Calculation of electronic spectra

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Radiative transitions

- Fermi's golden rule:

$$W_{i\to f} = \frac{2\pi}{\hbar} \left| \langle f | \hat{H}_{\text{int}} | i \rangle \right|^2 \delta(E_{\text{tot},f} - E_{\text{tot},i})$$

  - Conservation of energy: $E_{\text{tot}} = E_{\text{matter}} + E_{\text{light}}$.
  - $\hat{H}_{\text{int}}$ light-matter interaction

Radiative transitions

Light-matter interaction

- QED Hamiltonian: $\hat{H}_{\text{tot}} = \hat{H}_{\text{mat}} + \hat{H}_{\text{rad}} + \hat{H}_{\text{int}}$
- Electron in EM field: $\vec{p}_i \to \vec{p}_i + e\vec{A}$
  - $\vec{A}(\vec{r},t) = \sum_{\vec{k},\sigma} A_0(k)\vec{\epsilon}_{\vec{k}\sigma}\left(a_{\vec{k}\sigma}\mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}} + a^*_{\vec{k}\sigma}\mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}}\right)$
  - $\vec{\nabla}\cdot\vec{A} = 0$
  - $\mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}} \approx 1 + \mathrm{i}\vec{k}\cdot\vec{r}$
- After a bit of algebra:

$$\hat{H}_{\text{int}} = \sum_{i=1}^{N}\left(\underbrace{e\vec{r}_i\cdot\vec{E}_0(k)}_{\text{E1}} + \underbrace{\frac{e}{2m_e}\left(\hat{\vec{\ell}}_i + g_e\hat{\vec{s}}_i\right)\cdot\vec{B}_0(k)}_{\text{M1}} + \underbrace{\frac{1}{2}e\vec{r}_i\otimes\vec{r}_i : \vec{k}\otimes\vec{E}_0(k)}_{\text{E2}}\right)$$

- Relative strengths E1 : M1 : E2 $\approx 1 : 10^{-5} : 10^{-6}$

Radiative transitions

Experimental observables

- Absorption spectrum:

$$S_{\text{abs}}(\omega) = C\omega\sum_f\left|\langle f|\,\hat{\vec{D}}_e\,|i\rangle\right|^2\delta(E_f - E_i - \hbar\omega)$$

- Emission spectrum:

$$S_{\text{em}}(\omega) = C\omega^3\sum_f\left|\langle f|\,\hat{\vec{D}}_e\,|i\rangle\right|^2\delta(E_f - E_i - \hbar\omega)$$

with $\hat{\vec{D}}_e = -e\sum_{i=1}^{N}\vec{r}_i$ for E1 transitions.

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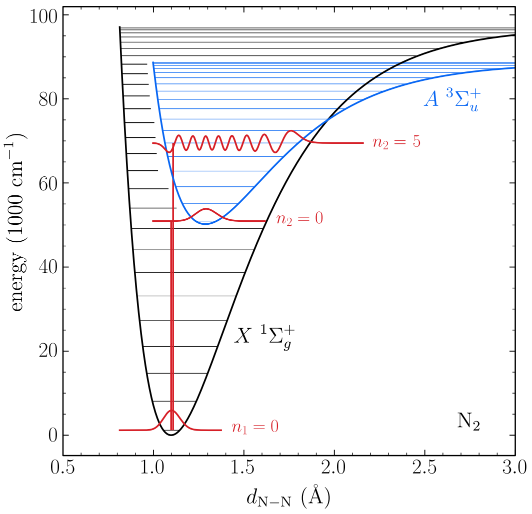
Electron-vibrational transitions

- Born-Oppenheimer wave functions:

$$|\Psi_1^{(\mathrm{tot})}\rangle = |\Psi_1\rangle\,|\zeta_{1n_1}\rangle \qquad \text{and} \qquad |\Psi_2^{(\mathrm{tot})}\rangle = |\Psi_2\rangle\,|\zeta_{2n_2}\rangle$$



Electron-vibrational transitions

- Born-Oppenheimer wave functions:

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- Vibrational wave function:

$$\zeta_{\alpha n_\alpha}(Q_\alpha) = \prod_{i=1}^{3\nu-6} \zeta_{\alpha i n_{\alpha i}}(Q_i)$$

- Transition dipole operator:

$$\hat{\vec{D}} = \underbrace{-e\sum_{i=1}^{N}\vec{r}_i}_{\vec{D}_{\mathrm{e}}} + \underbrace{e\sum_{j=1}^{\nu} Z_j\vec{R}_j}_{\vec{D}_{\mathrm{N}}}$$

- Matrix element:

$$\langle\Psi_2^{(\mathrm{tot})}|\,\hat{\vec{D}}\,|\Psi_1^{(\mathrm{tot})}\rangle = \langle\zeta_{2n_2}|\,\langle\Psi_2|\,\hat{\vec{D}}_{\mathrm{e}}\,|\Psi_1\rangle\,|\zeta_{1n_1}\rangle + \underbrace{\langle\Psi_2|\Psi_1\rangle}_{=0}\langle\zeta_{2n_2}|\,\hat{\vec{D}}_{\mathrm{N}}\,|\zeta_{1n_1}\rangle.$$

