

# Controlling materials with lattice vibrations

**Gael Privault**

Supervisors: E. Collet<sup>[1]</sup>, M. Lorenc<sup>[1]</sup>,

In collaboration with: I. Chaban<sup>[1]</sup>,  
A. Subedi<sup>[2]</sup>,

J.Y. Mevellec<sup>[3]</sup>, B. Corraze<sup>[3]</sup>, B. Humbert<sup>[3]</sup>, E. Janod<sup>[3]</sup>,  
N. Daro<sup>[4]</sup>, G. Chastanet<sup>[4]</sup>

1. Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France.
2. Institut des Matériaux Jean Rouxel, CNRS Université de Nantes, UMR 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes, France
3. CNRS, University of Bordeaux, ICMCB, UMR 5026, 87 Avenue du Docteur-Albert-Schweitzer, 33608 Pessac, France
4. Centre de Physique Théorique, École Polytechnique, CNRS, 91128 Palaiseau Cedex, France

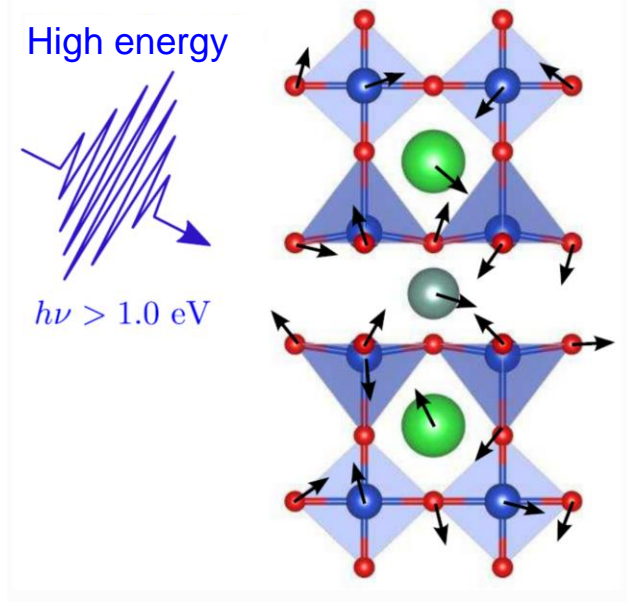


## Outlook :

- Photo-Induced Phase Transition (PIPT)
- Non-Linear Phononic
- Control of magnetic materials
- Ultrafast experimental set up

# Photo-Induced Phase Transition (PIPT)

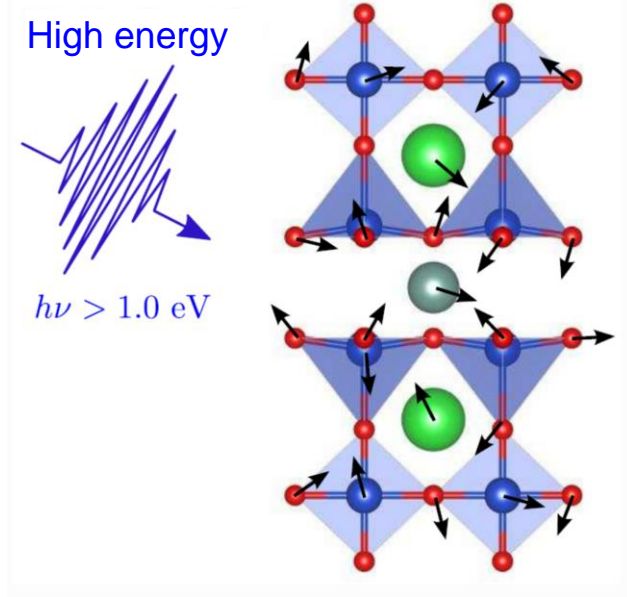
## Photo-Induced effect



[2] A. Subedi *et al. Phys. Rev. B* 89 (2014).

# Photo-Induced Phase Transition (PIPT)

## Photo-Induced effect



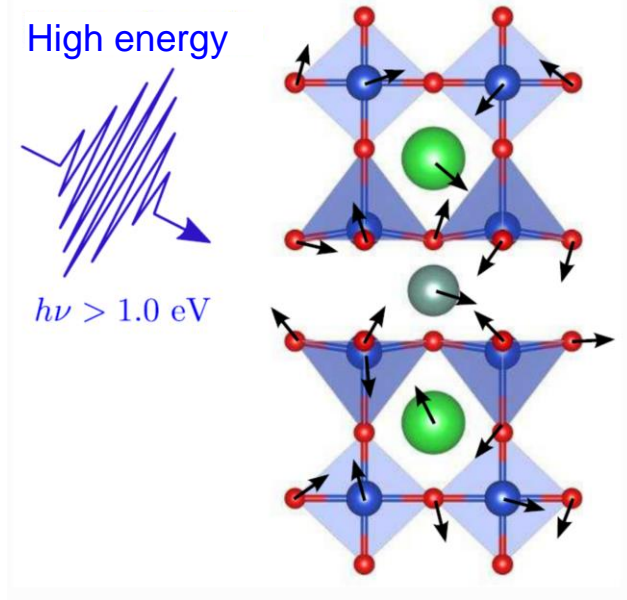
Reorganisation of  
electronic  
configuration



[2] A. Subedi *et al.* *Phys. Rev. B* 89 (2014).

