

## Electronic spectral characterization of doped systems of the Nd (III) ion in the solutions of some oximes

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### ABSTRACT

The Depoed systems of Nd(III) ion in the solution of various organic oximes have been characterized with respect to electronic spectral parameters viz. Slater-Condon ( $F_K$ ), Lande parameter ( $\zeta_{4f}$ ), intensity of hypersensitive band, bonding parameter ( $B$ ,  $b^{1/2}$  del) Judd-Ofelt parameter ( $T_\lambda$ ) and Racah parameter ( $E^K$ ). These various parameters prove the covalent nature of M-L and change in symmetry around Nd(III) ion. The study provides useful information about interelectronic repulsion and spin interaction involved in metal – ligand bond.

**Key words:** Electronic spectral parameters, oximes, Nd(III) ions.

### INTRODUCTION

A great deal of work has been reported on the measurement of  $f \rightarrow f$  transitions of free and aquo ions of lanthanides in different chemical enviromental<sup>1-4</sup>. In the studies of biological system and as diagnostic agent in clinical medicine, Lanthano ions have been found to be very useful and important<sup>5</sup>. Much work on metal chelates have been carried out with ligands having N and O as donor atoms<sup>6-7</sup>. In the present work Nd (III) ion has been doped in solutions of some organic oximes in the metal to ligand ratio of 1:1 and 1:2. The doped Nd(III) ion in solutions of organic oximes exhibit adsorption spectra characterized by bands in visible region, but these spectra have not been studied extensively<sup>8-10</sup> in terms of various electronic spectral parameters. The values of various electronic spectral parameters like Slater-Condon ( $F_K$ ), Lande parameter ( $\zeta_{4f}$ ), Nephelauxetic ratio ( $\beta$ ), bonding parameter ( $b^{1/2}$ ) Judd-Ofelt parameter ( $T\lambda$ ) and

Racah parameter ( $E^K$ ), which gives useful information regarding interelectronic repulsion, spin orbit interaction, Nephelauxetic effect and bonding in the complexes have been computed.

### EXPERIMENTAL

In the present study six organic oximes Acetoxime (L1), Acetophenoneoxime (L2), Benzophenoneoxime (L3), Diacetylmono oxime (L4), Cyclooctanoneoxime (L5) and Camphoreoxime (L6) have been used as ligands. All the chemicals and the solvent used were of analytical grade. The ligands were dissolved to prepare 0.32M and 0.16M solutions in 50% aqueous ethanol (solvent) at room temperature (32°C). Equal volume (10ml) of each of these 0.32M and 0.16M ligand solution was added in 10ml solution fo 0.16 Nd<sup>3+</sup>, to get six systems each of having metal to ligand ratio 1:2 and 1:1 respectively. This has been represented by using 'a' and 'b' along with ligand

