ELECTRONIC SPECTRAL INTENSITIES OF TRIVALENT NEODYMIUM – BRUCINE DOPED SYSTEMS IN ETHANOL MEDIUM AT pH 2 TO 6 WITH DIFFERENT METAL-LIGAND CONCENTRATION

*Anushree Arya[1] & Ravi Shankar Verma[2]

1. Department of Chemistry , M.D.(P.G.) College, Sri Ganganagar(Raj.)
2. Department of Chemistry, Govt. Dunger College, Bikaner(Raj.)

1. ABSTRACT:

We have observed ten bands for trivalent Neodymium ion in the region of 380-900 nm in ethanol medium. These bands are due to $^4P_{1/2}$, $^4G_{11/2}$,$^2G_{9/2}$,$^4G_{9/2}$,$^4G_{7/2}$, $^4G_{5/2}$,$^4F_{9/2}$,$^4F_{7/2}$,$^4F_{5/2}$ and $^4F_{3/2}$ levels . The transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ in Nd^{+3} ion has been considered as " Hypersensitive transition ". Electronic Spectral Intensities in terms of oscillator strengths (P_{obs}) and Judd-Ofelt parameters of the observed peaks have been calculated from the recorded absorption spectra of Nd- BRU Doped systems at different pH of solution with different concentration of Brucine ligands .The change in oscillator strength and Judd-Ofelt parameters of Nd- BRU Doped systems suggest, the existence of the species which is the bounded by the donor group of ligand at different pH of solution.

(KEYWORD :- Hypersensitive transition ,Oscillator strength , Judd-Ofelt parameters, BRU= Brucine)

2. INTRODUCTION: The absorption spectra due to 4f-4f transition in lanthanides is closely related to spectral intensities of coordinated complex . the spectral intensity of a Hypersensitive band is sensitive to the pH [1,2] ,concentration of ligand[3]and solvent[4] . In the present paper electronic spectral intensities (i.e. oscillator strength and Judd-Ofelt parameters)for the modified Nd (III) –Brucine doped systems at a broad range of pH i.e. 2 to 6 with metal-ligand ratio 1:1, 1:2 & 1:3 have been studied . Brucine is an alkaloid , It shows greater coordination behavior with trivalent Neodymium ion due to presence of 'N' and 'O' as donor atoms .

Judd[5,6,7]-Ofelt[8] derived an equation for oscillator strength (P) of a transition between a ground state (f^N ψJ) and an excited state (f^N ψJ') of the lanthanide ion in solution given as -

$$P_{ed} = \sum_{\lambda=2,4,6} T_\lambda \; \bar{\nu} [f^N \psi_J \| U^{(\lambda)} \| f^{N'} \psi_J']^2 \qquad \text{.....(1)}$$

Where the unit tensor operator [$U^{(\lambda)}$] connect the initial and final states via T_λ(λ=2,4,6) parameters .The oscillator strength (P) is the probability of an electronic transitions and can be given as -

$$P = (4.6 \times 10^{-9}) \times \in_{max} \times \Delta \bar{\nu} ½ \qquad \text{.....(2)}$$

Where $\in_{max}$ is the molar extinction coefficient of the peak maximum and $\Delta \bar{\nu}$ ½.is the half intensity band width , i.e. the width at ½ $\in_{max}$ .For the allowed transition P is equals to one .Since f ↔ f transitions are mostly induced electric dipole transitions , the value of P is of the order of 10^{-6} , i.e. P<<1. The value of oscillator strength magnetic dipole and electric quadrupole is of the

order of 10^{-8} and 10^{-10} respectively . The selection rule for these transitions are $\Delta J \leq 1$ and $\Delta J \leq 2$. In Judd-Ofelt parameters (T_λ), We have $\Delta J \leq \lambda$ i.e.for T_2,T_4 and T_6, we have $\Delta j \leq 2$, , $\Delta J \leq 4$ and $\Delta J \leq 6$, respectively.

The ratio of T_4/T_6 is found to be nearly constant for the systems having same symmetry[1,3] . Thus the Judd-Ofelt[7] parameters (T_λ) are characterstics intensity parameters for the intra f^N transitions observed in the lanthanide complexes (or doped systems). Therefore it has been found desirable to use the statistical method for computing T_λ parameters.

