

Gaël Privault

Ultrafast spectroscopy applied to photoinduced phase transition

At the Institut de Physique de Rennes

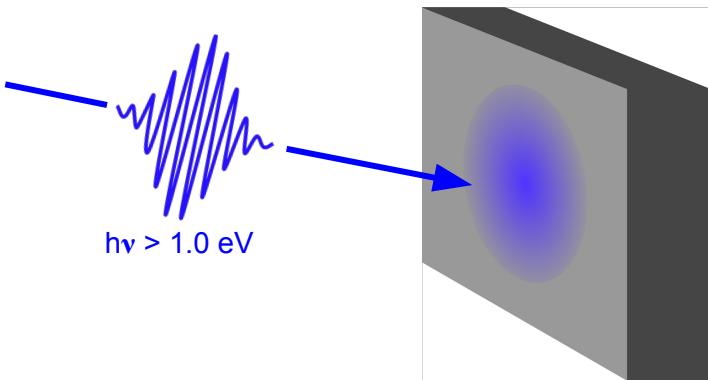
Supervisors : Eric Collet & Maciej Lorenc

**Fundings : ANR Electrophone,
Région Bretagne**

Collaboration IM Nantes (B. Humbert),
Polytechnique (A. Subedi)

Controlling material's states by light irradiation

Perturbation by light irradiation



Time resolved traces of optical transmission and reflection after light irradiation in $\text{Fe}(\text{phen})_2(\text{NCS})_2$ crystal

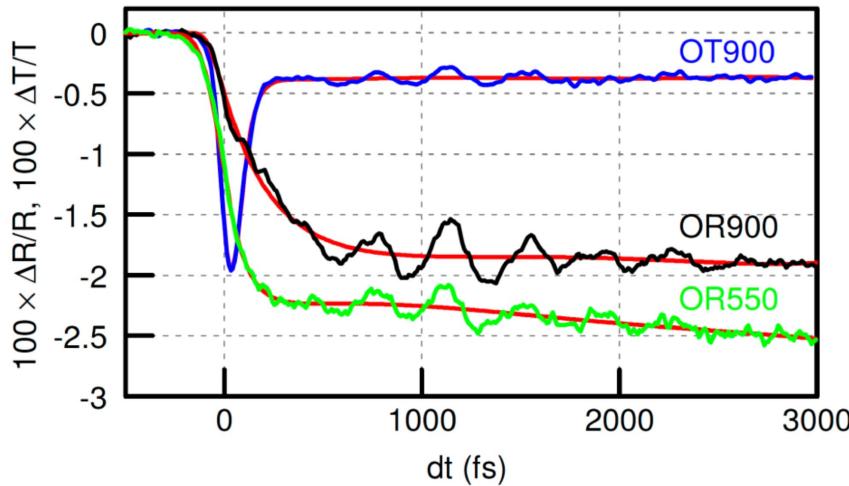
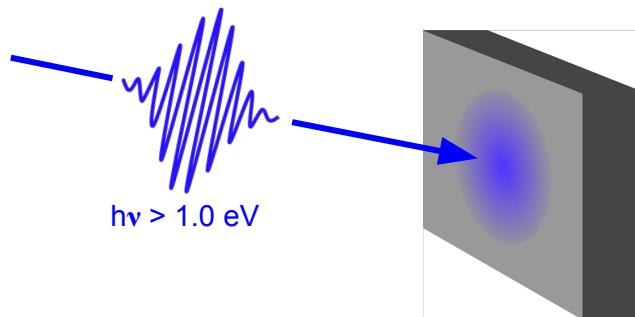


Photo-Induced Phase Transition (PIPT)

Coupling between electronic and structural reorganisation



Reorganisation of the
electronic
configuration

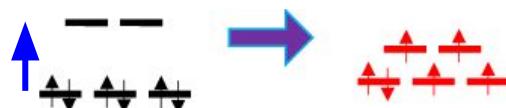
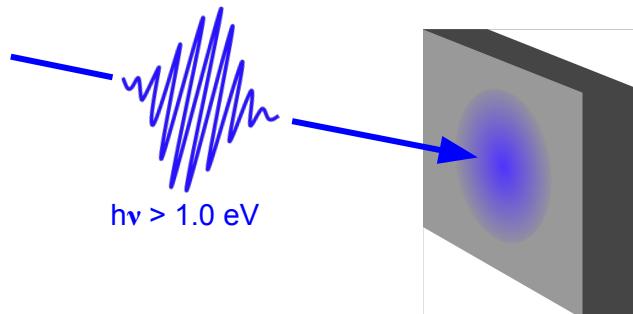
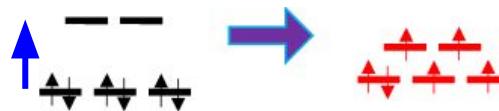


Photo-Induced Phase Transition (PIPT)

Coupling between electronic and structural reorganisation



Reorganisation of the electronic configuration



Structural reorganisation
oscillation of one vibrational mode Q_R

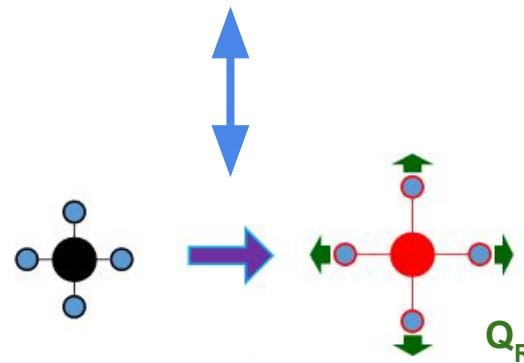
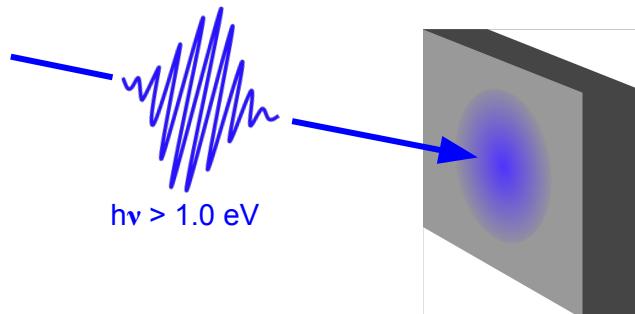
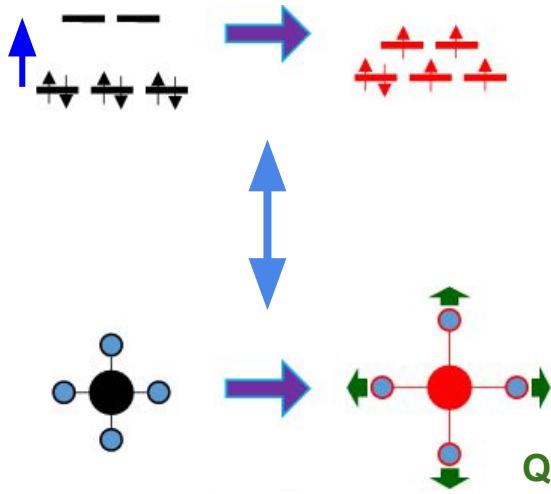


Photo-Induced Phase Transition (PIPT)

Coupling between electronic and structural reorganisation

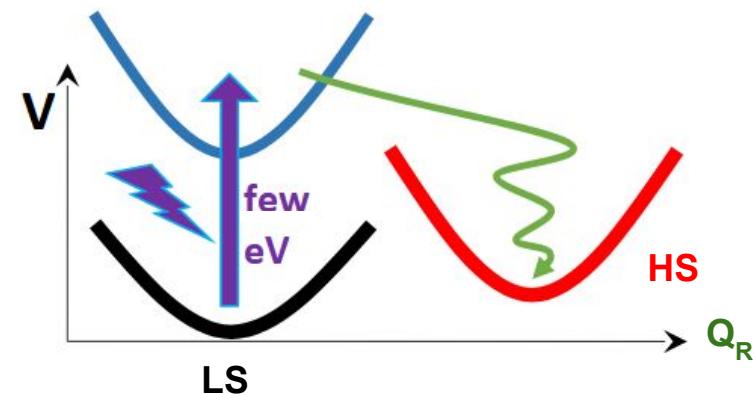


Reorganisation of the electronic configuration



Structural reorganisation
oscillation of one
vibrational mode Q_R

Change the equilibrium position

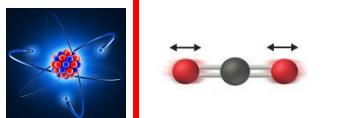


Pump-Probe spectroscopy

What timescale for ultrafast processes ?

