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# Symmetry-resolved THz, IR, Raman spectroscopies and DFT studies of lattice phonon modes in the spin crossover crystal [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>]

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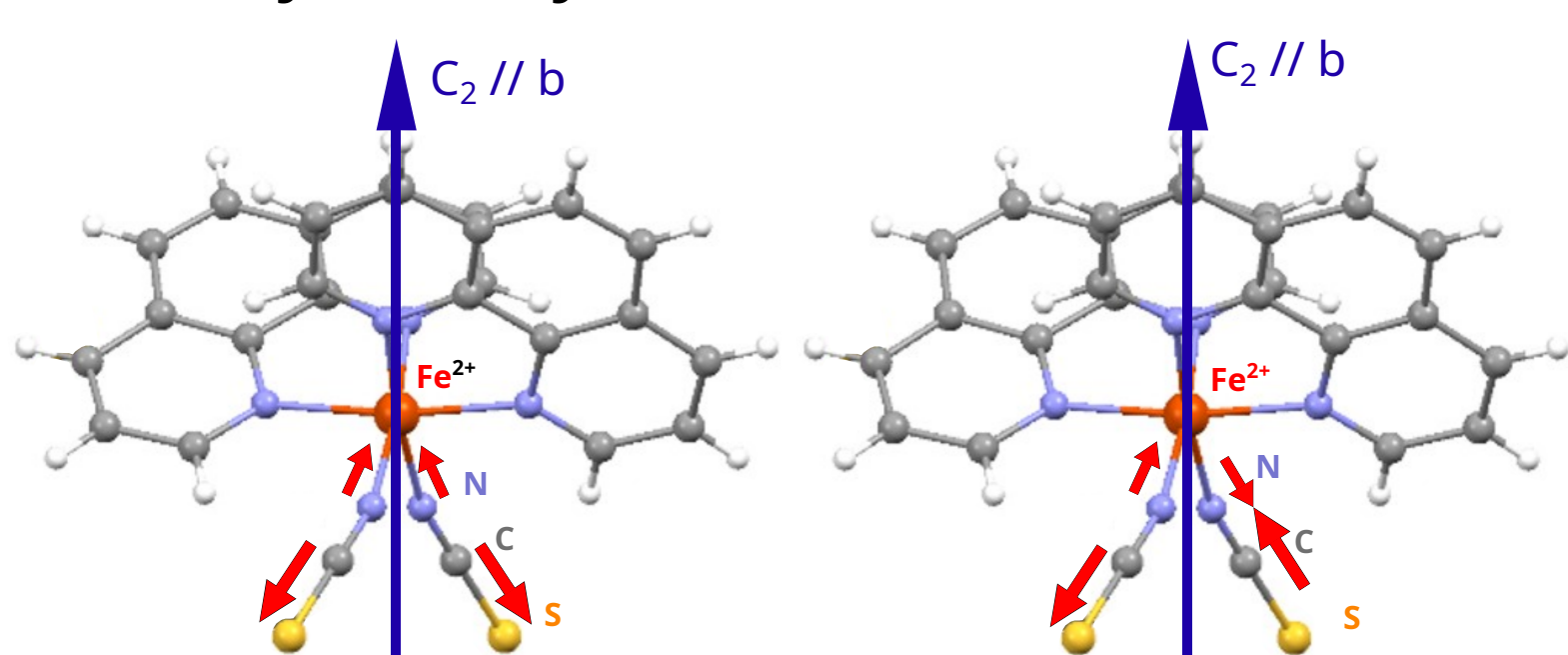
<sup>d</sup>. Centre de Physique Théorique, École Polytechnique, CNRS, 91128 Palaiseau Cedex, France

## 1) Isolated Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> molecule

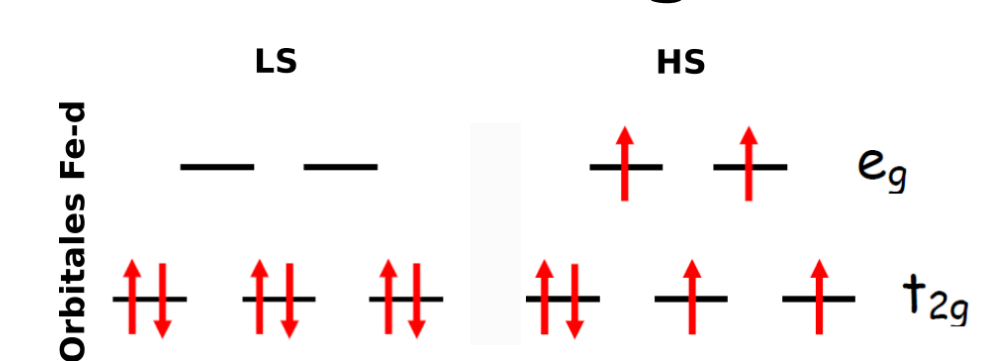
Isolated molecule

A Symmetry

B Symmetry



Fe<sup>2+</sup> : 3d<sup>6</sup> schematic electronic configuration



51 atoms  
x 3 degree of liberty  
= 153 modes

3 translation      3 rotation

147 vibrational modes

C <sub>2</sub>	E	C <sub>2</sub>	linear functions, rotations	quadratic functions
A	+1	+1	y, R <sub>y</sub>	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup> , xz
B	+1	-1	x, z, R <sub>x</sub> , R <sub>z</sub>	xy, yz