# Photo-Induced Phase Transition (PIPT)

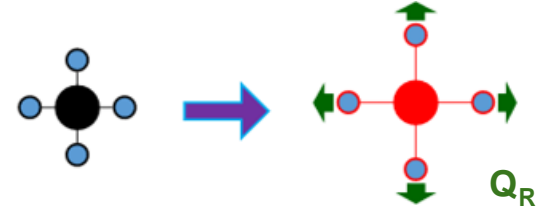
## Photo-Induced effect



Reorganisation of  
electronic  
configuration



Structural  
reorganisation :  
oscillation of the  
vibrational mode  $Q_R$

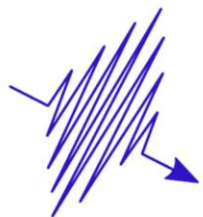


[2] A. Subedi *et al. Phys. Rev. B* 89 (2014).

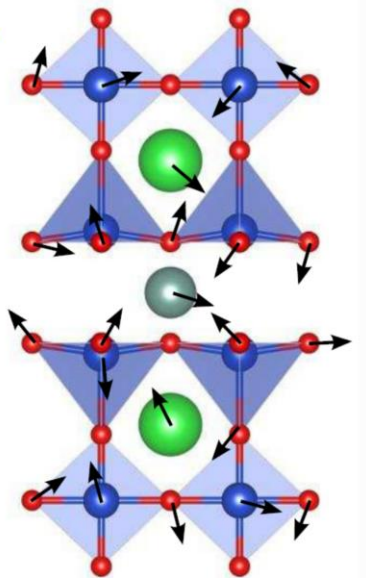
# Photo-Induced Phase Transition (PIPT)

## Photo-Induced effect

High energy



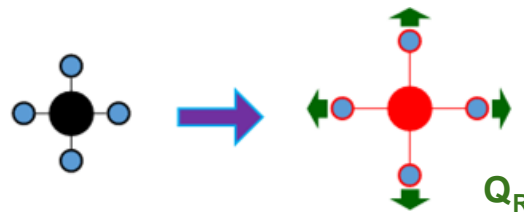
$h\nu > 1.0$  eV



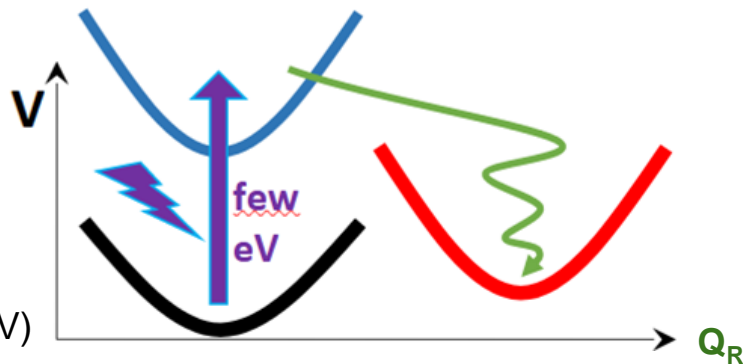
Reorganisation of electronic configuration



Structural reorganisation : oscillation of the vibrational mode  $Q_R$



Change the equilibrium position



[2] A. Subedi *al. Phys. Rev. B* 89 (2014).

Limitations :

- High energy excitation (eV)
- No selectivity
- Entropy increase

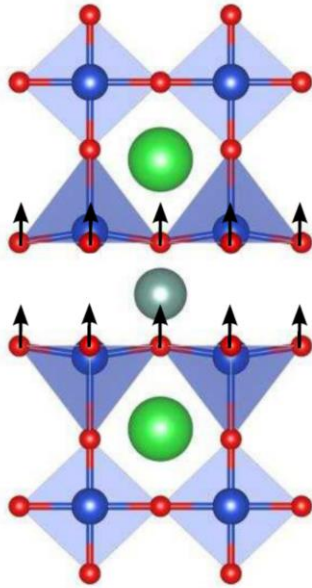
# Non-Linear Phononic (NLP)

## Resonant excitation of infrared active mode

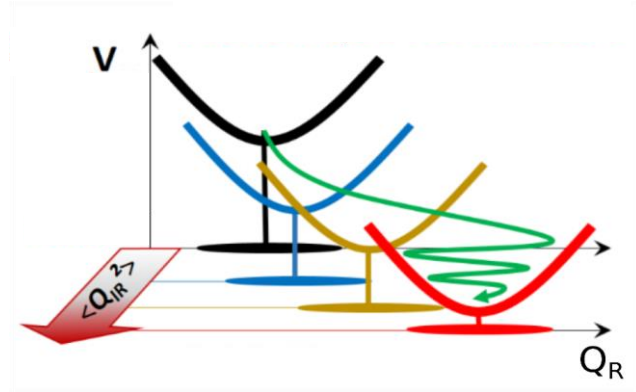
Low energy (IR)



$h\nu < 100$  meV



Change the  
equilibrium position



[2] A. Subedi *et al.* *Phys. Rev. B* 89 (2014).

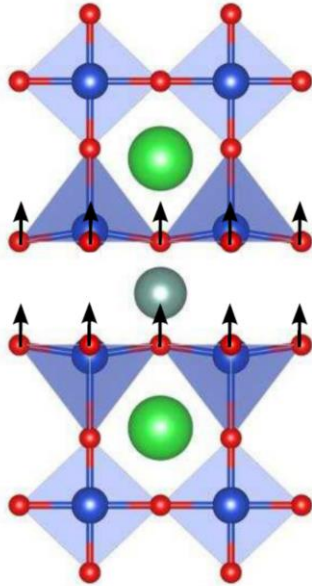
# Non-Linear Phononic (NLP)

