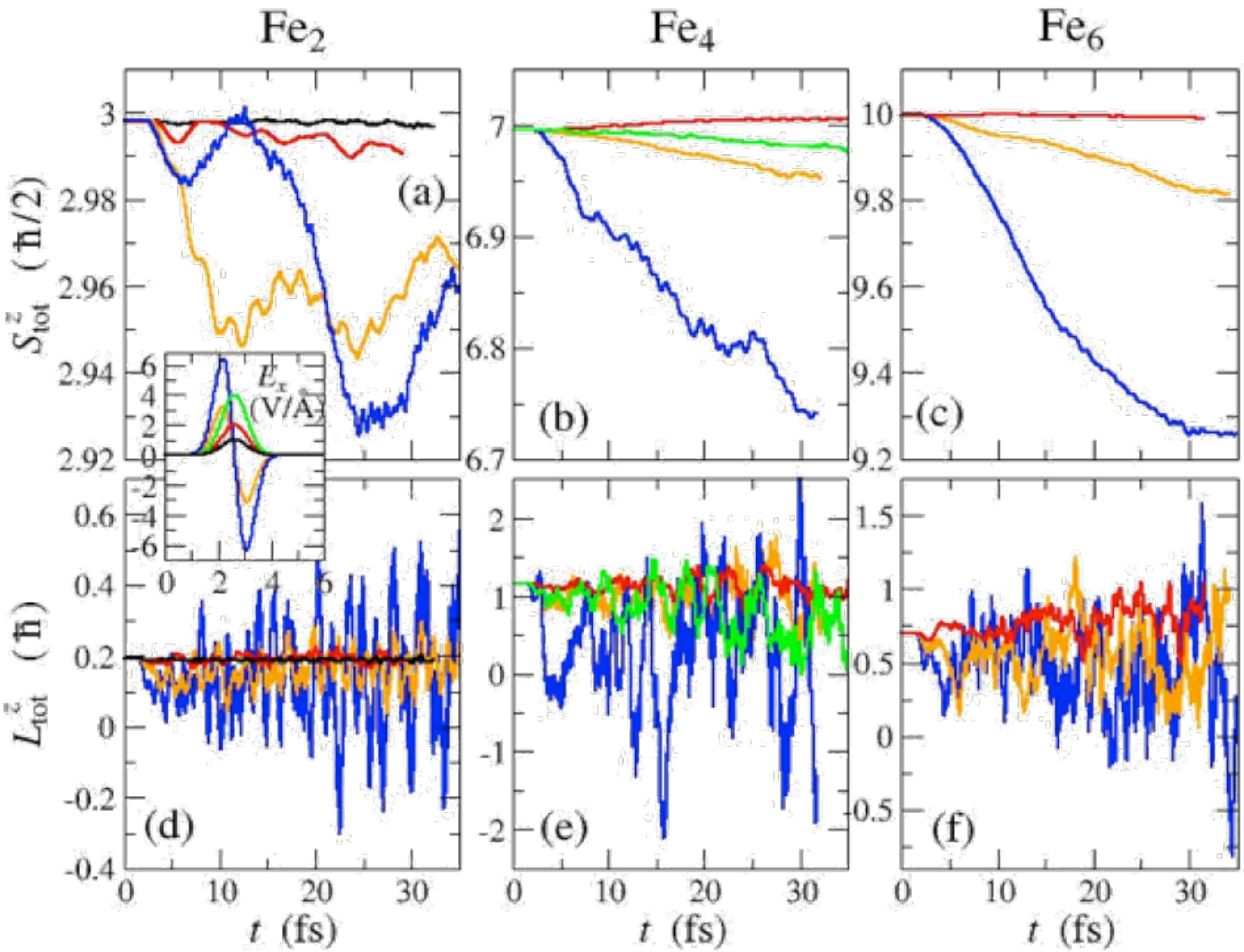
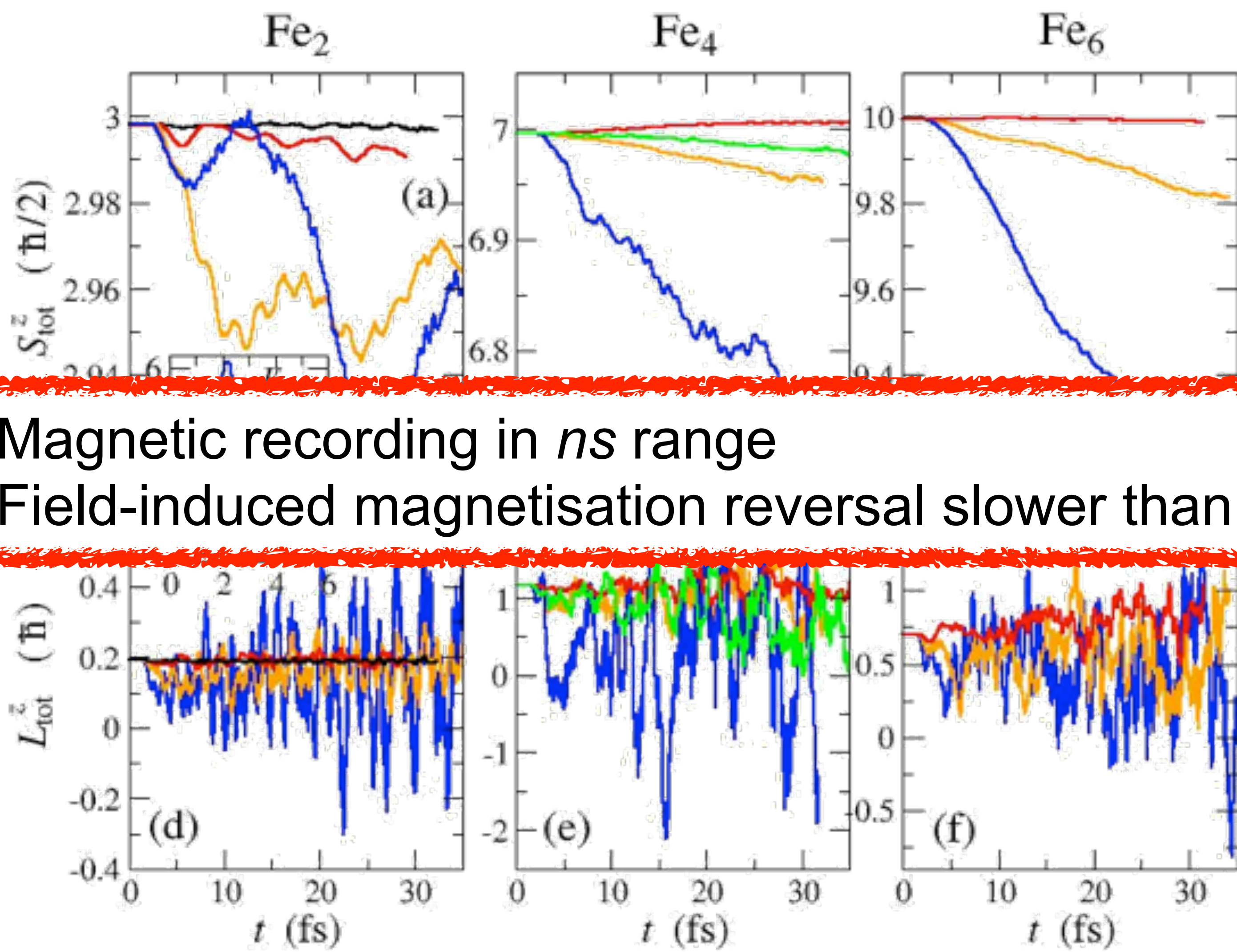


M. Stamenova, J. Simoni and S. Sanvito, arXiv:1511.00864

How can we model spin dynamics?

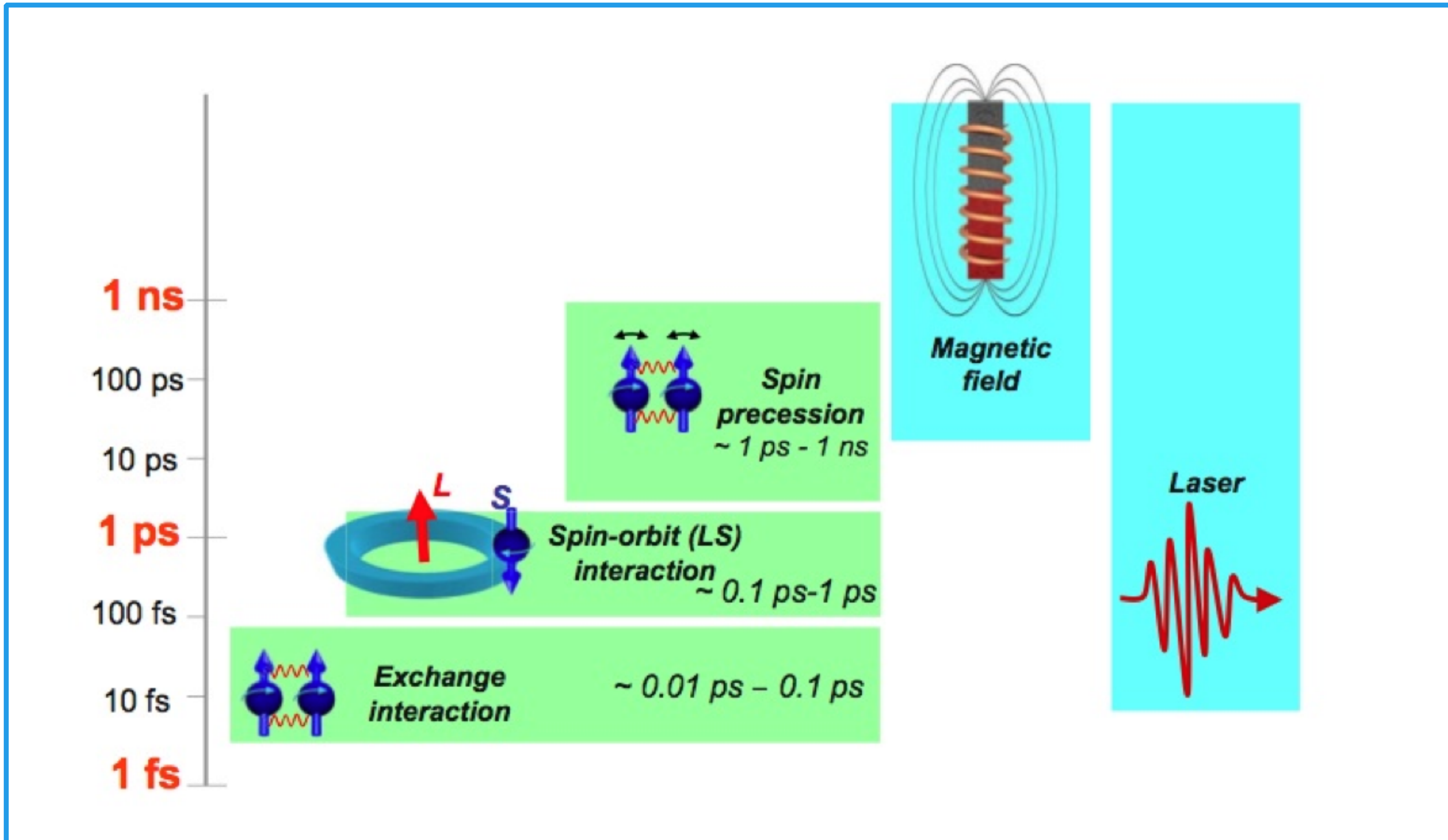


- Magnetic recording in *ns* range
- Field-induced magnetisation reversal slower than *ps*

M. Stamenova, J. Simoni and S. Sanvito, arXiv:1511.00864

How can we model spin dynamics?

Hund's (exchange) coupling saves the day



How can we model spin dynamics?

