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Electronic spectral studies on lanthanide(III) in mixed metal environments of the type [Ln(III)·DTPA·M(II)]: Ln(III)=Pr, Nd, Sm, Dy, Er, Tm and M(II)=Mn, Fe, Co, Ni, Cu, Zn

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Abstract

Electronic spectral studies of lanthanides (Ln) in mixed metal environments of the type [Ln(III)·DTPA·M(II)] (where Ln(III)=Pr, Nd, Sm, Dy, Er, Tm; and M(II)=Mn, Fe, Co, Ni, Cu and Zn) in aqueous phase at controlled pH (~4.00) have been carried out in order to evaluate electronic spectral parameters, viz: (i) oscillator strength (f_{JO}), (ii) Judd–Ofelt parameters (T_λ), (iii) interelectronic repulsion (Racah) parameters (δE^k) and (iv) nephelauxetic ratio ($\delta E^3/\delta E^1$) values in mixed metal environments and to examine their variations as a result of insertion of M(II) (3d transition metal) ions in a [Ln·DTPA] environment. Octadentate DTPA has been used as a bridging ligand between two elemental moieties, viz: Ln(III) and M(II). The electronic spectral parameters (f_{JO}), (T_λ) and ($\delta E^3/\delta E^1$) values show marked dependence on the nature of M(II) ions inserted in [Ln·DTPA] complex with a general sequence of Mn<Fe<Co<Ni<Cu>Zn indicating an allowed dependence of the spectral parameters on the nature of the M(II) ion. The variations in the spectral parameters have been discussed in light of partial covalency, symmetry around the Ln(III) cation and the degree of delocalisation of the 4f shell. *J* quantum number dependency of the electronic spectral parameters has also been discussed. © 1998 Elsevier Science S.A.

Keywords: Electronic spectral studies; Lanthanides; Oscillator strength; Judd–Ofelt parameters; Interelectronic repulsion (Racah) parameters; Nephelauxetic ratio

1. Introduction

The rare earth mixed metal complexes containing Fe, B, Ba have shown significant applications in the field of lasers [1], superconductors or supermagnets [2,3]. Perovskite type compounds with a stoichiometry of ABO_3 have been extensively studied for their structural flexibility of oxygen framework and symmetry distortions [4]. The mixed metal complexes are also of academic importance in view of the challenges faced in understanding the transition between their electronic and crystal field levels and their bonding modes [5]. Thus, keeping in view the applications of such mixed metal systems and in conformity with electronic spectral studies being carried out in our laboratories [6], the present work dealing with the electronic spectral investigations of the mixed complexes of the type [Ln(III)·DTPA·M(II)] (where Ln(III)=Pr, Nd, Sm, Dy, Er, Tm; DTPA=diethylene triamine pentaacetic acid; and M(II)=Mn, Fe, Co, Ni, Cu and Zn) in solution phase at varied pH have been undertaken. Spectral parameters, viz: oscillator strength (f_{JO}), (ii) Judd–Ofelt parameters (T_λ), interelectronic repulsion (Racah) parameters (δE^k) and the nephelauxetic ratio ($\delta E^3/\delta E^1$) have been evaluated so as to observe their variation as a result of insertion of M(II) ion in the [Ln(III)·DTPA] complex system.

2. Experimental details

Stock solutions of metal ions (3d and 4f) and ligand (DTPA) were prepared in double distilled water using standard Anal-R grade chemicals. Ln(III) and M(II) nitrates of 99.99% purity (supplied by Indian Rare Earths Ltd. or Sigma/Fluka AG) were used. Penta acid form of DTPA was dissolved in double distilled water using 0.5 mol dm^{-3} of sodium hydroxide solution. A 0.1 mol dm^{-3} HNO_3 solution was used as reference acid.

