Characterization of Some Pr(III) Complexes in Terms of Electronic Spectral Parameters

P. R. BHATI*, K. P. SONI, G. K. JOSHI AND S. N. SWAMI

Department of Chemistry, Government Dungar College
Bikaner-334 001, India

Pr(III) complexes from the ligands derived from methyl acetoacetate, ethyl acetoacetate, veratraldehyde, ethyl vanillin and 2,5 dimethoxy benzaldehyde forming Schiff-bases with ortho, meta and para phenylene diamines have been synthesized. The complexes have been characterized in terms of various Slater-Condon Landé and Judd-Ofelt parameters. The various trends in the parametric values have also been described. The involvement of 4f-orbital in the Pr(III) complexes including deviation in the symmetry have been discussed on the basis of electronic spectral parameters. The validity of the theories used has been established while comparing observed and calculated energies and intensities of the various bands in the present complexes on the basis of r.m.s. deviation. The trends of the curves observed in the solution spectra have also been discussed.

INTRODUCTION

Lanthanide (III) ions exhibit absorption spectra characterised by bands in visible region but these spectra have not been studied extensively[1-4] in terms of Slater-Condon-Landé and Judd-Ofelt parameters, covalent contributions to bond formation have been invoked to explain certain effects of the extremely complicated spectra resulting from the $f \leftrightarrow f$ electronic transitions[5-18] in the lanthanide ions. Although the bonding between the ligands and the lanthanide ions is sufficiently electrostatic yet with appreciable interactions between the 4f-orbitals and ligand orbitals[5-18]. The interelectronic repulsions and spin-orbit interactions involved in the metal-ligand bond may be given in terms of Slater-Condon-Landé parameters whereas the intensities of the various bands observed may be given in terms of Judd-Ofelt parameters in lanthanide complexes[5-18]. In the present paper some Pr(III) complexes have been characterised in terms of these electronic spectral parameters.

EXPERIMENTAL

Synthesis of Pr(III) Complexes

The complexes have been synthesized from the method described by Ansari and Ahmed[19] by refluxing the mixture of ethanolic solution of $PrCl_3 \cdot 6H_2O$ and the ligands in 1 : 1 molar ratio. In the reaction mixture the precipitation occurs with a change in colour from buff to dark reddish

brown. Complexes were found soluble in DMSO, N,N dimethylformamide and water acetic acid mixture. The ligands were also prepared by the condensation reaction in ethanol from o^-, p^- and m^- phenylene diamine and methyl acetoacetate, ethyl acetoacetate, veratraldehyde, ethyl vanilline and 2,5-dimethoxy benzaldehyde in the 1 : 2 molar ratio. AnalaR grade chemical were used for synthesis.

(a) *Solution Spectra*:   The solution spectra of the various complexes in the present work have been recorded by using the standard spectrophotometer in the region 350–750 nm.

(b) *Analytical and IR-Studies*:   The analytical and IR studies have been carried out at CDRI, Lucknow and AIIRA, Ahmedabad respectively. However metal percentage of the complexes have been estimated by using the standard methods[20]. These studies suggest the following molecular formulae for the present Pr(III) complexes.

(i) $Pr(Cl)(L)(H_2O)_4$, where L = MeAA-OPD, MeAA-PPD, MeAA-MPD, EtAA-OPD, EtAA-PPD, EtAA-MPD, EtV-OPD, EtV-PPD, EtV-MPD.

(ii) $Pr(L')(H_2O)_4Cl_3$, where L' = 2,5 DMB-OPD, 2,5 DMB-PPD, 2,5 DMB-MPD, V-OPD, V-PPD, V-MPD.

Parametric Calculations

As has been reported earlier[5-18] the following equations involving Slater-Condon-Landé and Judd-Ofeld theories to compute energy and intensity parameters resulting from f–f transitions have been employed in the present Pr(III) complexes.