Electron-vibrational transitions

- FC approximation:

$$\begin{aligned}\hat{\vec{D}}_{\mathrm{e}}(Q) \;&=\; \hat{\vec{D}}_{\mathrm{e}}(Q_1^{(0)}) + \cancel{\sum_{i=1}^{3\nu-6}\left(\frac{\partial\hat{\vec{D}}_{\mathrm{e}}}{\partial Q_i}\right)_{Q_1^{(0)}}\left(Q_i - Q_{1,i}^{(0)}\right)}\\ &\quad \cancel{+\frac{1}{2}\sum_{i=1}^{3\nu-6}\sum_{j=1}^{3\nu-6}\left(\frac{\partial^2\hat{\vec{D}}_{\mathrm{e}}}{\partial Q_i\partial Q_j}\right)_{Q_1^{(0)}}\left(Q_i - Q_{1,i}^{(0)}\right)\left(Q_j - Q_{1,j}^{(0)}\right) + \mathcal{O}(Q^3)}\end{aligned}$$

- Matrix element:

$$\langle\Psi_2^{(\mathrm{tot})}|\,\hat{\vec{D}}_{\mathrm{e}}\,|\Psi_1^{(\mathrm{tot})}\rangle = \underbrace{\langle\Psi_2|\,\hat{\vec{D}}_{\mathrm{e}}(0)\,|\Psi_1\rangle}_{\text{purely electronic}}\,\underbrace{\langle\zeta_{2n_2}(Q)|\,\zeta_{1n_1}(Q)\rangle}_{\text{FC integrals}}$$

Electron-vibrational transitions

- FC approximation:

$$\hat{\vec{D}}_\mathrm{e}(Q) = \hat{\vec{D}}_\mathrm{e}(Q_1^{(0)}) + \cancel{\sum_{i=1}^{3\nu-6}\left(\frac{\partial \hat{\vec{D}}_\mathrm{e}}{\partial Q_i}\right)_{Q_1^{(0)}}\left(Q_i - Q_{1,i}^{(0)}\right)}$$

$$\cancel{+\frac{1}{2}\sum_{i=1}^{3\nu-6}\sum_{j=1}^{3\nu-6}\left(\frac{\partial^2 \hat{\vec{D}}_\mathrm{e}}{\partial Q_i \partial Q_j}\right)_{Q_1^{(0)}}\left(Q_i - Q_{1,i}^{(0)}\right)\left(Q_j - Q_{1,j}^{(0)}\right) + \mathcal{O}(Q^3)}$$

- Matrix element:

$$\langle\Psi_2^{(\mathrm{tot})}|\,\hat{\vec{D}}_\mathrm{e}\,|\Psi_1^{(\mathrm{tot})}\rangle = \underbrace{\langle\Psi_2|\,\hat{\vec{D}}_\mathrm{e}(0)\,|\Psi_1\rangle}_{\text{purely electronic}}\underbrace{\langle\zeta_{2n_2}(Q)|\,\zeta_{1n_1}(Q)\rangle}_{\text{FC integrals}}$$

Franck-Condon integrals

Which modes are important?

- If $\Delta Q_i = Q_{2,i}^{(0)} - Q_{1,i}^{(0)} = 0$: only zero-phonon line (ZPL) contributes
- If $\Delta Q_i = Q_{2,i}^{(0)} - Q_{1,i}^{(0)} \neq 0$: non-trivial contribution
- Consider Taylor expansion of PESs:

$$U_1(Q) = U_1^{(0)} + \frac{1}{2}\sum_{i=1}^{3\nu-6}\left(\frac{\partial^2 U_1}{\partial Q_i^2}\right)_{Q_1^{(0)}}(Q_i - Q_{1,i}^{(0)})^2 + \ldots$$

$$U_2(Q) = U_2^{(0)} + \sum_{i=1}^{3\nu-6}\left(\frac{\partial U_2}{\partial Q_i}\right)_{Q_2^{(0)}}(Q_i - Q_{2,i}^{(0)}) + \frac{1}{2}\sum_{i=1}^{3\nu-6}\left(\frac{\partial^2 U_2}{\partial Q_i^2}\right)_{Q_2^{(0)}}(Q_i - Q_{2,i}^{(0)})^2 + \ldots$$

- Hellmann-Feynman:

$$\frac{\partial U_2}{\partial Q_i} = \langle\Psi_2|\frac{\partial \hat{H}_{el}}{\partial Q_i}|\Psi_2\rangle,$$

- Contributing Q_i's can be found from $\Gamma(\Psi_2)\otimes\Gamma(Q_i)\otimes\Gamma(\Psi_2)\ni\Gamma_1$

Franck-Condon integrals

Calculation

- Numerical integration
- Very simplistic, yet useful: single configurational coordinate model
  - One mode Q
  - Harmonic potentials
  - Equal curvatures

