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E: ISSN NO.: 2349-980X **Shrinkhla Ek Shodhparak Vaicharik Patrika**

Calculation of Electrostatic, Spin-Orbit Coupling and Configuration-Interaction Parameters For Ln (III) Bioactive System in UV-Visible Region

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Abstract

The free-ion energy bands of the Nd^{3+} ion have been determined from their UV Visible absorption spectra in alcoholic solution at room temperature. All the spectra of the rare earth ions arise from the internal configurational transitions within the 4f shell. In the free ion these transitions are forbidden by the parity rule of the electric dipole transitions In trivalent lanthanides, the free ion is only slightly perturbed by the electric field of the solution matrix. In solution spectra the crystal-field components are usually not resolved, so the observed absorption bands can only be characterized in terms of the free-ion levels involved. Energy-level assignments were determined by comparison with aqua ion spectra and on the basis of calculated and observed band intensities.

Sufficient numbers of assignments were made to justify inclusion of the effects of configuration interaction in the calculation of the energy-level parameters. Variation of the electrostatic, spin-orbit coupling and configuration-interaction parameters for lanthanide is examined. The present work reports the evaluation of various spectroscopic parameter for Nd^{3+} ion with 2HQ in alcoholic (Et-OH) and micellar medium viz (TX-100, HTAB and SDS). The spectroscopic analysis was done with the help of the Judd-Ofelt theory.

Keywords: Quinoline Derivatives, Nd^{3+} ion, Spin-orbit Coupling and Configuration-interaction Parameters.

Introduction

Theoretical interpretation of trivalent lanthanide absorption spectra has been correlate the experimentally observed energy levels with those calculated by diagonalization of the complete energy matrices of the appropriate f^N electron configurations[8-14]. In the present paper, we have examined the validityof the intensity relationships deduced by Judd and Ofelt. The energies and intensities of the absorption bands have been studied for the Nd^{3+} ion in different mediam. The observed spectral intensities were analyzed using the eigenvectors obtained from the energy-level calculation employed by Judd[15].

In this treatment of Nd^{3+} ion we obtain good agreement between theory and experiment for Nd^{3+} ions in different solution in terms of three parameters, T_λ).(λ=2, 4, 6). Our particular interest is in the behavior of these parameters under the influence of different medium and in the relationship that they bear to each other for lanthanides.

Aims of Study

The formation of a coloured complex between the metal and coloured or colourless ligand is the basis for the development of spectrophotometric studies. Investigations for lanthanide complexes in different medium particularly in micellar medium viz (TX-100, HTAB and SDS) and there is also a need to correlate different parameters such as intensity, energy or interaction and bonding parameters. The intensity parameters are Oscillator Strength ($Px10^6$) and Judd - Ofelt parameters (T_λ), Energy or Interaction perameters areSlater-Condon Parameters (F_2, F_4 and F_6) Lande Parameters or spin-orbit interaction parameters (ζ_{4f}) Racah Parameters or Energy parameters (E^1, E^2 and E^3).

Review of Literature

Spectroscopic properties of Ln(III) ions have been reported by Judd and Ofelt[1-2]. The Nd(III) ions have special spectroscopic properties

because the 4f valence shell has shielded from the environment around the lanthanide ion by higher lying closed shells[3]. Calculation of Judd-Ofelt parameters (T_λ) in some Nd(III) complexes has been carried out by using statistical method by G. K. Joshi[4] The solution and reflection spectra of some neodymium complexes have been investigated by Sinha S. P [5].Effect of solvent on sensitivity of hypersensitive transition for Ln (III) complexes with quinoline derivatives in doped system have been carried out by jatolia et al[6]. The thermodynamic parameters and steric environment of Nd(III) ion with a series of semicarbazone in standard alcoholic solution have been discussed on the basis of electronic spectral data[7].

Material and Method

Metal chloride of 99.9% and ligand was procured from Ms. Indian Earth limited. The solvents used in doped system are Ethyl Alcohol (AR 99.9%, Jiangsu-Hliaxi International Trade Co. Ltd., Made in China) and Triton-X-100 (100 CMC solution, Loba Chemia Pvt.Ltd., Mumbai, India).The saturated solution of ligand and metals Nd(III) ion 0.05 M were prepared in different solvents (Triton X-100 of 100 CMC (1.8×10^{-2} M, Sodium Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Bromide, (HTAB) of 100 CMC (9.2×10^{-2}M) is used for preparing saturated solution of ligand and metal. The UV-visible spectra from 400 nm to 900 nm were recorded on (5704-SS) UV Visible Double Beam spectrophotometer at room temperature in 1:3 ratio (Metal:Ligand) at Green chemistry research center (GCRC) Bikaner

