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Hypersensitivity in Lanthanoids: Symmetry Inversion or Covalency

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Explanation to the phenomenon of hypersensitivity has proved to be an intriguing problem. Hypersensitivity may refer to "an enhanced sensitivity of the intensity of specific electronic transitions to the chemical environment than the normal f-f transitions". Intensity and transition of the hypersensitive peaks are functions of the quantum numbers L and J of the ground state of the lanthanoid ions and generally, three selection rules: $\Delta J \leq 2$, $\Delta L \leq 2$ and somtimes $\Delta S \leq 0^3$ have been proposed to regulate the hypersensitive transitions. It was, however, noted that the transitions having a large contribution from magnetic dipole interactions ($\Delta J = 0, \pm 1$) may also vary little with a change in environment. Hypersensitivity is thus also called pseudo-quadrupolar transition because it follows electric quadrupole selection rule.

Several proposals have been made in order to elucidate the phenomenon of hypersensitivity (HST). Two prominent proposals have been advanced: (i) pseudoquadrapolar transition[1–6] and (ii) inclusion of spherical harmonics in the crystal field potential[7]. Besides the two proposals, the hypersensitivity has also been proposed to an account of[8] vibronic transition, increased covalency, the nephelauxetic effect, centre of inversion, double photon transition[9], in homogeneous dielectric[10, 11] dynamic coupling[12], crystal structures[13, 14] and distinguishing mechanism[15].

While examining the phenomenon of hypersensitivity in the solution spectra of lanthanoids, Judd[16] noticed that the hypersensitive bands are associated with large values of U^2 matrix elements thereby showing hypersensitivity to be associated with τ_2. Thus in view to examine the role of covalency and symmetry to the oscillator strength values for the hypersensitive or pseudo-hypersensitive transitions[17] the present attempt has been made to correlate the oscillator strength values of the HST transitions for Nd(III) and Er(III) in different environments (our values and the values reported by others in literature) with the T_λ ($\lambda = 2, 6$) and the β (β = nephelauxetic ratio, $\partial E^3/\partial E^1$) parameters. The ∂E^1 and ∂E^3 are the

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variations in the inter-electronic repulsion (Racah) parameters denoting the orbital and radial part.

According to Judd ofelt theory, the oscillator strength of a transition is given by

$$P = \Sigma\, vT_{\lambda}(f^{n}\psi J \,\|\, U^{\lambda} \,\|\, f^{n}\psi J) \tag{1}$$

where T_{λ} values are the parameters which depend on the nature of the effect which allows f-f transitions and the U^{λ} values are sums of the multiples of tensor operators within the variation of Ω. The U^{λ} parameters are less significant[12, 18] and are less affected by the environment . However, the E values show significant variation with the change in environment. Thus in view of Eq. (1) and the values of $\Sigma E \cdot U^{\lambda}$ ($\lambda = 2, 4, 6$) evaluated for Nd(III) and Er(III) (cf. Table-1) along with the variation in the $4f^{n}$, S, L, J and the theoretical and experimental values for Ω_{λ} ($\lambda = 2, 4, 6$) for aqua systems are recorded in Table-1.

TABLE-1

VARIATION IN THE $4f^{n}$, S, L, J AND (A) $\Sigma E \cdot U^{\lambda}$ $\lambda = 2, 4, 6$) VALUES, (B) THE THEORETICAL Ω_{λ} ($\lambda = 2, 4, 6$) VALUES, AND (C) THE EXPERIMENTAL Ω_{λ} ($\lambda = 2, 4, 6$) VALUES FOR AQUA SYSTEMS FOR Nd(III) AND Er(III) IONS

			(A)				
Ln(III)	f^{n}	S	L	J	$\Sigma E \cdot U^{2}$	$\Sigma E \cdot U^{4}$	$\Sigma E \cdot U^{6}$
Nd (III)	3	3/2	6	9/2	18264#	20779#	19594#
Er(III)	3	3/2	6	15/2	38532#	40232#	45426#
			(B)				
Ln(III)	f^{n}	S	L	J	Ω_2(*)	Ω_4(*)	Ω_6(*)
Nd(III)	3	3/2	6	9/2	3.04*	4.04*	5.04*
Er(III)	3	3/2	6	15/2	3.05*	5.05*	4.05*
			(C)				
Ln(III)	f^{n}	S	L	J	Ω_2	Ω_4	Ω_6
Nd(III)	3	3/2	6	9/2	2.25 (0.93)#	4.06 (5.00)#	9.47 (7.91)#
Er(III)	3	3/2	6	15/2	1/34 (1.59)#	2.19 (1.95)#	1.88 (1.90)#

