

Ground term L and J quantum number profiles of the oscillator strengths (f_{JO}) and pH values of some lanthanoids in aminopolycarboxylate ligand environments

PUSPANJALI ROUT, RASHMI SINGHAI, SUDHIR N LIMAYE*
and M C SAXENA

Department of Chemistry, Dr H S Gour University, Sagar 470 003, India

MS received on 19 April 1996; revised 25 June 1996

Abstract. Electronic spectral studies of some lanthanoids [(viz. Pr(III), Nd(III), Sm(III), Eu(III), Dy(III), Er(III) and Tm(III)] in aminopolycarboxylate (viz. IMDA, NTA, HEDTA, EDTA, CDTA and DTPA) environment have been undertaken with a view to evaluate the oscillator strengths (f_{JO}), Judd–Ofelt parameters (τ_j), inter-electronic repulsion Racah parameters (∂E^k) and nephelauxetic ratios ($\partial E^3/\partial E^1$). The parameters have been evaluated for the entire pH range (pH 2–9) with intervals of 0.5 in order to study the dependence of oscillator strengths on pH values. The extent of covalency (via parameter τ_2) and symmetry (via parameters τ_4 and τ_6) in the metal–ligand interaction have been estimated with the help of τ_j parameters. The values of oscillator strengths and Judd–Ofelt parameters have been discussed in the light of coordination number of lanthanoid metal ions, denticity and basicity of the ligands. The metal–ligand bonding pattern has been studied in the light of changes in Racah parameters and the nephelauxetic ratio. The oscillator strength values for some specific hypersensitive transitions and for the transition where U^{λ} values are significantly large have been studied as a function of ground term L and J quantum numbers of the lanthanoids.

Keywords. Lanthanoids; electronic spectra; nephelauxetic parameters; aminopolycarboxylates.

1. Introduction

According to several reports (Carnall *et al* 1965; Bukietynska and Choppin 1970; Choppin and Fellows 1974; Peacock 1975) the intensities of the so-called hypersensitive $f-f$ transitions are sensitive to changes in the immediate environment of lanthanoid ions [Ln(III)]. The mechanism (Judd 1962) and origin of hypersensitivity (Jorgensen and Judd 1964) have been discussed earlier. Some efforts have been made to utilise the electronic spectra of Ln(III) complexes for the evaluation of stability constants (Bukietynska *et al* 1981a) thermodynamic parameters (Bukietynska *et al* 1981b) and derivation of a nephelauxetic series (Jorgensen 1971b) for Ln(III) metal ions along the same lines as the nephelauxetic series (Jorgensen 1971b; Limaye and Saxena 1994) for d -transition metal ions.

The present work has been undertaken so as to study the pH dependence of the oscillator strength values, specially for the hypersensitive and/or those $f-f$ transitions for which U^{λ} (tensor operators) as well as the oscillator strength values are significantly

* For correspondence

large. The L and J quantum number profiles of the oscillator strength values have also been examined in order to seek probable correlation between the two, so as to throw light on the origin of hypersensitivity.

2. Experimental

Chemicals of standard purity (BDH AnalaR/Fluka/Sigma) were used. The lanthanoids Pr(III), Nd(III), Sm(III), Eu(III) and Dy(III) were used as their nitrates (99.99% purity). Er(III) and Tm(III) oxides were converted into their nitrates by dissolving the oxides in a minimum quantity of nitric acid. Stock solutions (0.125 M) of Ln(III) metal ions and ligands were prepared in double distilled water. The ligands IMDA, NTA, HEDTA, EDTA, CDTA and DTPA were used as their sodium salts. Metal and ligand solutions were mixed in 1:1 proportion to obtain ML complexes of 0.05 M final concentration. The electronic spectra of mixed solutions (ML complexes) were recorded at controlled pH values of 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0 on a Perkin-Elmer Lambda-3B self-recording spectrophotometer. The chart speed was kept at 80 nm/min and the sensitivity was monitored from 200 to 1000 mV. The procedure adopted for the evaluation of various spectral parameters viz., oscillator strengths (f_o), Judd-Ofelt parameters, variations in the inter-electronic repulsion Racah parameters and nephelauxetic ratio is the same as those reported earlier by us (Singhai *et al* 1995).