3. EXPERIMENTAL: Stock solution of .1M $NdCl_3$ was prepared from 99.9% Neodymium chloride, (Merk) in 50% ethanol solution. .1M, .2 M, .3 M solutions of Brucine were also made in 50% ethanol. Now 10 ml of each of these ligand solutions was added to 10 ml of .1M Nd (III) solution. In this way we got Nd (III) –BRU doped systems with different M:L Ratio (1 : 1, 1 : 2 & 1 : 3). Electronic spectra of Er(III) ion in such doped system was measured at pH 2 to 6. A carbonate free NaOH solution and HCl was used to adjust the pH of Nd (III) –BRU doped systems.

All electronic spectra were measured by Systronic-2202 UV-Visible double beam spectrophotometer in the range of 380-900 nm. pH was recorded by using systronic µ-pH system 361, pH meter at room temp. 100% C_2H_5OH (Merk) was used to make solutions.

4. OBERVATION AND CALCULATION –

4.1 OBERVATION

We have observed ten bands for trivalent Neodymium ion in the region of 380-900 nm in ethanol medium. These bands are due to $^4P_{1/2}$, $^4G_{11/2}$,$^2G_{9/2}$,$^4G_{9/2}$,$^4G_{7/2}$, $^4G_{5/2}$,$^4F_{9/2}$,$^4F_{7/2}$,$^4F_{5/2}$ and $^4F_{3/2}$ levels . The transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ in Nd^{+3} ion has been considered as Hypersensitive transition (Fig.4.1.1).

4.2 Calculation of Oscillator Strength and Judd-Ofelt Parameters

Oscillator strength of only hypersensitive peak was calculated by the relation[9,10] **:-**

$$P_{exp} = 4.60 \times 10^{-9} \times \Delta\nu_{½} \times \varepsilon_{max} \quad \text{.....(3)}$$

Mostly the spectral studies of the solution have been done by utilizing the matrix element of carnall et al [9]. In the calculation of T_λ parameters .The statistical method known as partial multiple regression method[10] , has been used. The equations for the partial multiple regression method [9,10]have the form

$$Ye = a + b_1 X_1 + b_2 X_2 + ... + b_p, X_p \quad \text{.....(4)}$$

where, there are P independent variables and the regression coefficients b_1, b_2 ..... bp are referred to as partial regression coefficients .The observed oscillator strength of the transition of energy ($\bar{\nu}$) can be expressed in terms of T_2, T_4 & T_6 parameters (Judd-Ofelt) as follows :-

$$P_{obs} = T_2 \bar{\nu} [U^{(2)}]^2 + T_4 \bar{\nu} [U^{(4)}]^2 + T_6 \bar{\nu} [U^{(6)}]^2 \quad \text{.....(5)}$$

The values of $[U^{(2)}]^2$,$[U^{(4)}]^2$ and $[U^{(6)}]^2$ have been taken from Carnall et al.[9] to compute the values of T_2,T_4 & T_6 parameters.The ten bands in the present Nd(III)-doped systems have been assigned the energy levels as$^4P_{1/2}$, $^4G_{11/2}$,$^2G_{9/2}$,$^4G_{9/2}$,$^4G_{7/2}$,

$^4G_{5/2}$,$^4F_{9/2}$,$^4F_{7/2}$,$^4F_{5/2}$ and $^4F_{3/2}$ .From the observed oscillator strength of the ten bands, equations of the form as given in eq. (4), have been obtained .Here we have the following –

$Y = Pobs/V$, $a = 0$, $b_1 = T_2$, $b_2 = T_4$, $b_3 = T_6$

$X_1 = [U^{(2)}]^2$, $X_2 = [U^{(4)}]^2$, $X_3 = [U^{(6)}]^2$

Now three steps are involved to complete the values of T_2 , T_4 and T_6 :-

STEP I From the equations so obtained, the values of a_{11}, a_{22}, a_{21}, a_{31}, a_{32}, and a_{33} have been calculated by using the following relations.

$a_{11} = \Sigma x_1^2$, $a_{22} = \Sigma x_2^2$, $a_{33} = \Sigma x_3^2$,

$a_{21} = \Sigma x_2 x_1$, $a_{31} = \Sigma x_3 x_1$, $a_{32} = \Sigma x_3 x_2$,

where $\Sigma x_1^2 = \Sigma X_1^2 - \frac{(\sum X_1)^2}{N}$, $\Sigma x_2^2 - \frac{(\sum X_2)^2}{N}$

$\Sigma x_3^2 = \Sigma X_3^2 - \frac{(\sum X_3)^2}{N}$, $\Sigma x_2 x_1 = \Sigma X_2 X_1 - \frac{\sum X_2 . \sum X_1}{N}$

$\Sigma x_3 x_1 = \Sigma X_3 X_1 - \frac{\sum X_3 . \sum X_1}{N}$, $\Sigma x_3 x_1 = \Sigma X_3 X_2 - \frac{\sum X_3 . \sum X_2}{N}$,

Here N = Number of levels fitted.