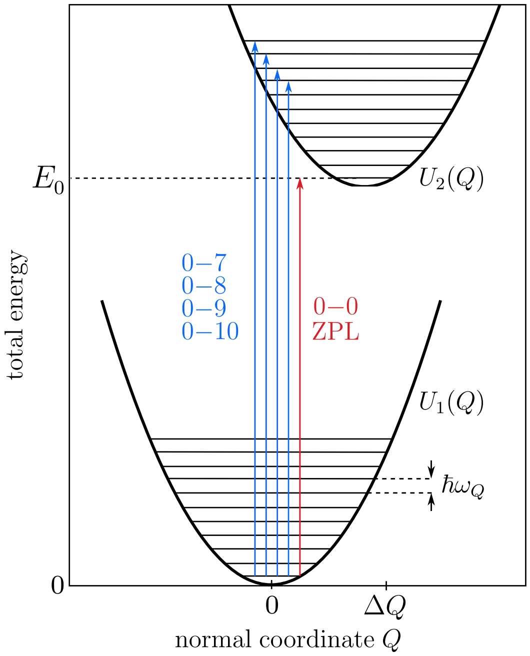
$$\begin{aligned} U_1(Q) &= U_1(0) + \frac{1}{2}KQ^2 \\ U_2(Q) &= U_2(0) + A_2 Q + \frac{1}{2}KQ^2 \end{aligned}$$

  - FC integral:

$$\begin{aligned} \langle \zeta_{2n_2}(Q) | \zeta_{1n_1}(Q) \rangle &= \sqrt{\frac{n_1!}{n_2!}}\,(-S)^{n_2-n_1}\,\mathrm{e}^{-S/2}\,L_{n_1}^{n_2-n_1}(S) \\ \langle \zeta_{20}(Q) | \zeta_{1n}(Q) \rangle &= \frac{\mathrm{e}^{-S}S^n}{n!} \end{aligned}$$

with $S = \frac{1}{2}\frac{M\omega_Q}{\hbar}\Delta Q^2$ and $\omega_Q = \sqrt{\frac{K}{M}}$.

Spectral shape



Spectral shape

- Sum over all electron-vibrational contributions:

$$S_{1\to 2}(\omega) = C_{1\to 2}\omega^{\beta} \sum_{i,j=1}^{3\nu-6} \sum_{n_{1i},n_{2j}=0}^{\infty} \left|\left\langle \zeta_{2n_{2j}}(Q_j) | \zeta_{1n_{1i}}(Q_i) \right\rangle\right|^2 \frac{\delta[E_0 \pm (n_{2j}\epsilon_{2j} - n_{1i}\epsilon_{1i}) - \hbar\omega]}{\mathrm{e}^{\frac{n_{1i}\epsilon_{1i}}{k_BT}} - 1}.$$

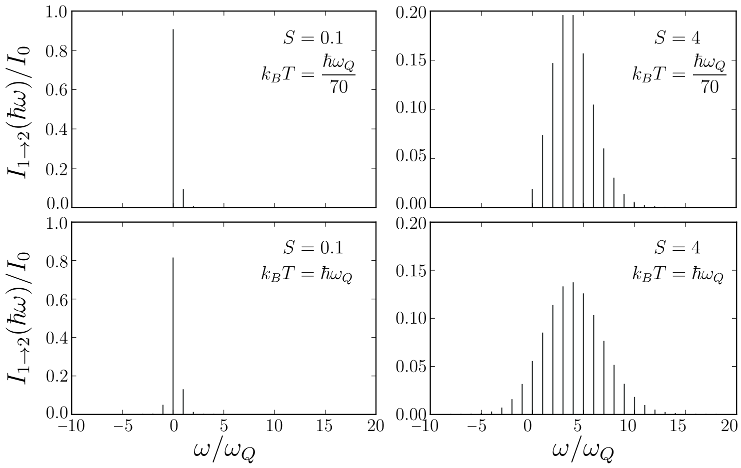
- For single configurational coordinate model:

$$C_{1\to 2}\omega^{\beta} \sum_{n=-\infty}^{\infty} \exp\left[\frac{n\hbar\omega_Q}{2k_BT} - S\coth\frac{\hbar\omega_Q}{2k_BT}\right] I_n\left[S\,\mathrm{csch}\left(\frac{\hbar\omega_Q}{2k_BT}\right)\right] \delta\left(E_0 \pm n\hbar\omega_Q - \hbar\omega\right)$$

  - Low-temperature limit:

$$S_{1\to 2}(\omega) = C_{1\to 2}\omega^{\beta} \sum_{n=0}^{\infty} \frac{\mathrm{e}^{-S}S^n}{n!}\delta(E_0 \pm n\hbar\omega - \hbar\omega),$$

Spectral shape



Spectral shape

- Sum over all electron-vibrational contributions
- More sophisticated: Time-dependent methods (Heller) and extensions[1]
- Less sophisticated: Simple Gaussian (high-S limit)