Electronic spectra for metal ion blank (0.025 mol dm^{-3}), 1:1 [Ln(III)·DTPA] and 1:1:1 [Ln(III)·DTPA·M(II)] were prepared in a similar manner as for their pH potentiometric titrations [7]. Total Ln(III) concentrations ~0.025 mol dm^{-3} were maintained throughout the binary

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and mixed metal sets. The electronic spectra of these sets were performed at controlled pH value of ~4.00 (observed to be a pH of optimum complexation, ascertained by a pH potentiometric titration for a representative case of [Pr(III)/Nd(III)·DTPA·M(II)] and SCOGS evaluation of the formation constants (details avoided for brevity)). The pH of the sets were maintained using an Orion-940 module. The electronic spectra were recorded on a Perkin-Elmer Lamda-3B UV-VIS spectrophotometer attached to an RX100 plotter. Fig. 1 records a representative electronic spectra for [Pr(III)·DTPA·M(II)] systems only. All the calculations were performed on a 40486 PC/AT-DX2 computer with a Calligra 24-pin DMP.

The values of the oscillator strengths and Judd–Ofelt parameters were evaluated using the Judd–Ofelt [8,9] approach, whereas the variations in interelectronic repulsion Racah parameters (IERP-Racah) for Ln(III) were evaluated using Wong's equations [10]. Pascal-compiled self-devised [11] computer software was used to evaluate spectral parameters using standard equations.

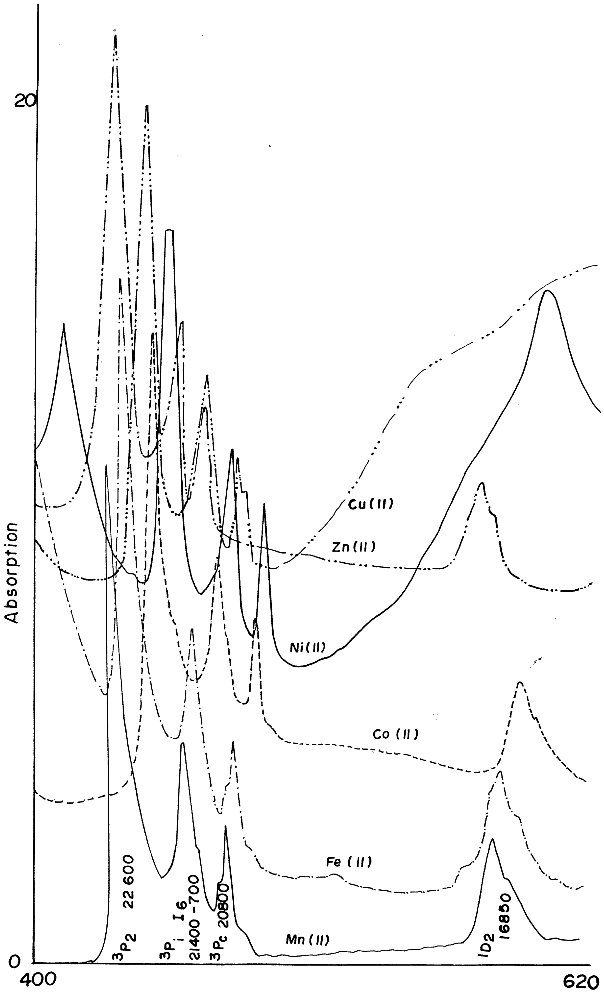

Fig. 1. Representative electronic spectra for [Pr(III)·DTPA·M(II)] mixed metal systems.

3. Result and discussion

Oscillator strength values for [Ln(III)·aqua], [Ln(III)·DTPA] and the [Ln(III)·DTPA·M(II)] mixed-metal systems at pH range of ~4.00 are reported in Table 1. Judd–Ofelt parameters (T_λ) (Table 2) and the variations in the IERP-Racah parameters (δE^k) and nephelauxetic ratio ($\delta E^3/E^1$) values for binary and corresponding mixed metal systems for Pr, Nd and Er only, at pH ~4.00 are reported in Table 3.

The oscillator strength values for some specific prominent assignments have been evaluated using the reduced equation

$$P = 4.318 \times 10^{-9} \times \frac{m^0 \times M_x \times M_y}{m' \times l \times c}$$

where m^0 and m' are the weighted averages of the peak surface and a unit square cm of the surface respectively (the same has been ascertained using weighted average methods also) M_x = rate of change of E (cm^{-1}) per cm of the electronic spectrum, M_y = sensitivity, l = thickness of the cell, and c = the total molar concentration.