STEP II From the values of a_{11}, a_{22}, a_{33}, a_{21}, , a_{31}, and a_{32} the values of C_{11}, C_{12}, C_{13}, C_{22}, C_{23} and C_{33}, have been obtained by the following instructions :-

Matrix for Calculating C_{ij} from a_{ij}

Line	**← Abbreviated Solution →**					
1	a_{11}	a_{21}	a_{31}	1.0	1.0	0
2	-	a_{22}	a_{32}	0	1.0	0
3	-	-	a_{33}	0	0	1.0
4	a_{11}	a_{21}	a_{31}	1.0 (d_{11})	0	0
5	1.0	b_{21}	b_{31}	e_{11}	0	0
6	-	$a_{22.1}$	$a_{32.1}$	$d_{11.1}$	$d_{12.1}$	0

7	-	1.0	$b_{32.1}$	$e_{11.1}$	$e_{12.1}$	0
8	-	-	$a_{33.12}$	$d_{11.12}$	$d_{12.12}$	$d_{13.12}$
9	-	-	1.0	$e_{11.12}$	$e_{12.12}$	$e_{13.12}$
10	-	-	-	C_{11}	C_{12}	C_{13}
11	-	-	-	-	C_{22}	C_{23}
12	-	-	-	-	-	C_{33}

Line **Instructions**

1, 2, 3 : Enter sums of squares and products

4 : Copy Line 1

5 : Divide each entry in line 4 by a_{11}

6 : $a_{22.1} = a_{22} - a_{21} \cdot b_{21}$

$a_{32.1} = a_{32} - a_{31} \cdot b_{21}$

$d_{11.1} = 0 - d_{11} \cdot b_{21}$

$d_{12.1} = 1 - 0x\ b_{21}$

7 : Divide each entry in line 6 by $a_{22.1}$

8 : $a_{33.12} = a_{33} - a_{31}b_{31} - a_{32.1}\ b_{32.1}$

$d_{11.12} = 0 - d_{11}b_{31} - d_{11.1}\ b_{32.1}$

$d_{12.12} = 0 - d_{12.1}\ b_{32.1}$

$d_{13.12} = 1.0$

9 : Divide each entry in line 8 by $a_{33.12}$

10,11,12 : $C_{11} = d_{11}\ e_{11} + d_{11.1}\ e_{11.1} + d_{11.12}\ e_{11.12}$

$C_{12} = d_{11.1}\ e_{12.1} + d_{11.12}\ e_{12.12}$

$C_{22} = d_{12.1}\ e_{12.1} + d_{12.12}\ e_{12.12}$

$C_{13} = d_{11.12}\ e_{13.12}$

$C_{23} = d_{12.12}\ e_{13.12}$

$C_{33} = d_{13.12}\ e_{13.12}$

STEP III From the values of C_{11}, C_{12}, C_{13}, C_{22}, C_{23} and C_{33}, the values of a, b_1, b_2 and b_3 have been computed by using the relations given below:-

$b_1 = C_{11}\,\Sigma x_1y + C_{12}\,\Sigma x_2y + C_{13}\,\Sigma x_3y$

$b_2 = C_{12}\,\Sigma x_1y + C_{22}\,\Sigma x_2y + C_{23}\,\Sigma x_3y$

$b_3 = C_{13}\,\Sigma x_1y + C_{23}\,\Sigma x_2y + C_{33}\,\Sigma x_3y$

$a = \overline{Y} - b_1\,\overline{X_1} - b_2\,\overline{X_2} - b_3\,\overline{X_3}$ where

$$\Sigma x_1y = \Sigma X_1Y - \frac{(\Sigma X_1.\Sigma Y)}{N}$$

$$\Sigma x_2y = \Sigma X_2Y - \frac{(\Sigma X_2.\Sigma Y)}{N}$$

$$\Sigma x_3y = \Sigma X_3Y - \frac{(\Sigma X_3.\Sigma Y)}{N}$$

$\overline{Y} = \frac{\Sigma Y}{N}$, $\overline{X_1} = \frac{\Sigma X_1}{N}$, $\overline{X_2} = \frac{\Sigma X_2}{N}$, $\overline{X_3} = \frac{\Sigma X_3}{N}$, N = No. of levels fitted. (N=9)

