EFFECT OF pH VARIATION ON INTENSITY PARAMETERS OF Er(III)-ATROPINE DOPED SYSTEMS HAVING DIFFERENT METAL – LIGAND RATIOS

*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: In this work we have made some modified doped systems of Er (III) ion with different concentration of Atropine ligand. and observed the effect of pH variation on electronic spectral parameters i.e. intensity parameters (oscillator strength & judd-ofelt parameters) of Er^{+3}-ATP doped systems. All these parameters give useful information regarding coordination sphere and bonding of Er^{+3}-ATP doped systems. The applicability of Judd-Ofelt theory of f-f transition has been established.

(**KEYWORD :-** Oscillator strength AND Judd-Ofelt parameters , ATP= Atropine)

2. **INTRODUCTION:** The spectral intensity of an absorption band is measured by in terms of its oscillator strength & Judd-Ofelt Parameters .The intensity parameters of the solution spectra of tri positive lanthanides have been interpreted in terms of Judd[1]-Ofelt[2] Theory. Oscillator strength is directly proportional to the area under absorption curve. T_λ parameters are generally called Judd-Ofelt parameters.The values of T_λ have been calculated from " partial and multiple regression" method[3].

In the present paper oscillator strength and judd-ofelt parameters for the modified Er (III) –Atropine 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 . Atropine is a tropane alkaloid . Er (III) –Atropine doped systems Er(III) ion is surrounded by solvent as well as ligand molecules.Calculation for oscillator strength & Judd-Ofelt parameters have been done for all Er (III) –Atropine doped systems.

3. EXPERIMENTAL: Stock solution of .1M $ErCl_3$ was prepared from 99.9% Erbium chloride, (Merk) in 50% ethanol solution. .1M, .2M, .3M solutions of AtropineSulphate were also made in 50% ethanol. Now 10 ml of each of these ligand solutions was added to 10 ml of .1M Er (III) solution. In this way we got Er (III) –Atropine doped systems of 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 Er(III)-Atropine doped systems.

4. OBERVATION AND CALCULATION - All electronic spectra were measured by Systronic-2202 UV-Visible double beam spectrophotometer in the range of 380-850 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.

For Er^{+3} doped systems, we have observed nine peaks in the region of 400-850 nm. These peaks are due to $^2G_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$ and $^4F_{11/2}$ The transition $^4I_{15/2}\rightarrow{}^2H_{11/2}$ in Er^{+3} ion has been considered as "Hypersensitive transition"[2], which is highly affected by different concentrations of ligand and pH of solution.

Oscillator strength of only hypersensitive peak was calculated by the relation **:-**

$$P_{obs} = 4.6 \times 10^{-9} \times \Delta\nu_{½} \times \varepsilon_{max} \quad \text{.....(3)}$$

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The calculations of Judd-Ofelt parameters (T_2, T_4 & T_6) and mostly the spectral studies of the solution have been done by utilizing the matrix element of carnall et al[4] by computerizing program.

TABLE : 1.00 COMPUTED VALUES OF OSCILLATOR STRENGTH AND ENERGIES OF VARIOUS BANDS OF Er(III) FREE ION

S.N.	Energy Levels	$P_{obs.} \times 10^6$	$P_{cal.} \times 10^6$	$E_{obs.}$	$E_{cal.}$
1		1.55	1.24	24622.80	24736.95
2	$^2G_{9/2}$	0.42	0.60	22560.14	22499.34
3	$^4F_{3/2}$	0.60	1.05	22175.51	22232.11
4	$^4F_{5/2}$	2.91	3.14	20513.13	20526.07
5	$^4F_{7/2}$	3.87	4.09	19130.42	19279.44
6	$^2H_{11/2}$	0.37	0.87	18451.26	18174.52
7	$^4S_{3/2}$	2.30	2.50	15319.23	15357.56
8	$^4F_{9/2}$	0.16	0.33	12451.98	12393.09
9	$^4I_{9/2}$	0.07	0.92	24622.80	24736.95
	rms deviation(σ)		**$=0.291 \times 10^{-6}$**		**=124.41**

TABLE : 2.00 COMPUTED VALUES OF JUDD-OFELT PARAMETERS OF Er (III) FREE ION

Judd -Ofelt Parameters	$T_2 \times 10^{-10}$	$T_4 \times 10^{-10}$	$T_6 \times 10^{-10}$	T_4/T_6
	1.8956	1.3155	2.13307	0.6167

