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

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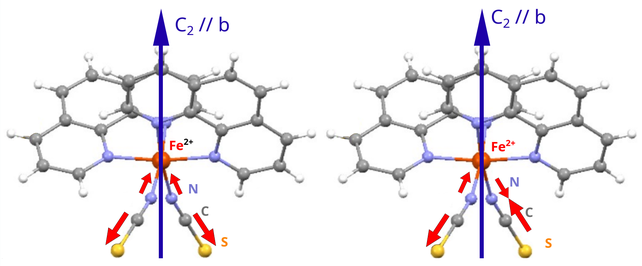
1) Isolated $Fe(phen)_2(NCS)_2$ molecule

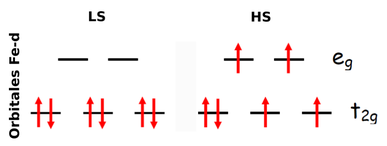
Isolated molecule



C_2	E	C_2	linear functions, rotations	quadratic functions
A	+1	+1	y, R_y	x^2, y^2, z^2, xz
B	+1	-1	x, z, R_x, R_z	xy, yz

C_2 symmetry:
2 types of modes:
A symmetry (identity) →
B symmetry →

Fe^{2+} : $3d^6$ schematic electronic configuration



51 atoms
x 3 degree of liberty
= 153 modes

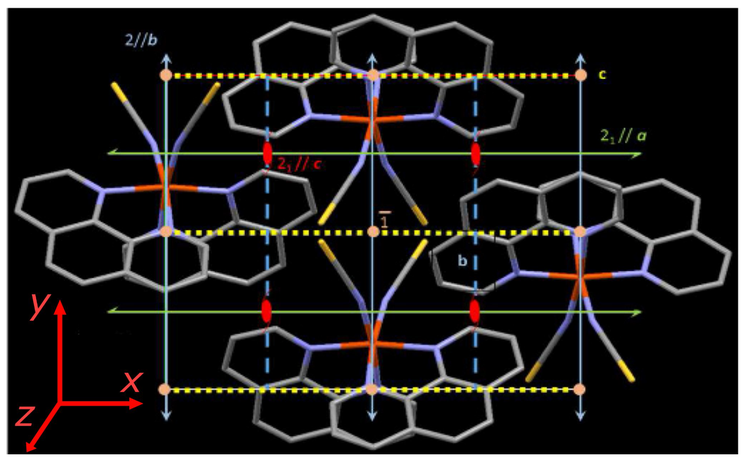
3 translation
3 rotation

147 vibrational modes

stretching N-CS modes[1]
HS 2040 cm^{-1} LS 2070 cm^{-1}
HS 2029 cm^{-1} LS 2061 cm^{-1}

2) In crystal: Pbcn space group

Crystal structure[2]



Crystalline point group (mmm)[2]

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_z	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_x	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	

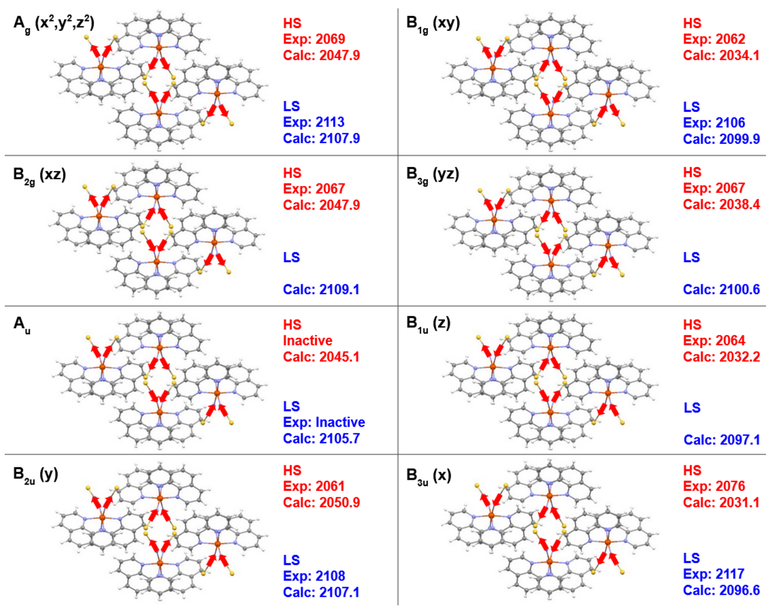
axes: 2//*b* 2_1 //*a*, 2_1 //*c*,
glide planes b⊥*a*, c⊥*b* n⊥*c*
$\bar{1}$ inversion symmetry

