



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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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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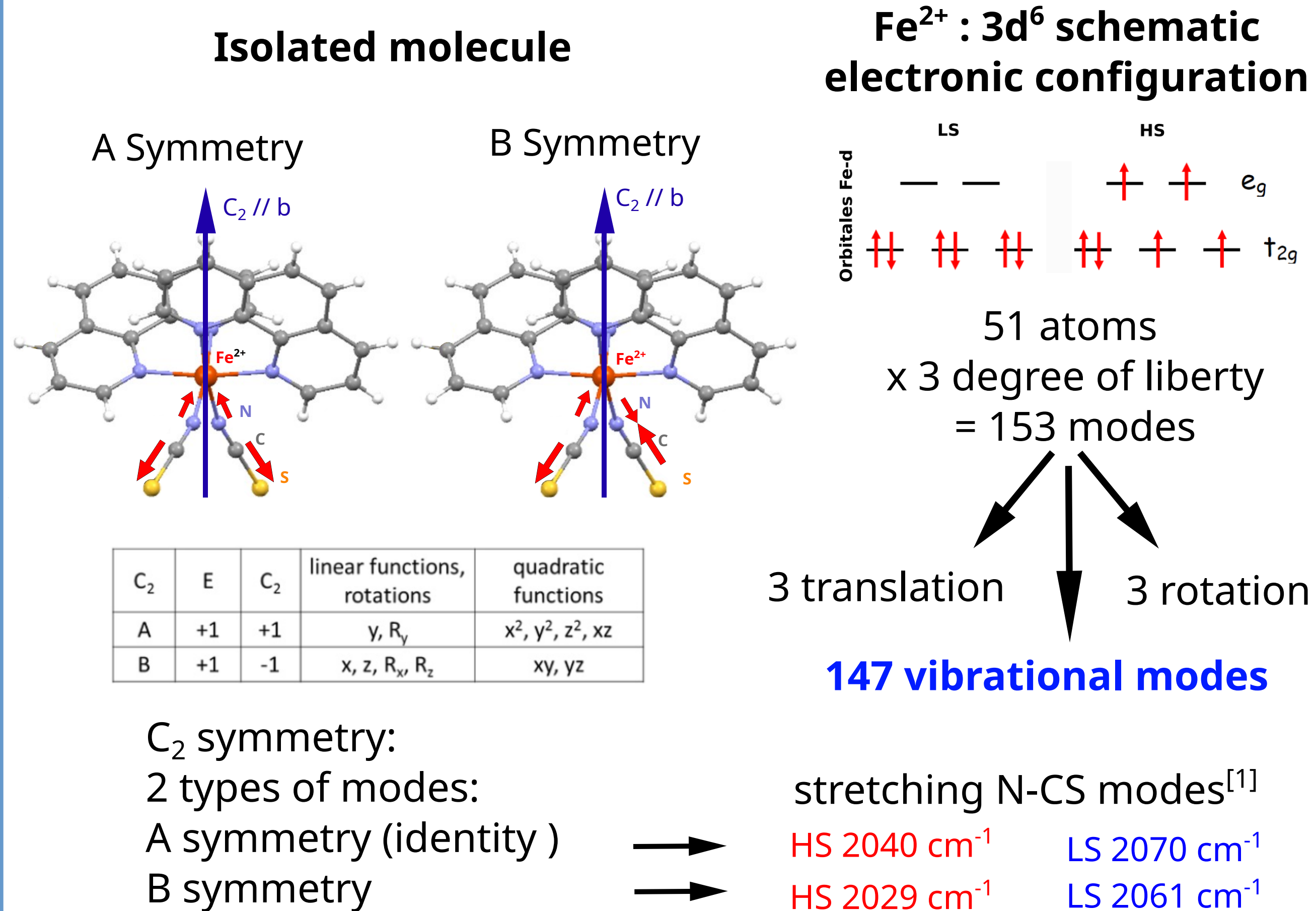
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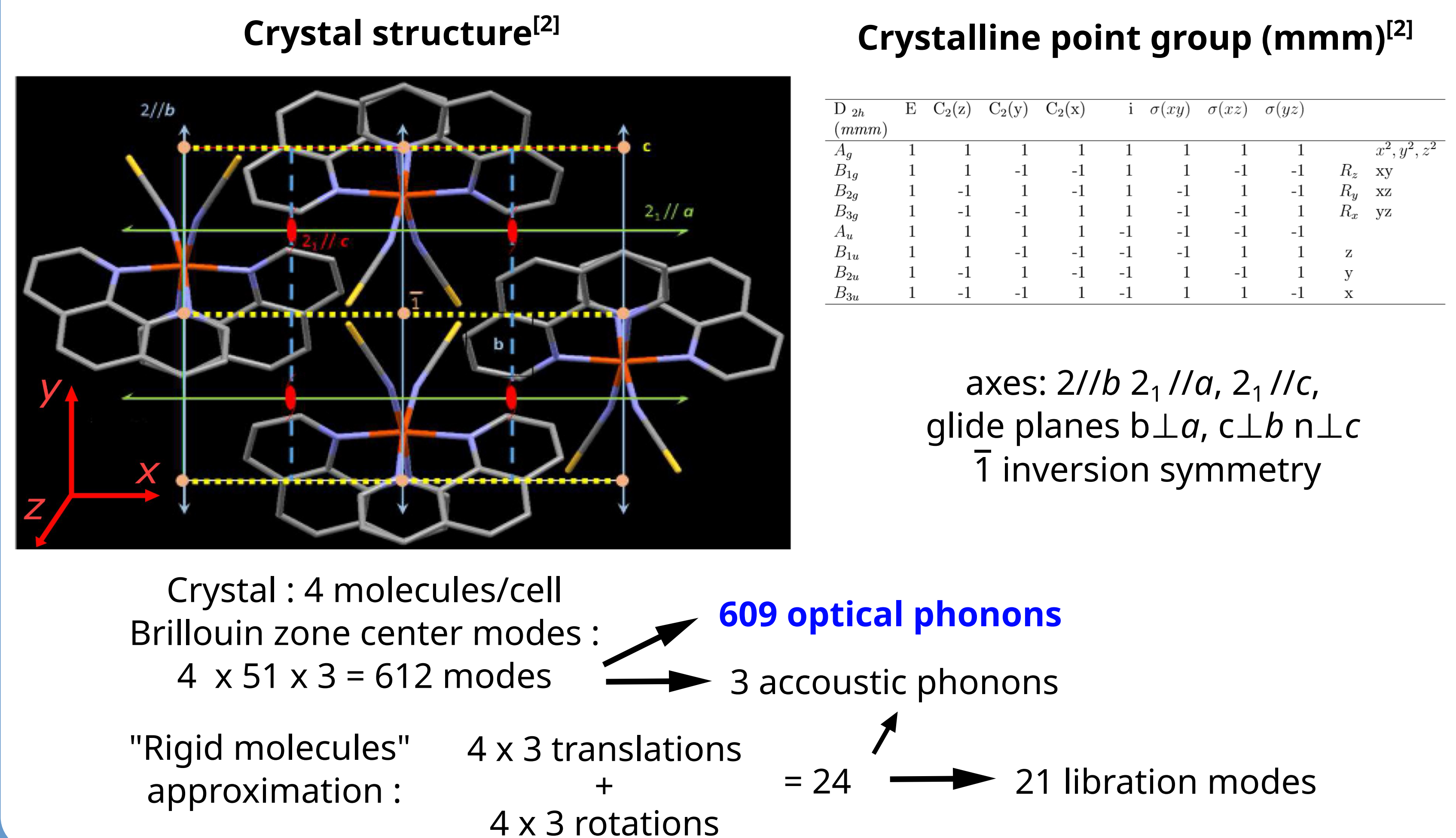
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1) Isolated Fe(phen)₂(NCS)₂ molecule

