Università degli Studi Firenze

Molecular Spin Qubits Studied by EPR and THz Spectroscopy

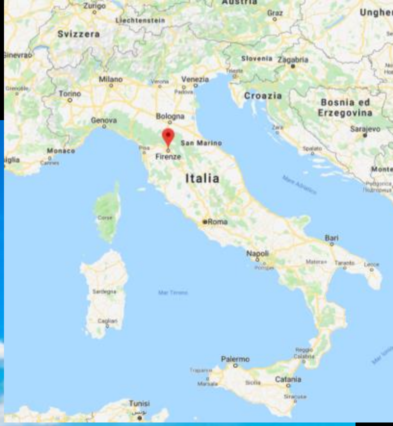
Lorenzo Tesi

PETER Workshop

Universität Stuttgart

19-06-2019


COMUNE DI
FIRENZE
My Home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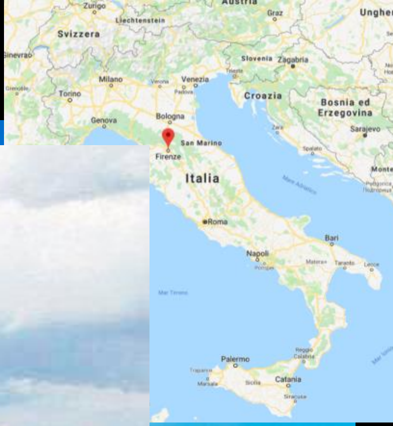
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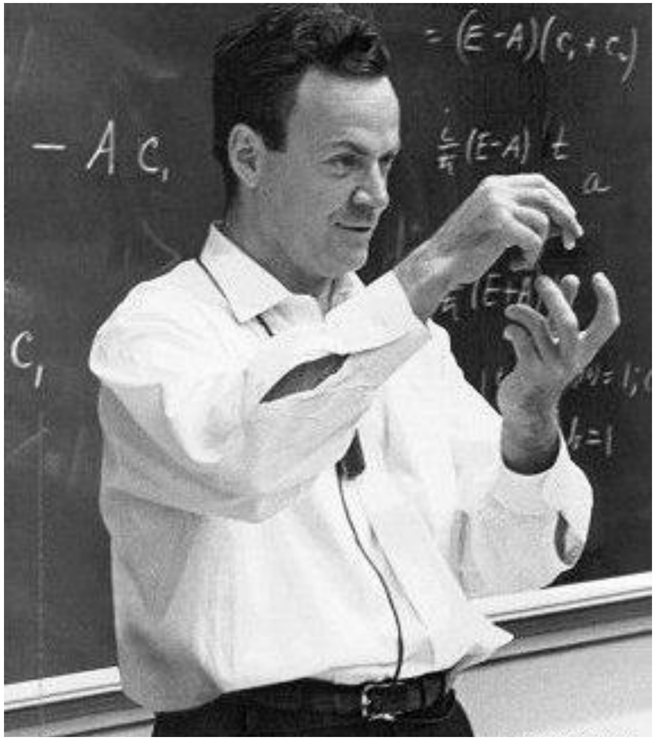
WHAT IS A QUBIT?



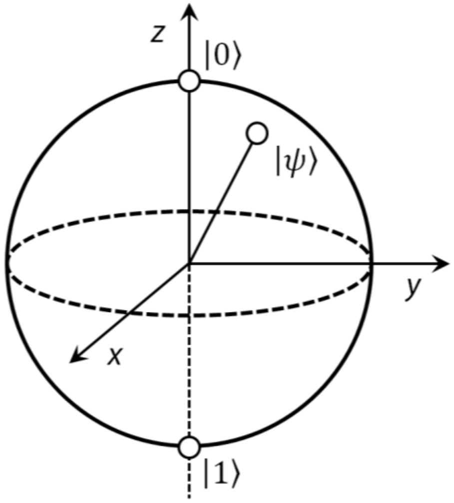
Richard Feynman, 1982

'If you want to make a simulation of nature you'd better make it quantum-mechanical'

Classical bit

$|\psi\rangle = |0\rangle \text{ or } |1\rangle$

Two possible states



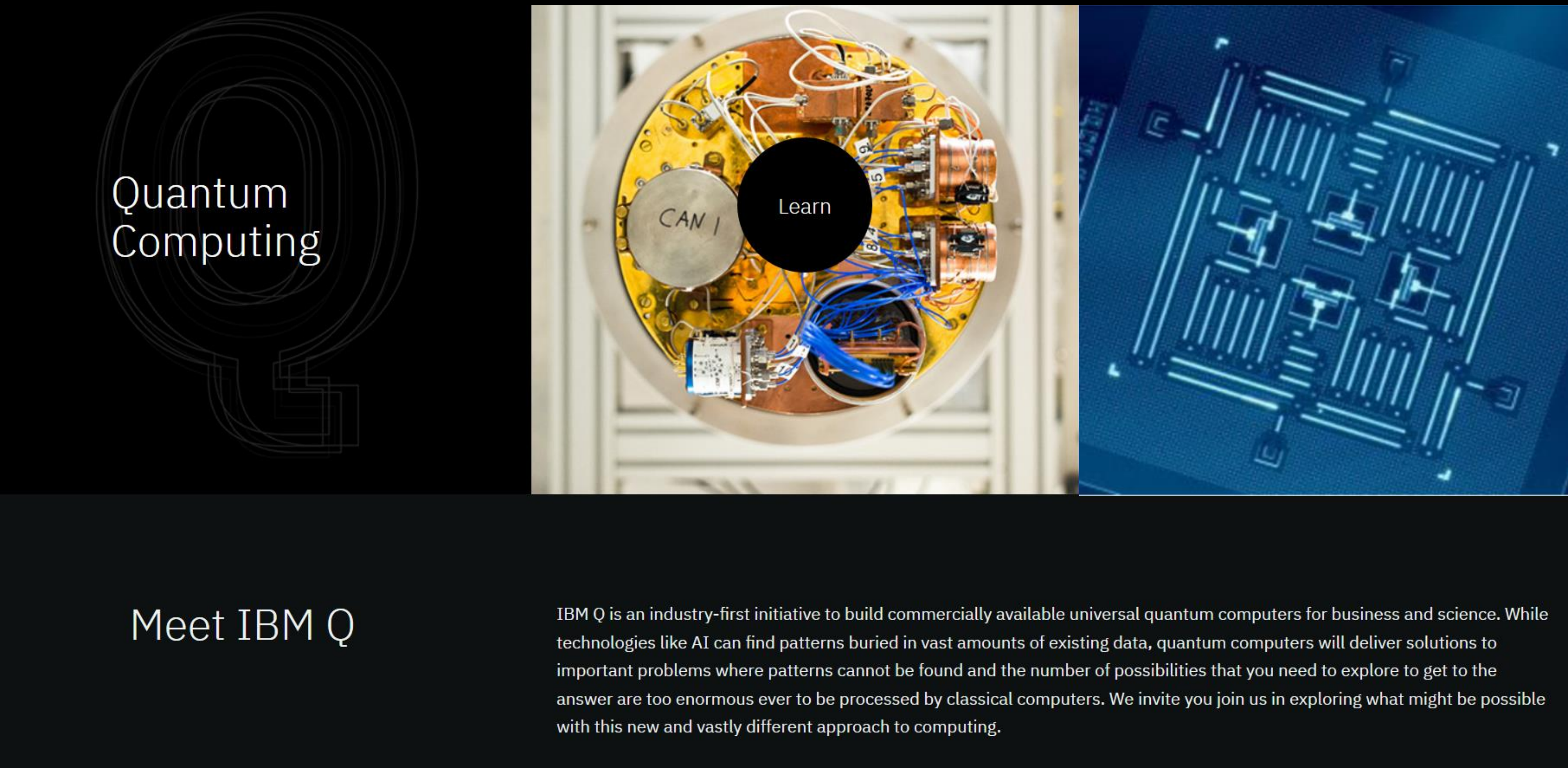
Quantum bit

$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$

Superposition state

Faster computation and data searching capabilities;
Quantum systems can be simulated.

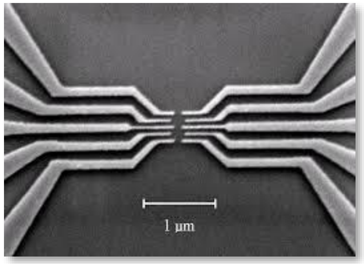
PROTOTYPE OF QUANTUM COMPUTER



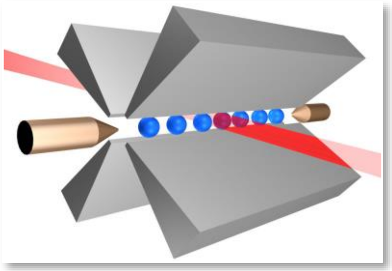
www.research.ibm.com

But also Google, Nasa, USA Energy Department, Alibaba, etc...

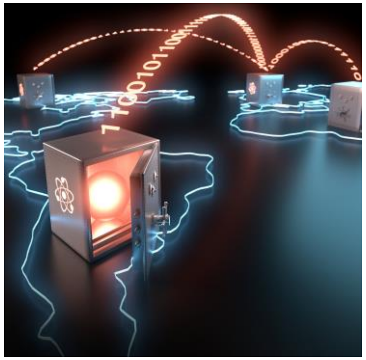
WHAT IS A QUBIT?



