F-element optical and NMR spectroscopy-insights from experiment and theory

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Optical Spectroscopy 1:

Lanthanides

Louise Natrajan

louise.natrajan@manchester.ac.uk
Research Themes

Pure oxidation state actinide compounds and fundamental chemistry

Transition metal polypyridyls: two photon spectroscopy

Geochemistry of Uranyl

Lanthanide upconverting nanoparticle enzyme biosensors and FRET
Optical Spectroscopy

- X-ray diffraction
- UV-vis-nIR
- Emission
- IR and Raman
- NMR
- EPR
- XAS (EXAFS, XANES)

Recommended reading:
Chemistry of the f-block elements-Helen Aspinall (Gordon and Breach)
The f elements-Nikolas Kaltsoyannis and Peter Scott (Oxford Chemistry Primers)
Principles of Fluorescence Spectroscopy-Joseph Lackowicz (Springer)
Useful Properties of the Lanthanides

Resulting from the ‘core like’ nature of the f-orbitals:

Catalytic convertors in car exhausts (CeO₂)

Lighting-fluorescent lamps

Imaging in medicine: MRI (Gd), luminescent cellular probes (e.g. Eu)
**Lanthanide Complexes as Luminescent Sensors and Probes**

**Applications:**

- Luminescent phosphors: lighting, displays, security encoding

**Biological Uses:**

- Structural probes (site symmetry, coordination number)
- Analytical probes (determining concentrations of analytes)
- Imaging probes for medical diagnosis e.g. tumour cell imaging


Near Infra-red Excitation/Emission

> 500 microns depth penetration of near infra-red light

Yb$^{3+}$, Nd$^{3+}$

3D optical imaging

Biological imaging
Photochemistry Re-cap:

Absorption of light:  Electronic transitions

- organic molecules, metal complexes (high $\varepsilon$)

Vertical absorption

Vibrational relaxation (VR)
Non-radiative de-activation

Vertical emission (radiative decay)
Kasha’s rule: emission from lowest vibrational (relaxed) state

Fluorescence - radiative decay between states of the same multiplicity (2S+1)
Photochemistry Re-cap:

**Hund’s Rule:** for every singlet excited state, there is a triplet state which lies lower in energy

**ISC** - intersystem crossing ($S_1 - T_1$):
- horizontal transition
- radiationless process between 2 states of different multiplicity

**Phosphorescence** - radiative decay between states of different multiplicity
El Sayed’s Rule

- Intersystem crossing is slow unless there is a change in orbital type

Spin-Orbit Coupling

- Crossing points occur on the $S_1$ and $T_n$ potential energy curves
- Application of a magnetic torque to an electron spin can result in a change in spin and a change in angular momentum
- Most common mechanism of ISC
- Improved with the addition of heavy atoms
Selection Rules

Spin Selection rule: $\Delta S = 0$ allowed transition

- Fluorescence $S_1^* \to S_0$, $\Delta S = 0$, allowed, fast decay (ns)
- Phosphorescence $T_1^* \to S_0$, $\Delta S = 1$, forbidden, slow (s)

Electronic transitions in lanthanides-Absorption

- f-f transitions (weak oscillator strengths, $\varepsilon \sim 1 \text{ M}^{-1} \text{ cm}^{-1}$, c.f. d-d transitions $\sim 100$ and $\pi-\pi \sim 10^5$)
- Laporte selection rules (centrosymmetric cxs (i): $\Delta l = 1$ and $g \rightarrow u$
- f-f $\Delta l = 0$, slow decay results in long lived emission
- Relaxation of the Laporte selection rule occurs by spin orbit coupling ($l$ and $s$)
- Described by Russell-Saunders coupling scheme
Example

- Line-like absorption and emission spectra
- Transitions between states derived from Russell-Saunders spin orbit coupling (J)
- Pale colours (formally forbidden transitions)

\[ \text{Pr(Tf}_2\text{N)}_3 \times 10^{-2} \text{ M in BumimTf}_2\text{N} \]
• Judd-Ofelt Theory