Theory

Fourteen bands $^4I_{9/2}\rightarrow{}^4D_{3/2}$, $^4I_{9/2}\rightarrow{}^2P_{1/2}$, $^4I_{9/2}\rightarrow{}^4G_{11/2}$, $^4I_{9/2}\rightarrow{}^2P_{3/2}$, $^4I_{9/2}\rightarrow{}^2G_{9/2}$, $^4I_{9/2}\rightarrow{}^4G_{9/2}$, $^4I_{9/2}\rightarrow{}^4G_{7/2}$, $^4I_{9/2}\rightarrow{}^2K_{13/2}$, $^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^4I_{9/2}\rightarrow{}^2G_{7/2}$, $^4I_{9/2}\rightarrow{}^4F_{9/2}$, $^4I_{9/2}\rightarrow{}^4F_{7/2}$, $^4I_{9/2}\rightarrow{}^4F_{5/2}$ and $^4I_{9/2}\rightarrow{}^4F_{3/2}$ in the case of Nd (III) system have been observed in the region 200 nm to 900 nm.

Oscillator Strength

The intensity of a band is measured in term of Oscillator strength which is expressed in term of molar extinction coefficient (ϵ) and the energy of transition in term of wave number (ν) by the following equation

$$P = 4.315 \times 10^{-9} \int \varepsilon \, d\nu \quad \text{---------- (1)}$$

$$P_{obs} \approx 4.6 \times 10^{-9} \times \varepsilon_{max} \Delta\nu^{1/2} \quad \text{---------- (2)}$$

According to Judd-Ofelt theory, the oscillator strength for transition of energy can be calculated by using Judd-Ofelt parameters (T_2, T_4 and T_6) with the help of formula-

$$P_{cal} = T_2 \nu [U^{(2)}]^2 + T_4 \nu [U^{(4)}]^2 + T_6 \nu [U^{(6)}]^2 \quad \text{---------- (3)}$$

Where $[U^{(2)}]^2$, $[U^{(4)}]^2$, $[U^{(6)}]^2$ are matrix elements [16-17].

Slater- Condon (F_2, F_4, & F_6) and Lande parameter (ζ_{4f})

The values of Slater-Condon parameters (F_k) and Lande para-meters (ζ_{4f}) are then evaluated using following equations-

$$F_k = F^o_k + \Delta F_k \quad \text{---------- (4)}$$

$$\zeta_{4f} = \zeta^o_{4f} + \Delta\zeta_{4f} \quad \text{---------- (5)}$$

Where, $\Delta F_k << F^o_k$, $\Delta\zeta_{4f} << \zeta^o_{4f}$ and F^o_k and ζ^o_{4f} are the zero -order values of Slater- Condon and spin-orbit interaction parameters as reported by Wong[18].

Result and Discussion

The values of the oscillator strength (P) for Nd(III) systems have order of 10^{-6} which shows the transitions are forbidden ones. The intensity of the hypersensitive transition $^4I_{9/2} \rightarrow {}^2G_{7/2}$ in the Nd (III) system depends much on the ligand. The higher values of oscillator strength (P) show lower symmetry in complexes[19]. The spectral intensities of observed bands have been `reported in terms of T_2, T_4 and T_6 parameters. These parameters include Slater Condon (F_K), Lande (ζ_{4f}) and Racah (E^k) parameters. Among F_2, F_4, F_6 and ζ_{4f} parameters, decrease has been observed with F_2 and ζ_{4f} parameters in comparison to free metal ions. This shows the expansion of 4f-orbital in the complex formation[20-21]. These observations show that on complexation, central metal ion expands, which has expected to decrease the interelectronic repulsions and spin orbitinteraction.

Conclusion

We have examined the validity of the intensity relationships deduced by Judd Ofelt.The energies and intensities of the absorption bands have been studied for the Nd^{3+}ion with 2HQ different medium. The observed spectral intensities were analyzed using the eigen vectors obtained from the energy-level calculation employed by Judd. Parameters include Slater Condon (F_K), Lande (ζ_{4f}) and Racah (E^k) parameters. Among F_2, F_4, F_6 and ζ_{4f} parameters, decrease has been observed with F_2 and ζ_{4f} parameters in comparison to free metalions. This shows the expansion of 4f-orbital in the complex formation

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Table: 1
Observed and calculated value of oscillator strength ($P_{obs}x10^6$) for various Absorption transitions of Nd (III)-2HQ Complex in organic and Micellar medium