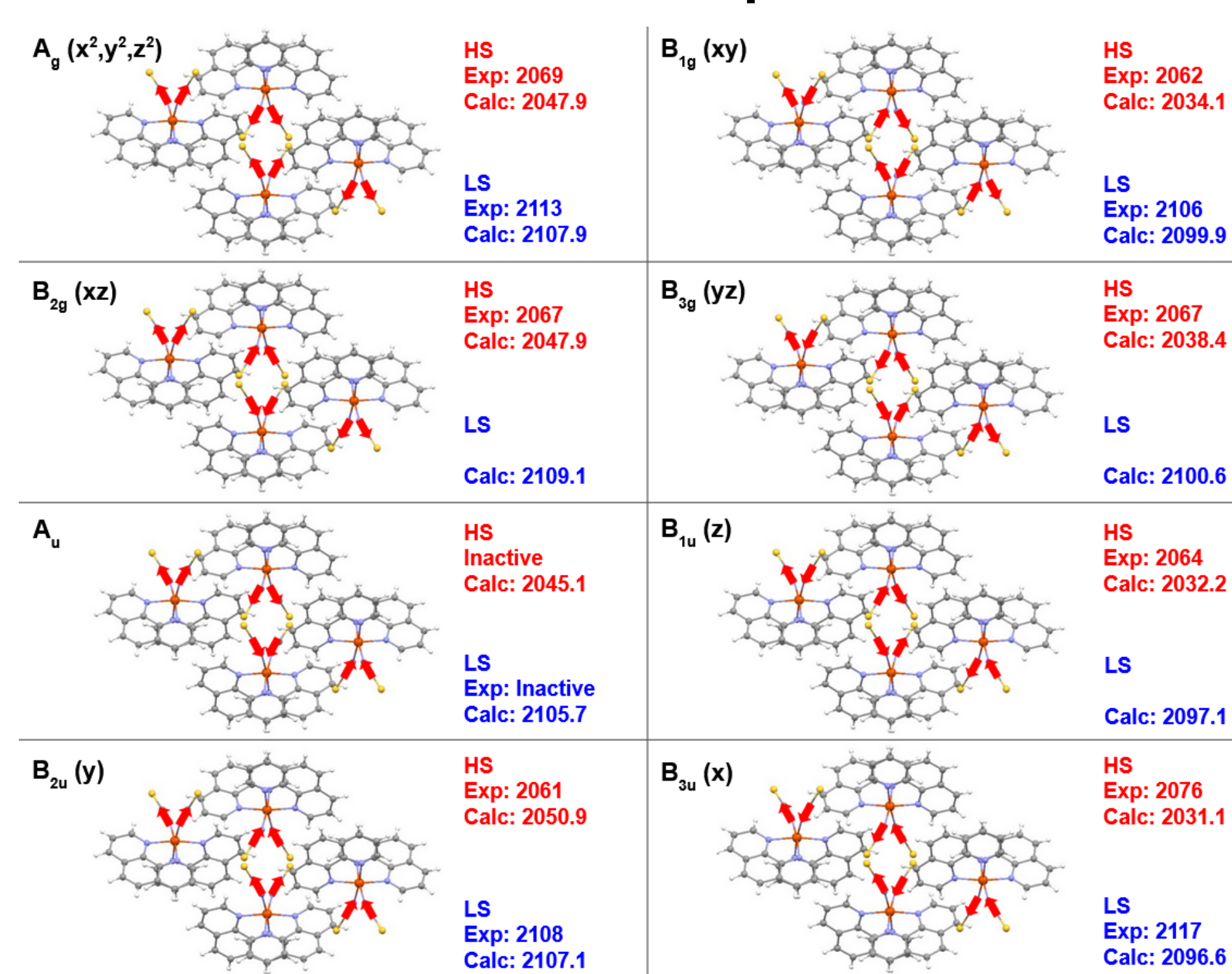


2) In crystal: Pbcn space group

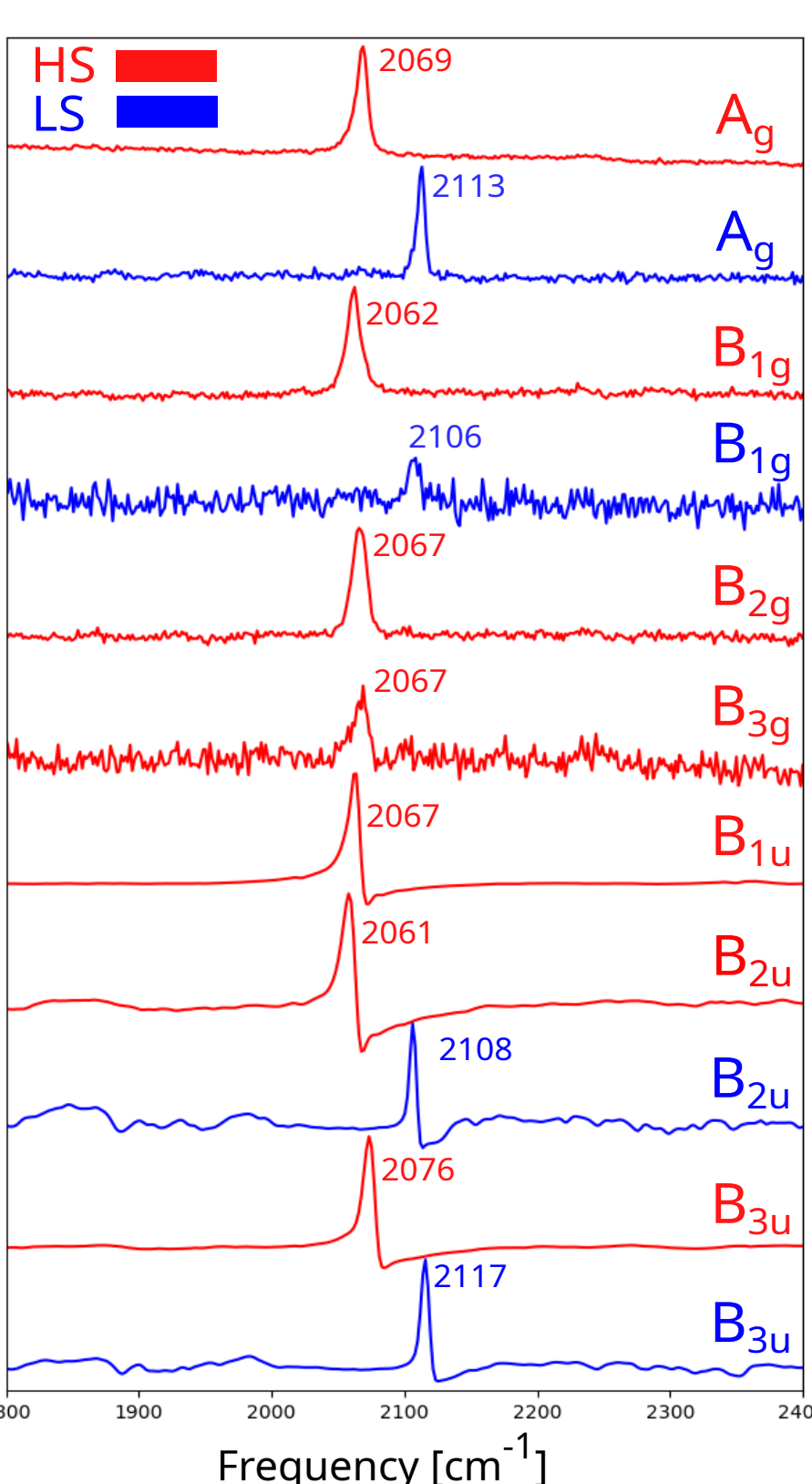


