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Vibronic coupling in a 4f qubit

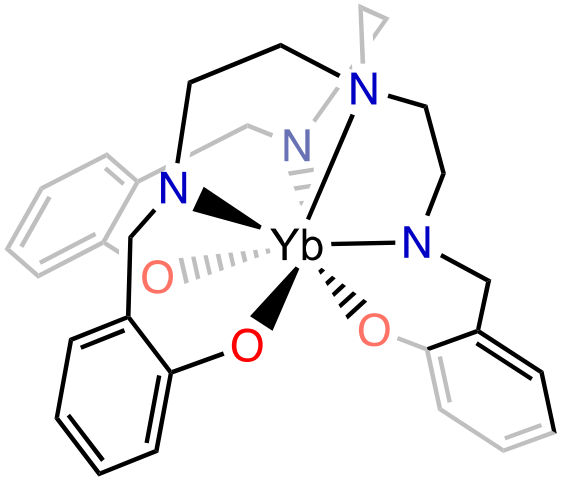
Jon G. C. Kragskow, Jonathan Marbey, Christian D. Buch, Joscha Nehrkorn, Mykhaylo Ozerov, Stergios Piligkos, Stephen Hill and Nicholas F. Chilton

Kragskow *et al.*, *Nature Communications*, 2022

Vibronic coupling

Coupling of electronic structure to vibrational motion – ever present phenomenon
e.g. Catalysis, Luminescence, Qubit decoherence, Single molecule magnets

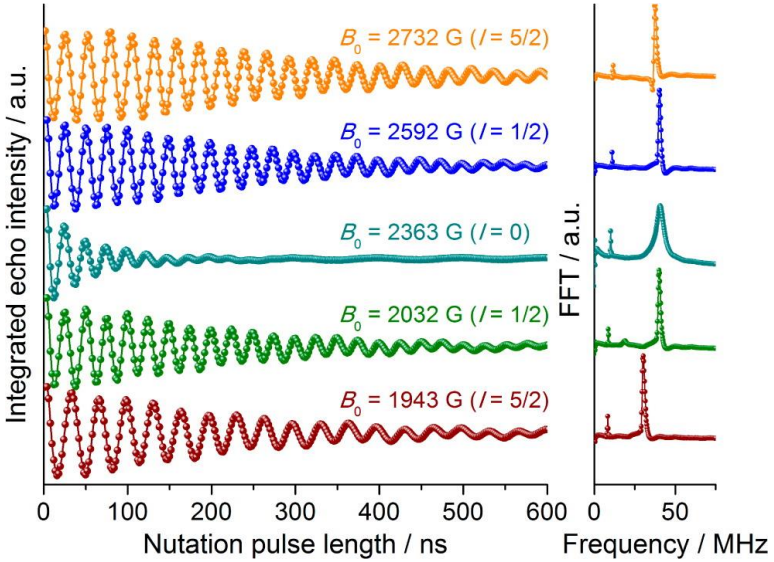
[Yb(trensal)] - Neutral, air-stable Yb(III) complex, C_3 symmetric, capped trigonal prism



Well-studied electronic structure and magnetic properties [1]

Promising molecular spin qubit [2]

Poor single molecule magnet [3]
Relaxation via two-mode pathway



[1] M. Flanagan *et al.*, *Inorg. Chem.*, 2002, **41**, 5024; [2] K. S. Pedersen *et al.*, *J. Am. Chem. Soc.*, 2016, **138**, 5801.
[3] K. S. Pedersen *et al.*, *Inorg. Chem.*, 2015, **54**, 7600;

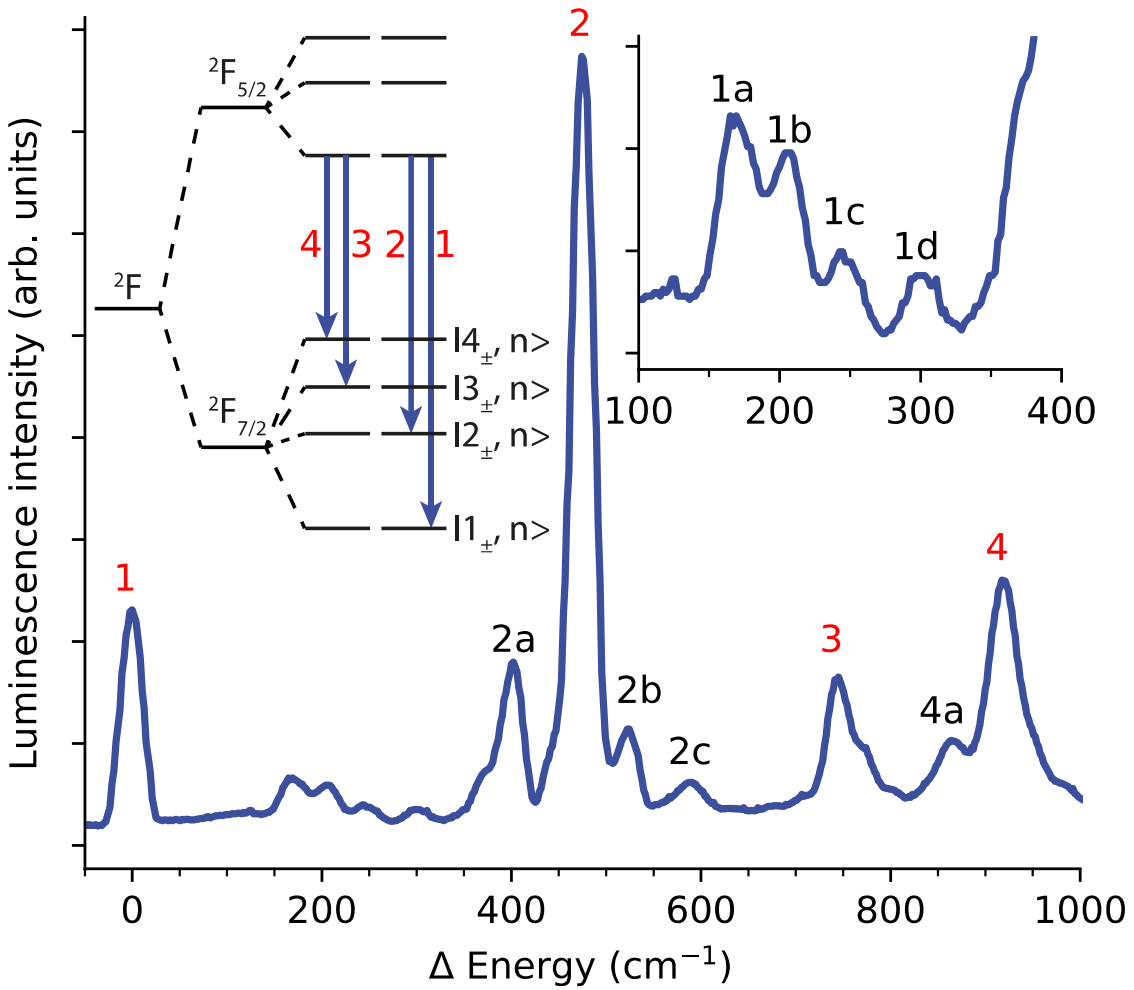
Electronic structure

Yb(III): $4f^{13}$, $^2F_{7/2}$ (Ground) and $^2F_{5/2}$

Solid-state luminescence at 5 K:[1]

- Excite to $J = 5/2$ and measure emission spectrum

- Peaks 1-4 = energies of $J = 7/2$ multiplet (within NIR region)
  - Peaks a-d ”vibrational sidebands”
    - Coupling?

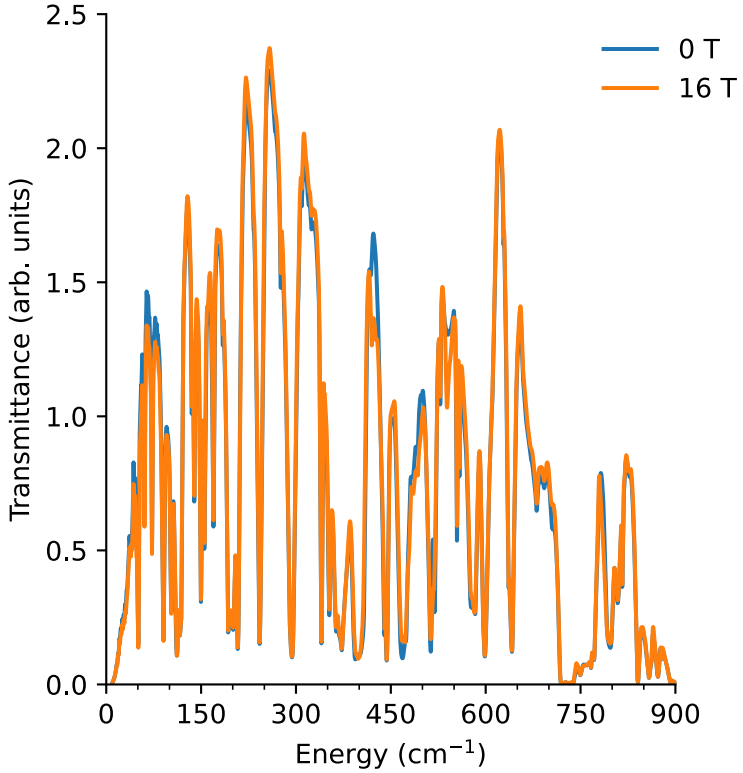


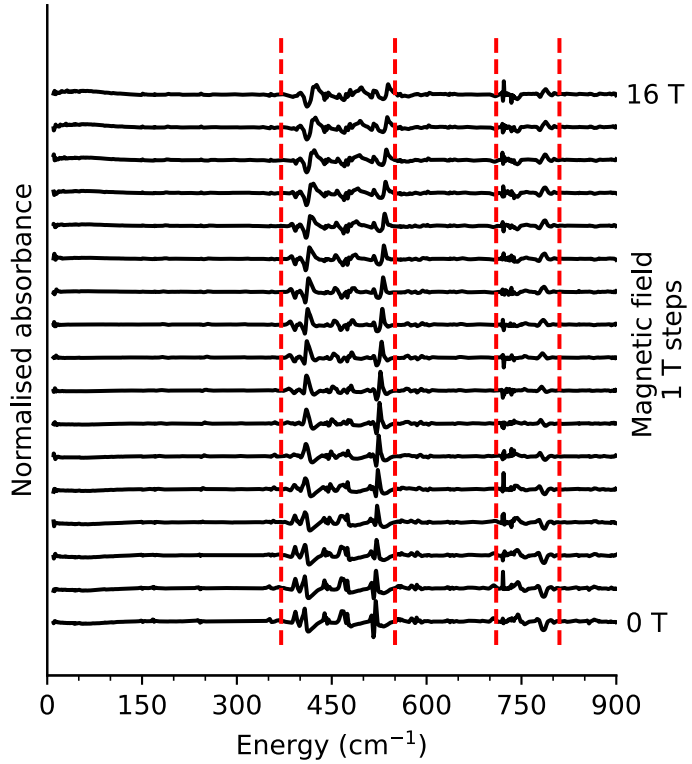
K. S. Pedersen *et al.*, *Inorg. Chem.*, 2015, **54**, 7600

FIRMS

Far-infrared magneto-spectroscopy (FIRMS)

- FTIR spectrum as a function of magnetic field at 4 K
- Normalise by average of all spectra to give field dependent signals