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[1] *Heller, E. J. J. Chem. Phys. 1975; Baiardi, Alberto, Bloino, Julien, and Barone, Vincenzo. J. Chem. Theory Comput. 2013.*

Electron-vibrational transitions

- FC approximation:

$$\begin{aligned}\hat{\vec{D}}_{\mathrm{e}}(Q) &= \hat{\vec{D}}_{\mathrm{e}}(Q_1^{(0)}) + \cancel{\sum_{i=1}^{3\nu-6}\left(\frac{\partial\hat{\vec{D}}_{\mathrm{e}}}{\partial Q_i}\right)_{Q_1^{(0)}}\left(Q_i - Q_{1,i}^{(0)}\right)} \\ &\quad \cancel{+\frac{1}{2}\sum_{i=1}^{3\nu-6}\sum_{j=1}^{3\nu-6}\left(\frac{\partial^2\hat{\vec{D}}_{\mathrm{e}}}{\partial Q_i\partial Q_j}\right)_{Q_1^{(0)}}\left(Q_i - Q_{1,i}^{(0)}\right)\left(Q_j - Q_{1,j}^{(0)}\right) + \mathcal{O}(Q^3)}\end{aligned}$$

- Matrix element:

$$\langle\Psi_2^{(\mathrm{tot})}|\,\hat{\vec{D}}_{\mathrm{e}}\,|\Psi_1^{(\mathrm{tot})}\rangle = \underbrace{\langle\Psi_2|\,\hat{\vec{D}}_{\mathrm{e}}(0)\,|\Psi_1\rangle}_{\text{purely electronic}}\underbrace{\langle\zeta_{2n_2}(Q)|\,\zeta_{1n_1}(Q)\rangle}_{\text{FC integrals}}$$

Oscillator strengths

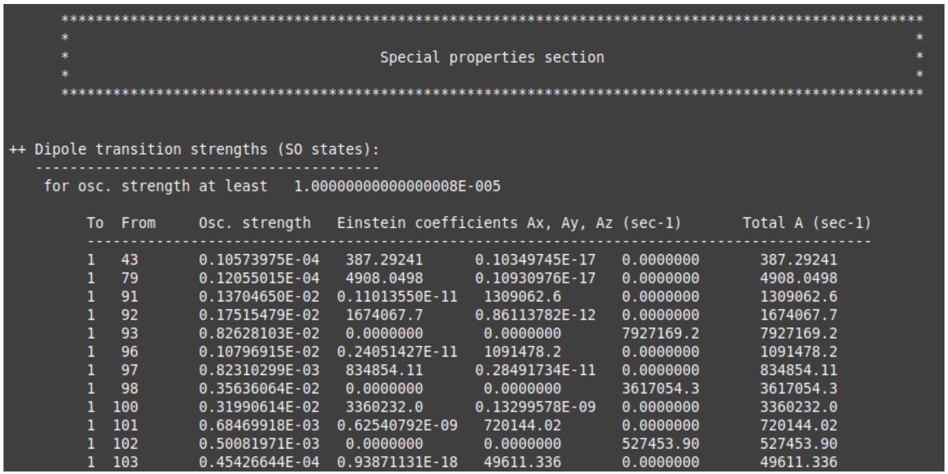
- Oscillator strength:

$$f_{1\to 2} = C\omega_0 \left| \langle \Psi_2 | \hat{\vec{D}}_e | \Psi_1 \rangle \right|^2$$

- Two flavours:
    - Dipole: $f^{\mathrm{D}}_{1\to 2} = C\omega_0 e^2 \left| \langle \Psi_2 | \sum_{i=1}^{N} \vec{r}_i | \Psi_1 \rangle \right|^2$
    - Velocity: $f^{\mathrm{V}}_{1\to 2} = C\frac{1}{\omega_0}\left(\frac{e\hbar}{m_e}\right)^2 \left| \langle \Psi_2 | \sum_{i=1}^{N} \vec{\nabla}_i | \Psi_1 \rangle \right|^2$
    - $f^{\mathrm{D}}_{1\to 2} = f^{\mathrm{V}}_{1\to 2}$ for exact eigenfunctions of $\hat{H}$

Oscillator strengths

Molcas: RASSI-SO output



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      *****************************************************************************************
      *                                                                                       *
      *                                 Special properties section                            *
      *                                                                                       *
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++ Dipole transition strengths (SO states):
   ---------------------------------------
    for osc. strength at least   1.00000000000000008E-005