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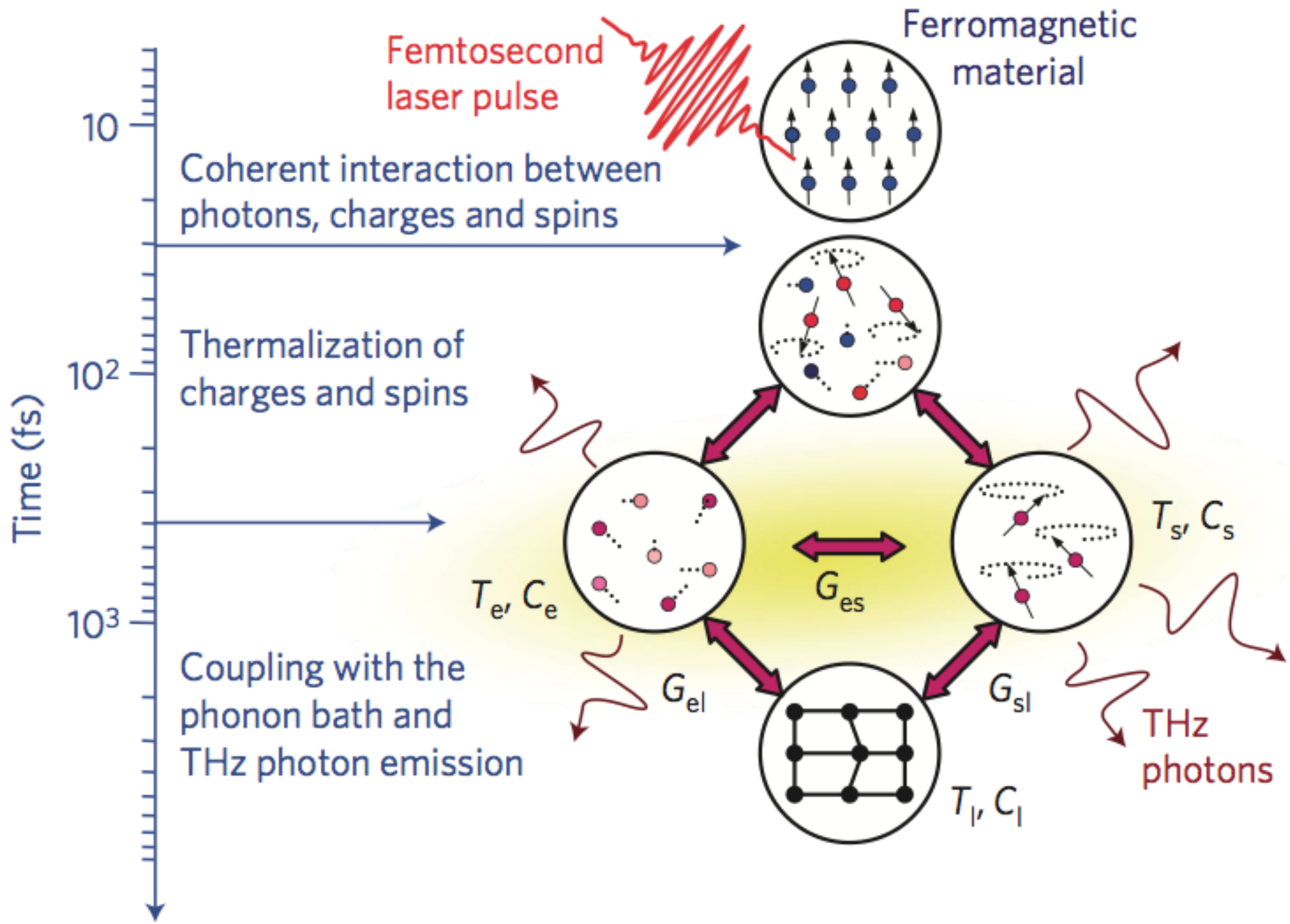
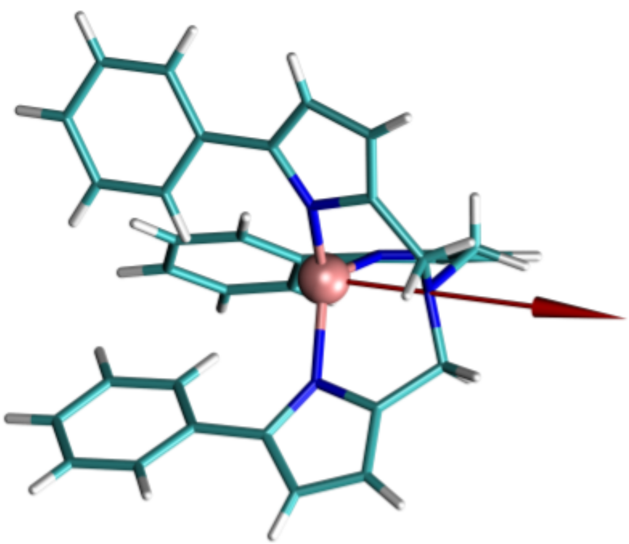
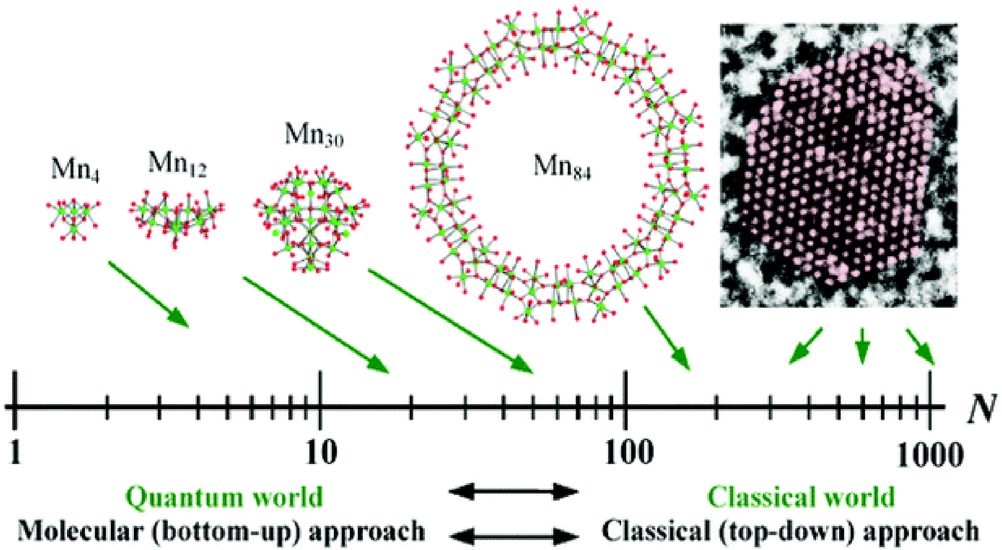
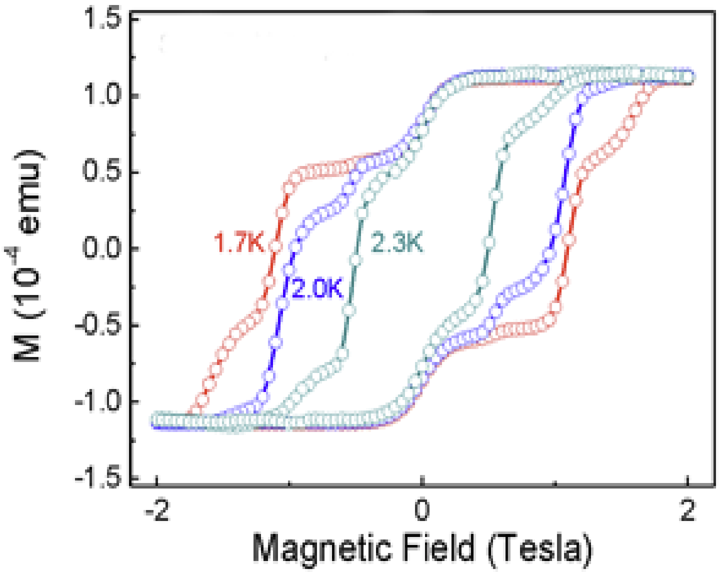


Single molecule magnets:
the relaxation puzzle

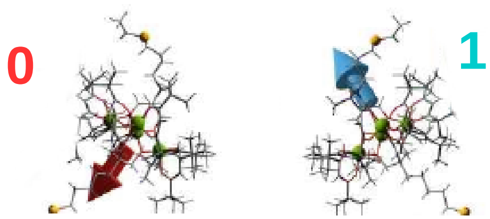


Single molecule magnets

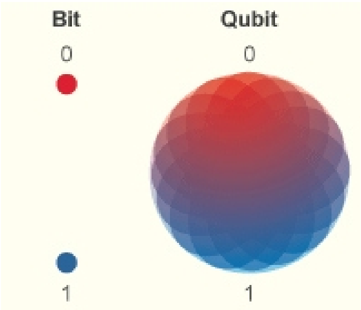




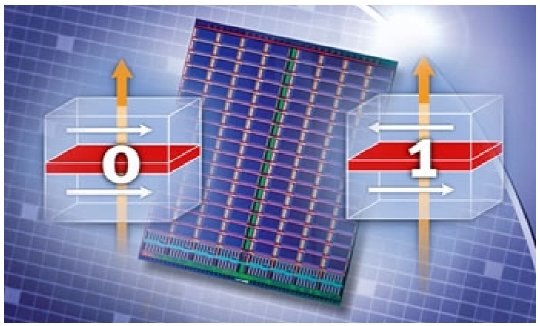
Data storage



Quantum logic



Spintronics



Single molecule magnets

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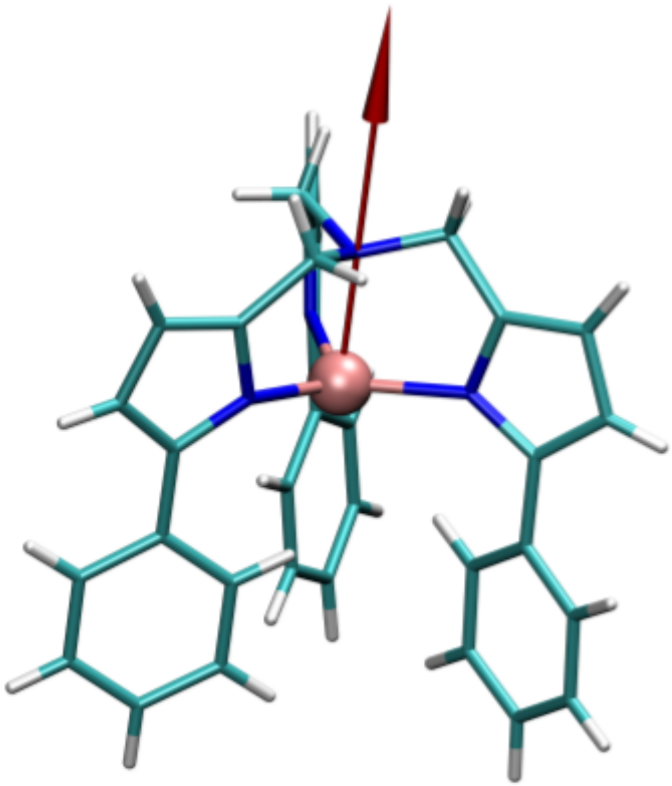
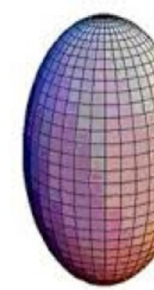
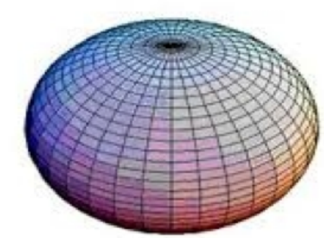
$$H_s = DS_z^2 + E\left(S_x^2 - S_y^2\right)$$



Axial anisotropy $D<0$



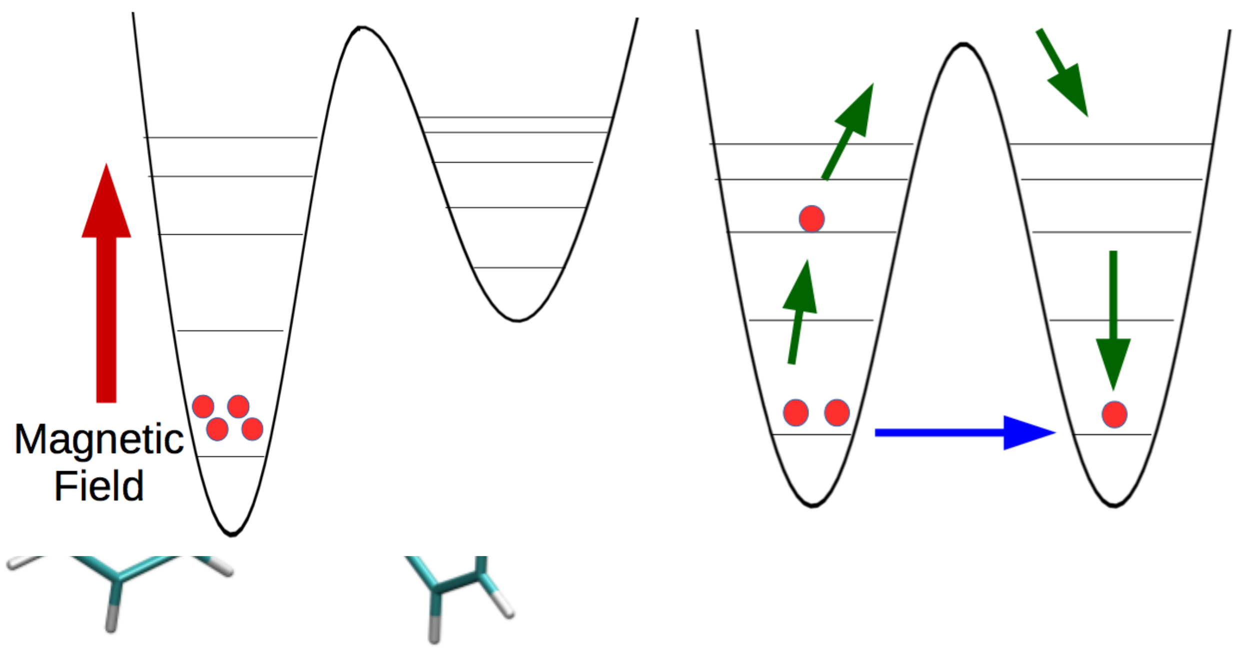
Axial anisotropy $D>0$



Rhomboic anisotropy $E \neq 0$

Spin relaxation

$$H_s = DS_z^2 + E\left(S_x^2 - S_y^2\right)$$



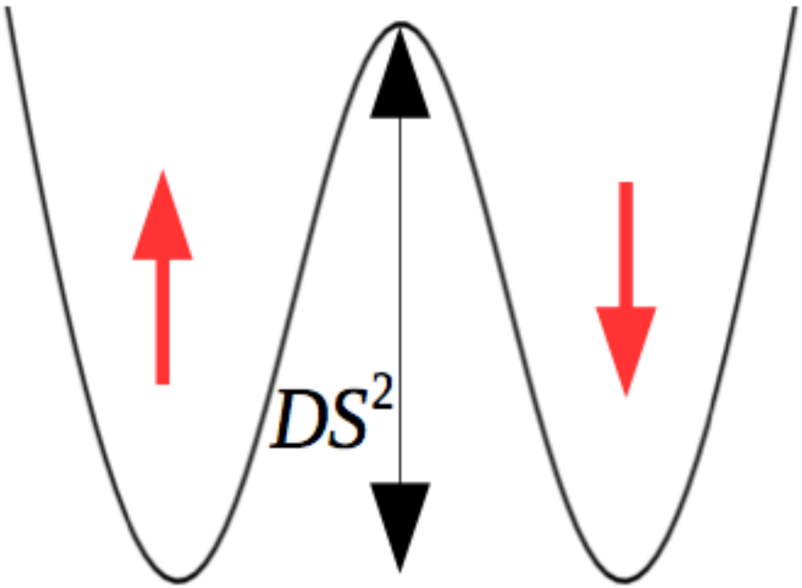
Direct relaxation - quantum tunnelling of the magnetisation

Orbach relaxation - over barrier relaxation

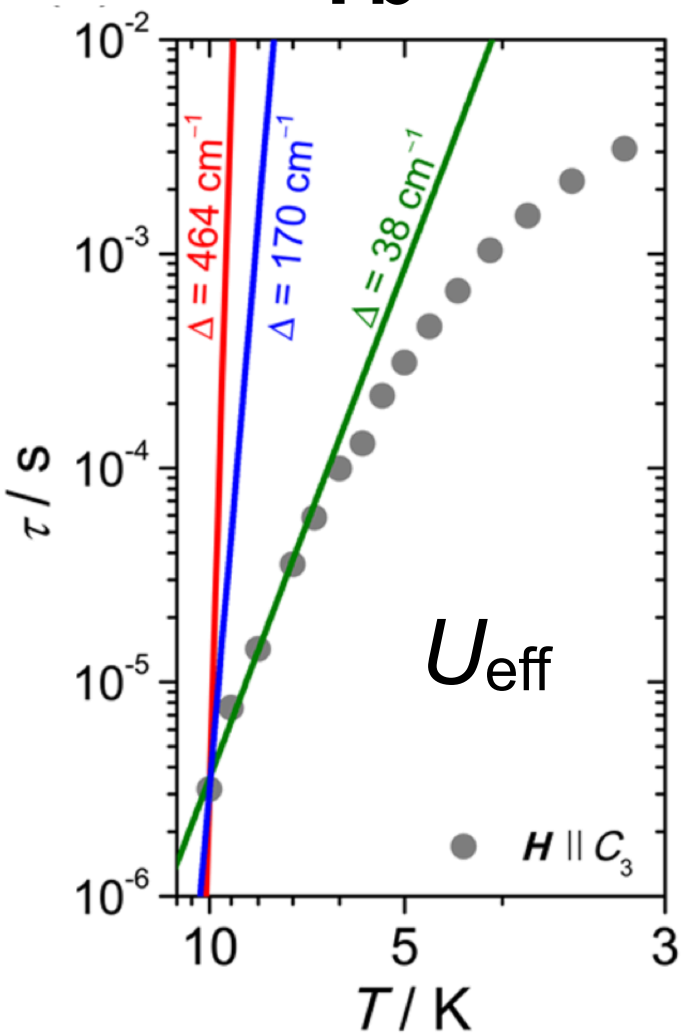
The problem

$$\tau = \tau_0 e^{U_{\mathrm{eff}}/k_{\mathrm{B}}T}$$

$$U_{\mathrm{eff}} = |D|S^2$$



Yb^{3+}



Inorg. Chem. **54**, 7600 (2015)

Co^{2+}

Table 1 | Selected examples for zero-field splitting parameters.