3) N-CS vibrational modes in crystal

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



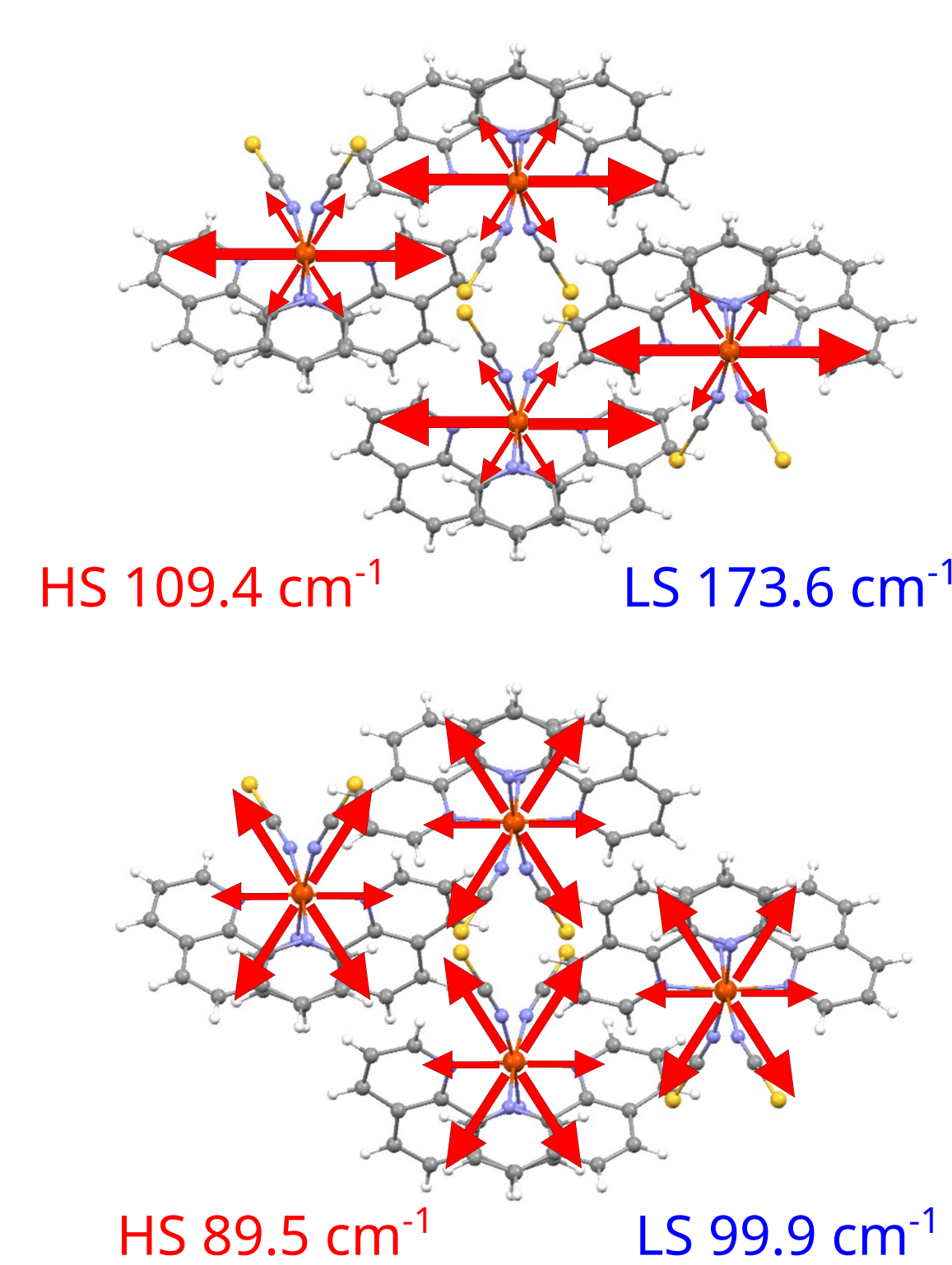