Oscillator strength values that are the measures of the sensitivity of a specific electronic transition to the change in environment or degree to which a specific transition is allowed, show a marked dependence on the cation environment. Higher values of f_{JO} for the mixed metal environments than their corresponding binary ones may be attributed to a preferably greater degree of allowance of the electronic transition in a mixed metal environments.

A perusal of the oscillator strength values show an increase for [Ln(III)·DTPA·M(II)] systems than the corresponding [Ln(III)·aqua] or [Ln(III)·DTPA] systems. This points to an M(II) ion-induced sensitivity of specific electronic transition. A close observation of the f_{JO} values, however, exhibits a general dependence on the 3d-metal ion showing a maximum in the f_{JO} values for Cu(II), indicating a possible f–d interelectronic interaction between the 4f and 3d electrons. This situation may be better visualised using the the Judd–Ofelt (T_λ) parameter calculated using Eq. (2)Eq. (3) (values reported in Table 2).

$$f_{\mathrm{JO}} = T_2 \nu U^2 + T_4 \nu U^4 + T_6 \nu U^6 + \ldots \tag{2}$$

$$T_\lambda = (2J+1)\tau_\lambda \tag{3}$$

Where f_{JO} are the pre-calculated values of the oscillator strengths evaluated for each spectral assignment and U^λ are the tensor operators for $\lambda = 2, 4, 6$.

The T_λ values (where $\lambda = 2, 4, 6$) which compose the oscillator strength values are indicative of (i) the mode of metal–ligand interaction (T_2) and (ii) the changes in symmetry (T_4, T_6) around the metal ion by the proximity of an adjacent M(II) ion. The T_λ parameters in general exhibit a sequence of $T_2 < T_4 < T_6$ which is indicative of

Table 1
Oscillator strength values (f_{JO}) for some specific electronic transitions [Ln(III)·DTPA·M(II)] at pH 4.00

