Journal of Chemistry and Chemical Sciences, *Vol.7(11), 1049-1051, November 2017* *ISSN 2229-760X (Print)*
(An International Research Journal), *www.chemistry-journal.org* *ISSN 2319-7625 (Online)*

Spectroscopic and Computational Studies of the Lanthanide Complexes

Wakeel Ahmed Dar[1] and Ruqiya Bhat[2]

[1]Department of Chemical Sciences,
Jamia Millia Islamia, New Delhi-110025, INDIA.
[2]Department of Physics,
University of Kashmir, Srinagar (J&K)-190006, INDIA.
email: Chemistakeel@gmail.com

(Received on: October 10, 2017)

ABSTRACT

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) 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: Lanthanide complexes, Sparkle model.

INTRODUCTION

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.[1, 2] 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 crystallography[3], NMR[4] and fluorescence spectroscopy.[5] 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 optoelectronics[3] and as luminescent labels in bio-immunoassays.[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]

Perspective

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] RM1[14] 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 $\exp(-\alpha r)$, where α 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-workers [16] 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 ZINDO[17] 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)]. Indeed, 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] modelling metal organic frameworks (MOFs),[29] light conversion devices of Tb(III),[30] and other problems.

CONCLUSIONS

The geometry of the lanthanide complexes are optimized using Sparkle models and the resulting parameters are utilized for determining the photophysical parameters: Judd–Ofelt intensity parameters, radiative parameters. The theoretical energy of the excited singlet and triplet states are calculated using configuration interaction single (CIS) based on the intermediate neglect of differential overlap/ spectroscopic (INDO/S) method,[31,32] implemented in the ZINDO program,[33] for the ground state geometry obtained using Sparkle model.

REFERENCES

1. K. Binnemans, *Handbook on the physics and chemistry of rare earths*, 35, 107-272 (2005).
2. F. Arnaudneu, *Chemical Society Reviews*, 23, 235-241 (1994).
3. Z. Ahmed and K. Iftikhar, *Inorg. Chem.*, 54, 11209-11225 (2015).
4. M. Irfanullah and K. Iftikhar, *J. Photochem. Photobiol., A*, 224, 91-101 (2011).
5. R. Ilmi and K. Iftikhar, *J Coord Chem*, 65, 403-419 (2012).
6. M. Sy, A. Nonat, N. Hildebrandt and L. J. Charbonniere, *Chem. Commun. (Cambridge, U. K.)*, 52, 5080-5095 (2016).
7. J.-C. G. Bunzli, *Coord. Chem. Rev.*, 293-294, 19-47 (2015).
8. A. V. M. de Andrade, N. B. da Costa Jr, A. M. Simas and G. F. de Sá, *Chem Phys Lett*, 227, 349-353 (1994).
9. M. J. S. Dewar and W. Thiel, *Journal of the American Chemical Society*, 99, 4907-4917 (1977).
10. M. J. S. Dewar and W. Thiel, *Journal of the American Chemical Society*, 99, 4899-4907 (1977).
11. P. Winget, A. H. C. Horn, C. Selçuki, B. Martin and T. Clark, *Journal of Molecular Modeling*, 9, 408-414 (2003).
12. J. J. P. Stewart, *Journal of Computational Chemistry*, 10, 209-220 (1989).
13. J. J. P. Stewart, *Journal of Computational Chemistry*, 10, 221-264 (1989).
14. G. B. Rocha, R. O. Freire, A. M. Simas and J. J. Stewart, *J Comput Chem*, 27, 1101-1111 (2006).
15. J. J. P. Stewart, *Journal of Molecular Modeling*, 13, 1173-1213 (2007).
16. A. V. M. de Andrade, N. B. da Costa Jr, O. L. Malta, R. L. Longo, A. M. Simas and G. F. de Sá, *Journal of Alloys and Compounds*, 250, 412-416 (1997).
17. M. C. Zerner, *ZINDO Manual; QTP, University of Florida: Gainesville, FL*, (1990).
18. G. B. Rocha, R. O. Freire, N. B. Da Costa, Jr., G. F. De Sa and A. M. Simas, *Inorg Chem*, 43, 2346-2354 (2004).
19. R. O. Freire, G. B. Rocha and A. M. Simas, *Inorg. Chem.*, 44, 3299-3310 (2005).
20. W. M. Faustino, O. L. Malta, E. E. Teotonio, H. F. Brito, A. M. Simas and G. F. de Sa, *J Phys Chem A*, 110, 2510-2516 (2006).
21. M. Galle, R. Puchta, J. R. van Eikema Hommes Nico and R. van Eldik, in *Zeitschrift für Physikalische Chemie*, vol. 220, p. 511 (2006).
22. R. O. Freire, N. B. da Costa Jr, G. B. Rocha and A. M. Simas, *J Organomet Chem*, 690, 4099-4102 (2005).
23. R. O. Freire, G. B. Rocha and A. M. Simas, *Chem Phys Lett*, 411, 61-65 (2005).
24. R. O. Freire, G. B. Rocha and A. M. Simas, *J. Comput. Chem.*, 26, 1524-1528 (2005).
25. R. O. Freire, G. B. Rocha and A. M. Simas, *Chem Phys Lett*, 425, 138-141 (2006).
26. R. O. Freire and A. M. Simas, *J. Chem. Theory Comput.*, 6, 2019-2023 (2010).
27. M. Seitz and N. Alzakhem, *Journal of Chemical Information and Modeling*, 50,217-220 (2010).
28. D. Sykes, I. S. Tidmarsh, A. Barbieri, I. V. Sazanovich, J. A. Weinstein and M. D. Ward, *Inorganic Chemistry*, 50, 11323-11339 (2011).
29. B. Rezaei, N. Askarpour and H. Hadadzadeh, *Electroanal*, 23, 1029-1037 (2011).
30. S. Biju, M. L. P. Reddy and R. O. Freire, *Inorganic Chemistry Communications*, 10, 393-396 (2007).