For Nd^{3+} Systems :-

C_{11}	=	0.4433	C_{12}	=	-0.01906
C_{13}	=	-5.2629	C_{22}	=	0.003024
C_{23}	=	0.1668	C_{33}	=	86.2946

5.00 Result & Discussion The transitions whose intensity is sensitive to ligands, pH of medium and coordination environment are known as hypersensitive transition [6,7]. The oscillator strengths of the observed peaks (P_{obs}) have been calculated from the recorded absorption spectra of trivalent Neodymium – Brucine Doped Systems in Ethanol medium at pH 2 to 6 with different Metal-Ligand concentration.Oscillator strength of hypersensitive bands tell us about coordination environment of metal ion[3,10,11]. Comparative absorption spectra of Ln (III) - doped system at different M:L Ratios at pH 2 to 6 clearly suggest the significant role of pH on complexation [1,2,10,12]. Value of P_{obs} ranges from 11.30 $\times 10^{-6}$ to 17.30 $\times 10^{-6}$ .Highest P_{obs} of hypersensitive band has been found for 1:1 M-L ratio at pH 6 . The value of r.m.s. deviation ranges from 2.48 $\times 10^{-6}$ to 3.64 $\times 10^{-6}$ .The small r.m.s. deviation between P_{obs} & P_{cal} values indicate applicability of Judd-Ofelt theory[10,11,12]

The general sequence of T_2, T_4 & T_6 for Nd(III)-doped system[1] is-

$T_4 > T_6 > T_2$

The value of T_2 varies from 0.001×10^{-9} to 0.33×10^{-9}. According to K. Bukietynska[1,2] values of T_2 parameter change significantly as a function of ligand concentration .The value of T_4 varies from 1.74 $\times 10^{-9}$ to 2.69 $\times 10^{-9}$ and the value of T_6 varies from 1.25 $\times$

10^{-9} to 1.83×10^{-9}.The variation in symmetry around Nd^{+3} ion is represented by the variation in T_4/T_6 values .The value of T_4/T_6 is varies from 1.2293 to 1.7232.

Nd (III)- BRU Doped systems may be characterized on the basis of T_4/T_6 parameters (Table 5.01) . T_4/T_6 parameters represent almost identical environment around Nd(III) ion (Fig.5.01).

6 CONCLUSION. With the help of intensity parameter and T_4/T_6 categorization we can predict that the more than one species can exist in Nd (III) -Brucine doped system with different concentration of ligands , a broad pH range of 2 to 6.

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8 REFERENCE

1. Bukietynska K., and A.Mondry 1987 Spectroscopy and Structure of Heavy Lanthanide Complexes with EDTA, Inorg. Chim. Acta, 130: 145-150
2. Bukietynska K. , and Mondry 1985 A. ,Spectroscopy and structure of neodymium complexes with EDTA, Inorganic Chimica Acta 110(1): 1-5,
3. Devlin Mark T, Stephens Eileen M. and. Richardson F.S 1988, Comparison of Electric –Dipole Intensity Parameters for a series of structurally related Neodymium, Holmium, and Erbium Complexes in aqueous solution Theory and Experiment , Inorg.Chem.Vol.27 No. 9: 1517-1524
4. Jatolia S.N. , Bhandari H.S., Bhojak N. , December 2014 Effect of solvent on sensitivity of hypersensitive transition for Pr (III) complexes with quinoline derivatives in doped systems , International advanced research journal in science ,Engineering and technology ,Vol.1, issue 4: 201-204
5. Judd B.R . 1962 ,Optical Absorption Intensities of Rare Earth Ions Phys. Rev.127:750
6. Judd B.R 1966, Hyper sensitive transition in Rare Earth Ions, Phys. Rev.,44 :839
7. Judd B.R 1979 Ionic transition hypersensitive to environment ,The Journal of Chemical Physics 70(11): 4830-4831
8. Ofelt G.S. 1962 Intensities of crystal spectra of Rare Earth Ions J.Chem.Phys. 37 : 511
9. Carnall W.T. Fields P.R.and Wybourne B.G. 1965 Spectral Intensities of Trivalent Lanthanide Ions. J. Chem. Phys. 42 :3797-3805
10. Verma R.S., Gupta Rama and .Joshi G.K October 2002 Calculation of Judd-Ofelt intensity parameters in some Er(III)- Doped systems using statistical method J.Indian Chem.Soc., Vol.79 : pp.802-806
11. Mishra Shubha , Wanker Sneha , Vishwakarma Preeti, Ghosh S.K. and Limaye S.N. 2015Variation in Electronic Spectral Parameters of Nd (III) and Er(III) with respect to ionic strength of the medium ,Chemical Science transactions 4(1) :95-100