Systems	Assignments/oscillator strength values ($\times 10^{-6}$)						
	$1D_2$ 16 850	$^3P_0$ 20 800	$^3P_1+{}^1I6$ 21 400–21 700	$^3P_2$ 22 600			
[Pr·DTPA·Mn]	0.80	0.52	1.19	4.34			
[Pr·DTPA·Fe]	1.28	0.43	1.15	3.78			
[Pr·DTPA·Co]	0.81	0.48	0.72	3.75			
[Pr·DTPA·Ni]	1.20	0.44	1.07	3.67			
[Pr·DTPA·Cu]	—	0.50	1.07	3.91			
[Pr·DTPA·Zn]	0.88	0.44	1.20	3.71			
Systems	$^4F_{3/2}$ 11 450	$^4F_{5/2}+{}^2H_{9/2}$ 12 500	$^4F_{7/2}+{}^4S_{3/2}$ 13 500	$^4G_{5/2}+{}^2G_{7/2}$ 17 300–17 400	$^2K_{13/2}+{}^4G_{7/2}$ 19 000–19 500	$^4D_{3/2}$ 28 300		
[Nd·DTPA·Mn]	0.70	5.90	6.33	8.36	3.84	5.44		
[Nd·DTPA·Fe]	0.72	6.07	6.37	8.35	3.99	—		
[Nd·DTPA·Co]	0.69	5.98	6.28	8.26	3.86	5.29		
[Nd·DTPA·Ni]	0.72	5.87	6.18	8.22	3.80	5.20		
[Nd·DTPA·Cu]	—	—	6.15	8.12	3.62	4.92		
[Nd·DTPA·Zn]	0.70	5.94	6.21	8.20	3.69	4.99		
Systems	$^4G_{5/2}$	$^4M1_{5/2}+{}^4I_{11/2}$	$^4I_{13/2}$	$^6P_{3/2}$	$^6P_{7/2}$	$^4D_{3/2}+{}^6P_{5/2}$		
	17 900	20 800	21 600	24 950	26 750	27 700		
[Sm·DTPA·Mn]	0.86	0.32	0.80	2.06	1.10	1.08		
[Sm·DTPA·Fe]	—	—	—	—	—	—		
[Sm·DTPA·Co]	—	—	0.81	1.88	1.12	1.01		
[Sm·DTPA·Ni]	0.74	0.33	—	—	—	—		
[Sm·DTPA·Cu]	—	—	—	1.87	1.06	1.05		
[Sm·DTPA·Zn]	0.80	0.32	0.88	1.98	1.01	1.29		
Systems	$^4F_{5/2}$ 12 400	$^6F_{3/2}$ 13 200	$^4I1_{5/2}$ 22 100	$^2K1_{7/2}+{}^4G_{11/2}$ 25 800	$^6P_{7/2}$ 28 500			
[Dy·DTPA·Mn]	2.24	0.52	0.78	2.98	3.75			
[Dy·DTPA·Fe]	—	—	—	—	—			
[Dy·DTPA·Co]	2.25	0.49	0.71	2.91	3.54			
[Dy·DTPA·Ni]	—	—	0.75	3.01	3.61			
[Dy·DTPA·Cu]	—	—	—	—	—			
[Dy·DTPA·Zn]	2.35	0.55	0.94	3.34	3.73			
Systems	$^4F_{9/2}$	$^4S_{3/2}$	$^2H_{11/2}$	$^4F_{7/2}$	^{4} F3/2	$^2G_{9/2}$	$^4G_{11/2}$	$^2K1_{5/2}$
	15 300	18 400	19 200	20 500	22 200	24 600	26 400	27 600
[Er·DTPA·Mn]	1.30	0.23	2.65	1.75	0.84	0.86	5.43	2.24
[Er·DTPA·Fe]	—	—	—	—	—	—	—	—
[Er·DTPA·Co]	1.24	—	—	—	—	0.94	5.28	2.13
[Er·DTPA·Ni]	1.35	—	2.67	1.82	0.61	—	—	—
[Er·DTPA·Cu]	—	—	—	—	—	—	—	—
[Er·DTPA·Zn]	1.37	0.24	2.70	1.88	0.80	1.06	5.27	2.46
Systems	$^3H_4$	$^3F_3$	$^3F_2$	$^1G_4$	$^1D_2$			
	12 700	14 500	15 300	21 300	27 900			
[Tm·DTPA·Mn]	1.59	2.46	0.21	0.50	1.55			
[Tm·DTPA·Fe]	—	—	—	—	—			
[Tm·DTPA·Co]	1.29	1.87	—	—	—			
[Tm·DTPA·Ni]	1.45	2.08	0.20	0.35	—			
[Tm·DTPA·Cu]	1.25	1.86	—	—	—			
[Tm·DTPA·Zn]	1.35	1.94	0.16	0.33	1.38			

the relative significance of these parameters in the Nd–M(II) interactions.

The observed sequence for the T_λ parameters is in accordance [12] with the general characteristics of lanthanide elements. Lanthanides have a deep filled 4f shell that experiences strong shielding effects making these orbitals less available for bonding and thereby leading to a predominantly ionic [Ln(III)–L] bond. Similarly a large

Table 2
Calculated values of Judd–Ofelt (T_λ) parameters for [Ln(III)·DTPA·M(II)] systems at pH 4.00

Parameter/M	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
[Pr·DTPA·M]						
T_2	1.66	1.44	1.30	1.06	0.96	1.23
T_4	16.67	14.44	13.09	10.68	9.87	12.32
T_6	118.83	108.85	105.37	105.63	100.88	103.76
[Nd·DTPA·M]						
T_2	2.54	2.01	2.64	2.59	2.63	2.62
T_4	27.80	27.99	30.45	26.47	26.52	27.74
T_6	84.52	72.89	73.54	74.00	71.42	74.75
[Sm·DTPA·M]						
T_2	0.00	—	0.00	—	0.00	0.00
T_4	1.05	—	1.05	—	1.56	1.18
T_6	39.18	—	35.80	—	38.56	45.72
[Dy·DTPA·M]						
T_2	−5.89	—	−3.45	—	—	2.10
T_4	−1.87	—	−1.90	—	—	2.20
T_6	14.82	—	11.73	—	—	12.34
[Er·DTPA·M]						
T_2	29.56	—	−29.08	−29.39	—	−28.53
T_4	3.58	—	2.41	21.85	—	3.37
T_6	24.17	—	24.43	49.84	—	25.87
[Tm·DTPA·M]						
T_2	−18.13	—	25.47	14.67	—	−16.74
T_4	−17.99	—	31.98	15.75	—	−16.64
T_6	17.14	—	52.89	16.22	—	13.58

cationic size associated with three concentric hydration zones may lead to greater perturbations in symmetry during viscinal metal–metal approach. The T_λ parameters in general exhibits a sequence $T_2 < T_4 < T_6$.