Note: The T_{λ} values (sec. B(*)) have been evaluated assuming the expression $P = aX + bY + cZ$ where X, Y and Z represent the Ω_2, Ω_4 and Ω_6 values which are assumed to be $1 + \lambda$, $2 + \lambda$ and $3 + \lambda$ for the evaluation of hypothetical values of Ω_{λ} and following the trend for *a, b* and *c* which correspond to the values of $\Sigma E \cdot U^{\lambda}$ ($\lambda = 2, 4, 6$) (*viz.* section A of this Table (# values) for Nd(III)/Er(III)).

A comparison of the values reported by us and the values reported in literature show a variety of sequences for Nd(III) in various ligands as well as crystal hosts. The observed types of sequences may are

$$\Omega_2 > \Omega_6 > \Omega_4 \quad (2A)$$

$$\Omega_4 > \Omega_6 > \Omega_2 \quad (2B)$$

$$\Omega_2 > \Omega_4 > \Omega_6 \quad (3A)$$

$$\Omega_6 > \Omega_4 > \Omega_2 \quad (3B)$$

$$\Omega_4 > \Omega_2 > \Omega_6 \quad (4A)$$

$$\Omega_6 > \Omega_2 > \Omega_4 \quad (4B)$$

Sequence (2A) represents the general sequence with respect to the $\Sigma\, EU^{\lambda}$ values which shows the even besides a change in the environment the complexes do not show any symmetry inversion whereas a reverse of the sequence (2B) represents a change in symmetry around the cation. It may be stated that the related magnitudes of the Ω_λ values may represent the degree of symmetry inversion which may lead to intermediate (miscellenous) sequences of Ω_λ values *viz.* (4; A, B). Sequence (3B) is the general sequence expected on account of the general features of lanthanoids. It may be stated in this regard that in case of lanthanoids the 4f-shells being deeply seated, the strong shielding mechanism makes these orbitals less available for bonding thereby, decreasing the covalency parameter, *i.e.*, Ω_2 whereas the large cationic size associated with three concentric hydration zones may cause greater disruption in symmetry during viscinal metal-matrix approach thereby increasing the Ω_6 values. Same authors have, however, reported a reverse sequence, *viz.*, sequence (3A) which states about a greater involvement of covalency parameters than the symmetry perturbation.

Carnall[19] has pointed out that the proportionality of the T_λ parameters using a crystal field model may be expressed as

$$T_\lambda = \langle r^{t+1} \rangle^2 \cdot R^{-2t-2} \quad (5)$$

whereas $\lambda = 2$ for t = 1, 3; $\lambda = 4$ for t = 3, 5 and $\lambda = 6$ for t = 5 ,7. This expects an order of decreasing sensitivity of the T_λ parameters to the environment giving a sequence $T_6 > T_4 > T_2$. Choppin[19, 20], Judd and Jorgenson[16, 21] and Reisfield[22] have individually observed this sequence for the sensitivity of these parameters towards the intensity of specific electronic transitions.

Nd(III) Systems

A perusal of Table-2 states variety of sequences obtained for Nd (III) in various environments. The studies reported by Mishra *et al.*[23] state a general sequence of' $\Omega_6 > \Omega 4 > \Omega_2$ for 140 systems, where as seven systems have been reported to have a sequence $\Omega_2 > \Omega_6 > \Omega_4$. Jayashanker *et al.*[24] have reported a sequence of $\Omega_2 > \Omega_6 > \Omega_4$ for around 15 systems, sequence $\Omega_4 > \Omega_6 > \Omega_2$ for seven systems, sequence $\Omega_2 > \Omega_4 > \Omega_6$ for 14 systems, sequence $\Omega_6 > \Omega_4 > \Omega_2$ for 9 systems, whereas miscellaneous sequence $\Omega_4 > \Omega_2 > \Omega_6$ and $\Omega_6 > \Omega_2 > \Omega_4$ were reported for two such systems. Authors in their studies have also reported a sequence $\Omega_6 > \Omega_4 > \Omega_2$ for around 24 binary and mixed systems.