(i) Slater-Condon-Landé Equation :

$$E_j(Fk, \xi_{4f}) = E_{0j}(F^0{}_k, \xi^0{}_f) + \frac{\delta E}{F_2} \times \Delta F_2 + \frac{\delta E_J}{\delta F_4} \times \Delta F_4$$

$$+ \frac{\delta E_J}{\delta F_6} \times \Delta F_6 + \frac{\delta E_J}{\delta J_{4f}} \times \Delta \xi_{4f}$$

(ii) Judd-Ofelt Equation :

$$P_{obs} = [U^{(2)}]\nu \times T_2 + [U^{(4)}]^2\nu \times T_4 + [U^{(6)}]^2\nu \times T_6$$

RESULTS AND DISCUSSIONS

In the present Pr(III) complexes, the solution spectra yield four bands viz. $^3H_4 \rightarrow {}^3P_2$; $^3H_4 \rightarrow {}^3P_1$ $^3H_4 \rightarrow 3P_0$ and $^3H_4 \rightarrow {}^1D_2$. The energies of the bands observed have been recalculated by applying Slater-Condon-Landé

MeAA = methylacetoacetate; EtAA = ethyl acetoacetate; EtV = ethyl vanilline; V = veratraldehyde; 2,5 DMB = 2,5 = dimethoxy benzaldehyde; OPD = *o*-phenylenediamine; PPD=p-phenylenediamine MPD = *m*-phenylenediamine.

equation in which computed parametric values from experimental energies have been used. The r.m.s. deviation between experimental and recalculated values of the bands varied from ± 94 to ± 158 cm^{-1}. These have been reported in Table 1.

The various energy parameters viz. F_2, F_4, F_6, β, $b^{1/2}$ and $\%^r F_2$ have been reported in Table 2. These parameters suggest that there is decrease in F_k-parameters when compared with the parametric values reported for free Pr(III) ion. This has been given in terms of percentage reduction in F_2-parameter, alongwith nephelauxetic ratio (β) and bonding parameter ($b^{1/2}$). The results show that the interelectronic repulsions have been decreased when Pr(III) ion forms complexes.

In the formation of complexes, spin-orbit-interactions have also been decreased. This has been given in terms of Landès parameter (ξ_{4f}) and has been reported alongwith Racah parameters in Table 3.

The intensity of the bands observed has been given in terms of oscillation strength (P). The values of intensity for the bands have been recalculated by applying the Judd-Ofelt equation in which computed parametric values from experimental intensities have been used. The r.m.s. deviation in between experimental and recalculated values for the oscillator strengths varies from $\pm 0.01 \times 10^{-6}$ to $\pm 0.08 \times 10^{-6}$. These have been reported in Table 4.

The Judd-Ofelt intensity parameters T_2, T_4 and T_6 have been reported along with the ratio T_4/T_6 in Table 5. A constancy in the ratio T_4/T_6 value suggests qualitatively to have a common symmetry in the series of complexes but in the present case the value of ratio has been slightly varied and hence the various complexes can be grouped according to the ratio value.

In the present series Pr(III) complexes the following inferences have been derived with respect to their spectral characterisations in terms of various spectral parameter.

(a) The order in terms of $B^{1/2}$ and $\%\ ^r F_2$

    (i) MeAA > EtAA

        When amines used are OPD, MPD and PPD for the formation of ligands.

    (ii) 2,5 DMB > Et.V > V

        When amines used are OPD, MPD and PPD for the formation of ligands.

(b) The order in terms of $\%\ \zeta_{4f}$.

    (i) Et.AA > MeAA

        When amines used are OPD, MPD and PPD for the formation of ligands.

