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RESEARCH ARTICLE

Variation in Electronic Spectral Parameters of Nd(III) and Er(III) with Respect to Ionic Strength of the Medium

SHUBHA MISHRA[1], SNEHA WANKAR[2],
PREETI VISHWAKARMA[2], S.K.GHOSH[1] and S.N.LIMAYE[2]

[1]School of Studies in Physics, Vikram University, Ujjain (M.P.), India
[2]Department of Chemistry, Dr. H. S. Gour University, A Central University,
Sagar (M.P.) 470003, India
snl222@yahoo.co.in

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Abstract: The 4*f* shells are known to have core like structure and were considered as least perturbed by changes around metal ion surroundings, however, there are evidences that the 4*f*-shells partially involved direct ligand interaction. Keeping in view this observation a systematic studies on the electronic spectral and radiative properties of [Ln(III).L] where L = HEDTA, EDTA and CDTA, in mediums of increasing ionic strengths (μ = 1.0 to 2.5) of $NaClO_4$ have been undertaken with a view to observe the effect of increased compactness of the medium on the electronic spectral parameters of Ln(III) ion. Variations in Oscillator strength, Judd-Ofelt parameter and radiative parameters have been examined as a function of ionic strength of medium, to explore their interdependence.

Keywords: Judd-Ofelt parameters, Transition probability, Branching ratio, Radiative life time

Introduction

The study[1] of the spectral parameters of Ln(III) especially Nd(III) and Er(III) has been of great interest in order of the co-ordination behavior[2] of Ln(III) ions. As regards to their ground term the two cations exhibit similar S and L terms with only difference in the J term only. The main features of the energy level structure are now well established in a wide range of host materials[3]. Ln(III) doped studies in different environments[4,5] have been most widely reported where the tapping of suitable relaxations are being used for Laser action at room temperature. Since, Neodymium Laser can operate with high efficiency[6]. According to Laporte's parity selection rule it states that *f*–*f* transitions are forbidden by the ED mechanism. But when the lanthanide ion is exposed under the influence of a ligand-field, the non-centrosymmetric interactions allow the mixing of electronic states of opposite parity into the 4*f* wave functions, which however, relaxes the selection rules and the transition becomes partially allowed; it is called an induced (or forced) electric dipole transition[7].

The Present work deals with the evaluation of spectral and radiative parameters of Nd(III) and Er(III) ions in HEDTA, CDTA and EDTA complexing agent environments within medium of varied ionic strength of $NaClO_4$. The Judd-Ofelt theory[8] has been applied to evaluate the oscillator strengths (P) and the symmetry parameters (τ_λ) and the radiative properties of Nd(III) and Er(III) ion in different environments. The transition probabilities (A_T) for intermediate transitions, relaxation timings T_R have been examined and the variations in the evaluated parameters have been observed and discussed in light of changes in the dielectric of the medium. Judd–Ofelt theory[9] defines that the susceptibility of the 4*f*- orbital and their electronic interaction in different environment are governed by the set of three intensity parameters $\Omega\lambda$ (λ= 2, 4, 6) (Tensor Operators) the susceptibility of the 4*f*- orbital and their electronic interaction in different environment indicative of direct Ln-ligand interaction, changes in symmetry and the nature of the environment around *4f*-Ln(III) ion.

Experimental

Experimental solution of metal ions were prepared by direct weighing, standards metal solution were prepared by dissolving their nitrates in double distilled water or directly in required volume of the experimental sets (or oxides in minimum quantity of perchloric acids). Preparation of five sets of solution as follows (Table 1):

Table 1. Preparation of sets

Ln (III)	Ligand	$NaClO_4$	Water	Ionic strength, μ
0.5M × 1 mL	0.5M × 1 mL	5M × 1.0 mL	3.0 mL	0.999
0.5M × 1 mL	0.5M × 1 mL	5M × 1.5 mL	2.5 mL	1.416
0.5M × 1 mL	0.5M × 1 mL	5M × 2.0 mL	2.0 mL	1.833
0.5M × 1 mL	0.5M × 1 mL	5M × 2.5 mL	1.5 mL	2.249
0.5M × 1 mL	0.5M × 1 mL	5M × 3.0 mL	1.0 mL	2.667