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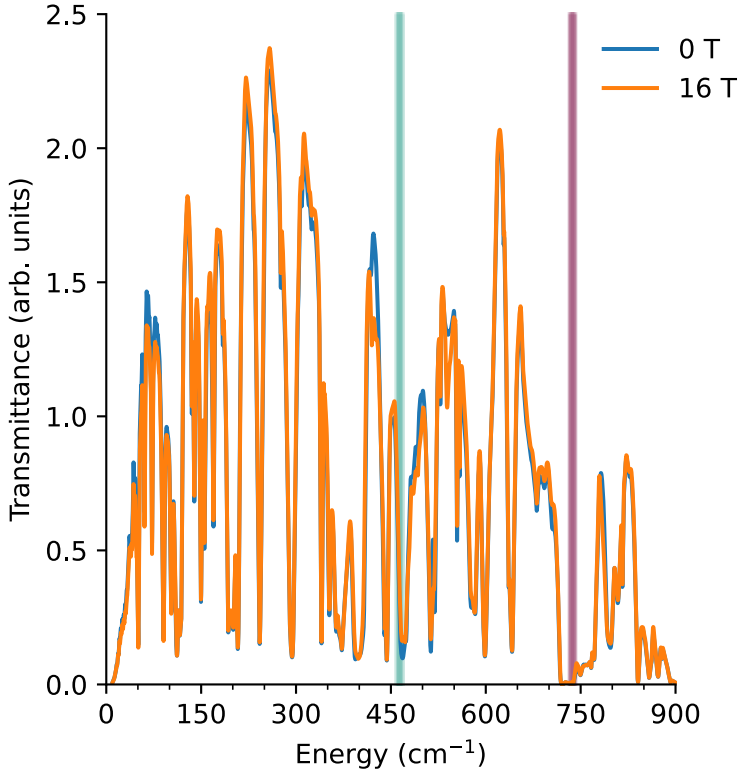
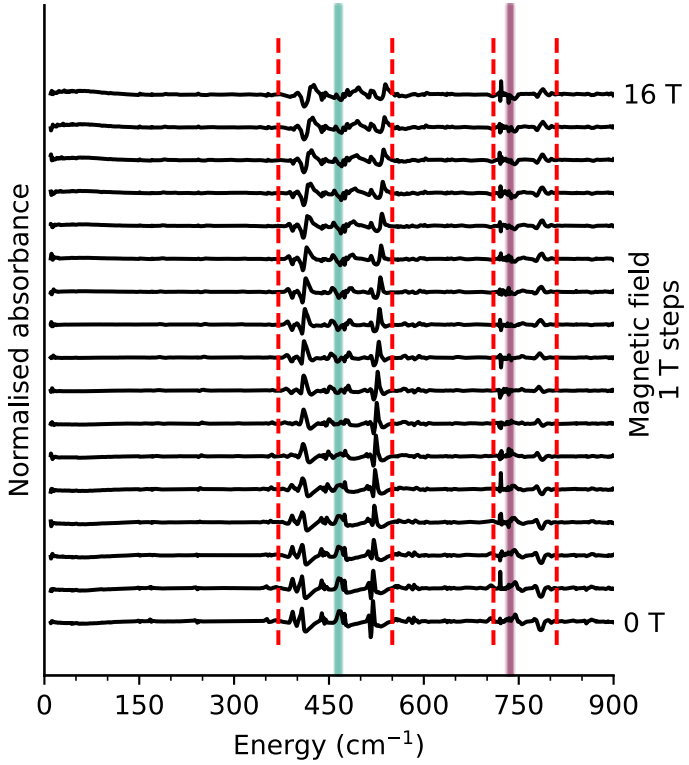
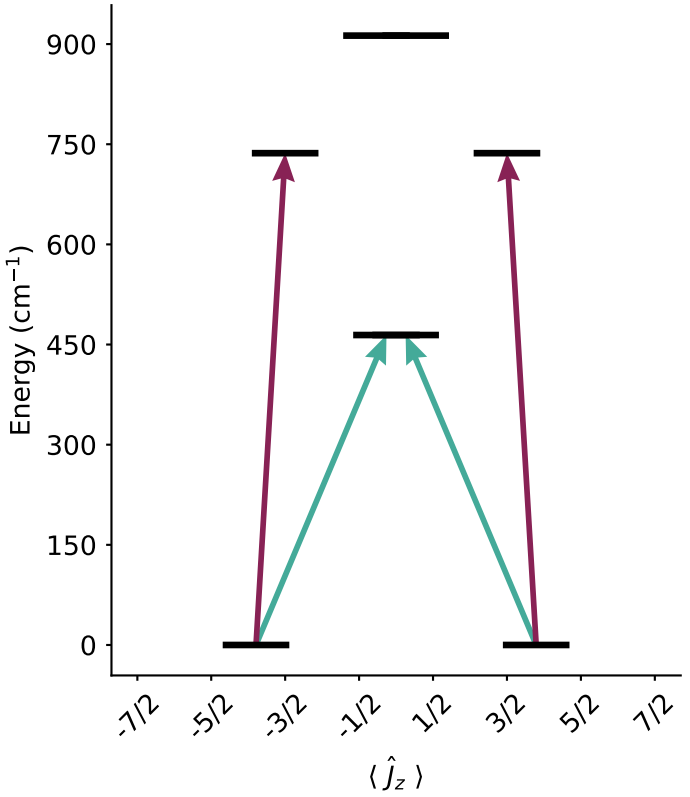






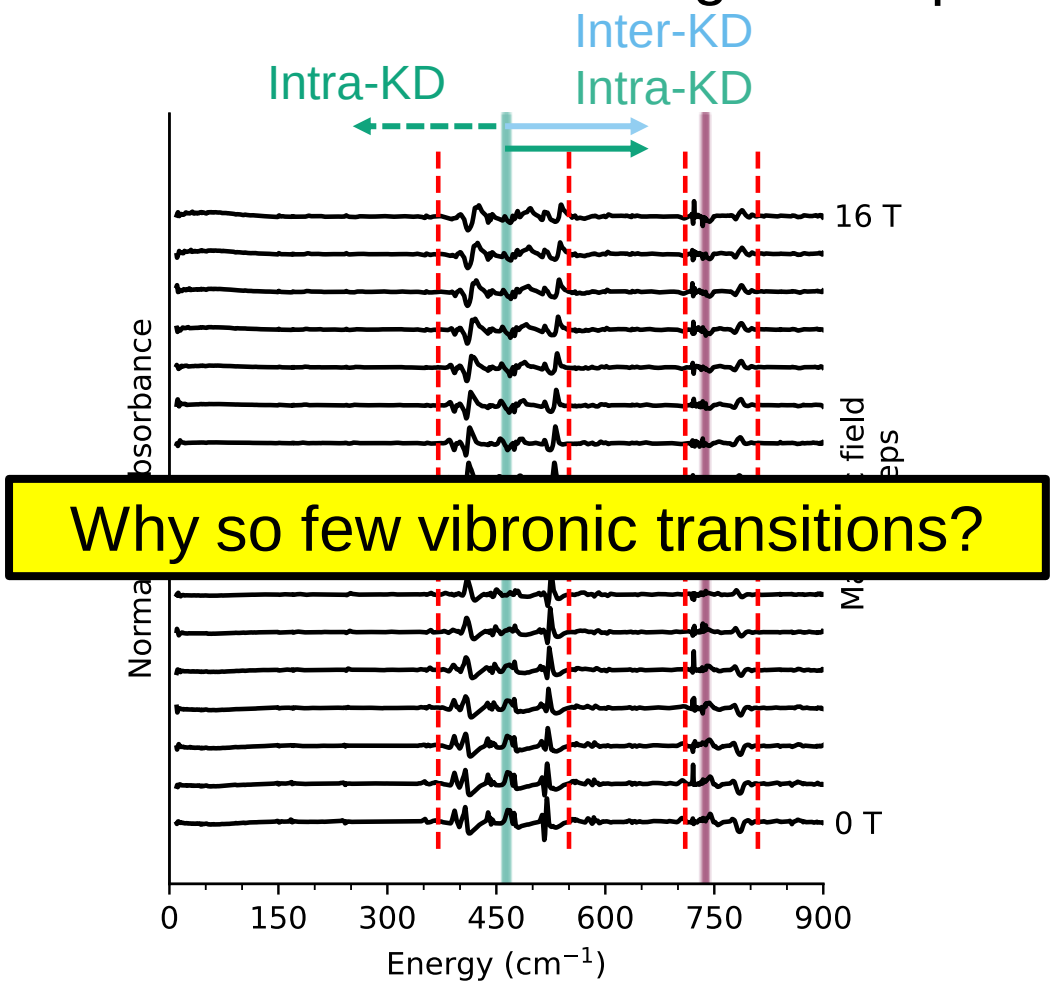
Field dependent signals

Purely vibrational (electric dipole, $\partial E/\partial B = 0$, MANY)

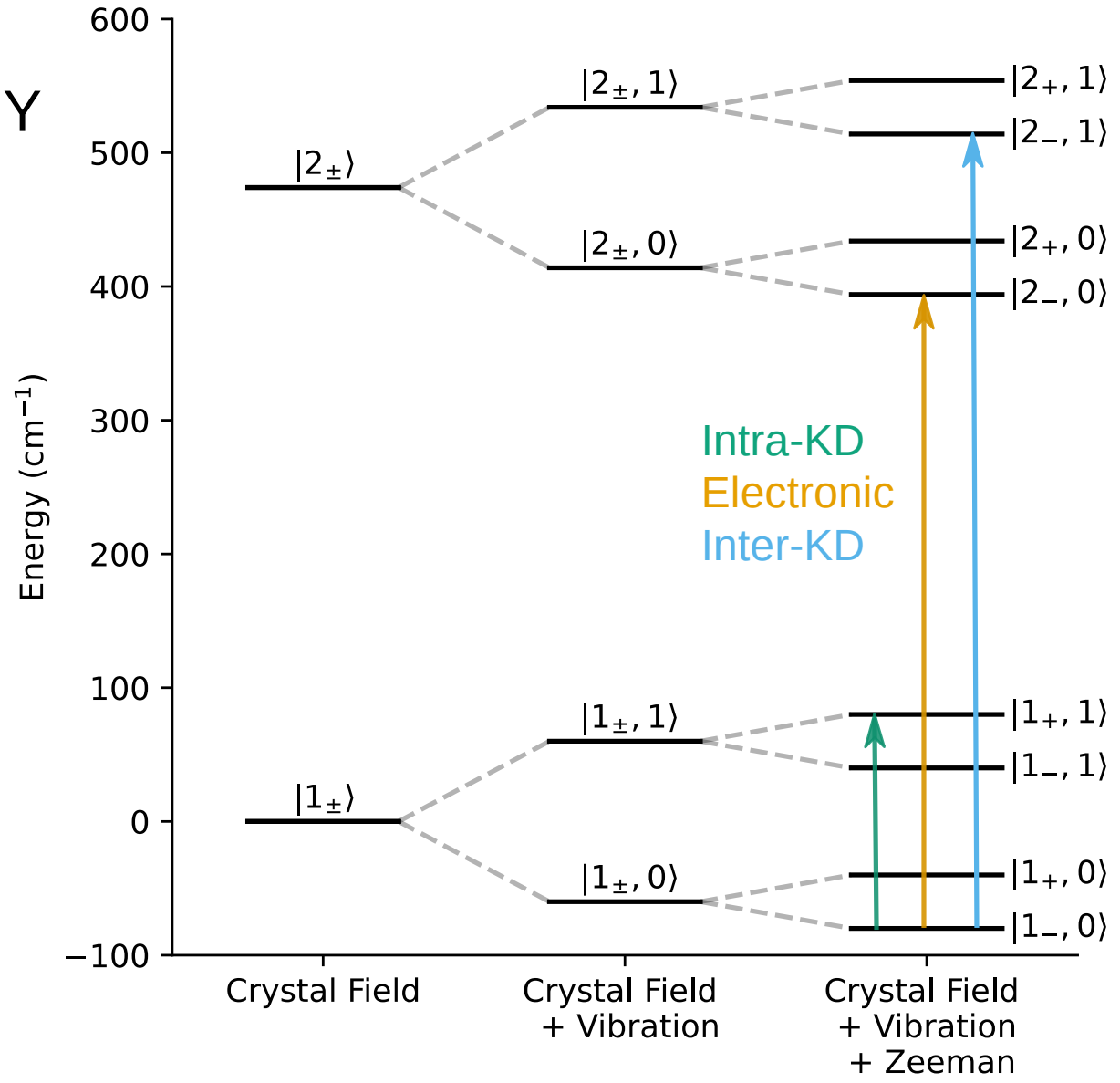
Field dependent signals

Purely electronic: magnetic dipole - FEW

Vibronic: electric and magnetic dipole - MANY



Why so few vibronic transitions?