Electronic dynamics

Atomic and molecular motions :
molecular/lattice vibrations



Main new television frequency : 1 kHz
1 image per millisecond

Fastest electronics

10^{-15}
fs

10^{-12}
ps

10^{-9}
ns

10^{-6}
μs

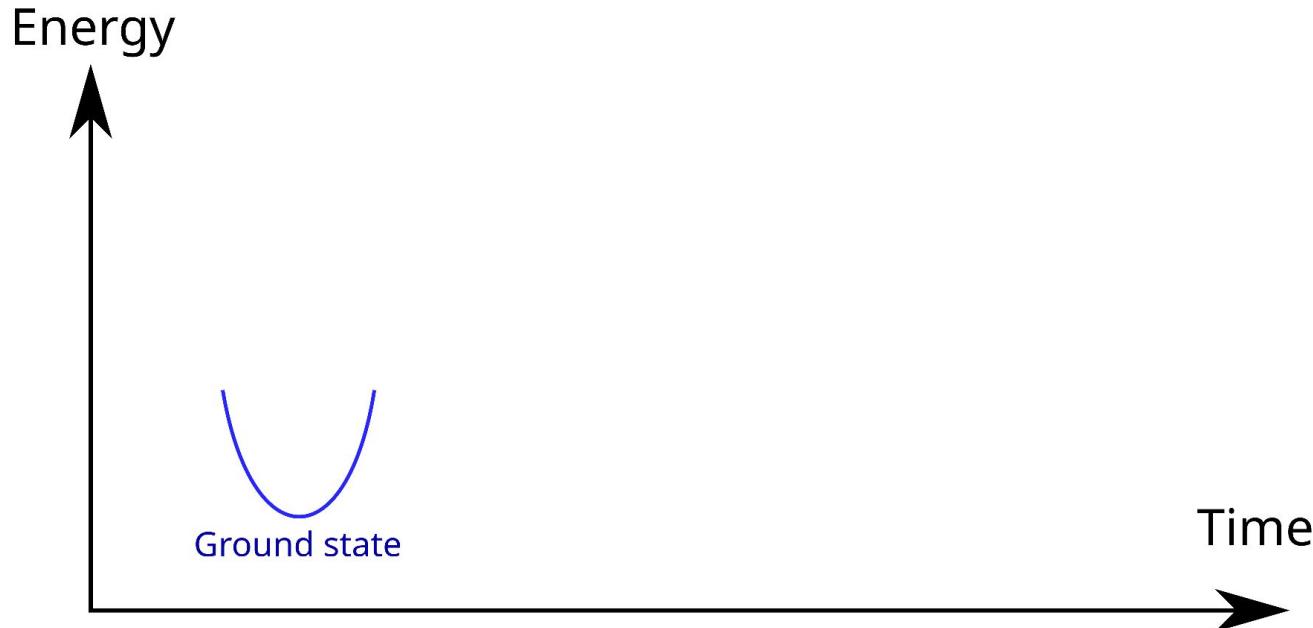
10^{-3}
ms

10^0
s

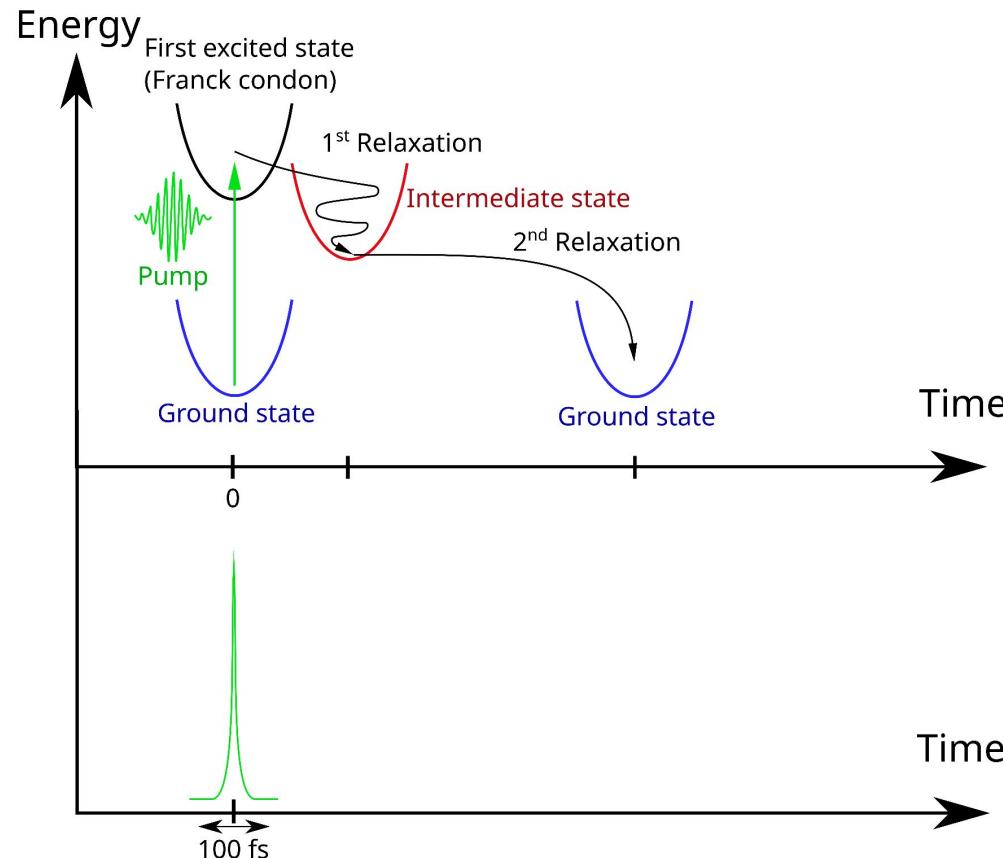
Time (s)

Probleme: How can we observe such phenomena ?