Carnall and others [13,14] have pointed out that the proportionality of the T_λ parameters using a crystal field model may be expressed as;

$$T_\lambda \sim \langle r^{t+1} \rangle^2 R^{-2t-2}$$

where $\langle r$ and $r \rangle$ denote the radius of electron nearer to the nucleus and radius of most distant electrons, respectively, and R = the distance between the ligand centre and the nucleus of rare earth, t is an integer. It has been observed that: for $\lambda = 2$, t is 1 and 3; for $\lambda = 4$, t is 3 and 5; and for $\lambda = 6$, t is 5 and 7. This implies an order of decreasing sensitivity of the T_λ parameters to the environment giving a sequence $T_2 < T_4 < T_6$.

Besides the general profile of the T_λ parameters, variation in the T_λ parameters with respect to 3d metal ions is interesting to observe. The overall sequence in the T_λ parameters for 3d metal ions is

$$\mathrm{Mn} < \mathrm{Fe} < \mathrm{Co} < \mathrm{Ni} < \mathrm{Cu} > \mathrm{Zn}$$

which is in agreement with the Irving William [15] series. It may be stated that the coordination polyhedra of the 3d metal ion (with its Jahn Teller distorted behaviour) seems to have significantly affected the symmetry parameters. The square planar geometry for Cu(II) may lead to lesser symmetry perturbations compared to the octahedral geometries for the rest of the 3d cations. There are, however, some deviations from the observed patterns

Table 3
Inter-electronic repulsion Racah (IERP) and nephelauxetic ratio values for [Ln(III)·DTPA·M(II)] at pH 4.00

Systems	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
[Pr·DTPA·M]						
δE^1	−245.0	−169.9	−169.9	−53.04	−90.57	−65.21
δE^3	12.81	−12.82	−11.92	−10.41	−12.64	−10.42
$\delta E^3/\delta E^1$	0.0522	0.0704	0.0753	0.0963	0.1395	0.1099
[Nd·DTPA·M]						
δE^1	14.66	22.35	37.36	34.74	11.82	19.64
δE^3	1.48	1.52	2.87	2.95	1.14	0.82
$\delta E^3/\delta E^1$	0.1008	0.0680	0.0768	0.0849	0.0981	0.0448
[Er·DTPA·M]						
δE^1	−75.29	−151.61	255.4	−103.2	−40.40	130.9
δE^3	−13.50	−11.25	21.25	−9.36	−4.02	5.88
$\delta E^3/\delta E^1$	0.1793	0.0742	0.0832	0.0906	0.0995	0.0449

which may be attributed to some significant steric perturbations.

An exact reflection of these steric situations may be better visualised from the variations in the interelectronic repulsion Racah (IERP-Racah) parameters and the nephelauxetic ratio values. Variations in the interelectronic repulsion Racah (IERP-Racah) parameters and the nephelauxetic ratio values have been determined using the following differential equations:

$$\Delta E = E_{oj} + (E_j/\delta E^1)\delta E^1 + (\delta E_j/\delta E^2)\delta E^2 + (\delta E_j/\delta E^3)\delta E^3 + (\delta E_j/\delta \xi_{4f})\delta \xi_{4f} \quad (4)$$

and

$$\mathrm{Nfe} = (\delta E^3/\delta E^1) \quad (5)$$

where $(\delta E^j/\delta E^3)$, $(\delta E_j/\delta \xi_{4f})$ are the partial derivatives and δE^k ($k = 1, 2, 3$) are the corrections to be applied to the free ions parameter E_j^k, ξ_{4f}^{o}, etc. The calculated values of E_{oj} and the partial derivatives for Coulomb matrix elements in terms of Racah (E^k) and other parameters have been used from the standard tables of Wong [10].