3. Results and discussion

Representative set of figures for [Pr(III).EDTA] systems at different pH values is shown in figure 1. The spectral band positions obtained for prominent electronic transitions have been used to evaluate (Singhai *et al* 1995, and references therein) the spectral parameters. The values of oscillator strengths for Pr(III), Nd(III), Sm(III), Eu(III), Dy(III), Er(III) and Tm(III) in different ligand environments at pH 3.0 to 5.0 (as representative cases) have been recorded in table 1. The values of Judd-Ofelt parameters for Ln(III) metal ions in each ligand environment (at pH 4.5) are recorded in table 2. The calculated values of nephelauxetic ratio ($\partial E^3/\partial E^1$) for Pr(III), Nd(III) and Er(III) are presented in table 3.

A perusal of the values of oscillator strength f_{jo} (table 1) shows that a maximum in these values lies at pH \approx 4 to 4.5. The oscillator strength values represent the degree of intensities of specific electronic transitions and are very sensitive to changes in the immediate vicinity of the metal ion and on its coordination state. The pH dependence of oscillator strength values in the present case clearly indicates a parallel correlation between the f_{jo} values and the degree of complexation, both of which attain higher values in the pH region \approx 4–4.5 as is known (Moeller *et al* 1965; Grietmon and Choppin 1977) for the present set of ligands.

It is interesting to note that the f_{jo} values lie in the general sequences IMDA < NTA < HEDTA \sim EDTA > CDTA > DTPA with respect to the ligands under study. A gradual increase from IMDA to EDTA may be a consequence of increase in the denticity of the aminopolycarboxylates and also the solution stability of the [(Ln(III).L) chelates in this order. Deviation at CDTA and DTPA may well be due to a loss of conformational freedom to a considerable extent in these cases (Ashcroft and Mortimer 1970).

