Int. J. Chem. Sci.: 6(3), 2008, 1606-1611

ELECTRONIC SPECTRAL PARAMETERS OF DOPED Er^{+3} ION WITH SOME ACIDIC LIGANDS IN ALCOHOLIC MEDIUM AT DIFFERENT pH VALUES

JOTI BALLA* and SUSHMA JAIN

Research Laboratory, Chemistry Department, Government Dungar College,
BIKANER – 334001 (Raj.) INDIA.

ABSTRACT

Absorption spectra of alcoholic solution of the Er^{+3} ion with saturated acidic ligands, viz, NA, SA, S'A, IAA and IBA have been recorded and the various parameters, viz, Judd–Ofelt parameter (T_λ), Slater–Condon (F_K), Lande's ($\zeta 4f$), Racah's (E_K), oscillator strength (P), nephelauxetic ratio and bonding parameter ($b^{1/2}$) have been studied.

Key words: Nicotinic acid, Stearic acid Europium, Sulphanilic acid, Indole acetic acid, Indole butyric acid, Electronic spectra.

INTRODUCTION

Considerable progress has been made in interpreting the optical spectra of Er^{+3} ion embedded in crystalline solids, in different solution media, in glass and in garnets[1].

Judd and Ofelt theory is the most widely applied method for analysing the spectroscopic properties of rare–earth in different hosts[2]. The absorption spectra of the Ln–ion in aqueous, acidic and molten solution have been reported. They correlated the experimental and theoretical energies and intensities.[1]

In persuation with earlier studies on the electronic spectra of Ln(III) cations in different complex environments, we are reporting the spectral characterization of various Er^{+3} systems in alcoholic medium involving acidic ligands, on the basis of Judd–Ofelt, Slater–Condon and other theories, which has used by earlier workers.[3]

---

* Author for correspondence

EXPERIMENTAL

To the saturated solution of nicotinic acid (NA), stearic acid (SA), sulphanilic acid (SA), indole acetic acid (IAA) and indole butyric acid (IBA), 0.014 M of Er $(NO_3)_3 . 5H_2O$ with 99.90% purity (purchased from friends agency, Bikaner) was added.

Absorption spectra of Er^{+3} complexes systems were recorded by using spectrophotometer (Spectronic–20) in the visible–region. pH of the system was measured and adjusted at 1, 2.5 and 4.0, respectively by using digital pH–meter (Model–III E).

RESULTS AND DISCUSSION

The computed values of various spectral parameters have been tabulated in Table 1.

Electronic energy levels

The absorption spectra of the Er–complexes consists of eight bands ($^2H_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$' $^4F_{7/2}$, $^4H_{11/12}$, $^4F_{9/2}$' $^4I_{9/2}$ and $^4S_{3/2}$. A bathochromic effect was observed as compared to those of the free ion, which is indicative of nephelauxetic effect on the 4f–orbitals of Er^{+3} ion coordinated with different ligands.

Using the energy expression in the Taylor series and partial multiple regression method, various energy parameters i.e. Slater–Condon parameter (F_K), Lande parameters (ζ4f) and Racah parameter (E^K) were evaluated.[4]

The values of F_K and ζ4f for Er–complexes (Table 1) are smaller than the corresponding parameters for the free ion. This confirms that central metal ions 4f–orbital expands on complexation, which results in a decrease in inter-electronic repulsion and spiin orbit interaction.

The small r.m.s. deviation in energies from ± 15014.86 to ± 15099.01 was found for Er^{+3} ion, and it demonstrates a good agreement between observed and calculated energy levels and proves the validity of Slater-Condon equation.[5]

The values of nephelauxetic ratio was found less than unity ($\beta < 1$) in all complex systems and the positive values of bonding parameters ($b^{1/2}$) supports for the covalent bonding in M–L bond[6] in Er^{+3} complexes, which has been reported in Table 1.

Table 1. Slater-Condon (F_K), Racah (E^K) Lande (ξ4f), nephelauxetic (β), bonding parameters ($b^{1/2}$) and Judd - Often (T_λ) parameters for doped systems