## Non-linear phononic

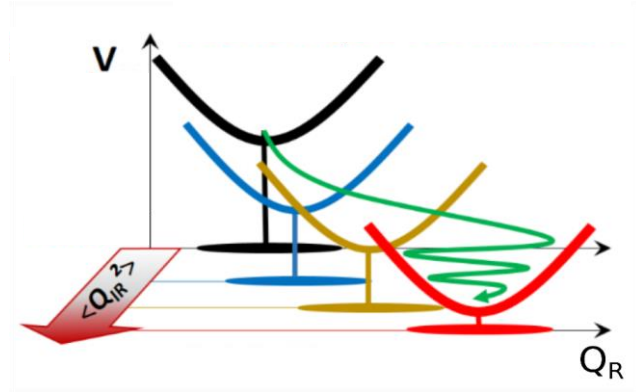
Low energy (IR)



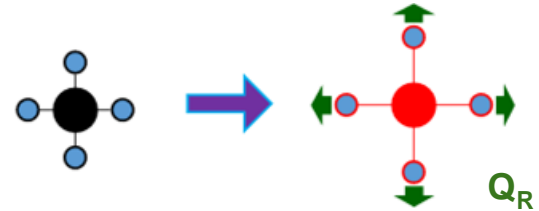
$h\nu < 100$  meV



Change the  
equilibrium position



Structural  
reorganisation :  
oscillation of the  
vibrational mode  $Q_R$



[2] A. Subedi *al. Phys. Rev. B* 89 (2014).



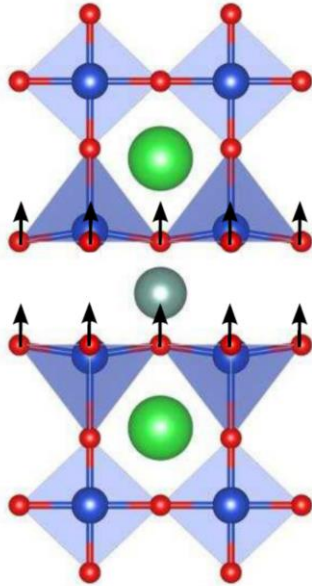
# Non-Linear Phononic (NLP)

## Non-linear phononic

Low energy (IR)

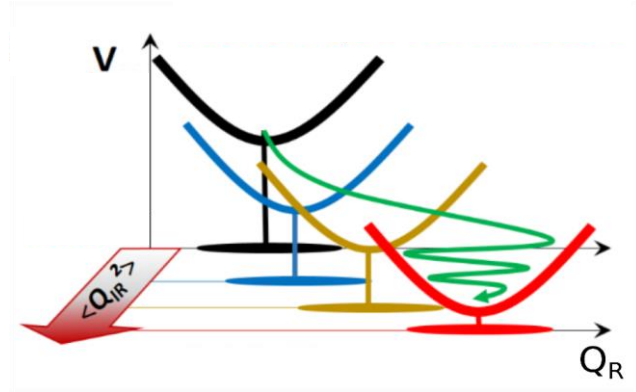


$h\nu < 100$  meV

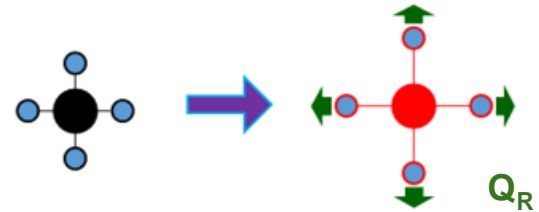


[2 A. Subedi *al. Phys. Rev. B* 89 (2014).

Change the  
equilibrium position



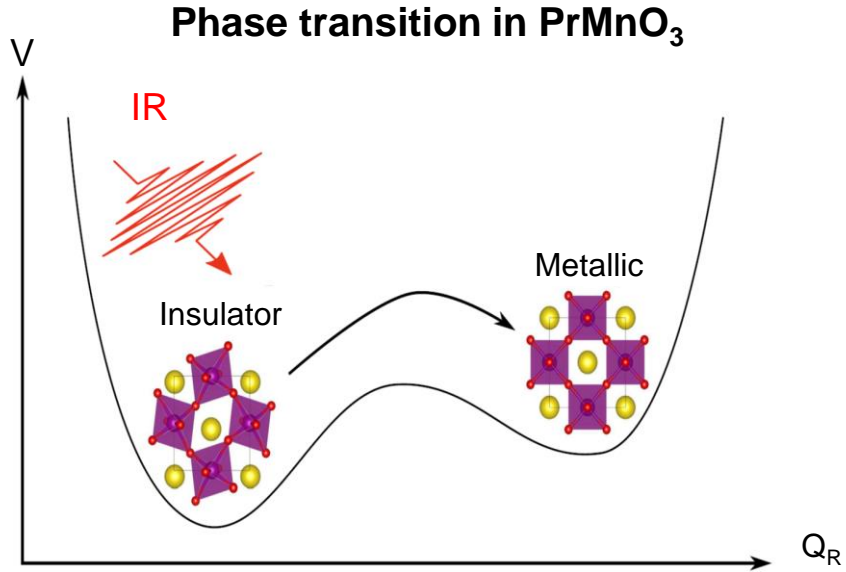
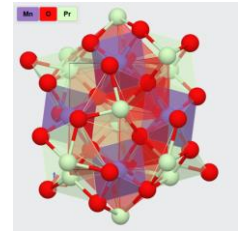
Structural  
reorganisation :  
oscillation of the  
vibrational mode  $Q_R$