Theoretical oscillator strengths $f(J, J')$ of the $J \rightarrow J'$ transition at the mean frequency $\nu$ is given for an electric dipole transition

$$f_{\text{cal}} = \frac{8\pi^2 m c \nu (n^2 + 2)^2}{27 h n (2J + 1)} \times \sum_{t=2,4,6} \Omega_i \left| \langle (S, L) J | U^t | (S', L') J' \rangle \right|^2$$

Only really works for doped solids in high symmetry (e.g. cubic)
Judd-Ofelt Celebration!
Russell Saunders Coupling

Electronic structure of the 4f elements

• Each state will have: \( S \) overall spin and \( L \) overall orbital angular momentum: \( 2S + 1L \) (d-orbitals)

• Spin and orbital angular momentums can couple: \( 2S + 1L \) \( J \)

• \( J \) takes values from \( |L+S| \)…\( |L-S| \)

Spin multiplicity \( 2S + 1 \), where \( S = \) overall spin

<table>
<thead>
<tr>
<th>Label</th>
<th>S</th>
<th>P</th>
<th>D</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
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<td>( L )</td>
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<td>4</td>
<td>5</td>
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</table>

\( 2S + 1L \) \( J \) \( J = L+S, L+S-1, L+S-2..., |L-S| \)
Hund’s Rules for Ground State

• Spin multiplicity must be the highest possible ($S_{\text{max}}$)
• If more than one term have the highest multiplicity, the term with the highest value of L is the ground state ($L_{\text{max}}$)
• The ground level has $J_{\text{min}}$ if the subshell is less than half full
• The ground level has $J_{\text{max}}$ if the subshell is greater than half full

Example: Nd$^{3+}$, f$^3$

\[
\begin{array}{ccccccc}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
3 & 2 & 1 & 0 & -1 & -2 & -3
\end{array}
\]

$m_l$

$L_{\text{max}} = 3 + 2 + 1 = 6 = I_{\text{state}}$

$J = |L+S|...|L-S| = 12/2 + 3/2, 12/2 + 3/2 -1...12/2 - 3/2$

$= 15/2, 13/2, 11/2, 9/2 = {}^4 I_{9/2}$
Russell Saunders Coupling: Nd$^{3+}$

- Transitions from excited state to ground $^4I_J$ ground state
- Series of absorption and emission lines
- Crystal field small-can be observed in some transitions (noteably Nd$^{3+}$, Yb$^{3+}$)

Pr$^{3+}$ ($f^2$):

\[ S = \frac{1}{2} + \frac{1}{2} = 1, \quad 2S+1 = 3 \]
\[ L = 3 + 2 = 5 = H \]
\[ J = 5+1…5-1, = 6, 5, 4 \]

Ground state = $^3H_4$
4f Emission Spectra

- Line-like emission spectra
- Long lived emission (milliseconds - microseconds)
- Range from UV (Gd$^{3+}$), to visible (Tm$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$) to near infra-red (Nd$^{3+}$, Pr$^{3+}$, Er$^{3+}$, Yb$^{3+}$)

Defining the Emissive State

- **Energy gap law:** emissive state is the one with the biggest energy gap to the next lowest state

- Energy gap = wavelength of emission
- Bigger gap = longer lifetime
- Tb$^{3+}$ and Eu$^{3+}$ millisecond lifetimes
- Non radiative quenching can reduce the lifetime e.g. by vibrations
Lifetimes

- It is the average time spent in an excited state before radiative decay.

- Given by the equation

\[ \tau_r = \frac{1}{k_f + k_{nr}} \]

- Units of lifetimes is usually ns.

- The inverse is ns\(^{-1}\) which is a rate.