Spectral analysis

The electronic spectra were recorded on a Systronics 2201 UV-Vis Double Beam Spectrophotometer. Cuvettes of 1 cm path length were used to keep reference / standard solution. The spectral recordings were for Neodymium and Erbium element has been recorded in the λ range of 330 nm–900 nm, 350 nm–700 nm respectively. The spectral recordings were then used for evaluation of electronic- spectral parameters using standard equations[10]. Judd-Ofelt parameter and radiative parameters for the fluorescent levels of Nd(III) and Er(III) ions at different ionic strength of $NaClO_4$ have been reported in Table 2. (Only the hypersensitive transitions have been reported for brevity, however, the values for other assignments may be obtained from author if desired).

Results and Discussion

It is observed from the spectral recordings (Figure 1 & 2) it may be stated that the first order interaction of Ln(III) with its environments is evident from shift in spectral band shapes, their size, position and intensity. These features are infact the outcome of the [Ln(III)-L] interaction leading to variations in their microscopic features-related with oscillator strengths, symmetry parameters and the relative excitation and relaxation in the intermediate levels leading to actual photonic emission.

The oscillator strength by definition is the susceptibility of specific electronic assignment to the environment. Physically it is a measure of the strength of transition equal to the ratio of[11] actual transition intensity in the aqueous phase to that of intensity radiated in ligand mediums by one electron oscillating harmonically in three directions express by three tensors proposed by Judd-Ofelt[8,12]. Thus, the changes in environment cause a change in the frequency of the oscillating 4*f*-electron thus reflecting changes in their response towards the induced electrical and magnetic dipoles imposed by encompassing radiation. These changes are often larger for the hypersensitive transitions and are significant enough to cause change in the oscillator strengths values.

A perusal of the oscillator strengths values for hypersensitive transitions for the two metal ions in three different ligand environments at five varied ionic strengths of $NaClO_4$ (Table 2) exhibit a general increase in the oscillator strengths values with increased ionic strength. This increase in oscillator strengths is a positive evidence of increased environmental perturbation due to increased compactness of the medium. The increase in perchlorate percentage result into concomitant increase in the charge dielectric of the metal ion surrounding causing an increase in oscillator strengths values.

Table 2. Variation in the Oscillator strength values for [Ln(III).L] complexes with varied ionic strengths of $NaClO_4$. Nd(III)-$^4I_{9/2}$, Er(III)-$^4I_{15/2}$

Assignment	Energy, cm^{-1}			Nd(III)	Oscillator Strength (P x 10^{-5})		
		Ligand	$\mu = 0.99$	$\mu = 1.41$	$\mu = 1.83$	$\mu = 2.2$	$\mu = 2.66$
$^4G_{5/2}$	17300	HEDTA	11.1508	18.4273	18.9151	21.4857	26.4535
		EDTA	9.94162	10.4693	11.5085	12.0959	12.9870
		CDTA	8.65056	9.65057	10.1208	10.7608	11.6479
$^4G_{7/2}$	19100	HEDTA	2.16290	2.97486	3.23652	3.50156	3.61005
		EDTA	2.01406	2.04994	2.06659	2.21198	.2.36477
		CDTA	1.39883	1.92251	2.00174	2.01828	2.15481
				Er(III)	Oscillator Strength (P x 10^{-5})		
$^2H_{11/2}$	19150	HEDTA	1.02805	1.04480	1.30667	1.63809	2.50051
		EDTA	3.87349	3.96226	3.97400	4.70701	5.18365
		CDTA	1.58507	1.81523	1.99109	2.28051	2.50647
$^4F_{7/2}$	20450	HEDTA	0.47490	0.55066	0.63882	0.72511	0.77066
		EDTA	1.60996	1.85199	2.14565	2.41590	2.55709
		CDTA	1.07396	1.17508	1.26883	1.29704	1.32335