C<sub>2</sub> symmetry:

2 types of modes:

A symmetry (identity)

B symmetry

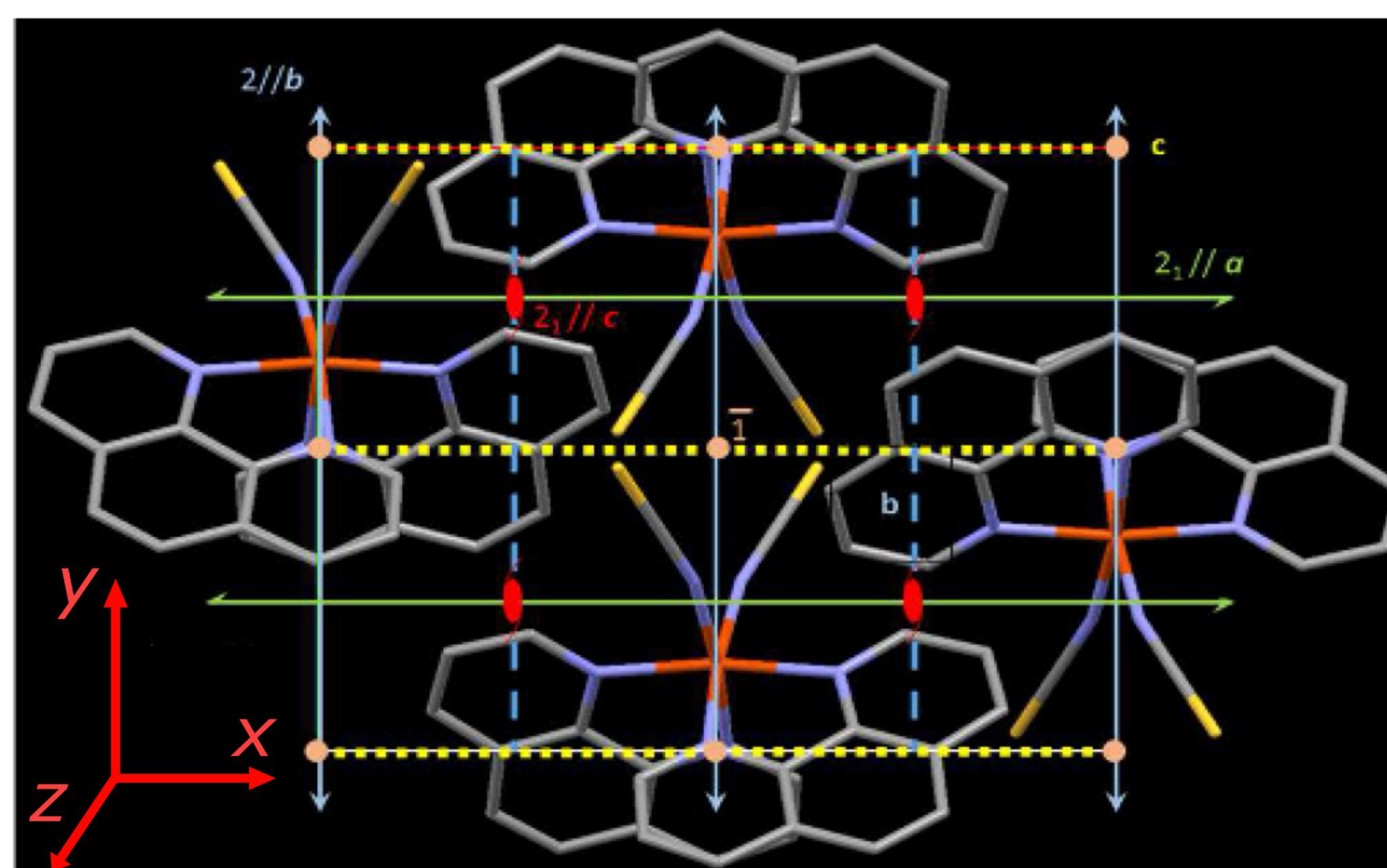
stretching N-CS modes<sup>[1]</sup>

HS 2040 cm<sup>-1</sup>      LS 2070 cm<sup>-1</sup>

HS 2029 cm<sup>-1</sup>      LS 2061 cm<sup>-1</sup>

## 2) In crystal: Pbcn space group

Crystal structure<sup>[2]</sup>



Crystalline point group (mmm)<sup>[2]</sup>

D <sub>2h</sub> (mmm)	E	C <sub>2</sub> (z)	C <sub>2</sub> (y)	C <sub>2</sub> (x)	i	σ(xy)	σ(xz)	σ(yz)	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>
A <sub>g</sub>	1	1	1	1	1	1	1	1	xy
B <sub>1g</sub>	1	1	-1	-1	1	-1	-1	-1	R <sub>z</sub>
B <sub>2g</sub>	1	-1	1	-1	1	-1	-1	-1	R <sub>y</sub>
B <sub>3g</sub>	1	-1	-1	1	1	-1	-1	-1	R <sub>x</sub>
A <sub>u</sub>	1	1	1	1	-1	-1	-1	-1	
B <sub>1u</sub>	1	1	-1	-1	-1	1	1	1	z
B <sub>2u</sub>	1	-1	1	-1	-1	1	1	1	y
B <sub>3u</sub>	1	-1	-1	1	-1	1	1	1	x