Quantum Dots
Nature **453** 1043-1049

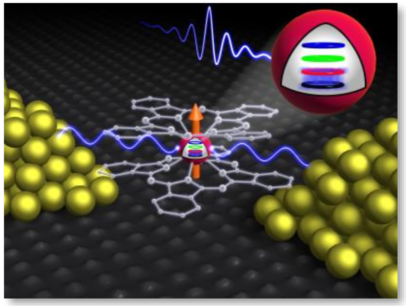


Ionic Traps
Nature **453**, 1008–1015

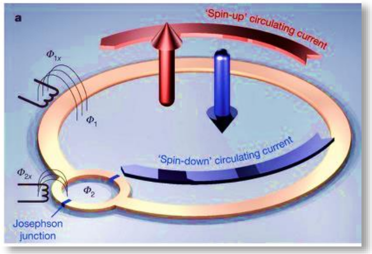


Photons
Nature **409**, 46-52

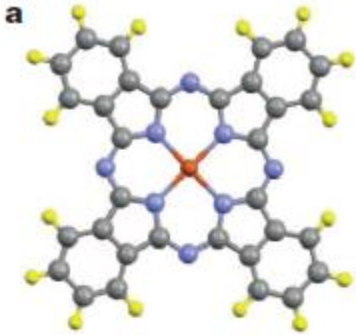
POTENTIAL QUBITS



Nuclear Spins
Nature **496**, 334–338

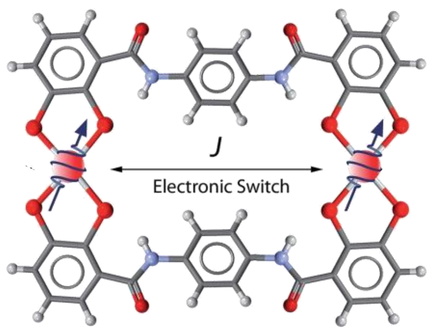


Superconducting Circuits
Nature **453**, 1031–1042



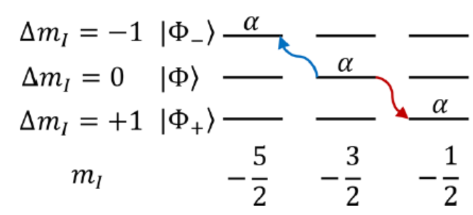
Electronic Spins
Nature **503**, 504-508

ADVANTAGES AND DRAWBACKS



- ✓ **Easily Interacting**
- ✓ **Scalable**
- ✓ **Easy quantum error correction**

BUT short coherence times



Spin-lattice Relaxation Time T_1

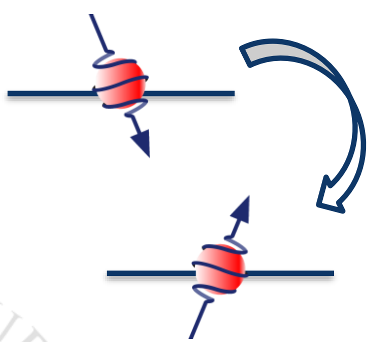
LIMITING FACTOR

Phase Memory Time T_m
(or Coherence Time)

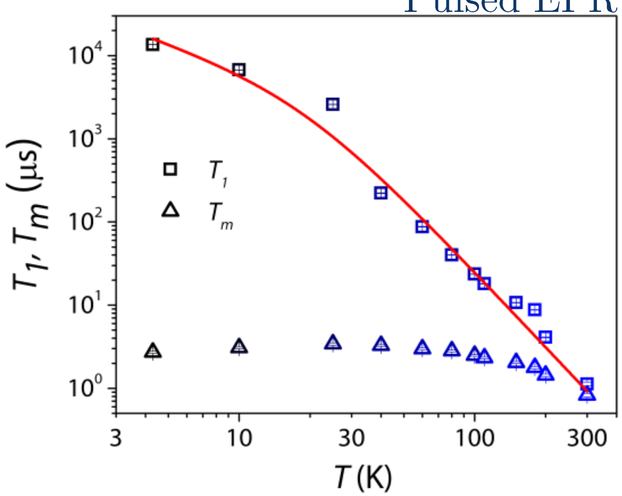
Classical Information Memory

$M_S = -½$

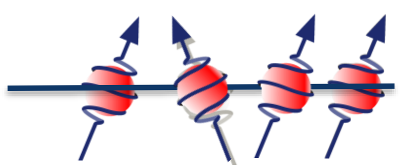
$M_S = +½$



Pulsed EPR



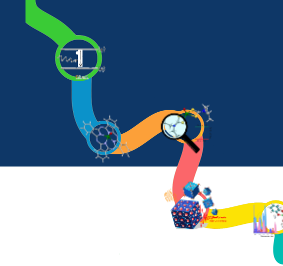
Quantum Information Memory

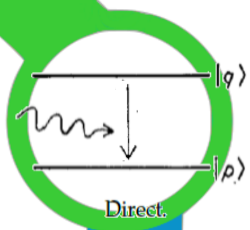


$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

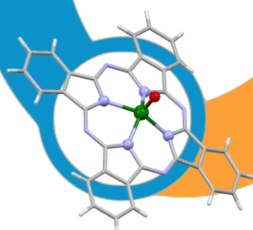
We need to identify the ingredients to lengthen the relaxation times!

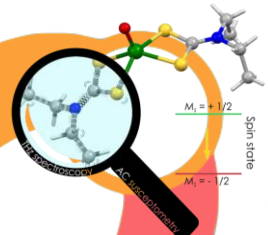
Outline





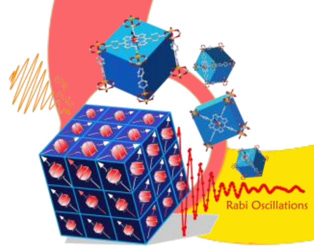
Part I
Spin-lattice Relaxation
Theoretical inputs

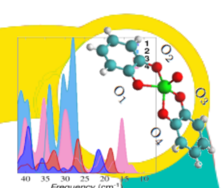




Part III
New evidences
from Terahertz spectroscopy

Part II
An example of
Molecular Spin Qubits



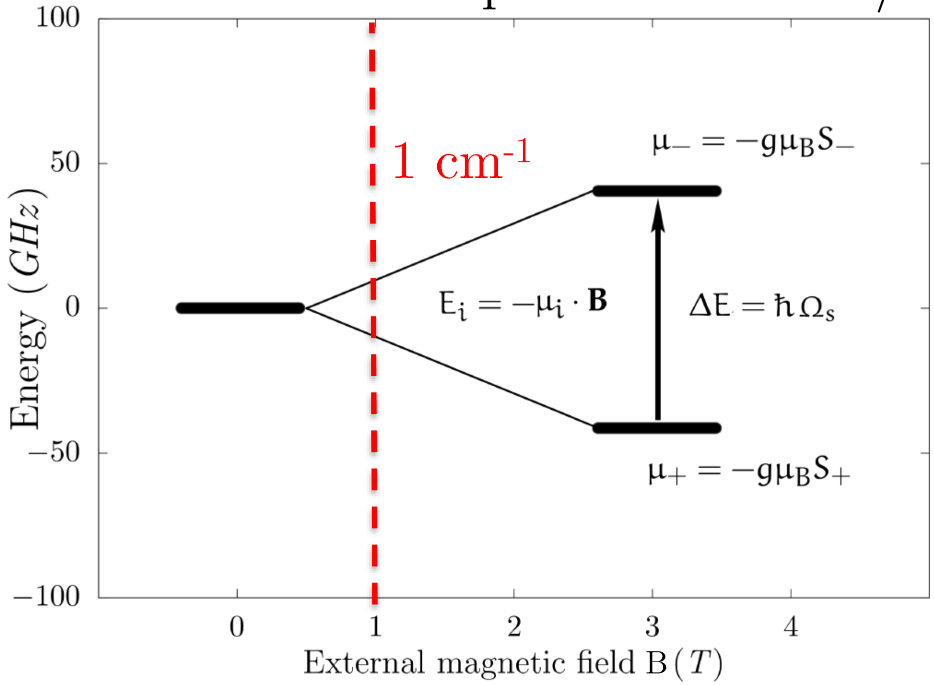


Part V
Developing a
theoretical framework

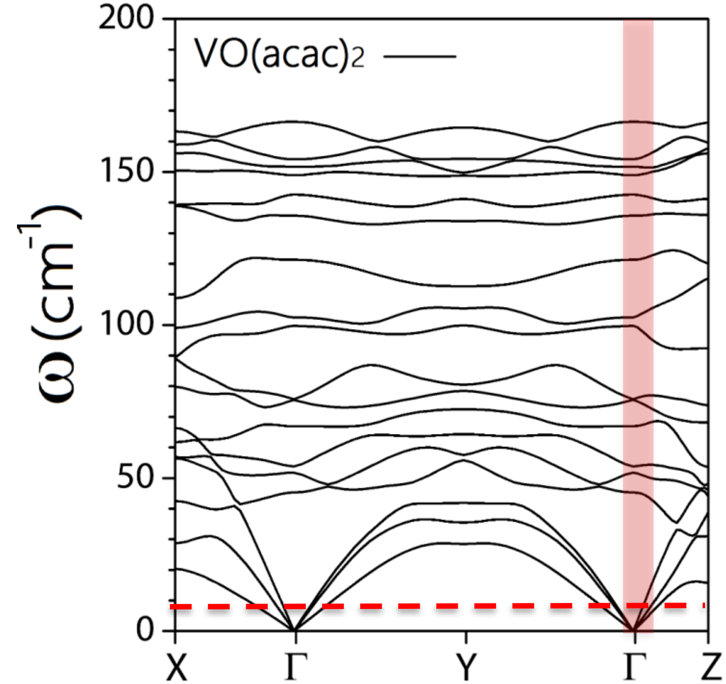
Part IV
Quantum MOF

CONCLUSIONS

Spin levels of S=1/2

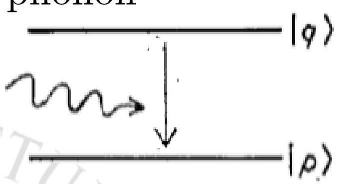


Lattice structure



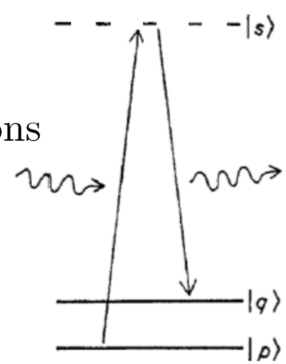
Main relaxation processes

One-phonon



Direct.

Two-phonons



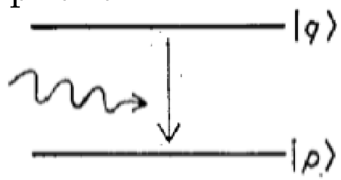
Raman.

The efficiency of spin-lattice relaxation is given by the **spin-orbit coupling**.

J. H. van Vleck, *Physical Review*, 1940, **57**, 426-447

Main relaxation processes

One-phonon



Direct.

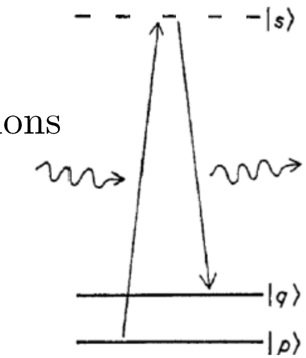
$$\frac{1}{T_1^D} = \frac{3}{2\pi}\left(\frac{\delta_{pq}}{\hbar}\right)^3 \frac{\coth(\delta_{pq}/2kT)}{\rho\hbar v^5}\ W_D^2$$

Temperature dependence Direct

$$\frac{1}{T_1} = aT$$

Magnetic field dependence of T_1

Two-phonons



Raman.