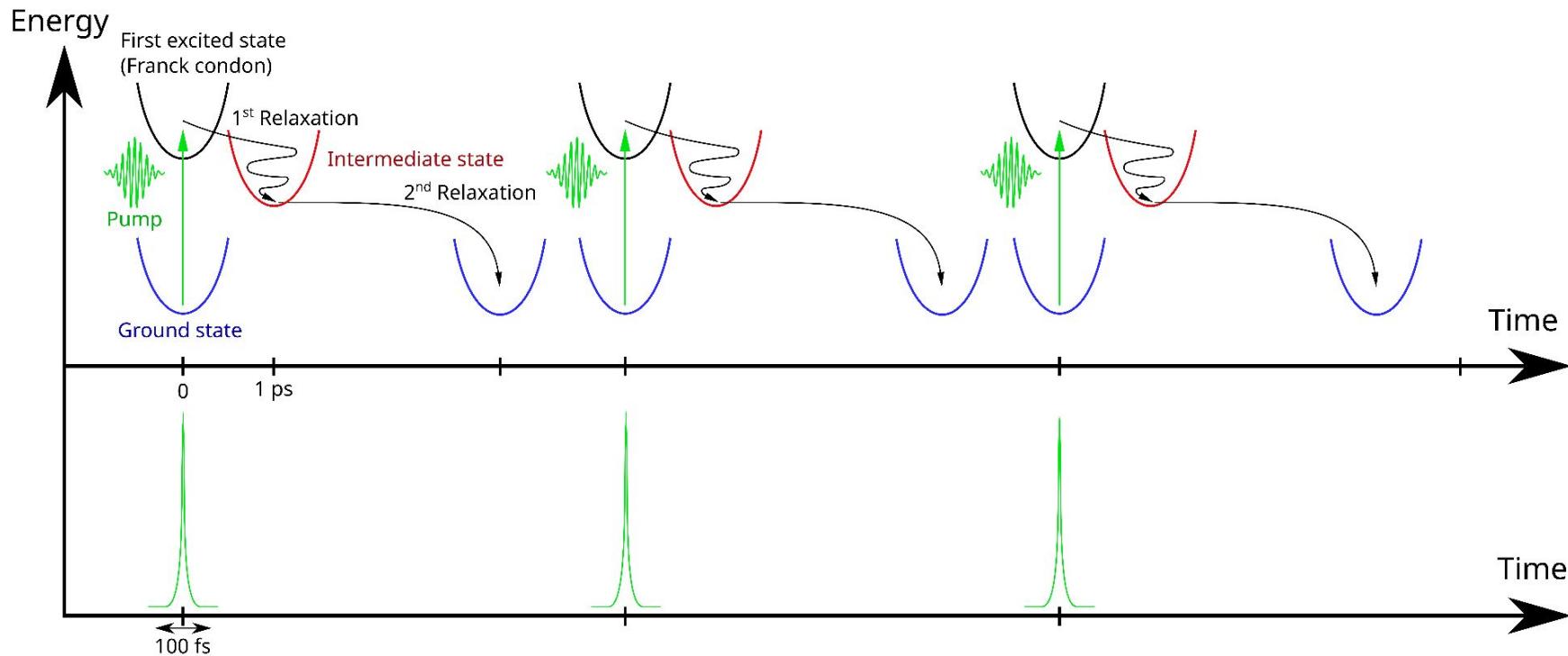
Pump-Probe spectroscopy



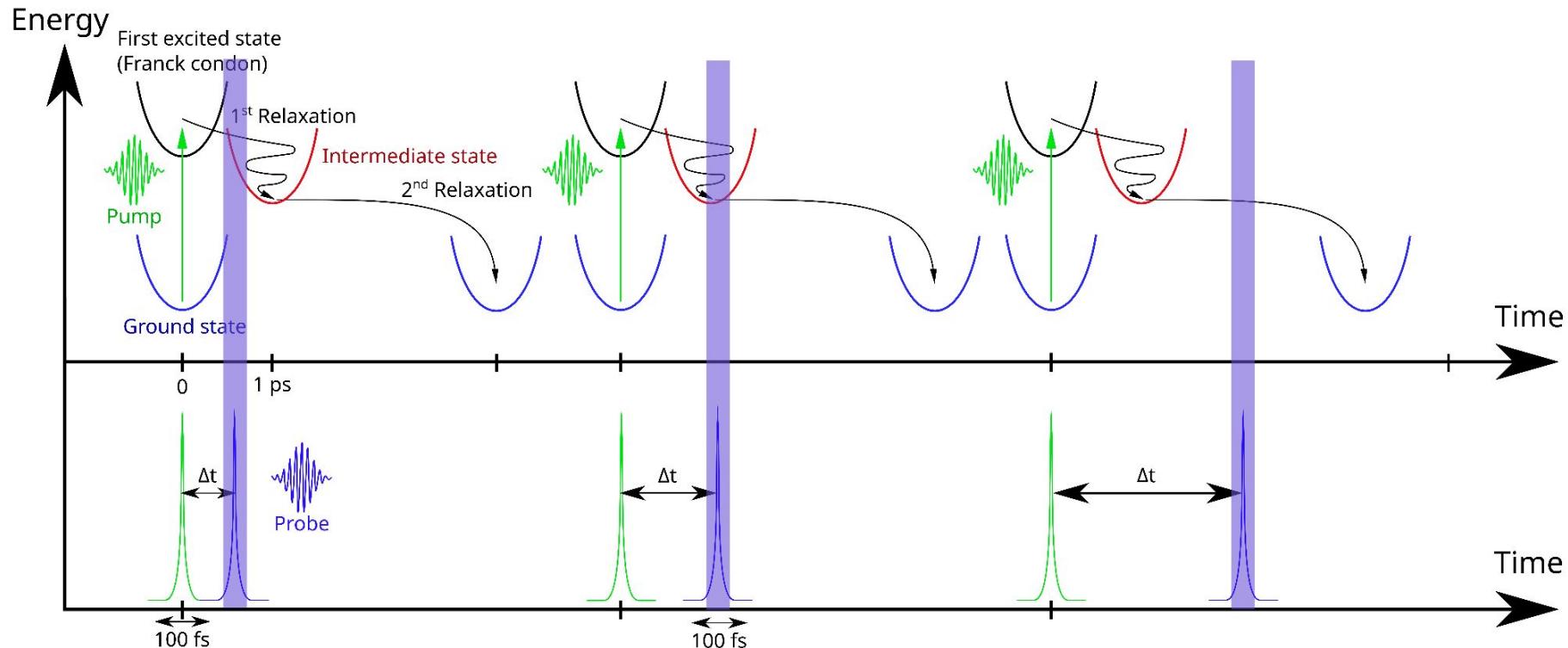
Pump-Probe spectroscopy



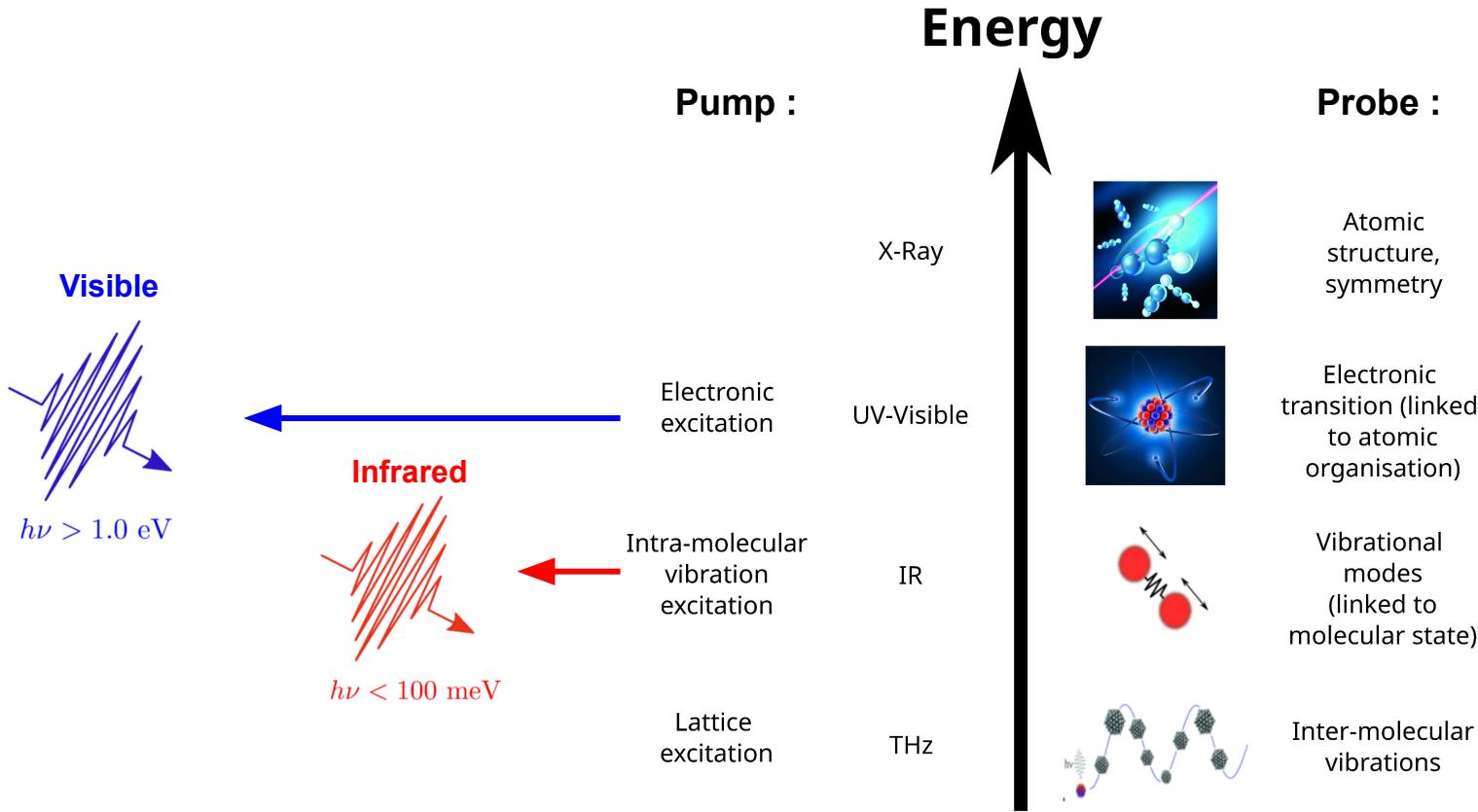
Pump-Probe spectroscopy



Pump-Probe spectroscopy



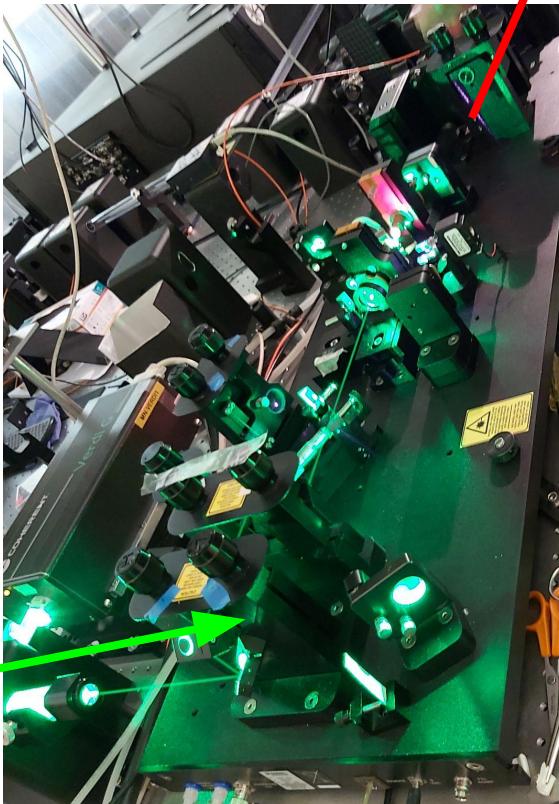
Pump-Probe spectroscopy : Which degrees of freedom ?