Table 1: Computed values of oscillator strength, Judd-Ofelt parameter

Table 2:Computed values of oscillator strength, Judd-Ofelt parameter

S No	Level	Nd <sup>3+</sup> + L4a		Nd <sup>3+</sup> + L4b		Nd <sup>3+</sup> + L5a		Nd <sup>3+</sup> + L5b		Nd <sup>3+</sup> + L6a		Nd <sup>3+</sup> + L6b				
		P obs		P cal		P obs		P cal		P obs		P cal				
		P	obs	P	cal	P	obs	P	cal	P	obs	P	cal	P	obs	P
1	2P <sub>1/2</sub>	8.99357	2.10589	1.0757	E-07	8.3421	5.00113	6.164	4.20819	6.9607	1.98336	6.10995	3.40145			
2	4G <sub>11/2</sub>	1.15611	1.95197	1.30063	E-07	2.85593	2.29793	3.22395	7.2703	E-07	E-07	E-07	E-07	E-07	E-07	E-07
3	2G <sub>9/2</sub>	4.26751	3.75552	6.54841	E-07	5.37041	1.24373	6.23647	4.43974	E-07	E-07	E-07	E-07	E-07	E-07	E-07
4	2K <sub>15/2</sub>	6.41853	3.19328	8.15327	E-07	4.79882	8.87168	5.11266	8.9815	E-07	E-07	E-07	E-07	E-07	E-07	E-07
5	4G <sub>9/2</sub>	1.13987	1.14702	1.78508	E-07	1.59978	2.69689	1.93645	1.91506	E-07	E-07	E-07	E-07	E-07	E-07	E-07
6	4G <sub>7/2</sub>	2.61673	2.82076	2.99999	E-06	3.99213	4.75757	4.20059	4.05769	E-06	E-06	E-06	E-06	E-06	E-06	E-06
7	4G <sub>5/2</sub>	1.88205	1.83551	2.9485	E-06	2.87134	1.96627	1.89559	1.71283	E-06	E-06	E-06	E-06	E-06	E-06	E-06
8	4F <sub>9/2</sub>	7.47286	5.89176	1.73248	E-05	8.94547	9.92924	9.25132	8.28498	E-05	E-05	E-05	E-05	E-05	E-05	E-05
9	4F <sub>7/2</sub>	6.79768	5.65054	1.05775	E-06	8.71586	1.00382	8.79881	1.03796	E-06	E-06	E-06	E-06	E-06	E-06	E-06
10	4F <sub>5/2</sub>	4.97025	5.50871	7.1701	E-06	8.10512	8.82538	9.06231	8.09124	E-06	E-06	E-06	E-06	E-06	E-06	E-06
11	4F <sub>3/2</sub>	2.51261	1.23644	3.78852	E-06	1.4915	3.63807	2.43163	3.54489	E-06	E-06	E-06	E-06	E-06	E-06	E-06
12	rms	$\sigma = \pm 6.75697 \times 10^{-7}$	$\sigma = \pm 1.12364 \times 10^{-6}$	$\sigma = \pm 9.03553 \times 10^{-7}$		$\sigma = \pm 9.03553 \times 10^{-7}$	$\sigma = \pm 6.7365 \times 10^{-7}$	$\sigma = \pm 6.7365 \times 10^{-7}$	$\sigma = \pm 6.7365 \times 10^{-7}$	$\sigma = \pm 8.1153 \times 10^{-7}$	$\sigma = \pm 8.1153 \times 10^{-7}$	$\sigma = \pm 5.944 \times 10^{-7}$				
13	T <sub>2</sub>	1.04592 E-09	1.7141 E-09	9.19977 E-10		8.14952 E-10		8.14952 E-10		1.4379 E-09		9.49069 E-10				
14	T <sub>4</sub>	2.37403 E-10	2.04738 E-10	5.6384 E-10		4.75105 E-10		4.75105 E-10		2.23503 E-10		3.85015 E-10				
15	T <sub>6</sub>	9.70804 E-10	1.51486 E-09	1.49555 E-09		1.55088 E-09		1.55088 E-09		1.47769 E-09		1.35358 E-09				
16	T <sub>4</sub> /T <sub>6</sub>	0.244542569	0.135152904	0.377012289		0.306344892		0.306344892		0.15132250.28441994						