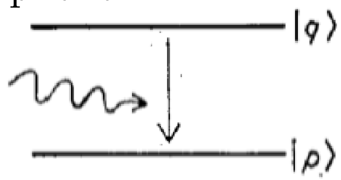
$$\frac{1}{T_1} \sim 8!\left(\frac{kT}{\hbar}\right)^9 \frac{W_R^2}{\Delta^2}\left(\frac{2V}{4\pi^2 M v^5}\right)^2$$

Temperature dependence Raman

J. H. van Vleck, *Physical Review*, 1940, **57**, 426-447

Main relaxation processes

One-phonon



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Temperature dependence Direct

$$\frac{1}{T_1} = aT$$

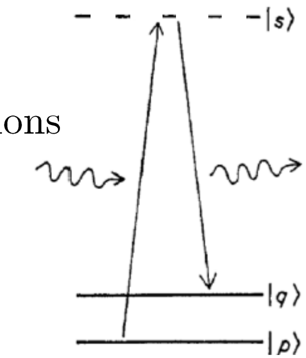
Magnetic field dependence of T_1

$$\frac{1}{T_1} = cB^4 + d\,\frac{1+eB^2}{1+fB^2}$$

direct

Brons-van Vleck

Two-phonons



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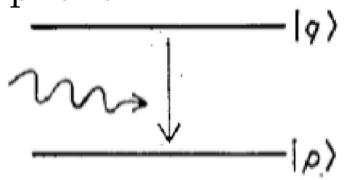
Main relaxation processes

One-phonon



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Brons-van Vleck

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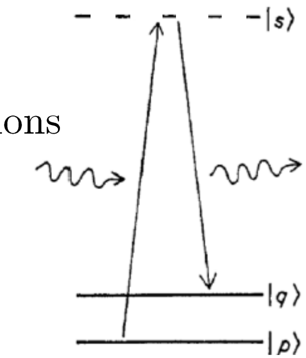

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$$\frac{1}{T_1} \sim 8!\left(\frac{kT}{\hbar}\right)^9 \frac{W_R^2}{\Delta^2}\left(\frac{2V}{4\pi^2 M v^5}\right)^2$$

Temperature dependence Raman

Debye model

$$\frac{1}{T_1} = a_{Ram}\left(\frac{T}{\theta_D}\right)^9 I_8\left(\frac{\theta_D}{T}\right)$$

$$I_8\left(\frac{\theta_D}{T}\right) = \int_0^{\theta_D} \frac{x^8 \exp x}{\exp(x-1)^2}\,dx$$

Local modes model

$$\frac{1}{T_1} = a_{loc}\frac{\exp(\hbar\omega)}{\left(\exp\left(\frac{\hbar\omega}{kT}\right)-1\right)^2}$$

J. H. van Vleck, *Physical Review*, 1940, **57**, 426-447

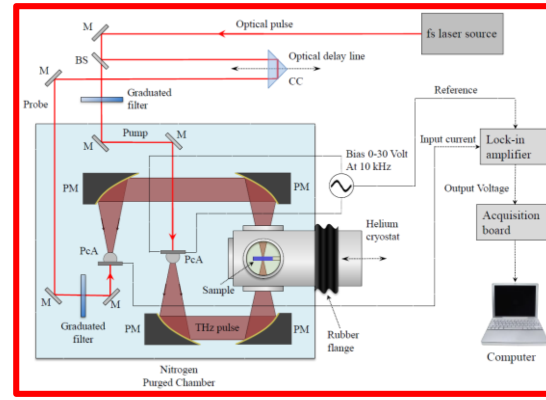
UNIVERSITÀ DEGLI STUDI FIRENZE

The Tools of Our Multitechnique Investigation

LAMM Laboratorio di Magnetismo Molecolare

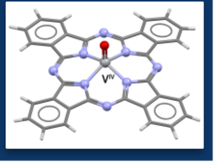
UNIVERSITÀ DEGLI STUDI DI TORINO

lens European Laboratory for Non-Linear Spectroscopy

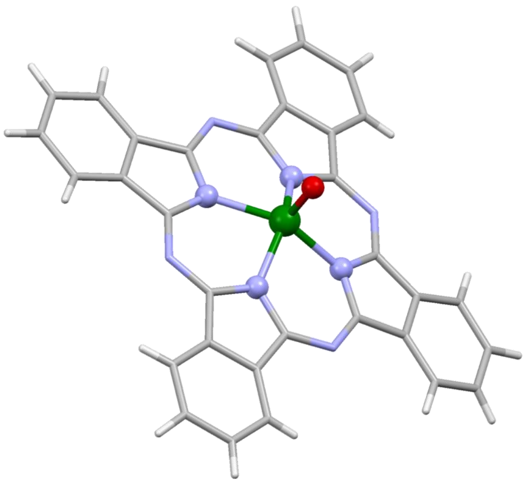


Continuous-wave EPR	AC susceptometry	Pulsed EPR	THz spectroscopy
↓	↓	↓	↓
Static Magnetic Properties	Magnetization Relaxation Time τ	Spin-Lattice Relaxation Time T_1; Phase Memory Time T_m	Low-energy vibrational spectrum

Part II
A Nice Example of Molecular Spin Qubit



M. Atzori, L. Tesi *et al.*, *JACS*, 2016



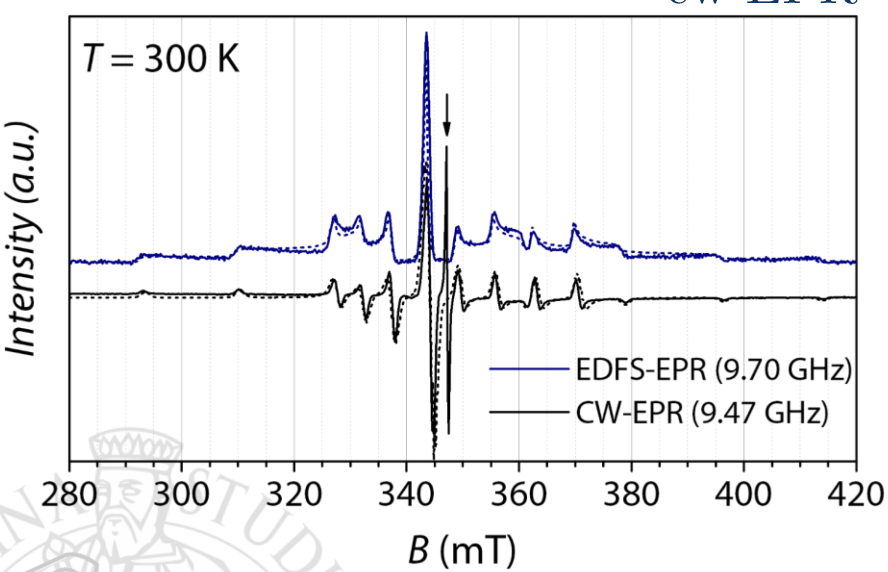
VOPc 0.1% in TiOPc

$S = 1/2 \quad I = 7/2$

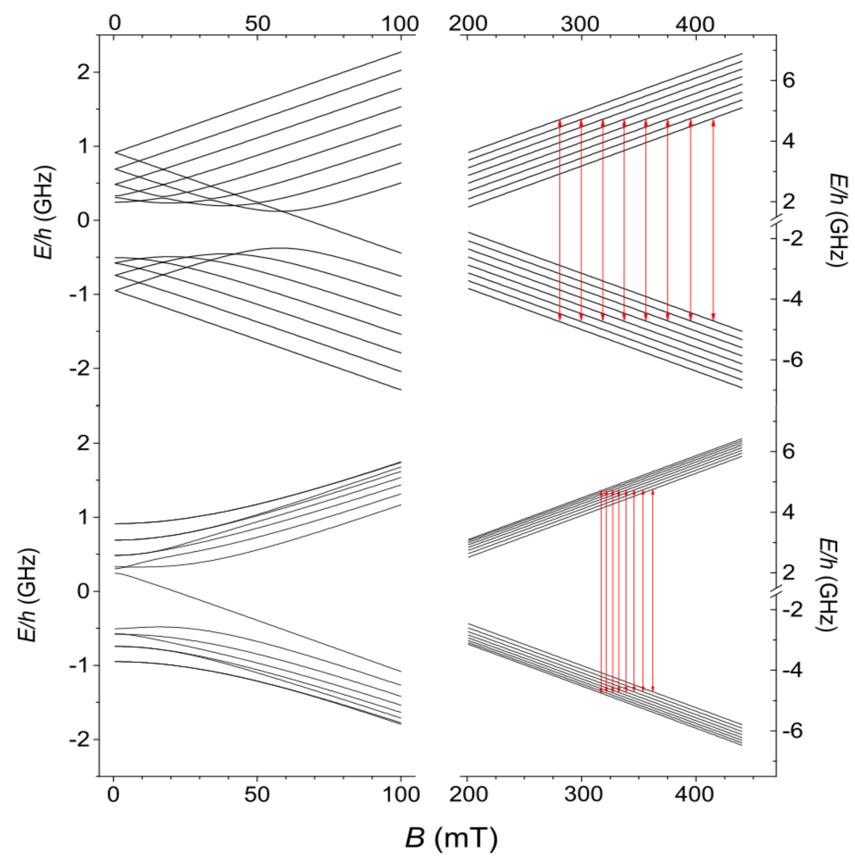
$$\mathcal{H} = \mu_B \boldsymbol{g} \cdot \hat{\boldsymbol{S}} \cdot \boldsymbol{B} + \hat{\boldsymbol{S}} \cdot \boldsymbol{A} \cdot \hat{\boldsymbol{I}}$$

