Variation in Symmetry Around Nd^{3+} Ion in Saturated Solution of Medicinal Compounds with Reference to Judd-Ofelt Electronic Spectral Parameter

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The stereo-environment of doped Nd^{3+} ion in various saturated solutions of some medicinal compounds has been studied for various electronic spectral parameters. The various electronic parameters, *viz.*, Slater-Condon (F_k), Landé parameter (ζ_{4f}), intensity of hypersensitive band ($^4G_{5/2}$), bonding parameter ($b^{1/2}$), Judd-Ofelt parameter (T_λ) and Racah parameter (E^k) for Nd^{3+} ion doped in saturated solution of thiabendazole, piperazine, mebendazole, pyrantel pamoate and albendazole have been studied.

INTRODUCTION

The chemistry of lanthanides continues to attract scientists because of its applications in various industries and biological studies. Recently it has been investigated that lanthanum is a substitute of Ca^{2+} ion in biological systems[1-3]. In the present discussion a study has been made to explore the extent of coordination behaviour of Nd^{3+} ion with some medicinally important compounds for their pharmaceutical application, on the ground of Judd-Ofelt and Slater-Condon theories[4]. The Ln^{3+} 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 present investigation has been undertaken with a view to make a comparative study of the various energy and intensity parameters resulting from f ↔ f transition in different energy levels of doped Nd^{3+} ion in alcoholic solution.

EXPERIMENTAL

The various saturated alcoholic solutions of thiabendazole (TBZ), piperazine (PPZ), mebendazole (MBZ), pyrantel pamoate (PP) and albendazole (ABZ) of I.P. grade have been prepared at room temperature and 0.1 g of NdCl$_3$·6H$_2$O salt per 10 mL of saturated solution has been added. Solution spectra of these saturated solutions have been recorded by using standard spectrophotometer in the range 400 to 900 nm.

RESULTS AND DISCUSSION

The values of various parameters have been reported in Tables 1–3. The

calculated parameters include oscillator strength (P), energy (E), Judd-Ofelt parameters (T_2, T_4 and T_6), Slater-Condon parameters (F_2, F_4 and F_6), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Racah parameters (E^1, E^2 and E^3), Landé parameter (ζ_{4f}), percentage reduction in F_2-parameter (% r F_2), percentage reduction in ζ_{4f}-parameter (% r ζ_{4f}), and r.m.s. deviation with respect to oscillator strength and energy (σ). The calculations of various parameters involve theories given by Slater-Condon-Landé and Judd-Ofelt as reported by earlier workers. The computerized programmes for the said calculations have already been set up in the present laboratory by earlier workers[5-8]. All the parameters show fair agreement with the theory involved in doped Nd^{3+} ion. The comparison of the observed and calculated values of the various energy levels shows the average r.m.s. deviation from ±44.00 to ±74.18. The red shift in all the energy bands compared with the free ion value supports the change in coordination environment around the central metal ion.

TABLE-1

ENERGIES (cm^{-1}) FOR Nd^{3+} DOPED PHARMACEUTICAL COMPOUNDS

Nd^{3+} Systems / Levels	Nd^{3+}-TBZ		Nd^{3+}-PPZ		Nd^{3+}-MBZ		Nd^{3+}-PP		Nd^{3+}-ABZ	
	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}
$^2P_{1/2}$	23148	23146	23148	23157	23148	23141	23148	23151	23148	23142
$^4G_{11/2}$	21552	21519	21459	21490	21739	21578	21505	21507	21645	21524
$^4G_{9/2}$	21186	21142	21142	21109	21277	21226	21277	21230	21277	21220
$^2G_{9/2}$	19531	19558	19455	19525	19531	19594	19531	19572	19531	19582
$^4G_{7/2}$	19157	19220	19157	19187	19157	19235	19157	19243	19157	19250
$^4G_{5/2}$	17241	17291	17241	17262	17241	17249	17241	17245	17241	17268
$^4F_{9/2}$	14619	14715	14663	14700	14663	14771	14663	14731	14619	14734
$^4F_{7/2}$	13423	13292	13369	13275	13369	13311	13369	13273	13369	13286
$^4F_{5/2}$	12469	12474	12469	12456	12469	12481	12469	12458	12469	12465
$^4F_{3/2}$	11494	11471	11481	11456	11481	11448	11468	11442	11494	11456
r.m.s. dev (±)	61.02		44.00		74.18		51.02		71.79	

The average value of F_4/F_6 in Nd^{3+} doped ion (0.155–0.160) is nearer to the value for free ion (0.153). The same trend has been observed for the ratio F_6/F_2 (0.016). The values of nephelauxetic ratio $\beta < 1$ and the values of bonding parameter ($b^{1/2}$) indicate covalent bonding to some extents in doped Nd^{3+} ion. The small value of $b^{1/2}$ and little variation in it suggests that the 4f-orbitals are very slightly involved in the bonding in the saturated solution with ligands.