Change the electronic  
configuration

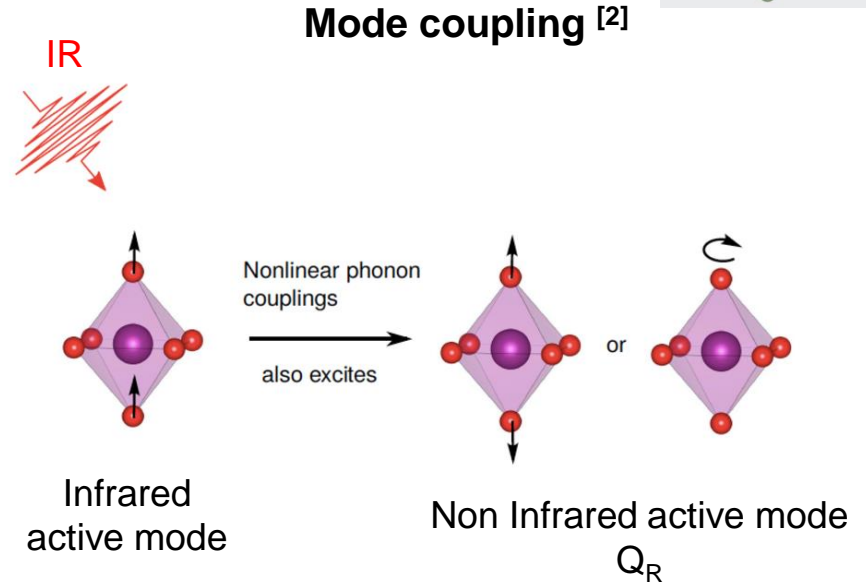
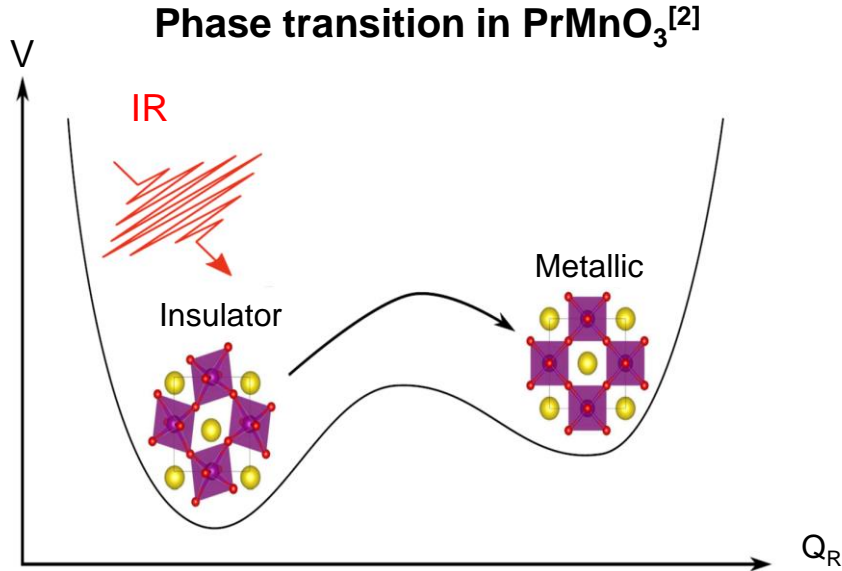
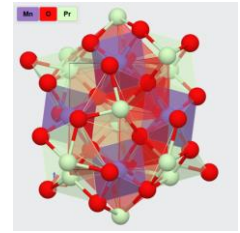


# Non-Linear Phononic (NLP)



[2] A. Subedi *et al.* *Phys. Rev. B* 89 (2014).

# Non-Linear Phononic (NLP)



The infrared vibration change the equilibrium structure of the crystal and modifies the electronic configuration

# Non-Linear Phononic: Theory

Double-potential well equation :

$$V(Q_R) = a Q_R^2 + b Q_R^3 + c Q_R^4$$

$Q_R$  : Amplitude of the Raman vibrational mode

$Q_{IR}$  : Amplitude of the IR vibrational mode

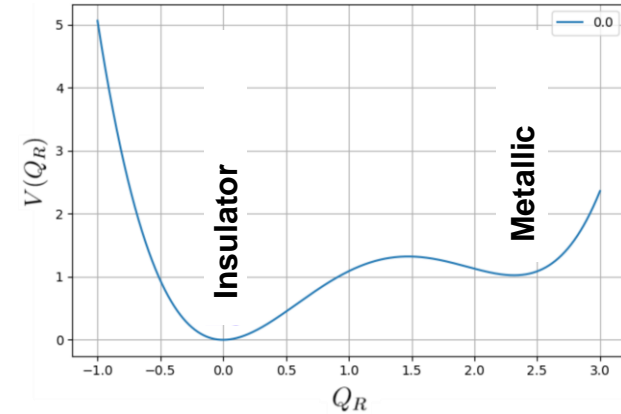
Double-potential well equation  
with the coupling terme :

$$V(Q_R) = a Q_R^2 + b Q_R^3 + c Q_R^4 - g Q_R Q_{IR}^2$$

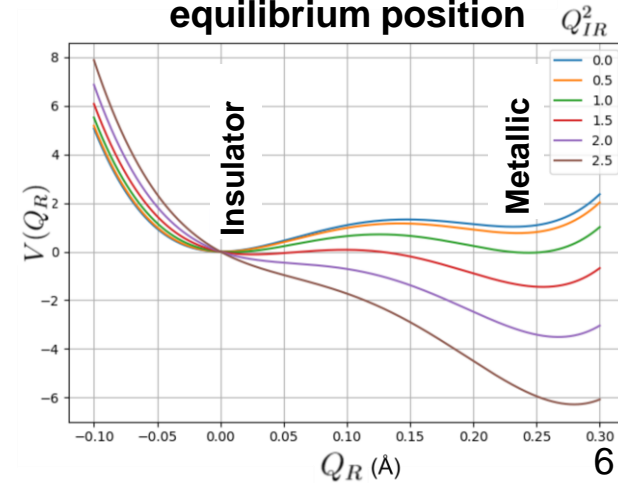
Coupling term relies on frequency shift  
and its sign can depend on  $Q_{IR}$

