

# Experimental and theoretical analysis of vibrational modes in

## Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> single crystal

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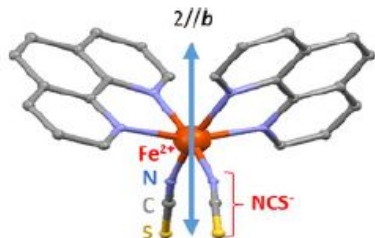
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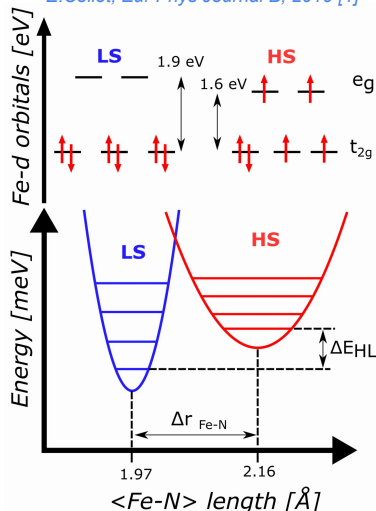
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### Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> molecule and energy diagram



E.Collet, Eur Phys Journal B, 2019 [1]



P. Gütllich, H.A. Goodwin, Spin crossover in Transition Metal compounds I, 2004 [2]

### Coupled electronic / structural reorganisation

### Spin transition driven by entropy difference (electronic and vibrational)

$$S_{vib}(T) = R \sum_{\lambda} \left( -\ln[1 - \exp^{-h\nu_{\lambda}/k_B T}] + \frac{h\nu_{\lambda}}{k_B T} \frac{1}{\exp(h\nu_{\lambda}/k_B T)} \right)$$

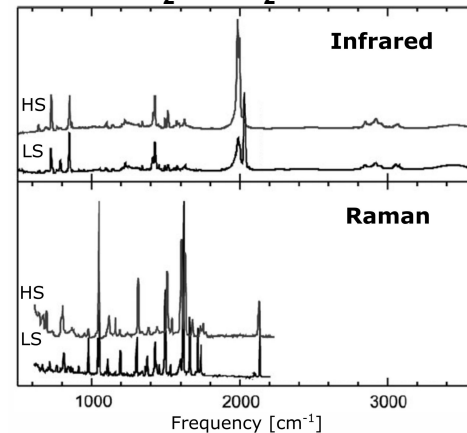
W. Nicolazzi, A. Bousseksou, C. R. Chimie 21, 2018 [3]

### Vibration modes characteristic of spin states

So far vibrational entropy mainly considered at a molecular level (147 modes)

What about crystals ? (612 modes)

### IR and Raman spectra of Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> in both state

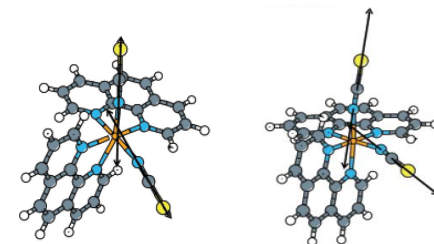


K. L. Ronayne et al, Phys Chemistry Chemical Physics, 2006 [4]

### N-CS vibrational mode representation and frequency

HS 2040 cm<sup>-1</sup>

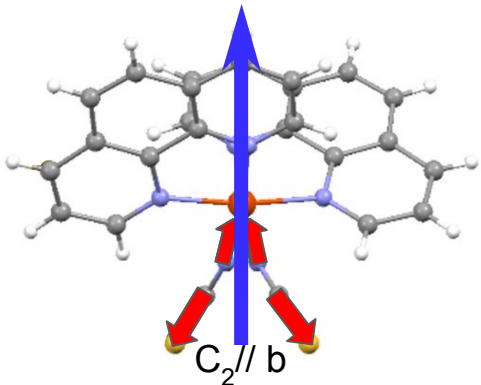
LS 2070 cm<sup>-1</sup>



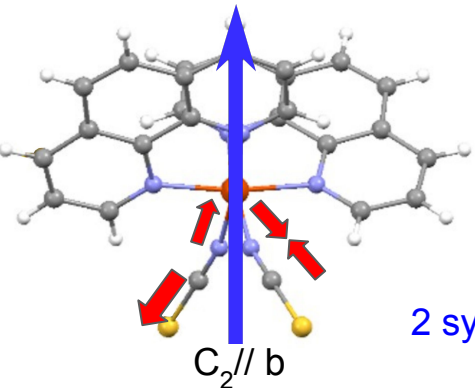
G. Brehm et al. J. Phys. Chem. 2002 [5]

