

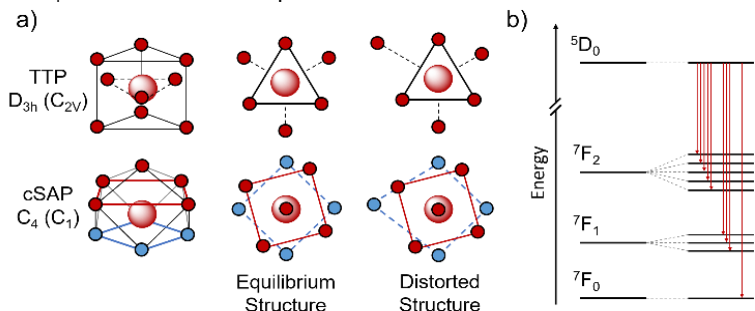
Revisiting the Fundamental Photophysical Properties of $f-f$ Electronic Transitions

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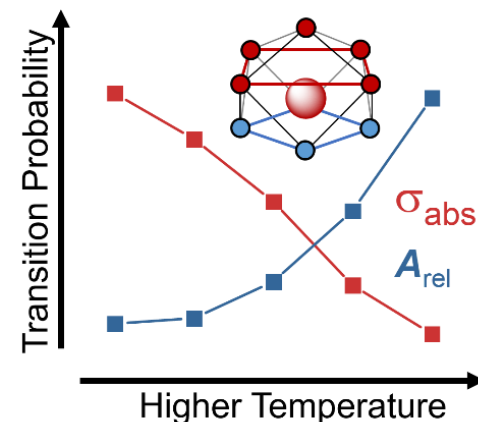
Motivation

The intrinsic optical transitions between f -orbitals continues to defy our conventional understanding of photophysics. As the optical spectra informs directly on the ligand field and thus relates to the structure of the metal complex, optical spectroscopy has the potential to reveal the solution structure of these complicated systems. This is a crucial step in the efforts to improve lanthanide separations and nuclear fuel recycling processes. However, our current understanding of the $f-f$ photophysics does not allow for such analysis. In this work we aim to change that, by probing the photophysical properties of $[\text{Eu}(\text{MeOH-d}_4)_9]^{3+}$ and $[\text{Eu}.\text{DOTA}(\text{MeOH-d}_4)]^-$ in MeOH-d_4 as a function of temperature.



Transition Probabilities

We find that the absorption cross section of the complexes decreases as the temperature increases while the relative emission transition probability increases. These observations seem conflicting at first, but can be explained by considering the experimental timescale of the two techniques. Ligand exchange for f -element complexes happens on a ns timescale. Compared to this, light absorption is instantaneous (fs timescale) while light emission is slow (ms timescale). The result of this is that in absorption spectroscopy we observe the average symmetry of the structure ensemble while in emission spectroscopy we observe a weighted average.



Rates and Quantum Yields

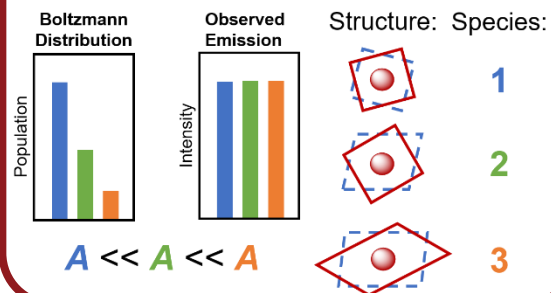
We find that the Quantum Yield increases for the two complexes as temperatures are increased. This is due to a large increase in the radiative rate constant while the non-radiative rate constant remains unchanged. This is contrary to organic fluorophores and phosphorescent transition metal complexes where vibronic couplings dominate the transition probabilities.

Photophysical data of $[\text{Eu}.\text{DOTA}(\text{MeOH-d}_4)]^-$ and $[\text{Eu}(\text{MeOH-d}_4)_9]^{3+}$ in MeOH-d_4

[Eu.DOTA(MeOH-d ₄)] ⁻						
Temperature	Φ ^a	k _r (s ⁻¹)	k _{nr} (s ⁻¹)	τ _{obs} (ms)	A _{MID} (s ⁻¹)	
10°C	0.46	189	219	2.45	19.85	
20°C	0.47	192	218	2.44	20.45	
30°C	0.51	214	208	2.37	22.39	
40°C	0.56	256	200	2.19	27.34	
50°C	0.61	323	206	1.89	34.02	
[Eu(MeOH-d ₄) ₉] ³⁺						
Temperature	Φ ^a	k _r (s ⁻¹)	k _{nr} (s ⁻¹)	τ _{obs} (ms)	A _{MID} (s ⁻¹)	
10°C	0.36	121	214	2.99	17.95	
20°C	0.37	126	210	2.98	18.45	
30°C	0.38	129	209	2.96	18.65	
40°C	0.38	131	211	2.92	18.77	
50°C	0.38	134	217	2.85	18.85	

Weighted Averages

The excited state lifetime of f -element complexes is slow (μs - ms) compared to molecular motion (ns). This allows for several conformations to be visited before emission occurs. As emission probability is directly linked to the symmetry a more distorted structure will be overrepresented in the emission spectrum even if it is only briefly populated.



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<https://doi.org/10.26434/chemrxiv.14096603.v1>