Experimental and theoretical analysis of vibrational modes in \( \text{Fe(phen)}_2(\text{NCS})_2 \) single crystal

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**Fe(phen)_2(NCS)_2** molecule and energy diagram

- **Coupled electronic / structural reorganisation**
- **Spin transition driven by entropy difference** (electronic and vibrational)

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

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)_2(NCS)_2** in both state
Fe(phen)$_2$(NCS)$_2$

4 molecules in unit cell
Pbcn space group
mmm point group

Molecule $C_2$ symmetry
Symmetry: A

two symmetries $\rightarrow$ eight symmetries

Crystal polarisation

IR or Raman
beam

y axis

x axis

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

**Δν(A_{g}) = 44 \text{ cm}^{-1}**  
**Δν(B_{3u}) = 41 \text{ cm}^{-1}**
Conclusion:
-Lattice mode measurements & calculations: \( \Delta S_{vib}^{\text{cell}} \neq 4 \Delta S_{vib}^{\text{molecule}} \) ?
-Infra red 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 Fe(phen)_2(NCS)_2 crystal, controlling spin state switching by resonant excitation of infrared modes.
References