A perusal of Table-1 and the hypothetically calculated values of Ω_λ for Nd(III) represents a sequence $\Omega_4 > \Omega_6 > \Omega_2$.

While correlating the oscillator strength (P) (figures not shown) values with $E \cdot \tau_2$ and $E \cdot \tau_6$, one may get a linear regression of a type $y = mx + c$ where 'c' is the intercept and 'm' is the slope $\Delta p/\Delta(E \cdot T_\lambda)$. For a larger value of slope, $\Delta(E \cdot T_\lambda)$ is expected to be small, whereas for the small slope values, $\Delta(E \cdot T_\lambda)$ is expected to be large. In view of Ω_λ sequence obtained for Nd(III) the two correlations may lead to smaller slope values for τ_6 and larger values for τ_2. The observed values for two correlations are m = 0.8315 for τ_2 and m = 0.7010 for τ_6 which states the same sequence of $\tau_6 > \tau_2$ for Nd(III) showing restriction of any symmetry inversion in case of Nd(III) complexes.

TABLE–2
JUDD-OFELT PARAMETERS (Ω_λ) FOR Nd(III) AND Er(III) IN VARIOUS HOSTS/ENVIRONMENTS

Systems	Sequence	Ref.
Aqua-ion	$\Omega_6 > \Omega_4 > \Omega_2$	[30]
CdBS	$\Omega_2 > \Omega_4 > \Omega_6$	[27]
LiCdBS; NaCdBS	$\Omega_6 > \Omega_2 > \Omega_4$	[27]
KCdBS	$\Omega_2 > \Omega_6 > \Omega_4$	[27]
GdCdBS	$\Omega_2 > \Omega_6 > \Omega_4$	[27]
LiBO	$\Omega_4 > \Omega_2 > \Omega_6$	[28]
MgLiBO	$\Omega_4 > \Omega_6 > \Omega_2$	[28]
CaLiBO	$\Omega_2 > \Omega_6 > \Omega_4$	[28]
SrLiBO	$\Omega_2 > \Omega_6 > \Omega_4$	[28]
BaLiBO	$\Omega_4 > \Omega_6 > \Omega_2$	[28]
$Nd(PO_3)_2P_2O_5$	$\Omega_2 > \Omega_6 > \Omega_4$	[29]
$49Mg(PO_3)_2 \cdot 50P_2O_5$	$\Omega_2 > \Omega_4 > \Omega_6$	[29]
$49Ca(PO_3)_2 \cdot 50P_2O_5$	$\Omega_6 > \Omega_4 > \Omega_2$	[29]
$49Sr(PO_3)_2 \cdot 50P_2P_5$	$\Omega_6 > \Omega_2 > \Omega_4$	[29]
$49Ba(PO_3)_2 \cdot 50P_2O_5$	$\Omega_6 > \Omega_4 > \Omega_2$	[29]
L27 : $33K_2O : 66.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[30]
H8 : $20MgO \cdot 15K_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[30]
H9 : $20CaO \cdot 15K_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[30]
H10 : $20SrO \cdot 15K_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[30]
H7 : $20BaO \cdot 15K_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[30]
$33Na_2O : 66.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[31]
$15MgO : 20Na_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[32]
$15CaO : 20Na_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[32]
$15SrO : 20Na_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[32]
$15BaO : 20Na_2O : 65.5SiO_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[32]
$25MgO : 10Al_2O_3 : 65P_2O_5$	$\Omega_2 > \Omega_4 > \Omega_6$	[32]
$25CaO : 10Al_2O_{365}P_2O_5$	$\Omega_2 > \Omega_6 > \Omega_4$	[32]
$25SrO : 10Al_2O_3 : 65P_2O_5$	$\Omega_2 > \Omega_6 > \Omega_4$	[32]