$g_x = g_y$	g_z	$A_x = A_y$	A_z
1.987(1)	1.966(1)	167.9(1) MHz	476.7(2) MHz

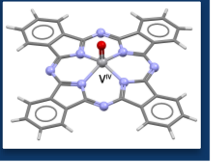
cw-EPR



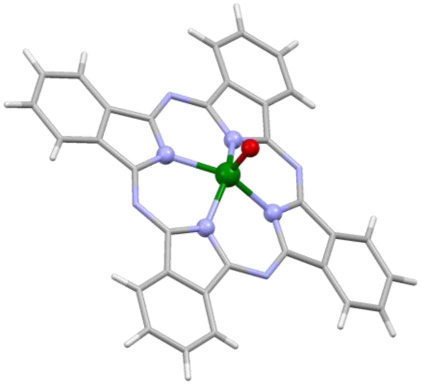
Spin levels composition



Part II
A Nice Example of Molecular Spin Qubit

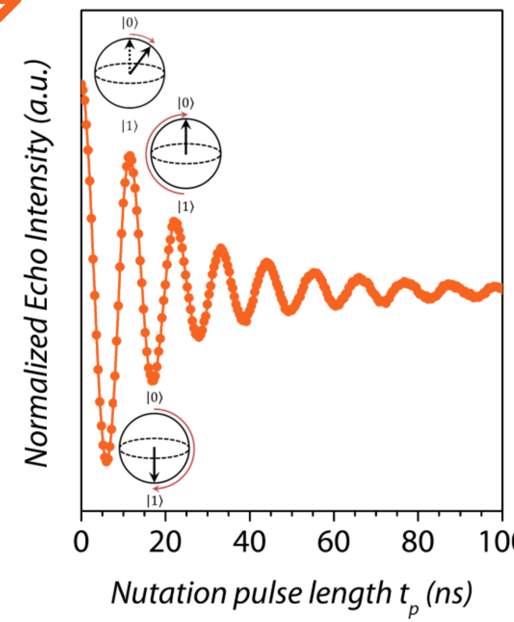


M. Atzori, L. Tesi *et al.*, *JACS*, 2016

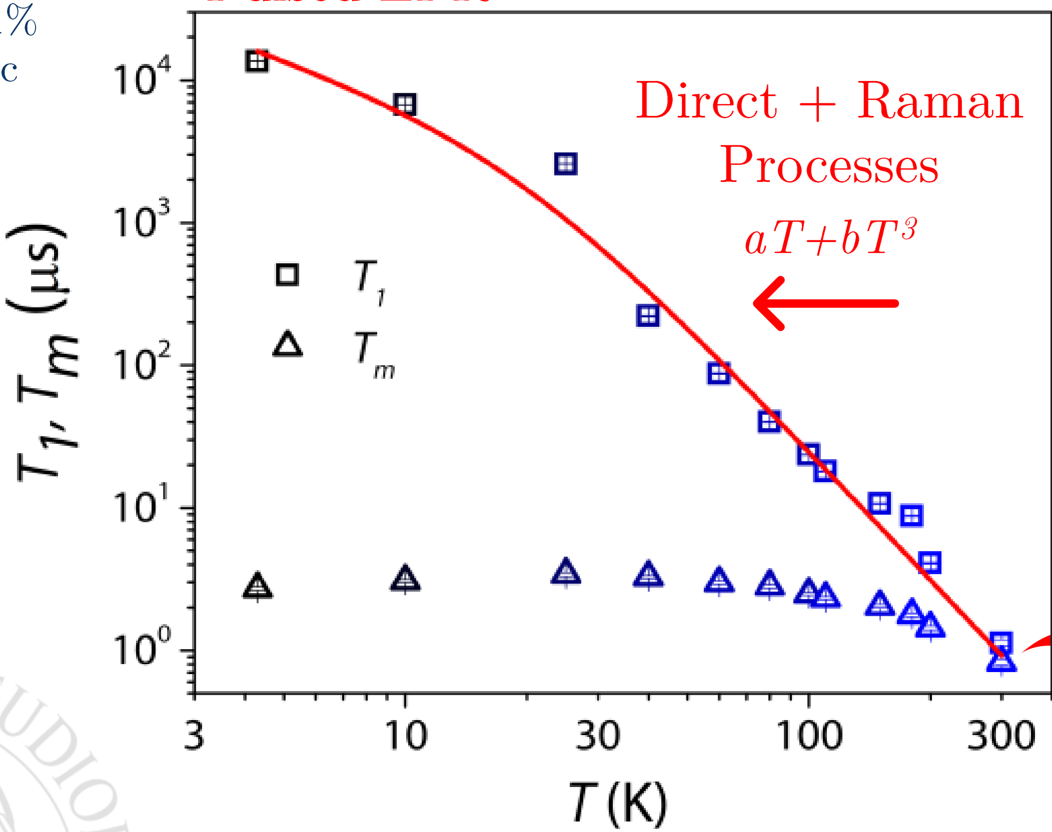


VOPc 0.1%
in TiOPc

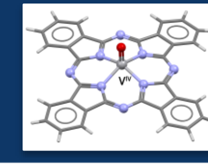
Quantum manipulation → Rabi oscillations



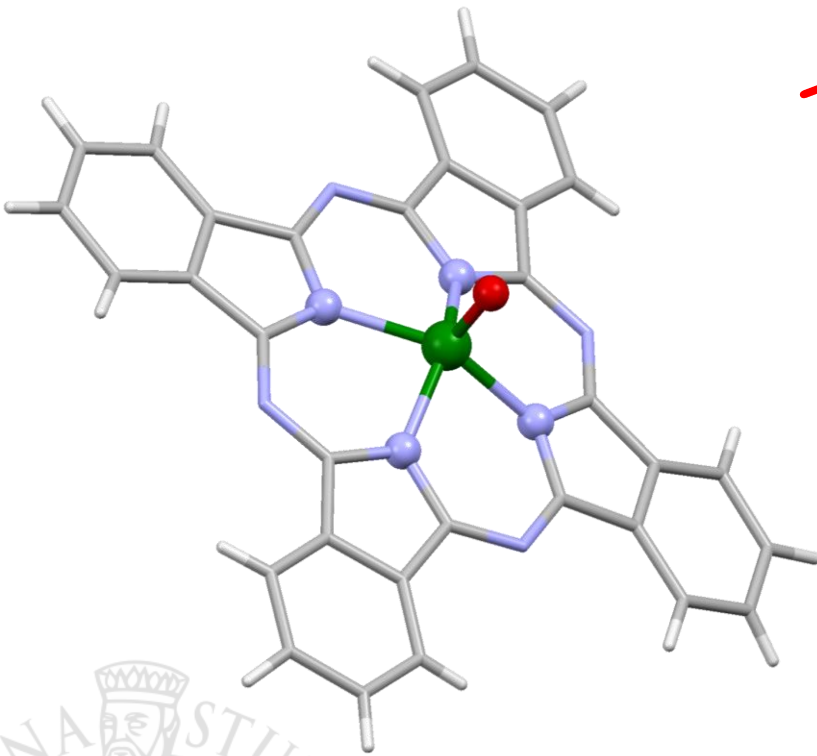
Pulsed EPR



0.83 μs
at 300 K



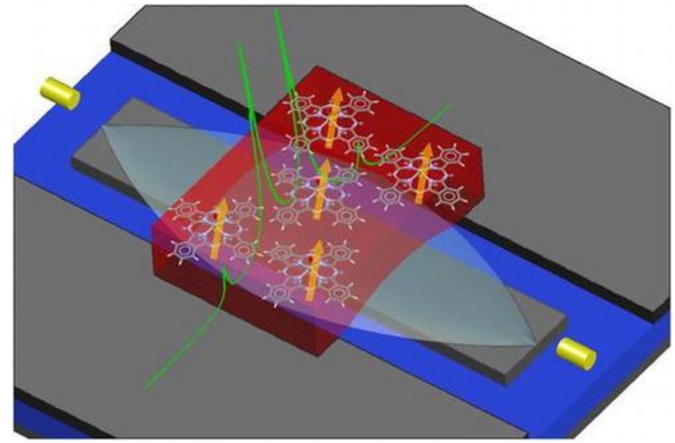
Room Temperature coherence of VOPc drew attention for other applications...



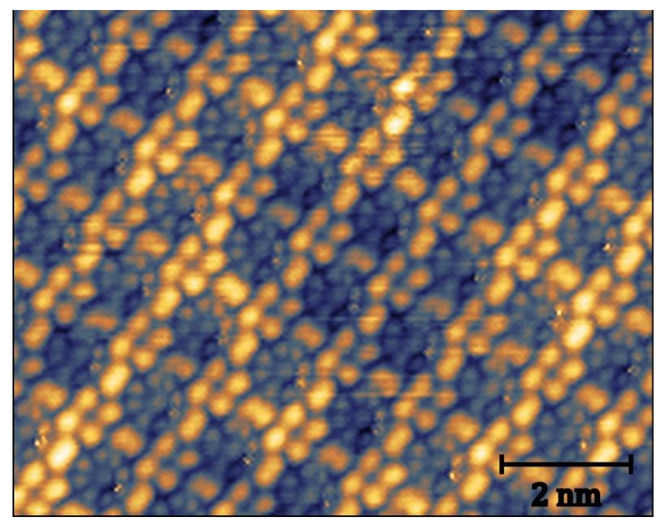
M. Atzori, L. Tesi *et al.*, *JACS*, 2016

UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

Superconducting planar resonator



C. Bonizzoni et al. *Sci. Reports* 2017



Max Planck Institute

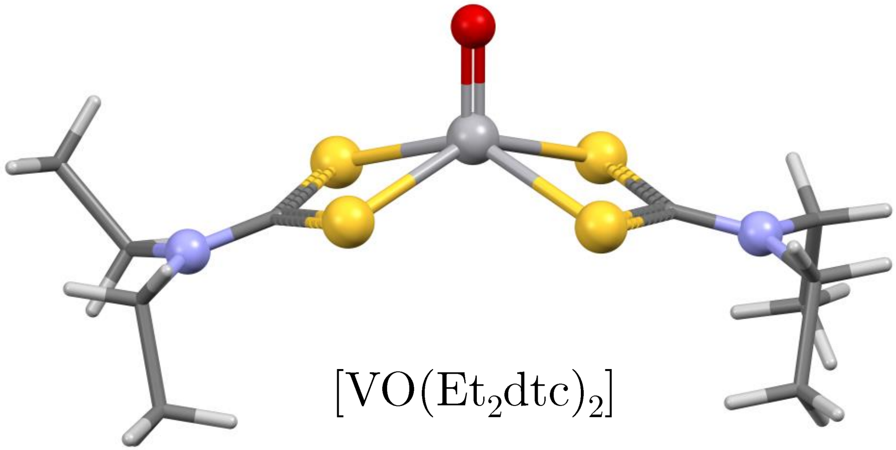
I. Cimatti et al. *Nano. Horizons* 2019

L. Malavolti et al. *Nano Letters* 2018

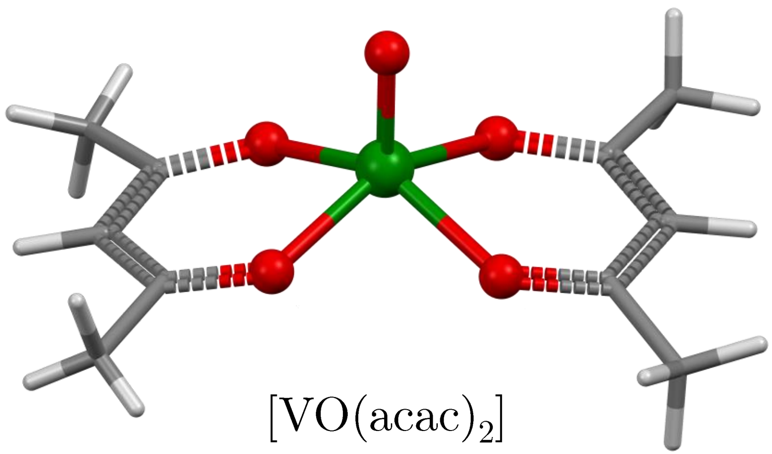
AC susceptometry and THz spectroscopy of the pure compounds