- The intrinsic lifetime is the average time spent in the excited state without non-radiative deactivation processes.

\[ \tau_n = \frac{1}{k_f} \quad k_f = \frac{\tau_r}{\Phi_f} \]
Lifetimes

• The intensity of emission after a pump pulse decays exponentially

• Taking the natural log of this gives a linear relationship between intensity and time

\[ I(t) = I_0 e^{-t/\tau} \]
\[ \ln[I(t)] = \ln(I_0) - t/\tau \]

• Methods used to measure lifetimes are a statistical methods based on the bulk solution

• Lifetimes are fitted using least squares regression

• Exchange processes which occur on timescales faster than the lifetime are averaged out. Exchange processes slower than the lifetime are resolved a separate lifetimes
Time Dependence of Emitted Light

\[ I(t) = I_0 e^{-kt} \]

- The lifetime of the excited state is given by: \( \tau = \frac{1}{k_{\text{obs}}} \) (s)

- During this time, a fraction \( 1/e \) of the excited molecules return to the ground state (\( e = 2.73 \))

Lifetimes of Ln\(^{3+} \) (\( \tau \)):
- Tb\(^{3+} \), Eu\(^{3+} \) milliseconds
- Sm\(^{3+} \), Dy\(^{3+} \), Yb\(^{3+} \), Er\(^{3+} \) microseconds
- Pr\(^{3+} \), Nd\(^{3+} \) nanoseconds (10 - 100’s)
Lifetime Determination from Kinetic Traces

1. Stepwise increase of time delay (manual or software driven)

*Tb^{3+}* complex in water: 0.1 ms steps (0.1 – 10 ms) at 545 nm

2. Time Correlated Single Photon Counting (TCSPC)

\[ \tau = 74 \text{ microseconds} \]

\[ \ln(\text{Emission Intensity}) \]

Sm\(^{3+}\) complex 200 microsecond range at 650 nm: Tail fit

3. Photodiode detection with an oscilloscope

Yb$^{3+}$ in water, Ge-diode detector, 980 nm, ns/µs timescale; Reconvolution fit with a scatterer

Grow-in Component (Rise Time)

- Grow in exponential fitted before decay-indicates slow energy transfer from sensitizer triplet state to Yb$^{3+}$ emissive excited state (corresponds to emission decay of the organic sensitizer)

- If different in D$_2$O than H$_2$O, indicates phonon assisted energy transfer is the rate determining step
Quantum Yields

A measure of the efficiency on fluorescence

$$\Phi_f = \frac{\text{Photons out}}{\text{Photons in}}$$

$$\Phi_f = \frac{k_f}{k_f + k_{nr}}$$

Excitation  Emission

[Graph showing fluorescence spectra with labels for Blank and Sample]

Integrating sphere
Hypersensitive Transitions

• In hypothetical Ln$^{3+}$, only magnetic dipole transitions are allowed: $\Delta L = 0, \Delta J = 0, 1$

e.g. $^5D_0 \rightarrow ^7F_1$ in Eu$^{3+}$

• In a complex, electric dipole (ED) transitions are induced: $\Delta L, \Delta J = 0, 2, 4, 6$ (0→0 forbidden)

• Some transitions acquire strength by both MD and ED e.g. Tb$^{3+}$

• Some transitions are sensitive to changes in symmetry and/or the inner coordination sphere.
• They display shifts in their maxima, splitting and intensity

**Hypersensitive transitions** - often quadrupolar transitions: $\Delta J = 2$

e.g. $^5D_0 \rightarrow ^7F_2$ in Eu$^{3+}$

   Mechanism: mixing of the 4f states with ligand states
Some Examples: Eu\(^{3+}\)

- Eu\(^{3+}\) ion in high symmetry environment
- \(\Delta J = 1, \Delta J = 2\) and \(\Delta J = 4\) transitions strong
- \(\Delta J = 0\) transition very weak

- Eu\(^{3+}\) ion low symmetry environment
- \(\Delta J = 1\) weak
- \(\Delta J = 0\) fairly strong
- \(\Delta J = 2\) very strong
- Split into two components
Hypersensitive Transitions in Nd$^{3+}$

Absorption

Nd(BrO$_3$)$_3$.9H$_2$O (s)