12. Jain Sushma and Verma R.S. 2002 Electronic spectral characterization of Pr (III) System involving some analytically important reagents at pH 5 in ethanol medium ,Oriental Journal of Chemistry, Vol 18(3) :517-520

Figure : 4.1.1 Electronic Absorption Spectra of .1M $NdCl_3$ (In 50% Ethyl alcohol)

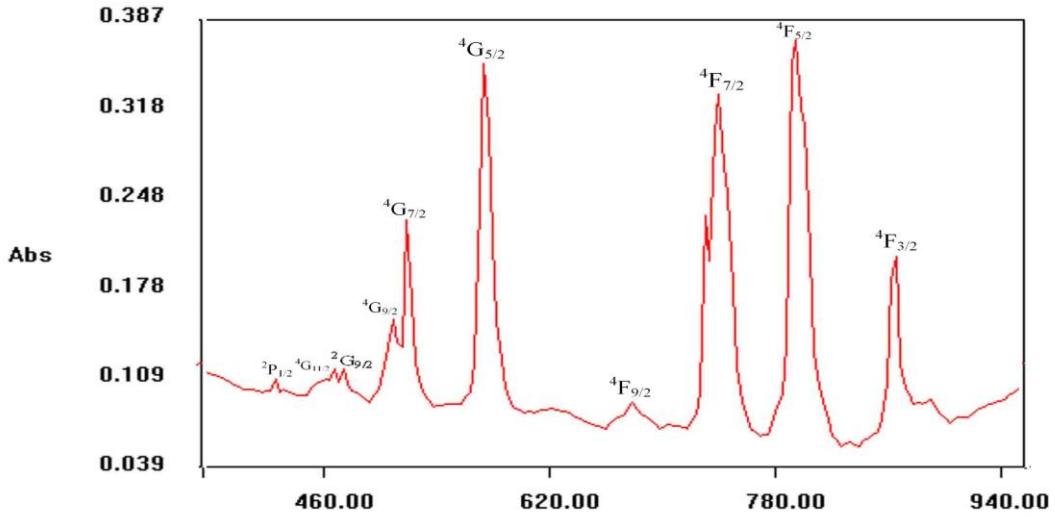

Figure : 4.1.2 A Comparative Absorption Spectra of .1M $NdCl_3$ + .1M Brucine(pH=2 to 6)

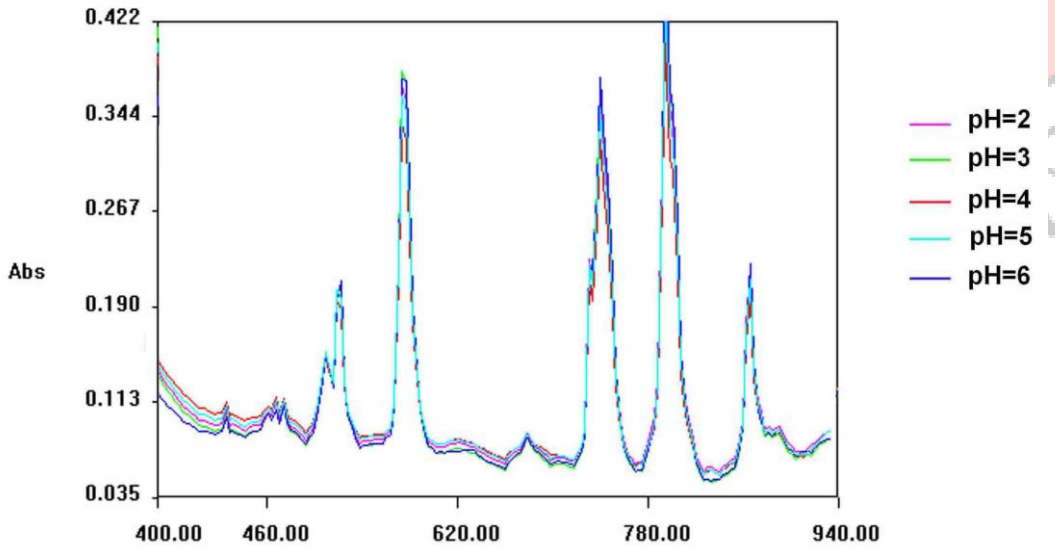

Figure : 4.1.3 A Comparative Absorption spectra of .1M $NdCl_3$ + .2M Brucine(pH=2 to 6)

