

Study of Energy Parameters of Some Er(III) Doped Systems

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An electronic spectral investigation of ten Er(III) doped systems has been attempted to evaluate electronic spectral parameters, viz., Slater-Condon (F_k), Racah (E^k), Landé (ζ_{4f}) and nephelauxetic ratio (β) in order to examine variation in these electronic spectral parameters as a result of change in ligand.

INTRODUCTION

The electronic spectra of lanthanides have earned much interest in the past.¹⁻⁴ Rare earths have acquired unique position in the field of biology and medicine.^{5, 6} In continuation with earlier studies, in the present report an electronic spectral investigation on Er(III) doped systems has been undertaken. In the doped system⁷, a constant amount of metal salt has been added to the saturated solution of ligand. In our study we have studied ten Er(III) doped systems. The systems include—diacetyl monoxime, α -benzoin oxime, ascorbic acid, aspartic acid, β -alanine, L-leucine, L-proline, arginine, L-cystine and hippuric acid as ligands. Er(III) ion yield eight bands in the 400–820 nm region. From the electronic spectra of Er(III) doped systems, Slater-Condon (F_2 , F_4 and F_6) parameter, Racah (E^1 , E^2 and E^3) and Landé (ζ_{4f}) parameter have been computed by using partial and multiple regression method.^{8, 9}

EXPERIMENTAL

The various saturated solutions at room temperature (35°C) in 50% ethanol were prepared for the ligands including aspartic acid, β -alanine, ascorbic acid, L-cystine, L-proline, arginine, hippuric acid, L-leucine, diacetyl monoxime and α -benzoin oxime (S.D. Fine Chem.) 0.05 g of $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% purity, Aldrich) were added to 10 mL of each saturated solution. The solution spectra of these systems recorded by using standard spectrophotometer (Systronics-106) in the 400–850 nm region. The calculation of the parameters done by using partial and multiple regression method.⁸

RESULTS AND DISCUSSION

The energies of the bands observed have been recalculated by applying the Slater Condon-Landé equation. The comparison of the observed and the calculated values of various energy levels have been tabulated in Tables 1 and 2. It shows that average rms deviations (σ) of the order of 15.34–55.93 cm^{-1} which

TABLE-1
COMPUTED VALUES OF ENERGIES (cm^{-1}) OF THE VARIOUS BANDS FOR Er(III) DOPED SYSTEMS

Levels	Diacetyl monoxime		α -Benzoin oxime		Aspartic acid		β -Alanine		Arginine	
	E_{obs} (cm^{-1})	E_{cal} (cm^{-1})	E_{obs} (cm^{-1})	E_{cal} (cm^{-1})	E_{obs} (cm^{-1})	E_{cal} (cm^{-1})	E_{obs} (cm^{-1})	E_{cal} (cm^{-1})	E_{obs} (cm^{-1})	E_{cal} (cm^{-1})
$^2\text{G}_{9/2}$	24610	24621.47	24605	24638.58	24620	24641.91	24580	24615.25	24570	24608.56
$^4\text{F}_{3/2}$	22518	22511.94	22520	22506.85	22520	22522.78	22520	22496.64	22500	22508.75
$^4\text{F}_{5/2}$	22223	22209.66	22220	22176.51	22271	22177.39	22223	22194.64	22271	22196.58
$^4\text{F}_{7/2}$	20500	20529.70	20490	20541.35	20530	20560.19	20490	20526.16	20491	20528.72
$^2\text{H}_{11/2}$	19267	19283.68	19193	19240.15	19193	19239.08	19194	19248.41	19230	19272.86
$^4\text{S}_{3/2}$	18360	18351.76	18538	18324.18	18330	18356.38	18350	18303.26	18325	18363.91
$^4\text{F}_{9/2}$	15350	15313.50	15350	15321.46	15340	15327.59	15320	15315.17	15350	15307.52
$^4\text{I}_{9/2}$	12370	12363.99	12380	12361.67	12380	12364.24	12370	12350.20	12380	12358.83
	$\sigma = 15.34 \text{ cm}^{-1}$		$\sigma = 34.26 \text{ cm}^{-1}$		$\sigma = 40.89 \text{ cm}^{-1}$		$\sigma = 34.38 \text{ cm}^{-1}$		$\sigma = 42.02 \text{ cm}^{-1}$	