Model

Add vibronic perturbation to model → 1st order corrections to wavefunction

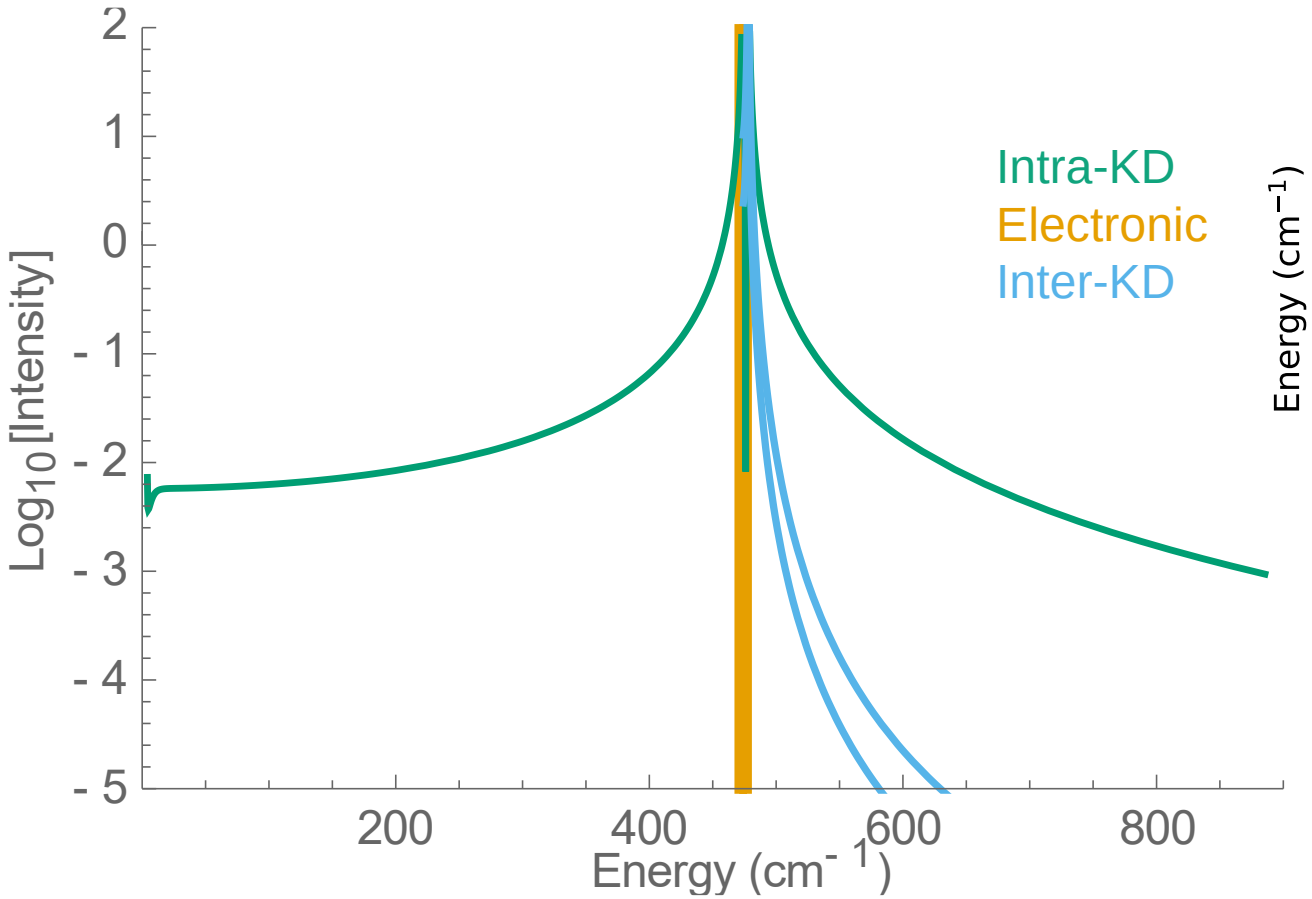
Calculate transition intensities as a function of mode energy.

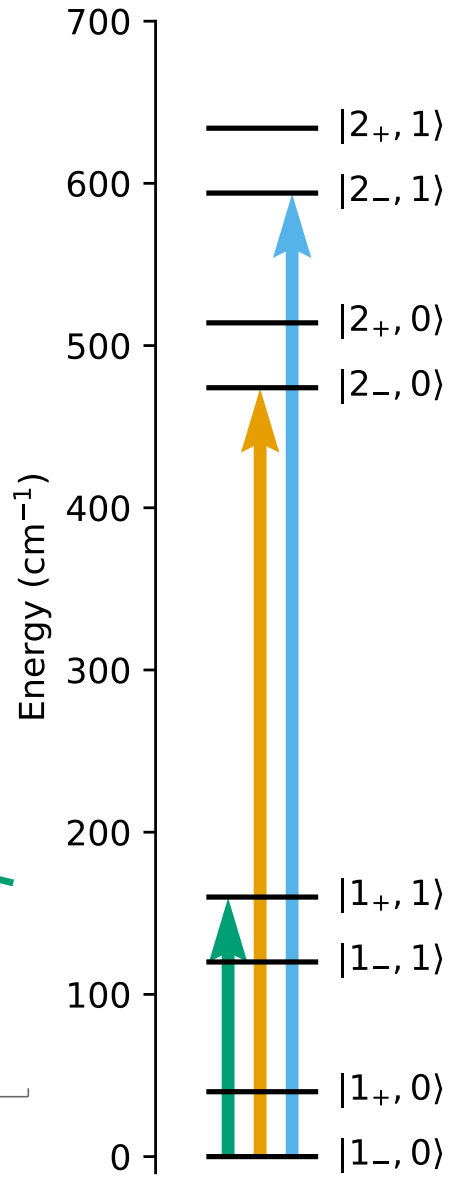
Intensity max when

$$\hbar\omega \approx \Delta$$

→ Spectral "Envelope effect"

Does not imply vibronic coupling is weak elsewhere!





Classification

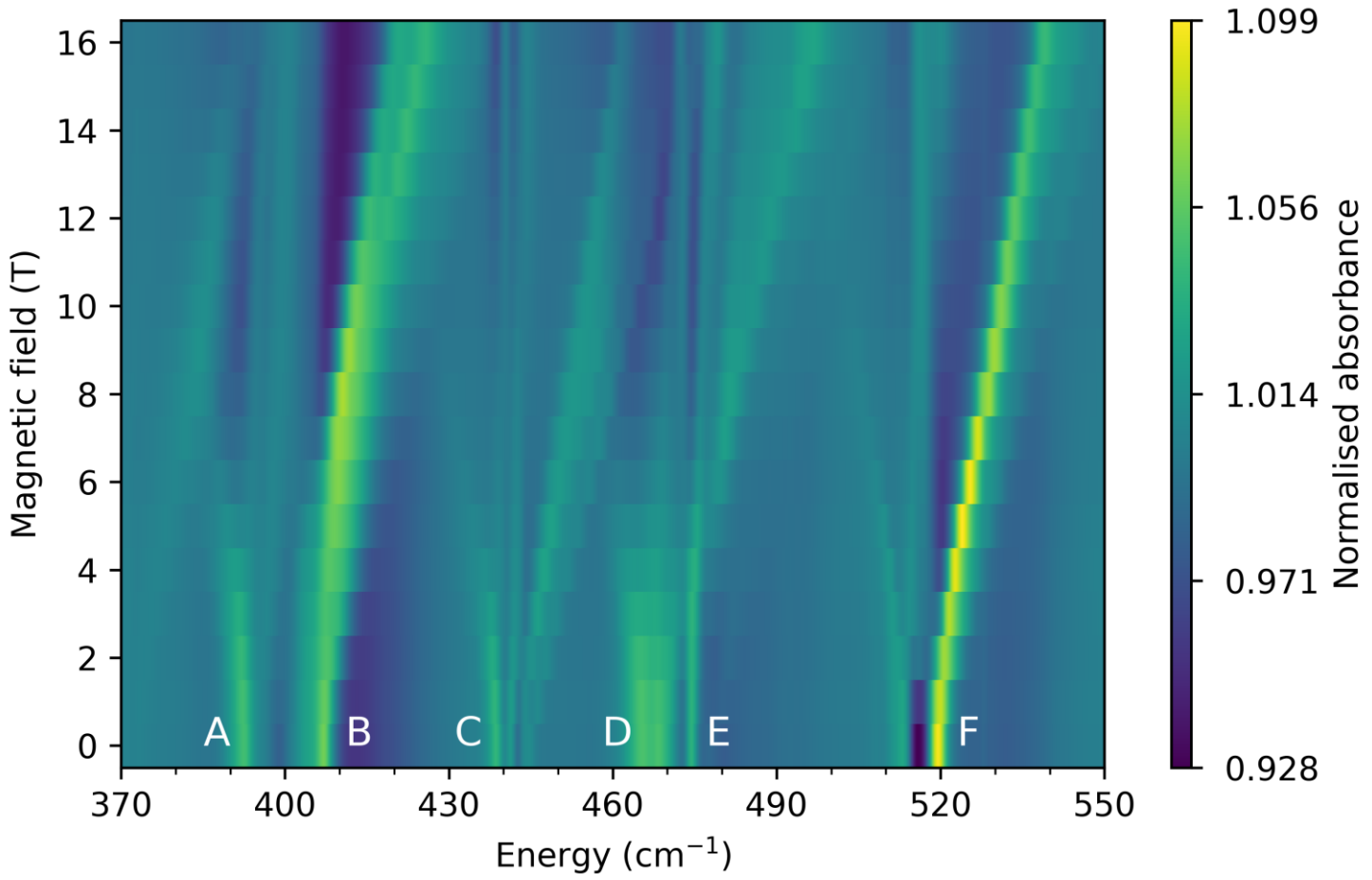
Can we classify the experimental features?