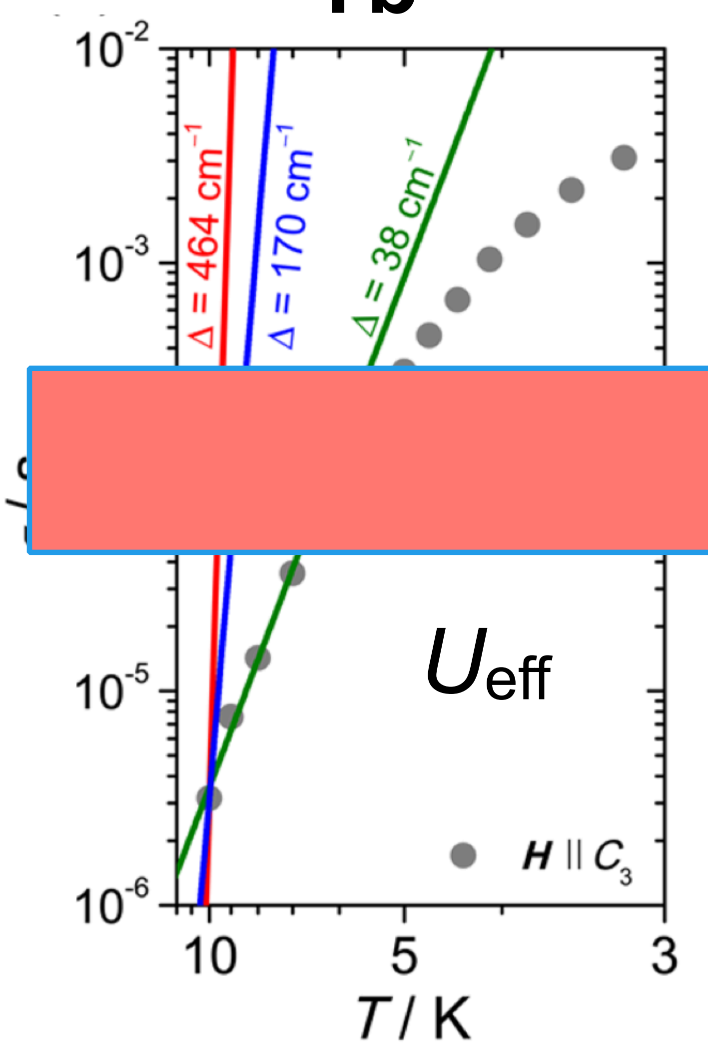
Compound	*D* (cm^{-1})	U_{eff} (cm^{-1})	Literature
$(Ph_4P)_2[Co(C_3S_5)_2]$	-161	33.9	Fataftah *et al.*[19]
$(HNEt_3)_2[Co(pdms)_2]$	-115	118	*
$(Ph_4P)_2[Co(SePh)_4]$	-83	19.1	Zadrozny *et al.*[20]
$[Co(AsPh_3)_2(I)_2]$	-74.7	32.6	Saber *et al.*[21]
$[Co(salbim)_2]$	+67	—	Šebová *et al.*[22]
$(Ph_4P)_2[Co(SPh)_4]$	-62	21.1	Zadrozny *et al.*[20]
$[Co\{NtBu)_3SMe\}_2]$	-58	75†	Carl *et al.*[24]
$[Co(acac)_2(H_2O)_2]$	+57	—	Gómez-Coca *et al.*[23]

Reported zero-field splitting *D*-values with $|D| > 50\ cm^{-1}$ and relaxation energy barriers U_{eff} of tetrahedral cobalt(II) complexes.
*This work
†In a 1,500 Oe applied magnetic field.

S=3/2

Nature Comm. **7**, 10467 (2016)

Yb^{3+}



Inorg. Chem. **54**, 7600 (2015)

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*This work
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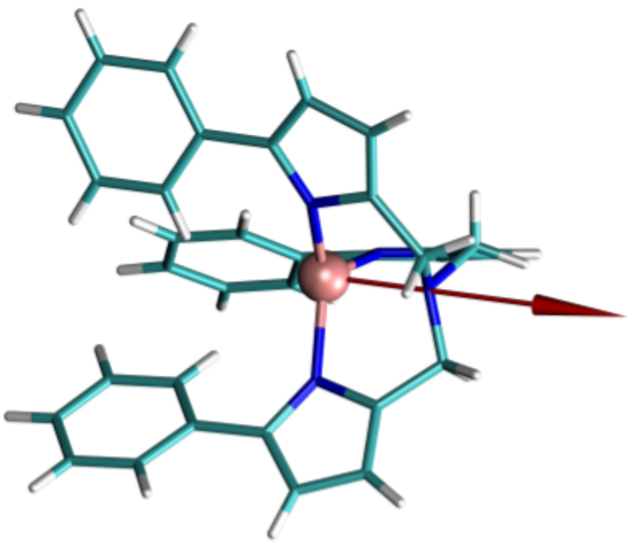
S=3/2

Nature Comm. **7**, 10467 (2016)

WHY ?

Microscopic picture

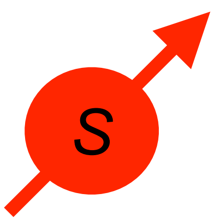


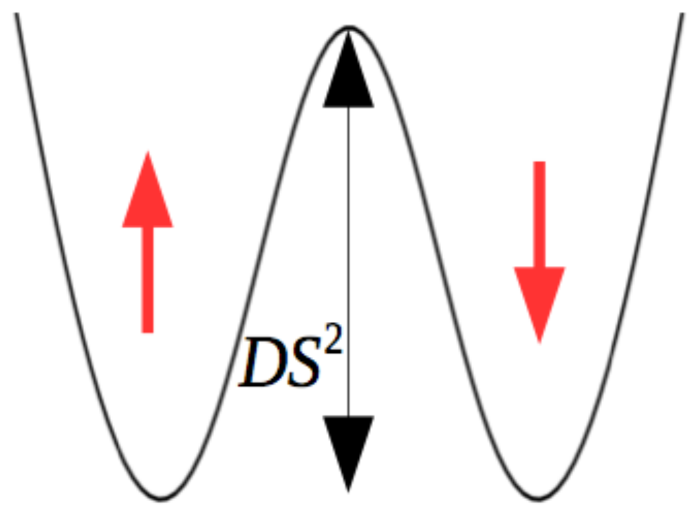
A. Lunghi, F. Totti, R. Sessoli and S. Sanvito, Nature Comm. **8**, 14620 (2017)

Interaction at play

$$H = \boxed{H_0} + H_{\mathrm{ph}} + H_{\mathrm{s-ph}}$$

$$H_0 = DS_z^2 + E\left(S_x^2 - S_y^2\right)$$





Interaction at play

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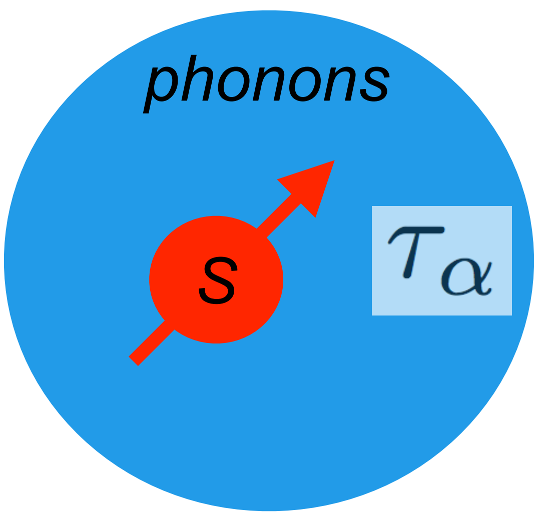
$$H = H_0 + \boxed{H_{\mathrm{ph}}} + H_{\mathrm{s-ph}}$$

$$H_{\mathrm{ph}} = \sum_{\alpha} \hbar\omega_{\alpha} \left(\frac{1}{2} + n_{\alpha}\right)$$



$$\hat{n}_{\alpha} = a_{\alpha}^{\dagger} a_{\alpha} \qquad \hat{q}_{\alpha} = \frac{1}{\sqrt{2}}(a_{\alpha}^{\dagger} + a_{\alpha})$$

$$\boxed{H_0 = DS_z^2 + E\left(S_x^2 - S_y^2\right)}$$

Interaction at play

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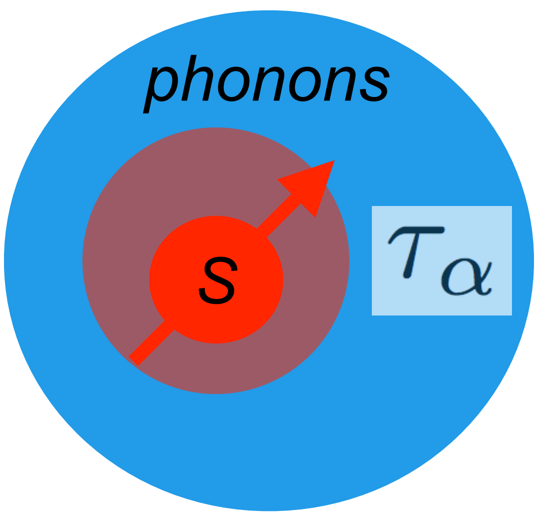
$$H = H_0 + H_{\mathrm{ph}} + \boxed{H_{\mathrm{s-ph}}}$$

$$H_{\mathrm{s-ph}} = \sum_\alpha \left(\frac{\partial H_0}{\partial q_\alpha}\right)_0 \hat{q}_\alpha$$



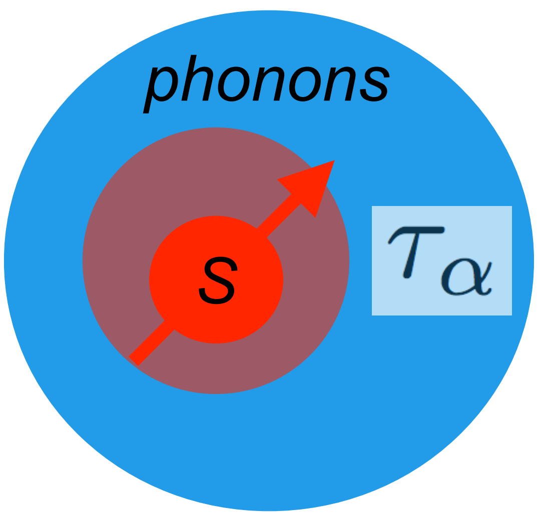
$$\hat{q}_\alpha = \frac{1}{\sqrt{2}}\left(a_\alpha^\dagger + a_\alpha\right)$$

$$H_{\mathrm{ph}} = \sum_\alpha \hbar\omega_\alpha \left(\frac{1}{2} + n_\alpha\right) + \sum_{\alpha,\beta,\gamma} V_{\alpha\beta\gamma} q_\alpha q_\beta q_\gamma$$

$$H_0 = DS_z^2 + E\left(S_x^2 - S_y^2\right)$$

Interaction at play

$$H = H_0 + H_{\mathrm{ph}} + H_{\mathrm{s-ph}}$$



$$H_{\mathrm{s-ph}} = \sum_\alpha \left(\frac{\partial H_0}{\partial q_\alpha}\right)_0 \hat{q}_\alpha$$

$$H_{\mathrm{ph}} = \sum_\alpha \hbar\omega_\alpha \left(\frac{1}{2} + n_\alpha\right) + \sum_{\alpha,\beta,\gamma} V_{\alpha\beta\gamma} q_\alpha q_\beta q_\gamma$$

$$H_0 = DS_z^2 + E\left(S_x^2 - S_y^2\right)$$

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The dynamics

A. Lunghi, F. Totti, R. Sessoli and S. Sanvito, Nature Comm. **8**, 14620 (2017)

The dynamics

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In principle ….

$$\frac{d\rho(t)}{dt} = \frac{i}{\hbar}[\rho(t), H]$$

Lattice ***always*** in thermal equilibrium

$$\tau_{\mathrm{S}} \gg \tau_{\mathrm{ph}}$$

Redfield equation for spin density matrix

$$\frac{\mathrm{d}p_a^{\mathrm{S}}(t)}{\mathrm{d}t} = \frac{2}{\hbar^2}\sum_\alpha \left|\left\langle a\left|\frac{\partial H_{\mathrm{S}}}{\partial q_\alpha}\right|b\right\rangle\right|^2 G(\omega_{ab}, \omega_\alpha)\, p_b^{\mathrm{S}}$$

$$\omega_{ab} = (E_a - E_b)/\hbar.$$

The dynamics

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What can I do about phonon-phonon interaction ?

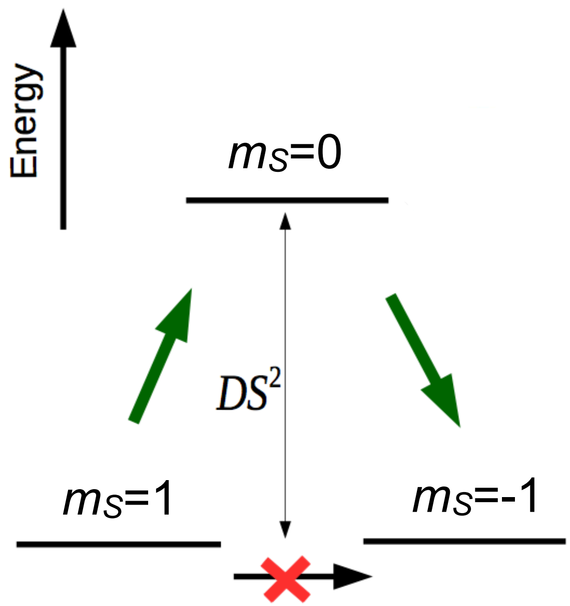
$$H_{\mathrm{ph}} = \sum_{\alpha} \hbar\omega_{\alpha} \left(\frac{1}{2} + n_{\alpha} \right) + \cancel{\sum_{\alpha,\beta,\gamma} V_{\alpha\beta\gamma} q_{\alpha} q_{\beta} q_{\gamma}}$$

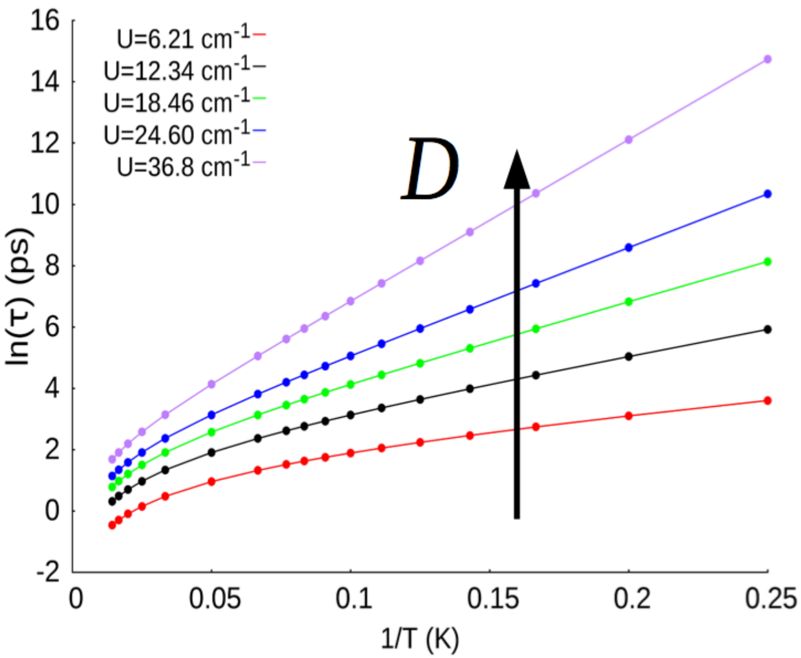
R. Orbach, Proc. R. Soc. A **264**, 458, (1961)

Orbach mechanism

One phonon only $\hbar\omega$

$$V = \left| \left\langle a \left| \frac{\partial H_S}{\partial q_\alpha} \right| b \right\rangle \right|^2$$





$$\tau = 1/V\, e^{U_{\text{eff}}/kT}$$

$$U_{\text{eff}} = |D|S^2$$

The dynamics

What can I do about phonon-phonon interaction ?

$$H_{\rm ph} = \sum_{\alpha} \hbar\omega_\alpha \left(\frac{1}{2} + n_\alpha \right) + \sum_{\alpha,\beta,\gamma} V_{\alpha\beta\gamma} q_\alpha q_\beta q_\gamma$$

The dynamics

What can I do about phonon-phonon interaction ?