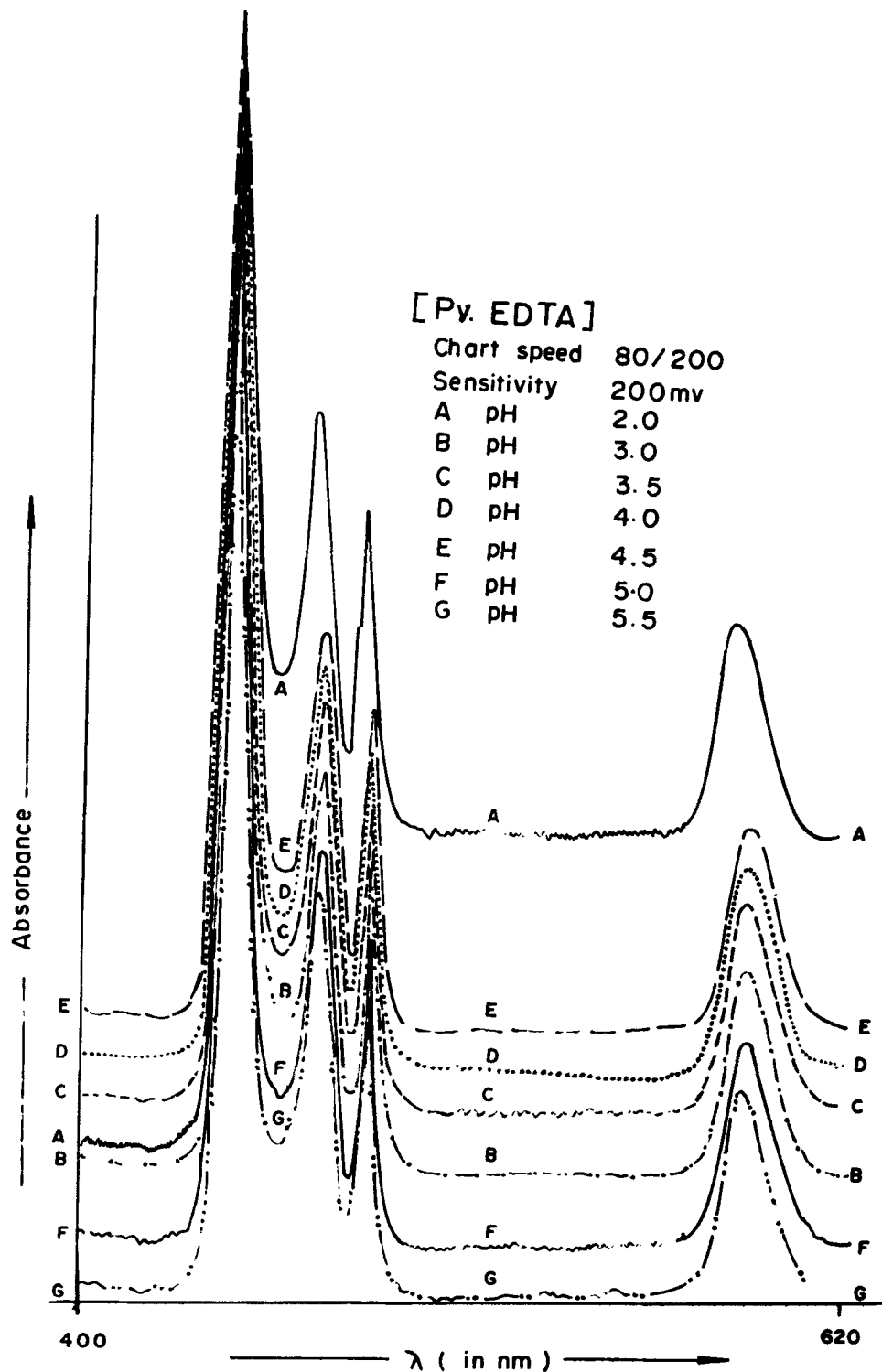


Figure 1. Representative electronic spectra for [Pr(III).EDTA] systems at different pH values.

Table 1. Oscillator strength values (f_{jo}) for some specific electronic transitions at controlled pH values.

[Ln(III).L] system	Assign- ment	Oscillator strengths at controlled pH values				
		3.00	3.50	4.00	4.50	5.00
[Pr(III).IMDA]	3P_0	14458.3	17455.3	23134.0	14443.2	23192.3
	3P_1	74497.9	77846.2	83095.5	83095.5	78074.2
[Pr(III).NTA]	3P_0	18309.2	24243.5	24455.2	24505.4	21216.4
	3P_1	73996.9	75893.8	76504.2	78606.3	70143.8
[Pr(III).HEDTA]	3P_0	14179.8	17007.3	19705.2	25090.3	16938.0
	3P_1	73039.7	74038.5	75128.3	77251.3	73020.4
[Pr(III).EDTA]	3P_0	13308.5	15251.8	17509.9	23375.9	21671.0
	3P_1	72397.5	73240.8	75591.6	74233.8	72193.5
[Pr(III).CDTA]	3P_0	16628.0	17223.6	18428.4	21561.3	20841.9
	3P_1	72723.6	74862.7	75334.2	74992.1	73404.1
[Pr(III).DTPA]	3P_0	14409.0	20236.8	17366.1	20393.6	20281.4
	3P_1	71658.8	72804.4	73624.9	74992.8	72254.1
[Nd(III).IMDA]	$^4F_{5/2}$	81347.1	89041.3	91275.3	91979.9	82175.6
	$^4G_{5/2}$	94659.2	94582.7	98907.7	98234.9	92427.3
	$^4G_{7/2}$	50506.7	59313.9	66034.8	72796.8	66041.5
[Nd(III).NTA]	$^4F_{5/2}$	77417.7	79647.3	84382.8	85651.4	82436.7
	$^4G_{5/2}$	86598.9	87276.0	89873.3	89878.6	84079.8
	$^4G_{7/2}$	56409.1	64049.3	76637.8	82961.3	74783.9
[Nd(III).HEDTA]	$^4F_{5/2}$	63299.9	65457.0	75610.6	78747.9	72301.7
	$^4G_{5/2}$	80372.3	87366.2	89766.6	85422.4	82049.9
	$^4G_{7/2}$	62403.0	66696.0	71886.9	72381.1	71569.2
[Nd(III).EDTA]	$^4F_{5/2}$	78656.1	80108.7	80298.8	79882.1	78604.2
	$^4G_{5/2}$	83681.5	86694.9	85823.8	85202.2	83325.1
	$^4G_{7/2}$	62312.1	64359.4	67725.9	67504.6	66253.4
[Nd(III).CDTA]	$^4F_{5/2}$	77245.5	84070.8	86324.7	82403.1	84264.8
	$^4G_{5/2}$	74198.5	82888.8	82283.3	83123.9	81061.5
	$^4G_{7/2}$	63107.2	67016.6	67814.2	67265.0	67137.8
[Nd(III).DTPA]	$^4F_{5/2}$	72712.6	72591.8	77335.4	75372.1	74327.1
	$^4G_{5/2}$	84501.6	88858.5	90292.6	84090.5	81138.9
	$^4G_{7/2}$	63318.6	66554.9	69163.7	72692.3	72203.0
[Sm(III).IMDA]	$^6P_{3/2}$	26481.2	29897.0	30059.8	34294.5	29460.5
[Sm(III).NTA]	$^6P_{3/2}$	26481.2	30803.1	33781.9	38280.1	29252.3
[Sm(III).HEDTA]	$^6P_{3/2}$	26461.4	30924.0	38815.8	35650.7	29180.2
[Sm(III).EDTA]	$^6P_{3/2}$	25432.6	28838.4	36587.3	36180.4	30193.4
[Sm(III).CDTA]	$^6P_{3/2}$	20537.9	25047.9	30076.6	30153.3	26033.6
[Sm(III).DTPA]	$^6P_{3/2}$	30765.0	34376.9	36327.5	39175.2	35006.9
[Eu(III).IMDA]	5L_6	12253.2	13067.8	13876.7	13834.1	15535.5
[Eu(III).NTA]	5L_6	11717.0	12435.1	13484.0	13463.7	12193.1