**Table 3: Energies of various peak**

S No	Level	Nd <sup>3+</sup> + Solvent		Nd <sup>3+</sup> + L1a		Nd <sup>3+</sup> + L1b		Nd <sup>3+</sup> + L2a		Nd <sup>3+</sup> + L2b		Nd <sup>3+</sup> + L3a		Nd <sup>3+</sup> + L3b	
		E obs	E cal	E obs	E cal	E obs	E cal	E obs	E cal	E obs	E cal	E obs	E cal	E obs	E cal
1	2P <sub>1/2</sub>	23292	23102.7	23289.4	23098.2	23290.2	23097.8	23290.9	23091.1	23299.4	23102.7	23291	23094.7	23289.9	23080.3
2	4G <sub>11/2</sub>	21641	21388.7	21619.1	21347.4	21635.6	21331.2	21619.2	21330.5	21619.8	21306.8	21629.2	21350.7	21606	21308.8
3	2G <sub>9/2</sub>	21236	21212.9	21230.0	21219.8	21261.0	21244.2	21241.7	21227.9	21230.3	21228.8	21240.9	21228.2	21249.9	21232.5
4	2K <sub>15/2</sub>	20945	21156.8	20953.5	21184.7	20959.8	21212.0	20952.4	21195.0	20959.9	21213.0	20951.5	21186.8	20949.4	21203.8
5	4G <sub>9/2</sub>	19498	19504.6	19498.5	19486.2	19508.6	19485.7	19494.7	19479.7	19505.1	19471.4	19507.4	19486.5	19495.9	19472.3
6	4G <sub>7/2</sub>	19.66	19192.6	19064.1	19192.8	19079.3	19199.5	19064.8	19190.7	19073.5	19192.6	19068.2	19189.7	19058.8	19190.5
7	4G <sub>5/2</sub>	17144	17155.5	17165.3	17139.5	17136.3	17124.9	17140.1	17125.0	17138.4	17123.6	17128.9	17127.1	17134.9	17116
8	4F <sub>9/2</sub>	14612	14676.8	14594.6	14649.9	14580.3	14646.4	14576.5	14643.2	14565.3	14630.5	14591.8	14562.8	14631.8	
9	4F <sub>7/2</sub>	13337	13203.4	13325.2	13173.7	13324.3	13161.5	13329.2	13161.9	13319.1	13149.9	13327.0	13173.0	13321.7	13148.5
10	4F <sub>5/2</sub>	12459	12385.0	12434.2	12360.1	12432.0	12384.4	12435.3	12348.9	12425.4	12389.4	12432.7	12357.5	12432.2	12337.6
11	4F <sub>3/2</sub>	11513	11383.1	11487.8	11370.4	11489.1	11360.1	11479.2	11360.5	11471.3	11358.9	11487.5	11363.1	11477.2	11353.3
12	σ rms		135.05		143.5		154.7		151.6		156.4		146.5		157.99

**Table 4: Energies of various peak**

S No	Level	Nd <sup>3+</sup> + L4a		Nd <sup>3+</sup> + L4b		Nd <sup>3+</sup> + L5a		Nd <sup>3+</sup> + L5b		Nd <sup>3+</sup> + L6a		Nd <sup>3+</sup> + L6b	
		E obs	E cal	E obs	E cal	E obs	E cal	E obs	E cal	E obs	E cal	E obs	E cal
1	2P <sub>1/2</sub>	23282.28	23098.68	23282.28	23083.69	23280.22	22976.82	23247.74	22943.66	23291.2	23078.2	23187.9	22951.8
2	4G <sub>11/2</sub>	21629.27	21374.86	21629.27	21324.0	21561.0	21430.0	21584.36	21348.0	21635.7	21349.0	21591.4	21368.6
3	2G <sub>9/2</sub>	21265.74	21236.71	21256.74	21238.18	21227.83	21161.83	21213.27	21167.6	21236.1	21217.6	21221.2	21206.0
4	2K <sub>15/2</sub>	20956.3	21183.91	20956.3	21203.31	20847.38	21032.23	20868.37	21067.48	20940.4	21171.7	20919.8	21091.9
5	4G <sub>9/2</sub>	19497.8	19497.51	19497.8	19480.65	19451.73	19488.98	19487.7	19474.25	19506.9	19484.8	1951.0	19489.6
6	4G <sub>7/2</sub>	19061.6	19192.5	19061.6	19194.9	19010.34	19140.74	19042.13	19165.64	19063.6	19187.9	19058.0	19175.2
7	4G <sub>5/2</sub>	17161.26	17128.444	17145.03	17120.87	17096.0	17116.84	17147.0	17135.9	17146.0	17132.9	17081.6	17120.1
8	4F <sub>9/2</sub>	14615.19	14670.98	14570.13	14641.0	14612.0	14684.07	14548.27	14629.6	14574.6	14650.1	14590.7	14651.3
9	4F <sub>7/2</sub>	13342.12	13185.36	13327.43	13156.91	13330.32	13211.83	13296.32	13169.66	13327.4	13172.8	13333.3	13175.9
10	4F <sub>5/2</sub>	12443.64	123.6689	12436.19	12344.66	12445.97	12387.36	12427.72	12360.05	12433.6	12358.7	12453.1	12361.8
11	4F <sub>3/2</sub>	11482.35	11365.25	11479.01	11358.89	11500.71	11358.15	11482	11361.44	11477.0	11365.7	11490.7	11352.8
12	σ rms		140.1753		15.6782		138.0242		149.9613		149.3		137.1