         To  From     Osc. strength   Einstein coefficients Ax, Ay, Az (sec-1)       Total A (sec-1)
         -----------------------------------------------------------------------------------------
         1   43       0.10573975E-04   387.29241      0.10349745E-17   0.0000000       387.29241
         1   79       0.12055015E-04   4908.0498      0.10930976E-17   0.0000000       4908.0498
         1   91       0.13704650E-02  0.11013550E-11   1309062.6       0.0000000       1309062.6
         1   92       0.17515479E-02   1674067.7      0.86113782E-12   0.0000000       1674067.7
         1   93       0.82628103E-02   0.0000000       0.0000000       7927169.2       7927169.2
         1   96       0.10796915E-02  0.24051427E-11   1091478.2       0.0000000       1091478.2
         1   97       0.82310299E-03   834854.11      0.28491734E-11   0.0000000       834854.11
         1   98       0.35636064E-02   0.0000000       0.0000000       3617054.3       3617054.3
         1  100       0.31990614E-02   3360232.0      0.13299578E-09   0.0000000       3360232.0
         1  101       0.68469918E-03  0.62540792E-09   720144.02       0.0000000       720144.02
         1  102       0.50081971E-03   0.0000000       0.0000000       527453.90       527453.90
         1  103       0.45426644E-04  0.93871131E-18   49611.336       0.0000000       49611.336
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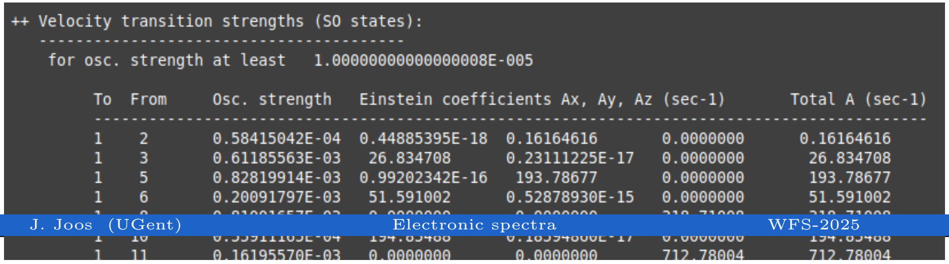

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++ Velocity transition strengths (SO states):
   ---------------------------------------
    for osc. strength at least   1.00000000000000008E-005

         To  From     Osc. strength   Einstein coefficients Ax, Ay, Az (sec-1)       Total A (sec-1)
         -----------------------------------------------------------------------------------------
         1    2       0.58415042E-04  0.44885395E-18  0.16164616       0.0000000       0.16164616
         1    3       0.61185563E-03   26.834708      0.23111225E-17   0.0000000        26.834708
         1    5       0.82819914E-03  0.99202342E-16   193.78677       0.0000000        193.78677
         1    6       0.20091797E-03   51.591002      0.52878930E-15   0.0000000        51.591002
         [illegible]
         [illegible]
         1   11       0.16195570E-03   0.0000000       0.0000000       712.78004        712.78004
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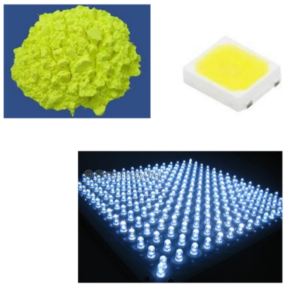
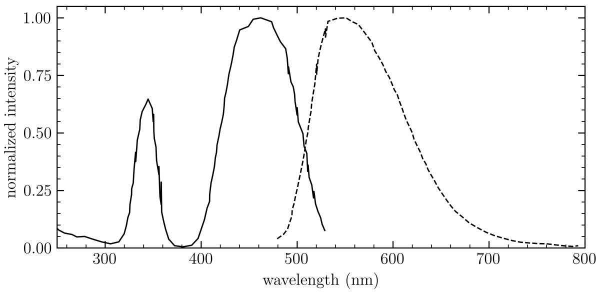
YAG:Ce^{3+}

- LED phosphor: blue excitation, yellow emission
- Single valence electron: $4f^1$ ground state; $5d^1$ excited state





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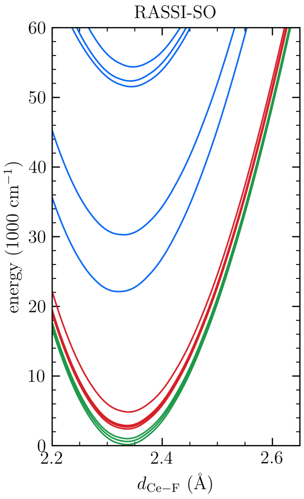
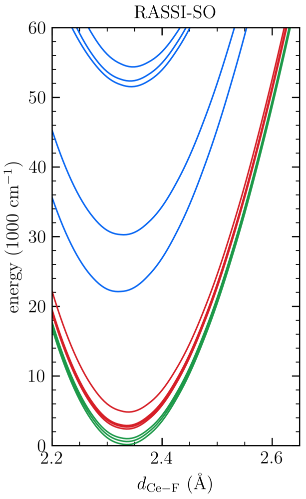
https://www.ledinside.com/
https://www.instrument.com.cn/
Bachmann, Ronda and Meijerink, Chem. Mater. ***21****, 2077 (2009)*