(Continued)

Table 1. (Continued)

[Ln(III).L] system	Assign- ment	Oscillator strengths at controlled pH values				
		3.00	3.50	4.00	4.50	5.00
[Eu(III).HEDTA]	5L_6	11104.6	16808.3	20638.7	20345.7	15797.7
[Eu(III).EDTA]	5L_6	11647.1	12809.2	13653.6	13763.7	13047.3
[Eu(III).CDTA]	5L_6	12318.6	12852.7	13252.7	13204.4	13140.0
[Eu(III).DTPA]	5L_6	13944.7	14350.4	14875.7	14873.5	13866.6
[Dy(III).IMDA]	$^6F_{5/2}$	7705.6	7333.2	7586.3	8624.4	7613.2
	$^4M_{19/2}$	12707.4	12538.6	10965.2	12015.1	13199.7
[Dy(III).NTA]	$^6F_{5/2}$	8367.5	7370.5	8875.8	7587.4	7234.2
	$^4M_{19/2}$	13967.2	15431.3	16403.9	16480.3	13203.4
[Dy(III).HEDTA]	$^6F_{5/2}$	7138.9	7348.9	7007.0	6856.4	6856.4
	$^4M_{19/2}$	12982.0	14026.4	14535.0	13881.8	12881.8
[Dy(III).EDTA]	$^6F_{5/2}$	6354.9	6587.1	6681.0	6939.2	6058.1
	$^4M_{19/2}$	13984.1	15798.1	17731.6	19222.7	16302.9
[Dy(III).CDTA]	$^6F_{5/2}$	7106.7	7029.9	7739.8	8023.2	7803.2
	$^4M_{19/2}$	19556.9	21104.1	23278.2	23175.5	21022.6
[Dy(III).DTPA]	$^6F_{5/2}$	5969.7	6947.6	7642.2	7731.2	8034.4
	$^4M_{19/2}$	11458.3	13371.4	17181.5	19626.5	12120.3
[Er(III).IMDA]	$^2H_{11/2}$	20664.8	21140.9	23568.5	26337.0	20855.2
	$^4G_{11/2}$	59216.6	62273.9	65603.4	65603.4	63273.5
[Er(III).NTA]	$^2H_{11/2}$	23063.5	25156.8	26209.9	25798.4	22665.8
	$^4G_{11/2}$	68906.8	77120.7	78160.9	77306.0	67759.3
[Er(III).HEDTA]	$^2H_{11/2}$	22235.0	23323.8	23408.7	23422.6	21345.3
	$^4G_{11/2}$	50485.2	65270.7	65935.3	69933.9	60403.9
[Er(III).EDTA]	$^2H_{11/2}$	23664.8	21140.9	21568.5	26337.0	20855.2
	$^4G_{11/2}$	56181.7	55457.9	63924.5	64550.0	63151.3
[Er(III).CDTA]	$^2H_{11/2}$	11381.5	11464.6	11124.7	11297.8	11663.7
	$^4G_{11/2}$	62586.3	67409.0	73631.6	74270.3	71699.7
[Er(III).DTPA]	$^2H_{11/2}$	22422.9	22288.3	22350.1	22325.9	27300.8
	$^4G_{11/2}$	57622.7	61391.0	66385.0	66005.9	61965.6
[Tm(III).IMDA]	3H_4	20525.1	20624.5	21155.1	20799.2	20580.6
	3F_3	25429.3	25173.0	29945.2	35201.8	35480.1
	1D_2	21120.1	23277.7	23941.3	24902.4	23791.8
[Tm(III).NTA]	3H_4	22688.7	23830.2	24962.3	26866.4	24302.4
	3F_3	28048.5	28393.4	36192.5	34057.6	31002.5
	1D_2	21243.3	22816.3	24386.1	23261.8	21004.6
[Tm(III).HEDTA]	3H_4	19962.9	20689.4	21854.5	20729.1	20438.5
	3F_3	27261.8	28665.6	35812.8	35601.0	31391.4
	1D_2	26965.0	27623.6	27711.5	28729.5	28074.6
[Tm(III).EDTA]	3H_4	20004.0	21431.2	22513.1	23596.9	20377.7
	3F_3	25722.2	29876.6	34731.9	35470.8	30709.5
	1D_2	17084.7	27117.8	28685.3	27702.8	27235.6