↓

Evidence of the role of low energy phonons in spin dynamics



$[VO(Et_2dtc)_2]$

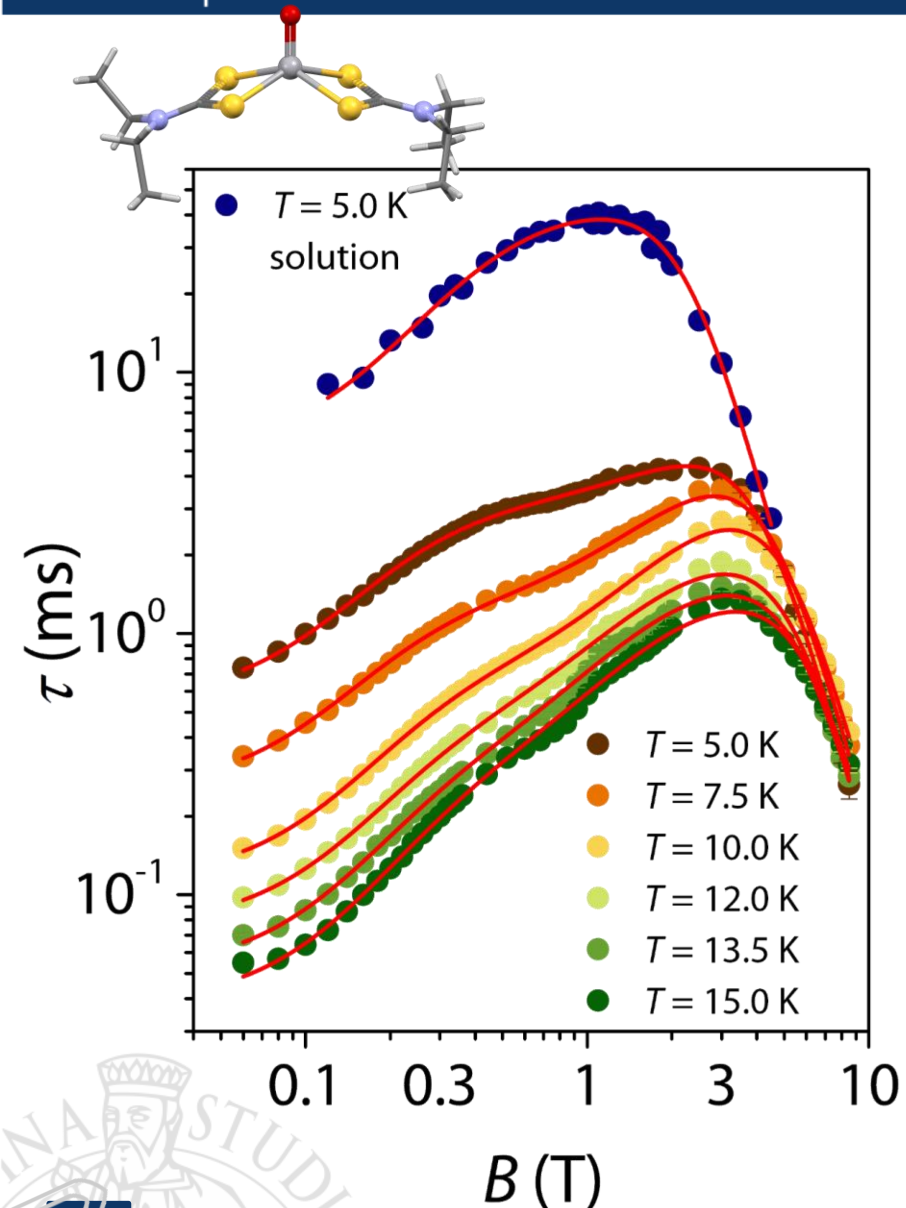


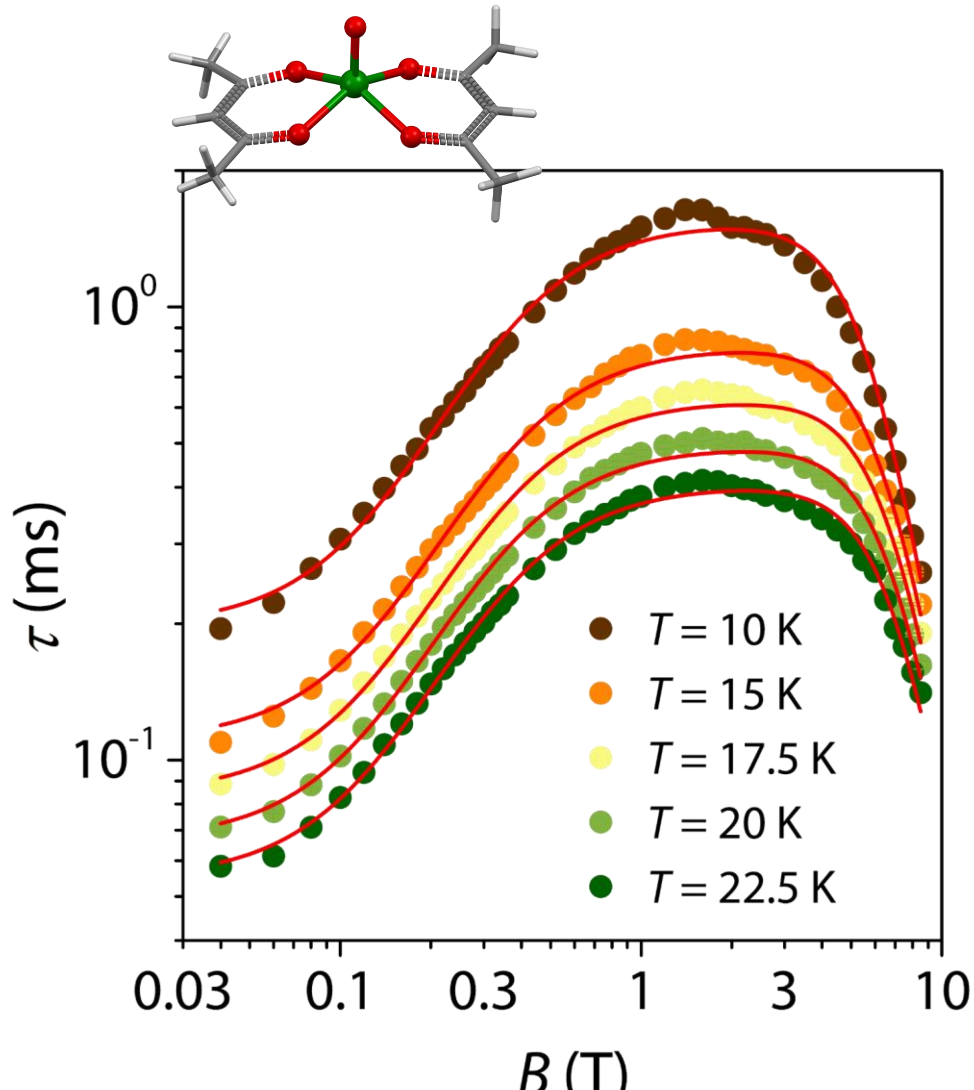
$[VO(acac)_2]$

(Et_2dtc = Ethyldithiocarbammate)
(acac = acetylacetonate)

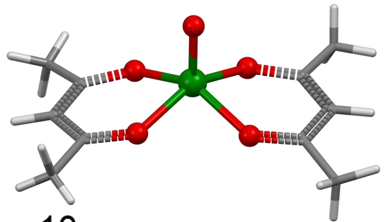
M. Atzori, L. Tesi *et al.*, *JACS*, 2017

AC susceptometry – B dependence of τ



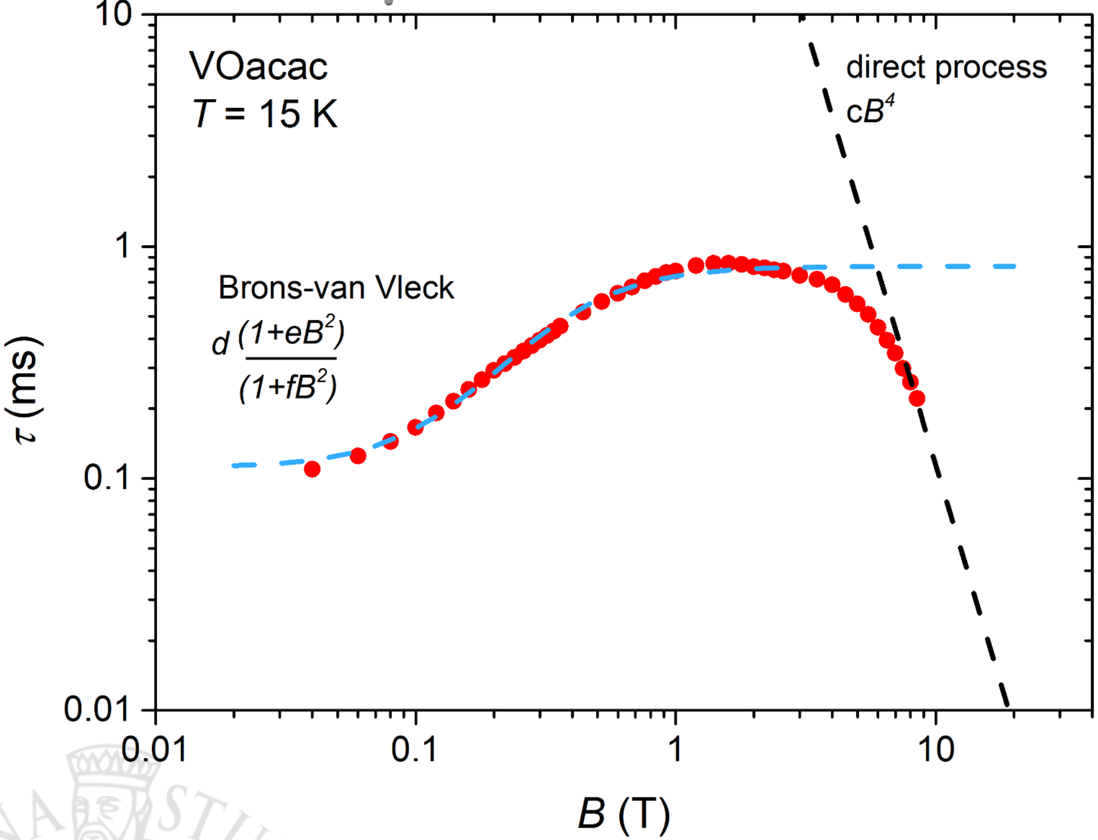


M. Atzori, L. Tesi *et al.*, *JACS*, 2017

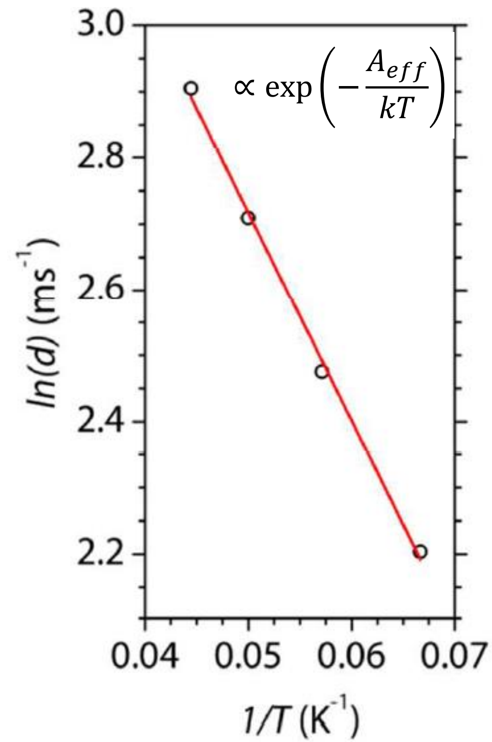


Direct + Brons-van Vleck model

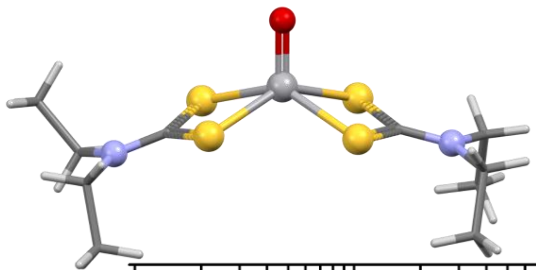
$$\tau^{-1} = cB^4 + d\,\frac{1+eB^2}{1+fB^2}$$