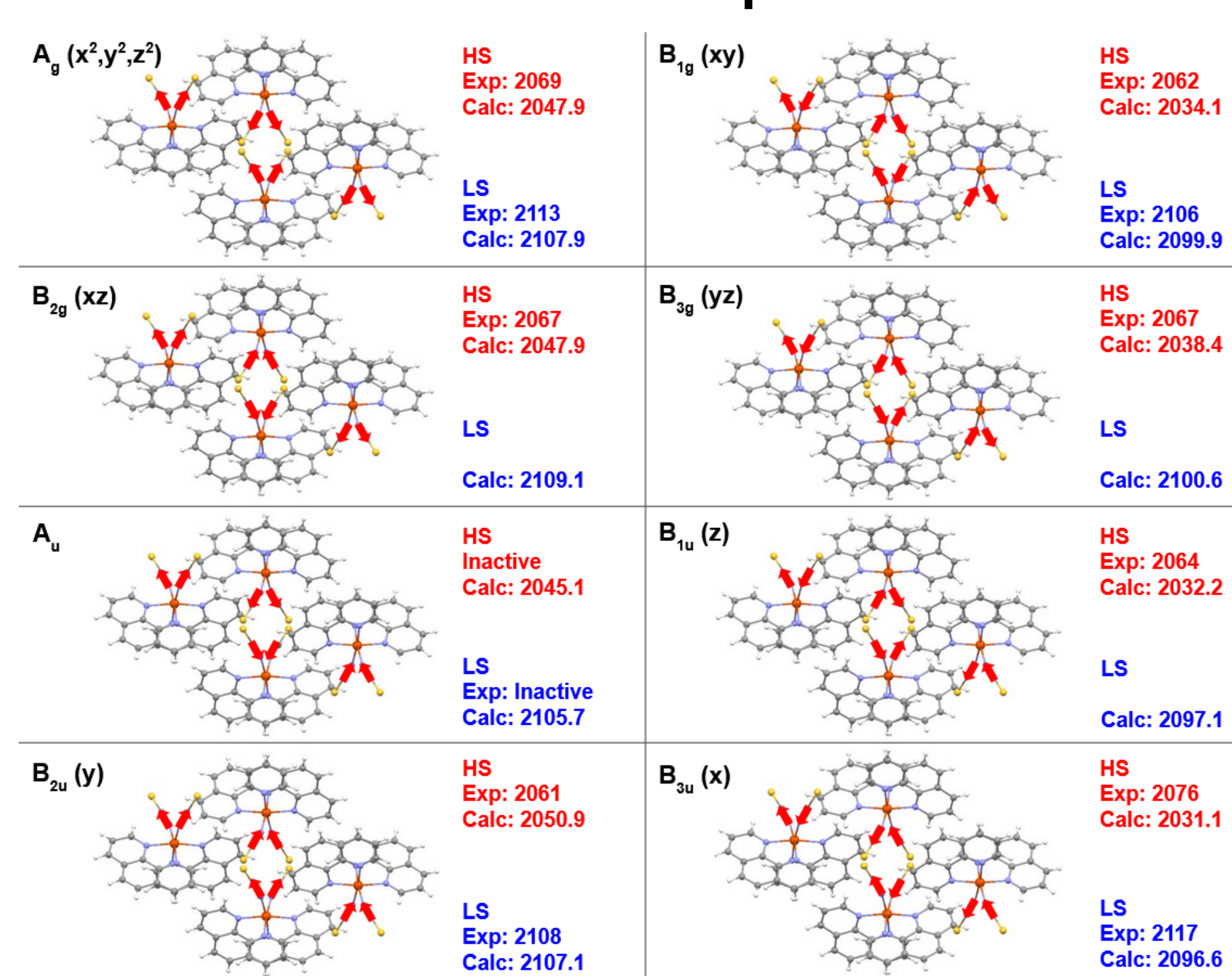
axes: 2//b 2<sub>1</sub>//a, 2<sub>1</sub>//c,  
glide planes b⊥a, c⊥b n⊥c  
↑ inversion symmetry

Crystal : 4 molecules/cell  
Brillouin zone center modes : 4 x 51 x 3 = 612 modes  
609 optical phonons  
3 acoustic phonons