Simultaneously, the Carnall's proposal[11] for T_λ parameter is $T_\lambda \sim < r^{t+1} >^2 . R^{-2t-2}$ where for $\lambda = 2$, t = 1 and 3; for $\lambda = 4$, t = 3 and 5 and for $\lambda = 6$, t = 5 and 7 expects a general trend $T_2 < T_4 < T_6$ for T_λ parameters where the experimental values obtained for the present case are in agreement with the theoretical range. Amongst τ_λ parameter τ_2 is concerned with direct metal ligand interaction whereas τ_6 exhibit the change in symmetry associated with metal ion surroundings. The general sequence obtained for the present set of complexes (Table 3) justify the smaller values of τ_2 due to lesser Ln(III)-L interaction and greater changes in τ_6 symmetry due to disruption of larger hydration zones associated with Ln(III) ions.

Also, variation profiles for the oscillator strengths values with respect to ionic strength have been plotted (Figures 3-6), where most the slopes have significant linear profile with R^2 (regression) values very near to 0.9 and 0.99. The ratio τ_2/τ_6 a semi empirical parameter indicative of a relative involvement of ionic charges and symmetry parameters exhibit a sequence Nd(III) < Er(III) which may be on account of increased ionic potential for Er(III) associated with Ln(III) contraction[13]. The two cations undertaken for studies are similar in both $4f^q$, S and L values, however, differ in their J terms. The observed difference in the spectral parameters is a difference expected on account of their ground term stability their concomitant[14] effect on the susceptibility and population of the excitation levels in the common external field. It is interesting to observe a drift in the bonding pattern from electronic to covalent electronic from Nd(III) to Er(III). The intermediate transition levels and their relative responses (especially for hypersensitive transition bands) have been tabulated (Table 4) for their transition probabilities, their branching ratio and the relaxation timings. The values exhibit a gradual change with respect to ionic strength of the medium. The drifts in relaxation timings serve as an evidence for the effective influence of environment of the electronic spectral parameters.

Table 3. Variation in the Judd-Ofelt parameters (τ_2 and τ_6) for [Ln(III).L] systems with varied ionic strengths of $NaClO_4$

Ligand	Nd(III)					Er(III)				
μ	μ=0.99	μ =1.41	μ =1.83	μ =2.25	μ =2.6	μ =0.99	μ =1.41	μ =1.83	μ =2.25	μ =2.6
HEDTA										
τ_2	16.9	22.0	19.7	19.5	19.7	13.0	13.5	14.4	13.2	9.90
τ_6	28.2	28.1	28.1	28.1	28.1	18.3	30.3	22.3	35.5	15.8
τ_2/τ_6	0.59	0.78	0.70	0.69	0.70	0.71	0.44	0.64	0.37	0.62
EDTA										
τ_2	21.6	18.2	20.3	22.0	20.7	13.2	13.1	13.1	13.1	13.1
τ_6	28.2	28.2	28.2	28.2	28.2	13.6	14.4	14.3	15.4	13.2
τ_2/τ_6	0.76	0.64	0.71	0.78	0.73	0.96	0.90	0.91	0.85	0.99
CDTA										
τ_2	17.7	20.4	22.5	21.6	21.5	13.3	12.8	13.2	13.0	12.8
τ_6	23.2	23.2	23.1	23.1	23.2	17.3	37.2	34.4	35.7	37.1
τ_2/τ_6	0.76	0.34	0.38	0.36	0.346	0.76	0.88	0.97	0.93	0.92