(Continued)

Table 1. (Continued)

[Ln(III).L] system	Assign- ment	Oscillator strengths at controlled pH values				
		3.00	3.50	4.00	4.50	5.00
[Tm(III).CDTA]	3H_4	20325.5	21059.5	21056.5	20302.3	20657.8
	3F_3	24768.9	26876.9	36974.8	36342.9	26603.5
	1D_2	17830.4	17790.8	26724.0	28814.6	27313.9
[Tm(III).DTPA]	3H_4	20085.8	21044.7	25177.8	26121.2	20659.2
	3F_3	23708.1	28106.7	33445.0	35180.9	33016.1
	1D_2	21999.7	23886.0	23815.6	24155.5	21622.5

Table 2. Calculated values of Judd–Ofelt (JO) parameters for Ln(III) ions in different ligand environments at pH 4.5.

Judd–Ofelt parameters	Ligand environment for Ln(III) ion					
	IMDA	NTA	HEDTA	EDTA	CDTA	DTPA
Pr(III)						
τ_2	0.44	—	0.47	—	0.63	0.99
τ_4	5.22	—	2.14	—	0.91	3.28
τ_6	22.70	—	– 34.31	—	24.20	29.90
Nd(III)						
τ_2	0.64	– 0.75	– 1.24	0.16	0.35	– 0.64
τ_4	1.74	1.73	2.87	5.75	4.24	2.04
τ_6	36.84	28.84	10.69	40.65	33.70	35.50
Sm(III)						
τ_2	0	0	0	0	0	0
τ_4	3.72	3.37	4.90	6.68	6.16	4.35
τ_6	17.26	15.80	19.89	51.50	48.10	25.30
Eu(III)						
τ_2	0	0	0	0	0	0
τ_4	– 2.52	– 1.74	– 5.38	– 3.03	– 3.72	– 3.39
τ_6	34.48	36.62	61.90	41.41	39.73	38.47
Dy(III)						
τ_2	0.95	0.89	0.15	0.54	0.28	0.72
τ_4	4.85	5.03	5.06	7.25	7.72	5.19
τ_6	27.00	27.20	25.90	37.50	35.40	23.90
Er(III)						
τ_2	– 0.59	0.19	0.14	0.13	0.80	0.76
τ_4	10.70	7.27	– 1.44	– 0.31	0.09	– 0.84
τ_6	39.03	25.40	28.20	14.10	13.71	23.40
Tm(III)						
τ_2	1.26	1.08	1.00	0.68	0.84	1.21
τ_4	1.49	1.27	0.74	0.59	0.76	1.40
τ_6	6.06	8.11	9.66	11.50	10.00	5.66

Table 3. Calculated values of IERP (Racah) ∂E^k and nephelauxetic ratio ($\partial E^3/\partial E^1$) for Ln(III) ions in various ligand environments and their total partial charge values.

[Ln(III).L] system	IERP (Racah) ∂E^k and nephelauxetic ratio ($\partial E^3/\partial E^1$) values			
	Pr(III)	Nd(III)	Er(III)	Partial charge
<i>IERP (Racah) ∂E^1</i>				
[Ln.IMDA] ⁺	81.60	124.24	39.95	
[Ln.NTA] ⁰	-39.00	71.03	84.79	
[Ln.HEDTA] ⁰	22.00	123.67	62.73	
[Ln.EDTA] ⁻¹	-22.00	63.86	50.50	
[Ln.CDTA] ⁻¹	-2.84	92.63	189.83	
[Ln.DTPA] ⁻²	-104.00	118.87	119.08	
<i>IERP (Racah) ∂E^3</i>				
[Ln.IMDA] ⁺	20.79	1.20	2.03	
[Ln.NTA] ⁰	-1.08	0.20	3.96	
[Ln.HEDTA] ⁰	-0.51	-1.60	5.19	
[Ln.EDTA] ⁻¹	-1.03	0.77	1.14	
[Ln.CDTA] ⁻¹	1.85	-3.22	-5.92	
[Ln.DTPA] ⁻²	11.00	3.44	2.52	
<i>$\partial E^3/\partial E^1$</i>				
[Ln.IMDA] ⁺	-0.0254	0.0097	0.0508	0.600
[Ln.NTA] ⁰	0.0271	0.0028	0.0466	0.819
[Ln.HEDTA] ⁰	0.0231	-0.0130	0.0828	1.311
[Ln.EDTA] ⁻¹	0.0454	0.0120	0.0192	1.257
[Ln.CDTA] ⁻¹	-0.0649	-0.0359	-0.0312	1.357
[Ln.DTPA] ⁻²	-0.0010	0.0290	0.0211	1.657