TABLE : 3.00 COMPUTED VALUES OF OSCILLATOR STRENGTH OF VARIOUS BANDS OF Er (III)-ATP DOPED SYSTEMS

.1M Er(III) + .1M ATROPINE 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.	$^2G_{9/2}$	0.32	1.21	1.04	0.39	0.68	0.81	0.03	1.26	0.03	0.77
2.	$^4F_{3/2}$	0.28	0.62	0.12	0.23	0.09	0.41	0.12	0.645	0.28	0.39
3.	$^4F_{5/2}$	1.10	1.04	1.87	0.38	0.93	0.68	0.42	1.07	0.50	0.65
4.	$^4F_{7/2}$	1.34	2.98	0.07	0.67	0.40	2.05	0.96	3.18	0.96	1.92
5.	$^2H_{11/2}$	4.43	4.27	2.74	2.01	3.58	3.46	4.39	4.79	3.78	3.91
6.	$^4S_{3/2}$	2.26	0.85	0.57	0.31	0.35	0.56	0.50	0.88	0.10	0.54
7.	$^4F_{9/2}$	3.07	2.24	0.65	0.33	2.37	1.67	2.89	2.66	1.60	1.50
8.	$^4I_{9/2}$	0.02	0.25	0.37	0.24	0.25	0.21	0.11	0.34	0.16	0.17
9.	$^4I_{11/2}$	2.12	0.91	1.99	0.37	2.15	0.61	2.42	0.94	1.40	0.66
	rms deviation (σ)	**$\sigma = 0.931 \times 10^{-6}$**		**$\sigma = 0.918 \times 10^{-6}$**		**$\sigma = 0.801 \times 10^{-6}$**		**$\sigma = 1.07 \times 10^{-6}$**		**$\sigma = 0.512 \times 10^{-6}$**	

TABLE : 4.00 COMPUTED VALUES OF OSCILLATOR STRENGTH OF VARIOUS BANDS OF Er (III)-ATP DOPED SYSTEMS

.1M Er(III) + .2M ATROPINE 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.	$^2G_{9/2}$	1.03	0.59	1.03	0.64	0.95	0.86	1.11	0.86	1.19	0.60

2.	$^4F_{3/2}$	0.06	0.30	0.12	0.32	0.19	0.45	0.19	0.45	1.90	0.31
3.	$^4F_{5/2}$	1.54	0.49	1.69	0.54	1.69	0.75	1.85	0.74	8.16	0.52
4.	$^4F_{7/2}$	1.82	1.57	1.93	1.66	2.25	2.08	2.50	2.06	5.90	1.45
5.	$^2H_{11/2}$	3.19	2.35	3.31	2.45	4.05	3.31	4.17	3.08	7.86	4.05
6.	$^4S_{3/2}$	0.62	0.41	0.62	0.44	0.31	0.62	3.14	0.61	3.35	0.43
7.	$^4F_{9/2}$	2.15	1.46	2.15	1.45	1.99	1.42	2.11	1.38	3.44	0.96
8.	$^4I_{9/2}$	1.52	0.23	1.52	0.20	1.52	0.12	2.17	0.11	4.34	0.07
9.	$^4I_{11/2}$	2.17	0.43	2.24	0.47	2.58	0.67	3.26	0.66	3.79	0.50
	rms deviation (σ)	**$\sigma = 0.90 \times 10^{-6}$**		**$\sigma = 0.924 \times 10^{-6}$**		**$\sigma = 0.915 \times 10^{-6}$**		**$\sigma = 1.26 \times 10^{-6}$**		**$\sigma = 3.39 \times 10^{-6}$**	

TABLE :5.00 COMPUTED VALUES OF OSCILLATOR STRENGTH OF VARIOUS BANDS OF Er (III)- .3M ATP DOPED SYSTEMS

.1M Er(III) + .3M ATROPINE 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.	$^2G_{9/2}$	0.99	1.06	1.11	1.24	1.27	1.68	1.11	1.15	5.16	2.37
2.	$^4F_{3/2}$	0.03	0.55	0.09	0.65	0.09	0.94	0.19	0.60	0.19	1.30
3.	$^4F_{5/2}$	1.62	0.91	1.77	1.08	2.08	1.57	1.77	1.00	8.62	2.14
4.	$^4F_{7/2}$	2.95	2.56	3.00	2.94	3.22	3.39	3.00	2.75	6.22	5.16
5.	$^2H_{11/2}$	4.39	4.11	4.46	4.38	4.40	4.19	4.49	4.17	8.27	6.66