Raman and Infrared measurements



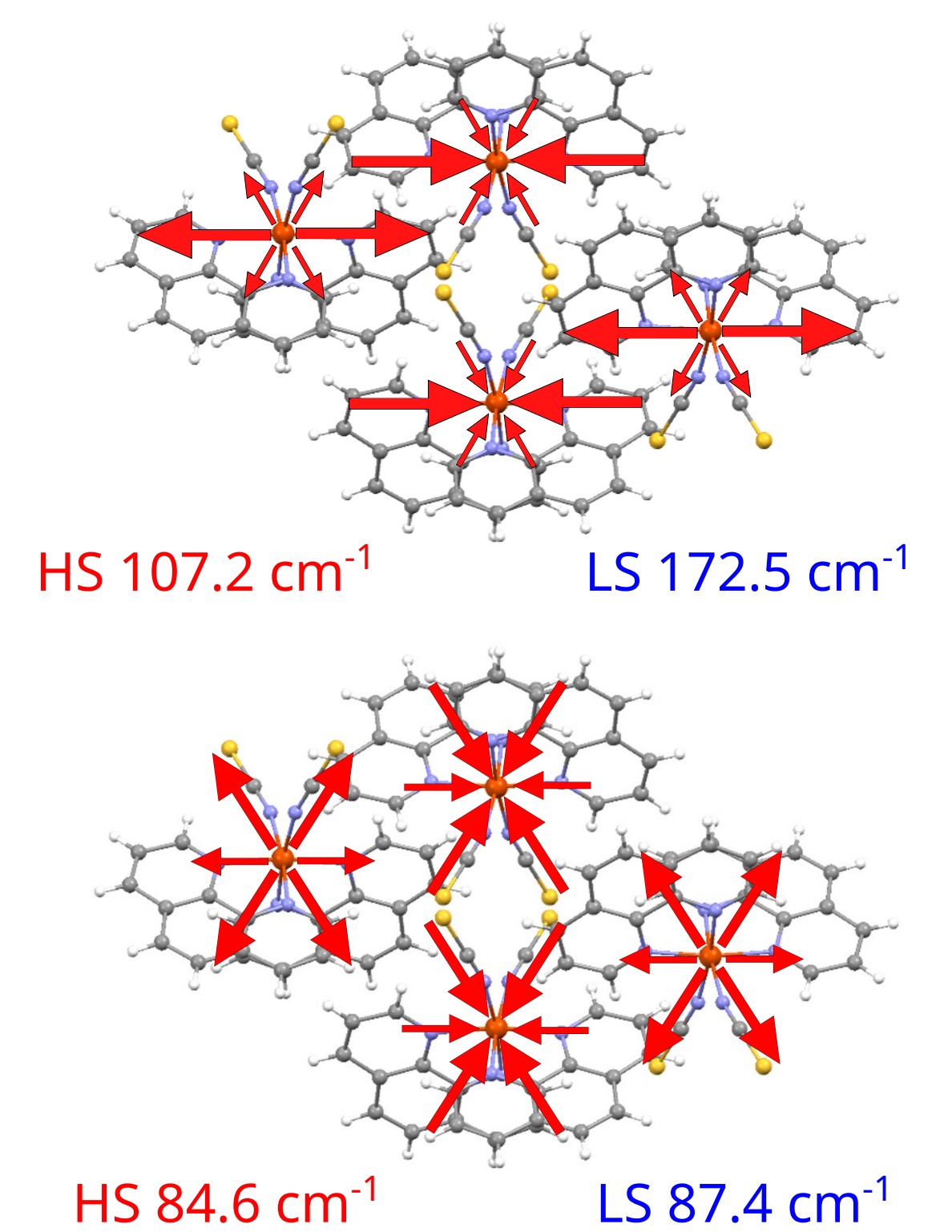
4) Breathing modes

DFT calculations :