Systems	Sequence	Ref.
$25BaO : 10Al_2O_3 : 65P_2O_5$	$\Omega_2 > \Omega_6 > \Omega_4$	[32]
$KZ : 70K_2SO_4 : 29ZnSO_4$	$\Omega_6 > \Omega_4 > \Omega_2$	[33]
$MKZ : 5MgSO_4{\cdot}35K_2SO_4 : 59ZnSO_4$	$\Omega_2 > \Omega_6 > \Omega_4$	[34]
$CKZ : 5CaSO_4{\cdot}35K_2SO_4 : 59ZnSO_4$	$\Omega_2 > \Omega_6 > \Omega_4$	[34]
$BKZ : 5BaSO_4{\cdot}35K_2SO_4 : 59ZnSO_4$	$\Omega_2 > \Omega_6 > \Omega_4$	[34]
$60BiCl_3 : 40KCl$	$\Omega_4 > \Omega_2 > \Omega_6$	[35]
$50ZnCl_2 : 40KI$	$\Omega_4 > \Omega_6 > \Omega_2$	[35]
Lead acetate glasses	$\Omega_6 > \Omega_2 > \Omega_4$	[26]
LSG–91H	$\Omega_4 > \Omega_6 > \Omega_2$	[36]
ED–2; S33	$\Omega_6 > \Omega_4 > \Omega_2$	[36]
$30LiSO_4 : 69.5Na_2SO_4$	$\Omega_2 > \Omega_6 > \Omega_4$	[37]
$15Li_2O{\cdot}20BaO : 65SiO_2$	$\Omega_2 > \Omega_6 > \Omega_4$	[30]
$20Na_2O : 79TeO_2$	$\Omega_4 > \Omega_6 > \Omega_2$	[30]
$Ga_2S_3 : La_2S_3 : Nd_2S_3$	$\Omega_2 > \Omega_6 > \Omega_4$	[38]
$Al_2S_3 : La_2S_3 : Nd_2S_3$	$\Omega_2 > \Omega_6 > \Omega_4$	[38]
$LiNO_3 + KNO_3$(melt)	$\Omega_2 > \Omega_6 > \Omega_4$	[39]
$Y_3Al_5O_{12}$	$\Omega_6 > \Omega_4 > \Omega_2$	[40]
LaF_3	$\Omega_4 > \Omega_6 > \Omega_2$	[41]
Y_2O_3	$\Omega_2 > \Omega_4 > \Omega6$	[41]
Sodium β'' alumina	$\Omega_2 > \Omega_4 > \Omega_6$	[42]
NdO_8 chromophore [18 systems]	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
NdO_8 chromophore [6 systems] [Inner Sphere Complexes]	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
NdO_6 inner sphere [2 systems]	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
Schiff base complexes [6 systems]	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
Mixed ligand complexes [22 systems]	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
Mixed ligand complexes [35 systems] [Nd(hist/cysteine)(diol) $(H_2O)_3$	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
Nd complexes of nucleic acid component [42 systems]	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
Nd-tris haloacetate trihydrated essentially other sphere [9 systems]	$\Omega_6 > \Omega_4 > \Omega_2$	[23]
Ω_λ Values or Er(III):	Sequence	Ref.
LiBO	$\Omega_2 > \Omega_4 > \Omega_6$	[28]
MgLiBO	$\Omega_2 > \Omega_4 > \Omega_6$	[28]
CaLiBO	$\Omega_2 > \Omega_6 > \Omega_4$	[28]
SrLiBO	$\Omega_2 > \Omega_6 > \Omega_4$	[28]
BaLiBO	$\Omega_2 > \Omega_6 > \Omega_4$	[28]
ZSS	$\Omega_2 > \Omega_4 > \Omega_6$	[43]
LSS	$\Omega_2 > \Omega_6 > \Omega_4$	[43]