## Molecule $C_2$ symmetry

Symmetry: A



Anti-symmetry: B



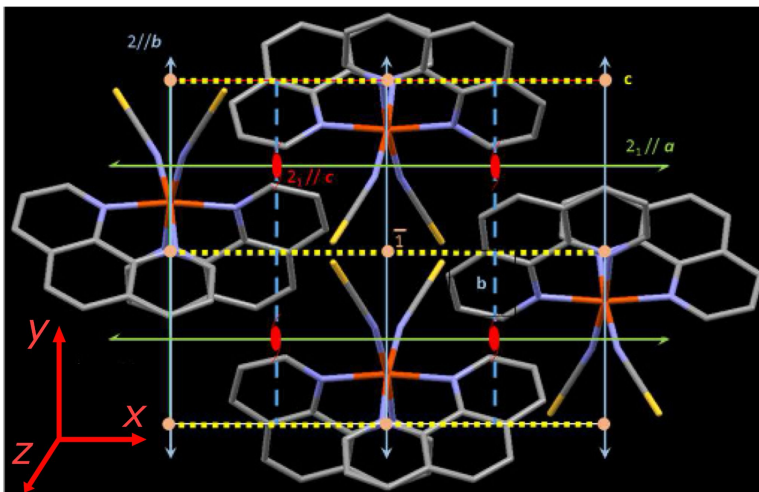
2 symmetries  $\longrightarrow$  8 symmetries