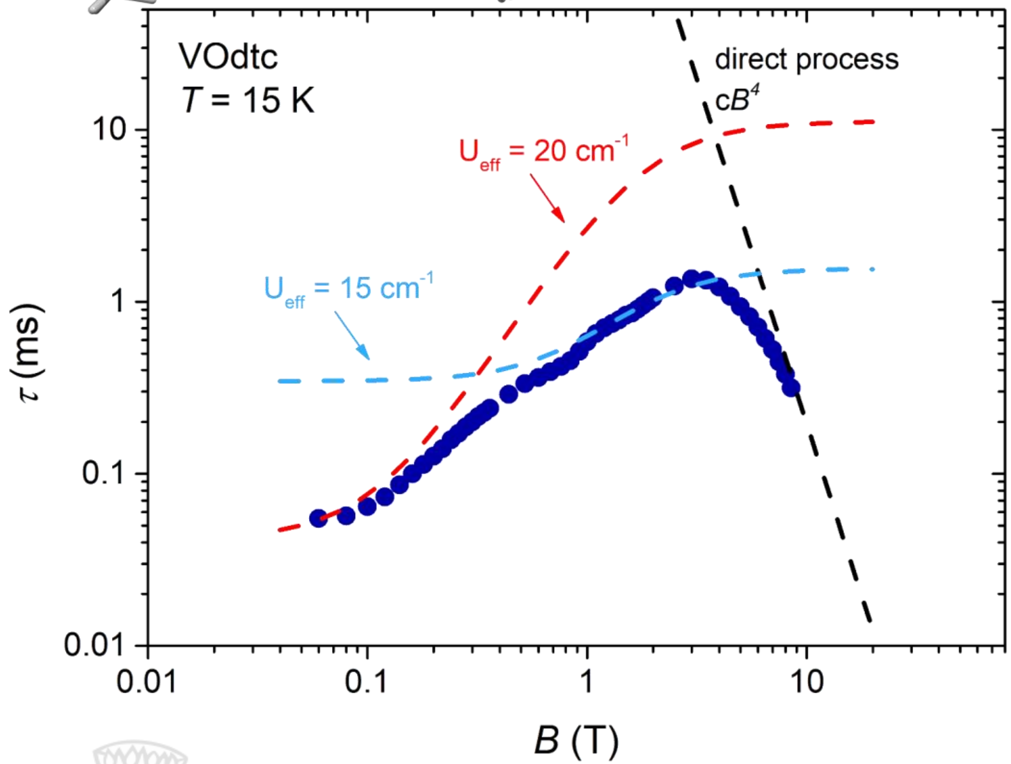


A_{eff}=22 cm^{-1}



M. Atzori, L. Tesi *et al.*, *JACS*, 2017

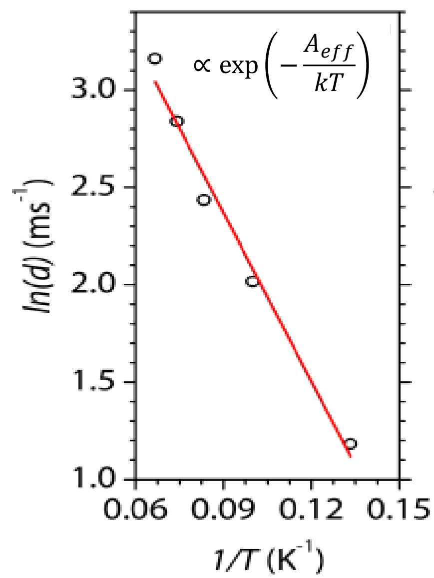




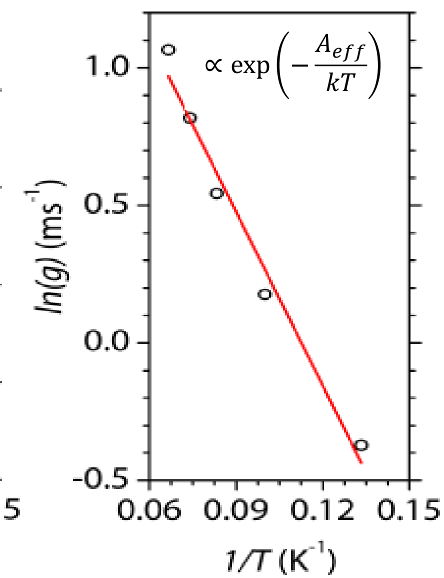
Direct + Brons-van Vleck model

$$\tau^{-1} = cB^4 + d\,\frac{1+eB^2}{1+fB^2} + g\,\frac{1+eB^2}{1+hB^2}$$

A_{eff}=20 cm^{-1}



A_{eff}=15 cm^{-1}

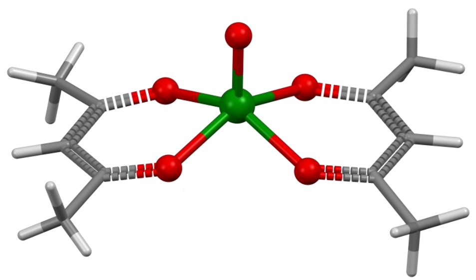


M. Atzori, L. Tesi *et al.*, *JACS*, 2017

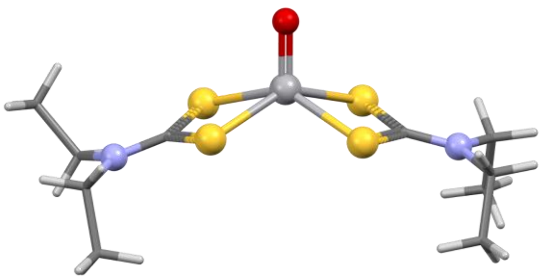
Correlation between the activation energy and phonon frequency:

From: A. Lunghi *et al.*, *Nature Comm. 8*, 14620 (2017)