A-D = intra-KD vibronic
$|1_{\pm}, 0\rangle \rightarrow |1_{\mp}, 1\rangle$

E = electronic
$|1_{\pm}, 0\rangle \rightarrow |2_{\pm}, 0\rangle$

F = inter- or intra-KD vibronic
$|1_{\pm}, 0\rangle \rightarrow |2_{\pm}, 1\rangle$ or $|1_{\pm}, 0\rangle \rightarrow |1_{\mp}, 1\rangle$

Which modes are responsible?



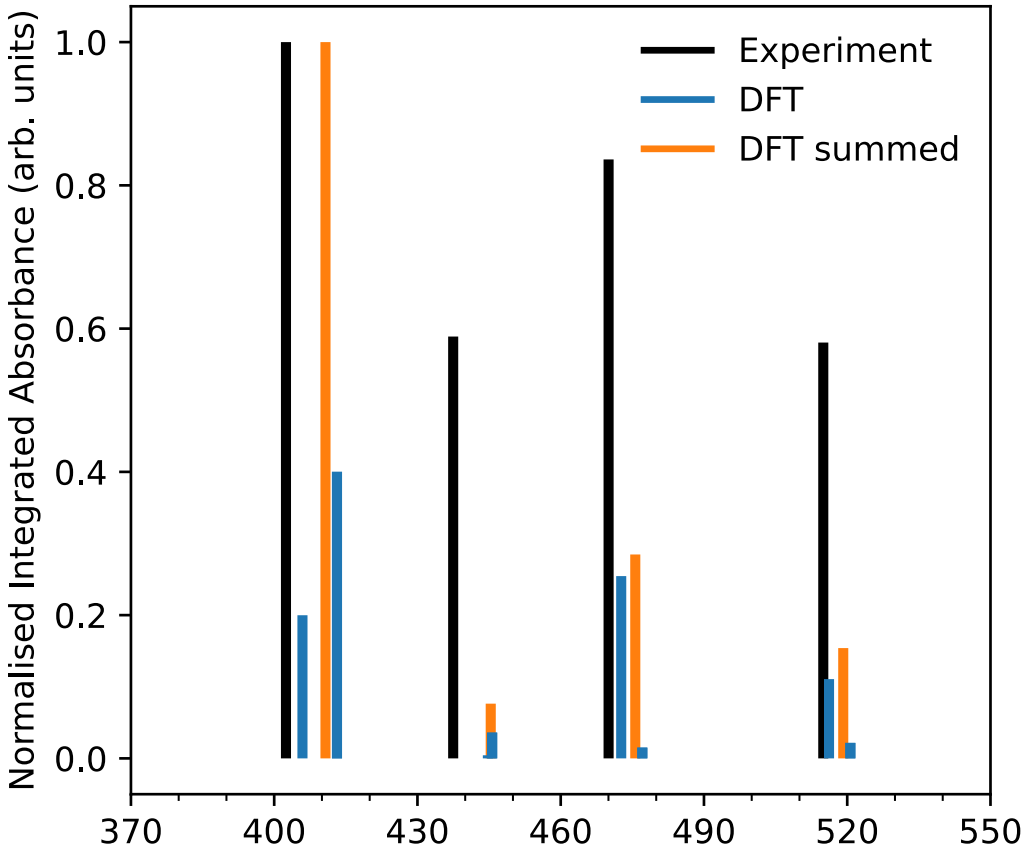
DFT vibrational modes

Unrestricted DFT (PBE0+D3) optimisation and frequency calculation

Very good agreement of experimental and DFT vibrational mode energies

In general, modes are motions of the entire molecule.

Given this level of agreement, can we simulate the FIRMS spectra *ab initio*?



Simulation

Use more sophisticated Hamiltonian than small model:

$$\hat{H}_{\mathrm{T}} = \hat{H}_{\mathrm{CF}} + \hat{H}_{\mathrm{Zee}} + \sum_{j} \left(\hat{H}_{\mathrm{vib},j} + \hat{H}_{\mathrm{coup},j} \right)$$

$$\hat{H}_{\mathrm{CF}} = \sum_{k\,=\,2,4,6} \sum_{q=\,-k}^{k} B_k^q \hat{O}_k^q$$ [CAS(13,7)SCF+CASPT2+SO]

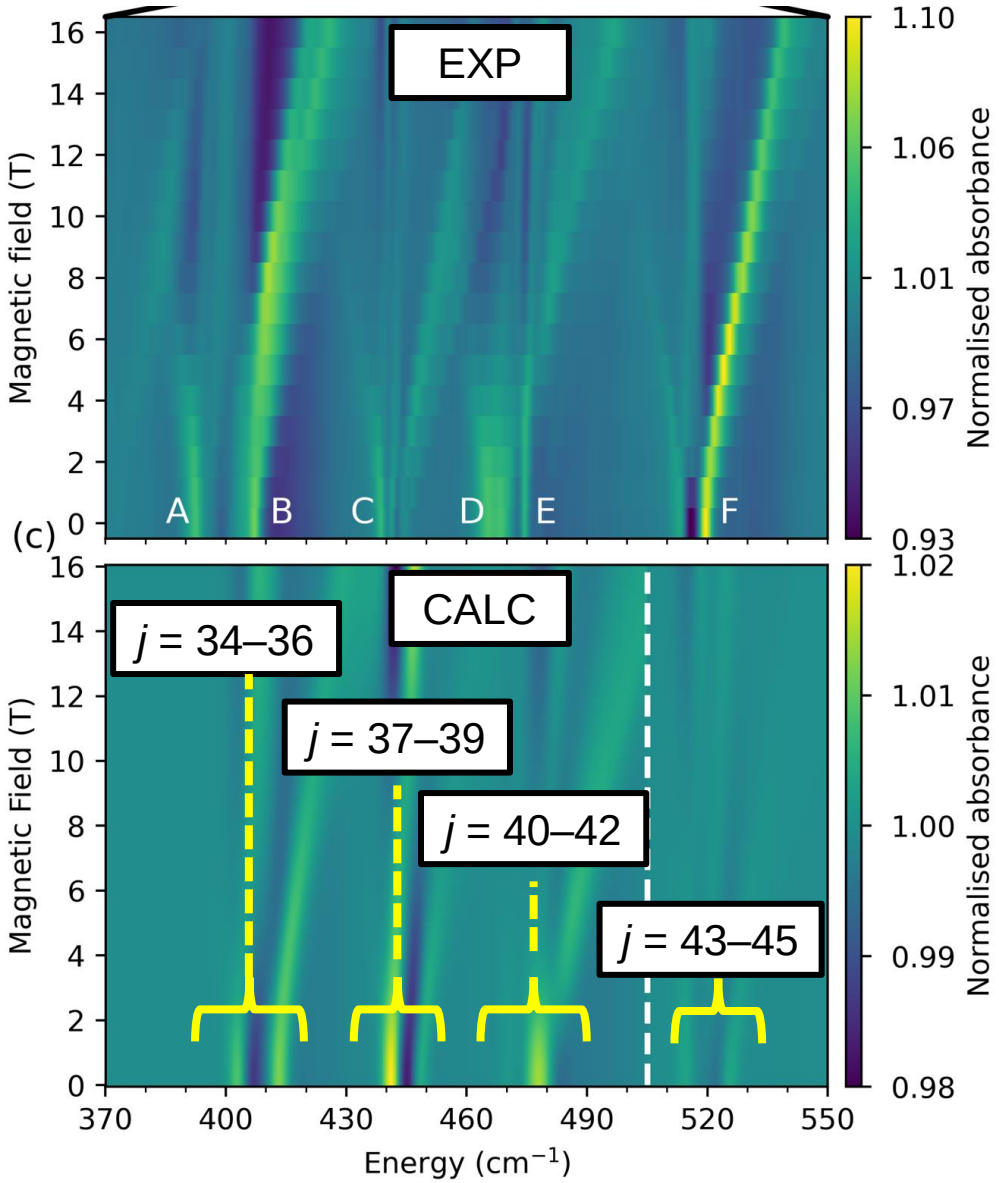
$$\hat{H}_{\mathrm{Zee}} = \mu_{\mathrm{B}} g_J \vec{B} \cdot \vec{\hat{J}}$$

$$\hat{H}_{\mathrm{vib},j} = \hbar \omega_j \left(n_j + \frac{1}{2} \right)$$ DFT [PBE0+D3]

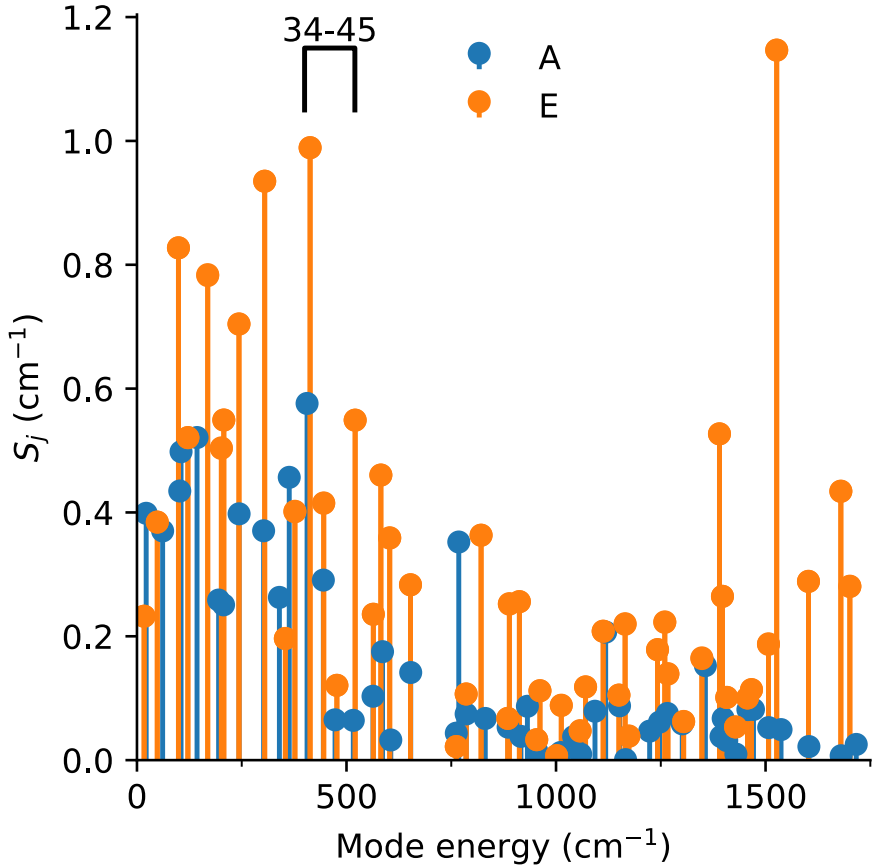
$$\hat{H}_{\mathrm{coup},j} = \sum_{k=2,4,6} \sum_{q=-k}^{k} Q_j \left(\frac{\partial B_k^q}{\partial Q_j} \right)_{\mathrm{eq}} \hat{O}_k^q$$ [CAS(13,7)SCF+SO] using DFT [PBE0] modes

Max. of 9 modes, and limit each to $|n = 0,1\rangle$ - hot bands negligible at 4 K

Simulation



$$S_j = \sqrt{\frac{1}{3}\sum_k \frac{1}{2k+1}\sum_{q=-k}^{k}\left|\left(\frac{\partial B_{k,q}}{\partial Q_j}\right)_{\mathrm{eq}}\right|^2}$$



C_3 : A (singly degen.) and E (doubly degen.) modes

Conclusions & Future Work

Successfully analysed and reproduced FIRMS map

FIRMS intensity dominated by envelope effect, not vibronic coupling.