Systems	Sequence	Ref.
CSS	$\Omega_2 > \Omega_4 > \Omega_6$	[43]
PSS	$\Omega_2 > \Omega_6 > \Omega_4$	[43]
MSS	$\Omega_2 > \Omega_4 > \Omega 6$	[43]
MPZS	$\Omega_2 > \Omega_6 > \Omega_4$	[44]
CPZS	$\Omega_2 > \Omega_6 > \Omega_4$	[44]
BPZS	$\Omega_2 > \Omega_6 > \Omega_4$	[44]
ZSP	$\Omega_2 > \Omega_6 > \Omega_4$	[45]
PSP	$\Omega_2 > \Omega_4 > \Omega_6$	[46]
SFP	$\Omega_4 > \Omega_2 > \Omega_6$	[47]
SBP	$\Omega_2 > \Omega_6 > \Omega_4$	[48]
SAP	$\Omega_2 > \Omega_6 > \Omega_4$	[49]
BTF	$\Omega_2 > \Omega_4 > \Omega_6$	[50]
BZYTLE	$\Omega_2 > \Omega_4 > \Omega_6$	[51]
PZGL	$\Omega_2 > \Omega_6 > \Omega_4$	[52]
ZBLA	$\Omega_2 > \Omega_4 > \Omega_6$	[53]
ZCBLAL	$\Omega_4 > \Omega_2 > \Omega_6$	[54]
FLSRP	$\Omega_2 > \Omega_6 > \Omega_4$	[55]
FLPH	$\Omega_2 > \Omega_4 > \Omega_6$	[56]
Phosphate	$\Omega_2 > \Omega_6 > \Omega_4$	[56]
Ge/Al silica	$\Omega_2 > \Omega_4 > \Omega 6$	[56]
FLZBLA	$\Omega_2 > \Omega_4 > \Omega_6$	[57]
Fluorohafnate	$\Omega_2 > \Omega_4 > \Omega_6$	[58]
$Zn(PO_3)_2$	$\Omega_2 > \Omega_4 > \Omega_6$	[59]
$Pb(PO_3)_2$	$\Omega_2 > \Omega_6 > \Omega_4$	[59]
TEO	$\Omega_2 > \Omega_4 > \Omega_6$	[60]
B25N	$\Omega_2 > \Omega_4 > \Omega_6$	[61]
Si	$\Omega_2 > \Omega_4 > \Omega_6$	[61]
S30N	$\Omega_2 > \Omega_4 > \Omega_6$	[61]
S25AN	$\Omega_2 > \Omega_4 > \Omega_6$	[61]
G1ON	$\Omega_2 > \Omega_4 > \Omega_6$	[61]
CaAl	$\Omega_2 > \Omega_4 > \Omega_6$	[61]
Al	$\Omega_2 > \Omega_4 > \Omega_6$	[61]
$LiNO_3 + KNO_3$(melt)	$\Omega_2 > \Omega_4 > \Omega_6$	[62]
$Er(dpm)_3$	$\Omega_2 > \Omega_6 > \Omega_4$	[62]
$ErCl_3(AlCl_3)_3$	$\Omega_2 > \Omega_4 > \Omega_6$	[62]
$ErBr_3$	$\Omega_2 > \Omega_6 > \Omega_4$	[62]
Aqua ion	$\Omega_4 > \Omega_6 > \Omega_2$	[62]
CH_3OH	$\Omega_4 > \Omega_2 > \Omega_6$	[62]
$ErW_{10}O_{35}^{-7}$	$\Omega_2 > \Omega_4 > \Omega_6$	[62]

Systems	Sequence	Ref.
Y_2O_2S	$\Omega_2 > \Omega_6 > \Omega_4$	[63]
$KCaF_3$	$\Omega_4 > \Omega_2 > \Omega_6$	[64]
LaF_3	$\Omega_2 > \Omega_6 > \Omega_4$	[62]
$YAlO_3$	$\Omega_4 > \Omega_2 > \Omega_6$	[62]
Y_2O_3	$\Omega_2 > \Omega_4 > \Omega_6$	[65]
Y_2SiO_5	$\Omega_2 > \Omega_4 > \Omega_6$	[66]
$Er(CCL_3COO)_3 \cdot 2H_2O$	$\Omega_2 > \Omega_4 > \Omega_6$	[67]
$LiErP_4O_{12}$	$\Omega_4 > \Omega_2 > \Omega_6$	[68]
ErP_5O_{14}	$\Omega_4 > \Omega_2 > \Omega_6$	[68]
Ammonium acetate	$\Omega_4 > \Omega_2 > \Omega_6$	[24]
Magnesium acetate	$\Omega_2 > \Omega_4 > \Omega_6$	[24]
Potassium acetate	$\Omega_2 > \Omega_4 > \Omega_6$	[24]
Sodium acetate	$\Omega_2 > \Omega_4 > \Omega_6$	[24]
Erbium	$\Omega_4 > \Omega_2 > \Omega_6$	[24]
BNa glass	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
BLi glass	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
BAl glass	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
BNaAl glass	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
BLiAl glass	$\Omega_4 > \Omega_2 > \Omega_6$	[25]
BNaLi glass	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
$57ZrF_4 - 34BaF_2 - 4AlF_3 - 3NaF_3 - 2ErF_3$	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
$19BaF_2 - 27ZnF_2 - 5YbF_3 - 27ThF_3 - 21LuF_3 - 1ErF_3$	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
$30BaF_2 - 20ZnF_2 - 30InF_3 - 84YbF_3 - 10ThF_3 - 2ErF_3$	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
$48(NaPO_3)_6 - 20BaCl_2 - 10ZnCl_2 - 20LiCl - 2ErCl_3$	$\Omega_2 > \Omega_4 > \Omega_6$	[25]
$50(NaPO_3)_6 - 18BaF_2 - 10ZnF_2 - 20LiF - 2ErF_3$	$\Omega_2 > \Omega_4 > \Omega_6$	[25]