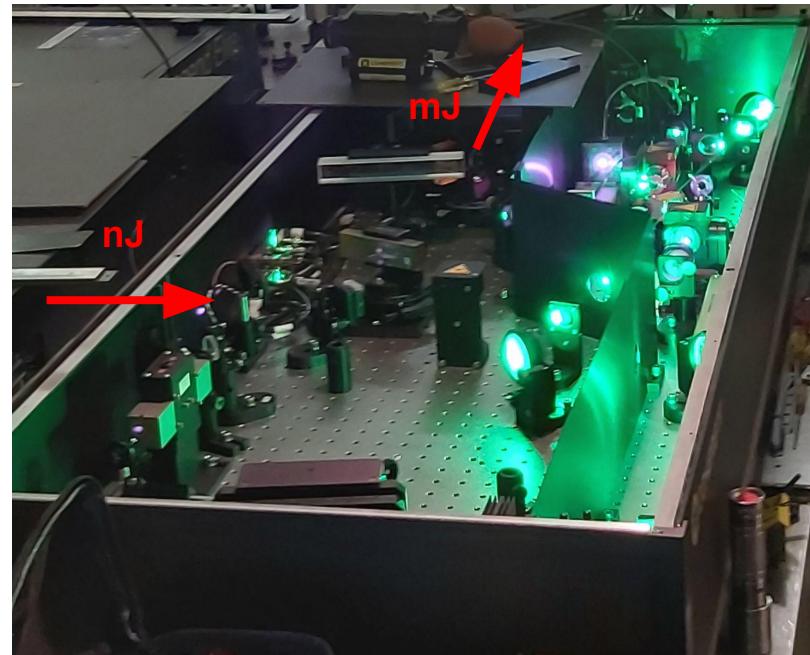
Experimental development

Pulsed laser generation

Pulses 10-100 fs
800 nm

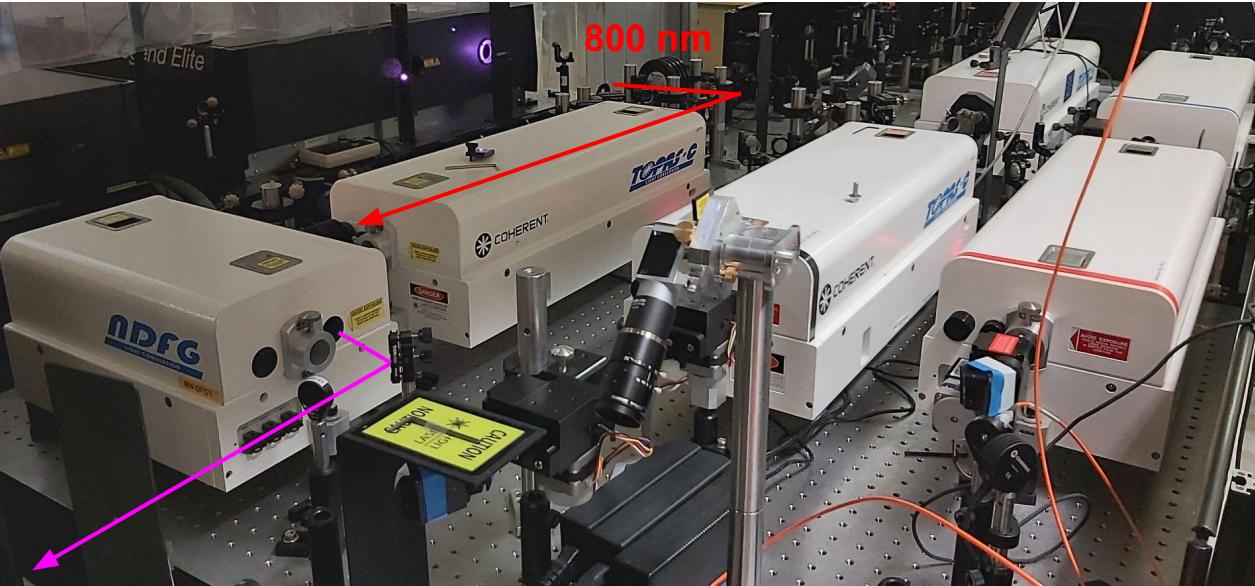


Laser Amplification

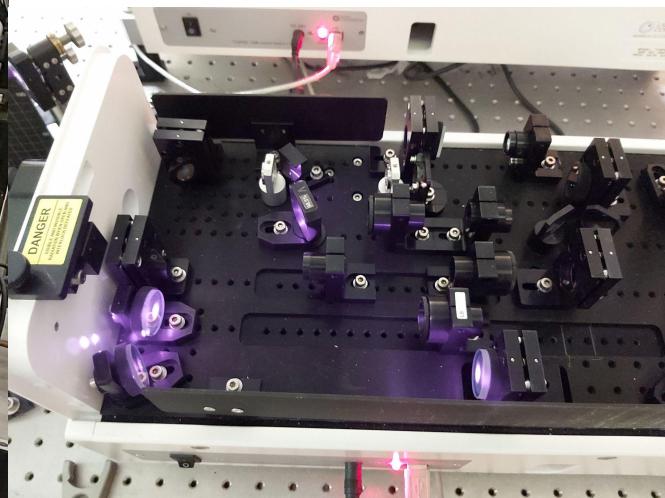


Experimental development

Infrared generation

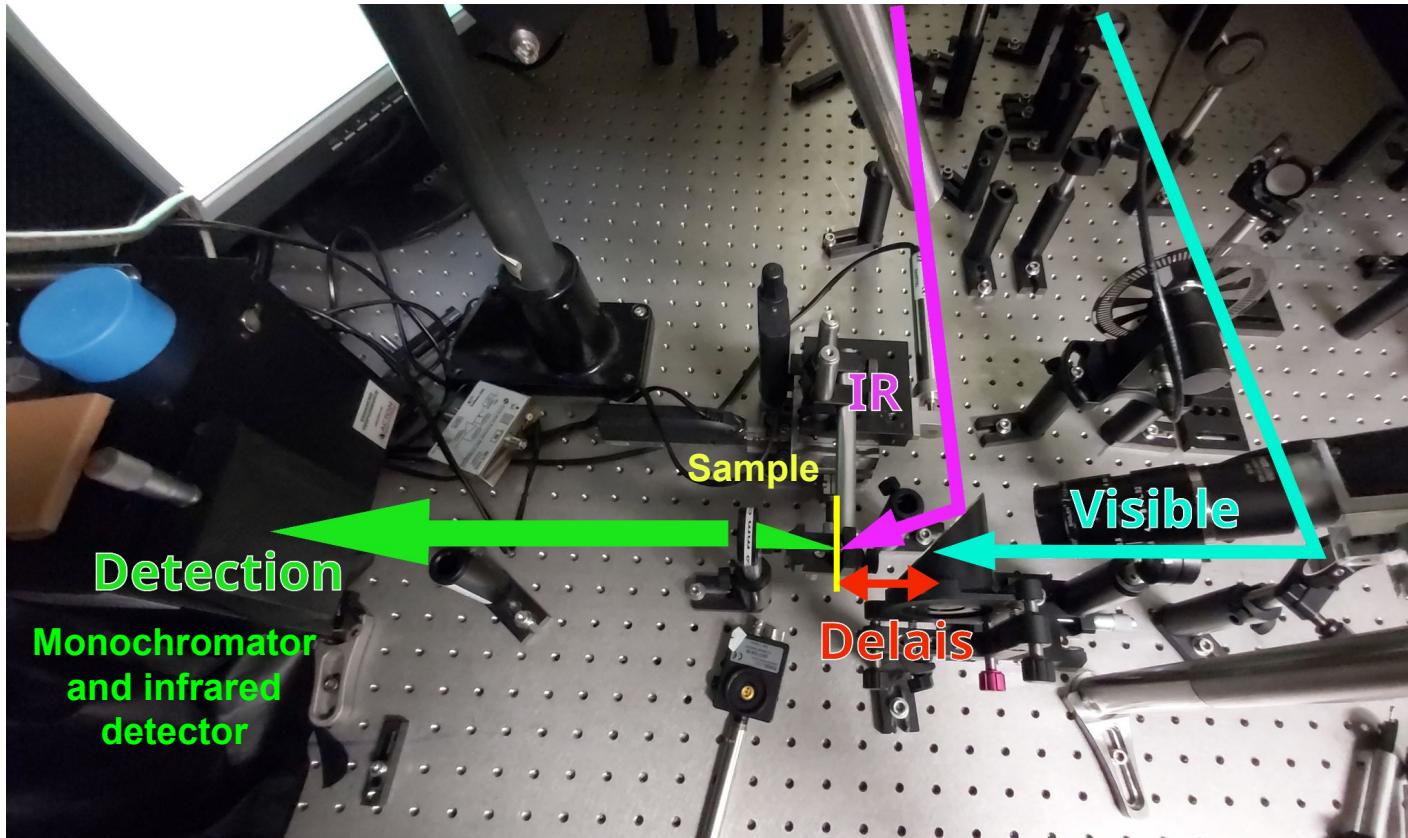


1300 - 10000 nm
7700 - 1000 cm^{-1}



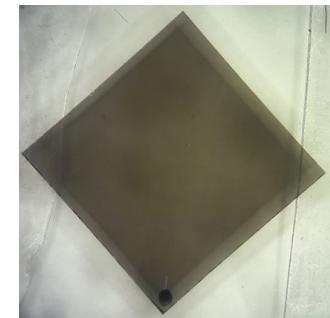
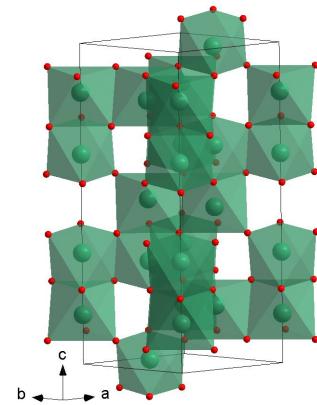
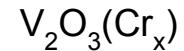
Experimental development