$$A_{eff} = \frac{\hbar\omega_v}{2}$$



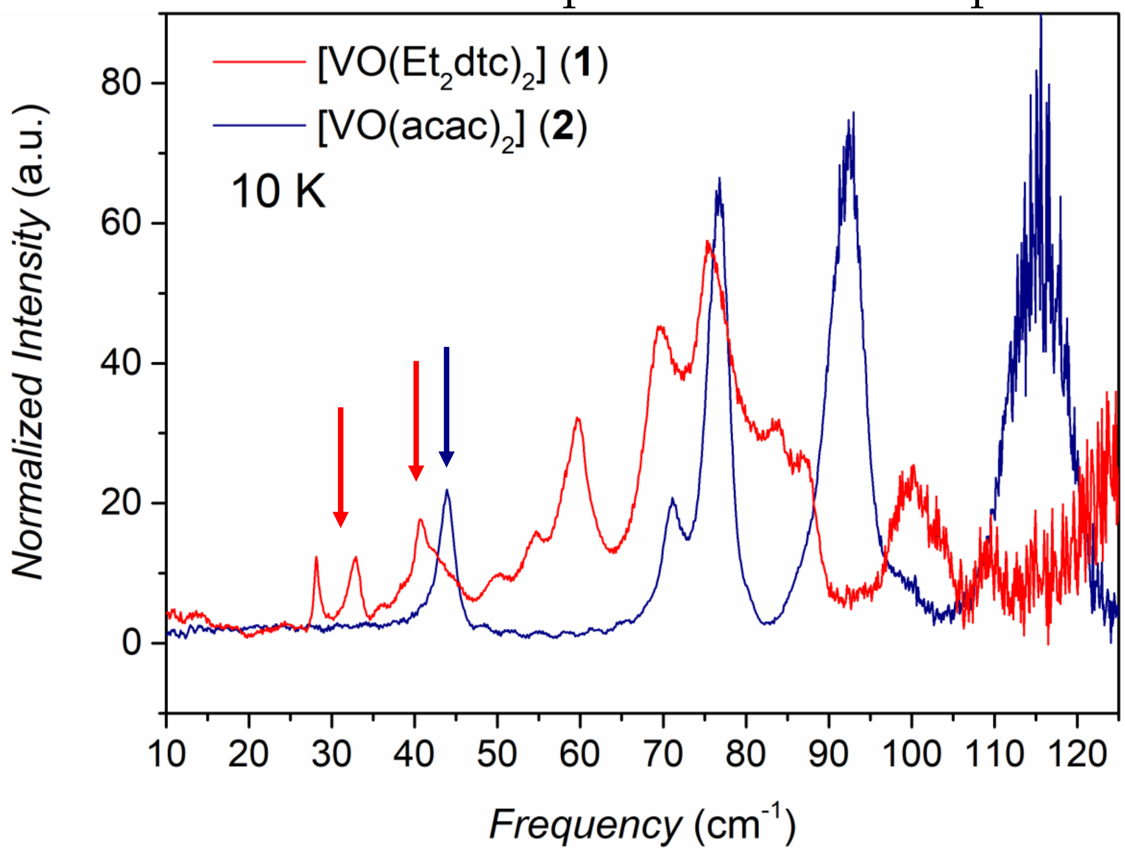
$A_{eff} = 22(2)\ cm^{-1}$



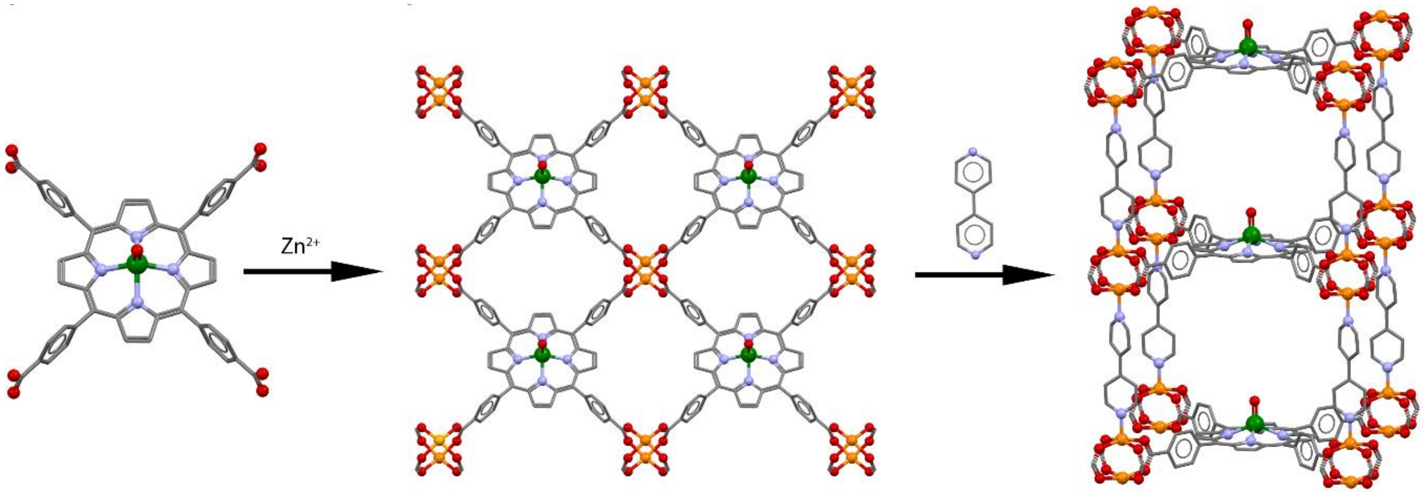
$A_{eff} = 15(2)\ cm^{-1}$

$A_{eff} = 20(2)\ cm^{-1}$

experimental THz spectra

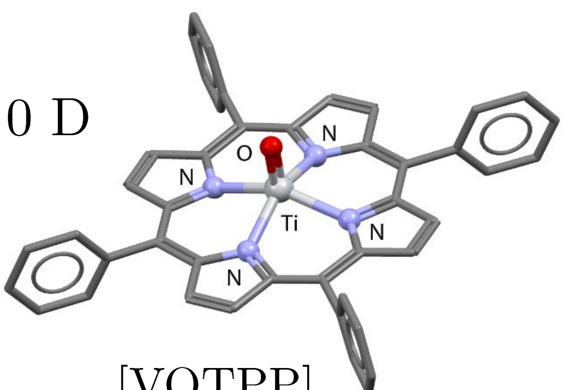


M. Atzori, L. Tesi *et al.*, *JACS*, 2017



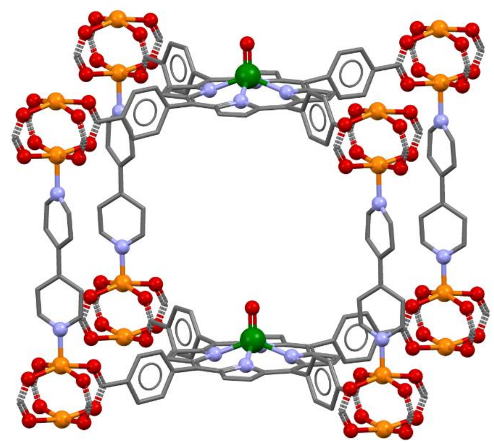
In collaboration with
Prof. M. Yamashita
and T. Yamabayashi

0 D



[VOTPP]
2% in [TiOTPP]

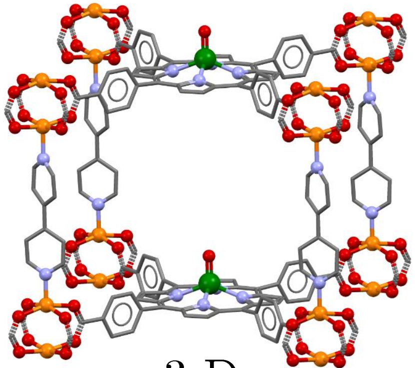
3 D

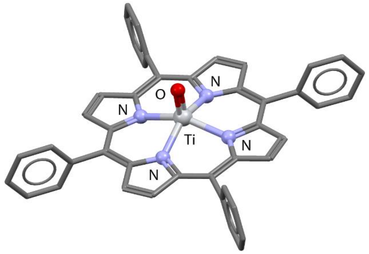


[VO(TCPP-Zn_2-bpy)]
5% in [TiO(TCPP-Zn_2-bpy)]

(VOTPP = tetraphenylporphyrinate)
(TCPP = tetracarboxylphenylporphyrinate)
(bpy = 4,4′-bipyridyl)

T. Yamabayashi, M. Atzori, L. Tesi *et al.*, *JACS*, 2018



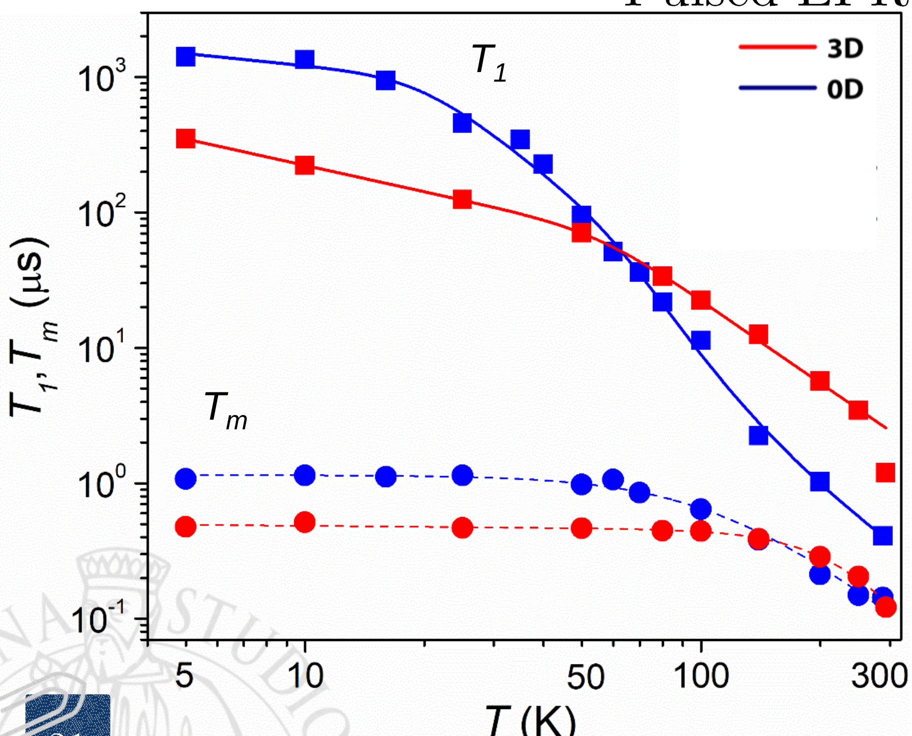


$$T_1^{-1} = a_{dir}T^{x} + a_{loc}\frac{e^{(\hbar\omega/k_BT)}}{(e^{(\hbar\omega/k_BT)}-1)^2}$$

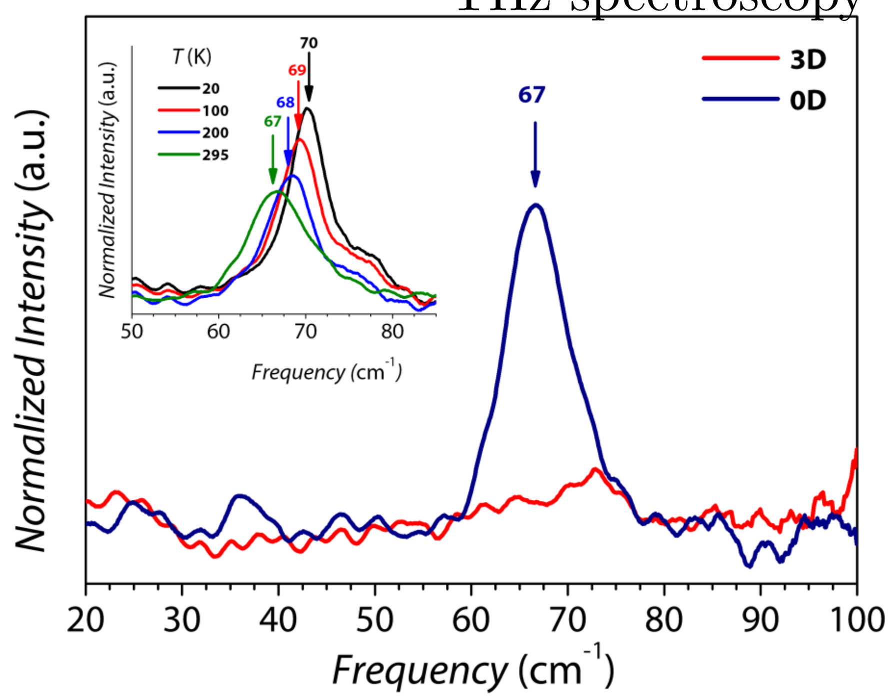
3D $\hbar\omega = 184(2)\ \mathrm{cm}^{-1}$

0D $\hbar\omega = 67(0)\ \mathrm{cm}^{-1} + \hbar\omega = 303(35)\ \mathrm{cm}^{-1}$