Er(III) Systems

A perusal of Table-2 represents a general sequence for $\Omega_6 > \Omega_4 > \Omega_2$ for Er(III), whereas carnall *et al.*[38] in their studies have reported a sequence $\Omega_4 > \Omega_6 > \Omega_2$. This states an inversion of symmetry in the Er(III) complexes as compared to Nd(III). Table-2 represents variety of sequences obtained for Er(III) in various environments. Jayashanker *et al.*[24, 27] in their studies have reported a sequence $\Omega_2 > \Omega_4 > \Omega_6$ for around 8 systems, $\Omega_2 > \Omega_6 > \Omega_4$ for around 14 systems, whereas sequence $\Omega_4 > \Omega_2 > \Omega_6$ for 2 systems. Similarly Rai *et al.*[25] in their studies have reported a sequence of $\Omega_2 > \Omega_4 > \Omega_6>$ for around 10 systems, whereas sequence $\Omega_4 > \Omega_2 > \Omega_6$ for one system. Authors in their studies have observed a sequence of $\Omega_4 > \Omega_6 > \Omega_2$ from their studies.

While correlating the oscillator strength (P) (figures not shown) values with $E \cdot \tau_2$ and $E \cdot \tau_6$ one may get a linear regression of a type $y = mx + c$. The m values obtained for the τ_2 and τ_6, regression are $m = 0.0515$ for τ_2 and $m = 0.0299$ for τ_6, which gives a general sequence of $\Omega_6 > \Omega_2$ for Er(III) complexes. The resemblance of the τ_λ values for hypothetical calculation and experimental values is, however, $\Omega_2 > \Omega_6$ which is in general a sequence of symmetry inversion. The aqua systems worked out by authors, however, rule out the possibility of any symmetry inversion.

Inference

A perusal of various patterns for Ω_λ values obtained for Nd(III) and Er(III) in various hosts/environments clearly indicates a difference in the mode of bonding pattern of Nd(III) and Er(III). The Nd(III) systems have shown a greater dependence on symmetry parameters as compared to that of the covalent model regulating hypersensitivity whereas the HST transitions in Er(III) have, however, shown greater dependency on covalency model than the symmetry perturbation. A comparison of general reported sequence of Ω_λ for various hosts and the hypothetical relationship obtained for two cations, Nd (III) and Er(III) under study, suggest a partial restricted symmetry inversion for Nd(III) ions in various hosts whereas a general symmetry inversion in case of Er(III) complexes. The aqueous systems, however, have not shown any symmetry inversion. It may be stated that the two cations have almost similar values for same $4f^q$, S (spin quantum number), and L (orbital angular momentum), (3, 3/2, 6 respectively) but have difference only in their J (total quantum number) values (9/2 for Nd(III) and 15/2 for Er(III)) suggesting a J-dependent behaviour of susceptibility and intensity of the hypersensitive transitions.

It is, however, necessary to note that the present conclusions have been drawn only on the basis of τ_2 and τ_6 parameters, whereas the exact explanation of this phenomenon may be drawn taking into consideration all the parameters discussed in para 2. To seek a quantitative explanation for the overall mechanism, it is necessary to make a theoretical approach similar to that for crystal field. The phenomenon seems to be directly affected by chemical bonding and the solution to the problem probably lies under the influence of dielectric conditions at the ion site, configuration mixing between $4f^n$ and the nephelauxetic phenomenon with dynamic coupling. The picture is yet blurred and needs a greater attention for a more refined case.

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REFERENCES

1. C.K. Jorgenson and B.R. Judd, *Mole. Phys.*, **8**, 281 (1964).
2. N.S. Poluektor, N.A. Nazenko and V.T. Misshchenko, *Dokl. Akad. Nauk. USSR*, **265**, 1190 (1982).
3. J.C.G. Bunzli, Lanthanoid Probes in Life, Medical and Environmental Sciences, Elsevier, Amsterdam, Ch. 7 (1991).
4. N.S. Poluektor, *Dokl. Akad. Nauk. USSR*, **224**, 150 (1975).
5. O.L. Malta, *Mole. Phys.*, **42**, 65 (1981).