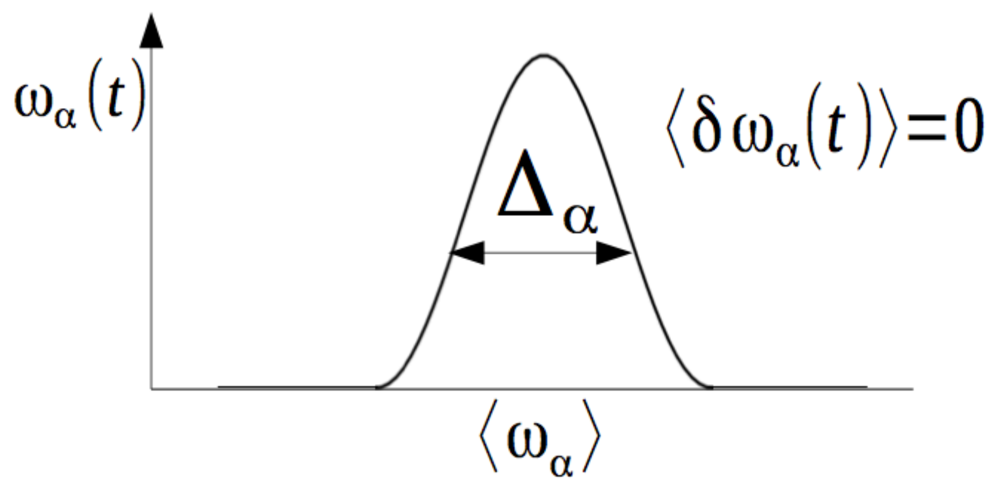
$$H_{\rm ph} = \sum_{\alpha} \hbar\omega_{\alpha} \left(\frac{1}{2} + n_{\alpha}\right) + \sum_{\alpha,\beta,\gamma} V_{\alpha\beta\gamma} q_{\alpha} q_{\beta} q_{\gamma}$$

$$H_{\rm ph} = \sum_{\alpha} \hbar\omega_{\alpha}(t) \left(\frac{1}{2} + n_{\alpha}\right)$$

Stochastic treatment of lattice dynamics

$$H_{\mathrm{ph}} = \sum_{\alpha} \hbar\omega_{\alpha}(t)\left(\frac{1}{2} + n_{\alpha}\right)$$

$$\omega_{\alpha}(t) = \langle\omega_{\alpha}\rangle + \delta\omega_{\alpha}(t)$$



R. Kubo, J. of Math. Phys. **4**, 174 (1963)

Stochastic treatment of lattice dynamics

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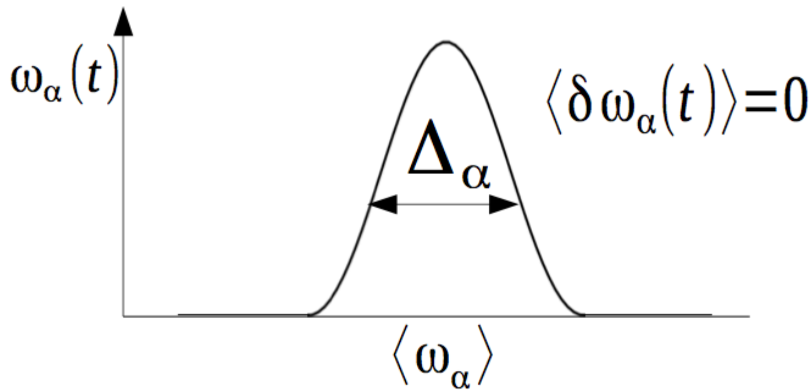
$$G(\omega_{ab},\omega_\alpha) = \frac{\Delta_\alpha}{\Delta_\alpha^2 + (\omega_{ab}-\omega_\alpha)^2}\bar{n}_\alpha + \frac{\Delta_\alpha}{\Delta_\alpha^2 + (\omega_{ab}+\omega_\alpha)^2}(\bar{n}_\alpha + 1)$$



$$\Delta_\alpha^2 = \frac{\partial \langle H_{\rm ph}\rangle}{\partial (kT)} = \frac{(\hbar\omega_\alpha)^2\, e^{\hbar\omega_\alpha/kT}}{(e^{\hbar\omega_\alpha/kT}-1)^2}$$

Non-resonant: *Orbach mechanism*

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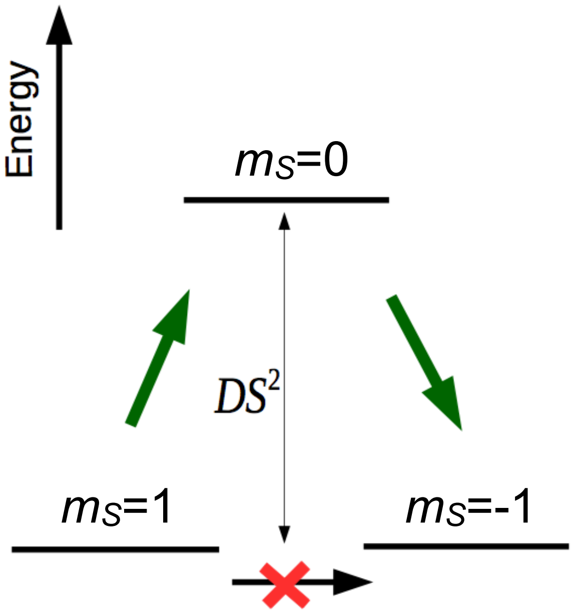
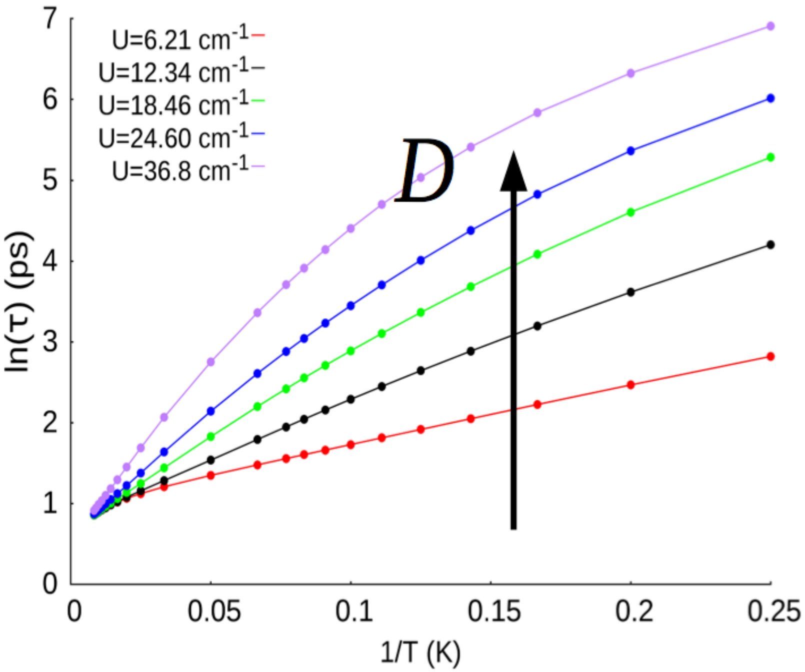
One phonon only $\hbar\omega$

$$V = \left| \left\langle a \left| \frac{\partial H_S}{\partial q_\alpha} \right| b \right\rangle \right|^2$$





$$\tau = \frac{\hbar\omega}{V}\left[e^{\frac{1}{2}\frac{\hbar\omega}{kT}} + \frac{(|D|S^2 - \hbar\omega)^2}{(\hbar\omega)^2} e^{\frac{3}{2}\frac{\hbar\omega}{kT}}\right]$$

Non-resonant: *direct relaxation*

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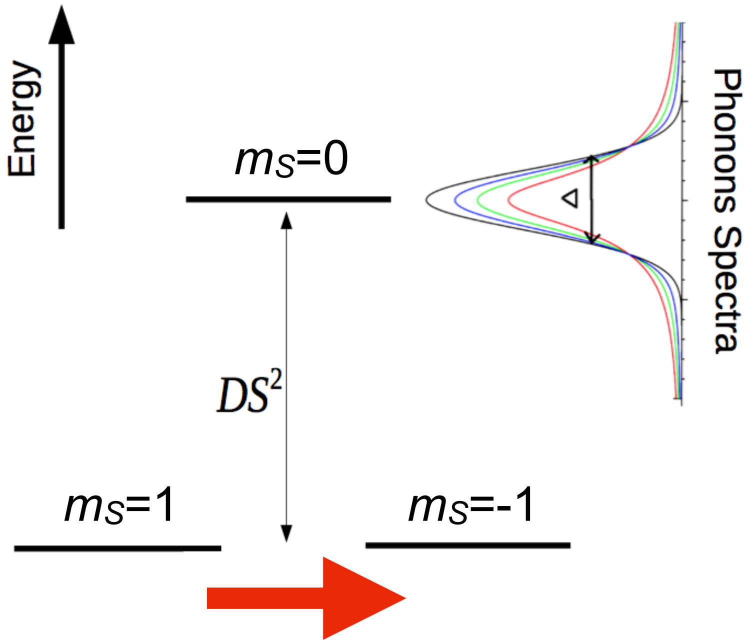
One phonon only $\hbar\omega$

$$V = \left| \left\langle a \left| \frac{\partial H_S}{\partial q_\alpha} \right| b \right\rangle \right|^2$$



$$\tau = \frac{\hbar\omega}{V} e^{\frac{1}{2}\frac{\hbar\omega}{kT}}$$

Stochastic treatment of lattice dynamics

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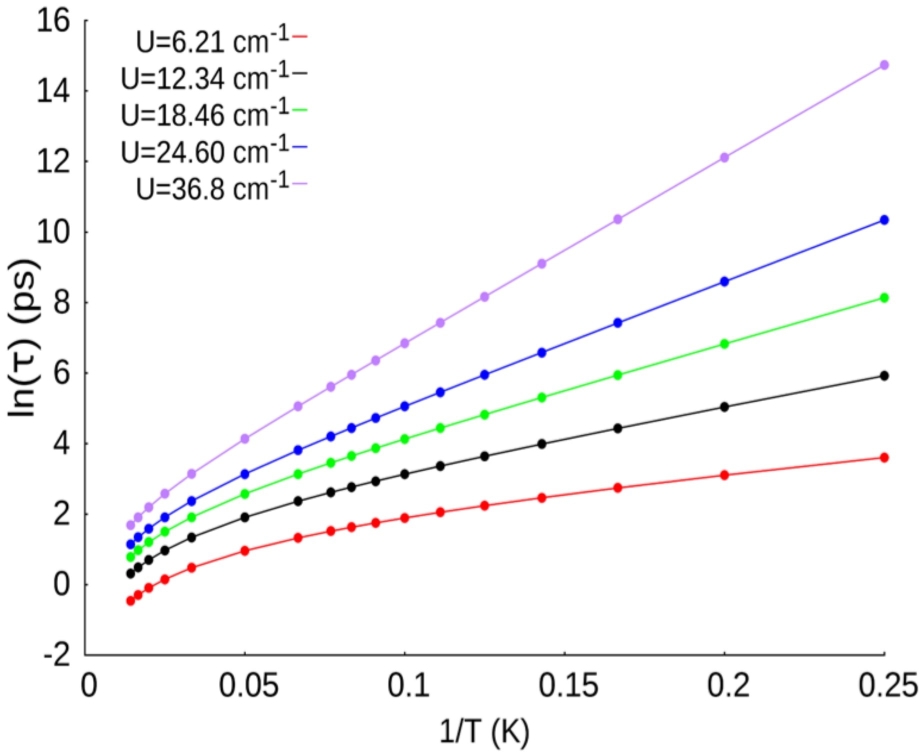
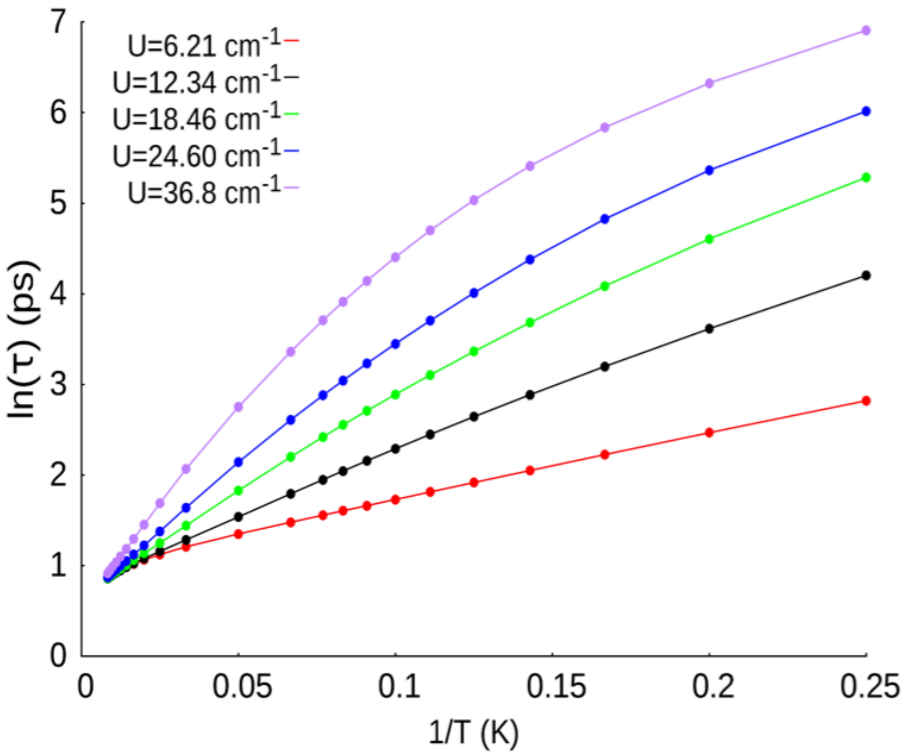
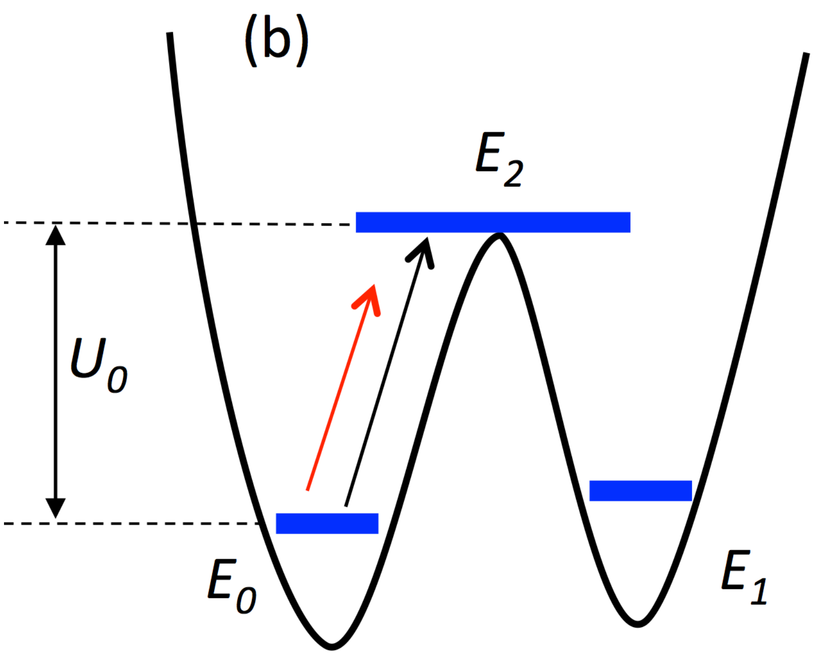
Harmonic phonon