## $Fe(phen)_2(NCS)_2$

4 molecules in unit cell

Pbcn space group

mmm point group

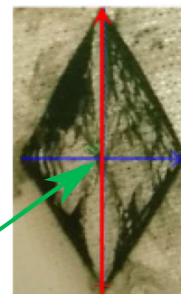


## Crystal polarisation

IR or Raman beam

Y

y axis



x axis

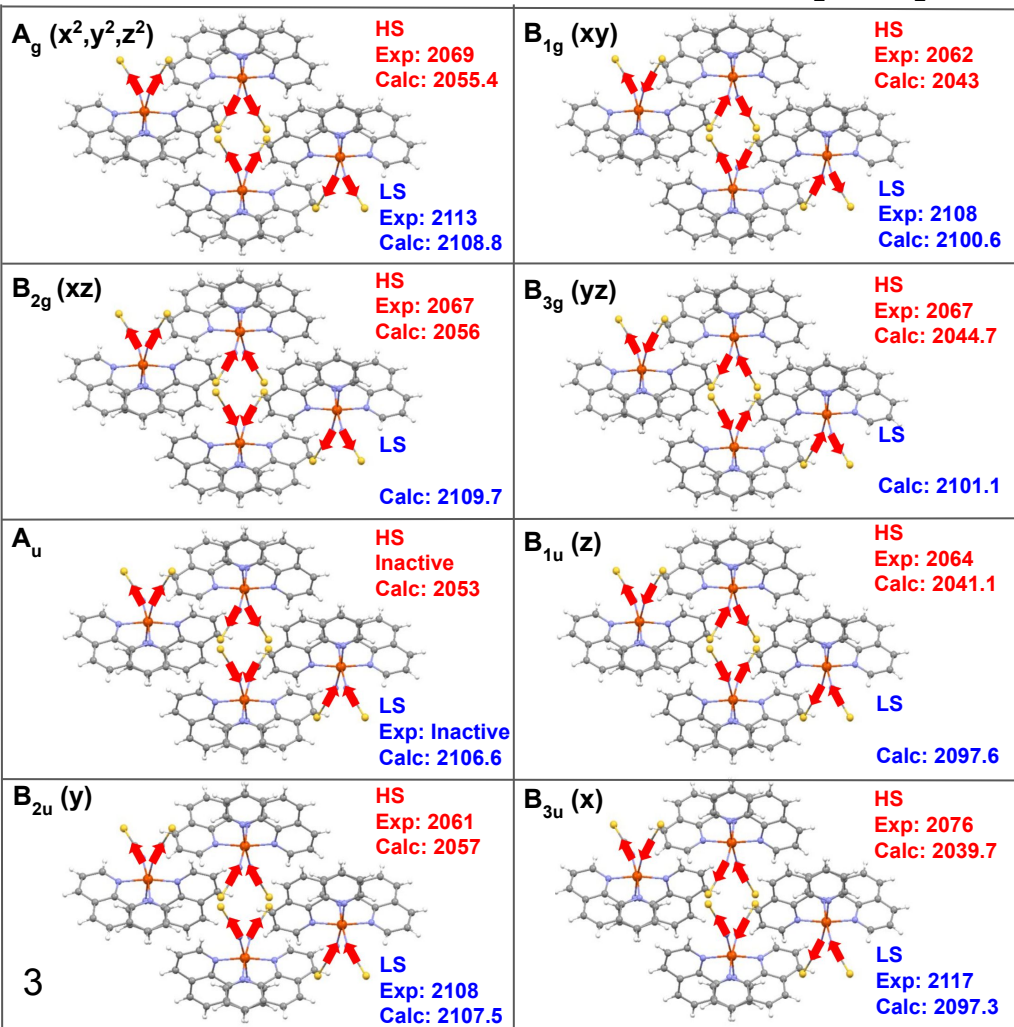
## Crystalline point group

$D_{2h}$ (mmm)	$E$	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$A_g$	1	1	1	1	1	1	1	1	$x^2, y^2, z^2$
$B_{1g}$	1	1	-1	-1	1	1	-1	-1	$R_x$ $xy$
$B_{2g}$	1	-1	1	-1	1	-1	1	-1	$R_y$ $xz$
$B_{3g}$	1	-1	-1	1	1	-1	-1	1	$R_z$ $yz$
$A_u$	1	1	1	1	-1	-1	-1	-1	
$B_{1u}$	1	1	-1	-1	-1	-1	1	1	$z$
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	$y$
$B_{3u}$	1	-1	-1	1	-1	1	1	-1	$x$

Raman

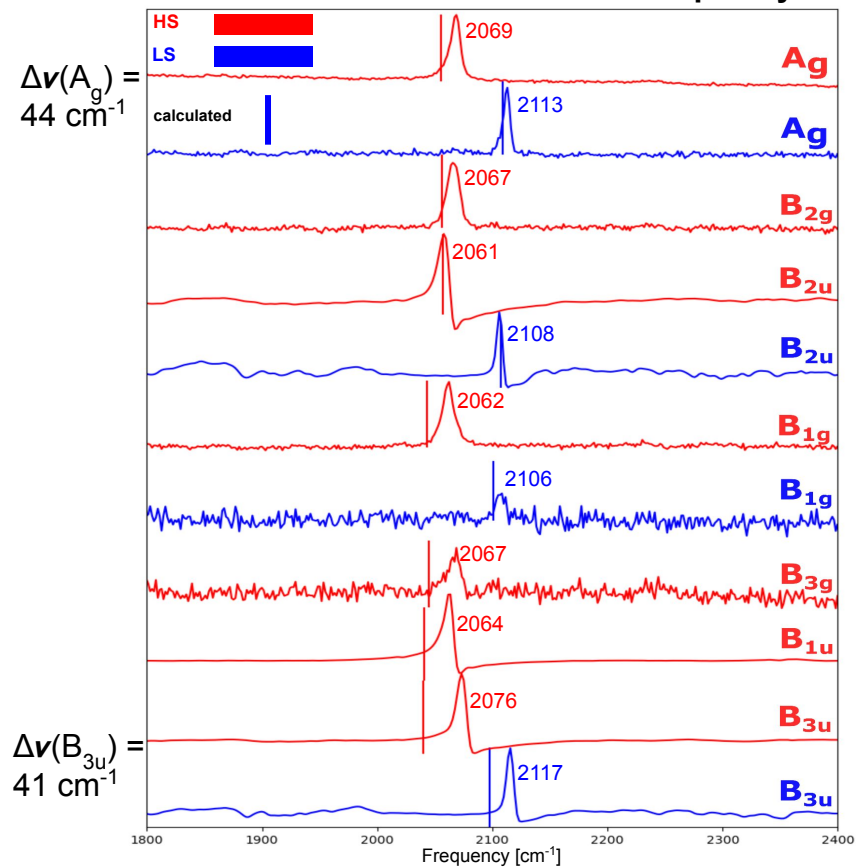
Infrared

# N-CS vibrational symmetry in the Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> cell



The vibrational spectra of 4 molecules in crystal is more complex than the one of the isolated molecule : different symmetries