Focalisation and detection



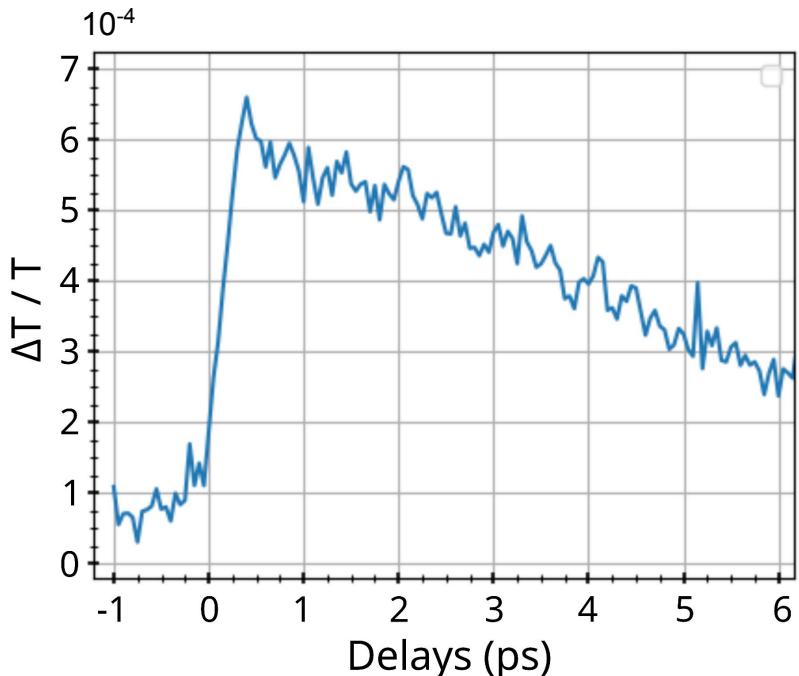
Femtosecond experiments IR/Visible : Time resolved measurements

Oxide :



Femtosecond experiments IR/Visible : Time resolved measurements

Variation of the transmission in V_2O_3 (Cr doped) as a function of time



Pump : 6000 nm
/ 1666 cm^{-1}
/ 0.2 eV

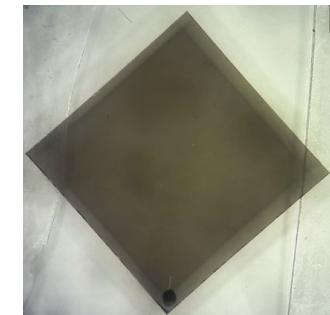
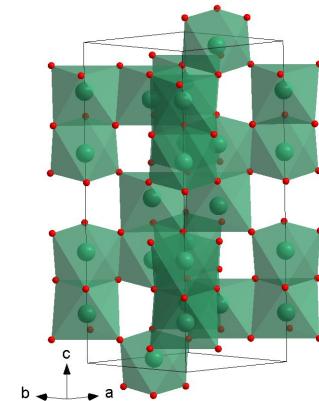
Probe : 800 nm
/ 12500 cm^{-1}
/ 1.54 eV

Thickness : 100 nm

Temporal
resolution :
100 fs

Oxide :

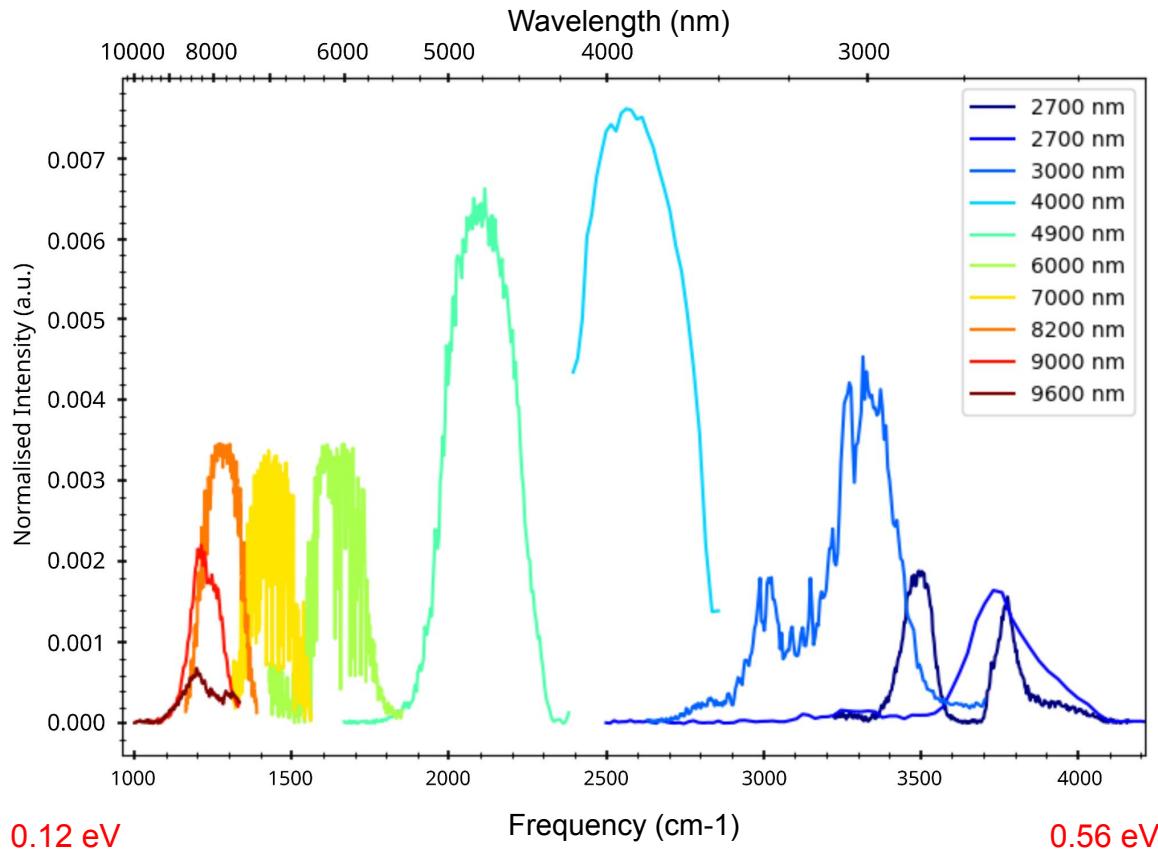
$\text{V}_2\text{O}_3(\text{Cr}_x)$



→ Pompe-Probe experiment Vis/IR ready

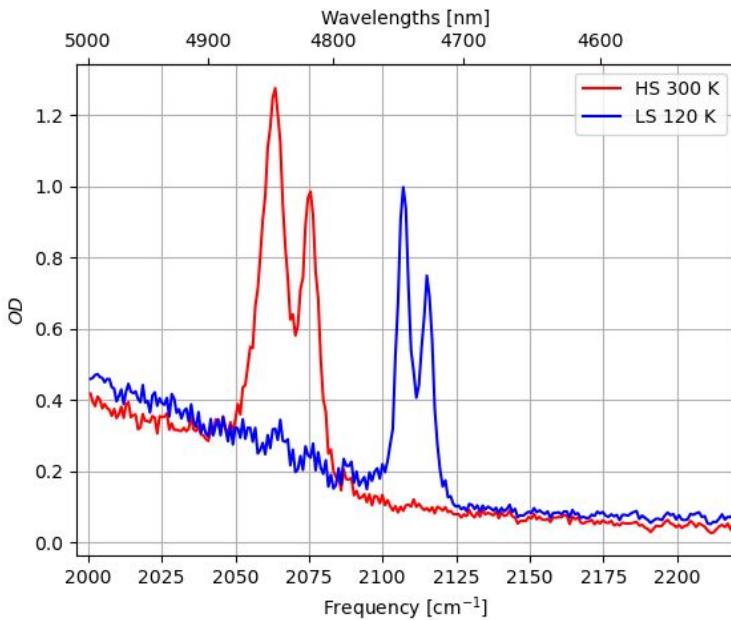
Characterization of the infrared generation

Tunability of the infrared beam



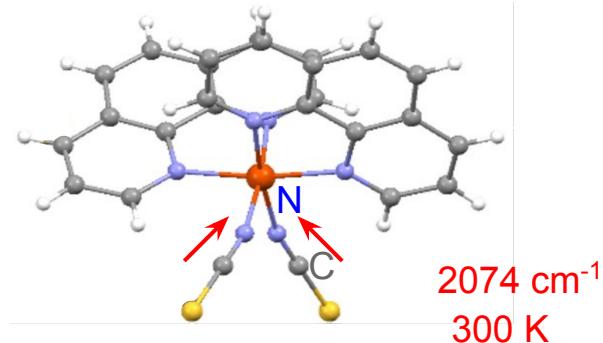
Infrared vibrational spectroscopy

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

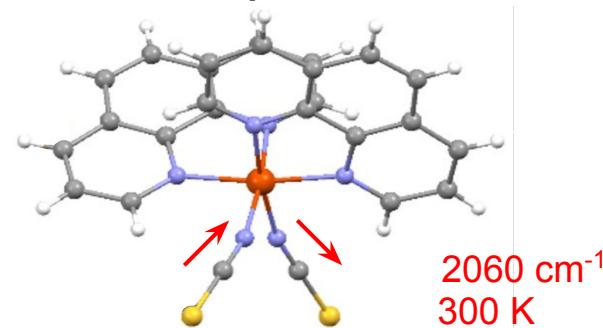


→ Frequency shift

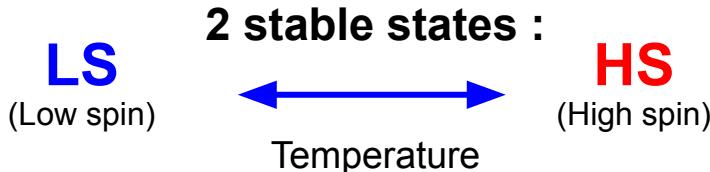
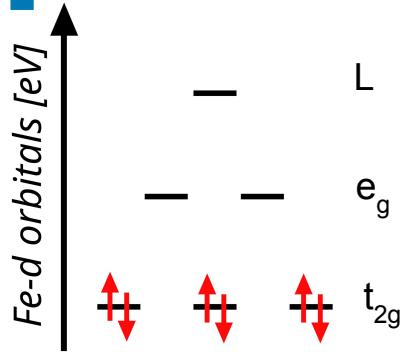
Infrared vibrational mode N-CS in phase