The intensities of the observed bands have been given in terms of oscillator strength (P). The r.m.s. deviation with respect to oscillator strength (P) within the range of $\pm 1.44 \times 10^{-6}$ to $\pm 1.98 \times 10^{-6}$ has been reported in Table-2. The small deviation for the calculated and observed (P) value suggests the validity of Judd-Ofelt equation for f $\leftrightarrow$ f transition for the present study.

TABLE-2

THE OSCILLATOR STRENGTH ($P \times 10^6$) FOR Nd^{3+} DOPED
PHARMACEUTICAL COMPOUNDS

Nd^{3+} Systems / Levels	Nd^{3+}-TBZ		Nd^{3+}-PPZ		Nd^{3+}-MBZ		Nd^{3+}-PP		Nd^{3+}-ABZ	
	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$
$^2P_{1/2}$	1.95	1.39	2.46	1.47	2.03	1.13	2.59	0.46	2.11	1.56
$^4G_{11/2}$	1.98	0.43	1.92	0.42	1.71	0.33	2.01	0.46	2.14	0.45
$^4G_{9/2}$	4.60	3.35	3.71	3.36	4.01	2.59	4.89	3.81	4.40	3.58
$^2G_{9/2}$	2.45	0.84	1.76	0.83	1.47	0.64	2.69	0.93	2.31	0.89
$^4G_{7/2}$	4.99	6.86	5.90	6.83	4.73	5.37	6.86	7.96	6.41	7.36
$^4G_{5/2}$	18.10	20.80	15.50	18.20	14.10	16.20	20.80	23.70	18.60	21.50
$^4F_{9/2}$	1.93	1.04	2.30	1.00.	1.91	0.76	2.57	1.07	2.08	1.05
$^4F_{7/2}$	8.19	9.23	7.84	8.63	5.54	6.53	7.96	9.07	7.84	9.12
$^4F_{5/2}$	8.27	11.90	7.99	11.60	6.40	8.84	8.82	12.70	8.65	12.30'
$^4F_{3/2}$	3.48	5.07	3.80	5.27	2.46	4.03	4.20	6.03	3.49	5.56
r.m.s. dev $\times 10^6 (\pm)$	1.89		1.73		1.44		1.98		1.89	

TABLE-3

SLATER-CONDON (F_K), RACAH (E^K) LAND'E ($\zeta 4f$), NEPHELAUXETIC (β),
BONDING PARAMETER ($B^{1/2}$) AND JUDD-OFELT (T_λ) PARAMETER FOR
Nd^{3+} DOPED SYSTEMS

Nd^{3+} Systems / Parameters	Nd^{3+}-TBZ	Nd^{3+}-PPZ	Nd^{3+}-MBZ	Nd^{3+}-PP	Nd^{3+}-ABZ
F_2	329.97	330.71	328.78	327.90	328.11
F_4	51.54	51.19	51.33	52.39	52.29
F_6	5.24	5.29	5.23	5.23	5.21
F_4/F_6	0.156	0.155	0.156	0.160	0.159
F_6/F_2	0.016	0.016	0.016	0.016	0.016
E^1	5054.95	5062.50	5037.69	5058.96	5053.31
E^2	23.56	23.79	23.49	23.04	23.08
E^3	494.09	493.17	492.06	492.61	493.35
ζ_{4f}	854.92	855.24	874.01	859.13	858.39
% rζ_{4f}	3.28	3.25	1.13	2.81	2.89
β	0.995	0.997	0.992	0.989	0.989
$b^{1/2}$	0.049	0.036	0.065	0.074	0.072
$T_2 \times 10^{10}$	5.72	3.60	4.20	5.86	5.32
$T_4 \times 10^{10}$	15.70	16.70	12.80	19.50	17.60
$T_6 \times 10^{10}$	14.60	13.50	10.20	14.00	14.30
T_4/T_6	1.08	1.24	1.26	1.40	1.23
% rF_2	0.36	0.13	0.72	0.98	0.92

The T_4/T_6 ratio has been reported in Table-3. It qualitatively suggests to have a common symmetry around the Nd^{3+} ion in the solution.

The hypersensitive transition (which is sensitive to environmental changes) $^4I_{9/2} \leftrightarrow {}^4G_{5/2}$ exihibits the increase in the intensity with the increase in covalency around the Nd^{3+} ion in the solution. The hypersensitivity has been found to be proportional to nephelauxetic ratio (β). This is in conformity with the observations reported earlier by Peacock for the hypersensitive bands.

The trend of decrease in ζ_{4f} value for the Nd^{3+} ion doped in saturated solution in comparison to free value (884.99 cm^{-1}) varies from 854.92 cm^{-1} to 874.01 cm^{-1} and suggests fair interaction as given in Table-3. The various other parameters have their usual significance as reported earlier.

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