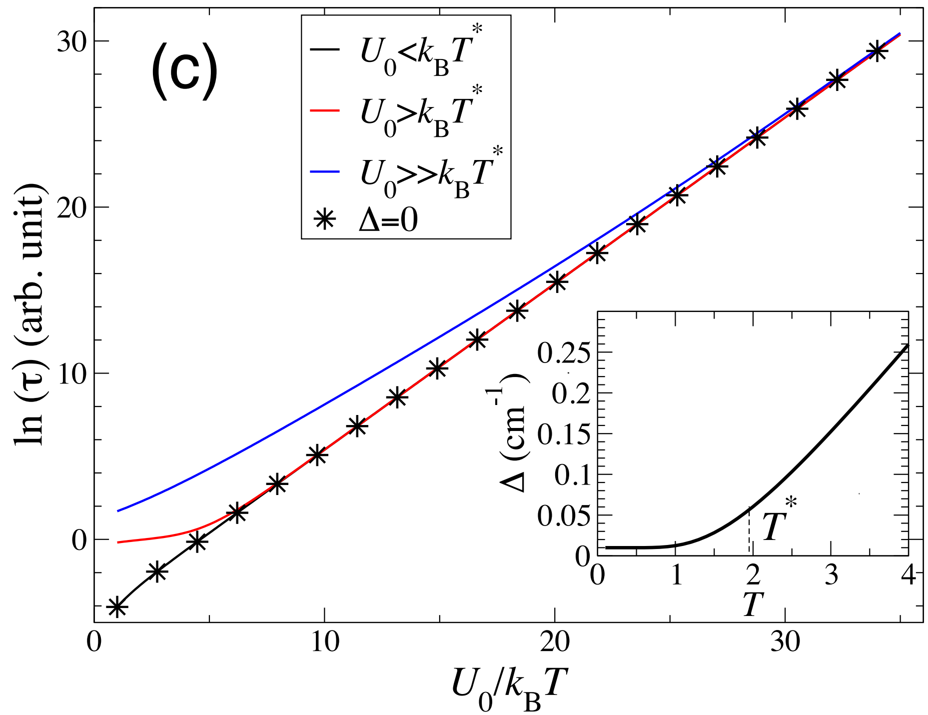


Anharmonic phonon



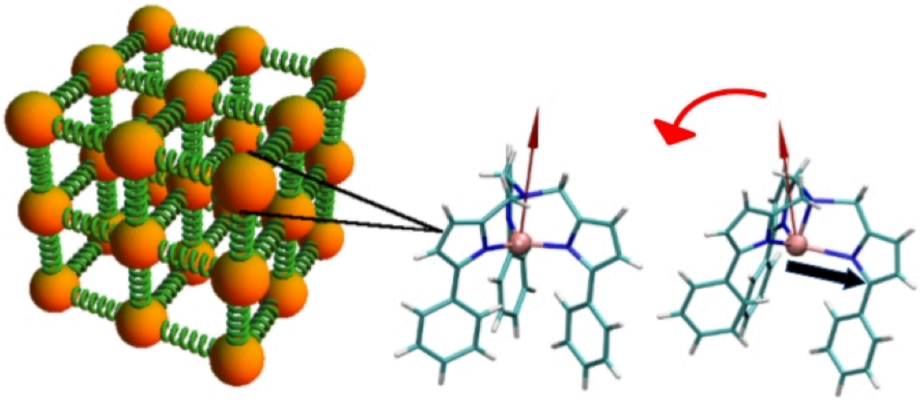
T-dependent phonon linewidth





$$\Delta_\alpha^2 = \frac{\partial \langle H_{\rm ph} \rangle}{\partial (kT)} = \frac{(\hbar\omega_\alpha)^2 \, e^{\hbar\omega_\alpha/kT}}{(e^{\hbar\omega_\alpha/kT} - 1)^2}$$

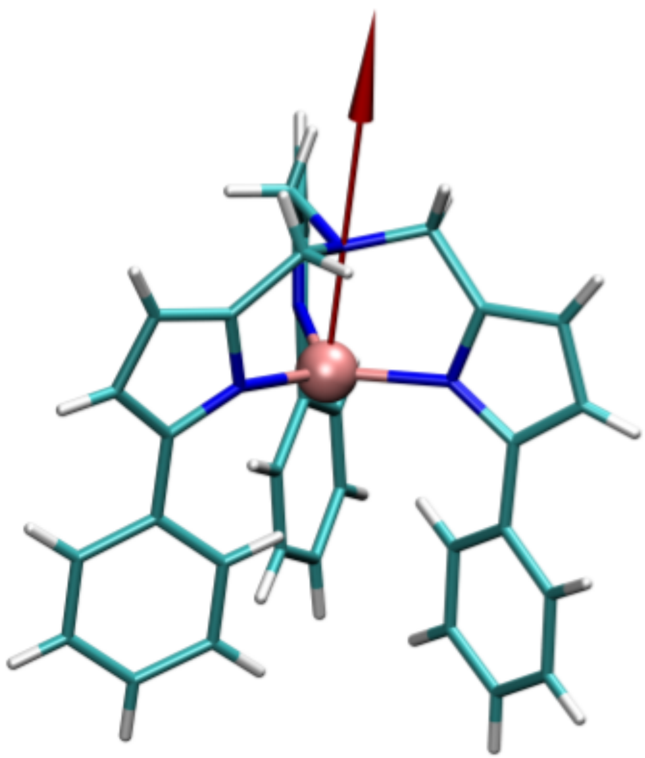
First principles level



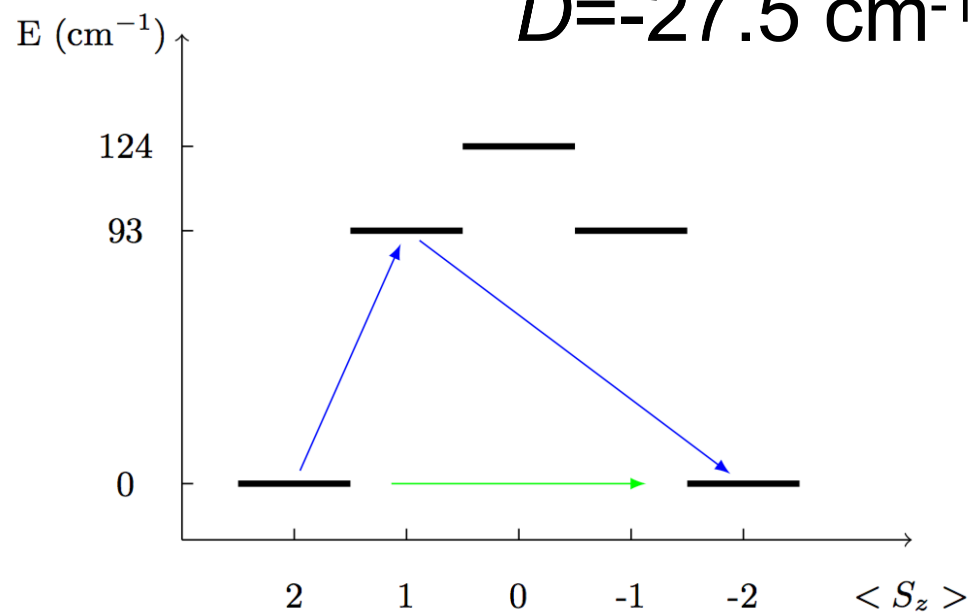
The case of Fe(II)

$[(tph^{Ph})Fe]^-$

S=2



D=-27.5 cm^{-1}



W. H. Harmann, J. Am. Chem. Soc. **132**, 18115 (2010)

General calculation scheme

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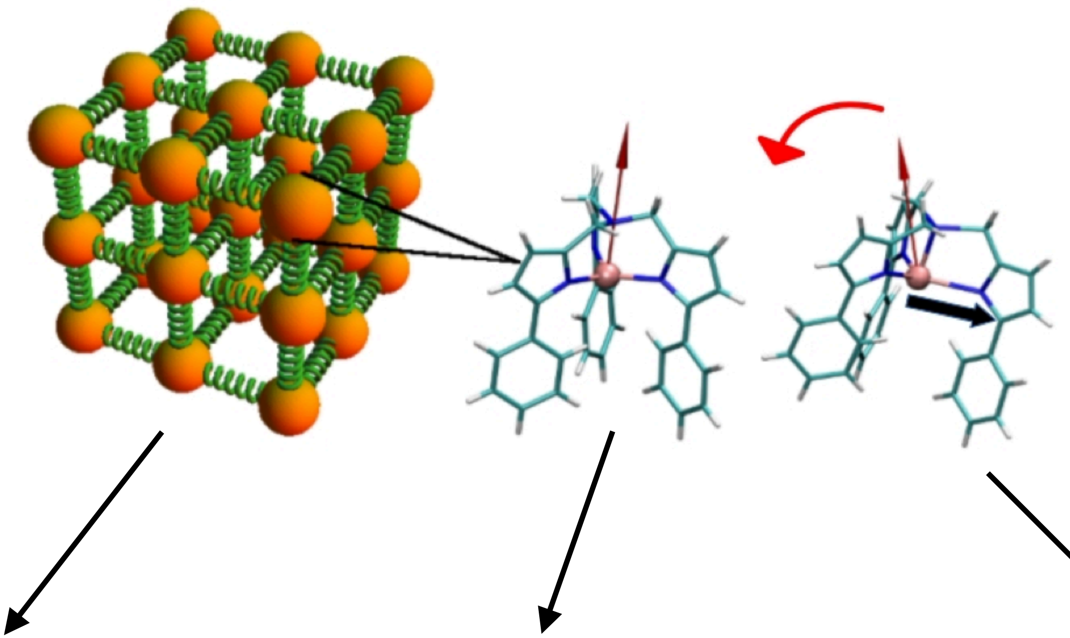

Phonons

Hamiltonian

Dynamics

From DFT at the Gamma point

From post Hartee-Fock (CASSCF)

From Redfield equation

Phonons

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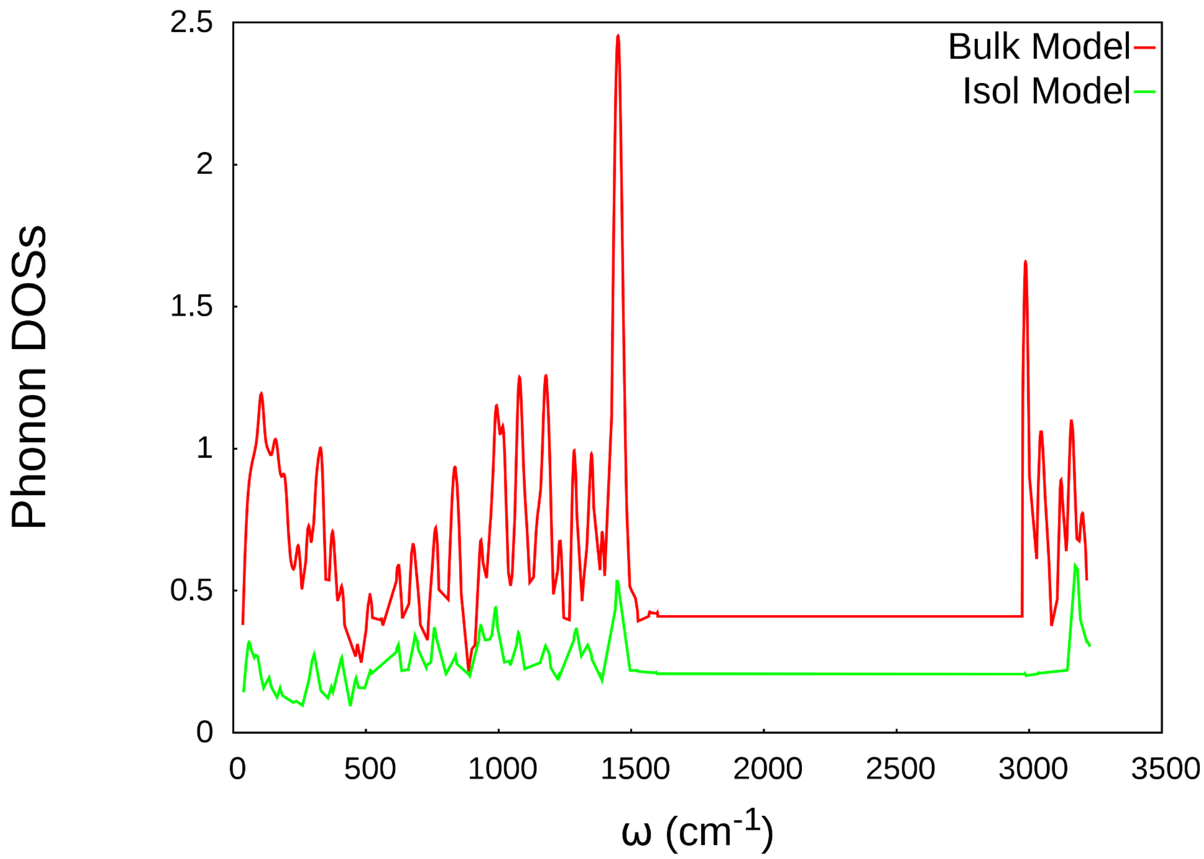
[(*tph*^{Ph})Fe]$^{-}$ single crystal:

- Symmetry
- 2 SMM per cell+2 counterions
- 228 atoms



Hamiltonian

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$$\langle SM_S|H|SM'_S\rangle = \langle SM_S|H_\mathrm{S}|SM'_S\rangle$$

