Asian Journal of Chemistry; Vol. 24, No. 10 (2012), 4597-4600

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Electronic Spectral Parameters of Doped Pr(III) and Nd(III) Ions in the Saturated Solutions of Some N and O Donor Biologically Important Ligands in DMF Medium

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(*Received*: 13 August 2011; *Accepted*: 9 May 2012) AJC-11446

The study of interaction of biologically important compounds with Pr(III) and Nd(III) ions in the form of doped model have been discussed in the terms of electronic spectral parameters *viz*. Oscillator strength (P), Judd-Ofelt (T_λ), Racah parameter (E_k), Slater- Condon parameter (F_k), Lande parameter (ζ4F), Bonding parameters ($b^{1/2}$), Naphelauxetic ratio (β), per cent covalency (δ), rms deviation (σ) and Peacock constant (K) have been evaluated. The study infers the change in absorption spectra of doped Pr(III) and Nd(III) ion with some biologically important ligands (*viz*. ascorbic acid, biotin, gibberalic acid, indoleacetic acid, indole-3-butyric acid, kinetin, niacin, pyridoxine, thiamin and 4-chlorophenoxyacetic acid). The doped model involves small concentration of Pr(III) ion salt (0.0435 g) and Nd(III) ion salt (0.0438 g) in saturated solution of ligand in DMF solvent at 298 K. In this comparative study, we observed that Pr(III) shows better complexation than Nd(III) ion and the complexing efficiency of biotin ligand with Pr(III) and Nd(III) is greatest among all the ten ligands.

Key Words: Electronic Spectral Parameters, Doped Pr(III) and Nd(III).

INTRODUCTION

The tripositive lanthanide ions have unique spectroscopic properties. The chemistry of lanthanides continues to attract scientist because the complexes of lanthanide metal ion with organic reagents are significant due to its application in various industries, biochemical fields, laser material, electroluminescent devices, immunoassay sensors and shift reagent for NMR spectroscopy[1,2]. The biological action of lanthanide ion is based upon the use of rare earth ion as a substitute or antagonist of Ca^{2+} in variety of cellular and sub cellular reactions[3]. The lanthanide ion exhibits absorption spectra characterized by the bands in the visible region but these spectra have not been studied extensively in terms of various electronic spectral parameters. The discovery of the corresponding elements and their displays as optical fibers and amplifiers, lasers responsive luminescent stains for biomedical analyzed and in celluio sensing assessment of the luminescence efficiency of lanthanide containing emissive molecular edifices[4]. A sustained research activity has been devoted to lanthanide complexes because of their successful application as diagnostic tools in biochemical analysis as MRI contrast agent[5,6]. Lanthanide ions are use as hosts for optical devices. Rare earth doped heavy metal fluoride glasses are transparent from ultraviolet to the infrared region. Fluoride glasses have smaller multiphonon emission rates and are chemically stable[7,8]. In the presence of Zn(II) and Ca(II) Pr(III) gives better complexation and covalent character with dimethyl glyoxime[9]. Borate, phosphorus and borophosphoruate glasses are much useful as host materials for laser action and amplifiers[10,11].

The 4*f* shell is efficiently shielded by the close 5*s* and 5*p* shell, the ligand environment has only a weak influence on the electronic cloud of the lanthanide ion. Owing to the poor thermodynamic stability of lanthanide complexes modified doped system is undertaken to record solution spectra in solvent using standard spectrophotometer[12]. The present investigation has been undertaken with a view to make a comparative study of a various energy and intensity parameters resulting from *f-f* transition in different energy levels of doped Pr(III) and Nd(III) ions in DMF solvent. Ten compounds *e.g.*, ascorbic acid, biotin, gibberalic acid, indole acetic acid, indole-3-butyric acid, kinetin, niacin, pyridoxine, thiamin, 4-chlorophenoxyacetic acid have been used as ligands. A constant amount of $Pr(NO_3)_3.6H_2O$ and $Nd(NO_3)_3.6H_2O$ has been added to each of the saturated solution of ligand in DMF solvent. Pr(III) ion spectra is measured in 390-650 nm region. It yields four bands in visible region and Nd(III) spectra is measured in 400-900 nm region, it gives ten bands in visible region. The calculations involve the Judd-Ofelt equation and the other relation described in literature[13,14]. On examining the electronic spectral parameters of the systems under study the covalency is inferred to some extent to metal-ligand bonding. The study also provides some useful information regarding validity of Judd-Ofelt equation and relation proposed by Peacock. The study also provides beneficial information about interelectronic repulsion, spin orbit interaction and comparative[15] study of complexation behaviour of Pr(III) and Nd(III) ions with biologically important compounds.