$$g \propto \left( \frac{\omega_{IR}}{\omega_R} \right)^2$$

Phenomenological  
adiabatic potential

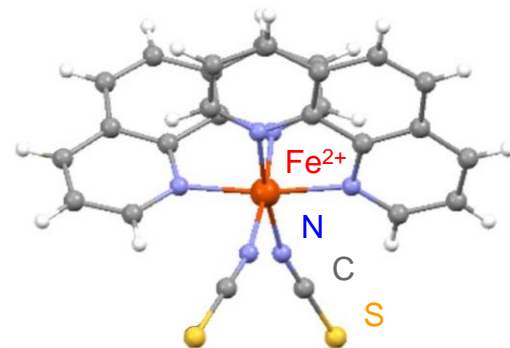


Coupling effect on the  
equilibrium position  $Q_{IR}^2$



# The spin-crossover crystal: $\text{Fe}(\text{phen})_2(\text{NCS})_2$

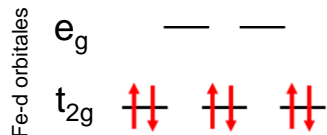
Representation of the  
isolated molecule



**LS**

(Low spin)

$T < 180 \text{ K}$



**2 Stable states :**

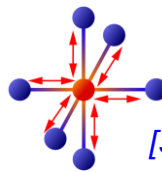
Temperature

$\text{Fe}^{2+} : 3d^6$

schematic electronic configuration

Fe-N distances

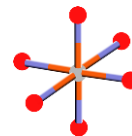
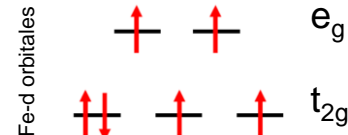
Breathing mode :  $Q_R$



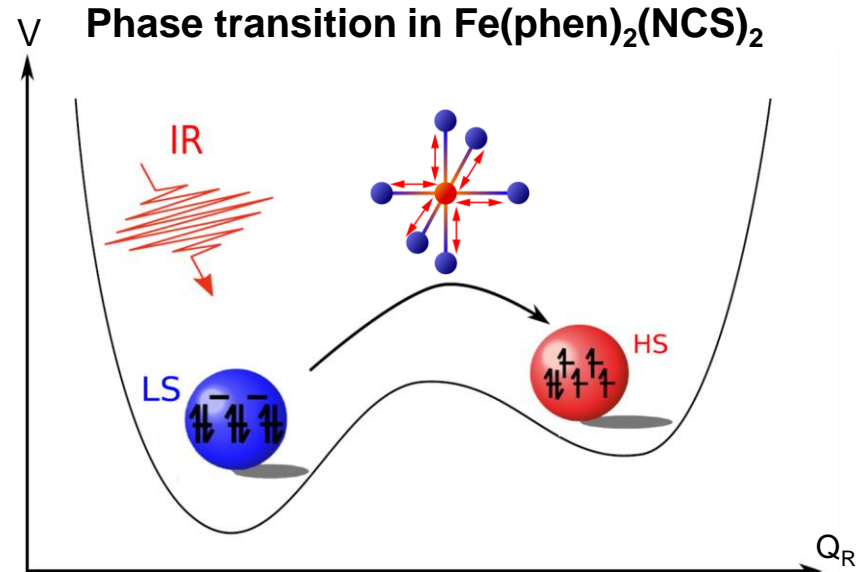
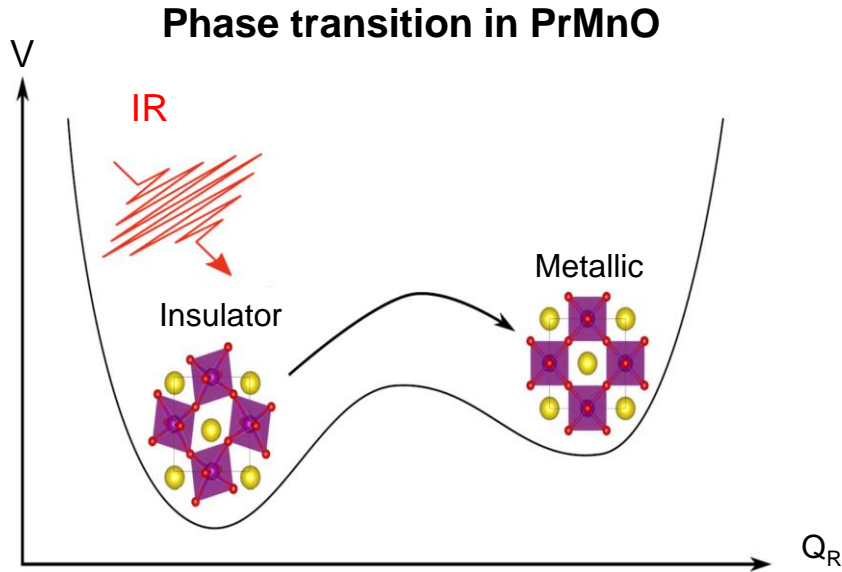
**HS**

(High spin)

$T > 180 \text{ K}$



# The spin-crossover crystal: $\text{Fe}(\text{phen})_2(\text{NCS})_2$



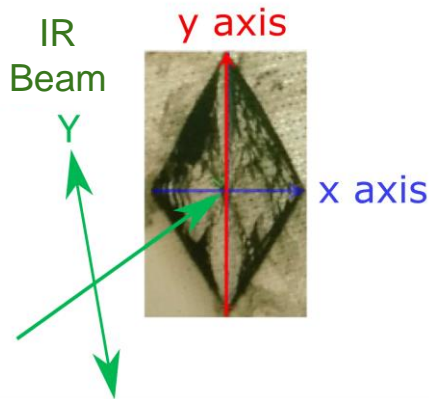
[2] A. Subedi *et al. Phys. Rev. B* 89 (2014).