From an electronic structure theory: CASSCF

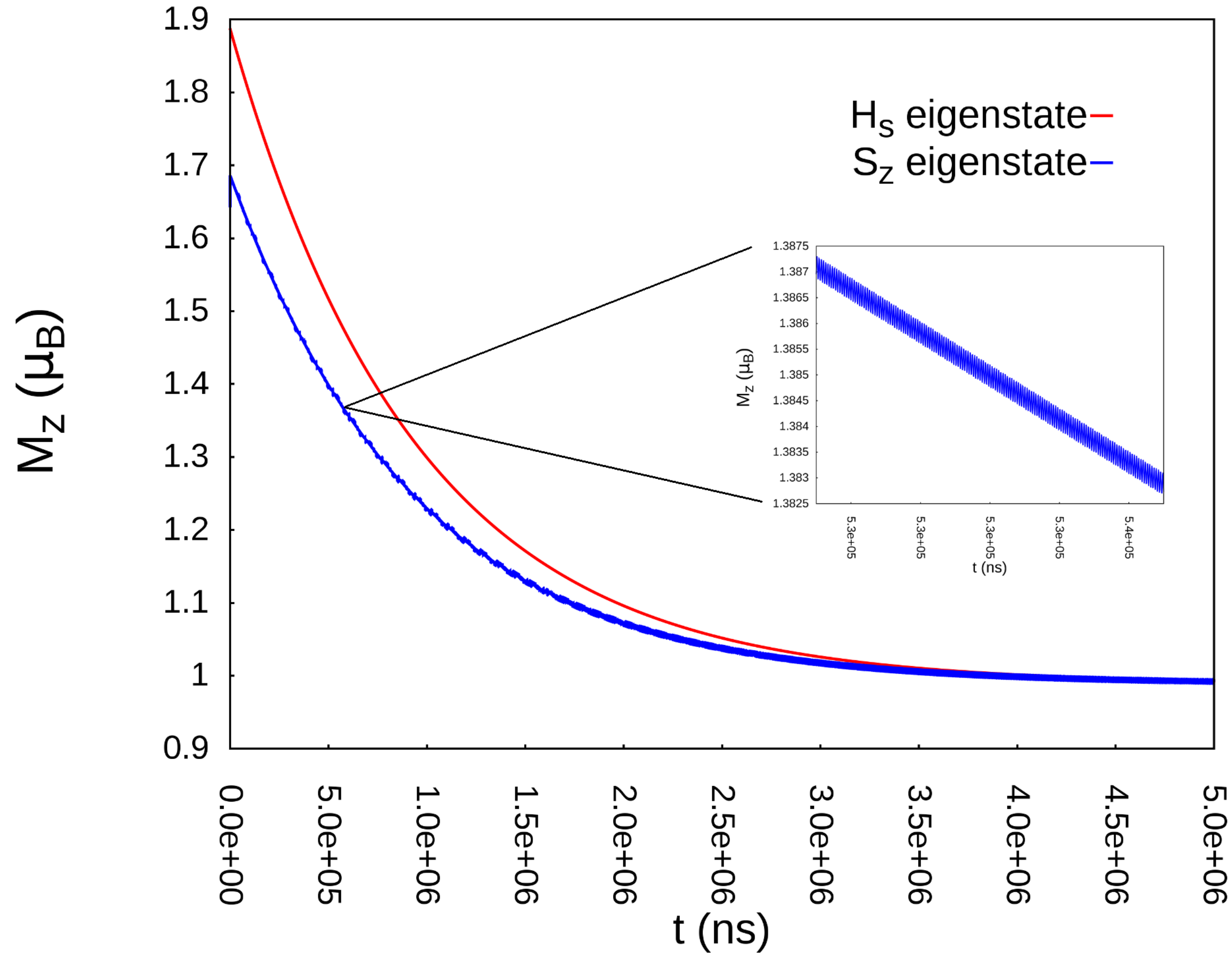
Define H_S

Same for spin-phonon coupling

$$\sum_{i\ldots j}\langle b|\frac{\partial^n H_0}{\partial q_i\ldots\partial q_j}|a\rangle = \sum_{i\ldots j}\frac{\partial^n}{\partial q_i\ldots\partial q_j}\langle b|H_0|a\rangle = \sum_{i\ldots j}\frac{\partial^n}{\partial q_i\ldots\partial q_k}\langle b|H_\mathrm{S}|a\rangle$$

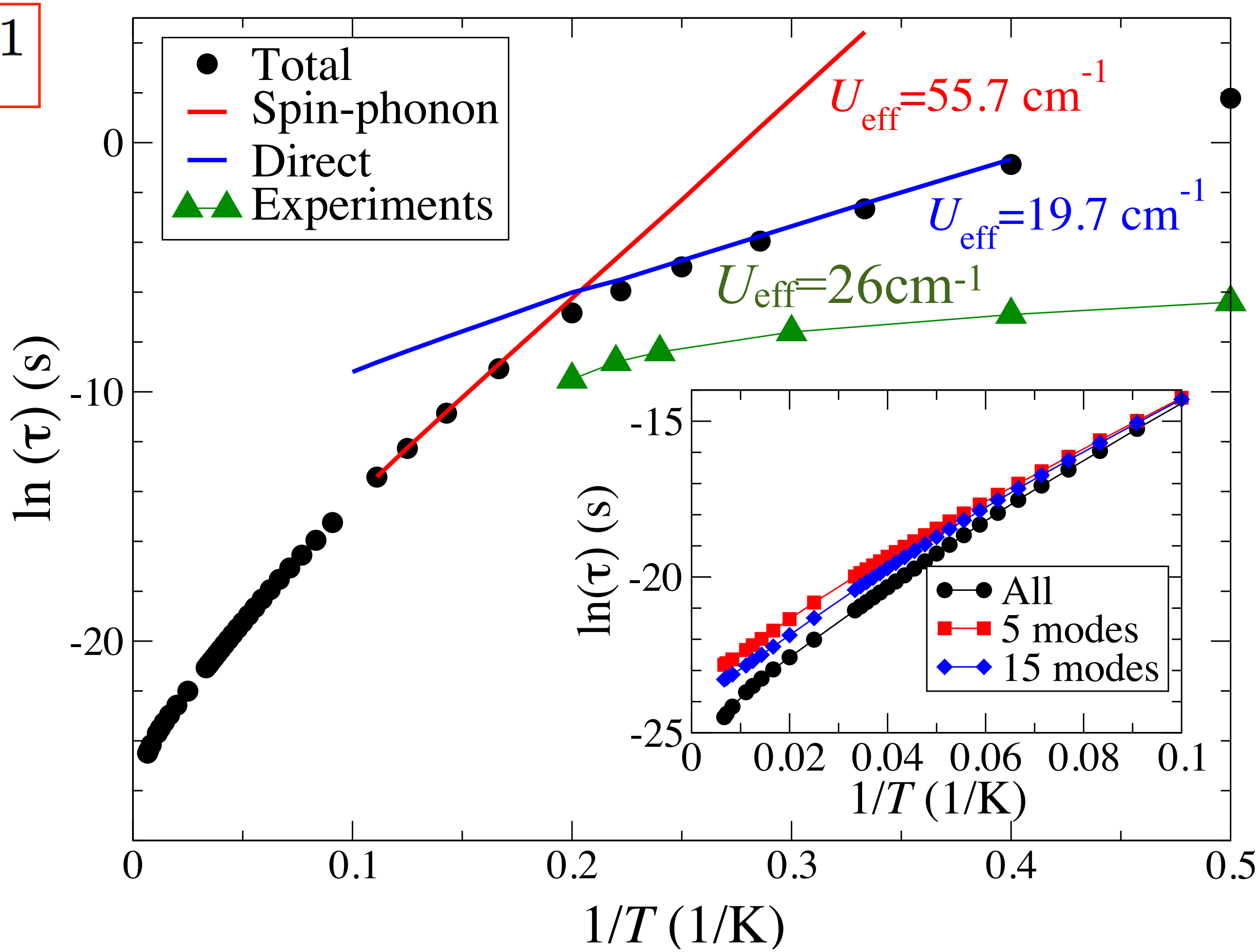
Spin dynamics

$$M_z(t) = (M_z(0) - M(\infty))e^{-t/\tau} + M_z(\infty)$$



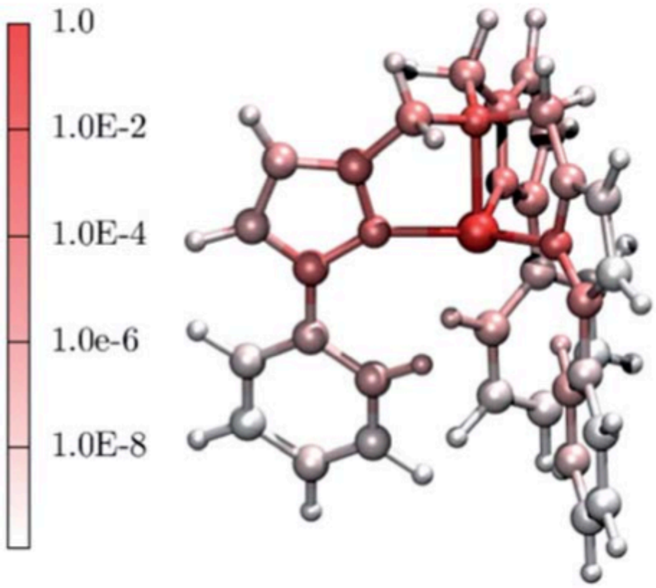
Results

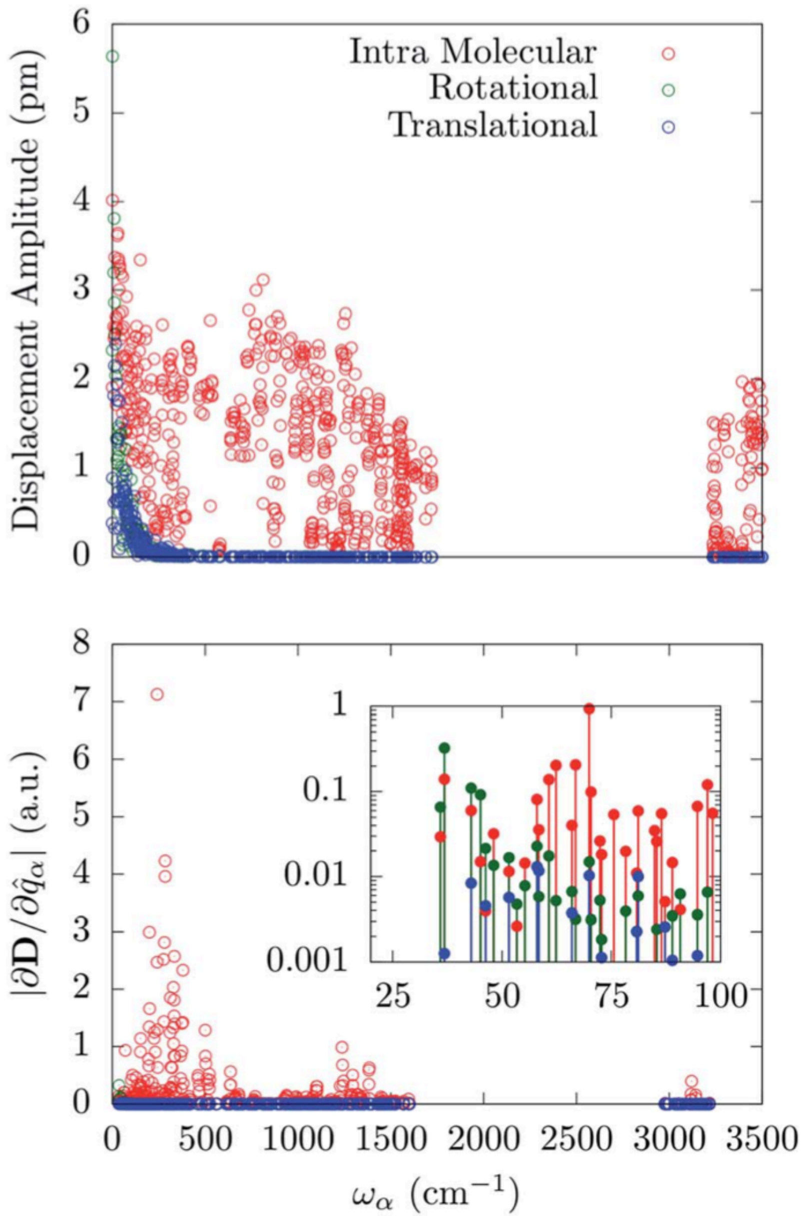
$$\hbar\omega_0 = 36\ \mathrm{cm}^{-1}$$



$$U_{\mathrm{eff}} = 19.7\mathrm{cm}^{-1} \sim \frac{1}{2}\hbar\omega_0 \qquad U_{\mathrm{eff}} = 55.7\mathrm{cm}^{-1} \sim \frac{3}{2}\hbar\omega_0$$

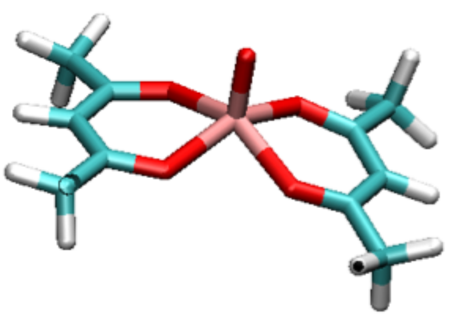
Which phonons matter?