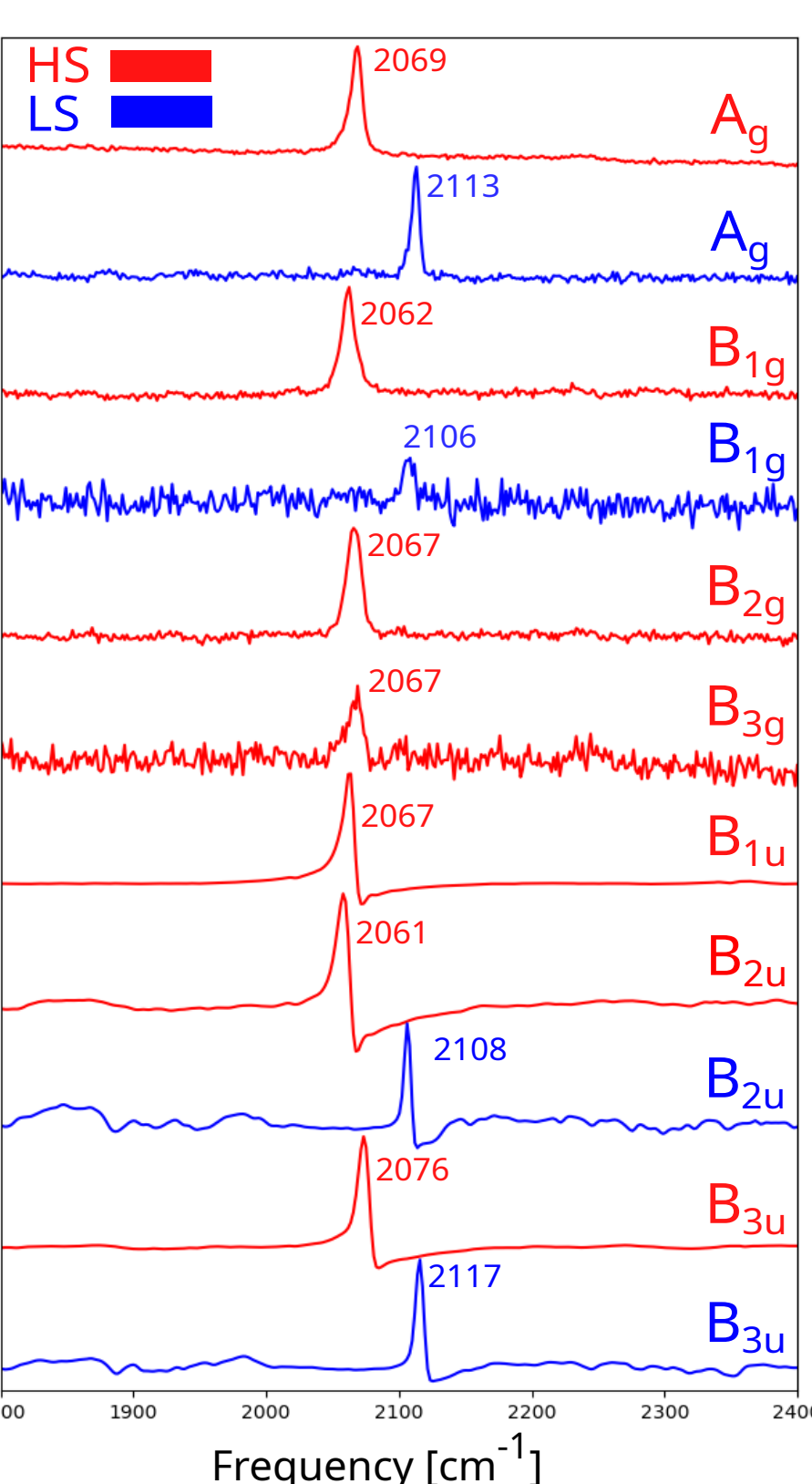
"Rigid molecules" approximation : 4 x 3 translations + 4 x 3 rotations = 24 → 21 libration modes

## 3) N-CS vibrational modes in crystal

Different symmetries and frequencies Density Functional Theory calculations vs IR and Raman experiments