Different types of A_g breathing modes

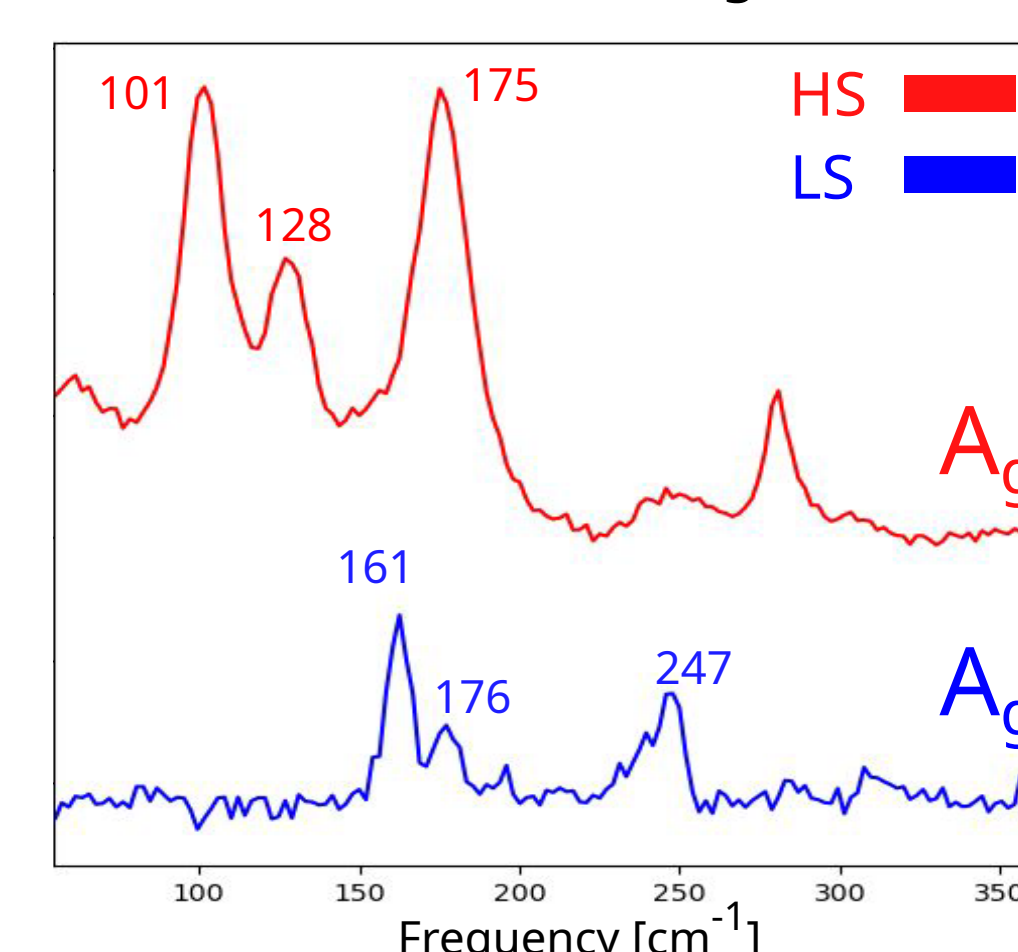