Beginning to deepen understanding of vibronic coupling and symmetry

Future:

- Single crystal measurements
- Explore other SMMs experimentally and computationally – e.g. Dy^{3+} complexes

Acknowledgements

Luminescence/Synthesis

Christian Buch
Stergios Piligkos

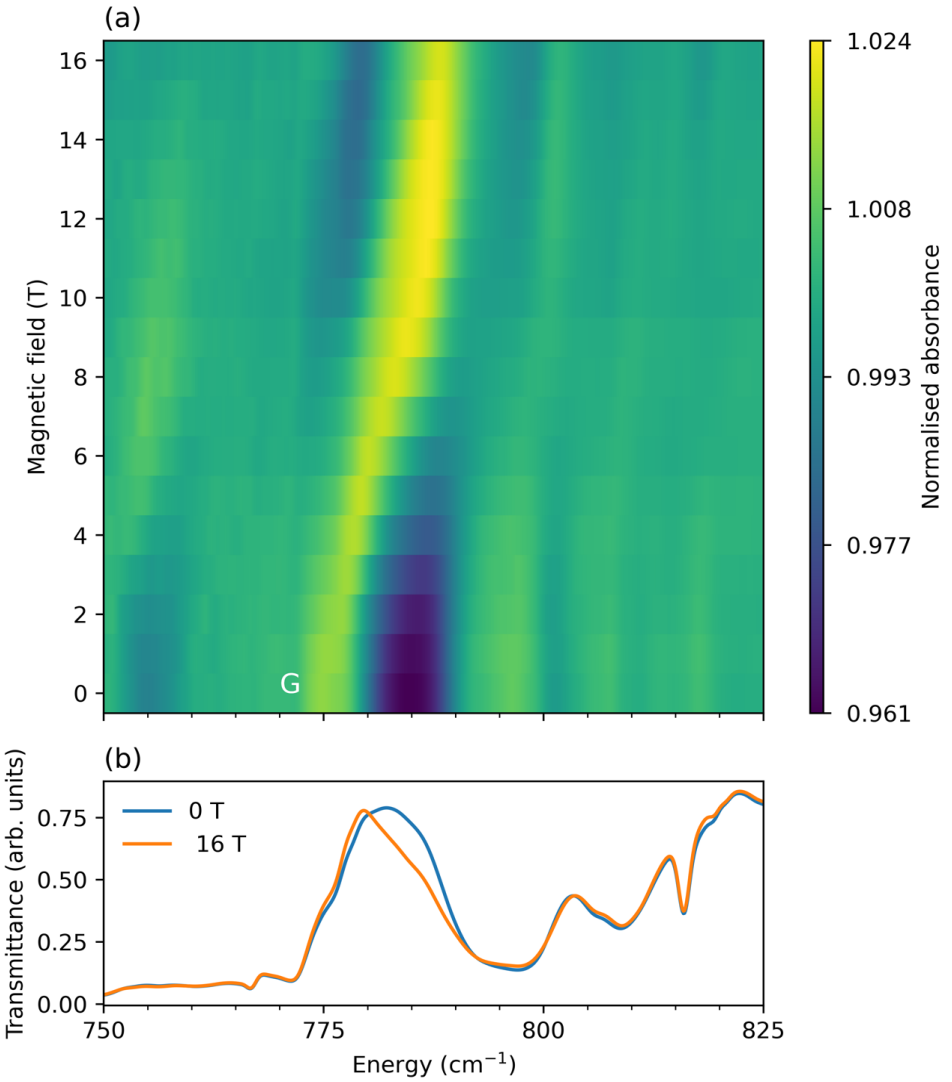
FIRMS

Jon Marbey
Joscha Nehrkorn
Mykhaylo Ozerov
Steve Hill

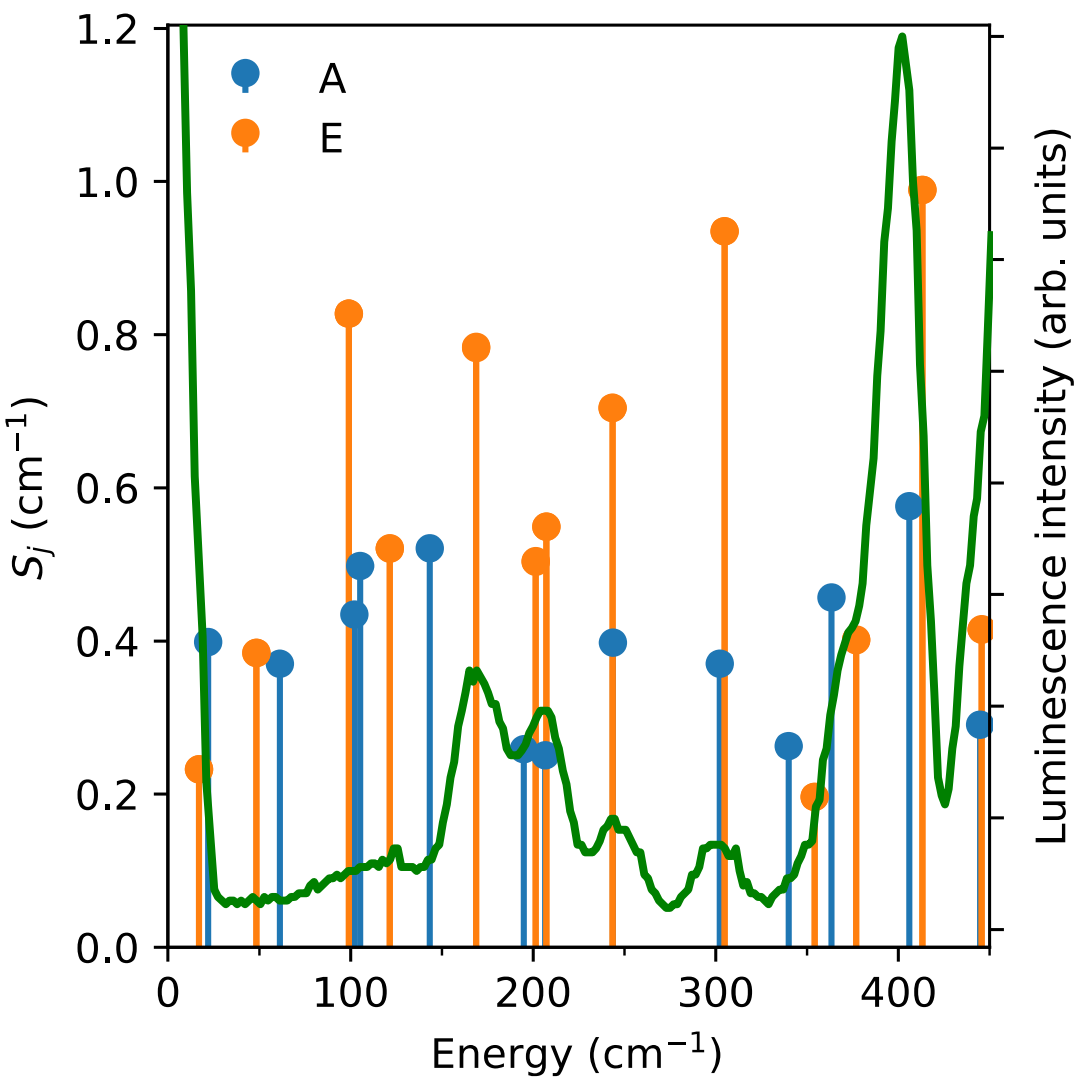
Supervision

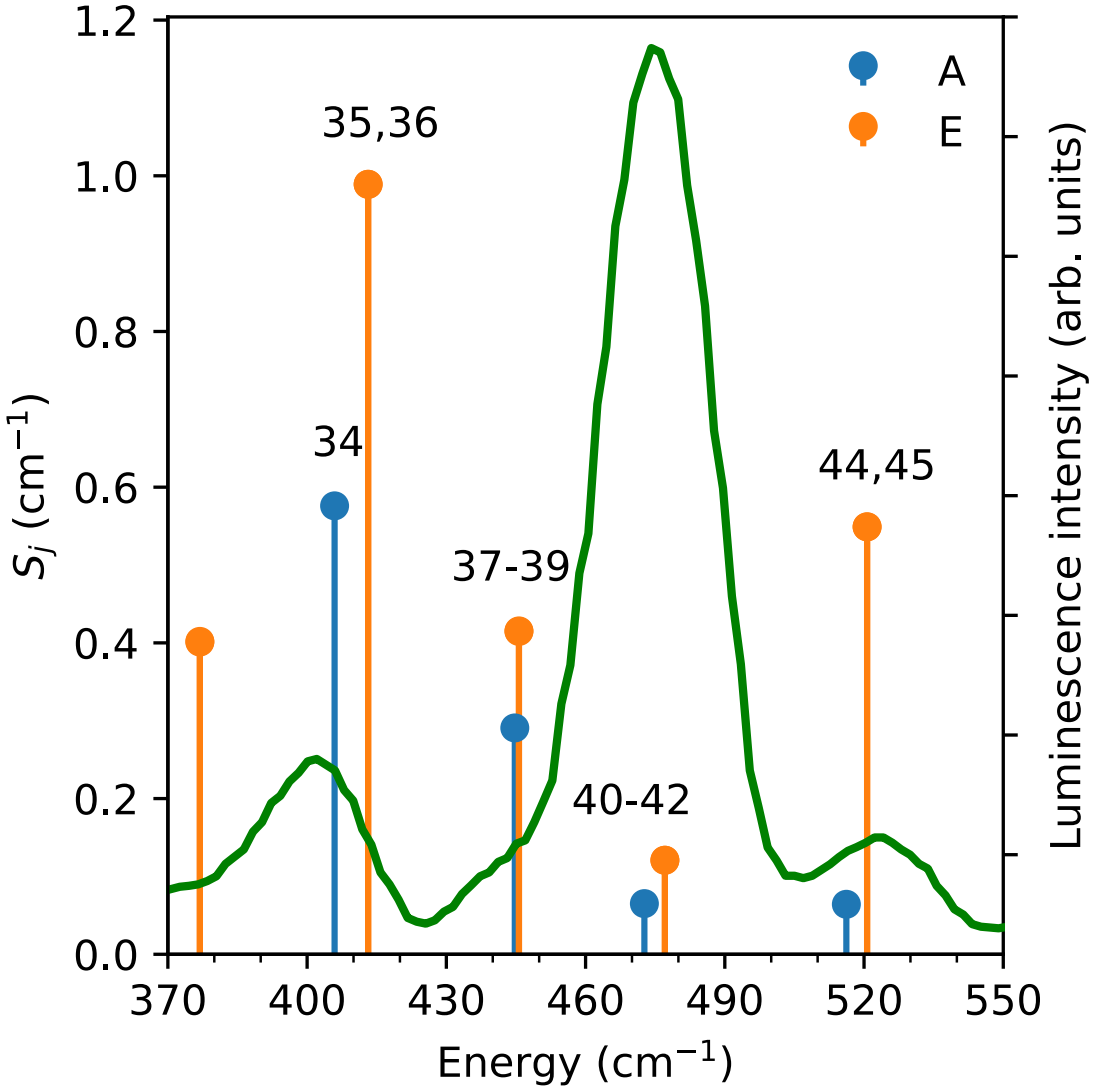
Nicholas Chilton

Band 2

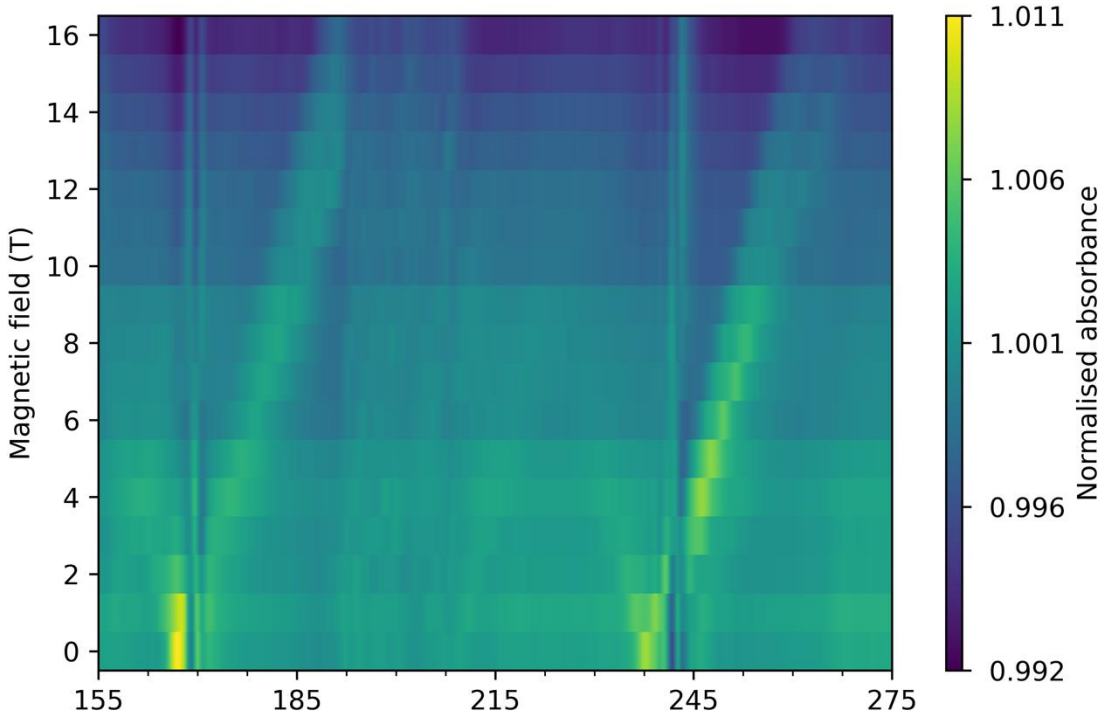

(a)
Magnetic field (T)
16
14
12
10
8
6
4
2
0
G
1.024