EXPERIMENTAL

Standard grade chemicals $Pr(NO_3)_3.6H_2O$ and $Nd(NO_3)_3{\cdot}6H_2O$ (99.9 % purity) (procured from Indian rare earths) and biologicallyimportant compounds ascorbic acid, biotin, gibberalic acid, indole acetic acid, indole-3-butyric acid, kinetin, niacin, pyridoxine, thiamin, 4-chlorophenoxyacetic acid (SD fine) were used. In this present study DMF solvent was used. Saturated solutions of ligands were prepared in DMF and 0.0435 g of $Pr(NO_3)_3{\cdot}6H_2O$ or 0438 g $Nd(NO_3)_3{\cdot}6H_2O$ was added to saturated solution of ligand (10 cm^3). Spectra of these solutions were recorded by using standard spectrophotometer (SL 164 double beam UV-Visible) at 298 K. In 390-650 nm range four peaks corresponding to $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^3H_4 \rightarrow ^1D_2$ transition have been obtained for Pr(III) and in the range of 400-900 ten peaks corresponding to $^4I_{9/2} \rightarrow ^2P_{1/2}$, $^4I_{9/2} \rightarrow ^4G_{11/2}$, $^4I_{9/2} \rightarrow ^4G_{9/2}$, $^4I_{9/2} \rightarrow ^2G_{9/2}$, $^4I_{9/2} \rightarrow ^4G_{7/2}$, $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^4I_{9/2} \rightarrow ^4F_{9/2}$, $^4I_{9/2} \rightarrow ^4F_{7/2}$, $^4I_{9/2} \rightarrow ^4F_{5/2}$ and $^4I_{9/2} \rightarrow ^4F_{3/2}$ transition have been obtained for Nd(III) ion.

RESULTS AND DISCUSSION

The present study shows that the *f-f* transitions result from spin orbit interaction in metal and ligands. A change in various energy and intensity parameters (T_2, T_4, T_6) have been observed[16]. The red shift is observed in all the energy bands from that of aquo Pr(III) and Nd(III) ions has been observed. The transition $^3H_4 \rightarrow ^3P_2$ (occurring a 5200 cm^{-1}) of Pr(III) which satisfies selection rules $\Delta S = 0I\Delta LI$ and $I\Delta JI \leq 2$ depends on $U^{(2)}$ matrix elements and show substantial changes even minor changes in the coordination environment. Such transition is called hypersensitive transition. It is not generally studied in solution spectral analysis. But it is not so in the case of transition to $^3H_4 \rightarrow ^3P_2$, $^3H_4 \rightarrow ^3P_1$, $^3H_4 \rightarrow ^3P_0$ and $^1D_2$ of Pr(III). These transitions are regarded as the 'ligand mediated pseudo-hypersensitivity' or 'pseudo-hypersensitivity transitions[17,18]. For Nd(III) ion transition $^4I_{9/2} \rightarrow ^4G_{5/2}$ is called hypersensitive transition. Pr(III) and Nd(III) showed an appreciable red shift with respect to corresponding free ion on complexation but the intensity of the 4*f*-4*f* bands increased significantly.

The energy of 4*f*-4*f* transition consists of two major components. Columbic represented by Slater condon parameters (F_K) and spin orbit interaction represented by Landeζ4F between 4*f* electrons. While $f^K$and A_{SO} are the angular components spin orbit columbic interaction as given by the following relation[19].

$$E = f^K F_K + A_{SO}\zeta 4F$$

The observed band energies as E_{obs} and the zeropoint energy E_{oj} and partial derivatives of Pr(III) and Nd(III) ions are used. The correction factors ΔE^K and $\Delta\zeta 4F$ have been calculated by the least squares fit method. The calculated correction factors are than added to the zero order parameters to obtain the Racah parameter (E^K) and the spin orbit interaction parameters ζ4F. The Slater integrals (F_K) have been evaluated from Racah parameters using relevant expressions. The rms deviations between the energies $E_{(cal)}$ calculated using these parameters and the observed energies E_{obs} are experimental limits. The value of oscillator strengths ofthe complex are found to be higher as compared to free ion which shows higher complexation. Hence, it may be concluded that higher magnitude of oscillator strength indicates inner sphere complexation. The relation among different F^K parameters is found to be $F_2 > F_4 > F_6$ and $E_1 > E_3 > E_2$.