6. G.R. Choppin, D.E. Henrie and K. Buijs, *Inorg. Chem.*, **5**, 1743 (1966).
7. B.R. Judd, *J. Chem. Phys.*, **44**, 839 (1966).
8. G.R. Choppin and D.E. Henrie, *J. Chem. Phys.*, **49**, 477 (1968).
9. J.D. Axe, *Phys. Rev.*, **136**, A42 (1964).
10. F.S. Mason, R.D. Peakock and B. Stewart, *Mole. Phys.*, **30**, 1829 (1975).
11. ________, *Chem. Phys. Lett.*, **29**, 149 (1974).
12. B.R. Judd, *J. Chem. Phys.*, **70**, 4830 (1979).
13. J.L. Rayan and C.K. Jorgenson, *J. Chem. Phys.*, **70**, 2845 (1966).
14. ________, *Inorg. Chem.*, **8**, 2053 (1969).
15. B.R. Judd, American Chemical Society, Series 47, Ch.13, p. 667 (1980).
16. ________, *Phys. Rev.*, **127**, 750 (1962).
17. R. Reisefield and C.K. Jorgenson, Lasers and Excited States of Rare Earths, Pergamon Press, p. 24, Tables 2–8 (1977).
18. G.R. Choppin, D.E. Henrie and R.L. Fellows, *Coord. Chem. Rev.*, **18**, 199 (1976).
19. W.T. Carnall, P.R. Fields and B.G. Wybourn, *J. Chem. Phys.*, **42**, 3727 (1965).
20. G.R. Choppin, D.E. Henrie and R.L. Fellows, *J. Chem. Phys.*, **52**, 2875 (1970); **49**, 477 (1968).
21. R. Reisefield and C.K. Jorgenson, *Solid State Commun.*, **13**, 281 (1973).
22. ________, *Struct. and Bond.*, **13**, 13 (1973).
23. S.N. Mishra and S.O. Sommerer, *Rev. in Inorg. Chem.*, **12**, 3 (1992)
24. S.V.J. Lakshman and C.K. Jayashankar, *Spectrochim. Acta*, **40A**, 695 (1984).
25. B. Sharma, D.K. Rai and S.B. Rai, *Indian J. Phys.*, **70B**, 397 (1996).
26. Y.C. Ratnakaram, N. Sudharani and S. Buddhudu, *Bull. Mater. Sci.*, **19**, 581 (1996).
27. V.V.R.K. Kumar and C.K. Jayashanker, *Physica B*, **226**, 313 (1996).
28. A.R. Devi and C.K. Jayashanker, *Materials Chem. and Phys.*, **42**, 106 (1995).
29. M.J. Weber, R.A. Saroyan and R.C. Ropp, *J. Non-Cryst. Solids*, **44**, 137 (1981).
30. R. Reisefield and C.K. Jorgenson, in: K.A. Gcshneidner (Jr.) and Eyring (Eds.), Handbook on Phys. and Chem. of Rare Earths, Vol. IX, Elsevier, Amsterdam, Ch. 58 (1987).
31. R.R. Jacobs and M.J. Weber, *IEEE J. Quantam Electronics*, **QE–12**, 102 (1976).
32. T. Izumitani, H. Toratani and H. Kuroda, *J. Non.–Cryst. Solids*, **28**, 209 (1978).
33. S.V.J. Lakshman and A. Suresh Kumar, *J. Less-Common Met.*, **126**, 257 (1986).
34. Y. Subramanyam, L.R. Moorthy and S.V.J. Lakshman, *J. Phys. Chem. Solids*, **51**, 123 (1990).
35. M.J. Weber, D.C. Zeigler and C.A. Angell, *J. App. Phys.*, **53**, 4344 (1982).
36. W.F. Krupke, *IEEE J. Quantum Electronics*, **QE-10**, 450 (1974).
37. S.V.J. Lakshman and Y.C. Ratnakaram, *Phys. Chem. Glasses*, **29**, 26 (1988).
38. C.K. Jayashanker, F.S. Richardson and M.F. Reid, *J. Phys. Condensed Mat.*, **6**, 5919 (1994).
39. W.T. Carnall, in: K.A. Gcshneidner (Jr.) and Eyring (Eds.), Handbook on Phys. and Chem. of Rare Earths, Vol. III, North Holland, Amesterdam, Ch. 24 (1987).
40. A.A. Kaminskii, Laser Crystals, Springer, New York (1981).
41. W.F. Krupke, *Phys. Rev.*, **145**, 325 (1966).
42. H. Dai and O.M. Stafsudd, *J. Phys. Chem. Solids*, **52**, 367 (1991).
43. S.V.J. Lakshman and Y.C. Ratnakaram, *Phys. Chem. Glasses*, **94**, 222 (1987).
44. Y. Subramanyam, L.R. Moorthy and S.V.J. Lakshman, *Mater. Lett.*, **9**, 277 (1990).
45. S.V.J. Lakshman and A. Suresh Kumar, *Phys. Chem. Glasses*, **29**, 146 (1988).
46. ________, *J. Phys. Chem. Solids*, **49**, 133 (1988).
47. ________, *Lanthanide Actinide Res.*, **2**, 243 (1988).