Variation in symmetry around the Ln(III) metal ions as a result of chelation with the aminopolycarboxylates results in a systematic and parallel change in the values of Judd-Ofelt parameters (τ_λ) as may be seen from the experimental data in table 2. The τ_λ values show a general trend $\tau_2 < \tau_4 < \tau_6$, which indicates an increasing degree of involvement of these parameters in the intensity of specific transitions. The τ_2 parameters, which are covalency susceptible, are expected to be smaller in magnitude in view of a predominantly ionic nature of Ln(III).L bonding (Moeller *et al* 1965). The τ_4 and τ_6 parameters are susceptible to changes in symmetry around the central metal ion; in the present case their larger values are a consequence of considerable symmetry changes in the coordination sphere due to higher denticities and greater complexing tendencies of the interacting ligands. Comparison of the τ_λ parameters reveals that the τ_6 values are higher for EDTA and HEDTA as compared to those with CDTA and DTPA. A similar sequence has also been observed for the oscillator strength values as explained above.

A significant inference related to the nature of the Ln(III).L bonding pattern may be drawn from comparison of the τ_λ values for Nd(III) and Er(III) cations. The

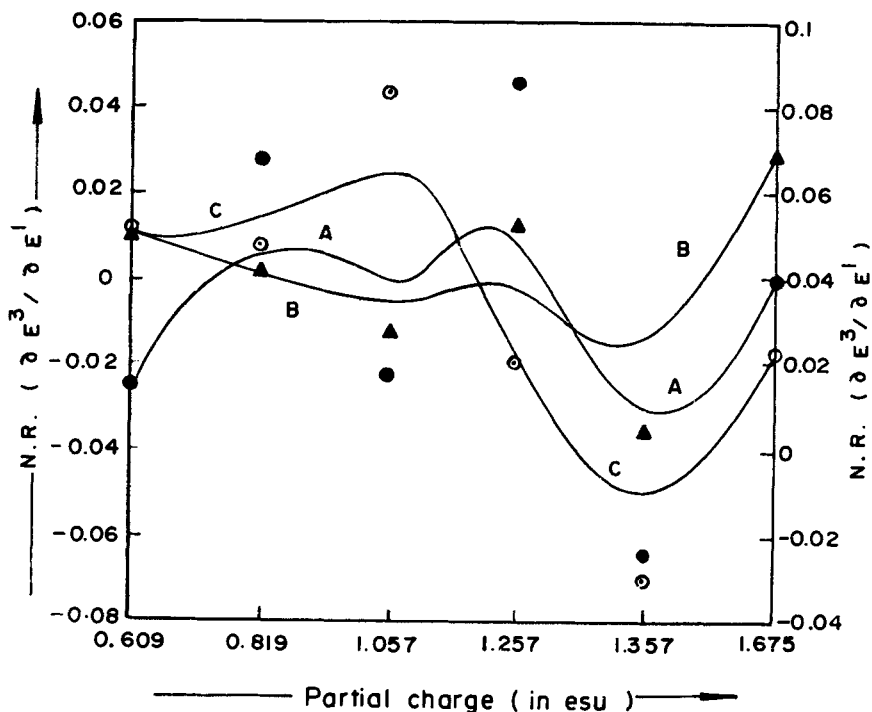


Figure 2. Variation profiles of the nephelauxetic ratios ($\partial E^3/\partial E^1$) as a function of partial charge on ligand donor atoms [A = Pr(III); B = Nd(III); C = Er(III)].

observed trend Er(III) > Nd(III) in τ_2 values appears to be a function of cation size. Both Nd(III) ($4f^3$) and Er(III) ($4f^{11}$) are identical with regard to their orbital angular momentum [$L = 6$] and total spin [$S = 3/2$] quantum numbers. Nd(III) being larger in size makes a distant approach, thereby decreasing the covalency in the Ln(III)-L interaction whereas Er(III) being smaller in size experiences a closer interaction causing a greater degree of partial covalency, thereby increasing the values of τ_2 parameters. Also, the τ_6 parameters are simultaneously larger for Er(III) than for Nd(III), which may be due to greater disruption of the hydration sphere due to closer approach in the case of Er(III). The τ_2 parameters exhibit, in general, a slight increase from pre-Gd elements to post-Gd elements. This is suggestive of a gradual increase with a change in the mode of Ln(III)-L interaction, from a predominantly ionic to partial ionic-covalent character as we traverse the Ln(III) series from lighter to heavier lanthanoids.

