

Mechanisms of Luminescence in Lanthanide Complexes: A Crucial Role of Metal–Ligand Covalency

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A current understanding of the luminescence of lanthanide complexes is based on the phenomenological Judd–Ofelt (JO) theory. However, the mechanisms of electric-dipole transitions lying at its basis were never subjected to a rigorous analysis.

Herein we investigate the contributions to the electric-dipole transitions in the Er^{3+} : ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ band of an Er-trensral complex using state-of-the-art *ab initio* calculations. We find that the conventional JO mechanism based on the electrostatic crystal field yields only a quarter of the integral intensity of this band. Accordingly, three quarters of it is contributed by covalent binding of erbium and ligand orbitals via three major mechanisms, the 4f ligand and ligand–ligand electric-dipole transitions and covalent enhancement of the hybridization of 4f and even empty orbitals of erbium. We expect that these findings will inspire the design of efficient rare-earth luminescent materials.

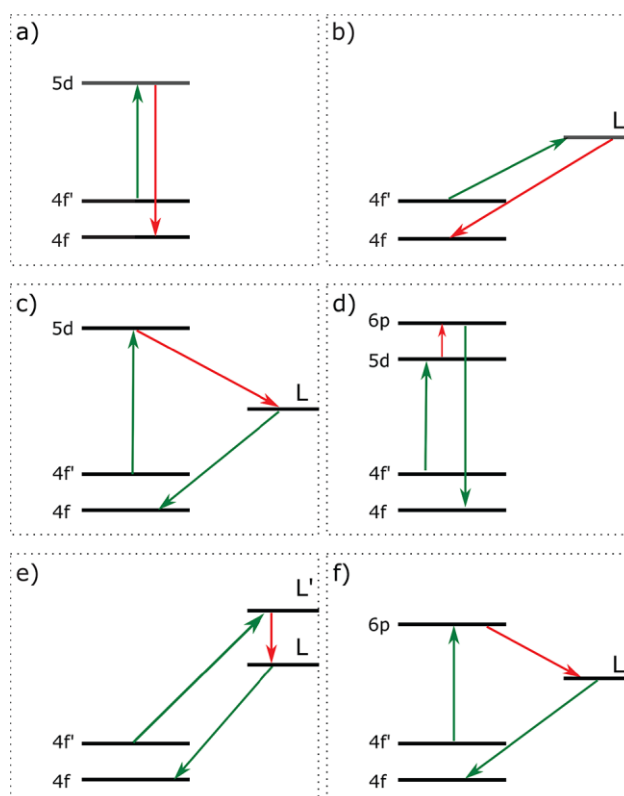


Figure: Six mechanisms of electric dipolar transitions between 4f orbitals in Ln complexes. Red arrows stand for electric dipolar coupling, and green arrows denote covalent (when relevant) and electrostatic crystal field admixtures of excited Ln and ligand orbitals. The label “5d” in the above scheme stands for “all even empty orbitals of the lanthanide” and label “6p” stands for “all odd empty orbitals of the lanthanide”.

Reference

[1] L. Ungur, B. Szabo, Z. A. AlOthman, A. A. S. Al-Kahtani, L. F. Chibotaru *Inorg. Chem.* **2022**, *61*, 5972–5976. <https://doi.org/10.1021/acs.inorgchem.2c00071>.