The observed values for the IERP-Racah parameters (Table 3) show that the values for IERP-Racah parameters and the nephelauxetic ratio values lie well within the theoretically calculated ranges of δE^1 and $\delta E^3 \sim 1\%$ of E^k and $-0.0913 < \delta E^3/\delta E^1 < 0.214$ which justifies the validity of the present calculations. This also indicates towards a positive deformation in the 4f electronic wavefunction in the changed environment. A perusal of these values in the light of 3d metal ion exhibit a sequence

$$\mathrm{Mn} < \mathrm{Fe} < \mathrm{Co} < \mathrm{Ni} < \mathrm{Cu} > \mathrm{Zn}$$

which is the general order of stability for the 3d metal ions. Fig. 2 exhibits a variation in the $\delta E^3/\delta E^1$ values for Pr, Nd and Er mixed environments with respect to M(II) ions. The plots show a maxima at Cu(II), which may be attributed to a greater release in the interelectronic repulsion parameters associated with a closer Ln(III)–M(II) ion approach due to less repulsive square planar geometry.

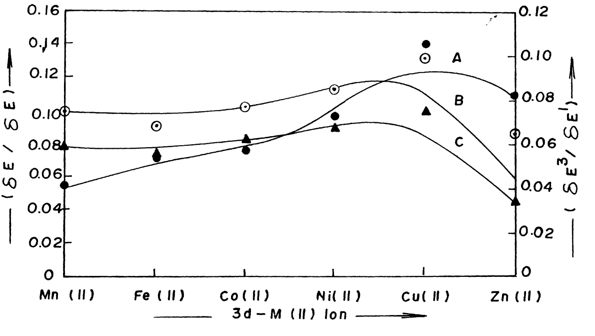

Fig. 2. Variation in $(\delta E^3/\delta E^1)$ values for (A) Pr(III), (B) Nd(III) and (C) Er(III) with respect to 3d metal ions.

A close perusal of the spectral parameters for the isoelectronic Nd(III) and Er(III) suggests that the two lanthanides possess similar values for spin (S) and orbital angular momentum (L) quantum number. S and L are the same 3/2 and 6, respectively, for both lanthanides, only J values are different: Nd(III) $J = {}_{9/2}$ and Er(III) $J = {}_{15/2}$. Thus the variation in the spectral parameters indicates a J dependency of these parameters.

3.1. *J correlations*

In lanthanides where the 4f orbitals are effectively shielded by the outer lying orbitals and the ligand field stabilisation energy (l.f.s.e.) has negligible effects, the Ln–L (L = ligand) interactions are expected to be predominantly ionic. The response of specific 4f orbitals can be ascertained through the changes in their interelectronic repulsion (Racah) parameters (IERP) and their coefficients composed of S (total spin) and L (total orbital angular momentum) quantum numbers [16]. The L values have long been used as fundamental properties to study the periodicity in lanthanides [6]. The f–f transitions in lanthanides are believed to occur from one J state to another and hence the justification [17] in seeking a correlation between E_{av} (where $E_{av} = \Sigma(E \times U^{\lambda})/\Sigma U^2$ where E is the energy of the electronic transitions (in cm^{-1}) for assignments having $U^2 > 0.2$ [6]) or oscillator strength values and $4\mathrm{f}^q$ or J quantum numbers of lanthanides.

The plots of E_{av} values [18] for specific electronic assignments (of Table 4) and f_{JO} values (only for Mn(II) and Zn(II) as representative cases) evaluated for some electronic assignments for Pr(III), Nd(III), Sm(III),

Table 4
Hypersensitive transitions of standard [6] and doped Ln(III) ions, values of tensor operators (ΣU^2) and average energies (ΣE_{av}) of transitions