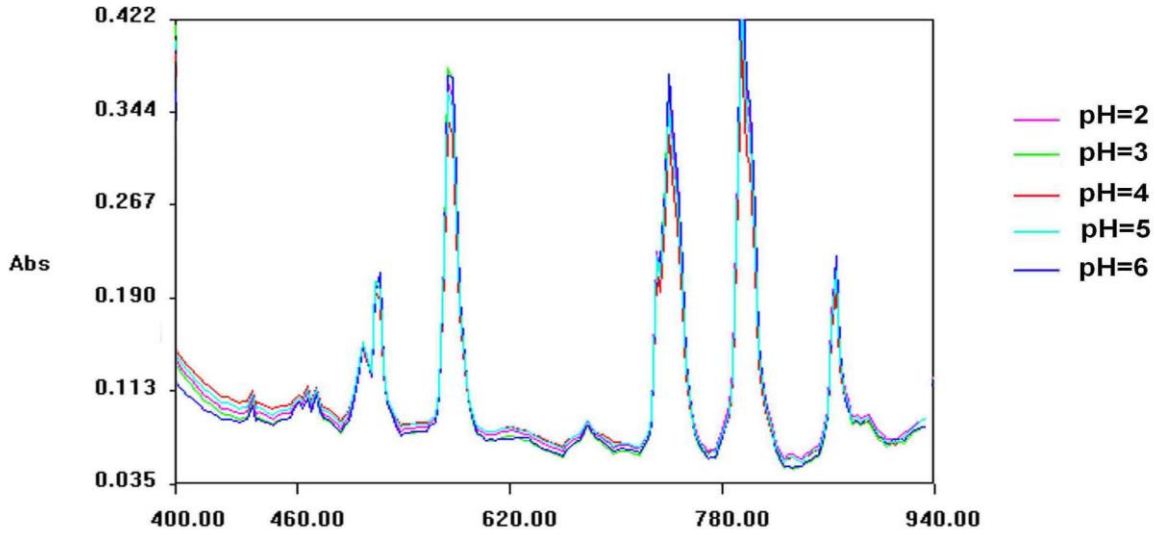

Figure : 4.1.4 A Comparative Absorption Spectra of .1M $NdCl_3$ + .3M Brucine(pH=2 to 6)