1.008
0.993
0.977
0.961
Normalised absorbance
(b)
Transmittance (arb. units)
0.75
0.50
0.25
0.00
0 T
16 T
750
775
800
825
Energy (cm^{-1})

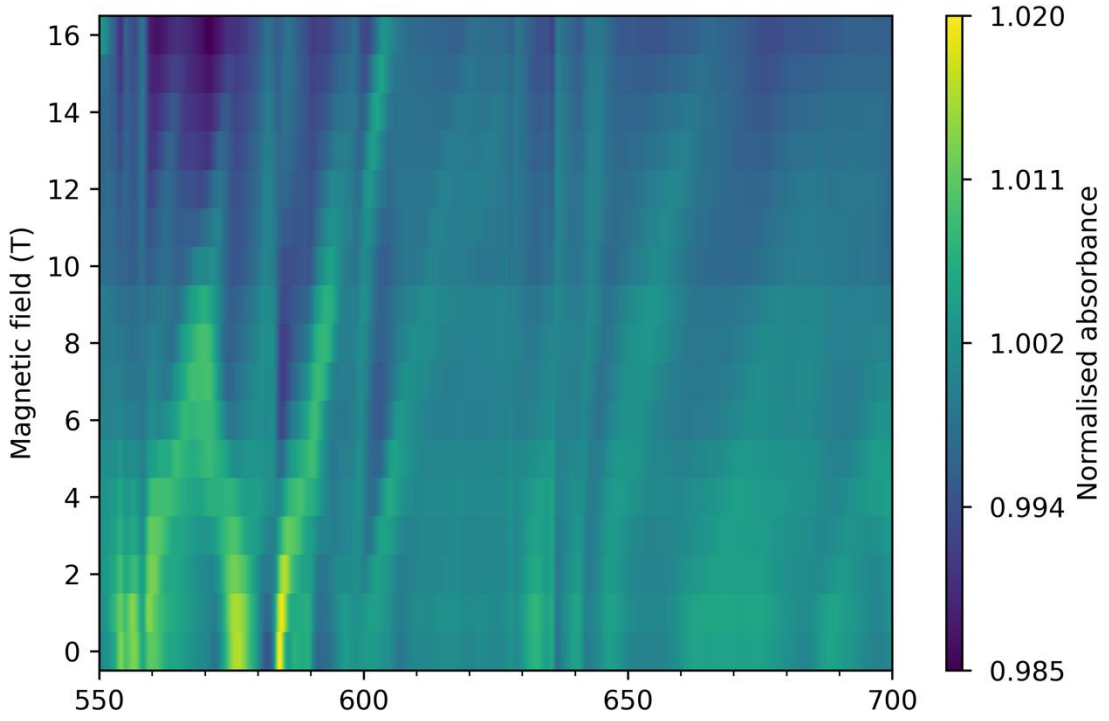
Strength and Luminescence





Weaker signals



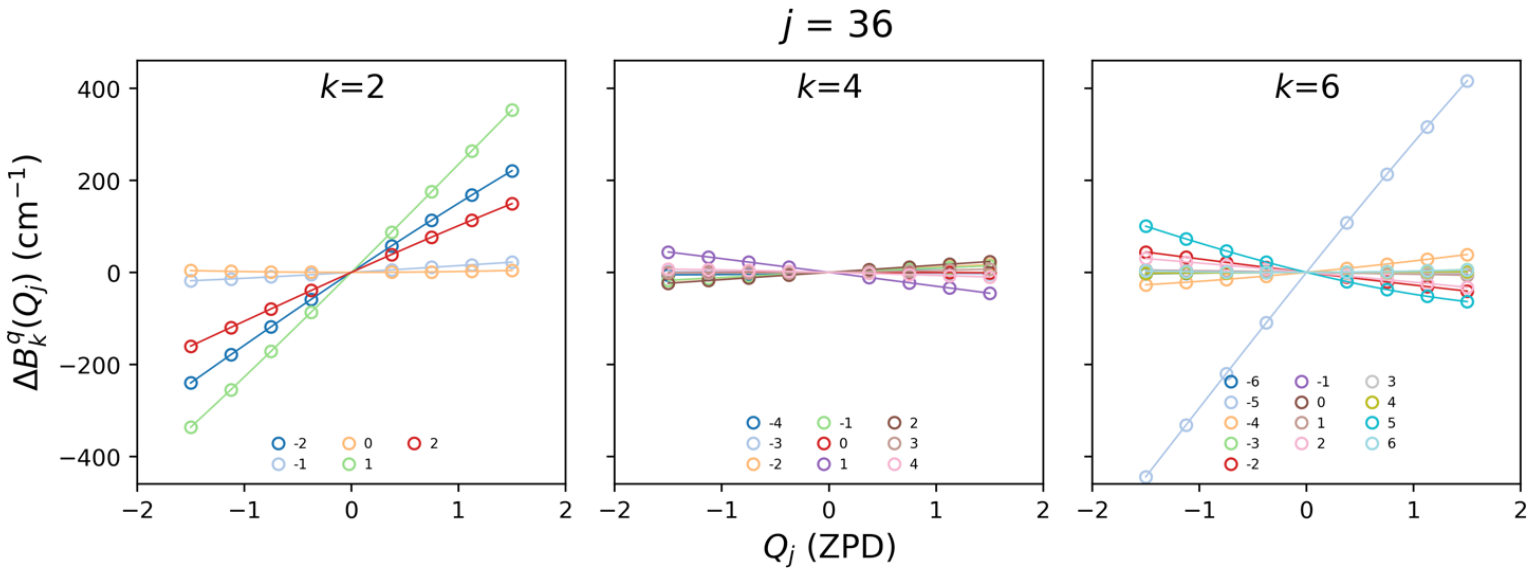


Coupling

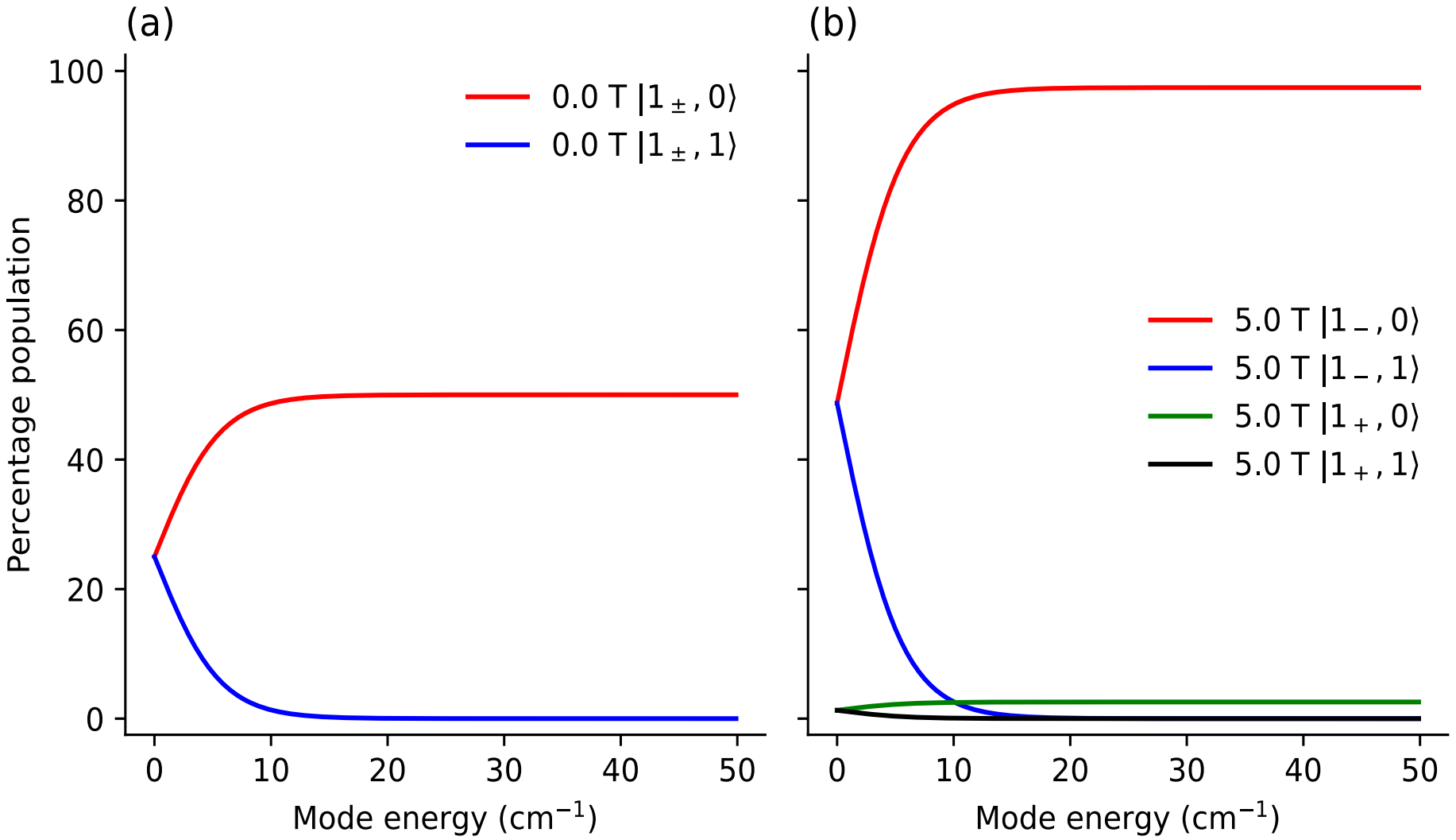
Coupling Hamiltonian in CF framework – linear term in expansion of parameters as function of vibrational mode displacement

$$\hat{H}_{\mathrm{coup},j} = \sum_{k=2,4,6} \sum_{q=-k}^{k} Q_j \left(\frac{\partial B_k^q}{\partial Q_j}\right)_{\mathrm{eq}} \hat{O}_k^q$$