TABLE 1

COMPUTED VALUES OF ENERGIES IN cm⁻¹ FOR THE BANDS OF Pr(III) COMPLEXES WITH LIGANDS DERIVED FROM VERATRALALDEHYDE, ETHYL VANILLINE AND 2,5 DMB AND WITH β-KETO ESTER AND o^-, m^-, p^- PHENYLENEDIAMINE

S. No.	Level Pr(III) Complexes	$^3P_2$		$^3P_1$		$^3P_0$		$^1D_2$		dev($\pm$)
		E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	
1.	Pr-Me.AA-OPD	22446	22340	21213	21220	20738	20774	16914	17078	$\pm$ 99
2.	Pr-Et.AA-OPD	22421	22248	21118	21163	20748	20780	16874	17038	$\pm$ 122
3.	Pr-V-OPD	22473	22328	21208	21214	20746	20777	16891	17040	$\pm$ 105
4.	Pr-Et.V-OPD	22421	22322	21208	21199	20704	20746	16891	17062	$\pm$ 101
5.	Pr-2,5 DMB-OPD	22462	22380	21222	21241	20734	20757	16912	17090	$\pm$ 99
6.	Pr-MeAA-PPD	22468	22356	21228	21232	20738	20776	16914	17085	$\pm$ 104
7.	Pr-EtAA-PPD	22461	22335	21223	21228	20733	20804	16911	17084	$\pm$ 108
8.	Pr-V-PPD	22461	22336	21188	21217	20733	20770	16911	17074	$\pm$ 105
9.	Pr-EtV-PPD	22471	22316	21164	21189	20682	20601	16863	17050	$\pm$ 128
10.	Pr-2,5 DMB-PPD	22396	22310	21119	21178	20661	20708	16835	17041	$\pm$ 112
11.	Pr-MeAA-MPD	22421	22336	21231	21210	20703	20749	16891	17065	$\pm$ 158
12.	Pr-EtAA-MPD	22471	22312	21186	21204	20746	20768	16877	17066	$\pm$ 125
13.	Pr-V-MPD	22471	22330	21208	21204	20703	20745	16863	17062	$\pm$ 124
14.	Pr-EtV-MPD	22446	22345	21186	21214	23703	20744	16920	17072	$\pm$ 94
15.	Pr-2,5 DMB-MPD	22421	22300	21231	21196	20746	20780	16863	17061	$\pm$ 119

MeAA = Methyl aceto acetate
EtAA = Ethyl aceto acetate
V = Veratraldehyde
EtV = Ethylvanilline
2,5 DMB = 2,5 dimethoxy benzaldehyde
OPD = Ortho-phenylen diamine (buff colour)
PPD = Para-phenylene diamine (slightly reddish colour)
MPD = Meta-phenylene diamine (slight reddish purple)

TABLE 2

COMPUTED VALUES OF VARIOUS SPECTROSCOPIC PARAMETERS
F_k, β, $b^{1/2}$ and %$^r F_2$ OF Pr(III) COMPLEXES WITH β-KETO ESTER
VERATRALDEHYDE, ETHYL VANILINE, 2,5.DMB AND $^-$o, $^-$m, $^-$p
PHENYLENEDIAMINE, SCHIFF'S BASES

S. No.	Parameters Pr(III) Complexes	F_2 (in cm^{-1})	F_4 (in cm^{-1})	F_6 (in cm^{-1})	β	$b^{1/2}$	%$^r F_2$
1.	Pr–Me.AA–OPD	311.65	43.02	4.71	0.96758	0.12732	3.24
2.	Pr–Et AA–OPD	312.64	43.16	4.72	0.97065	0.12114	3.03
3.	Pr–V–OPD	311.86	43.03	4.71	0.96822	0.12606	3.18
4.	Pr–EtV–OPD	311.09	42.95	4.70	0.96585	0.13067	3.41
5.	Pr–2,5DMB–OPD	310.80	42.91	4.70	0.96494	0.13240	3.51
6.	Pr–Me.AA–PPD	311.51	43.00	4.71	0.96716	0.12814	3.28
7.	Pr–Et.AA–PPD	312.41	43.12	4.72	0.96995	0.12258	3.01
8.	Pr–V–PPD	311.53	43.00	4.71	0.96722	0.12802	3.28
9.	Pr–EtV–PPD	310.63	42.88	4.69	0.96441	0.13340	3.56
10.	Pr–2,5DMB–PPD	310.23	42.83	4.69	0.96317	0.13570	3.68
11.	Pr–Me.AA–MPD	310.98	42.93	4.69	0.96246	0.13700	3.45
12.	Pr–Et.AA–MPD	311.98	43.06	4.71	0.96861	0.12528	3.14
13.	Pr–V–MPD	310.96	42.92	4.69	0.96545	0.13143	3.44
14.	Pr–EtV–MPD	310.83	42.91	4.69	0.96505	0.13219	3.50
15.	Pr–2,5 DMB–MPD	312.16	43.09	4.71	0.96917	0.12416	3.08
*	Pr^{-3} free ion	322.09	44.46	4.87	—	—	—