symbol (eg. L1a for M:L = 1:2, and L1b for M:I = 1:1). Solution spectra of these twelve systems were recorded by using standard spectrophotometer (Biomate UV-Visibile Spectrophotometer v7.07) in the range of 390 to 900 nm.

## RESULTS AND DISCUSSION

The calculation of parameters viz. Judd-Ofelt ( $T_e$ ) Slater-Condon ( $(F_K)$ , Lande ( $\xi_{4f}$ ), Racah ( $E^K$ ) have been computed by the programme developed by earlier workers<sup>8-9</sup>. The computed values of oscillator strength, Judd-Ofelt parameter (Table-1 and -2), energies of various peak (Table -3 and -4), Slater-Condon ( $F_K$ ), Lande ( $\xi_{4f}$ ), Racah ( $E^K$ ) parameters, nephelauxetic ratio ( $\alpha$ ) and bonding parameters (Table-5) have been tabulated.

### Spectral Intensity Parameters

The oscillator strength ( $P_{obs}$ ) values vary from  $9.9716 \times 10^{-7}$  to  $1.1236 \times 10^{-6}$  for hypersensitive transition  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$  which indicates the increase in intensity with increase in covalency of system (complex). There is much variation in Judd-Ofelt parameter, shows that the sequence  $T_4 < T_2 < T_6$  in most of the cases (except L4), which is in good agreement with lanthanide metal ion characteristics<sup>6</sup>. The deep lying 4f sub shell experiencing intense shielding make these orbital less available for bonding, thereby leading to lesser degree of metal-ligand interactions. The ratio  $T_4/T_6$  indicates symmetry around the cation and varies from 0.1351 to 0.3770. On the basis of  $T_4/T_6$  values, the doped Nd<sup>3+</sup> ion systems have been classified in the following systems.

1. SYSTEM-A:-  $T_4/T_6$  values varying in between 0.1351 to 0.2103. Ligands were L2b, L3b, L4b & L6b.
2. SYSTEM-B:-  $T_4/T_6$  values varying in between 0.2445 to 0.2844. Ligands were L2a, L3a, L4a & L6a.
3. SYSTEM-C:-  $T_4/T_6$  values varying in between 0.2994 to 0.3770. Ligands were L1b, L1b, L5a & L5b.

These three SYSTEMS (A, B&C) reveal that on changing the metal to ligand ratio for ligands L2, L3, L4 and L5, symmetry around the cation or symmetry of stereo environment around the doped Nd<sup>3+</sup> ion changes.