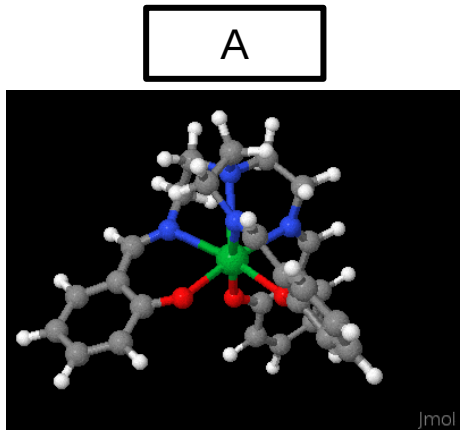
$\left(\frac{\partial B_k^q}{\partial Q_j}\right)_{\mathrm{eq}}$ calculated *ab initio* [CAS(13,7)SCF+SO] using DFT [PBE0] modes

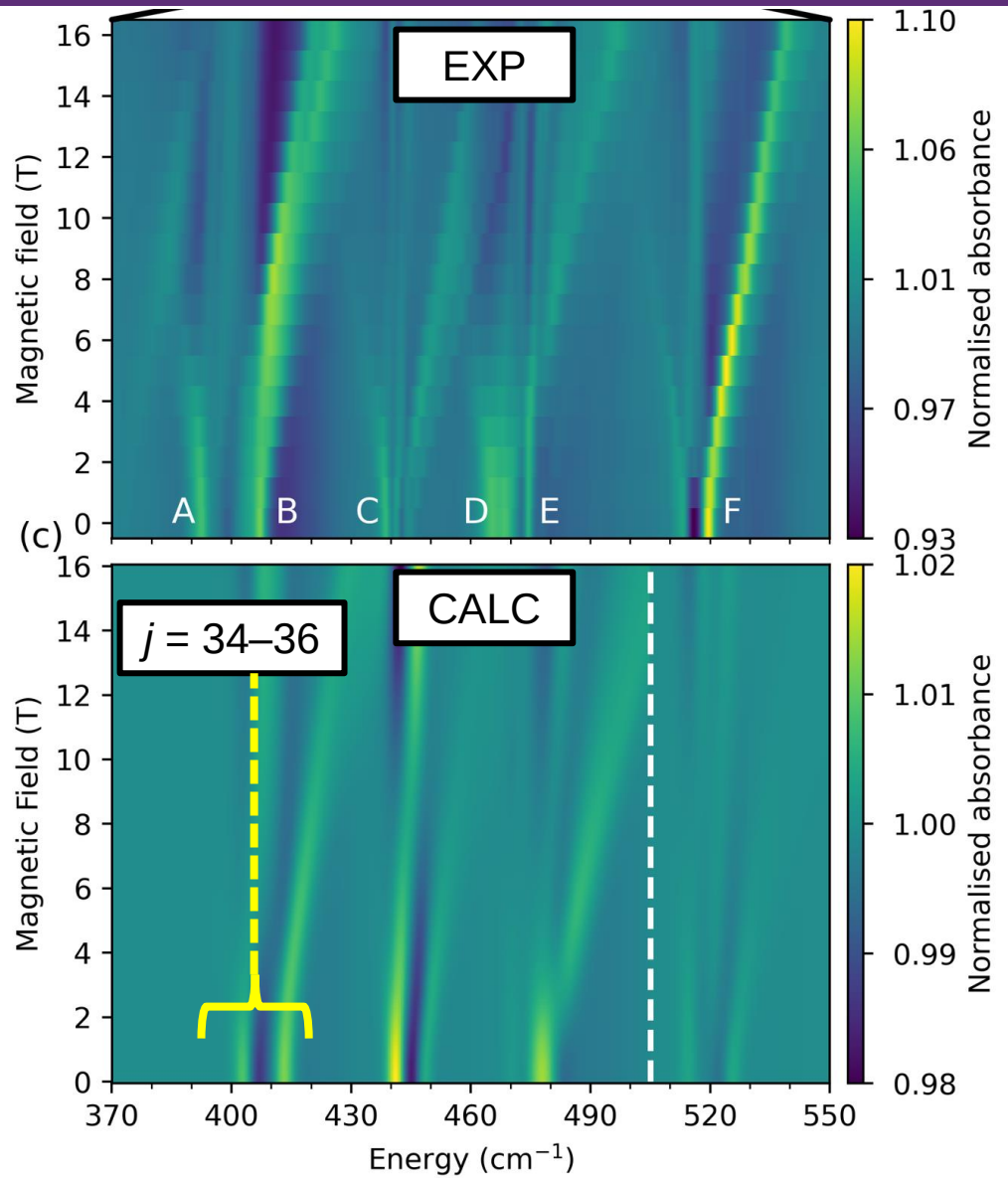


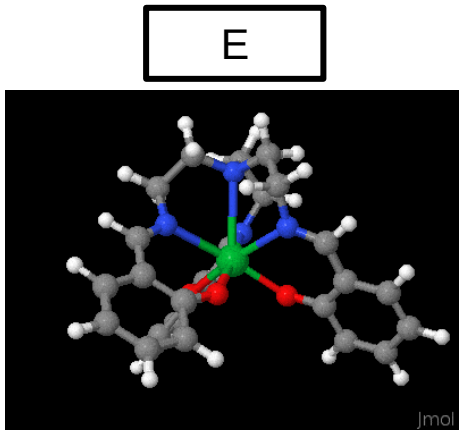
Populations

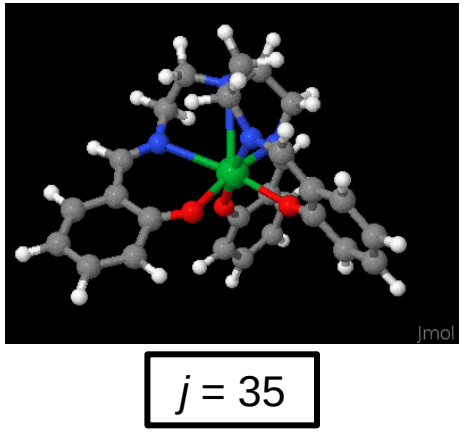


Simulation









Ab initio transition intensities

Vibrational = electric dipole

Electronic = Magnetic dipole

Vibronic = both

Simulation

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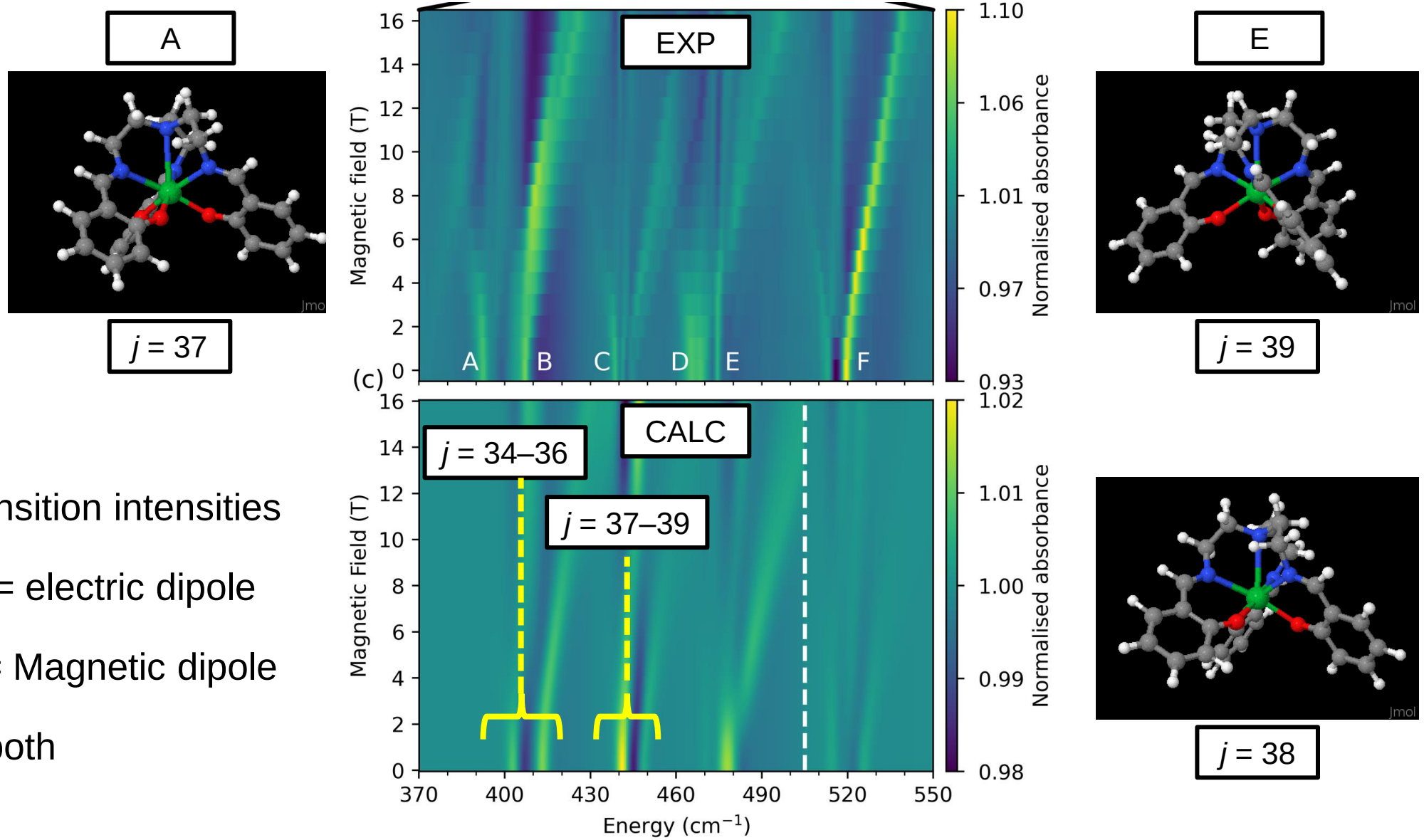
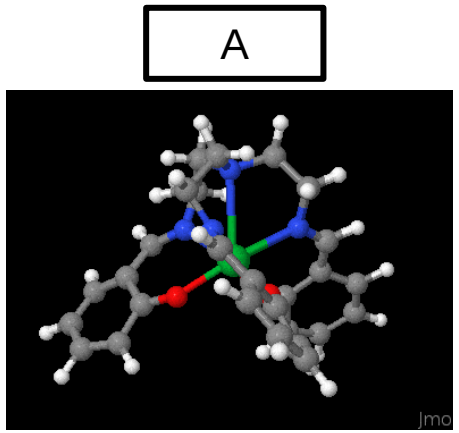
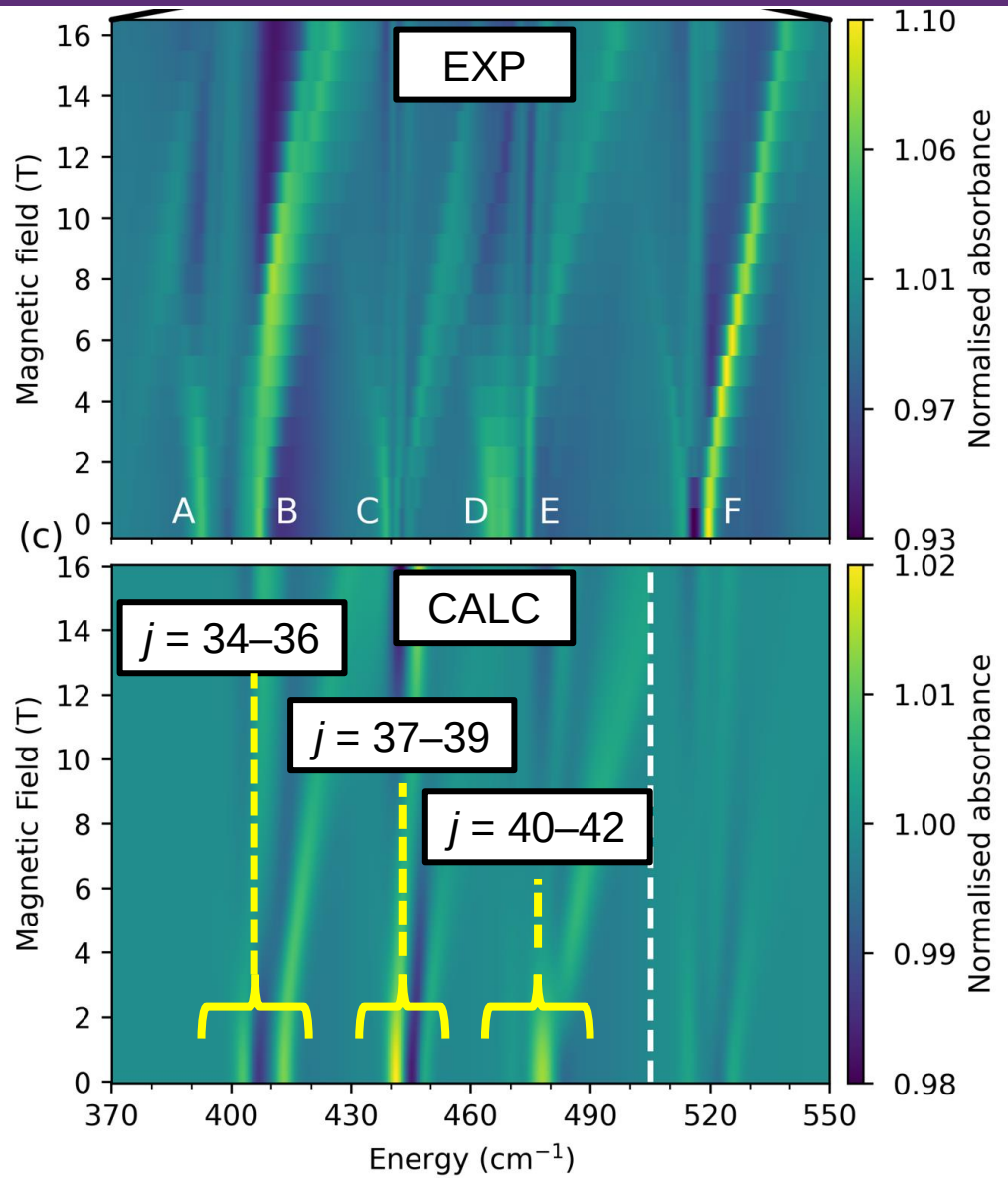