Pr(III) gives four bands in the range of 390-650 nm region and Nd(III) gives ten bands in the range of 400-900 nm. The comparative interaction of biologically important ligands with Pr(III) and Nd(III) ion in term of covalency and symmetry may therefore be given on basis of present doped model. On examining electronic spectral parameters ofthe system it proves the validity of Judd-Ofelt equation under study. The covalency is inferred to some extent in metal ligand bonding. The study also provides some useful information regarding inter electronic repulsion and spin orbit interaction.

The different parameters reported in Tables 1 to 4 have been calculated by the theories given by Slater condon, Lande and Judd-Ofelt[13,14]. The computerized programme for the said calculation has been reported by the earlier worker. From the observations and calculations the following points may be concluded.

(1) Large variation in the intensities of the oscillator strength P_{obs} has been observed in the present study. From the value of oscillator strength, it has been found that both metal Nd(III) and Pr(III) show better complexation with ligands. From the result it has been found that biotin shows the best complexation with both metal ion Pr(III) (P_{obs}) 15.0 × 10^{-5}) and Nd(III) (P_{obs}) 19.1 × 10^{-5}) among all the ligands under study.

(2)The value of nephelaxetic ratio β has been found less than one in all the systems and the value of $b^{1/2}$ is positive they indicates low covalent bonding[20-22]. In case of Pr(III) systems-Biotin shows lowest value of β (0.9546) highest value of $b^{1/2}$ (0.1505). Therefore Pr(III)-biotin system has more covalent character while in Nd(III)-systems Indole acetic acid shows more covalent character. The value of β is very less in Pr(III)-system (0.9546 to 0.9646) than Nd(III)-system (0.9904 to 0.9925). Therefore Pr(III) systems have more covalent character.

(3) The value of Sinha's covalency parameter δ % varies from 1.79 % to 4.75 % for Pr(III) systems and 0.756 % to 0.979 % for Nd (III) systems. Therefore Pr(III) systems have higher covalent character than Nd(III) systems. From the result it has been found that Pr(III) biotin-system (4.75 %) has highest covalent character among all ten systems and Nd(III) indole acetic acid system (0.979 %) has highest covalent character among all the ten ligands.

(4) The Lande parameter indicates decrease in spin orbit interaction. The value of ζ4F for all Nd(III) and Pr(III) systems has been found to be less than free ion value. The greater decrease ζ4F value indicates decrease in interelectronic repulsion and spin orbit interaction, which suggests expansion of the central metal ion orbits on complexation[23]. The greater decrease in ζ4F value has been observed in Pr(III)-Kinetin system (673) and Nd(III)-gibberalic acid system (877) from free ion value.