Ln(III)	Ground state	Excited state	ΣU^2	ΣE_{av} ($\times 10^9/\mathrm{cm}^{-1}$)
Ce(III)	${}^2F_{5/2}$	${}^3H_5$;	—	—
Pr(III)	${}^3H_4$	${}^3F_2$	0.509	5.200
Nd(III)	${}^4I_{9/2}$	${}^4G_{5/2}$; ${}^2G_{7/2}$	0.974	17.333
Pm(III)	${}^5I_4$	${}^5G_2$; ${}^5G_3$	0.886	17.950
Sm(III)	${}^6H_{5/2}$	${}^6F_{1/2}$; ${}^6F_{3/2}$	0.338	6.483
Eu(III)	${}^7F_0$, ${}^7F_1$	${}^5D_2$; ${}^5D_0$	0.004	1.940
Gd(III)	${}^8S_{7/2}$	—	—	—
Tb(III)	${}^7F_6$	${}^7F_5$	0.538	2.100
Dy(III)	${}^6H1_{5/2}$	${}^6F_{11/2}$	1.285	6.296
Ho(III)	${}^5I_8$	${}^5G_6$	1.736	22.793
Er(III)	${}^4I1_{5/2}$	${}^2H_{11/2}$; $4G_{11/2}$	1.631	23.418
Tm(III)	${}^3H_6$	${}^3F_4$; ${}^3F_2$	0.774	7.947
Yb(III)	${}^2F_{7/2}$	—	—	—

Dy(III), Er(III) and Tm(III) (assignments: Pr(III), $^3P_0$; Nd(III), $^4G_{5/2}$; Sm(III), $^4F_{1/2}$; Dy(III), $^6F_{11/2}$; Er(III), $^2H_{11/2}$; and Tm(III), $^3F_3$) vs. the number of 4f electrons (I) and the J value (II) of the lanthanides are given in Fig. 3. Plots E represent the E_{av} values, whereas A and B represent values of oscillator strength (f) for Mn(II) and Zn(II), respectively. These plots exhibit a semi-sigmoid (inverted tulip type) shape with varied amplitudes, which appears to depend on the relative response of specific $4f^q$ configuration towards the interacting environment and the relative complexing tendencies of the matrix donor atoms. The observed shape of the variation profiles is characteristic of the Ln(III) ions and indicates that the general f shell feature of the Ln(III) cations is preserved in the Ln(III)–M(II) ion interactions. Both the variation profiles in parts I and II of Fig. 3 follow the sequence in J values and hence maxima appear at $Nd^{3+}(4f^3)$, $Pm^{3+}(4f^4)$, $Ho^{3+}(4f^{10})$ and $Er^{3+}(4f^{11})$ in the two sets of curves. The relative sequence $Ho^{3+}(4f^{10})$, $Er^{3+}(4f^{10})$, $>Na^{3+}(4f^3)$, $Pm^{3+}(4f^4)$, is seen for E_{av} values, whereas for f_{JO} values the observed sequence is $Nd^{3+}(4f^3)$, $Pm^{3+}(4f^4)$, $>Ho^{3+}(4f^{10})$, $Er^{3+}(4f^{11})$ because of the inverse relationship between J_o and J values.

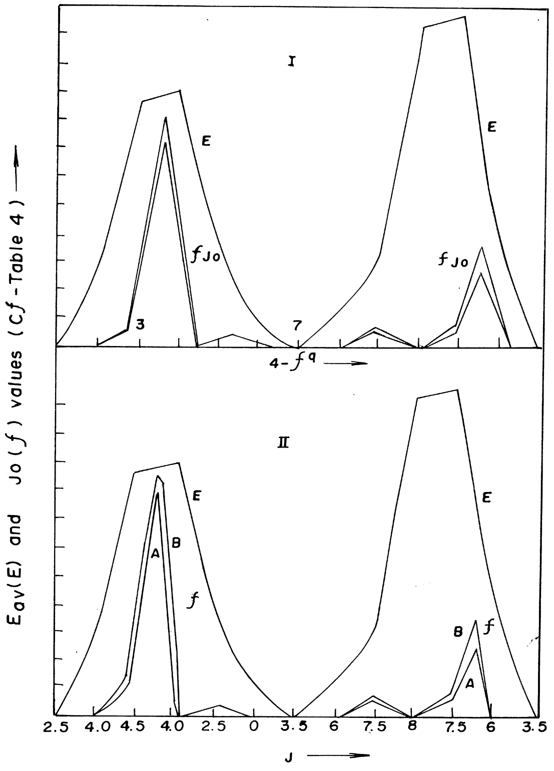

Fig. 3. Variation profiles of E_{av} (E) and standard f_{JO} (f) values for some electronic transitions vs. (I) the number of 4f electrons ($4f^q$) and (II) the total momentum (J) values for Ln(III) ions. (NB: A and B represent the f_{JO} values obtained for Mn(II) and Zn(II) mixed metal environments.)