48. ________, *Phys. Chem. Glasses*, **30**, 35 (1989).

49. ________, *J. Phys. Chem. Solids*, **49**, 807 (1988).

50. D.C. Yeh, R.R. Petrin, W.A. Sibley, V. Madigou, J.L. Adam and M.J. Suscavage, *Phys. Rev.*, **B39**, 80 (1989).

51. D.C. Yeh, W.A. Sibley, M.J. Suscavage and M.G. Drexhage, *J. Appl. Phys.*, **62**, 266 (1987).

52. R. Reisefield, G. Katz, N. Spector, C.K. Jorgenson, C. Jacoboni and R. De Pape, *J. Solid State Chem.*, **41**, 253 (1982).

53. M.D. Shinn, W.A. Sibley, M.G. Drexhage and R.N. Brown, *Phys. Rev.*, **B27**, 6635 (1983).

54. B. Villacampa, V.M. Orera, R.I. Marino, R. Cases, P.J. Alonso and R. Alcala, *Mater. Res. Bull.*, **26**, 741 (1991).

55. M. Ledig, E. Heumann, D. Ehrt and W. Seeber, *Opt. Quant. Elec.*, **20**, S107(1990).

56. S. Zemon, G. Lambert, L.J. Andrews, W.J. Miniscalo, B.T. Hall, T. Wei and R.C. Folweiler, *J. Appl. Phys.*, **69**, 6799 (1991).

57. R. Reisefield, G. Katz, C. Jacoboni, M.G. Drexhage and R. De Pape, *J. Solid State Chem.*, **48**, 323 (1983).

58. R. Cases and M.A. Chamarro, *J. Solid State Chem.*, **90**, 313 (1991).

59. G. Ingletto, M. Bettinelli, L. Di Sipio, F. Negrisolo and C. Aschieri, *Inorg. Chim. Acta,* **188**, 201 (1991).

60. W. Ryba-Romanowski, *J. Lumin.*, **46**, 163 (1990).

61. S. Tanabe, T. Ohyagi, S. Todoroki, T, Hanada and N. Soga, *J. Appl. Phys.*, 73, 8451 (1993).

62. R. Reisefield, C.K. Jorgenson, In: K.A. Gcshneidner (Jr.) and Eyring (Eds.), Handbook on Phys. and Chem. of Rare Earths, Vol. IX, Elsevier, Amesterdam, Ch. 58 (1987).

63. Yu P. Timofeev, N.K. Tkhan and S.A. Fridman, *Opt. Spectrosc.*, **69**, 220 (1990).

64. C.Y. Chen, W.A. Sibley, D.C. Yeh and C.A. Hunt, *J. Lumin.*, **43**, 185 (1989).

65. W.F. Krupke, *IEEE J. Quant. Electron.* **QE-7**, 153 (1971); *Phys. Rev.*, **145**, 325 (1966).

66. C. Li, C. Wyon and R. Moncorge, *IEEE J. Quant. Elect.*, **28**, 1209 (1992).

67. J. Legendziewicz, G. Oczko and G. Meyer, *Polyhedron*, **16**, 1921 (1991).

68. W. Ryba-Romanowski, Z. Mazurak, B. Jezowska-Trzebiatowska, D. Schultze and C.W. Waligora, *Phys. Status Solidi*, **A62**, 75 (1980).

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