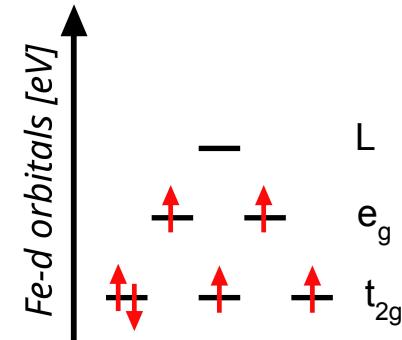
Infrared vibrational mode N-CS anti-phase



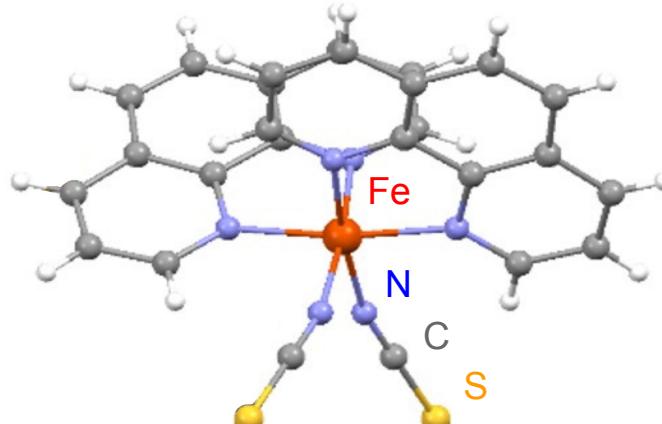
The Fe(phen)₂(NCS)₂ a spin crossover crystal



Schematic electronic configuration for a octahedral symmetry

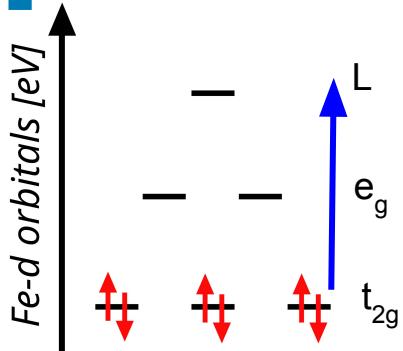


Molecular representation

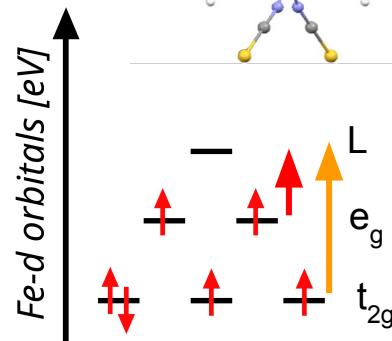
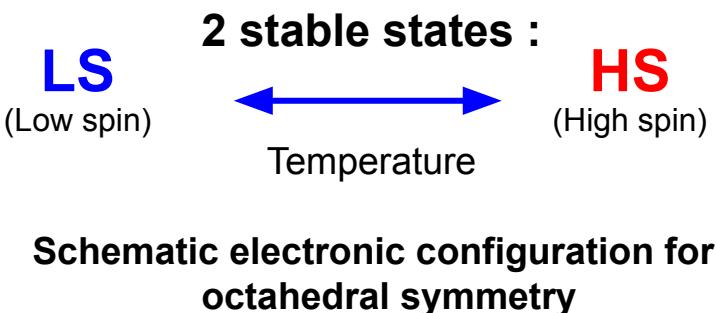


L : ligand orbital,
t_{2g} and e_g : Fe-d orbitals

The Fe(phen)₂(NCS)₂ a spin crossover crystal



Diamagnetic



Optical properties

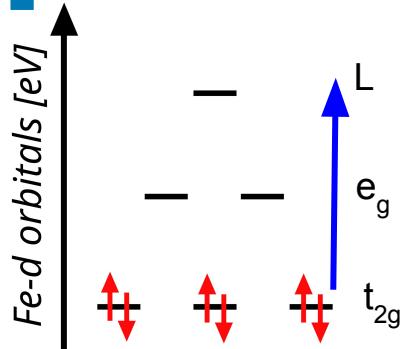


Magnetic properties

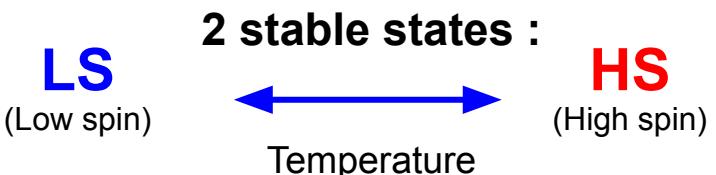
Paramagnetic

L : ligand orbital,
t_{2g} and e_g : Fe-d orbitals

The Fe(phen)₂(NCS)₂ a spin crossover crystal

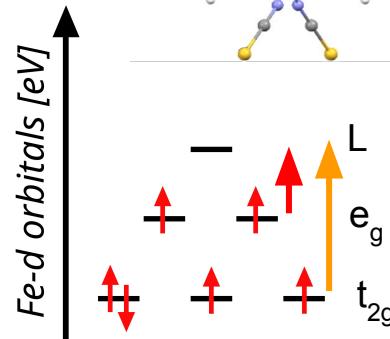


Diamagnetic

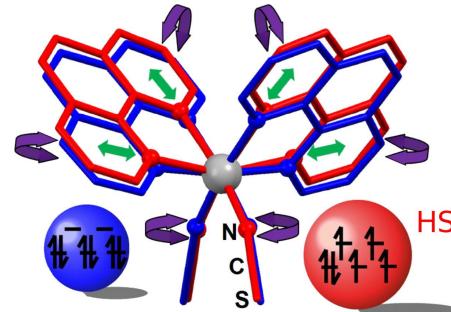
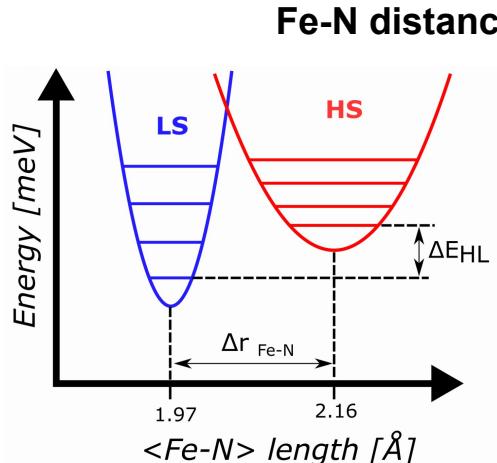