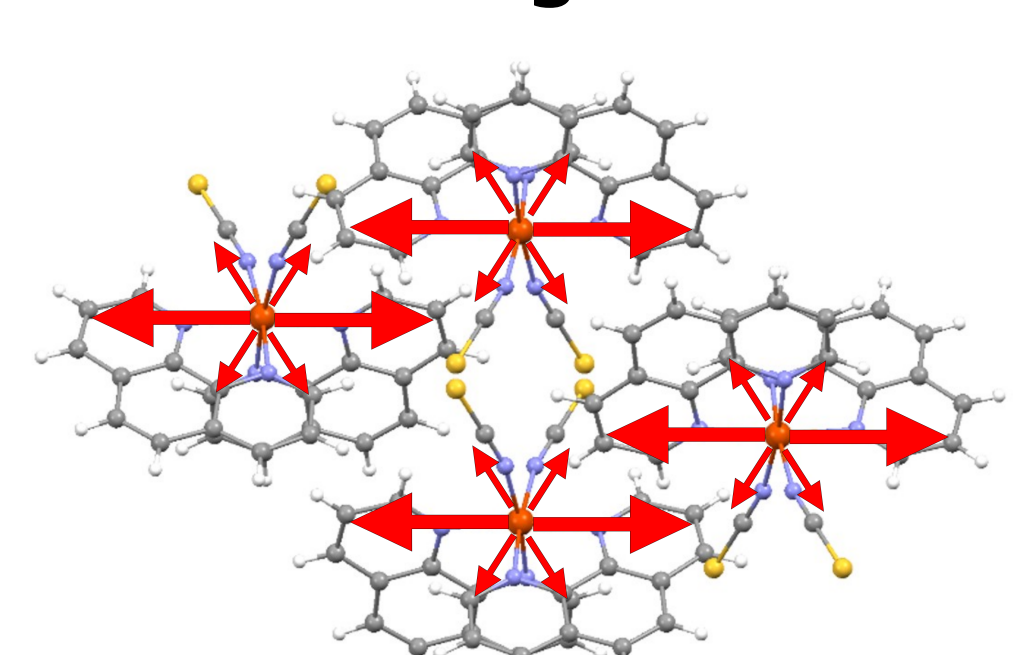
Raman and Infrared measurements



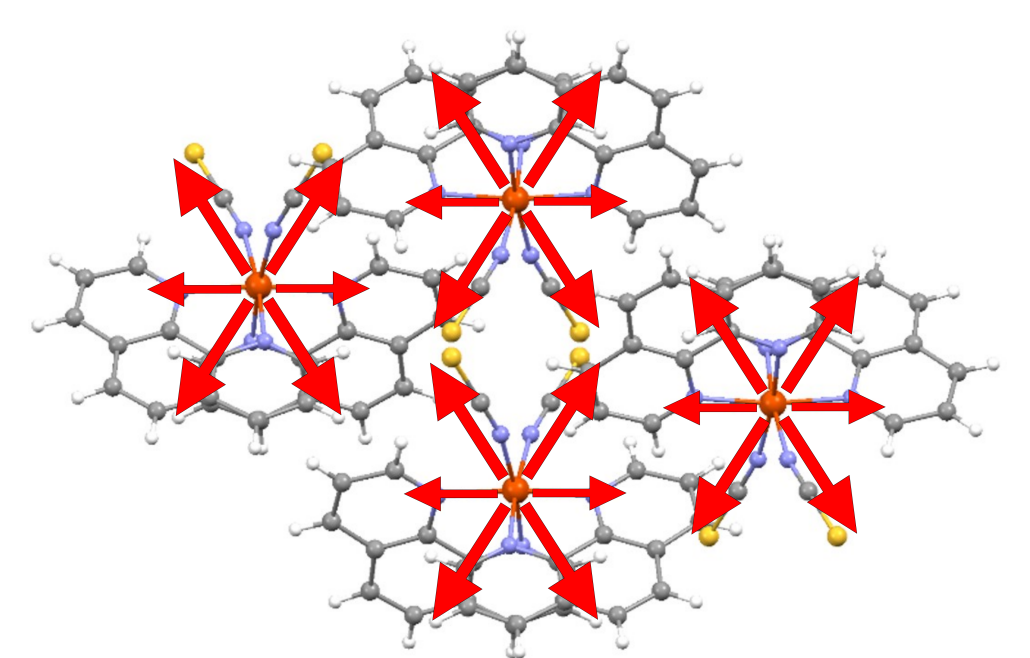
## 4) Breathing modes

DFT calculations :

