

Theoretical Modeling of Lanthanide Complexes-A Review

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ABSTRACT

The theoretical modeling of the Eu(III) system emphasis on the understanding of the ground state geometries of the complexes under investigation. In recent years, the geometry around the Ln(III) ion is usually obtained through X-ray analysis or other relevant techniques. In most of the cases good quality crystals are not obtained. In such cases one relies on the theoretical simulation of their equilibrium structures. Simas and co-workers (1994)⁸ developed a semi-empirical model for the calculation of ground state geometries for the lanthanide complexes. This model was named as 'Sparkle Model' for the computation of lanthanide complexes and has been successfully applied to the lanthanide complexes.

Keywords: Theoretical modeling of the Eu(III) system, Ln(III) ion, Sparkle Model.

DISCUSSION

The study of stable and efficiently luminescent Eu(III) complexes have been a subject of interest in view of their potential applications as luminescent centers in optoelectronics¹ and as luminescent labels in bio-immunoassays.² The huge interest has been paid to the synthesis and studies of lanthanide complexes using a variety of ligands including β -diketones in recent years.^{3, 4} There are many methods which have been used systematically to investigate the lanthanide complexes in solid and solution states such as single crystal X-ray crystallography¹, NMR⁵ and fluorescence spectroscopy.⁶ The Eu(III) complexes show strong antenna (ligands) centered absorption in UV-region and efficient ligand to europium energy transfer and intense lanthanide ion centered emission in the visible region (red colour emission).⁷ On the designing of highly luminescent Eu(III) complexes, the study of 4f-4f absorption spectroscopy and photoluminescent properties of these systems are important. The theoretical modelling of the Eu(III) system emphasis on the understanding of the ground state geometries of the complexes under investigation. In recent years, the geometry around the Ln(III) ion is usually obtained through X-ray analysis or other relevant techniques. In most of the cases good quality crystals

are not obtained. In such cases one relies on the theoretical simulation of their equilibrium structures. Simas and co-workers (1994)⁸ developed a semi-empirical model for the calculation of ground state geometries for the lanthanide complexes. This model was named as 'Sparkle Model' for the computation of lanthanide complexes and has been successfully applied to the lanthanide complexes. The Sparkle model serves as the fundamental tool for the computational studies of the electronic and optical properties of the lanthanide complexes. The most widely used successful methods are MNDO,^{9, 10} AM1,¹¹ PM3,^{12, 13} RM1¹⁴ and PM6.¹⁵ In these models, the programme is implemented in MOPAC where Ln(III) ion was replaced by the coulomb potential represented by a +3 point charge, superimposed on a repulsive radial potential of the form $\exp(-ar)$, where a effectively attributes a size to the combined spherical potential, preventing the ligand atoms from collapsing towards the Ln(III) ion. Simultaneously, the three lanthanide electrons are set into the unoccupied orbitals of the ligands, and are then slightly polarized towards the lanthanide ion. The success of the sparkle model can be ascribed to the fact that the bond between the Ln(III) ions and ligands are typically electrostatic in nature. Simas (1997) and co-workers¹⁶ developed a method to obtain the UV-spectra of the complexes due to the ligands by replacing the lanthanide ion by a point charge +3, followed by ZINDO¹⁷ calculation. The same workers (2004)¹⁸ upgraded the Sparkle model by introducing Gaussian functions to the expression which computes the core-core energy. However, the upgraded Sparkle model with full proficiency was announced in 2005 with an enhanced parameterization for Eu(III), Gd(III) and Tb(III) within AM1.¹⁹ At that time the Sparkle model was applied to alkali and alkaline earth complexes.^{20, 21} Afterwards, the Sparkle model was extended to all other Ln(III) ions within AM1,²²⁻²⁴ PM3,²⁵ and PM6.^{26, 27} Seitz and Alzakhem thoroughly studied the accuracy of the Sparkle model of over 650 lanthanide complexes and found them, especially Sparkle/AM1 model, amazingly accurate for the important middle lanthanide ions [Eu(III), Gd(III) and Tb(III)].

CONCLUSION

In conclusion, during the passage of time, the Sparkle model has been upgraded and has been successfully applied to numerous research based problems, such as the study of energy transfer in Ir(III)/Eu(III) dyads,²⁸ modeling metal organic frameworks (MOFs),²⁹ light conversion devices of Tb(III),³⁰ and other problems.

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