$\sigma =$ rms deviation

TABLE-2
COMPUTED VALUES OF ENERGIES (cm^{-1}) OF THE VARIOUS BANDS FOR Er(III) DOPED SYSTEMS

Levels	Hippuric acid		L-Leucine		L-Proline		L-Cystine		Ascorbic acid	
	$E_{\text{obs}} (\text{cm}^{-1})$	$E_{\text{cal}} (\text{cm}^{-1})$	$E_{\text{obs}} (\text{cm}^{-1})$	$E_{\text{cal}} (\text{cm}^{-1})$	$E_{\text{obs}} (\text{cm}^{-1})$	$E_{\text{cal}} (\text{cm}^{-1})$	$E_{\text{obs}} (\text{cm}^{-1})$	$E_{\text{cal}} (\text{cm}^{-1})$	$E_{\text{obs}} (\text{cm}^{-1})$	$E_{\text{cal}} (\text{cm}^{-1})$
${}^2\text{G}_{9/2}$	24540	24615.72	24605	24658.92	24590	24622.76	24580	24599.95	24570	24619.13
${}^4\text{F}_{3/2}$	22500	22473.42	22520	22495.29	22510	22513.00	22509	22505.05	22520	22490.83
${}^4\text{F}_{5/2}$	22223	22170.99	22201	22193.89	22242	22206.59	22280	22183.36	22220	22201.95
${}^4\text{F}_{7/2}$	20450	20489.54	20449	20519.04	20490	20545.96	20450	20525.45	20480	20514.67
${}^2\text{H}_{11/2}$	19193	19283.00	19193	19266.16	19193	19249.28	19230	19266.88	19194	19261.26
${}^4\text{S}_{3/2}$	18300	18323.52	18380	18282.18	18380	18317.35	18320	18376.77	18358	18289.62
${}^4\text{F}_{9/2}$	15350	15304.33	15350	15321.28	15350	15326.50	15350	15300.80	15320	15312.70
${}^4\text{I}_{9/2}$	12400	12380.38	12400	12372.56	12370	12351.54	12370	12357.07	12380	12353.73
	$\sigma = 52.89 \text{ cm}^{-1}$		$\sigma = 55.93 \text{ cm}^{-1}$		$\sigma = 41.00 \text{ cm}^{-1}$		$\sigma = 53.17 \text{ cm}^{-1}$		$\sigma = 42.97 \text{ cm}^{-1}$	

σ = rms deviation

TABLE-3
COMPUTED VALUES OF VARIOUS ELECTRONIC SPECTRAL PARAMETERS FOR Er(III) DOPED SYSTEMS

S. No.	Er(III) doped systems	F ₂	F ₄	F ₆	F ₄ /F ₂	F ₆ /F ₂	E ¹ (cm ⁻¹)	E ² (cm ⁻¹)	E ³ (cm ⁻¹)	ζ _{4f} (cm ⁻¹)	β	b ^{1/2}
1.	Diacetyl monoxime	435.89	65.01	7.3417	0.1491	0.01684	6691.99	32.472	633.80	2409	0.9868	0.0812
2.	α-Benzoin-oxime	432.38	65.40	7.1678	0.1512	0.01657	6636.28	31.810	634.03	2412	0.9789	0.1027
3.	Aspartic acid	431.89	65.83	7.0851	0.1524	0.01640	6625.09	31.550	636.59	2400	0.9778	0.1053
4.	β-Alanine	434.21	64.65	7.2910	0.1489	0.01679	6658.60	32.364	631.84	2422	0.9830	0.0921
5.	Arginine	435.37	65.27	7.2854	0.1499	0.01673	6682.30	32.280	635.18	2399	0.9857	0.0845
6.	Hippuric acid	434.92	64.99	7.3780	0.1494	0.01696	6692.02	32.400	631.05	2414	0.9846	0.0877
7.	L-Leucine	433.97	64.71	7.3560	0.1491	0.01695	6672.83	32.360	629.58	2435	0.9825	0.0935
8.	L-Proline	434.02	64.72	7.2482	0.1491	0.01669	6649.33	32.280	632.96	2422	0.9826	0.0932
9.	L-Cystine	434.99	65.57	7.2443	0.1507	0.01665	6677.91	32.100	636.40	2389	0.9848	0.0871
10.	Ascorbic acid	435.10	64.37	7.3770	0.1479	0.01695	6677.43	32.620	630.16	2430	0.9851	0.0863
11.	Free ion	441.68	68.32	7.4900	0.1547	0.01690	6855.00	32.126	645.57	2471	-	-

indicate good results even though the radial eigen function has been assumed to be hydrogenic and also best fit for the partial regression method.^{8,9} The red shifts in all the energy bands from that of free ion support the complexation.¹⁰

The various energy parameters F_K ($K = 2, 4, 6$), *i.e.*, Slater-Condon parameter, β -Nephelauxetic ratio, ζ_{4f} Landé parameter and $b^{1/2}$ bonding parameter (extent of covalency) have been reported in Table-3. In the present system, decrease in F_2 , E^K and ζ_{4f} indicate decrease in interelectronic repulsion and spineorbital interaction which suggests expansion of the central metal ion orbital on complexation and is in accordance with the theory of $f \leftrightarrow f$ transition reported earlier.¹⁻⁴

The value of F_4/F_2 for Er(III) doped systems ranges from 0.1479 to 0.1524. This value is larger than that calculated by using Hartree and Fock method (≈ 0.138) but it nearer to the value for the free ion (0.1513)^{11, 12}. The same trend has been observed for the ratio F_6/F_2 .

The values of nephelauxetic ratio $\beta < 1$ and bonding parameter $b^{1/2}$ indicate covalent bonding in Er(III) doped systems. The small value of $b^{1/2}$ and little variation in it suggest that 4f orbitals are very slightly involved in the bonding of lanthanide complexes. Since lanthanide complexes are kinetically less stable, so instead of making complexes, we have used lanthanide ion doped systems for spectral studies.

ACKNOWLEDGEMENTS

The authors are thankful to Sh. S.L. Jain, Vice Principal and Dr. P.C. Tater, Head, Department of Chemistry, for providing necessary facilities. One of the authors, R.S. Verma, is highly thankful to UGC for awarding him teacher fellowship. The authors also thank Dr. R.P. Mathur and Dr. Kirty Mahur for helpful discussion and suggestions.

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