Different types of A<sub>g</sub> breathing modes

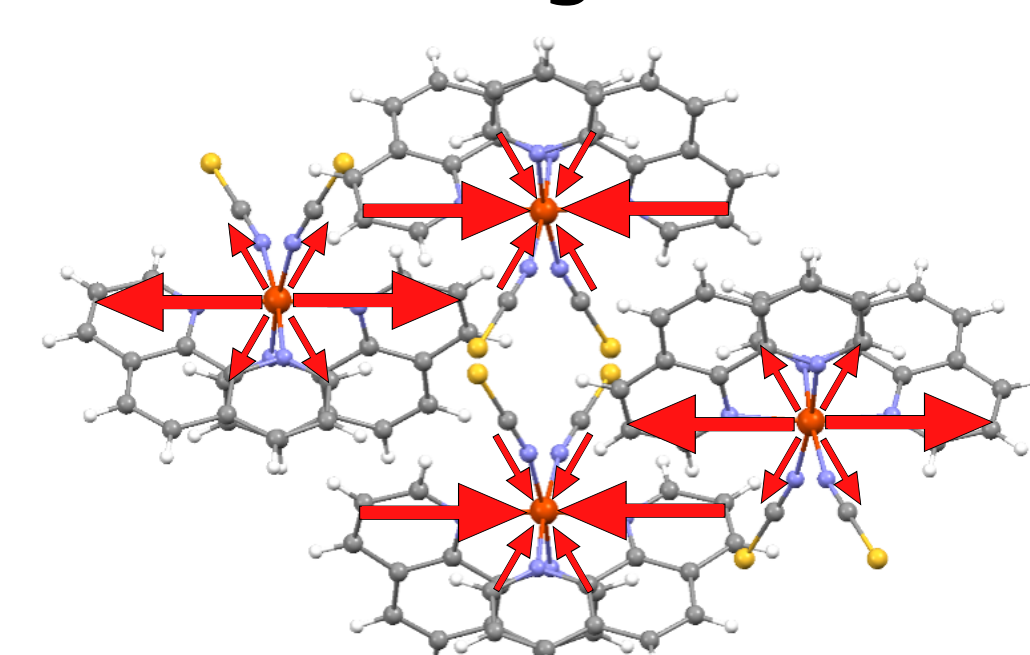


HS 109.4 cm<sup>-1</sup>      LS 173.6 cm<sup>-1</sup>

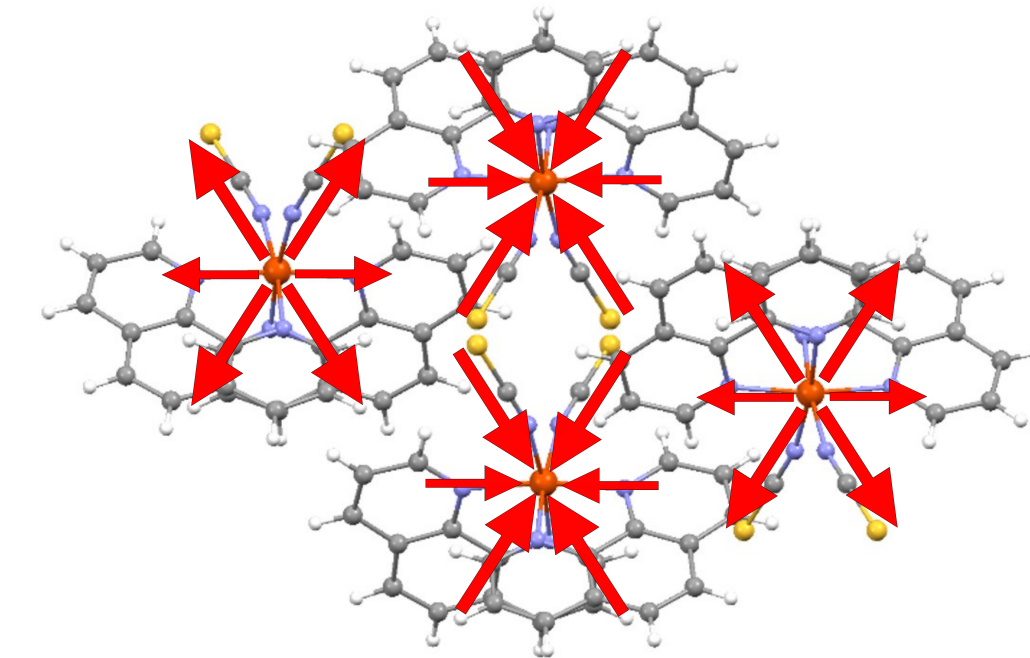


HS 89.5 cm<sup>-1</sup>      LS 99.9 cm<sup>-1</sup>

Different types of B<sub>2u</sub> breathing modes



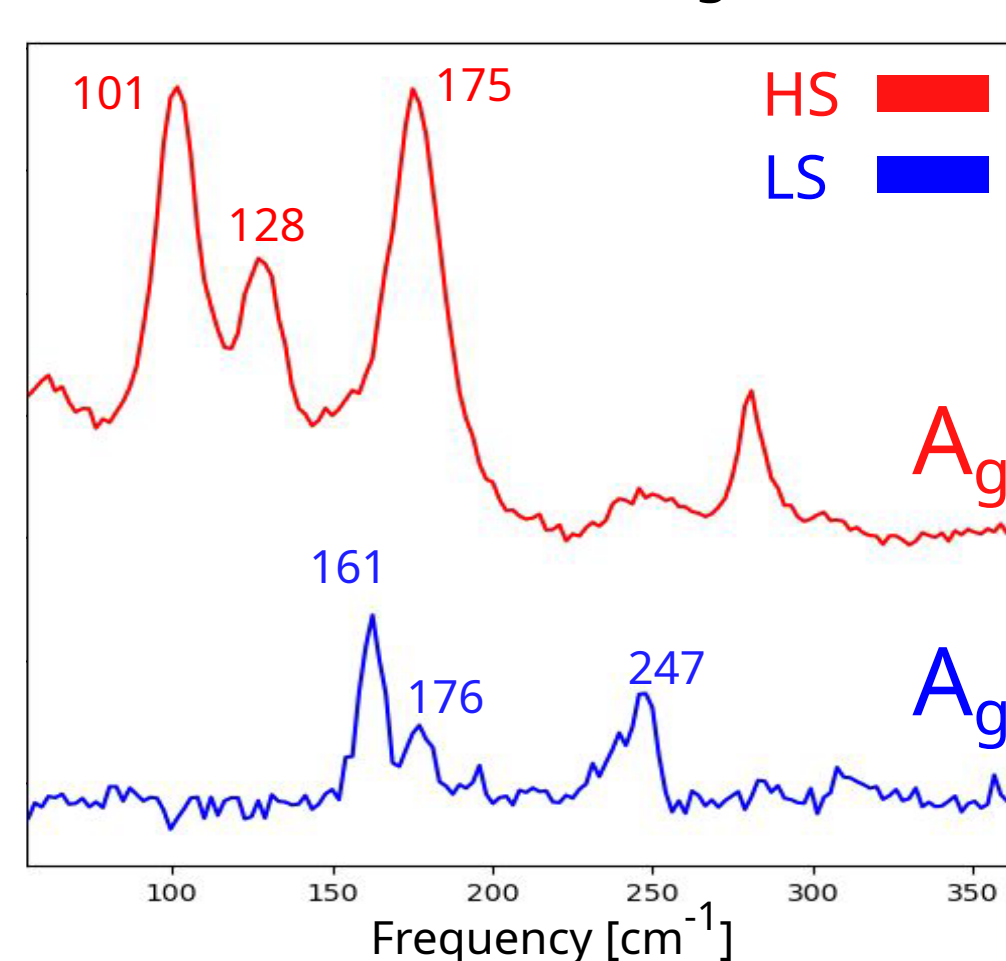
HS 107.2 cm<sup>-1</sup>      LS 172.5 cm<sup>-1</sup>