TABLE-1
COMPUTERIZED VALUES OF OSILLATOR STRENGTH, Tλ *etc*. FOR Pr(III)SYSTEM

S. No.	System	Oscillator strength × 10^5				Tλ × 10^8				rms σ × 10^8	$\bar{\nu}$ of $^3P_2$	$P_{obs}/\bar{\nu}$ T_6 × 10^2
		$^3P_{2(o)}$ $^3P_{2(c)}$	$^3p_{1(o)}$ $^3p_{1(c)}$	$^3P_{0(o)}$ $^3P_{0(c)}$	$^2D_{1(o)}$ $^2D_{1(c)}$	T_2	T_4	T_6	T_4/T_6			
1	Pr + DMF + As	9.128	2.919	2.046	2.611	-1.320	0.68	2.82	0.241	4.74	22472	14.4
		9.128	2.919	2.036	2.611							
2	Pr + DMF + B	15.20	6.918	3.925	4.450	-0.115	1.50	4.60	0.326	9.09	22421	14.7
		15.20	6.918	3.906	4.454							
3	Pr + DMF + GA	10.10	2.070	1.760	2.950	-0.260	0.53	3.20	0.166	4.09	22472	14.0
		10.10	2.070	1.756	2.943							
4	Pr + DMF + IAA	9.680	5.840	2.710	2.440	-9.430	1.18	2.90	0.413	6.29	22472	14.9
		9.680	5.840	2.705	2.443							
5	Pr + DMF + IBA	9.940	4.800	2.400	2.900	-0.297	1.01	2.81	0.337	5.57	22472	14.7
		9.940	4.894	2.396	2.899							
6	Pr + DMF + K	7.744	2.086	1.825	2.220	-0.860	0.54	2.40	0.226	4.23	22471	14.4
		7.744	2.086	1.817	2.220							
7	Pr + DMF + Ni	9.350	4.325	2.052	2.699	-1.020	0.89	2.83	0.314	4.77	22471	14.7
		9.350	4.390	2.052	2.699							
8	Pr + DMF + Py	8.272	3.105	1.507	2.400	-0.338	0.64	2.55	0.250	3.49	22472	14.4
		8.272	3.105	1.507	2.400							
9	Pr + DMF + Th	9.243	3.120	1.298	2.653	-1.160	0.61	2.88	0.212	3.01	22421	14.3
		9.243	3.120	1.292	2.611							
10	Pr + DMF + 4-Cl	7.649	3.470	1.850	2.560	-1.930	0.73	2.32	0.213	4.29	22471	14.3
		7.649	3.470	1.844	2.160							

As = ascorbic acid, B = biotin, GA = gibberalic acid, IAA = indoleacetic acid, IBA = indole-3-butyric acid, K = kinetin, Ni = niacin, Py = pyridoxine, Th = thiamin, 4-Cl = 4-chlorophenoxyacetic acid.

TABLE -2
COMPUTERIZED VALUES OF VARIOUS PARAMETERS for Pr(III) SYSTEM

S. No	System	F_2	F_4	F_6	rF_2 (%)	ζ4F	E_1	E_2	E_3	β	$b^{1/2}$	δ (%)	rms
1	Pr free ion	322.09	44.46	4.87	-	738	4729.00	24.78	478.43	-	-	-	-
2	Pr + DMF + As	309.00	42.60	4.66	4.19	722	4530.74	23.70	458.08	0.9581	0.1447	2.02	175.97
3	Pr + DMF + B	307.00	42.44	4.64	4.53	743	4514.44	23.61	456.43	0.9546	0.1505	4.75	173.97
4	Pr + DMF + GA	308.00	42.54	4.65	4.30	722	4525.17	23.67	457.51	0.9569	0.1467	2.16	105.44
5	Pr + DMF + IAA	311.00	42.87	4.69	3.57	679	4559.69	23.85	461.00	0.9642	0.1337	1.79	117.25
6	Pr + DMF + IBA	309.00	42.65	4.66	4.07	694	4536.20	23.72	458.63	0.9592	0.1427	2.04	131.39
7	Pr + DMF + K	311.00	42.89	4.69	3.53	673	4561.80	23.86	461.22	0.9646	0.1329	3.66	130.72
8	Pr + DMF + Ni	310.00	42.78	4.68	3.78	682	4549.89	23.80	460.01	0.9621	0.1375	3.93	122.04
9	Pr + DMF + Py	309.00	42.59	4.66	4.21	727	4529.66	23.69	457.97	0.9579	0.1451	2.10	180.07
10	Pr + DMF + Th	309.00	42.66	4.67	4.03	688	4537.83	23.73	458.79	0.9596	0.1421	4.21	105.94
11	Pr + DMF + 4-Cl	311.00	42.87	4.69	3.57	679	4559.00	23.85	461.00	0.9642	0.1337	3.71	219.16

As = ascorbic acid, B = biotin, GA = gibberalic acid, IAA = indoleacetic acid, IBA = indole-3-butyric acid, K = kinetin, Ni = niacin, Py = pyridoxine, Th = thiamin, 4-Cl = 4-chlorophenoxyacetic acid.