Because the mode coupling depends on the  $g$  sign :  
different vibrational modes can favor different spin state

$$g Q_R Q_{IR}^2$$

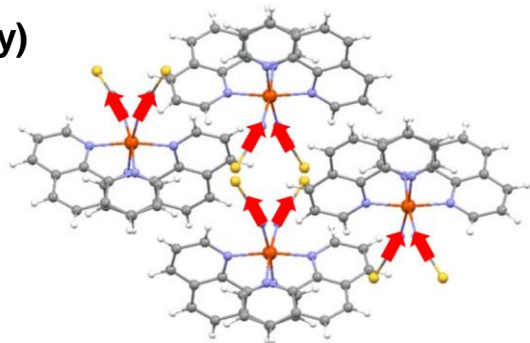
# The spin-crossover crystal: Fe(phen)2(NCS)2

Polarisation dependence



Representation of  $B_{2u}$  N-CS vibration in the primitive cell, frequencies calculated and measured

$B_{2u}$  (y)

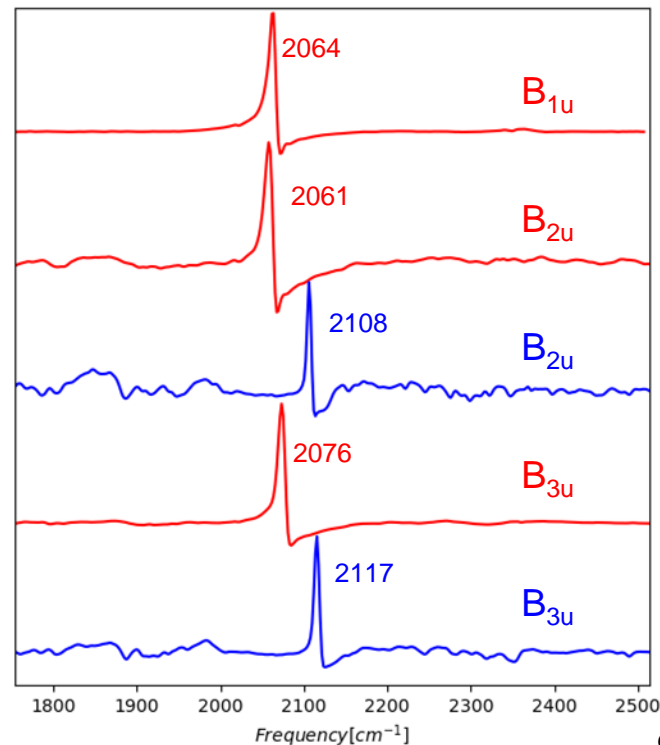


HS  
Exp: 2061  
