

Europium Luminescence: Electronic Densities and Superdelocalizabilities for a Unique Adjustment of Theoretical Intensity Parameters

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INTRODUCTION

We advance the concept that the charges, g_i , and polarizabilities, α_i , for europium complexes, within SOM and Judd-Ofelt theory, can be effectively and uniquely modeled by energy variations resulting from perturbations on the semiempirical electronic wave function of the complex. In our conceptualization, the charges will be determined from first order perturbation theory, and the polarizabilities from second order perturbation theory.

METHODS

All Sparkle calculations were carried out using MOPAC2012, and all RM1 orbital model for europium calculations were carried out by a version of the same software we modified. Subsequently, routines within LUMPAC were then coded to implement the new methodology being advanced here, and will be made available from <http://www.lumpac.pro.br>.

RESULTS AND DISCUSSION

With only three adjustable constants, we introduce expressions that relate the charge factors g_i to electronic densities q_i ,

$$g_i = Q \cdot q_i$$

$$q_\mu = 2 \sum_{i'}^{occ} \sum_p^{N_\mu} |c_{pi'}^\mu|^2$$

and the polarizabilities α_i to superdelocalizabilities SE_σ that we derived specifically for this purpose

$$\alpha_i = SE_i \cdot D + C$$

$$SE_\sigma = 2 \sum_{i'}^{occ} \sum_p \sum_q \frac{c_{pi'}^\sigma c_{qi'}^\sigma}{\epsilon_{i'}}$$

where i' runs over all occupied molecular orbitals of the complex, p and q run over all atomic orbitals of atom μ , and $c_{pi'}^\sigma$ and $c_{qi'}^\sigma$ are the corresponding linear coefficients.

The three constants Q , D , and C , are then adjusted iteratively until the calculated intensity parameters, corresponding to the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions, converge to the experimentally determined ones.

From the converged values of the constants, we then define a binary outcome acceptance attribute for the adjustment, and show that when the adjustment is acceptable, the predicted geometry is, in average, closer to the experimental one. This methodology advanced was tested on all thirteen europium complexes whose crystallographic structures could be obtained from the Cambridge Crystallographic Database, and whose values of Ω_2^{exp} and Ω_4^{exp} have been published.

CONCLUSIONS

The procedure advanced in this work, is seemingly a robust one, and leads to a unique set of g and α necessary for the prediction of the intensity parameters. An important consequence is that the terms related to dynamic coupling and electric dipole mechanisms will be unique. Hence, the important energy transfer rates will also be unique, leading to a single predicted intensity parameter for the $^5D_0 \rightarrow ^7F_6$ transition.

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