Different types of B_{2u} breathing modes

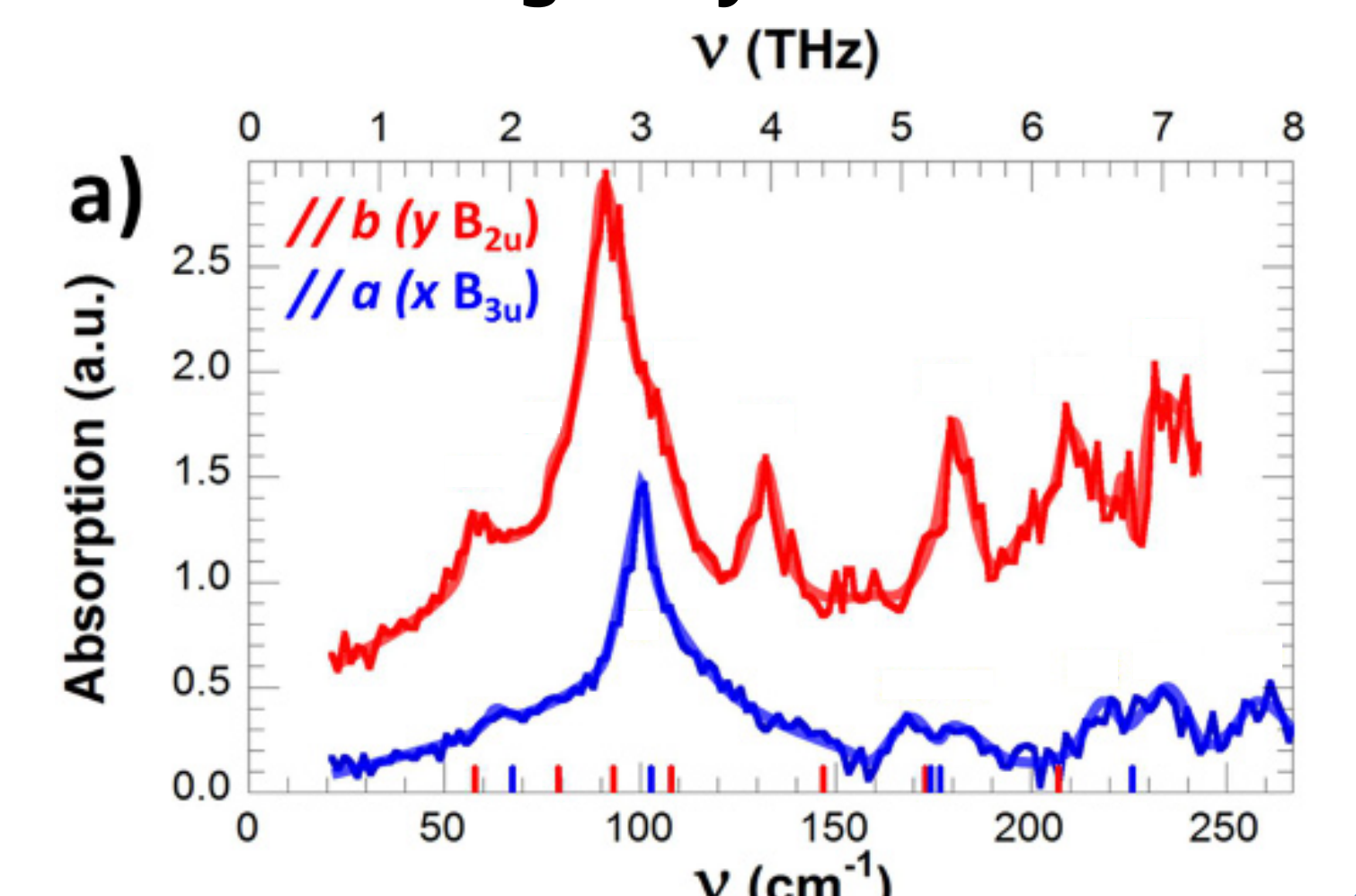


Measurements :