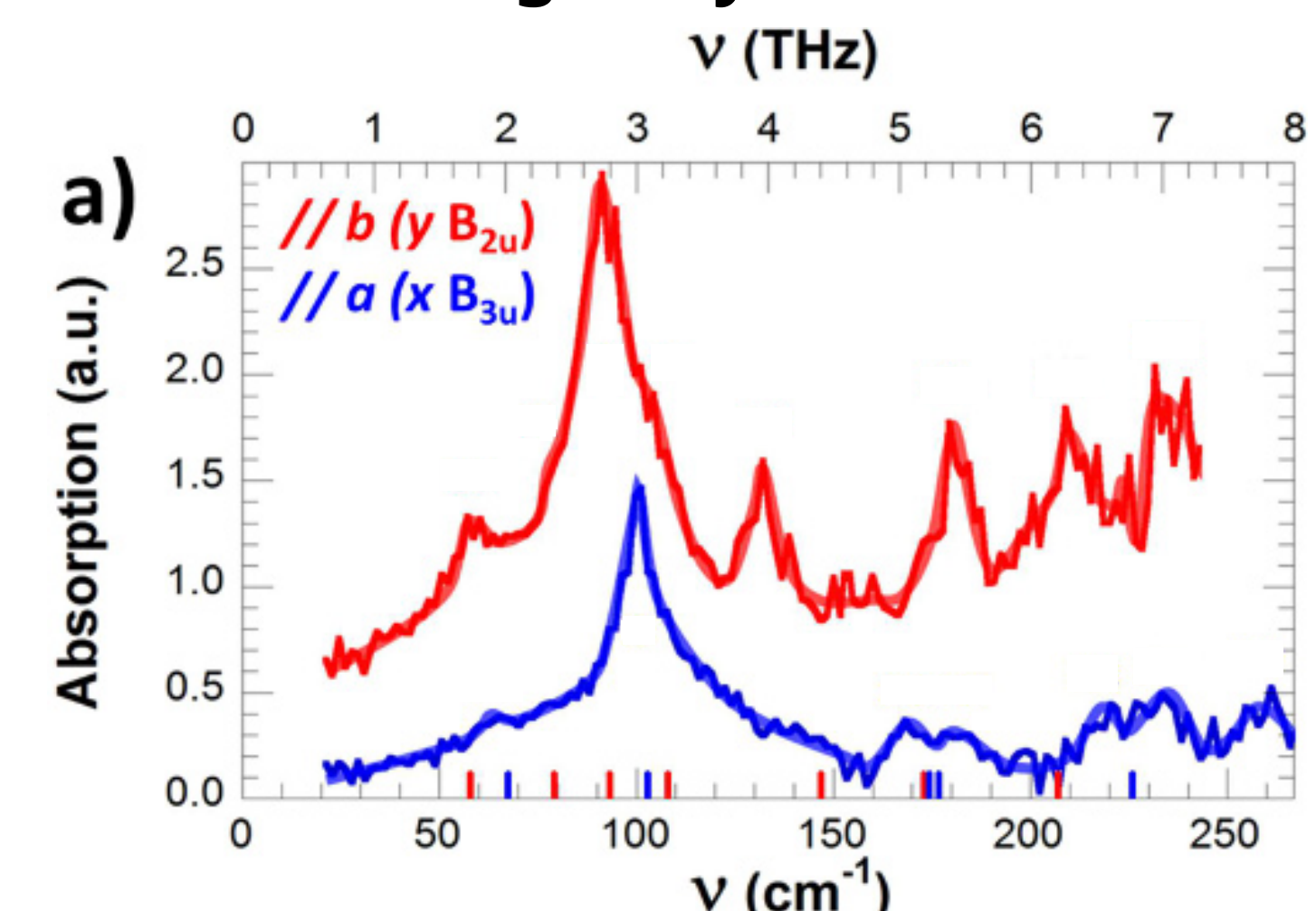
HS 84.6 cm<sup>-1</sup>      LS 87.4 cm<sup>-1</sup>

Measurements :