TABLE 3

COMPUTED VALUES OF VARIOUS SPECTROSCOPIC PARAMETERS
(E^k and ξ_{4t}) OF Pr(III) COMPLEXES WITH β-KETO ESTER AND
VERATRALDEHYE, ETHYL VANILLINE, 2,5 DMB SCHIFF'S BASES

S. No.	Parameters Pr(III) Complexes	E^1 (in cm^{-1})	E^2 (in cm^{-1})	E^3 (in cm^{-1})	ξ_{4t} (in cm^{-1})	%$^r \xi_{4t}$
1.	Pr–Me.AA–OPD	4575.58	23.93	362.61	654.38	11.69
2.	Pr–Et.AA–OPD	4590.10	24.01	464.08	623.83	15.81
3.	Pr–V–OPD	4578.59	23.95	462.91	658.05	12.26
4.	Pr–EtV–OPD	4567.39	23.89	461.78	658.05	11.19
5.	Pr–2,5DMB–OPD	4563.07	23.87	461.34	672.99	9.18
6.	Pr–Me.AA–PPD	4573.58	23.92	462.41	659.26	11.03
7.	Pr–Et.AA–PPD	4586.79	23.99	463.74	644.10	13.08
8.	Pr–V–PPD	4573.89	23.92	462.44	655.06	11.60
9.	Pr–EtV–PPD	4560.56	23.85	461.09	661.94	10.67
10.	Pr–2,5DMB–PPD	4554.72	23.82	460.50	665.61	10.17
11.	Pr–Me.AA–MPD	4565.78	23.88	461.62	661.59	10.72
12.	Pr–Et.AA–MPD	4580.45	23.96	463.11	644.84	12.98
13.	Pr–V–MPD	4565.31	23.88	461.59	660.68	10.84
14.	Pr–EtV–MPD	4554.29	23.87	461.40	665.65	10.17
15.	Pr–2,5 DMB–MPD	4583.07	23.97	463.37	640.25	13.60
*	Pr^{-3} free ion	4729.00	24.78	476.13	741.00	—

TABLE 4

COMPUTED VALUES OF OSCILLATOR STRENGTH OF THE BANDS OBSERVED FOR Pr^{3+} COMPLEXES WITH VARIOUS β-KETO ESTER AND VERATRALDEHYDE, ETHYL, VANILINE, 2,5.D.M.B. SCHIFF BASES