The changes in the IERP-Racah parameters (∂E^k) and the nephelauxetic ratio values ($\partial E^3/\partial E^1$) (table 3) for Pr(III), Nd(III) and Er(III) are in good agreement with the above observations. The variations in these parameters are indicative of the deformability of their f -orbitals under the ligand environment. A dependence of the nephelauxetic parameters on the effective charge of the ligand donor atoms calculated on the basis of Pearson's HSAB theory have also been attempted. A maximum in the ($\partial E^3/\partial E^1$) parameters at EDTA (figure 2) with deviations for CDTA and DTPA suggests a deformability of the f -electron wave function under the effect of ligand

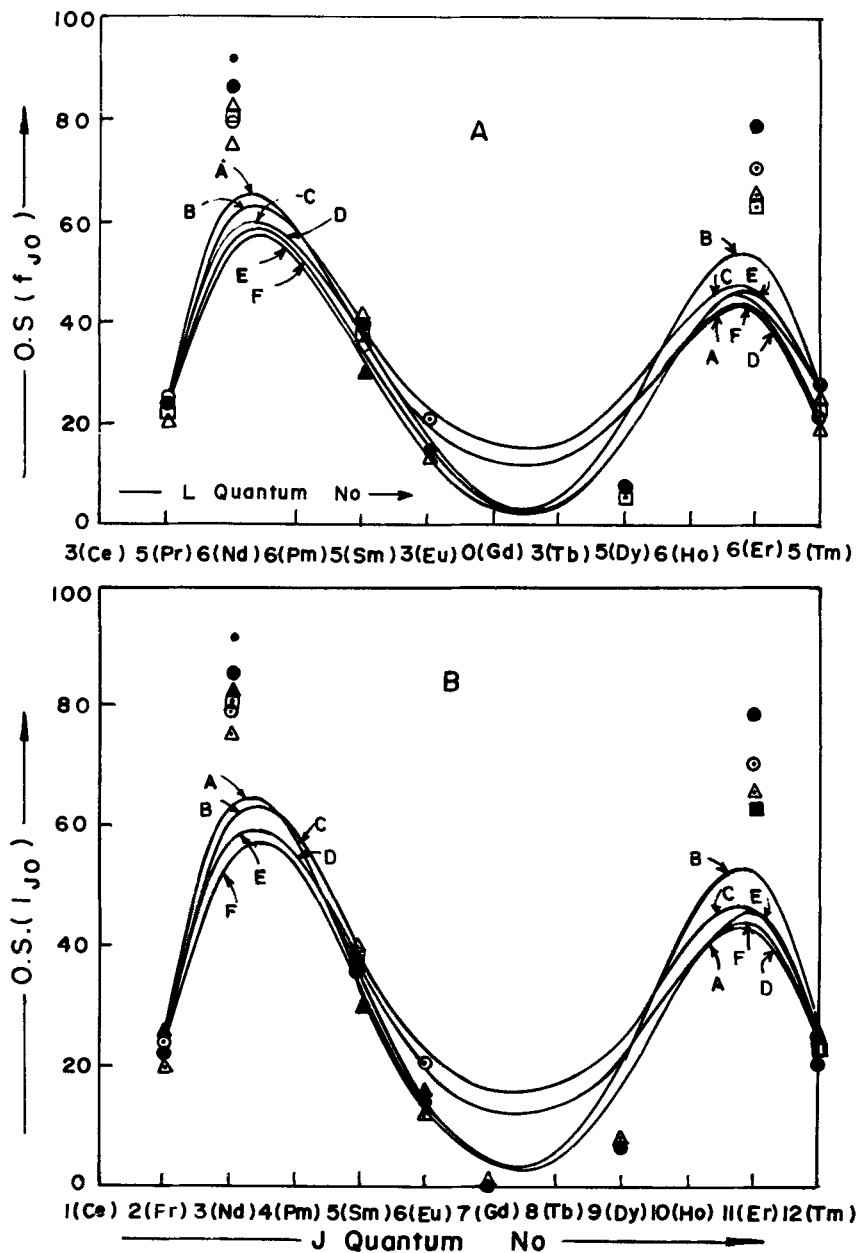


Figure 3. Variation profiles of oscillator strength (f_{j0}) values as a function of L (A) and J (B) quantum numbers of lanthanoids for the [Ln(III).aminopolycarboxylate] systems (A = IMDA; B = NTA; C = HEDTA; D = EDTA; E = CDTA; F = DTPA).