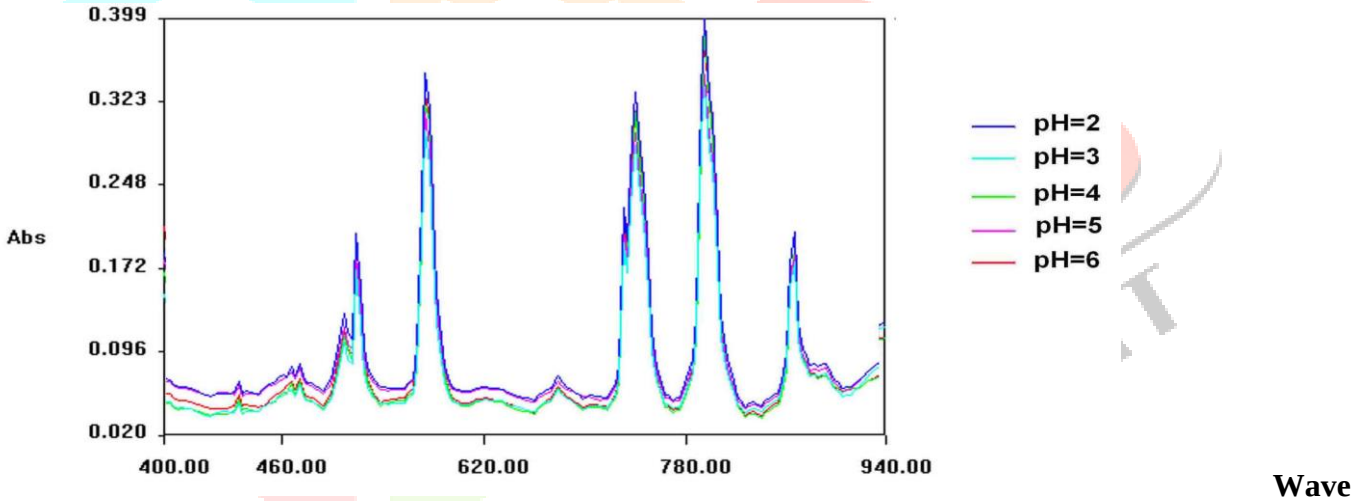

Table : 4.2.1 CALCULATED VALUES OF OSCILLATOR STRENGTH OF VARIOUS BANDS OF 0.1 M Nd (III) –0.1 M BRU DOPED SYSTEMS

.1M Nd (III) + .1M BRUCINE DOPED SYSTEM											
S No	Energy Levels	pH = 2		pH = 3		pH = 4		pH = 5		pH = 6	
		P_{obs} $\times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$
1.	$^4P_{1/2}$	2.40	2.09	2.33	2.26	2.33	2.08	2.51	1.99	2.31	1.92
2.	$^4G_{11/2}$	1.59	0.56	1.62	0.59	1.59	0.56	1.68	0.56	1.65	0.48
3.	$^4G_{9/2}$	4.90	4.67	4.29	4.96	4.20	4.64	3.85	4.60	4.34	4.10
4.	$^2G_{9/2}$	5.84	1.17	5.84	1.23	5.80	1.16	5.92	1.16	5.76	1.01
5.	$^4G_{7/2}$	2.14	9.33	2.25	9.99	2.23	9.34	2.18	9.18	2.29	8.50
6	$^4G_{5/2}$	15.60	19.00	16.80	20.60	16.50	20.0	16.20	19.80	17.30	19.80
7.	$^4F_{9/2}$	3.63	1.31	3.52	1.35	3.52	1.29	3.70	1.34	3.49	1.07
8.	$^4F_{7/2}$	7.29	11.10	7.18	11.40	7.25	11.0	7.30	11.50	7.12	8.87
9.	$^4F_{5/2}$	14.10	15.90	14.50	16.60	13.60	15.70	14.30	15.90	10.60	13.40
10.	$^4F_{3/2}$	4.99	7.68	5.33	8.24	5.06	7.63	4.34	7.43	6.22	6.91
	r.m.s. deviation (σ)	$\sigma = 3.42 \times 10^{-6}$		$\sigma = 3.64 \times 10^{-6}$		$\sigma = 3.39 \times 10^{-6}$		$\sigma = 3.50 \times 10^{-6}$		$\sigma = 2.94 \times 10^{-6}$	

Table : 4.2.2 CALCULATED VALUES OF OSCILLATOR STRENGTH OF VARIOUS BANDS OF 0.1M Nd (III) –0.2 M BRU DOPED SYSTEMS

.1M Nd (III) + .2M BRUCINE DOPED SYSTEM										
S No	Energy Levels	pH = 2		pH = 3		pH = 4		pH = 5		pH = 6	
		$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$	$P_{obs} \times 10^{-6}$	$P_{cal} \times 10^{-6}$
1.	$^4P_{1/2}$	2.18	1.77	2.18	1.89	2.22	1.82	2.29	1.71	2.36	1.62
2.	$^4G_{11/2}$	1.58	0.50	1.45	0.56	1.49	0.54	1.54	0.50	1.58	0.45
3.	$^4G_{9/2}$	4.20	4.09	4.77	4.50	4.34	4.29	4.99	4.04	4.60	3.70
4.	$^2G_{9/2}$	4.88	1.03	4.92	1.140	5.00	1.09	5.08	1.02	5.00	0.92
5.	$^4G_{7/2}$	2.01	8.10	2.08	8.80	2.09	8.42	2.09	7.94	2.02	7.34
6	$^4G_{5/2}$	13.60	16.70	13.80	17.60	13.40	16.90	13.10	16.20	12.20	14.80
7.	$^4F_{9/2}$	2.81	11.90	2.78	1.36	2.88	1.29	2.96	1.21	2.96	1.07
8.	$^4F_{7/2}$	6.88	10.30	6.88	11.80	6.65	11.20	6.41	10.60	5.95	9.15
9.	$^4F_{5/2}$	12.40	14.20	14.70	15.90	14.00	15.10	13.30	14.20	11.70	12.80
10.	$^4F_{3/2}$	4.04	6.60	3.07	7.16	3.14	6.85	3.05	6.45	3.57	6.01
	r.m.s. deviation (σ)	$\sigma = 2.95 \times 10^{-6}$		$\sigma = 3.46 \times 10^{-6}$		$\sigma = 3.28 \times 10^{-6}$		$\sigma = 3.09 \times 10^{-6}$		$\sigma = 2.74 \times 10^{-6}$	