Calc: 2050.9

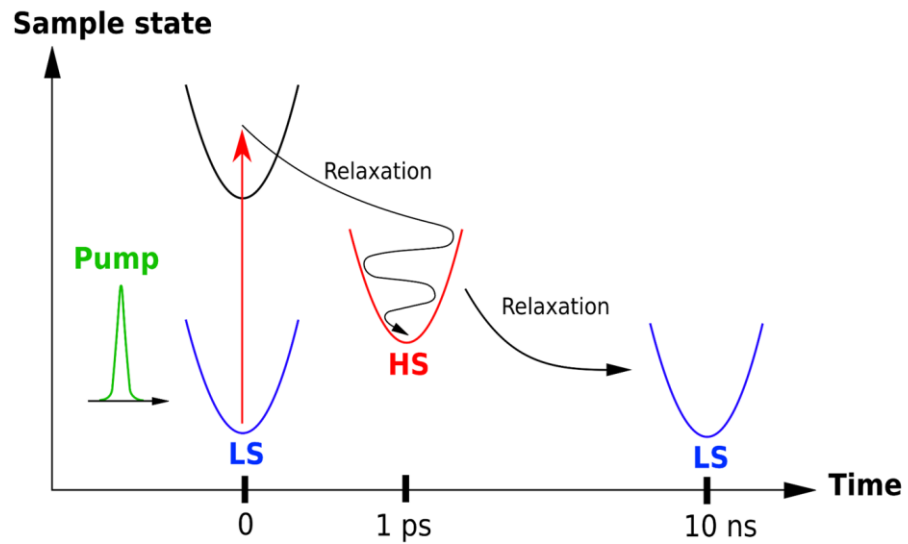
LS  
Exp: 2108  
Calc: 2107.1

Looking for  $Q_{IR}$

Infrared measured (IMN)  
N-CS modes frequency

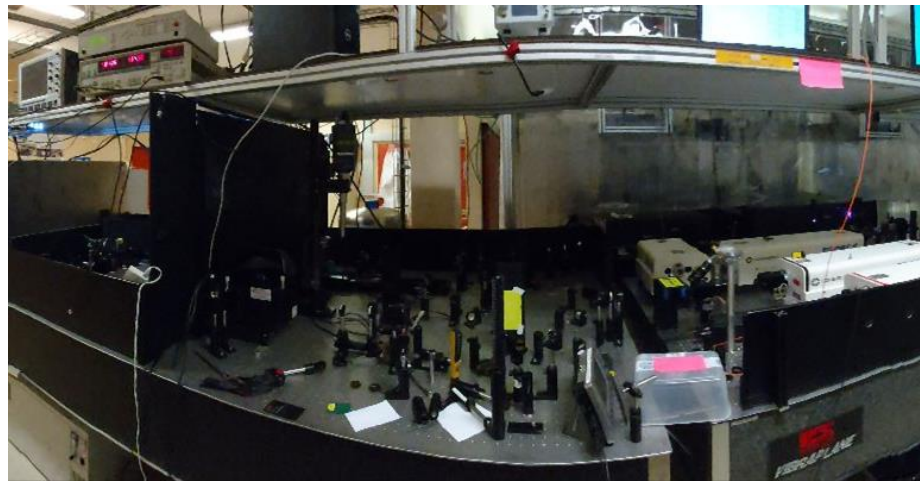
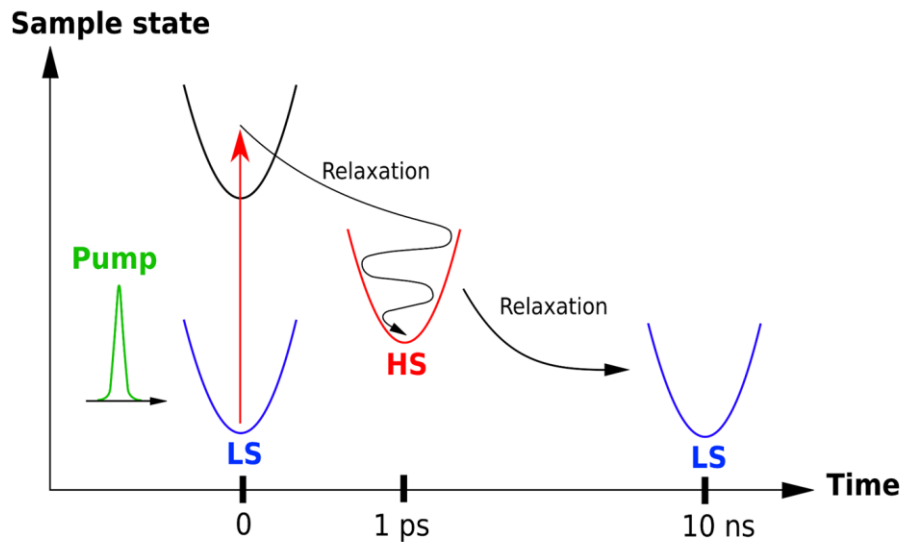


# Pump probe experiment





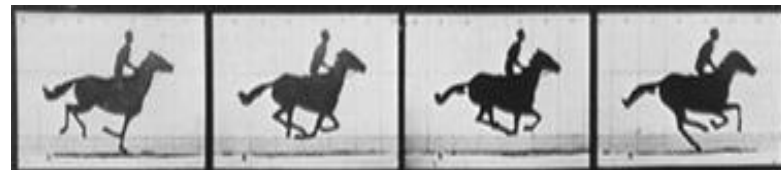
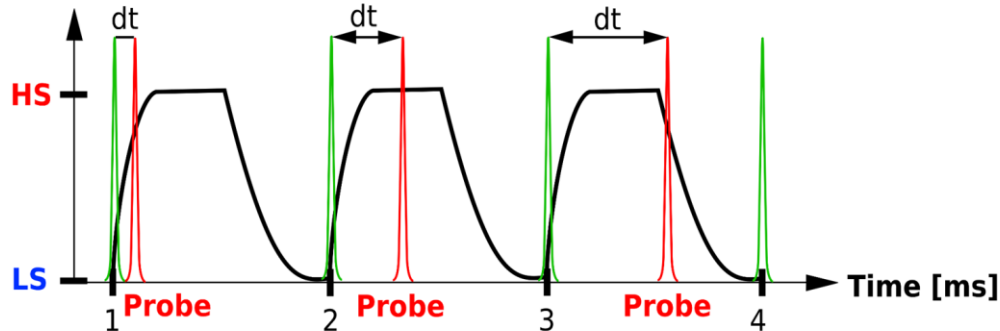
# Pump probe experiment



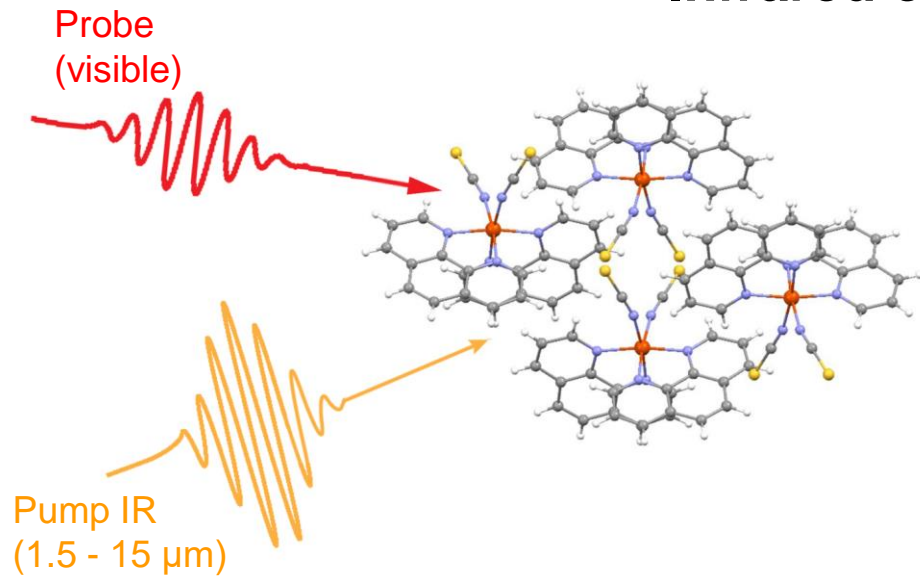
Delay the probe (dt)