donor atoms. Similarly, a comparison of the values of $(\partial E^3/\partial E^1)$ for Nd(III) and Er(III) indicates a change in the mode of interaction from ionic to iono-covalent from Nd(III) to Er(III).

3.1 *L* and *J* correlations

Spectral parameter (oscillator strengths, f_{JO}) values have been plotted against the total angular momentum quantum numbers (*L*) and the total quantum numbers (*J*) of the Ln(III) cations in order to seek a probable correlation between these (f_{JO} vs *L* and f_{JO} vs *J*). The variation profiles of f_{JO} vs *L* and f_{JO} vs *J* for the six Ln(III) aminopolycarboxylate systems are reproduced in figures 3A and 3B respectively.

In the lanthanoids, where the 4*f*-orbitals are effectively shielded by the outer lying orbitals and the ligand field stabilisation energy (lfse) effects are negligible, the Ln(III)-*L* interactions are expected to be predominantly ionic. The response of specific f^q -orbitals can be ascertained only through the changes in their inter-electronic repulsion Racah parameters and their coefficients composed of *S* and *L* quantum numbers (Limaye *et al* 1991; Limaye and Saxena 1992). The *L* values have long been used as a fundamental property to study the periodicity in lanthanoids (Limaye 1994). The *f*-*f* transitions in lanthanoids are believed to occur from one *J* state to another and hence the justification in seeking a correlation between oscillator strength values and *J* quantum numbers of lanthanoids.

The plots of f_{JO} vs *L* as well as *J* values exhibit a semi-sigmoid shape with varied amplitudes which appear to depend on the denticity and complexing tendency of the ligands. Smooth plots without any deviation indicate that the general *f*-shell feature of the Ln(III) cations is preserved in the (Ln(III).*L*) systems.

Acknowledgement

The authors are thankful to Prof S P Banerjee, for encouragement. RS and PR are thankful to the University Grants Commission, New Delhi and the Madhya Pradesh Council of Science and Technology, Bhopal for the award of project fellowships.

References

- Ashcroft S J and Mortimer C T 1970 *Thermochemistry of transition metal complexes* (London/New York: Academic Press) p. 123
- Bukietynska K and Choppin G R 1970 *J. Chem. Phys.* **50** 2875
- Bukietynska K, Mondry A and Osmeda E 1981 *J. Inorg. Nucl. Chem.* **43** (a) 1311, (b) 1321
- Carnall W T, Fields P R and Wybourn B G 1965 *J. Chem. Phys.* **42** 3797
- Choppin G R and Fellows R L 1974 *J. Coord. Chem.* **3** 209
- Grietmon T F and Choppin G R 1977 *J. Inorg. Nucl. Chem.* **39** 2021, 2026
- Jorgensen C K 1971a *Modern aspects of ligand field theory* (Amsterdam: North Holland) **23** 193
- Jorgensen C K 1971b *Modern aspects of ligand field theory* (Amsterdam: North Holland) **26** 293
- Jorgensen C K and Judd B R 1964 *Mol. Phys.* **8** 281
- Judd B R 1962 *Phys. Rev.* **127** 750
- Limaye S N 1994 *Tetrad effect in solution stabilities of lanthanoid complexes: A nephelauxetic phenomenon* D Sc thesis, Dr H S Gour University, Sagar
- Limaye S N and Saxena M C 1992 *Indian J. Chem.* **A31** 403
- Limaye S N and Saxena M C 1994 *J. Indian Inst. Sci.* **74** 611
- Limaye S N, Kopyrin A A and Saxena M C 1991 *J. Inst. Chem. (India)* **63** 215
- Moeller T, Ferrus R, Feistel G, Martin D F, Thompson L C and Randall W J 1965 *Chem. Rev.* **65** 1
- Peacock R D 1975 *Struct. Bonding* **22** 83
- Singhai R, Limaye S N and Saxena M C 1995 *Proc. Indian Acad. Sci. (Chem. Sci.)* **107** 523