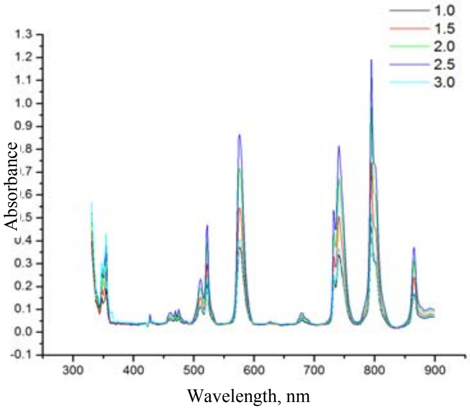

Figure 1. Absorption spectra of Nd(III)

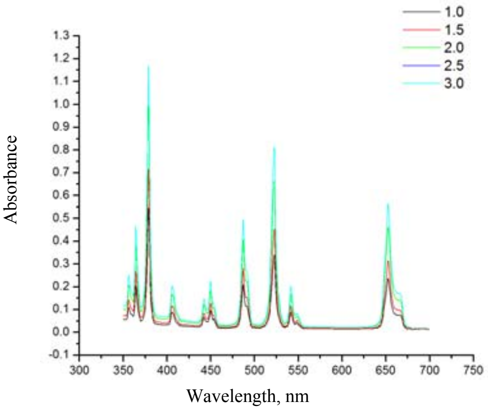

Figure 2. Absorption spectra of Er(III)

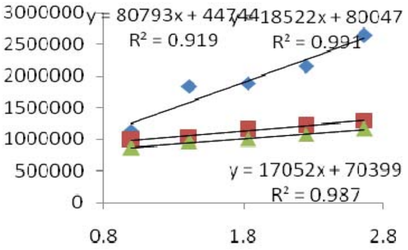

Figure 3. Nd(III) $^4G_{5/2}$

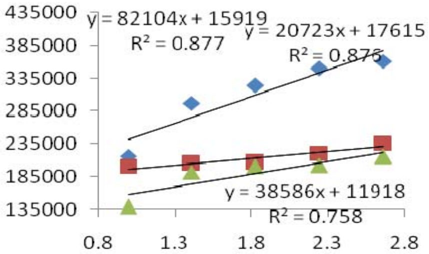

Figure 4. Nd(III) $^4G_{7/2}$

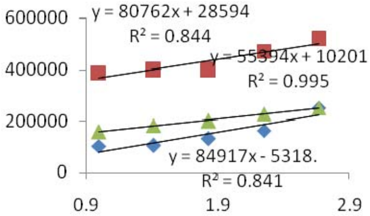

Figure 5. Er(III) 2H11/ 2

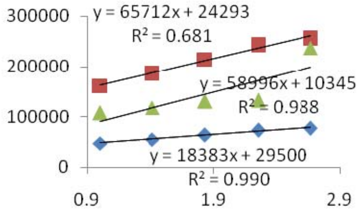

Figure 6. Er(III) 4F7/ 2

Table 4. Variation in the Total Transition probability (AT) for [Ln(III).L] systems with varied ionic strengths of $NaClO_4$

Assignment	Energy, cm^{-1}			Nd(III)	Total Transition probability (A_T)		
		Ligand	$\mu = 0.99$	$\mu = 1.41$	$\mu = 1.83$	$\mu = 2.25$	$\mu = 2.66$
$^4G_{5/2}$	17300	HEDTA	15796.9	21177.2	20852.6	18105.7	20138.1
		EDTA	20359.4	16753.2	18422	21307.4	17741.4
		CDTA	18649.5	16685.3	22053.9	20529.8	19559.6
$^4G_{7/2}$	19100	HEDTA	12636.3	16731.8	16404.3	14456.7	16095.0
		EDTA	16124.7	13374.6	14635.1	16822.8	14161.9
		CDTA	14726.6	13207.4	17277.5	16112.5	15385.0

Conclusion

The involvement of ionic charges and symmetry parameters exhibit a sequence Nd(III) < Er(III) which may be on account of increased ionic potential for Er(III) associated with Ln(III) contraction. It has been conclude that that the electronic spectral parameters of Ln(III) ion got perturb in different chemical environment. The 4*f* orbital shows the change in the core like behavior because of the exposing in different environment.

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