Low frequency Raman measurements, A_g modes

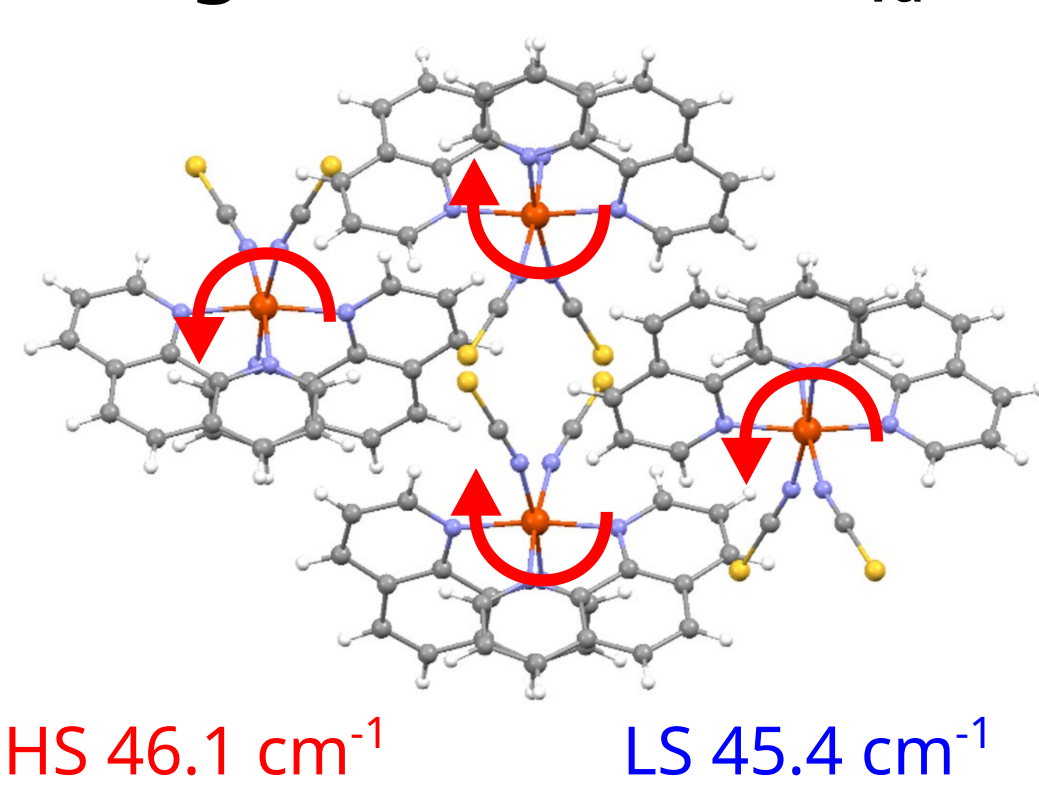


THz absorption on Fe(phen)₂(NCS)₂ single crystal^[2]

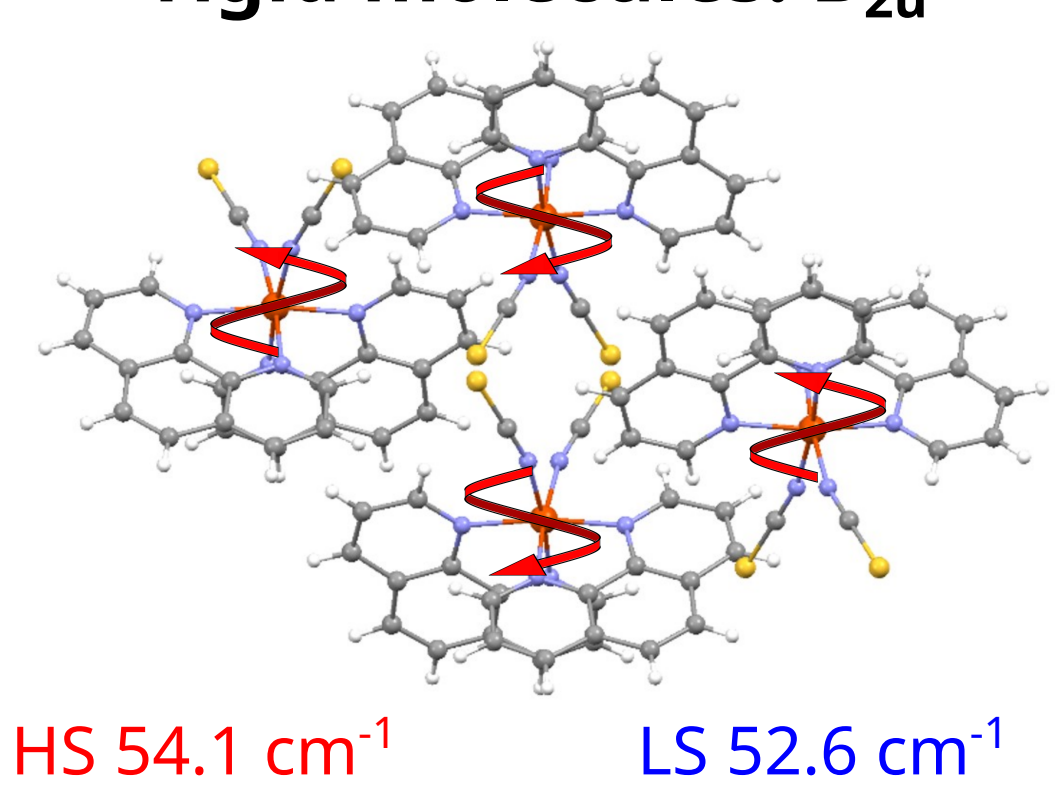


5) Libration modes

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



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



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)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)