CN = 9

[Nd(H$_2$O)$_9$]$^{3+}$(aq)

CN = 9

NdCl$_3$.6H$_2$O (s)

CN = 9

$^{2}H_{9/2},^{4}F_{5/2} \leftrightarrow ^{4}I_{9/2}$

Emission

$^{4}F_{3/2} \rightarrow ^{4}I_{13/2}$

Other Transitions: Absorptions

• f-d transitions: allowed by Laporte’s selection rule

Highly energetic except for Ce\(^{3+}\), Pr\(^{3+}\) and Tb\(^{3+}\) (4f to 5d)

\[ [\text{Ce} (\text{H}_2\text{O})_9]^{3+}, \text{D}_{3h} \text{ symmetry} \]

\[ \epsilon \sim 800 \text{ M}^{-1} \text{ cm}^{-1} \]

Ce\(^{3+}\) [Xe]5d\(^1\) generates two levels, \( ^2D_{3/2} \) and \( ^2D_{5/2} \)
• 4 transitions
LMCT Transitions

- Occurs in complexes with ligands that can be oxidised (redox reaction) - Laporte allowed
- Therefore the metal must have an accessible +2 oxidation state

\[
\text{Ar} + \text{Eu}^{3+} \rightarrow \text{Ar}^+ + \text{Eu}^{2+} \quad \text{Transient Ligand radical} + \text{Eu(II)}
\]

Sensitised Emission

• The special case of 4f elements: indirect excitation

• In view of weak f-f oscillator strengths, direct excitation (f-f absorption) is inefficient

• Laporte selection rule overcome by the ‘antenna effect’

Organic chromophore: \( h\nu_1 + Ar \rightarrow ^1Ar^* \rightarrow ^3Ar^* \rightarrow Ln^* \rightarrow Ln + h\nu_{Ln} \)

Eu β-diketonates

\[ [\text{Eu(dbm)}_4][\text{NEt}_4] \]
Dbm = dibenzoylmethane

Courtesy of Helen Aspinall, Liverpool University, UK.
Jablonski Diagram

Sensitised emission: Energy level scheme

- Heavy atom effect
  - promotes ISC

Competing pathways:
- Ligand fluorescence
- Ligand phosphorescence
- Back energy transfer

Triplet mediated sensitisation path

Relative Energy (cm$^{-1}$)

$S_0$ $T_1$ $5D_2$

$k_{isc}$ $k_{bet}$ $k_{et}$

$k_{fluorescence}$ $k_{phosphorescence}$

$7F_6$ $7F_5$ $7F_4$

$7F_3$ $7F_2$ $7F_1$

$7F_0$

Eu$^{3+}$

Ligand
Double electron transfer quenches the Eu\(^{3+}\) emission (NR decay)

• Competitive radiative decays (Eu emission + phosphorescence)
• Non radiative LMCT decay to ground state

**LMCT Sensitised Yb$^{3+}$ Emission**

- Alternative mechanism of energy transfer
- Fast energy transfer-mediated via an orbitally allowed transition

For NIR emitting Ln$^{3+}$, a wider range of chromophores can be used: e.g.

\[
\text{Ar}(S_0)\text{Ln}^3+ \rightarrow \text{Ar}(S_1)\text{Ln}^3+ \rightarrow \text{Ar}(T_1)\text{Ln}^3+ \rightarrow \text{Ar}^*\text{Ln}^2+ \rightarrow \text{Ar}(S_0)(\text{Ln}^3)^* \rightarrow \text{Ar}(S_0)\text{Ln}^3+
\]

Excitation Spectra

**Excitation spectrum**: Quanta of light emitted at a given wavelength as a function of excitation wavelength; the excitation spectrum follows the absorption spectrum, as the number of photons emitted is directly proportional to the amount of light absorbed.