Schematic electronic configuration for a octahedral symmetry

Optical Magnetic properties

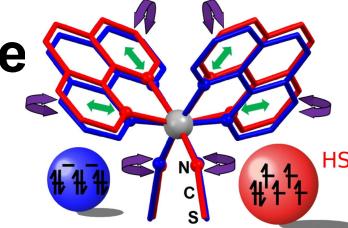


Paramagnetic

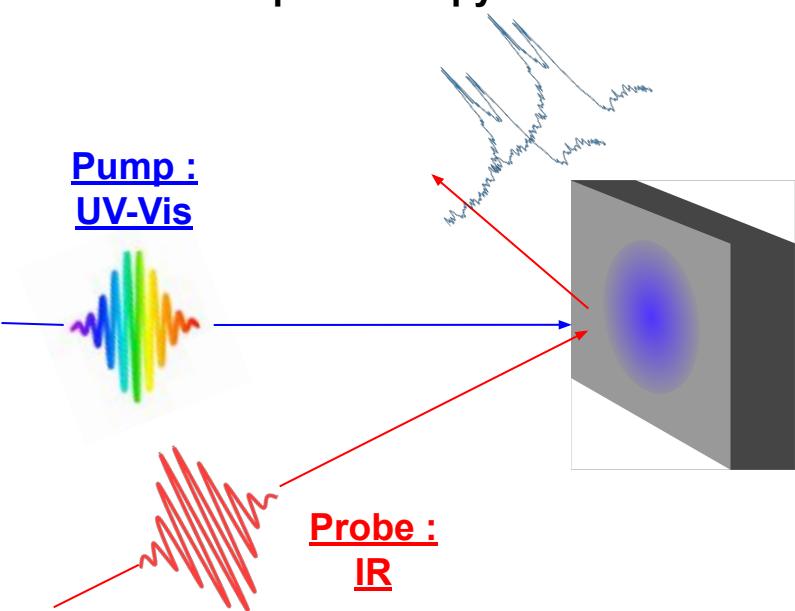


L : ligand orbital,
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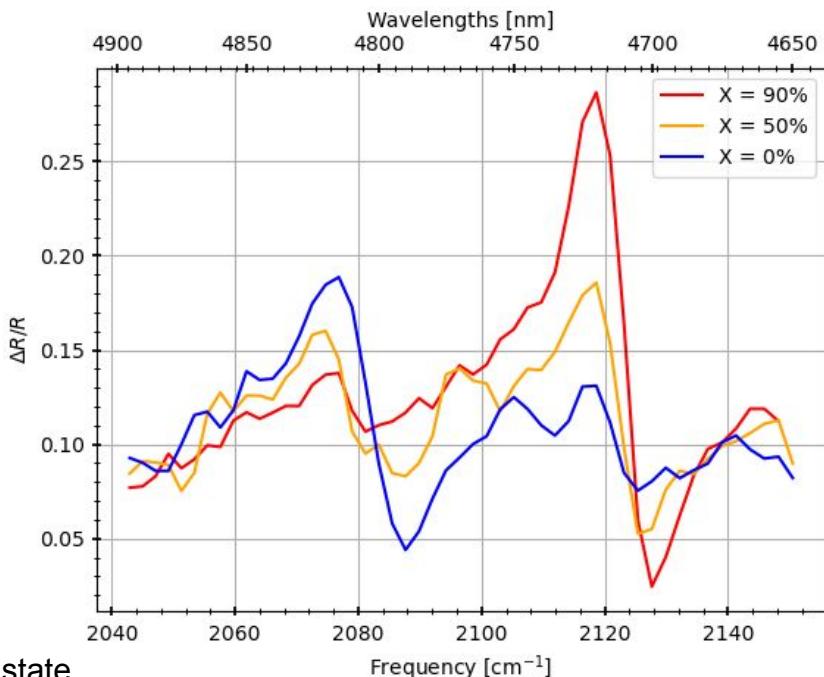
Application of the Pump-Probe experiment to the molecular crystal



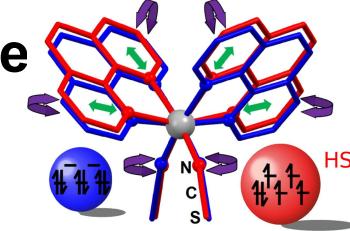
Time-resolved infrared spectroscopy



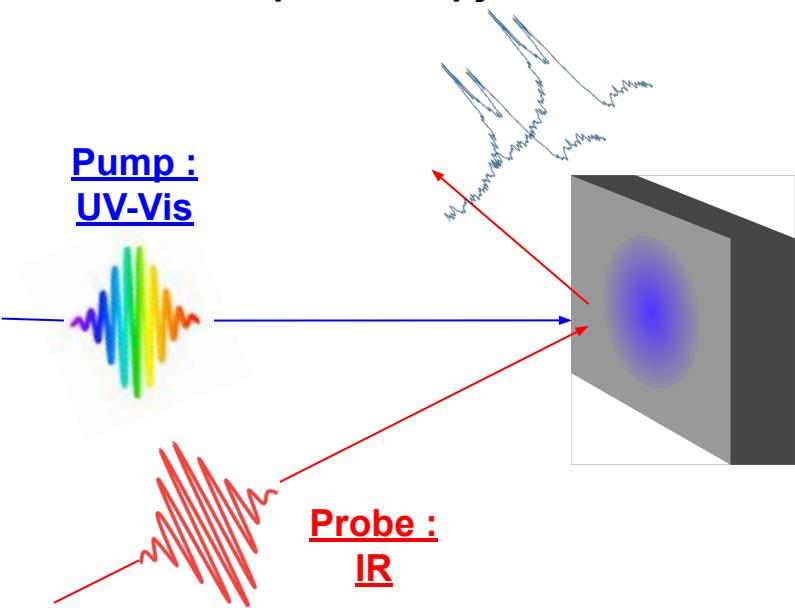
Frequency dependance of the vibrational modes to the spin state



Application of the Pump-Probe experiment to the molecular crystal



Time-resolved infrared spectroscopy



Pump :

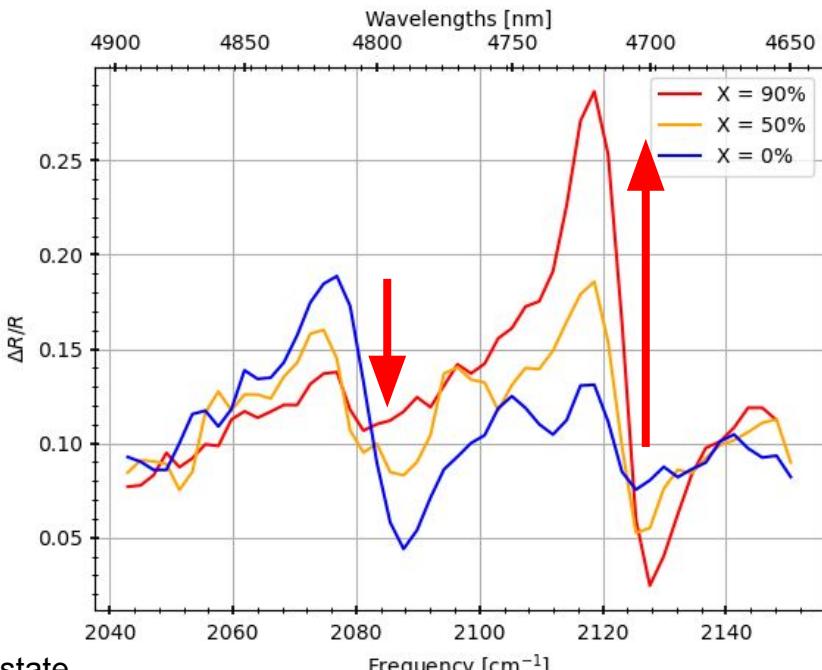
UV-Vis

Probe :

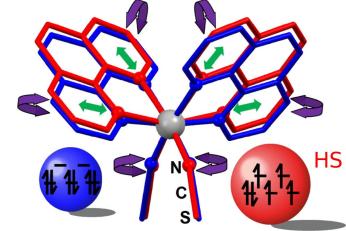
IR

X = % of HS state

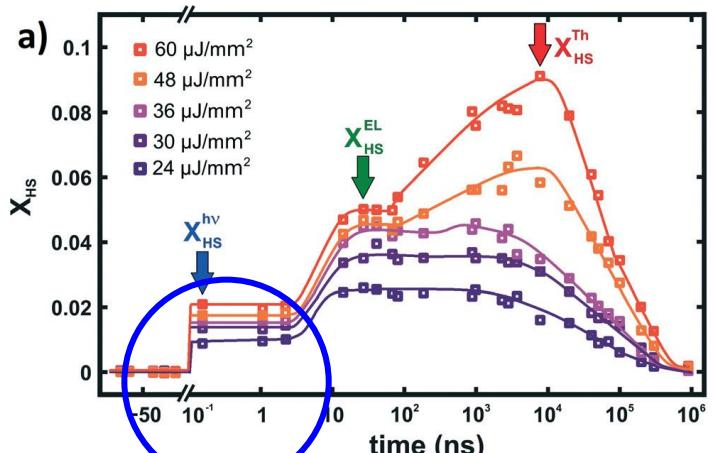
Frequency dependance of the vibrational modes to the spin state



Different generated dynamics with their timescales



Time resolved dynamics of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ for different excitation densities



Schematic representation of the out-of-equilibrium dynamics

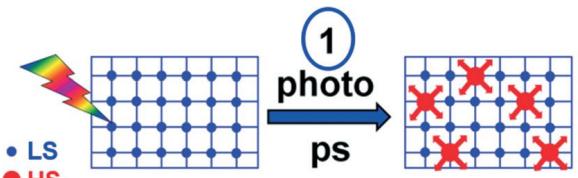
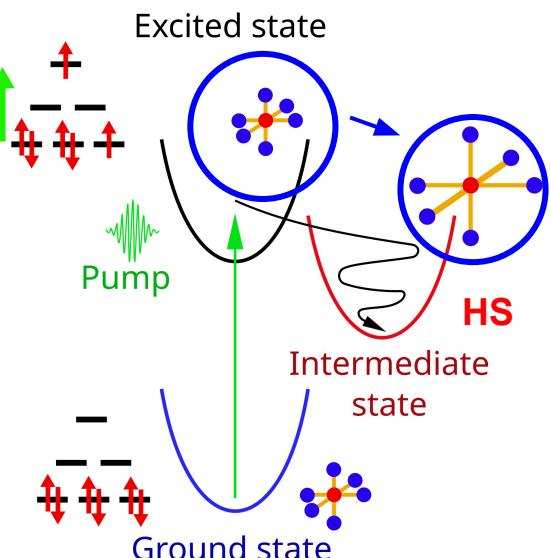
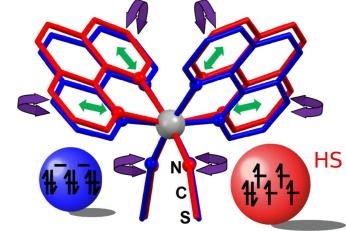