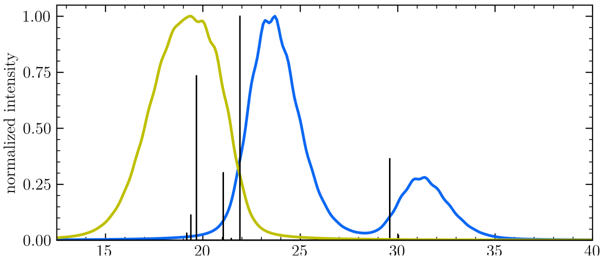
Potential energy curves

- SA-CASSCF/MS-CASPT2/RASSI-SO
- Single point calculations along "*ad hoc*" breathing mode



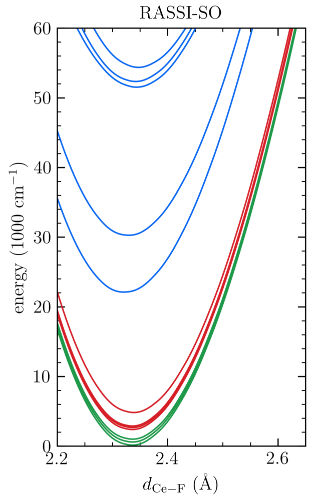
Absorption and emission spectra

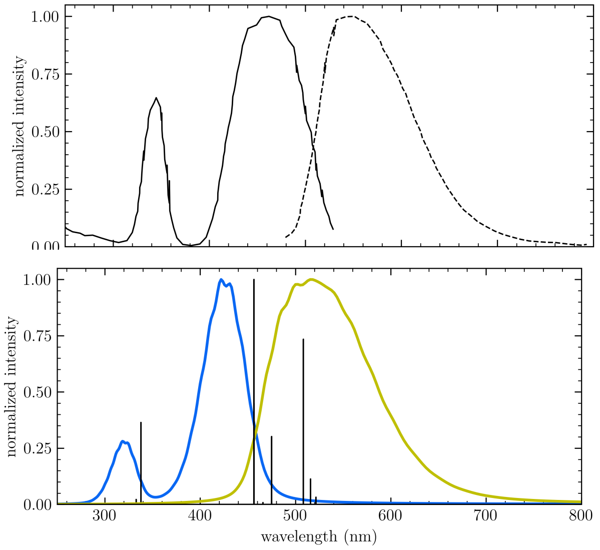




Absorption and emission spectra

Absorption spectrum





Bachmann, Ronda and Meijerink, Chem. Mater. ***21****, 2077 (2009)*

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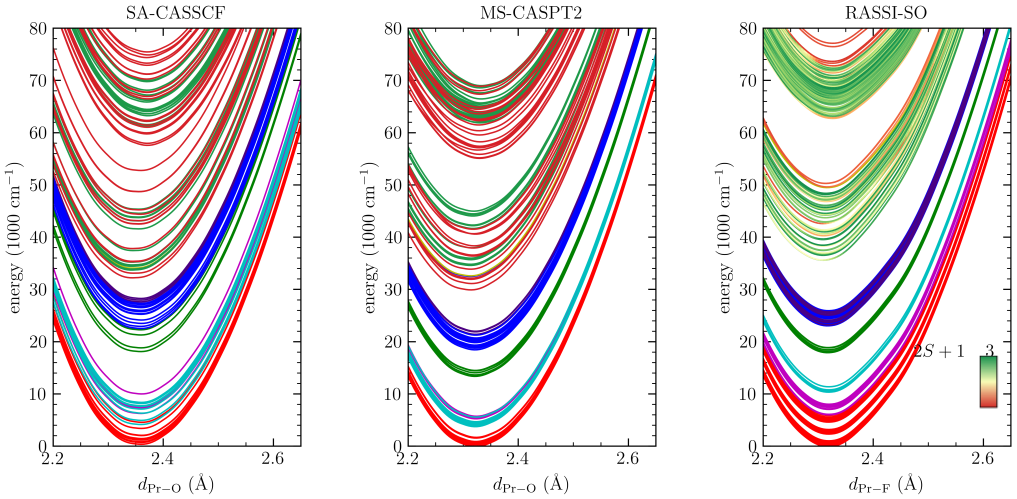
Exercise: Potential energy curves en spectra for YAG:Pr^{3+}

1. Introduce an “ad hoc” breathing mode, $Q_{\mathrm{Pr-O}}$ for the PrO_8^{13-} cluster in YAG.
2. Perform single-point SA-CASSCF/MS-CASPT2/RASSI-SO calculations to get the states of the $4f^2$ and $4f5d$ configurations for a range of geometries along the breathing mode.
3. Construct potential energy curves for all states and plot the configuration coordinate diagram.
4. Make a table with equilibrium values for $Q_{\mathrm{Pr-O}}$ and vibrational frequencies for a small number of relevant electronic states.
5. From the RASSI-SO output, extract oscillator strengths and simulate the absorption spectrum of Pr^{3+} in YAG.
6. Simulate the emission spectrum from the lowest $4f5d$ state.

