



An Explanation of Hypersensitive Transition (HST) through Judd-Ofelt Covalency and Symmetry Parameters.

SUJEET JAIN

Department of Physics & Electronics,
Dr. Hari Singh Gour University Sagar (M.P.)-470003, India

ABSTRACT

Explanation to the phenomenon of hypersensitivity has been observed to be an intriguing problem. Hypersensitivity has been exhibited in the electronic spectra as “enhanced sensitivity of the intensity of specific electronic transitions to the chemical environment with respect to normal f-f transitions”. Intensity and position of the hypersensitive peaks have been observed to be function of quantum numbers (S, L and J) of the ground state of the Lanthanide (III) ions. Generally, three selection rules: $\Delta J \leq 2$, $\Delta L \leq 2$ and sometimes $\Delta S \leq 0$ 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. Systemic investigation of the intensity regulating parameters for lanthanide elements of lighter and heavier groups, as explained by Judd-Ofelt, has been made. The Judd-Ofelt parameters Ω_λ ($\lambda=2,4,6$) in different matrix environments have been observed for selfed data obtained in literature. It has been observed that the sequence $\Omega_2 < \Omega_4 < \Omega_6$ change from pre-Gd elements to post-Gd elements. The changes in this sequence has been examined and explained in height of cation size and matrix nature.

Keywords: Hypersensitivity, Judd-Ofelt theory, Transition

INTRODUCTION

The 4f transitions, which are sensitive to environment, are known as hypersensitive transitions that obey the some selection rules. The hypersensitive bands are normally associated with the larger value of $\|U^2\|^2$ matrix elements and therefore the hypersensitivity is intimately related to Ω_λ parameters (1,2). Several proposals have been made in order to elucidate the phenomenon of hypersensitivity (HST). Two prominent proposals have been advanced: (i) pseudoquadrupolar transition (3,4) and (ii) inclusion of spherical harmonics in the crystal field potential (5,6). Besides the two proposals, the hypersensitivity have also been proposed to an account or vibronic transition, increased covalency, the nephelauxetic effect (7), centre of inversion, double photon transition in homogeneous dielectric dynamic coupling, crystal structures (8) and distinguishing mechanism.

While examining the phenomenon of hypersensitivity in the solution spectra of lanthanides, Judd (9,11) 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 the present attempt has been made to correlate the oscillator strength values of the HST transitions for Pr (III) in different environments with the T_λ ($\lambda=2,4,6$) Parameters (12, 13).

EXPERIMENTAL

In the present case the glasses of following composition were prepared using fusion method. Glass: - 99 $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ + 1 PrNO_3 . The $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and PrNO_3 of AR standard were taken into the borosil crucible and then heated to 600°C to 700°C in a furnace for 30 minutes. The melted substance was then poured onto a glass sheet and pressed by another glass so that the doped sample found should become transparent and is converted in form of a palate. In present case, a palate formed had a diameter of 2.4 cm and thickness 0.069 cm. The refractive index was measured by laser beam technique.

The chart speed was maintained at 160 nm per minutes and sensitivity 100-500/1000 nm as desired for specific spectral reading. Figure 1 show the spectra of Pr (III) ion in Glass.

RESULT AND DISCUSSION

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

$$P = \sum v T_{\lambda} (f^n \psi_j \| U^{\lambda} \| f^n \psi_j) \quad (1)$$

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 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 $\sum E.U^{\lambda}$ ($\lambda = 2, 4, 6$) evaluated for various lanthanides along with the variation in the $4f^n$, S, L, J and the theoretical and experimental values for Ω_{λ} ($\lambda = 2, 4, 6$) are recorded in Table.

A comparison of the values reported by us and the values reported in literature shows a variety of sequences for various crystal hosts. The observed types of sequences may are:

$$\Omega_2 > \Omega_6 > \Omega_4 \quad (i)$$

$$\Omega_4 > \Omega_6 > \Omega_2 \quad (ii)$$

$$\Omega_2 > \Omega_4 > \Omega_6 \quad (iii)$$

$$\Omega_6 > \Omega_4 > \Omega_2 \quad (iv)$$

$$\Omega_4 > \Omega_2 > \Omega_6 \quad (v)$$

$$\Omega_6 > \Omega_2 > \Omega_4 \quad (vi)$$

Sequence (i) represents the general sequence with respect to the $\sum E U^{\lambda}$ 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 (ii) 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 (miscellaneous) sequences of Ω_{λ} values viz. (v,vi). Sequence (vi) is the general sequence expected on account of the general features of lanthanides. It may be stated in this regard that in case of lanthanides 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. Carnall (10) has pointed out that the proportionality of the T_{λ} parameters using a crystal field model may be expressed as

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

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 $T_6 > T_4 > T_2$.

A comparison of the values reported by us and the values reported in literature show a variety of sequence for Pre Gd to Post Gd,

$$T_1 = T_2, T_4, T_6$$

Where $T_2 =$ Covalency

$$T_4 =$$
 Environment

$$T_6 =$$
 Environment

For Pre Gd $T_2 < T_4 < T_6$

For Post Gd $T_6 < T_4 < T_2$

$$T_6 \geq T_2$$

CONCLUSION

A perusal of various patterns for Ω_{λ} values obtained for Pr (III) in various hosts / environments clearly indicates a difference in the mode of bonding pattern, greater dependency of symmetry parameters and covalency models.

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Table:- Variation in the $4f^n$, S, L, J and (I) $\sum E.U^\lambda$ ($\lambda=2, 4, 6$) values, (II) The theoretical Ω_λ ($\lambda=2, 4, 6$) values and (III) The Experimental Ω_λ ($\lambda=2, 4, 6$) values for Pr (III) ions.

Ln(III) f^n	S	L	J	$\sum E.U^2$	(I)		$\sum E.U^6$	
Pr(III) 2	2/2	5	8/2	16850	$\sum E.U^4$	20800	21550	
Ln(III) f^n	S	L	J	Ω_2 (*)	(II)		Ω_6 (*)	
Pr(III)	2	2/2	5	8/2	10.28	Ω_4 (*)	0.35	1.350
Ln(III) f^n	S	L	J	Ω_2	(III)		Ω_6	
Pr(III)	2	2/2	5	8/2	378.32	Ω_4	12.88	49.74