TABLE-3
COMPUTERIZED VALUES OF OSILLATOR STRENGTH, Tλ *etc*. FOR Nd(III) SYSTEM

System	Oscillator strength × 10^5										Tλ × 10^8				rms σ × 10^8	$\bar{\nu}$ of $^4G_{5/2}$	$P_{obs}/\bar{\nu}$ T_6 × 10^2
	$^2P_{1/2(c)}$ $^2P_{1/2(o)}$	$^4G_{11/2(c)}$ $^4G_{11/2(o)}$	$^4G_{9/2(c)}$ $^4G_{9/2(o)}$	$^2G_{9/2(c)}$ $^2G_{9/2(o)}$	${}_4G^{7/2(c)}$ ${}^4G^{7/2(o)}$	$^4G_{5/2(c)}$ $^4G_{5/2(o)}$	$^4F_{9/2(c)}$ $^4F_{9/2(o)}$	$^4F_{7/2(c)}$ $^4F_{7/2(o)}$	$^4F_{5/2(c)}$ $^4F_{5/2(o)}$	$^4F_{3/2(c)}$ $^4F_{3/2(o)}$	T_2	T_4	T_6	T_4/T_6			
Nd + DMF + As	0.580	0.193	1.500	0.376	3.27	13.7	0.486	4.27	5.36	2.17	0.558	0.659	0.687	0.960	3.25	17182	116.20
	0.578	0.196	1.530	0.378	3.27	13.7	0.485	4.27	5.36	2.17							
Nd + DMF + B	0.401	0.148	1.180	0.296	3.01	19.1	0.398	3.49	4.16	1.56	1.010	0.456	0.564	0.809	6.75	17241	196.41
	0.394	0.144	1.170	0.295	3.02	19.1	0.397	3.49	4.16	1.56							
Nd + DMF + G	0.352	0.149	1.050	0.275	2.08	7.27	0.385	3.57	4.08	1.42	0.265	0.400	0.583	0.685	3.15	17241	73.31
	0.355	0.147	1.050	0.271	2.08	7.27	0.386	3.57	4.09	1.42							
Nd + DMF + IAA	0.254	0.120	0.836	0.221	1.65	5.99	0.328	3.06	3.37	1.08	0.236	0.288	0.506	0.569	3.56	17301	68.41
	0.256	0.121	0.845	0.214	1.64	5.99	0.326	3.07	3.37	1.08							
Nd + DMF + IBA	0.191	0.108	0.730	0.195	1.49	6.79	0.305	2.88	3.08	.877	0.322	0.217	0.481	0.452	1.81	17211	82.01
	0.187	0.108	0.730	0.199	1.49	6.79	0.305	2.88	3.03	.878							
Nd + DMF + K	0.343	0.121	0.927	0.236	1.93	7.54	0.313	2.81	3.40	1.31	0.290	0.390	0.442	0.863	1.46	17301	98.59
	0.343	0.121	0.926	0.239	1.93	7.54	0.313	2.81	3.40	1.31							
Nd + DMF + Ni	0.441	0.120	1.020	0.249	2.41	11.6	0.289	2.42	3.34	1.56	0.504	0.501	0.373	1.342	3.06	17241	180.37
	0.439	0.124	1.010	0.254	2.41	11.6	0.289	2.42	3.34	1.56							
Nd + DMF + Py	0.436	0.126	1.050	0.257	2.57	13.5	0.303	2.57	3.46	1.56	0.637	0.495	0.401	1.235	2.21	17182	187.96
	0.437	0.129	1.050	0.253	2.57	13.5	0.301	2.57	3.46	1.56							
Nd + DMF + Th	0.374	0.158	1.120	0.291	2.08	5.47	0.422	3.88	4.43	1.52	0.135	0.425	0.639	0.665	3.08	17211	49.73
	0.375	0.154	1.120	0.288	2.08	5.47	0.418	3.88	4.42	1.52							
Nd + DMF + 4-Cl	0.570	0.191	1.500	0.376	3.34	14.8	0.486	4.31	5.32	2.14	0.642	0.648	0.687	0.944	4.43	17123	125.80
	.570	0.190	1.500	0.374	3.35	14.8	0.484	4.31	5.32	2.14							

As = ascorbic acid, B = biotin, GA = gibberalic acid, IAA = indoleacetic acid, IBA = indole-3-butyric acid, K = kinetin, Ni = niacin, Py = pyridoxine, Th = thiamin, 4-Cl = 4-chlorophenoxyacetic acid.