Solution: Potential energy curves

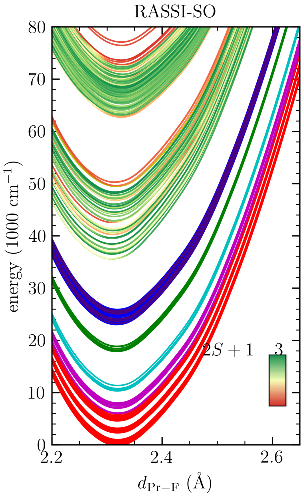
Energy level scheme

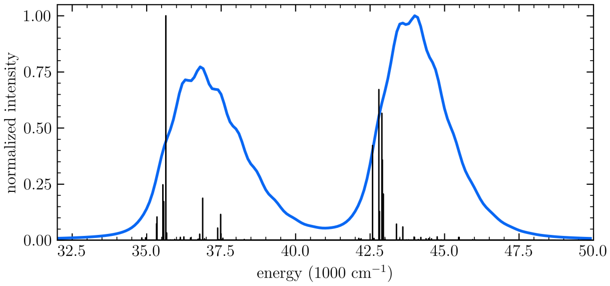


Solution: Potential energy curves

Absorption spectrum

- $4f^2(^3H_4, 1.A) \rightarrow 4f5d$ (i.e. state 1 → states 91-...)





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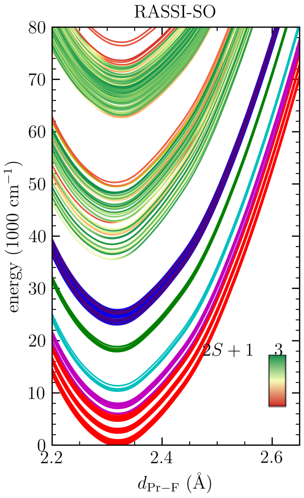

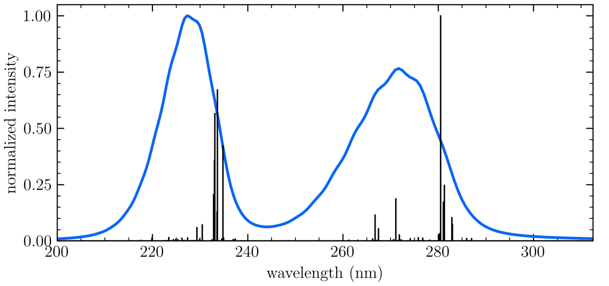

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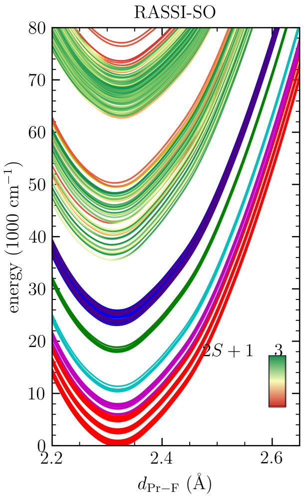
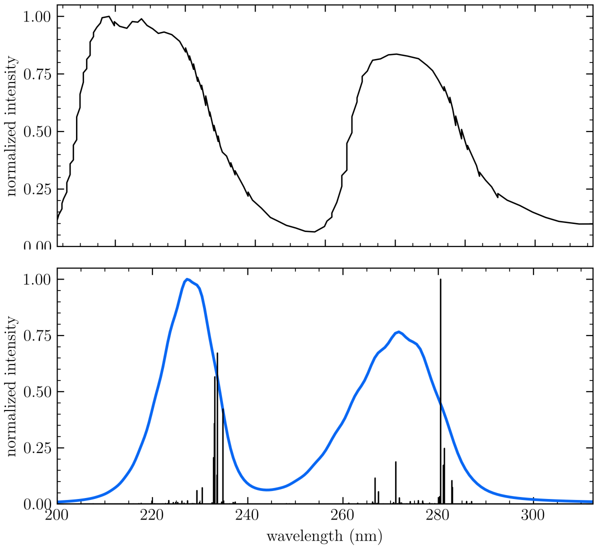


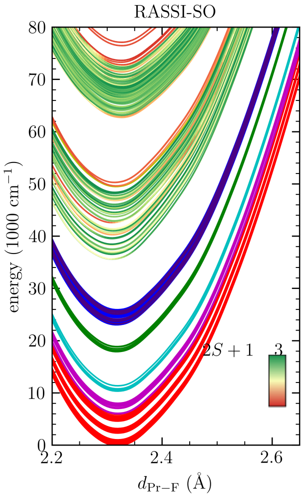


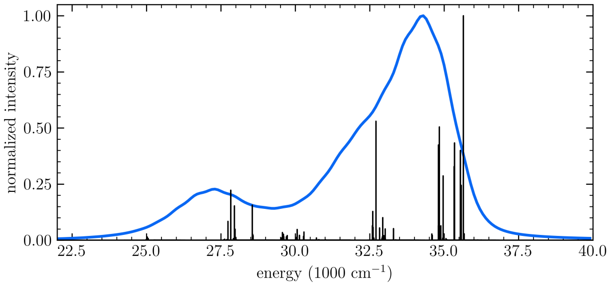
M. Wisniewska et al., IEEE Trans. Nucl. Sci. ***49****:3, 926 (2002)*