A. Lunghi, et al., Chem. Sci. **8**, 6051 (2017)

Tiny energy barriers

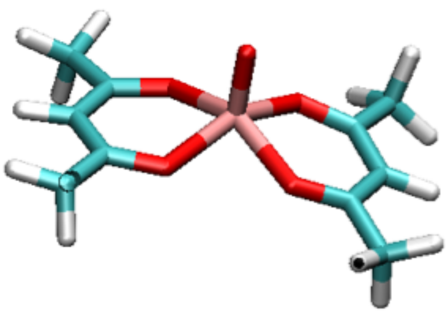


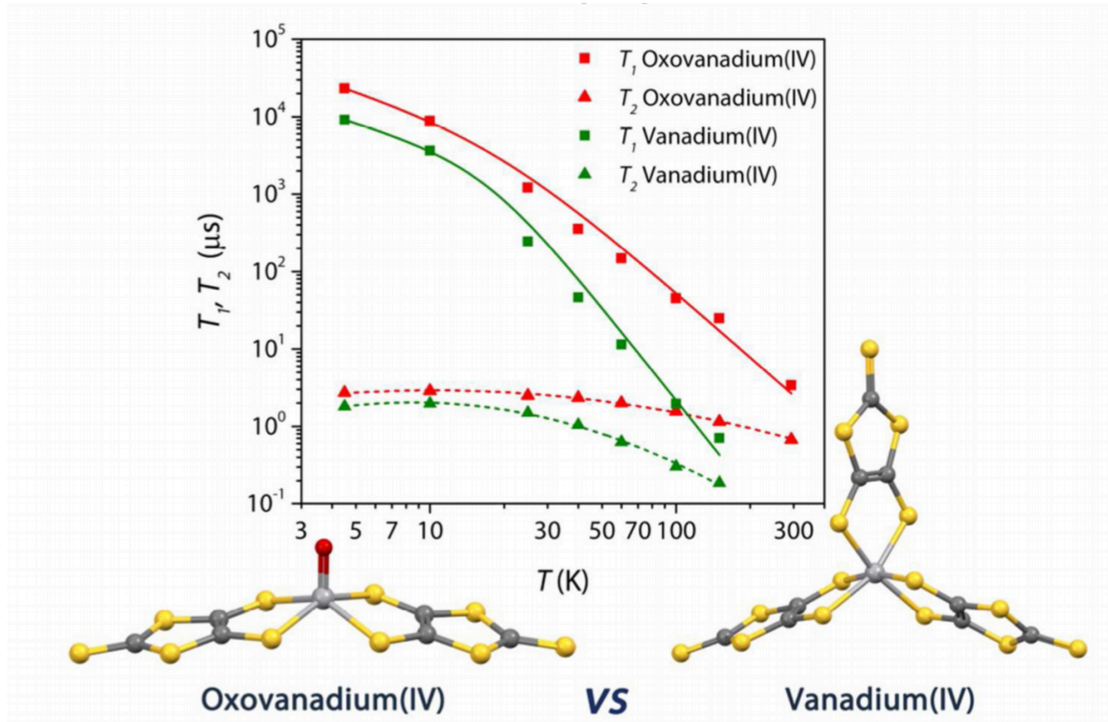
The case of vanadiles

M. Atzori, et al., JACS. **138**, 11234 (2016)

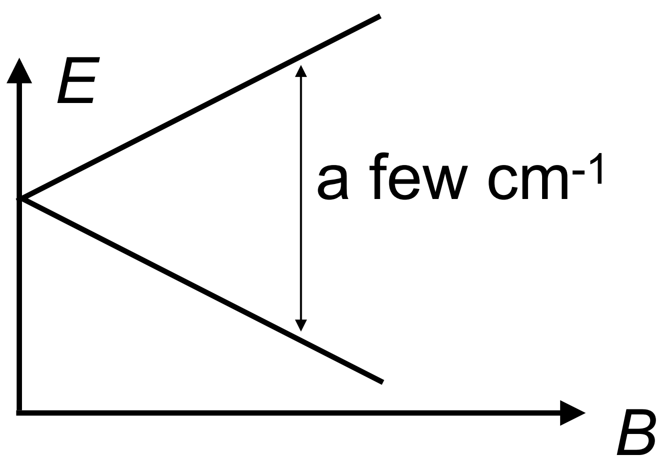
VO(*acac*)$_2$

V(IV) S=1/2





$$E = \mu_{\mathrm{B}} g B \hat{S}_z$$

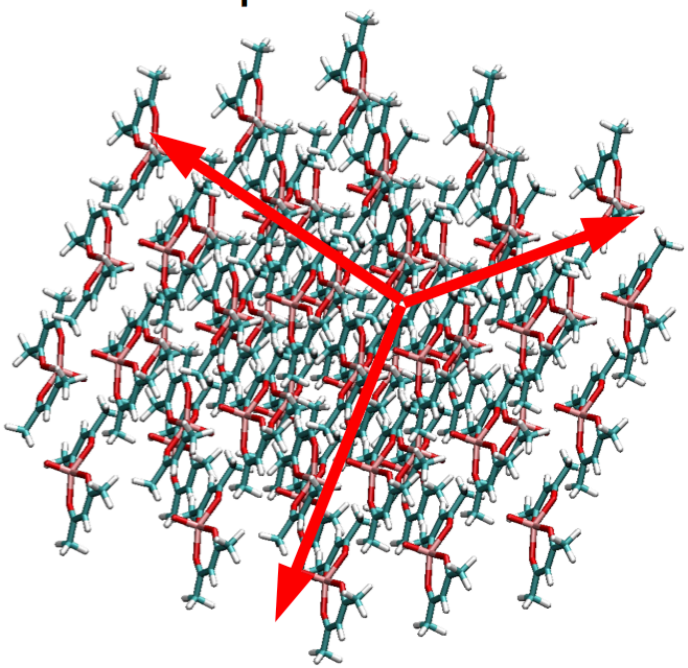


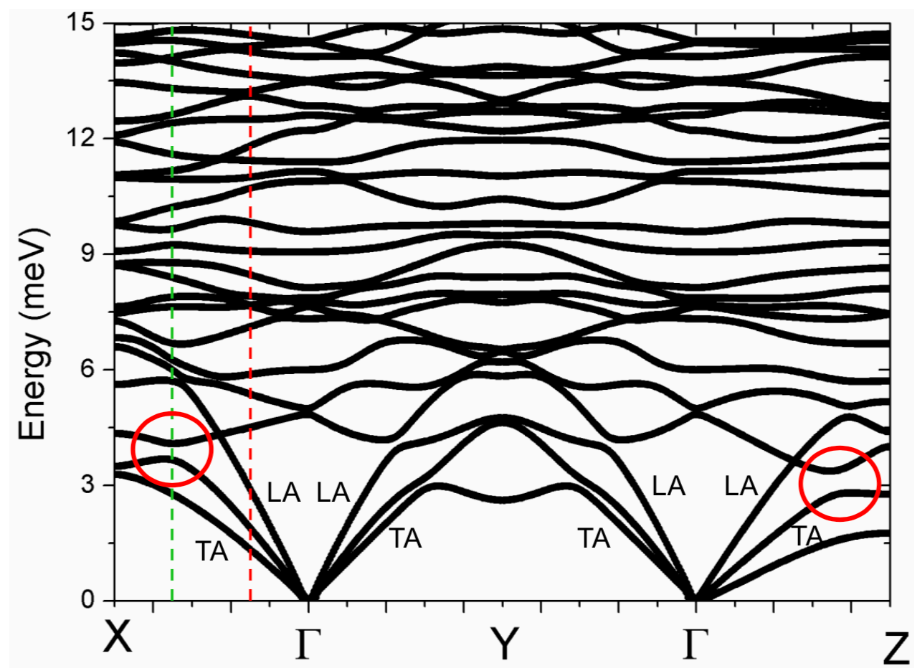
How can you relax at ~1 cm^{-1}

The case of vanadiles

$$\hat{H}_s = \sum_{i}^{N_s} \beta_i \vec{\mathbf{B}} \cdot \mathbf{g}(i) \cdot \vec{\mathbf{S}}(i) + \frac{1}{2} \sum_{ij}^{N_s} \vec{\mathbf{S}}(i) \cdot \mathbf{D}(ij) \cdot \vec{\mathbf{S}}(j)$$

3x3x3 Supercell: 1620 Atoms

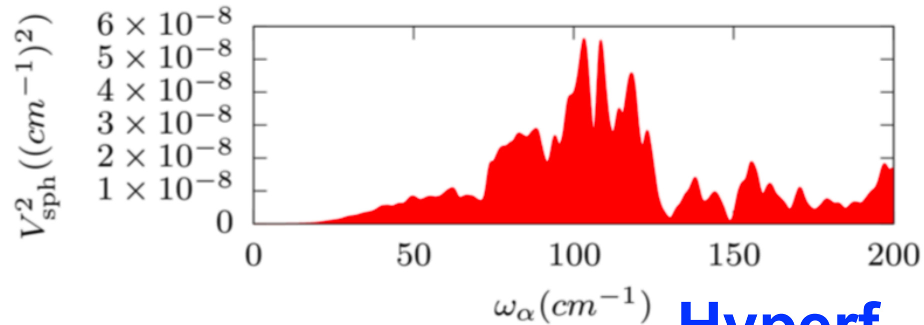




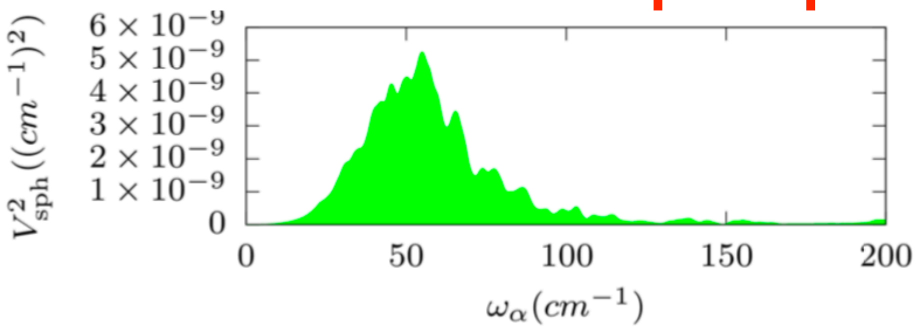
A. Lunghi and S.Sanvito, arXiv:1903.01424 (2019)

The case of vanadiles

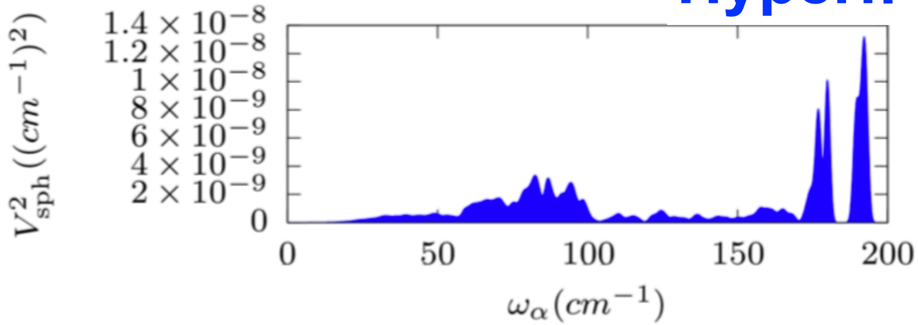
Zeeman



Spin-spin



Hyperf.



$$\frac{\partial \hat{H}_{\mathrm{s}}(i)}{\partial Q_{\alpha\mathbf{q}}} = \beta_i \vec{\mathbf{B}} \cdot \frac{\partial \mathbf{g}(i)}{\partial Q_{\alpha\mathbf{q}}} \cdot \vec{\mathbf{S}}(i) + \vec{\mathbf{S}}(i) \cdot \frac{\partial \mathbf{A}(ii)}{\partial Q_{\alpha\mathbf{q}}} \cdot \vec{\mathbf{I}}(i) +$$

Zeeman+hyperf

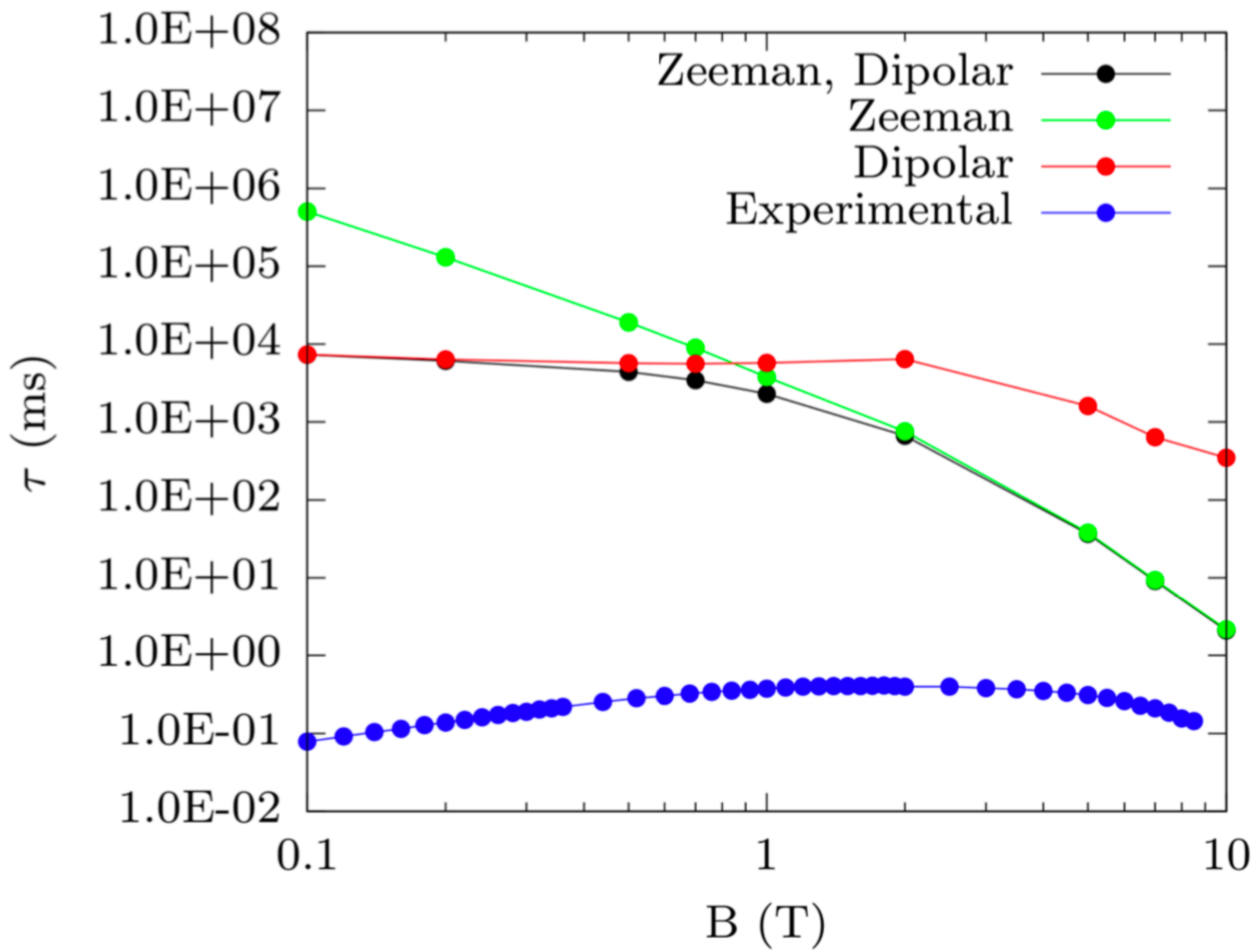
$$+ \sum_{j}^{N_s} \vec{\mathbf{S}}(i) \cdot \frac{\partial \mathbf{D}^{\mathrm{dip}}(ij)}{\partial Q_{\alpha\mathbf{q}}} \cdot \vec{\mathbf{S}}(j) \, .$$

Spin-spin

The case of vanadiles

Experiments: L. Tesi et al., Dalton Trans. **45**, 16635 (2016)