S. No.	Pr^{+3} Complexes	$^3P_2$		$^3P_1$		$^3P_0$		$^1D_2$		dev($\pm$) σ
		$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	
1a.	Pr-Me.AA-OPD	20.86	20.88	8.37	8.36	5.62	5.59	6.01	5.87	0.07
b.	Pr-Me.AA-PPD	20.25	20.18	8.96	8.96	5.42	5.41	6.52	6.52	0.03
c.	Pr-Me.AA-MPD	17.97	17.96	5.04	5.06	1.86	1.85	4.98	4.97	0.03
2a.	Pr-Et.AA-OPD	16.41	16.35	8.50	8.36	4.53	4.55	4.70	4.70	0.08
b.	Pr-Et.AA-PPD	16.19	19.18	8.89	8.88	4.47	4.46	5.48	5.49	0.01
c.	Pr-Et.AA-MPD	17.02	17.01	7.83	7.82	2.40	2.39	4.81	4.80	0.01
3a.	Pr-Vera-OPD	23.21	22.20	9.56	9.55	5.88	5.87	6.31	6.33	0.02
b.	Pr-Vera-PPD	29.86	29.83	10.40	10.38	4.93	4.91	8.51	8.51	0.02
c.	Pr-Vera—MPD	19.21	18.20	7.94	7.97	2.13	2.12	5.06	5.05	0.01
4a.	Pr-Et.V-OPD	17.75	17.75	8.38	8.37	4.10	4.11	5.10	5.10	0.01
b.	Pr-Et.V-PPD	29.65	29.65	9.88	9.87	7.38	7.29	8.55	8.54	0.01
c.	Pr-Et.V-MPD	16.72	16.71	6.80	6.79	2.47	2.46	4.61	4.62	0.01
5a.	Pr-2,5.DMB-OPD	35.30	35.28	10.12	10.11	4.86	4.85	10.80	10.08	0.01
b.	Pr-2,5.DMB-PPD	22.16	22.15	7.86	7.86	5.70	5.71	6.25	6.24	0.01
c.	Pr-2,5.DMB-MPD	17.16	17.15	8.50	8.49	2.45	2.44	4.82	4.82	0.01

TABLE 5

COMPUTED VALUES OF T_λ PARAMETER OF Pr(III) COMPLEXES WITH
β-KETO ESTER AND VERATRALDEHYDE, ETHYL VANILLINE AND
2,5 DMB SCHIFF'S BASE

S. No.	Parameter Pr^{3+} Complexes	$T_2 \times 10^{10}$	$T_4 \times 10^{10}$	$T_6 \times 10^{10}$	T_4/T_6
1a.	Pr–Me.AA–OPD	58.02	19.40	63.49	0.31
b.	Pr–Me.AA–PPD	43.65	19.91	60.99	0.33
c.	Pr–Me.AA–MPD	59.20	09.55	56.61	0.17
2a.	Pr–Et.AA–OPD	24.80	18.10	49.05	0.37
b.	Pr–Et.AA–PPD	36.38	18.50	58.18	0.32
c.	Pr–Et.AA–MPD	38.28	14.17	52.15	0.27
3a.	Pr–Vera–OPD	42.80	21.40	67.22	0.32
b.	Pr–Vera–PPD	42.98	21.20	92.36	0.26
c.	Pr–Vera–MPD	54.73	13.94	56.09	0.25
4a.	Pr–Et.V–OPD	27.55	17.30	53.81	0.32
b.	Pr–Et.V–PPD	44.76	24.02	90.98	0.26
c.	Pr–Et.V–MPD	65.92	12.58	51.55	0.25
5a.	Pr–2,5.DMB–OPD	52.53	20.74	110.40	0.19
b.	Pr–2,5.DMB–PPD	55.05	18.89	67.98	0.28
c.	Pr–2,5.DMB–MPD	48.35	15.14	52.44	0.29

    (ii) 2,5 DMB > Et.V < V
        When amines used are OPD and PPD.
    (iii) 2,5 DMB > EtV < V
        When amines used in MPD for the formation of ligands.
  (c) The order in terms of T_4/T_6 ratio
    (i)   OPD > PPD > MPD
        When carbonyl compounds used are EtAA, EtV and V for the
        formation of ligands.
    (ii) MPD > PPD > OPD
        When 2,5 DMB has been used for the formation of ligands.
    (iii) PPD > OPD > MPD
When MeAA has been used for the formation of ligands.