**Table 5: Computed values of Slater-Condon ( $F_K$ ), Lande ( $\xi_{4f}$ ), Racah ( $E^K$ ) parameters, nephelauxetic ratio ( $\beta$ ) and bonding parameters**

S.N.	Systems	M : L	$F_2$	$F_4$	$F_6$	$E^1$	$E^2$	$E^3$	$\xi_{4f}$	$\beta$	$b_{1/2}$	$\delta\%$	%r $\xi_{4f}$
1	Nd <sup>3+</sup> + solvent		325.77	53.05	5.237	5060.5379	22.586	490.1736	853.41	0.9825	0.0935	1.78117	3.460407
2	Nd <sup>3+</sup> + L1a	1:2	324.77	53.78	5.234	5070.7221	22.230	490.0799	845.09	0.9795	0.1012	2.092905	4.401584
3	Nd <sup>3+</sup> + L1b	1:1	323.97	54.20	5.230	5074.2750	21.997	489.7257	843.80	0.9771	0.1070	2.34367	4.547511
4	Nd <sup>3+</sup> + L2a	1:2	324.19	54.02	5.230	5071.5020	22.082	489.7063	844.01	0.9778	0.1055	2.270403	4.523756
5	Nd <sup>3+</sup> + L2b	1:1	234.12	54.34	5.242	5081.4874	21.978	489.8776	839.15	0.9775	0.1060	2.30179	5.073529
6	Nd <sup>3+</sup> + L3a	1:2	324.56	53.72	5.235	5067.8503	22.227	489.5826	848.07	0.9789	0.1028	2.155481	4.06448
7	Nd <sup>3+</sup> + L3b	1:1	232.51	54.36	5.219	5072.4873	21.885	489.5891	840.85	0.9757	0.1102	2.49052	4.881222
8	Nd <sup>3+</sup> + L4a	1:2	324.81	53.47	5.237	5063.6137	22.341	489.4096	852.92	0.9796	0.1010	2.082483	3.515837
9	Nd <sup>3+</sup> + L4b	1:1	323.67	54.24	5.219	5070.5020	21.941	489.6401	843.08	0.9762	0.1091	2.438025	4.628959
10	Nd <sup>3+</sup> + L5a	1:2	324.40	51.97	5.151	5002.8402	22.729	488.3383	868.51	0.9784	0.1040	2.207686	1.752262
11	Nd <sup>3+</sup> + L5b	1:1	322.16	53.64	5.085	5013.6101	21.873	489.9568	846.21	0.9716	0.1191	2.923014	4.274887
12	Nd <sup>3+</sup> + L6a	1:2	324.36	53.73	5.217	5062.5469	22.187	489.8163	846.71	0.9783	0.1042	2.218133	4.218326
13	Nd <sup>3+</sup> + L6b	1:1	321.78	53.64	5.089	5011.3200	21.832	489.2161	852.92	0.9705	0.1215	3.03967	3.515837
14	Nd <sup>3+</sup> (free ion)	-	331.16	50.71	5.150	5024.0000	23.900	497.0000	884.00	-	-	-	-

### **Slater-Condon, Racah, Lande and Bonding Parameters**

Taking the free/aqua ion as standard the ligand cause a slight red shift of the bands. The  $\delta$  RMS values of energies ( $E_{\text{obs}}$  and  $E_{\text{Cal}}$ ) of various peaks vary from 137.1 to 157.99 cm $^{-1}$ , which is even more in comparison, when solvent acts as ligand (135.05), indicates the red shift. REd shift may be conveniently used as a measure of metal-ligand covalent bonding. The effect may be visualized to be due to an expansion of wave function which results from the interactions between the metal cation and the bonding anion. The value of nephelauxetic ratio ( $\beta$ ) has been found to be less than one in all the systems irrespective to their metal-ligand ratio. Positive value of  $b^{1/2}$  indicates some covalent character in the metal-ligand bond.

The parametric values reveal a remarkable variation in spin orbit interaction Parameters. It's

value ranges from 839.15 to 868.51. The percentage reduction (%  $\xi_{4f}$ ) value comes to be from 1.752 to 5.073. The decrease in values of Slater-Condon, Lande and Racah parameters of the doped systems as compared to those of free metal ion may be attributed to chelation of Nd $^{3+}$  ion with the ligand present in the surrounding environment, and thus indicates the expansion of metal orbital which is in accordance with the theory of origin of intensity of intra – f $\leftrightarrow$ f transitions.

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