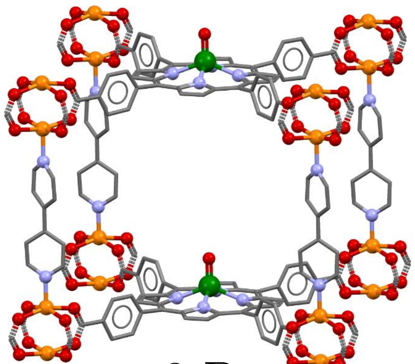
Pulsed EPR



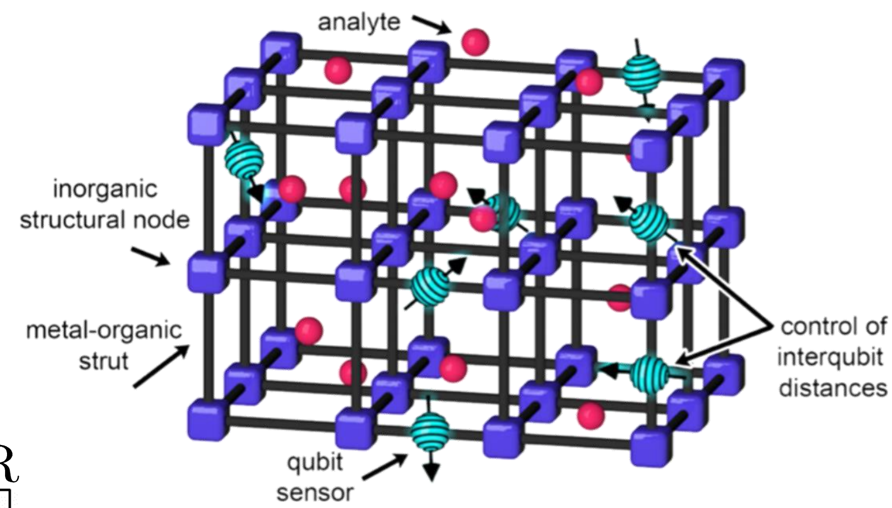
THz spectroscopy



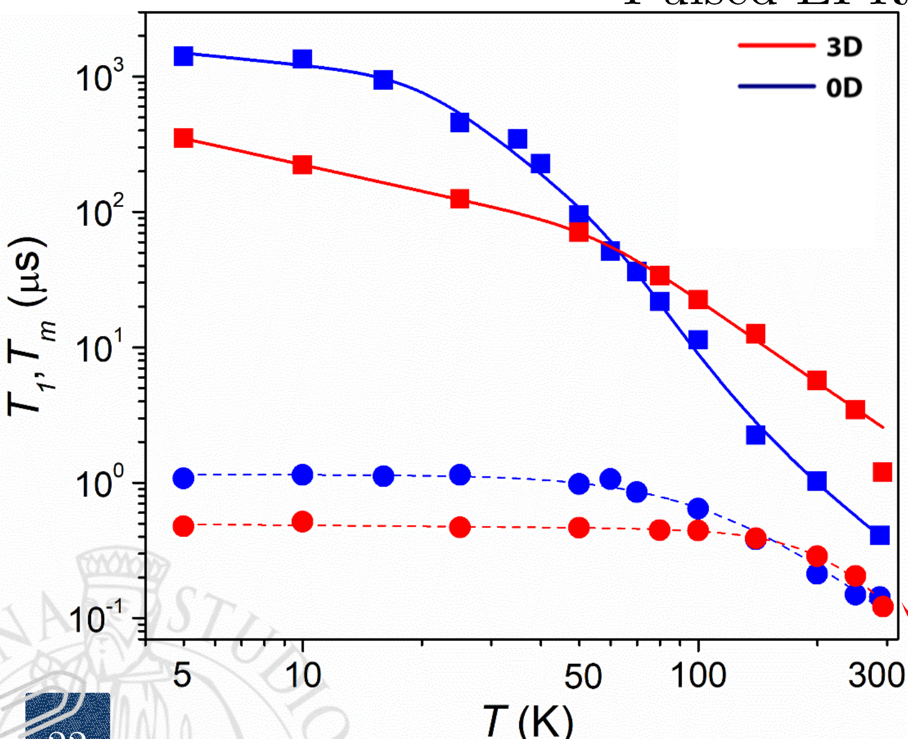
T. Yamabayashi, M. Atzori, L. Tesi *et al.*, *JACS*, 2018

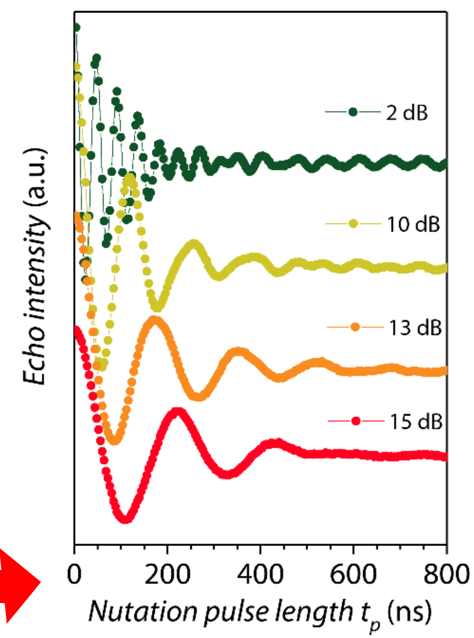


3 D



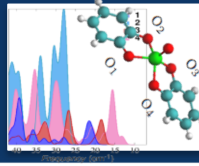
Pulsed EPR

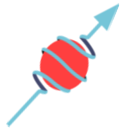




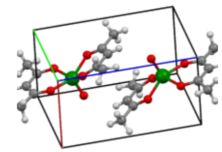
Rabi oscillations

T. Yamabayashi, M. Atzori, L. Tesi *et al.*, *JACS*, 2018

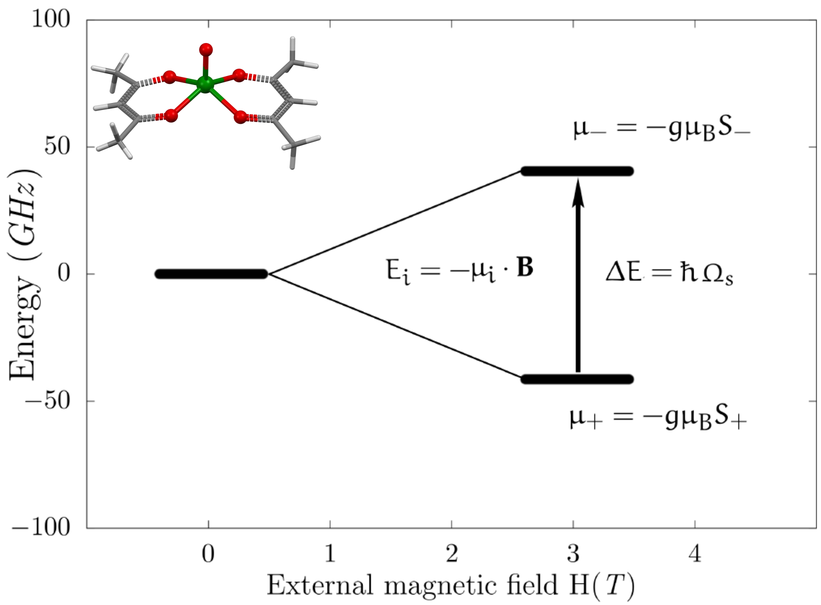


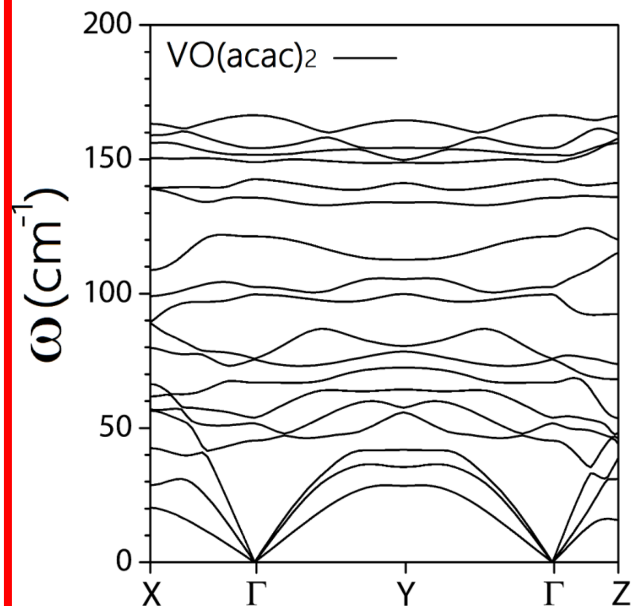


Spin system



Lattice system





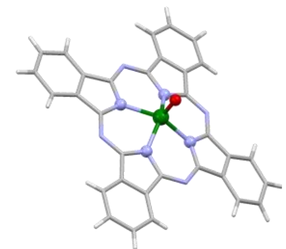
A. Albino, S. Benci, L. Tesi *et al.*, *ArXiv*, 2019
A. Lunghi, S. Sanvito, *ArXiv*, 2019

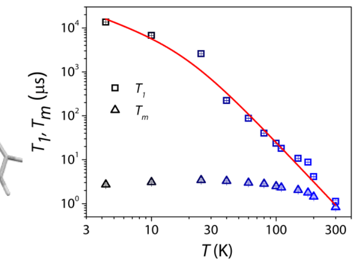
Spin-phonon coupling

by *ab initio* methods

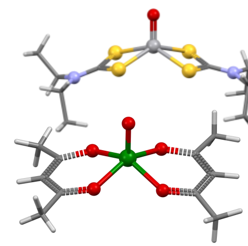
Conclusions

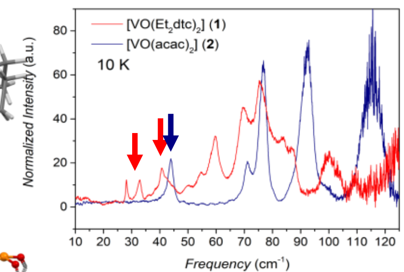
- Vanadyl phthalocyanine shows long coherence times also at room temperature. This, together with the possibility to easily deposit it on surface makes it an interesting MSQ system;



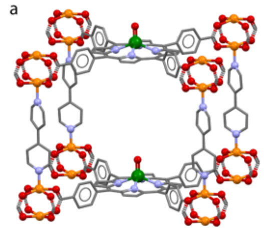


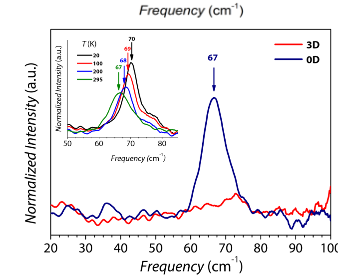
- We have evidenced the role of low energy vibrational modes in spin dynamics by combining the results of ac susceptibility (τ vs B) and pulsed EPR (T_1 vs T) measurements with THz spectroscopy;



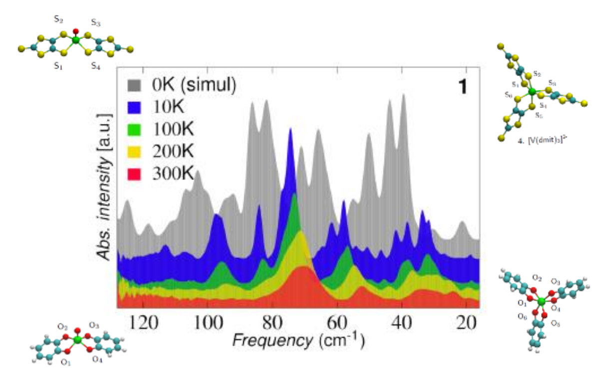


a





- Ab initio calculations can be used to simulate the spin-phonon coupling, this is an important step toward a better understand of the spin-lattice relaxation mechanisms. It is important to check the quality of the simulation in the THz range.



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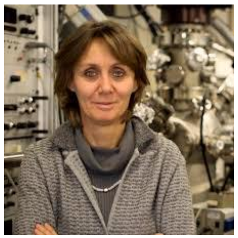
Acknowledgments

The Florence group

LAMM
Laboratorio di Magnetismo Molecolare


Prof. R. Sessoli


Prof. L. Sorace


Dr. M. Atzori


F. Santanni

THz spectroscopy

lens
European Laboratory for Non-Linear Spectroscopy


Prof. R. Torre


S. Benci

UNIVERSITÀ DEGLI STUDI DI TORINO

Pulsed EPR


Prof. M. Chiesa


Dott. E. Morra

Trinity College Dublin

Theoretical calculations


Dr. A. Lunghi


A. Albino

AND YOU

FOR THE

ATTENTION!