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

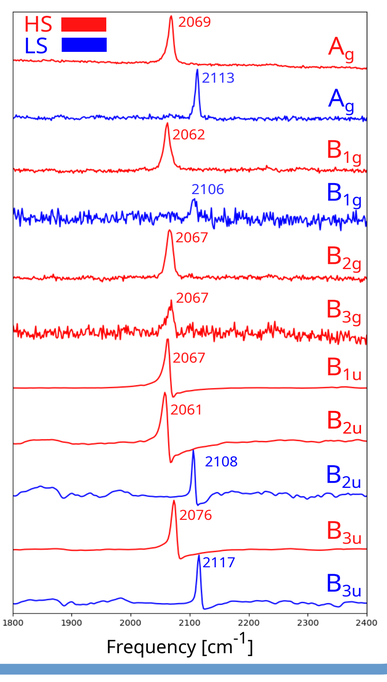
"Rigid molecules" approximation : 4 x 3 translations + 4 x 3 rotations = 24 → 21 libration modes

3) N-CS vibrational modes in crystal

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



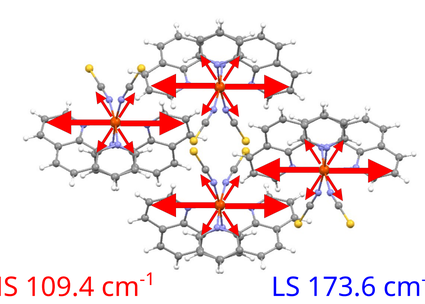
Raman and Infrared measurements



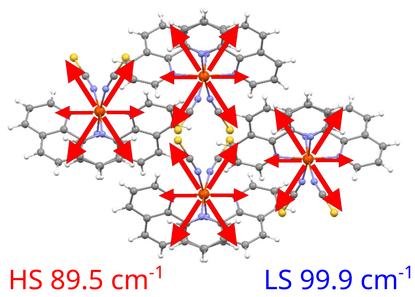
4) Breathing modes

DFT calcultations :

Different types of A_g breathing modes

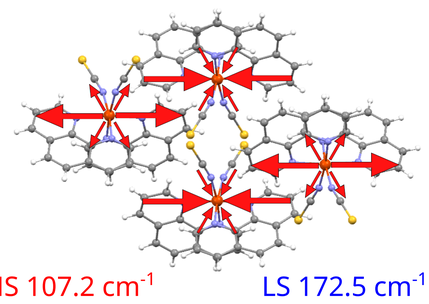


HS 109.4 cm^{-1} LS 173.6 cm^{-1}

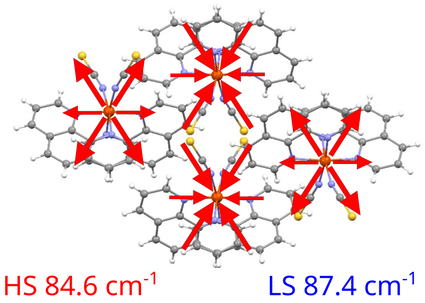


HS 89.5 cm^{-1} LS 99.9 cm^{-1}

Different types of B_{2u} breathing modes



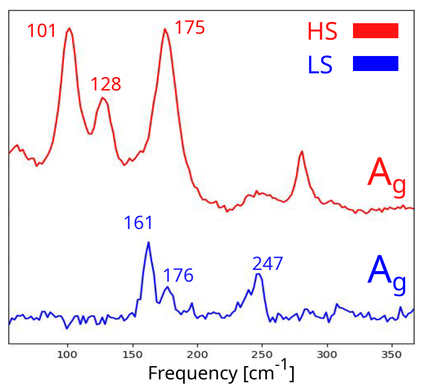
HS 107.2 cm^{-1} LS 172.5 cm^{-1}



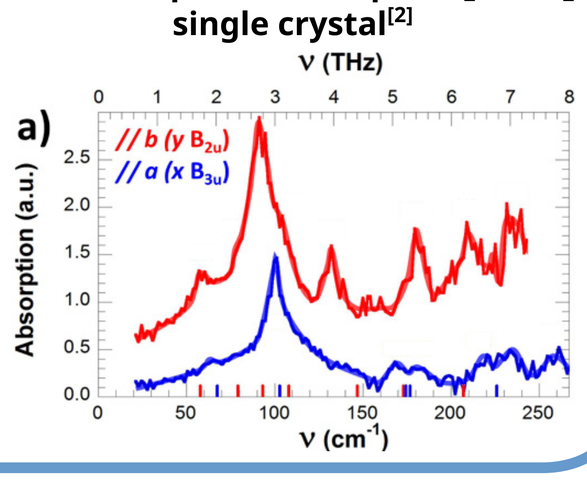
HS 84.6 cm^{-1} LS 87.4 cm^{-1}

Measurements :

Low frequency Raman measurments, A_g modes



THz absorption on $Fe(phen)_2(NCS)_2$ single crystal[2]



5) Libration modes

Rotation mode of almost rigid molecules: B_{1u}

HS 46.1 cm^{-1} LS 45.4 cm^{-1}

Screwing mode of almost rigid molecules: B_{2u}

HS 54.1 cm^{-1} LS 52.6 cm^{-1}

DFT calculated frequencies

6) Conclusion

- Vibrationnal modes in crystal correspond to different combinaisons 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 vibrationnal 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 $Fe(phen)_2(NCS)_2$ 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 $[Fe(phen)_2(NCS)_2]$ studied by THz, IR, Raman spectroscopies and DFT calculations ». Eur. Phys. J. B (2019)

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