4. Conclusions

On the basis of all above observations it may be stated that the oscillator strength values show a marked difference in their magnitude with a change in environment which shows a dependence on the nature of 3d metal ions. The T_λ values shows a general sequence which is in accordance with the lanthanide bonding and symmetry characteristics. As regards the variation in the interelectronic repulsion parameters or the nephelauxetic ratio values and their dependence on the nature of the 3d metal ion indicates a possible f–d inter-electronic interaction in the 4f and 3d electronic wavefunctions. It appears that the intensities and positions of specific electronic transitions (HST for reference) are influenced by induced ligand fields, i.e. the symmetry of the complex, the degree of covalency, the basicity of the ligand and the effective charge on the ligand donor atom. Therefore, a quantitative aspect of the mechanism (of HST) should, therefore, also take into account the role played by these factors.

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References

[1] M.J. Weber, Lanthanide and Actinide Chemistry and Spectroscopy, ch. 14, American Chemical Society Publ., 1980, p. 275.
[2] J.A. Alonso, M.T. Casais, C. Cascales, I. Rasines, Eur. J. Solid State Inorg. Chem. 28 (1991) 639.
[3] A. Salinas-Sanchez, R. Saez-Puche, M.A. Alario-Franco, Eur. J. Solid State Inorg. Chem. 28 (1991) 653.
[4] A. Correia Dos Santos, F.M.A. Da Costa, Eur. J. Solid. State Inorg. Chem. 28 (1991) 635.
[5] J.R. Quagliano, F.S. Richardson, M.F. Reid, J. Alloys Compounds 180 (1992) 131.
[6] P. Rout, R. Singhai, S.N. Limaye, M.C. Saxena, Proc. Indian Acad. Sci. (Chem. Sci.) 108 (4) (1996) 361; R. Singhai, S.N. Limaye, M.C. Saxena, Proc. Indian Acad. Sci. (Chem. Sci.) 107 (5) (1995) 532; Sepectrochim. Acta Part A 53 (5) (1997) 353.
[7] H.M. Irving, H.S. Rossotti, J. Chem. Soc. (1953) 3397; (1954) 2904.
[8] B.R. Judd, Phys. Rev. 127 (1962) 750.
[9] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
[10] E.Y. Wong, J. Chem. Phys. 35(2) (1961) 544.
[11] S.N. Limaye, Tetrad Effect in Solution Stabilities of Lanthnide Complexes; A Nephelauxetic Phenomenon, D.Sc. Thesis, Dr. H.S. Gour University, 1994.

[12] S.N. Limaye, M.C. Saxena, J. Indian Acad. Sci. (Bangalore) 74 (1994) 611; S.N. Limaye, A.A. Kopyrin, M.C. Saxena, J. Inst. Chem. (India) 63 (1991) 215.
[13] W.T. Carnall, P.R. Fields, B.G. Wybourne, J. Chem. Phys. 42 (1965) 3797.
[14] R.D. Peacock, Struct. Bonding 22 (1975) 83.
[15] S.N. Limaye, M.C. Saxena, Indian J. Chem. 31(A) (1992) 403.
[16] C.K. Jorgensen, Eur. J. Solid State Inorg. Chem. 28 (1991) 139.
[17] R. Reisfeld, C.K. Jorgensen, Lasers and Excited States or Rare Earths, Springer Verlag, Berlin, 1977, pp. 138–140.
[18] N.S. Poluektov, N.A. Nazarenko, V.T. Mischenko, S.V. Beltyukova, 1st Intern. Symp. on Ree Spectroscopy, Wraclow, Poland, World Sci. Publ. Co., Pvt. Ltd., 1984, pp. 363.