Low frequency Raman measurements, A<sub>g</sub> modes

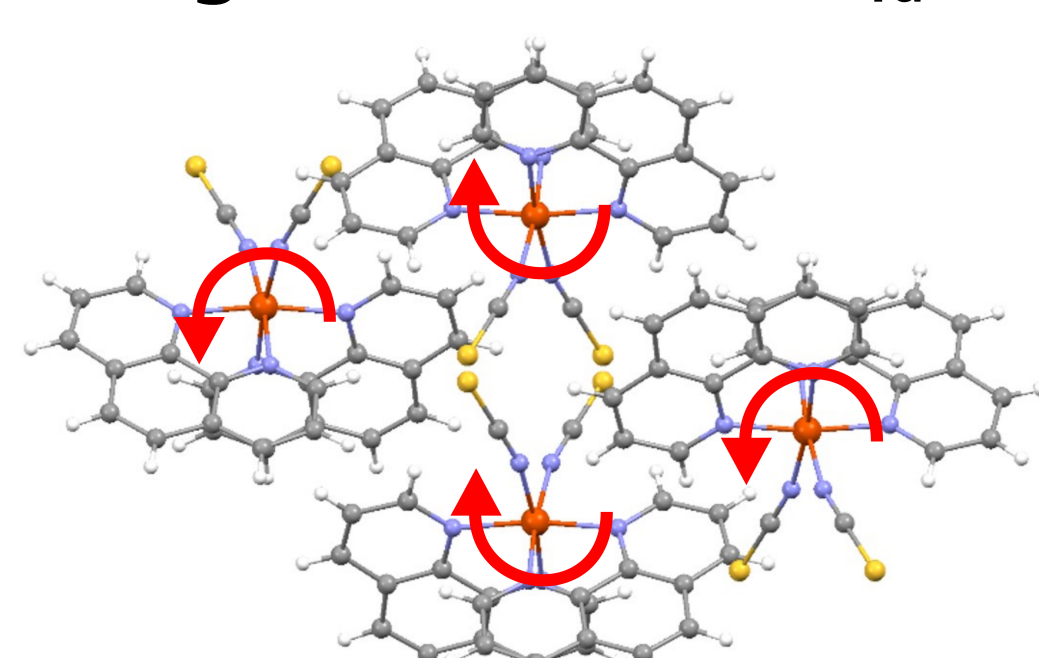


THz absorption on Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> single crystal<sup>[2]</sup>



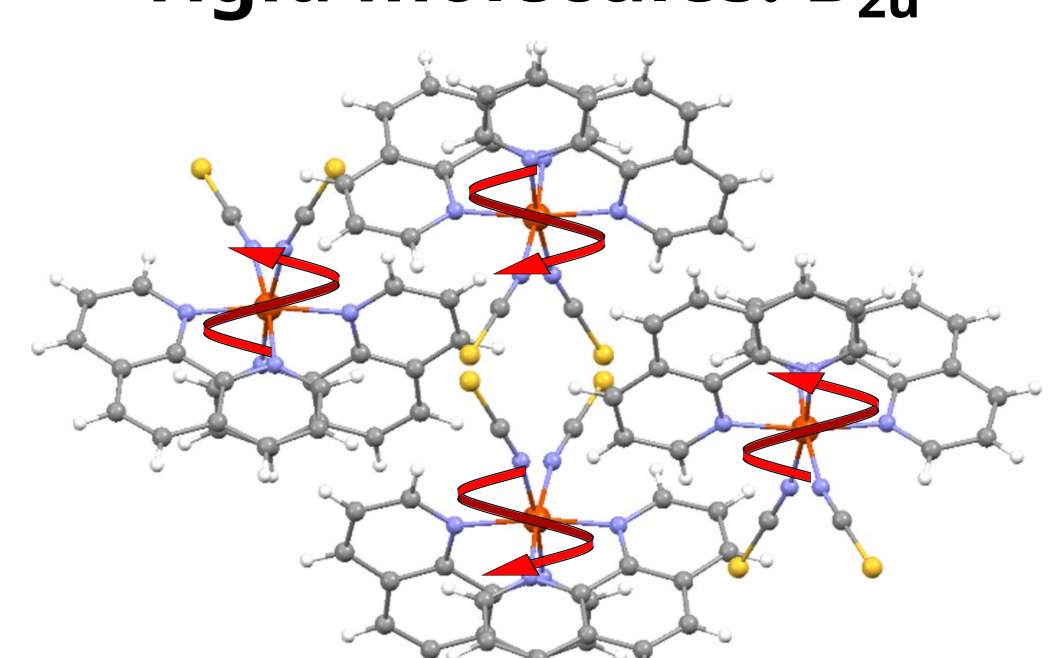
## 5) Libration modes

Rotation mode of almost rigid molecules: B<sub>1u</sub>



HS 46.1 cm<sup>-1</sup>      LS 45.4 cm<sup>-1</sup>

Screwing mode of almost rigid molecules: B<sub>2u</sub>



HS 54.1 cm<sup>-1</sup>      LS 52.6 cm<sup>-1</sup>

DFT calculated frequencies

## 6) Conclusion

- Vibrational modes in crystal correspond to different combinations of in-phase/out-of phase vibrations of the molecules in the unit cell
- There are different frequencies for the different symmetries
- The modes can be selectively probed by polarized IR, THz and Raman spectroscopies
- In this complex there is a mixing of intra-molecular and libration nature of the low frequency modes: the rigid approximation is not correct
- This complex and rich phonon structure should be taken into account for the vibrational entropy

## 7) References

- [1] G. Brehm et al. "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)
- [2] 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)