COMPLEX		Nd(III)-2HQ (EtOH)		Nd(III)-2HQ (TX-100)		Nd(III)-2HQ (HTAB)		Nd(III)-2HQ (SDS)	
S.N.	Energy Levels	$P_{obs}x10^6$	$P_{cal}x10^6$	$P_{obs}x10^6$	$P_{cal}x10^6$	$P_{obs}x10^6$	$P_{cal}x10^6$	$P_{obs}x10^6$	$P_{cal}x10^6$
1	$^4I_{9/2} \rightarrow {}^4D_{3/2}$	7.827	7.223	19.069	9.266	4.759	4.817	6.214	9.277
2	$^4I_{9/2} \rightarrow {}^2P_{1/2}$	4.068	1.257	2.098	1.651	7.820	0.867	5.447	1.549
3	$^4I_{9/2} \rightarrow {}^4G_{11/2}$	3.804	0.421	8.322	4.485	1.232	0.212	5.467	0.696
4	$^4I_{9/2} \rightarrow {}^2P_{3/2}$	2.855	0.650	2.855	0.851	0.225	0.446	2.553	0.805
5	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	1.450	1.408	1.850	1.434	1.896	0.799	7.602	2.183
6	$^4I_{9/2} \rightarrow {}^4G_{9/2}$	1.829	0.606	4.303	0.609	2.929	0.279	5.883	1.063
7	$^4I_{9/2} \rightarrow {}^4G_{7/2}$	1.808	5.530	1.521	5.658	7.955	3.249	7.940	8.356
8	$^4I_{9/2} \rightarrow {}^2K_{13/2}$	1.829	33.727	1.826	30.705	5.046	20.694	1.836	50.468
9	$^4I_{9/2} \rightarrow {}^4G_{5/2}$	1.158	4.241	1.858	3.572	1.756	2.370	1.886	6.867
10	$^4I_{9/2} \rightarrow {}^2G_{7/2}$	40.934	44.011	38.830	39.680	25.783	27.256	60.396	65.503
11	$^4I_{9/2} \rightarrow {}^4F_{9/2}$	2.638	2.000	1.938	1.872	2.654	0.940	2.935	3.513
12	$^4I_{9/2} \rightarrow {}^4F_{7/2}$	1.555	7.133	3.601	6.297	2.243	2.625	1.854	13.994
13	$^4I_{9/2} \rightarrow {}^4F_{5/2}$	11.579	20.490	12.034	21.496	6.395	10.225	20.626	34.176
14	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	2.638	9.498	2.727	11.759	3.899	6.017	3.563	12.920
15	r.m.s.(σ)	9.390		9.294		4.996		14.487	
	dev. (±)								

Table -2
Computed values of judd Ofelt Parameter (Tλ), Symmetry Parameter (T4/T2), and Coordination Parameter (T_4/T_6) of Nd (III)-2HQ Complex in alc. and micellar medium

S.N.	Parameter	Nd(III)-2HQ (EtOH)	Nd(III)-2HQ (TX-100)	Nd(III)-2HQ (HTAB)	Nd(III)-2HQ (SDS)
1	T2 x 10^9	17.181	14.302	10.633	23.561
2	T4 x 10^9	1.213	1.595	0.844	0.641
3	T6 x 10^9	1.060	0.931	0.389	1.442
4	T4/T6	1.144	1.714	2.170	0.444
5	T4/T2	0.071	0.112	0.079	0.027

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Table -3

Lande ζ_{4f} (cm^{-1}) Racah E_k (cm^{-1}) perameters and Hydrogenic Ratio (F_4/F_2) , (F_6/F_2) and (E_1/E_3) , (E_2/E_3) of Nd (III)-2HQ Complexes in Alcoholic and micellar medium

Complex		Nd(III)-2HQ	Nd(III)-2HQ	Nd(III)-2HQ	Nd(III)-2HQ
S.N.	Perameters	(EtOH)	(TX-100)	(HTAB)	(SDS)
1	E_1	5093.91	5082.68	5139.78	4994.52
2	E_2	24.45	25.04	23.86	26.55
3	E_3	513.25	511.15	516.35	511.36
4	F_2	338.94	340.16	338.84	343.23
5	F_4	51.54	50.28	53.30	46.61
6	F_6	5.10	5.15	5.11	5.07
7	ζ_{4f}	750.01	783.32	717.76	796.12
8	%r ζ_{4f}	13.66	9.82	17.37	8.35
9	%r F_2	1.57	1.22	1.60	0.33
10	F_4/F_2	0.152	0.148	0.157	0.136
11	F_6/F_2	0.015	0.015	0.015	0.015
12	E_1/E_3	9.925	9.944	9.954	9.767
13	E_2/E_3	0.048	0.049	0.046	0.052

Figure: Electronic spectra of Nd (III)-2HQ in different medium