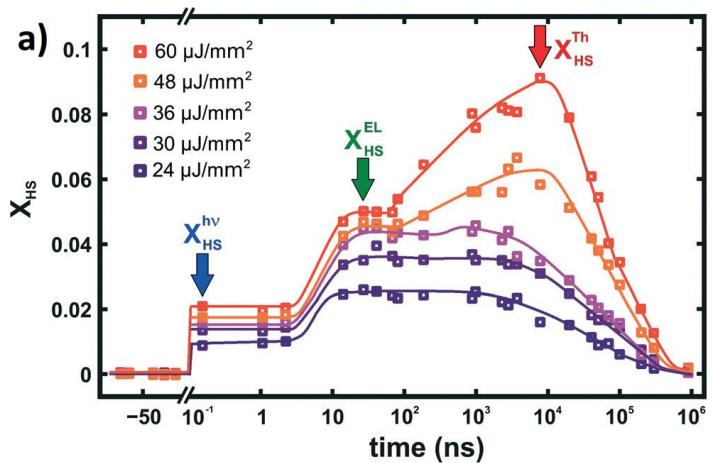
Photo-Induced effect



Different generated dynamics with their timescales

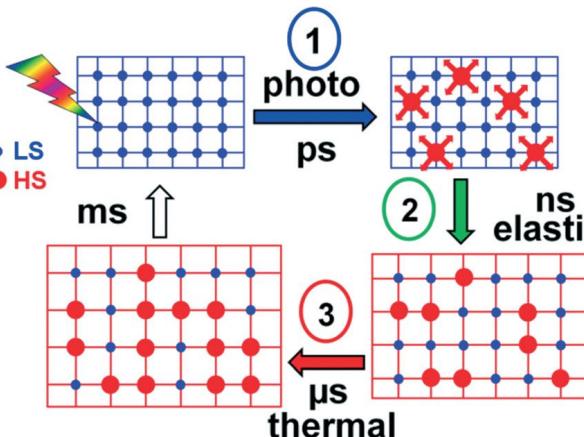


Time resolved dynamics of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ for different excitation densities



On $\text{Fe}(\text{phen})_2(\text{NCS})_2$ monocrystal at 140 K

Schematic representation of the out-of-equilibrium dynamics



Thermalisation effect

Thermo elastic effect

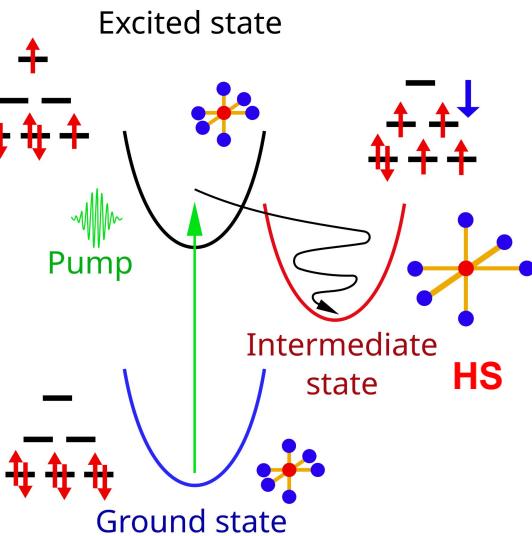
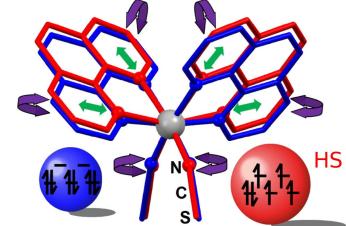


Photo-induced phase transition study with infrared spectroscopy



Time-resolved infrared spectroscopy

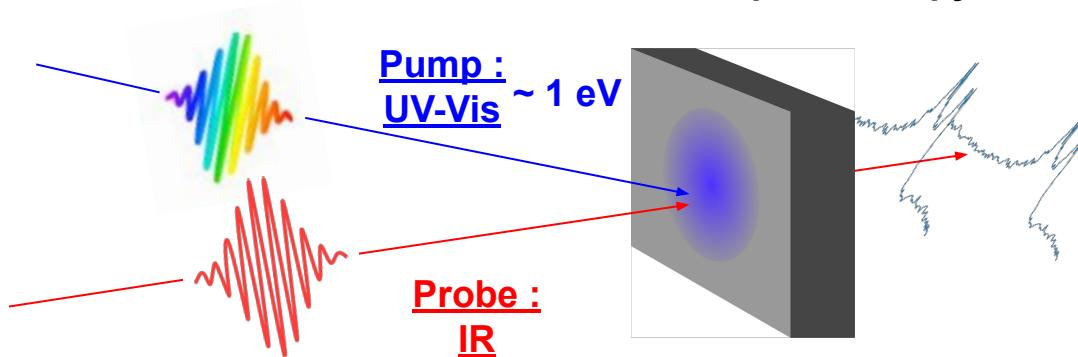
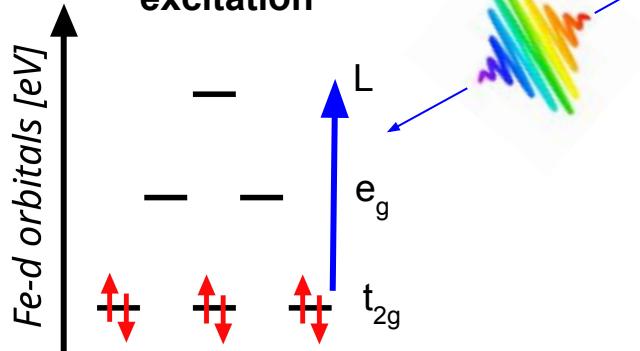


Photo-induced excitation



Generated phenomenon

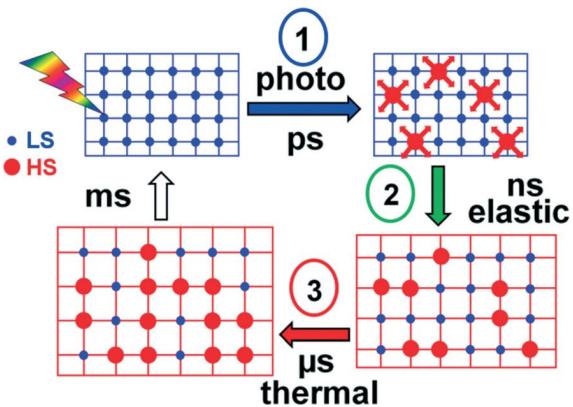
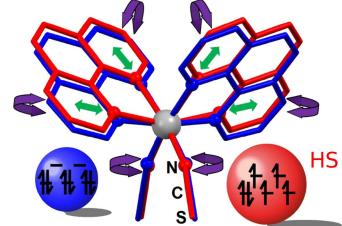
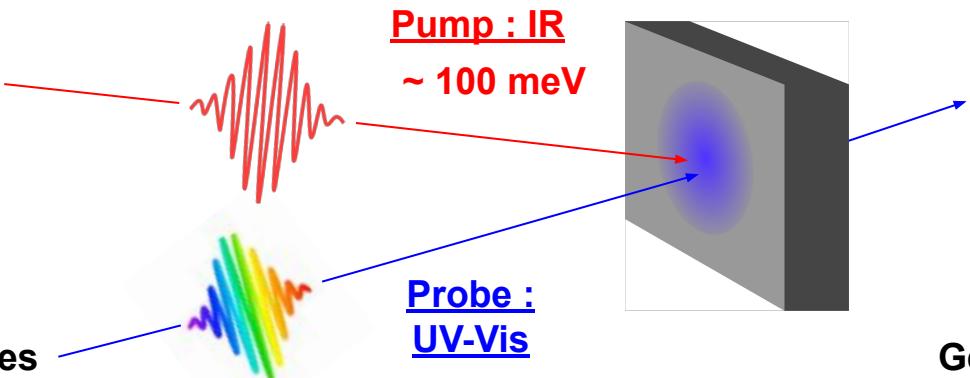


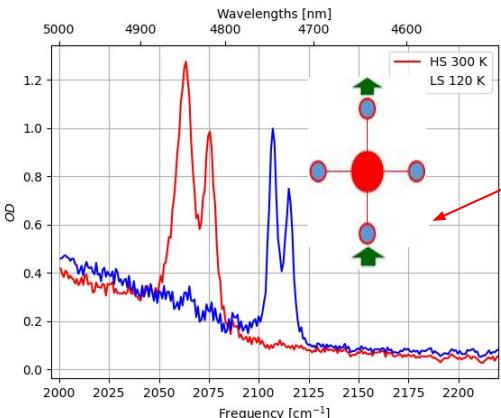
Photo-induced phase transition study with infrared spectroscopy



Time-resolved infrared spectroscopy



Vibrational modes



Non-linear phononic

Generated phenomenon ?