Solution: Potential energy curves

Emission spectrum

- $4f5d(16.B_2) \rightarrow 4f^2$ (i.e. state 91 → states 1-90)





Solution: Potential energy curves

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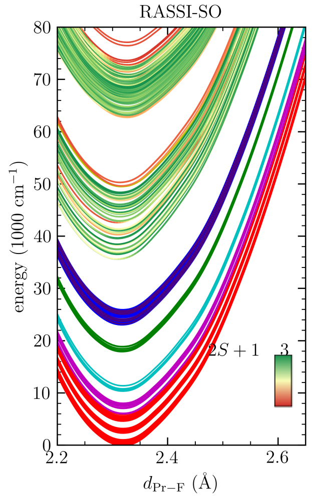

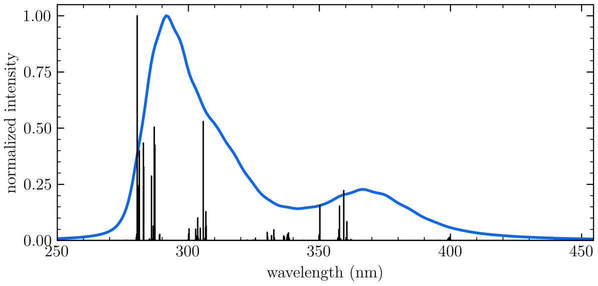

Solution: Potential energy curves

Emission spectrum

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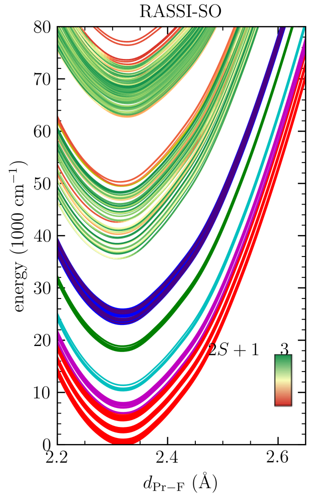
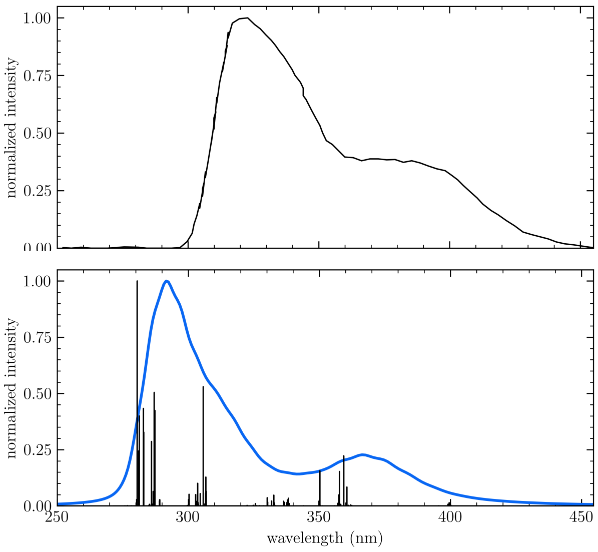
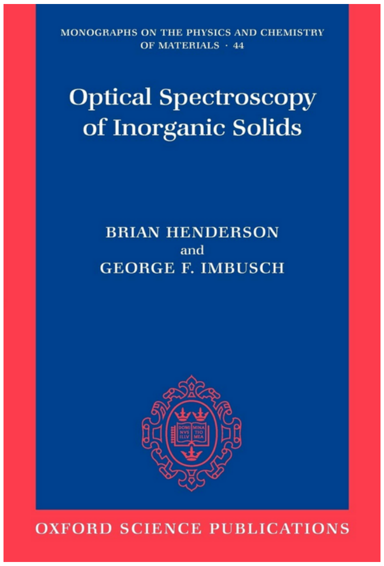




M. Wisniewska et al., IEEE Trans. Nucl. Sci. ***49****:3, 926 (2002)*

Literature



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Optical Spectroscopy
of Inorganic Solids

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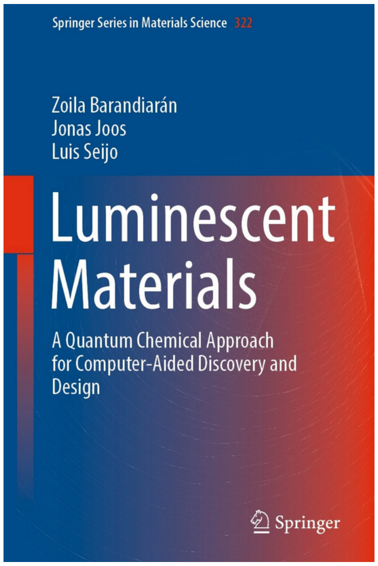

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