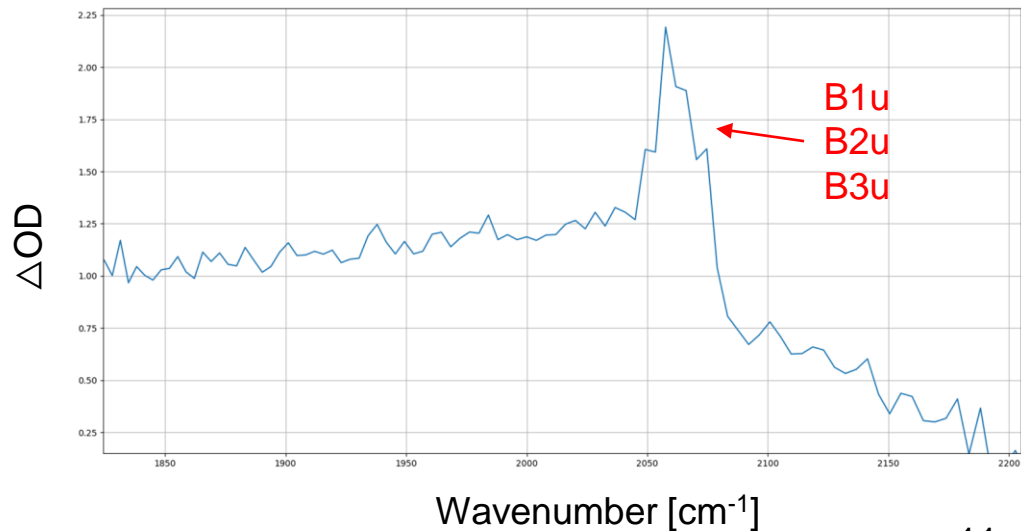
Get the movie of this phenomena



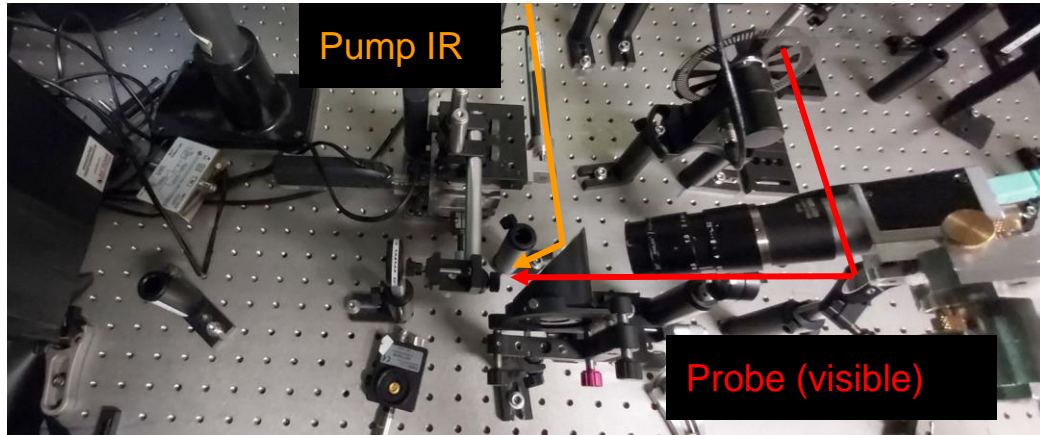
# Infrared experiment



Absorption spectrum of  $\text{Fe}(\text{phen})_2(\text{NCS})_2$

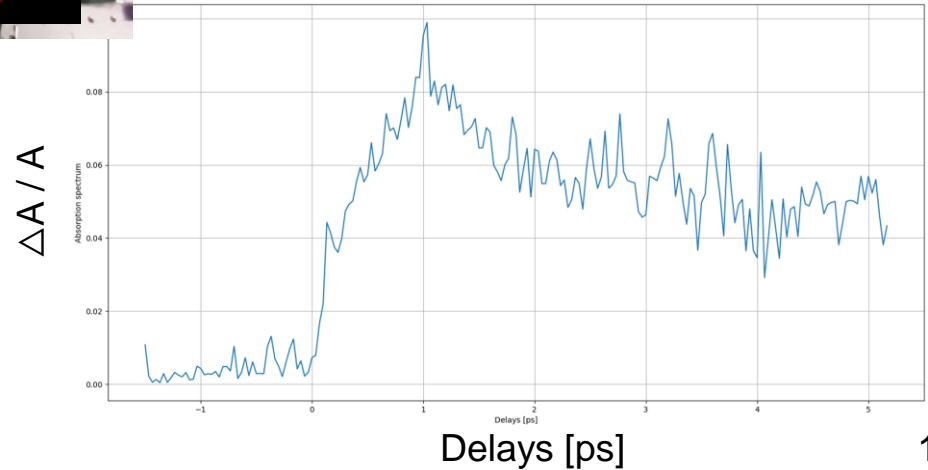


# Firsts results



Same time (resolution of femtoseconds)  
Same place (resolution of microns)

Time zero with Germanium filter



## Conclusion :

- We have identify the Infrared and Raman vibrational modes of the  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  sample
- A.Subedi is calculating the coupling terme between boths vibrational modes
- We are building an Ultrafast Infrared experiment in the lab

# References

- [1] **A. Subedi**, Microscopic theory of non linear phononics, presentation (Junes 2018) Rennes
- [2] **A. Subedi al.** « Theory of nonlinear phononics for coherent light control of solids » , Phys. Rev. B 89, 220301(R) (2014).
- [3] **E. Collet et al.** « Lattice phonon modes of the spin crossover crystal [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>] studied by THz, IR, Raman spectroscopies and DFT calculations ». Eur. Phys. J. B (2019)
- [4] **R. Bertoni**, « Ultrafast Photo-switching of Spin Crossover Crystal Coherence and Cooperativity », these of physics, under the direction of Maciej Lorenc, Rennes, Institut de Physique de Rennes (2013) page 17