Table : 4.2.3 CALCULATED VALUES OF OSCILLATOR STRENGTH OF VARIOUS BANDS OF 0.1 M Nd (III) –0.3 M BRU DOPED SYSTEMS

.1M Nd (III) + .3M BRUCINE DOPED SYSTEM										
S No	**Energy Levels**	**pH = 2**		**pH = 3**		**pH = 4**		**pH = 5**		**pH = 6**	
		$P_{obs} \times 10^{-6}$	**$P_{cal} \times 10^{-6}$**	**$P_{obs} \times 10^{-6}$**	**$P_{cal} \times 10^{-6}$**	**$P_{obs} \times 10^{-6}$**	**$P_{cal} \times 10^{-6}$**	**$P_{obs} \times 10^{-6}$**	**$P_{cal} \times 10^{-6}$**	**$P_{obs} \times 10^{-6}$**	**$P_{cal} \times 10^{-6}$**
1.	$^4P_{1/2}$	1.53	1.69	1.38	1.54	1.29	1.57	1.22	1.58	1.16	1.68
2.	$^4G_{11/2}$	1.08	0.47	1.11	0.428	0.91	0.44	0.85	0.44	0.96	0.47
3.	$^4G_{9/2}$	3.24	3.86	3.55	3.49	3.68	3.59	2.50	3.63	3.15	3.82
4.	$^2G_{9/2}$	4.28	0.96	3.92	0.874	3.52	0.90	3.44	0.91	4.32	0.95
5.	$^4G_{7/2}$	2.10	7.67	1.92	6.95	1.83	7.14	1.72	7.21	1.90	7.58
6	$^4G_{5/2}$	12.70	15.80	11.30	14.10	11.70	14.70	11.50	14.70	12.00	15.20
7	$^4F_{9/2}$	2.46	11.00	2.35	0.994	2.21	1.03	2.07	1.05	2.14	1.10
8.	$^4F_{7/2}$	6.10	9.47	5.40	8.50	5.69	8.85	5.75	8.99	5.77	9.40
9.	$^4F_{5/2}$	11.50	13.20	10.60	12.00	10.70	12.40	12.10	12.50	11.60	13.10
10.	$^4F_{3/2}$	3.68	6.28	3.30	5.71	3.37	5.84	3.43	5.90	3.39	6.23
	r.m.s. deviation (σ)	**$\sigma = 2.75 \times 10^{-6}$**		**$\sigma = 2.48 \times 10^{-6}$**		**$\sigma = 2.53 \times 10^{-6}$**		**$\sigma = 2.63 \times 10^{-6}$**		**$\sigma = 2.82 \times 10^{-6}$**	

Table : 4.2.4 COMPUTED VALUES OF JUDD-OFLET PARAMETERS OF Nd (III) –BRU DOPED SYSTEM

Nd (III) + BRU DOPED SYSTEM						
S No	**Judd-Ofelt Parameters**	**pH=2**	**pH=3**	**pH=4**	**pH=5**	**pH=6**
A	**.1M Nd(III) + .1M BRU DOPED SYSTEM**					
1	$T_2 \times 10^{-9}$	0.01	0.02	0.08	0.11	0.17
2	$T_4 \times 10^{-9}$	2.48	2.69	2.47	2.37	2.28
3	$T_6 \times 10^{-9}$	1.69	1.71	1.66	1.77	1.32
4	T_4/T_6	1.4692	1.5696	1.4842	1.3409	1.7232
B	**.1M Nd(III) + .2M BRU DOPED SYSTEM**					
1	$T_2 \times 10^{-9}$	0.04	0.02	0.02	0.04	0.11
2	$T_4 \times 10^{-9}$	2.10	2.25	2.16	2.03	1.92
3	$T_6 \times 10^{-9}$	1.58	1.83	1.73	1.63	1.40
4	T_4/T_6	1.3294	1.2293	1.2468	1.2443	1.3742
C	**.1M Nd(III) + .3M BRU DOPED SYSTEM**					
1	$T_2 \times 10^{-9}$	0.33	0.03	0.02	0.02	0.001
2	$T_4 \times 10^{-9}$	2.01	1.74	1.87	1.89	2.00
3	$T_6 \times 10^{-9}$	1.45	1.25	1.35	1.38	1.44
4	T_4/T_6	1.3903	1.3966	1.3823	1.3707	1.3906

Table : 5.01

Group	T_4/T_6	Nd-BRU Doped Systems (pH 2-6)
A	1.22 to 1.24	M-L ratio 1:2 ,(pH=3,4,5)
B	1.32 to 1.39	M-L ratio 1:1 (pH= 5) M-L ratio 1:2(pH=2,6) M-L ratio 1:3(pH=2,3,4,5,6)
C	1.46 to 1.48	M-L ratio 1:1 (pH=2,4)
D	1.56	M-L ratio 1:1(pH=3)
E	1.72	M-L ratio 1:1(pH=6)

Fig.5.01 VARIATION IN SYMMETRY AROUND Nd(III) ION IN Nd(III)-BRU DOPED SYSTEMS