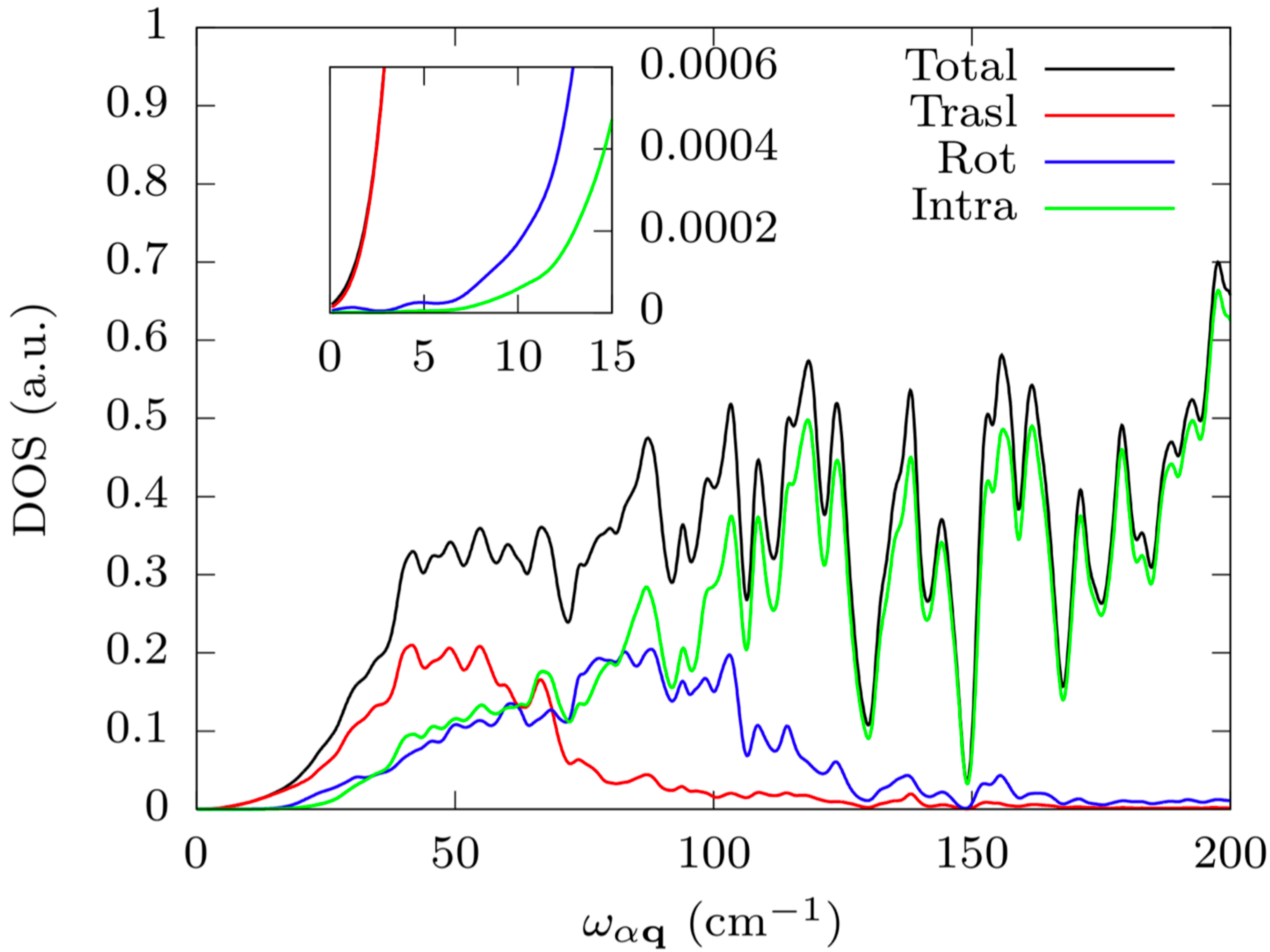
20 K



A. Lunghi and S.Sanvito, arXiv:1903.01424 (2019)

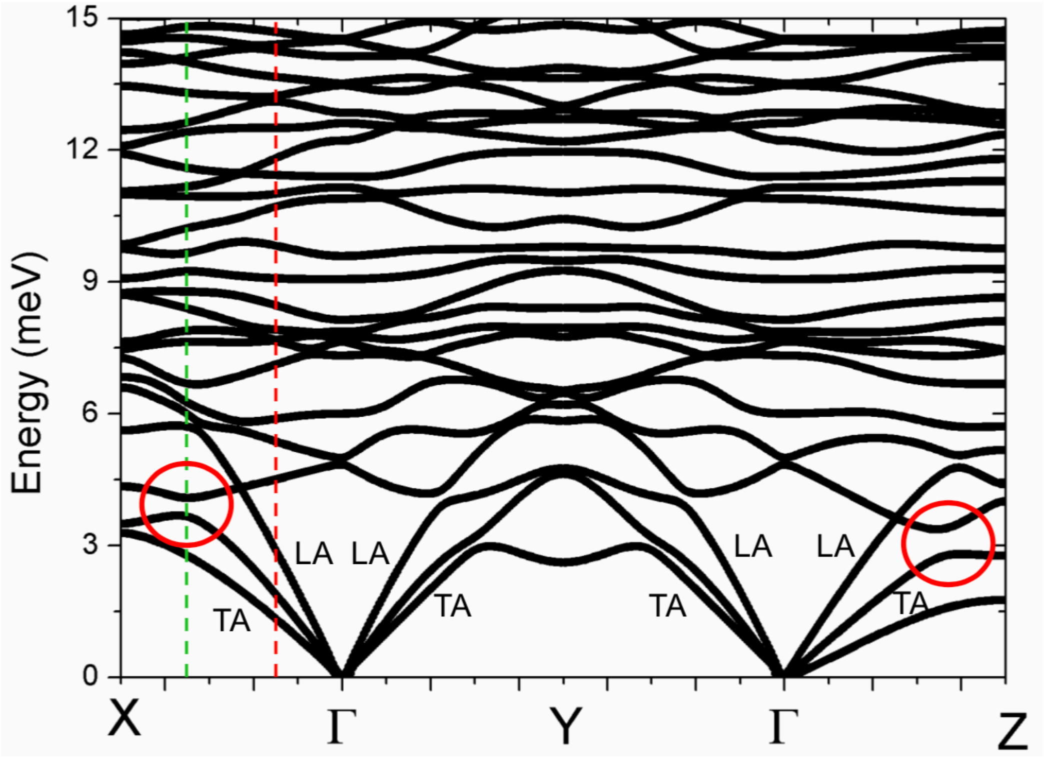
The case of vanadiles

CRANN

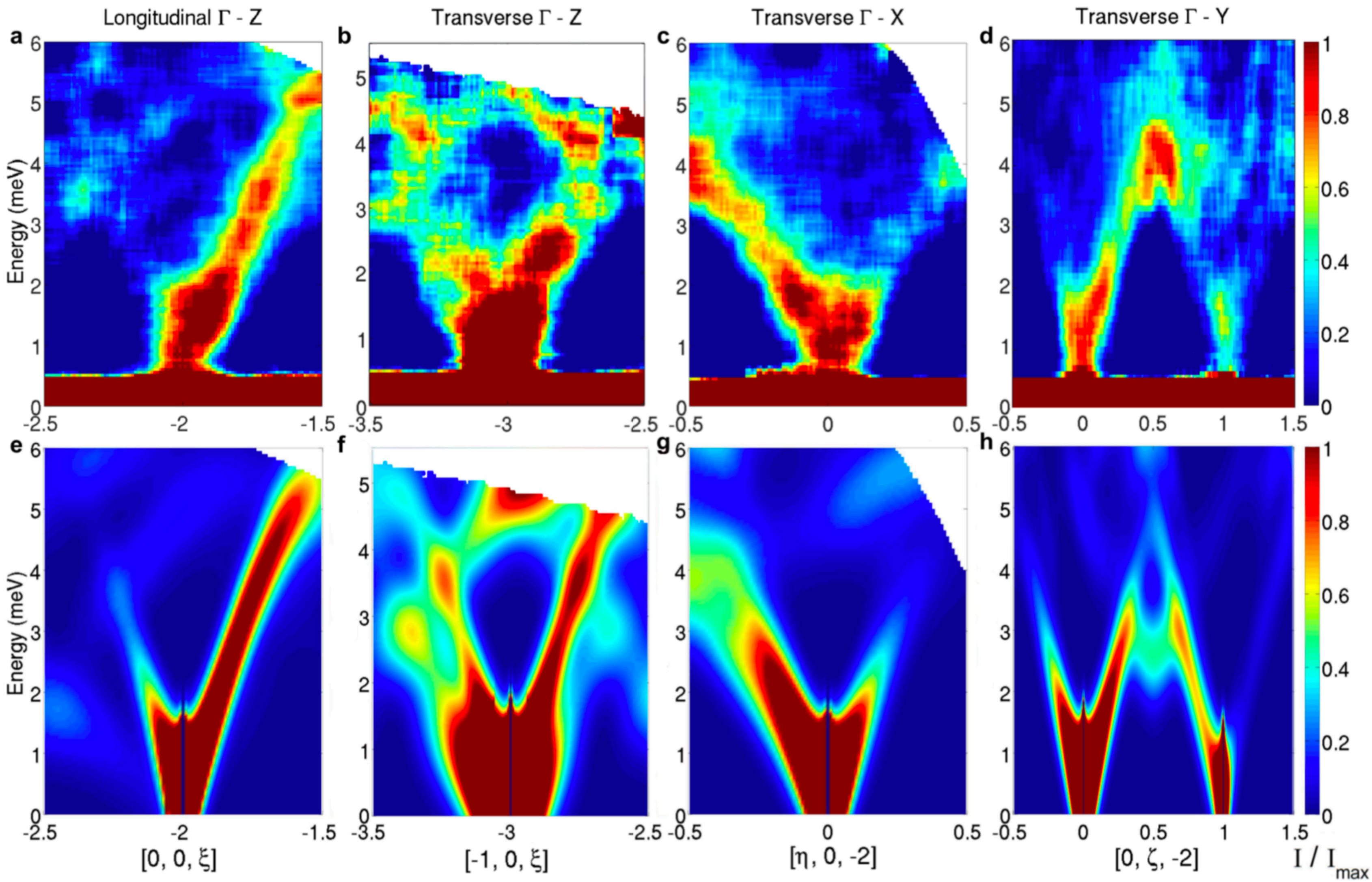


The case of vanadiles

CRANN

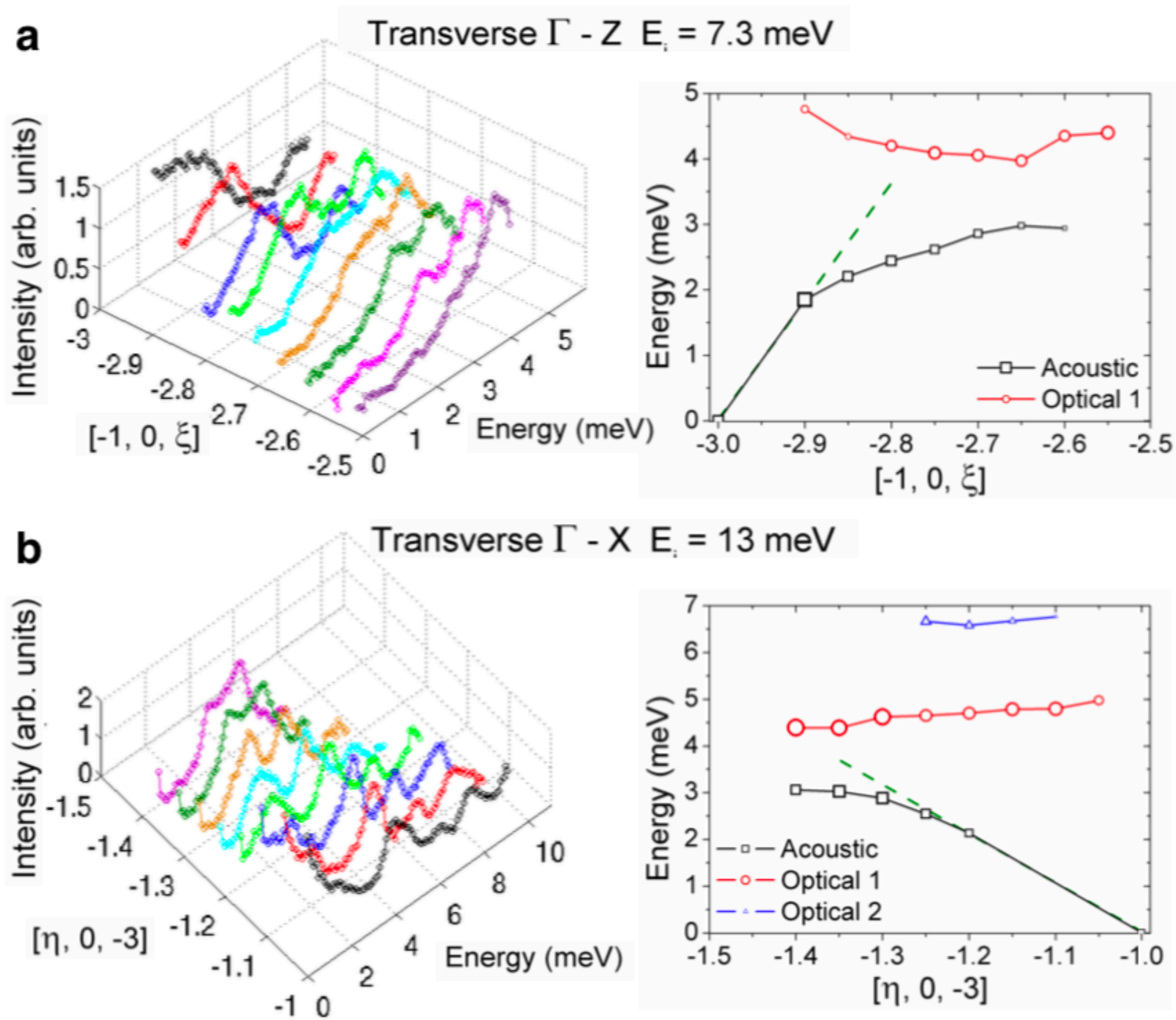


The case of vanadiles



E. Garlatti et al., under review

The case of vanadiles



E. Garlatti et al., under review

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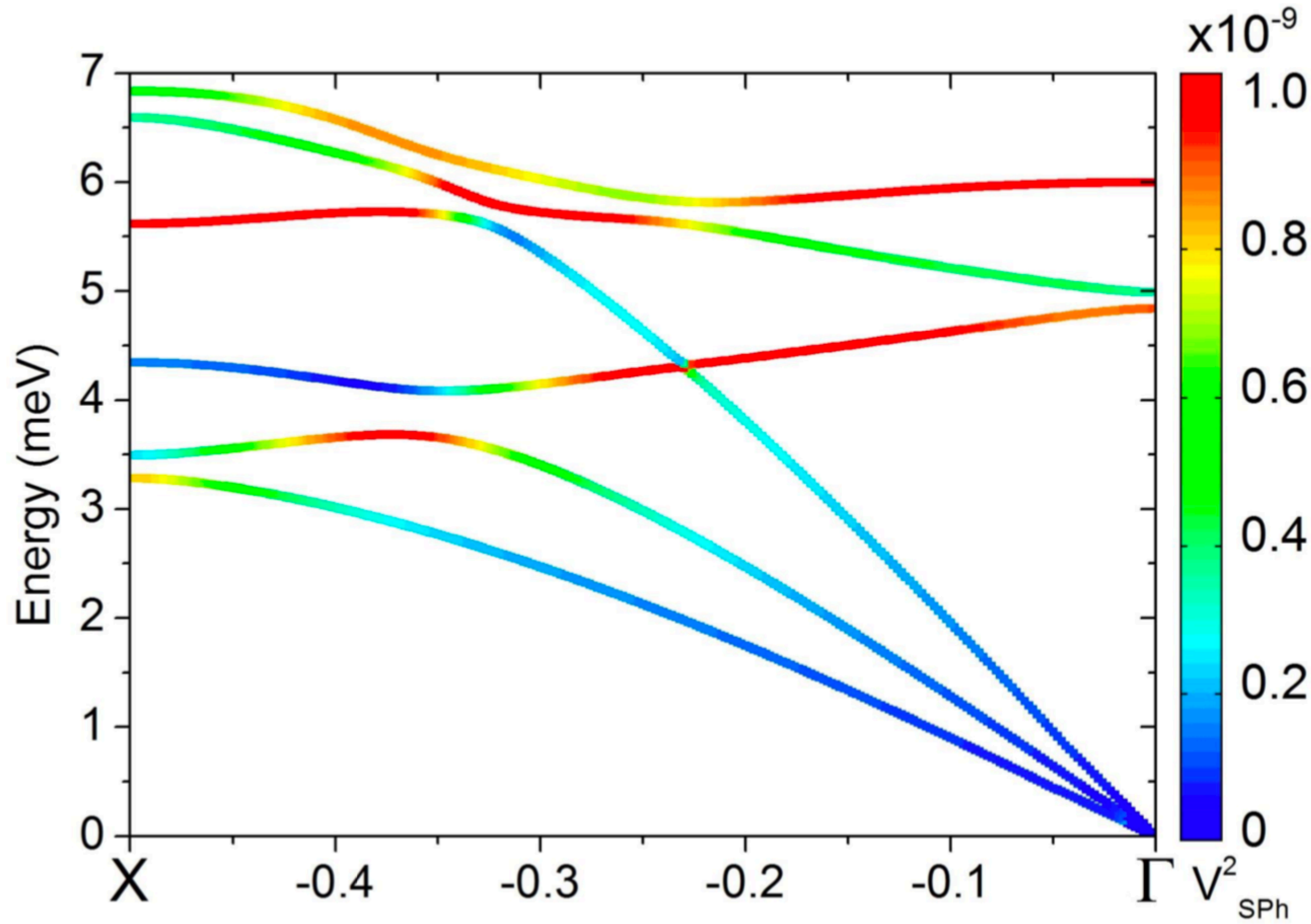

Conclusion: design rules

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Controlling the anisotropy barrier is not enough to control relaxation

- Increase the first phonon frequency
- Reduce spin-phonon coupling
- Try to avoid phonon resonant conditions
- **Full design requires handling large number of degrees of freedom and dynamical quantities**

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September 2019

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Spin-phonon coupling: the funny case of spin relaxation in magnetic molecules

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