Trends in Solution Spectra

The solution spectra showing absorption trends in the cases of ligands derived from PPD and OPD have been shown in Fig. 1 and 2. The spectra have been well distinguished as far as intensities of the various bands are concerned. The solution spectra of these complexes appear to have a strong absorption in the UV region as the curve have the beginning with high absorption near 400 nm. The effect of absorption band in the UV region has been minimised in all the complexes at the band
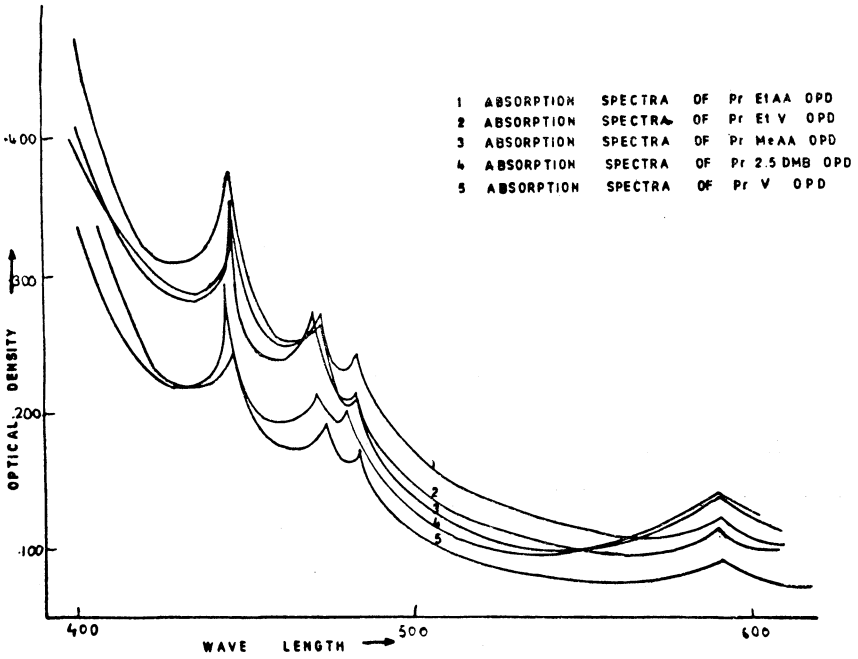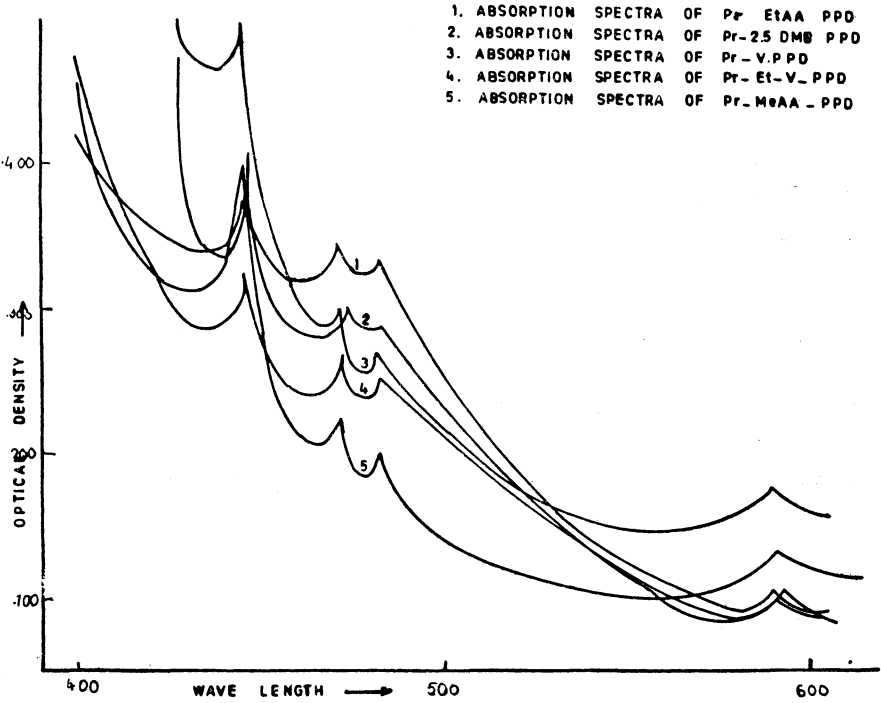
1 ABSORPTION   SPECTRA   OF   Pr EtAA OPD
2 ABSORPTION   SPECTRA   OF   Pr Et V OPD
3 ABSORPTION   SPECTRA   OF   Pr MeAA OPD
4 ABSORPTION   SPECTRA   OF   Pr 2.5 DMB OPD
5 ABSORPTION   SPECTRA   OF   Pr V OPD