Excitation (ligand)  Emission (f-f)

• Ln excited states are quenched by: O-H, N-H and C-H vibrations
• Limited quenching by O-D oscillators: - (Hooke’s law)
Calculating the Inner Sphere Hydration Number (q)

• Lanthanide coordination compounds are labile:

\[
[Ln(H_2O)_9]^{3+} + H_2O \rightleftharpoons [Ln(H_2O)_8(H_2O)]^{3+} + H_2O
\]

• Use quenching of O-H vs. O-D oscillators to determine \( q \)

**Horrocks Equation:** \( q = A(k_{H_2O} - k_{D_2O} - B) \)

\( k = \) rate constant of decay = \( 1/\tau \)

\( A, B = \) proportionality constants

\( A \) corrects for inner sphere quenching

\( B \) corrects for outer sphere quenching

A and B values have been determined for Eu\(^{3+}\), Tb\(^{3+}\), Yb\(^{3+}\) (Nd\(^{3+}\) and Sm\(^{3+}\))


Q. For the Eu$^{3+}$ complex determine q:
\[ \tau_{H2O} = 0.63 \text{ milliseconds (ms)} \]
\[ \tau_{D2O} = 2.60 \text{ milliseconds} \]

\[ q = A(k_{H2O} - k_{D2O} - B) \]
\[ A = 1.2 \text{ ms} \]
\[ B = 0.25 \]
\[ q = 1.2((1/0.63 - 1/2.60) - 0.25) \]

→ q= 1.1 ie. one molecule of water is coordinated to europium
Luminescent Chemical Sensors

The spectroscopic properties of the lanthanides make them ideal luminescent probes:

• Line like emission spectra: easily identifiable spectral fingerprint
• Long luminescent lifetimes
• Large Stokes’ shift ($\Delta \lambda$ absorption and emission)

**Time-gating:** removal of background fluorescence

**Time-resolved luminescence:** allows high signal to noise ratios

- Excite with UV pulse
- Allow background fluorescence to decay
- Collect Ln$^{3+}$ emission (Eu, Tb)
Macrocyclic Complexes

- Free Ln$^{3+}$ ions are toxic to living organisms
- For biological applications e.g. imaging agents, multidentate or macrocyclic ligands are often employed
- Using the chelate effect to create kinetically stable complexes
- Coordinatively saturated complexes- to exclude water molecules from the inner coordination sphere

e.g.

- $H_4$DOTA
- DOTAM
- $H_3$DTPA
Ln$^{3+}$ Luminescence as a Signalling Method

A. Modification of the Ln$^{3+}$ inner coordination sphere

- Binding of an analyte reduces O-H quenching and $q$ decreases

B. Modulation of the energy transfer processes

- Binding of an analyte switches on or off the Ln$^{3+}$ emission

Courtesy of Jean-Claude Bünzli
Example: pH Sensor

Change in Eu$^{3+}$ coordination sphere reflected in ratio of hypersensitive transitions

Example: Anion sensors

Bicarbonate sensor-ratiometric probe

Lactate and citrate assay

Example: Peptide Conjugates and Targeted Imaging

• Tb$^{3+}$ complex coupled to a peptidic vector-Tuftsin

• Affinity for macrophage cells

• Targetted probes/imaging agents

$\tau_{H2O} = 1.67$ ms

$\tau_{D2O} = 3.25$ ms

$q = 1.2$

<table>
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<tr>
<th>Z</th>
<th>Element</th>
<th>Symbol</th>
<th>Electronic configuration</th>
<th>Ground level</th>
<th>Radius Ln$^{3+}$ (Å)</th>
<th>µ$_{\text{eff}}$ cal</th>
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<td>58</td>
<td>Cerium</td>
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</table>

Properties of the lanthanide ions. Note: $\mu_{\text{eff}}$ – the calculated values and show good agreement with experimental values with the exceptions of Sm$^{3+}$ ($\mu_{\text{eff}}$ exp = 1.4 -1.7) and Eu$^{3+}$ ($\mu_{\text{eff}}$ exp = 3.3-3.5) due to their excited states being close to their ground state.