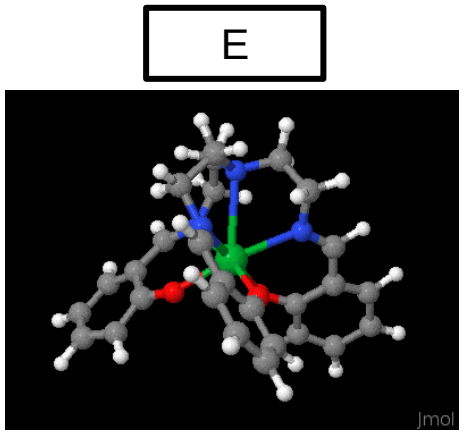


Simulation



$j = 40$





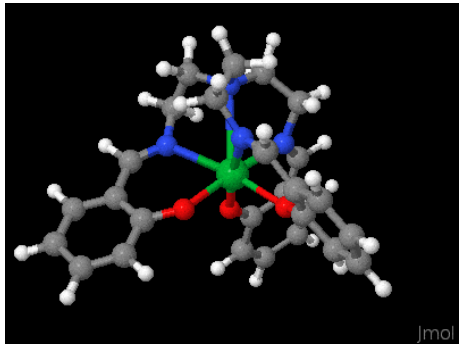
$j = 42$

Ab initio transition intensities

Vibrational = electric dipole

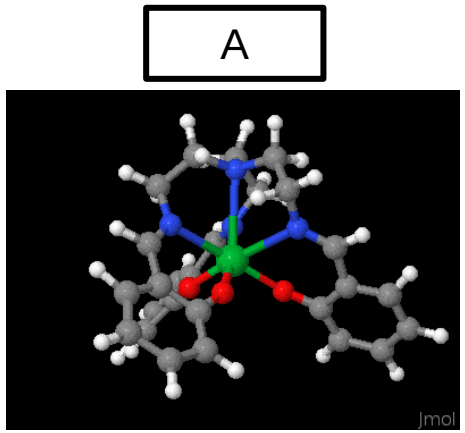
Electronic = Magnetic dipole

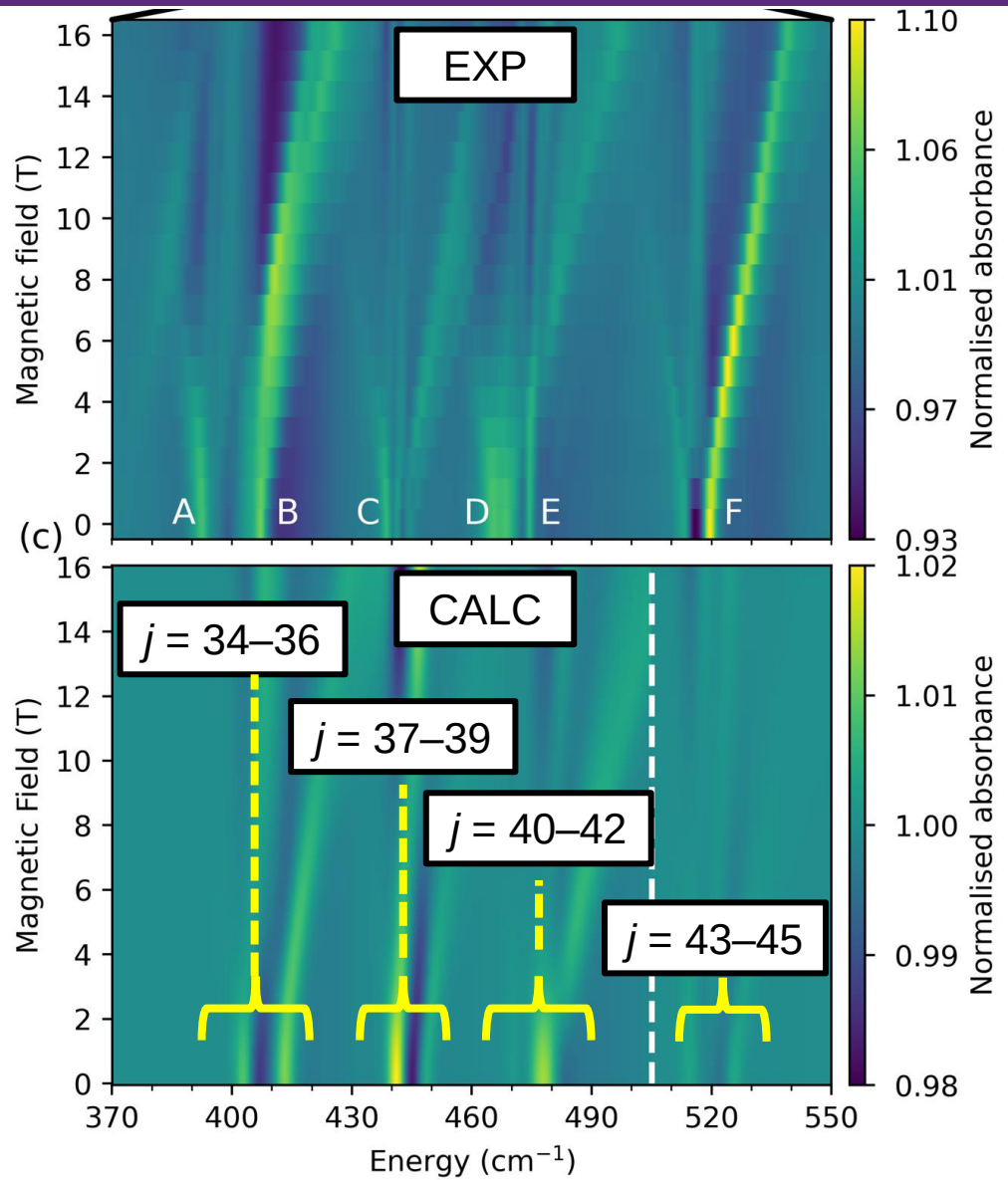
Vibronic = both

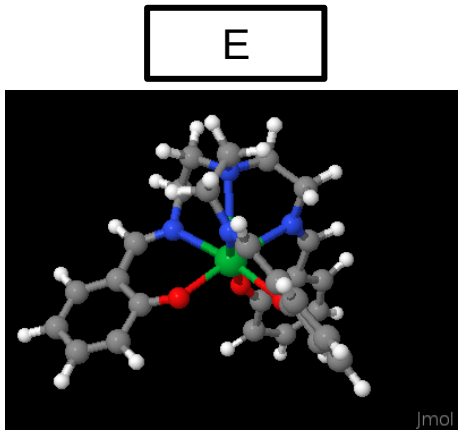


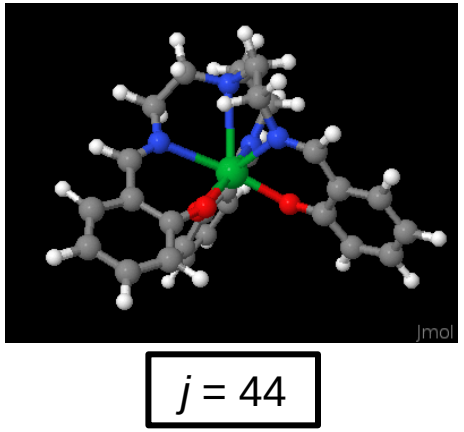
$j = 41$

Simulation









Ab initio transition intensities

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Electronic = Magnetic dipole

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