TABLE-4
COMPUTERIZED VALUES OF VARIOUS PARAMETERS FOR Nd(III) SYSTEM

System	F_2	F_4	F_6	rF_2 (%)	ζ4F	ζ4F (%)	E_1	E_2	E_3	β	$b^{1/2}$	δ (%)	rms
Free ion	331.16	50.71	5.15	-	884.0	-	5024	23.90	497	-	-	-	-
Nd + DMF + As	329.00	50..54	5.28	0.678	881	0.3075	5031	23.81	489	0.9919	0.0632	0.817	88.09
Nd + DMF + B	329.00	50.80	5.27	0.744	883	0.0998	5034	23.68	489	0.9913	0.0658	0.878	113.32
Nd + DMF + GA	329.00	50.70	5.21	0.655	877	0.7677	5020	23.70	492	0.9922	0.0624	0.786	108.90
Nd + DMF + IAA	328.00	50.81	5.21	0.843	883	0.0558	5017	23.60	491	0.9903	0.0694	0.979	71.10
Nd + DMF + IBA	329.00	50.75	5.18	0.772	883	0.1413	5012	23.62	492	0.9910	0.0668	0.908	75.09
Nd + DMF + K	329.00	50.70	5.24	0.693	882	0.2146	5024	23.71	491	0.9918	0.0640	0.827	119.70
Nd + DMF + Ni	329.00	50.83	5.28	0.736	881	0.2949	5036	23.69	489	0.9914	0.0655	0.867	126.73
Nd + DMF + Py	328.00	50.84	5.24	0.832	880	0.4063	5026	23.62	490	0.9904	0.0690	0.969	88.94
Nd + DMF + Th	329.00	50.61	5.27	0.627	881	0.3300	5031	23.79	490	0.9925	0.0612	0.756	85.64
Nd + DMF + 4-Cl	329.00	50.61	5.26	0.648	881	0.3210	5029	23.78	490	0.9923	0.0621	0.776	99.92

As = ascorbic acid, B = biotin, GA = gibberalic acid, IAA = indoleacetic acid, IBA = indole-3-butyric acid, K = kinetin, Ni = niacin, Py = pyridoxine, Th = thiamin, 4-Cl = 4-chlorophenoxyacetic acid.

On comparing results Pr(III) systems show greater decrease in ζ4F parameter than Nd(III) systems.

(5) According to theory of *f-f* transition decrease in F_2 parameter indicates decrease in interelectronic repulsion and may be attributed to chelation of metal ion with ligand present in surrounding environment[24]. Very much decrease in F_2 parameter has been found in Pr(III)-biotin system (307) and in Nd(III)-indoleacetic acid-system (328). On comparing results, Pr(III) systems (307 to 311) show greater decrease in F_2 parameter than Nd(III) systems (328 to 329), indicating better complexation is observed in Pr(III) system.

(6) Parameter T_2 and T_6 also show dependence on the status of metal ion. Parameter T_2 and T_6 which are symmetry denoting parameter expected to be large on account of large cationic size of Pr(III) and Nd(III) with large hydration zones. These factors are expected to cause greater perturbations in the symmetry around the coordination sphere during a vicinal Ln(III)-L interaction thereby increasing the magnitude of these values. In Pr(III) system, the negative value of T_2 parameter have no physical significance but in Nd(III) systems higher value of T_2 parameters with biotin shows better inter ligand interaction. The changes in T_6 value may be reflection of changes in symmetry associated with bonding mechanism for the ligand during inter ligand interaction[25].

From the result it has been found that greater change in symmetry has been found in Pr(III)-biotin system and Nd(III) ascorbic acid system and Nd(III) 4-chlorophenoxyacetic acid system. From the values of T_4/T_6 it has been found that there is very slight deviation from symmetry in both Pr(III) and Nd(III) system. On comparing both systems Pr(III) system show more deviation from symmetry than Nd(III) systems.

(7) The value of Peacock constant K has been found almost constant in all Pr(III) systems (14.0 to 14.9) where as there is some deviation (49.73 to 196.41) in Nd(III) systems.

(8) Small values of rms deviation for P_{obs} and P_{cal} for all bands in Pr(III) systems (1.46 to 6.75) and Nd(III) systems (3.01 to 9.09) proved the validity of Judd-Ofelt equation.

(9) Validity of Slater Condon and Lande theory has been proved by the rms deviation (rms σ) values of energies of all the bands for Pr(III) systems (105.44 to 180.07) and Nd(III) systems (71.10 to 126.73).

ACKNOWLEDGEMENTS

The authors are grateful to National Research Centre of Equines (NRCE) Bikaner, India for providing the necessary research facilities.

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