Fig. 1

1. ABSORPTION   SPECTRA   OF   Pr EtAA   PPD
2. ABSORPTION   SPECTRA   OF   Pr-2.5 DMB   PPD
3. ABSORPTION   SPECTRA   OF   Pr – V.P PD
4. ABSORPTION   SPECTRA   OF   Pr– Et– V– PPD
5. ABSORPTION   SPECTRA   OF   Pr–MeAA – PPD

Fig. 2

near 590 nm. A similar trend has also been observed in the complexes derived from MPD.

ACKNOWLEDGEMENT

REFERENCES

1. D.G. Karrakar, *J. Chem. Edu.*, 47, 424 (1970).

2. O. Johnson, *J. Chem. Edu.*, 47, 431 (1970).

3. S.P. Vasireddy and V. Ramachandra Rao, *J. Inorg. Nucl. Chem.*, 39, 311 (1977).

4. A. Kahn, A.M. Lejus, M. Madsac, J. Thery, D. Vivien and J.C. Bernier, *J. Appl. phys.* 52, 6864 (1981).

5. W.T. Carnall, H. Crosswhite and H.M. Crosswhite. Energy Level, Structure and Transition Probabilities of the Trivalent Lanthanides in LaF₃, Department of Physics, The Johns Hopkins University, Baltimore, Maryland, 21218.

6. W. T. Carnall, G. L. Goodman, R. S. Rana, P. Vandevelde, L. Fluyt and C. G. Walrand, *J. Less-Common Metals* 116, 17 (1986).

7. W. T. Carnall, P. R. Fields and B. G. Wybourne, *J. Chem. Phys.* 42, 3797 (1965).

8. S. P. Tandon and P. C. Mehta, *J. Chem. Phys.*, 52, 5417 (1970).

9. ———, *J. Chem. Phys.*, 52, 4313 (1970).

10. R. C. Mathur, S. S. L. Surana and S. P. Tandon, *Indian J. Pure & Appl. Phys.*, 17, 452 (1979).

11. S. S. L. Surana, Megh Singh and Sudhindra N. Misra, Intensity Analysis of $f \longleftrightarrow f$ Transitions and Energy Interaction Parameters in Studies of the Structure of Lanthanide Haloacetates in Solutions.

12. S. S. L. Surana, R. C. Mathur and S. P. Tandon *Spectroscopy Letters*, 11, 389 (1978).

13. G. K. Joshi, M. P. Bhutra and Sudhindra N. Misra, *J. Inorg Nucl. Chem.*, 43, 525 (1981).

14. G. K. Joshi, *Indian J. Pure & Appl. Phys.*, 21, 224 (1983).

15. S. V. J. Lakshman and S. Buddnudu., *J. Quant. Spectrosc. Radiat. Transfer*, 24, 251 (1980).

16. P. C. Vyas, C. K. Ojha, (Mrs.) S. Mittal and G. K. Joshi, *J. Indian Chem. Soc.*, 65, 611 (1988).

17. S. P. Tandon, A. Gokhroo, M. P. Bhutra, S. S. L. Surana and K. Tandon, *J. Chem. Phys.,* **86**, 7243 (1987).

18. B. K. Gupta, G. K. Joshi and P. R. Bhati, *Indian J. Pure & Appl. Phys.,* **28**, 525 (1990).

19. M. Shameem Ansari and Naseer Ahmed, *J. Inorg. Nucl. Chem.*, **38**, 1232 (1976).

20. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, ELBS and Longmans Green & Co. Ltd., London (1961).

21. G. K. Joshi, Megh Singh and Sudhindra N. Misra, *Indian J. Chem.*, **23A**, 329 (1984).