Raman and Infrared measured (IMN) and calculated N-CS modes frequency



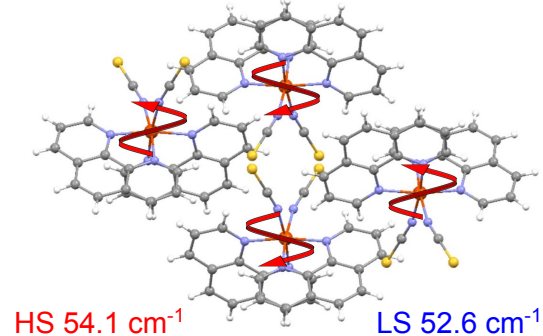
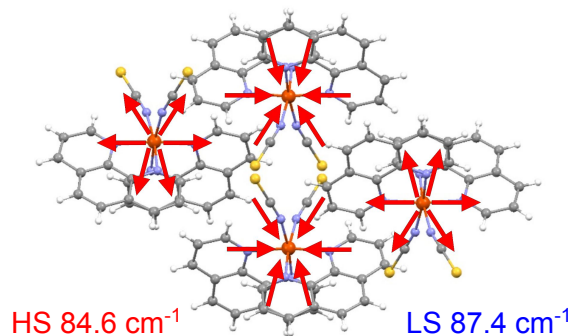
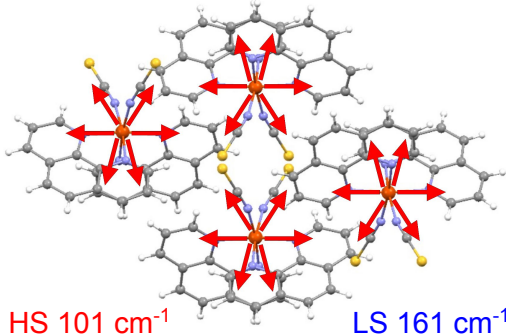
-Lattice vibrational modes as combinations of molecular modes different symmetries  
(exemple : breathing mode:  $A_g$   $B_{2u}$   $A_u$  et  $B_{2g}$ )

- Librations modes : (almost rigid molecules) translations / rotations

Representation of  $A_g$  totally symmetric breathing mode

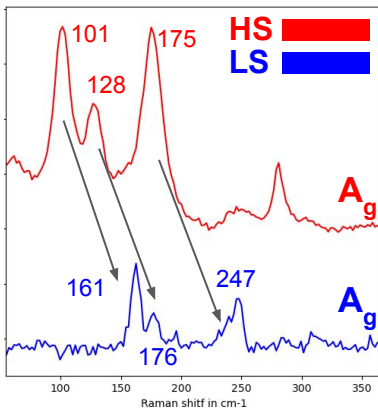
Representation of  $B_{2u}$  breathing mode

Librational mode  $B_{2u}$



Low frequency measurements for the  $A_g$  mode

Raman experiment (IMN)



Simplified equation : 
$$\Delta S_{vib} = \Delta S_{vib}^{HS} - \Delta S_{vib}^{LS} = R \sum_{\lambda=1}^k \ln \left( \frac{\nu_{\lambda}^{LS}}{\nu_{\lambda}^{HS}} \right)$$

**Conclusion :**

- Lattice mode measurements & calculations:  $\Delta S_{vib}(\text{cell}) \neq 4 \Delta S_{vib}(\text{molecule})$  ?
- Infrared and Raman experiments: identify the vibrational modes symmetry & frequencies
- The vibrational crystal spectrum is more complex than the isolated molecule, because those modes contains combinations of different symmetry for intra & inter molecular mode. Moreover librational and acoustics modes should be take into account
- Next step: Non-linear phononic with  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  crystal, controlling spin state switching by resonant excitation of infrared modes.

# References

- [1] **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) <https://doi.org/10.1140/epjb/e2018-90553-2>
- [2] **P. Gütllich, H.A. Goodwin**, “Spin crossover in Transition Metal compounds I” , 2004
- [3] **W. Nicolazzi, A. Bousseksou**, “Thermodynamical aspects of the spin crossover phenomenon”, C. R. Chimie 21 (2018) <https://doi.org/10.1016/j.crci.2018.10.003>
- [4] **K. L. Ronayne et al.** « Vibrational spectrum of spin crossover complex [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>] studied in IR and Raman spectroscopy, nuclear inelastic scattering and DFT calculations » . Physical Chemistry Chemical Physics DOI: 10.1039/b610634j
- [5] **G. Brehm, M. Reiher, and S. Schneider**, “Estimation of the Vibrational Contribution to the Entropy Change Associated with the Low- to High-Spin Transition in Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> Complexes: Results Obtained by IR and Raman Spectroscopy and DFT Calculations”, J. Phys. Chem. A 2002, 106, 12024-12034
- [6] **A. Subedi al.** « Theory of nonlinear phononics for coherent light control of solids » , Phys. Rev. B 89, 220301(R) (June 2014). 10.1103/PhysRevB.89.220301