pH Value	Spectral parameters Er^{+3} systems	F_2	F_4	F_6	% rF_2	β	$b^{½}$	E^1	E^2	E^3	ζ4f	$T_2 \times 10^9$	$T_4 \times 10^9$	$T_6 \times 10^9$
4.0	Er^{+3} – NA	431.034	66.785	7.118	0.601	0.994	0.055	6650.026	31.168	636.039	2470.099	0.355	0.226	0.106
4.0	Er^{+3} – SA	432.592	68.256	7.143	0.242	0.998	0.035	6705.318	30.869	640.843	2429.683	0.027	0.013	0.100
4.0	Er^{+3} – S'A	430.946	67.592	7.084	0.621	0.994	0.056	6662.536	30.862	638.535	2470.782	0.395	0.015	0.084
4.0	Er^{+3} – IAA	429.898	67.892	6.988	0.863	0.991	0.066	6640.546	30.571	640.313	2466.273	0.596	0.018	0.203
4.0	Er^{+3} – IBA	428.216	67.824	6.874	1.251	0.988	0.079	6600.377	30.318	640.844	2467.533	0.812	0.089	0.534
2.5	Er^{+3} – NA	431.943	66.844	7.168	0.391	0.996	0.042	6669.650	31.287	363.169	2469.401	0.334	0.005	0.045
2.5	Er^{+3} – SA	432.371	66.736	7.152	0.293	0.997	0.038	6666.659	31.358	637.154	2466.067	0.315	0.019	0.088
2.5	Er^{+3} – S'A	428.294	68.382	7.106	1.233	0.988	0.079	6667.026	30.321	635.036	2468.827	0.498	0.021	0.069
2.5	Er^{+3} – IAA	429.205	68.066	6.944	1.023	0.990	0.072	6629.917	30.402	640.845	2463.135	0.983	0.083	0.433
2.5	Er^{+3} – IBA	426.942	68.093	6.886	1.545	0.985	0.088	6600.109	30.096	638.884	2470.759	0.911	0.097	0.498
1.0	Er^{+3} – NA	432.482	68.074	7.138	0.267	0.997	0.037	6673.114	31.247	638.435	2470.692	0.270	0.007	0.145
1.0	Er^{+3} – SA	431.716	67.449	7.099	0.444	0.996	0.047	6668.173	31.007	639.080	2469.379	0.380	0.022	0.083
1.0	Er^{+3} – S'A	427.069	68.752	6.926	1.515	0.985	0.087	6626.869	29.921	639.206	2435.445	0.639	0.017	0.044
1.0	Er^{+3} – IAA	429.537	68.371	7.011	0.946	0.991	0.069	6655.264	30.389	639.968	2450.332	0.862	0.052	0.354
1.0	Er^{+3} – IBA	425.223	69.033	6.779	1.941	0.981	0.099	6587.114	29.509	648.138	2457.554	1.149	0.122	0.546

Spectral intensities

The absorption intensities, presented as Oscillator strength, were calculated from the expression.

$$f = 4.32 \times 10 \int \varepsilon(\nu)\, d\nu \qquad \ldots(1)$$

Where, $\in_{max}$ is molecular absorptivity and dν is the half–band width. Applying Judd–Ofelt theory to the measured intensities of the spectral lines, the Judd–Ofelt parameter (T_λ=T_2, T_4, T_6) were calculated. The r.m.s. deviation with respect to (P) oscillator strength is within the range of 5.101×10^{-7} to 23.848×10^{-7}. The small deviation for the calculated and observed (p) value suggests the validity of Judd–Ofelt equation for f–f transition.

The T_4/T_6 ratio value suggests the stereo environment around the Er^{+3} ion in the solution. The systems have been grouped into two categories (0.0504 to 0.1919) and (0.1920 to 0.3905). The complex system is in same category as a common symmetry around the central metal ion (Er^{+3}).

Hypersensitive transition

For Er^{+3} ion, $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition is the hypersensitive transition. It is an absolute magnitude of oscillator strength measure, that how sensitive a given transition is to the environment?

Table 2: The oscillator strength ($p \times 10^6$) for hypersensitive peak $^{2H}{}_{11/2}$ for Er^{+3} doped systems

pH Value	Er^{+3} Systems	$^2H_{11/2}$	
		$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
4	Er^{+3} – NA	5.73	5.32
4	Er^{+3} – SA	4.44	3.99
4	Er^{+3} – S'A	6.26	5.76

Cont…

pH Value	**Er^{+3} Systems**	**$^2H_{11/2}$**	
		$P_{exp} \times 10^6$	**$P_{cal} \times 10^6$**
4	Er^{+3} – IAA	9.42	8.83
4	Er^{+3} – IBA	14.29	12.99
2.5	Er^{+3} – NA	5.35	4.79
2.5	Er^{+3} – SA	5.20	4.71
2.5	Er^{+3} – S'A	7.85	7.24
2.5	Er^{+3} – IAA	17.27	15.17
2.5	Er^{+3} – IBA	16.20	14.37
1	Er^{+3} – NA	4.57	4.10
1	Er^{+3} – SA	6.12	5.63
1	Er^{+3} – S'A	9.90	9.08
1	Er^{+3} – IAA	14.87	13.07
1	Er^{+3} – IBA	19.85	17.93

Maximum interaction of metal ligand bonding and decrease in bond length have been observed with increase in basic character of ligands. In all the systems, oscillator strength (P) for hypersensitive transition has been increased with basicity of ligands. The observed values for this transition have been reported in Table 2.

ACKNOWLEDGEMENTS

Authors are thankful to Department of chemistry, Dungar College, Bikaner and Mrs. A. R. Neela Dixit and Mr. M. R. Yadav, Delhi Science Library, Delhi University for their supportive attitude during research survey.

REFERENCES

1. S. V. J. Lakshman and C. K. Jayasankar, Spectrochim. Acta, **40A,** 695–704 (1984).
2. Huaishan Wang, Guodong Qian, Zhiyu Wang and Minquan Wang, Spectrochim. Acta Part, **A–62,** 146 (2005).
3. Sushma Jain and G. K. Joshi, Asian J. Chem., **13**, (2001).
4. S. V. J. Lakshman and L. Rama Moorthy, J. Less–common Metal, **112,** 109 (1985).
5. Atul Arora, Anu Sharma, Kirty Mathur and R. P. Mathur, Asian J. Chem., **15,** (2003).
6. B. Keshavan and P. G Chandra Shekara, J. Indian Chem, Soc., **76,** 182–184 (1999).

Accepted : 18.03.2008