6.	$^4S_{3/2}$	0.73	0.75	0.36	0.89	0.34	1.31	1.12	0.83	2.43	1.78
7.	$^4F_{9/2}$	1.86	1.80	1.90	1.94	0.49	0.42	2.06	1.86	3.36	1.92
8.	$^4I_{9/2}$	0.83	0.17	0.55	0.50	0.55	0.47	0.69	0.15	0.61	0.26
9.	$^4I_{11/2}$	1.31	0.817	1.34	0.95	2.79	1.39	1.40	0.88	2.42	1.90
	rms deviation (σ)	**$\sigma = 0.433 \times 10^{-6}$**		**$\sigma = 0.395 \times 10^{6}$**		**$\sigma = 0.759 \times 10^{-6}$**		**$\sigma = 0.423 \times 10^{-6}$**		**$\sigma = 2.52 \times 10^{-6}$**	

TABLE : 6.00 COMPUTED VALUES OF JUDD-OFELT INTENSITY PARAMETERS FOR .1M Er (III) + ATROPINE DOPED SYSTEM

S No	Judd-Ofelt Parameters	pH=2	pH=3	pH=4	pH=5	pH=6
A	**.1M Er(III) + .1M ATROPINE DOPED SYSTEM**					
1	$T_2 \times 10^{-10}$	2.23	1.95	1.80	2.36	2.22
2	$T_4 \times 10^{-10}$	0.93	-1.10	0.84	1.33	0.68
3	$T_6 \times 10^{-10}$	2.08	0.77	1.39	2.15	1.33
4	T_4/T_6	0.4489	-1.4062	0.60	0.6222	0.5125
B	**.1M Er(III) + .2M ATROPINE DOPED SYSTEM**					
1	$T_2 \times 10^{-10}$	1.01	1.12	1.91	1.78	2.59
2	$T_4 \times 10^{-10}$	0.92	0.82	0.43	0.37	0.25

3	$T_6 \times 10^{-10}$	0.99	1.09	1.51	1.50	1.06
4	T_4/T_6	0.9279	0.7566	0.2852	0.2506	0.2439
C	**.1M Er(III) + .3M ATROPINE DOPED SYSTEM**					
1	$T_2 \times 10^{-10}$	2.33	2.55	3.85	2.39	4.99
2	$T_4 \times 10^{-10}$	0.61	0.49	-2.20	0.53	-1.4
3	$T_6 \times 10^{-10}$	1.84	2.17	3.13	2.01	4.31
4	T_4/T_6	0.3364	0.2263	-0.7146	0.2662	-.3248

5. RESULT & DISCUSSION 4*f*-orbitals of Er^{+3} are deeply embedded however 4*f*- orbitals partially involved direct ligand interaction[5], We have been found that electronic spectral parameters of Er^{+3} ions also change with Change in pH & M:L ratio. Oscillator strength of observed bands of different Er^{+3}- Atropine doped systems at pH 2 to 6 have been given in table no. 4 to 6 . The values of P_{obs} have been compared with P_{cal} (using Judd-Ofelt equation[5-7]) at different pH 2 to 6 .The r.m.s. deviation varies 0.512×10^{-6} to 1.07×10^{-6}(For 0.1M Er(III) + 0.1M Atropine Doped system), 0.915×10^{-6} to 3.39×10^{-6} (For 0.1M (Er(III) + 0.2M Atropine Doped system) and $0.395 \times 10^{-6}$to 2.52×10^{-6} (For 0.1M Er(III) + 0.3M Atropine Doped system). The small deviation[6] for the P_{cal}. and P_{obs} values suggest the validity of Judd-Ofelt equation for f-f transition for the systems under study. Properties of Er^{+3}– Atropine doped systems also vary with concentration of Ligands(Table no.4,5,6,&7). The values of T_λ parameters for all Er^{+3}- Atropine doped systems , pH 2 to 6 shows a general sequence[7]

$$T_2 > T_4 > T_6$$

The Judd-Ofelt parameters i.e. T_2,T_4 , T_6 & T_6/T_4 for Er^{+3} free ion and Er^{+3}- Atropine Doped Systems have been reported in table no. 3 & 7. The value of T_λ parameters change significantly on varying the concentration of ligands and pH of medium[5] .It is well known that T_2 parameters shows high sensitivity towards coordination changes while T_2 & T_6 have been found to exhibit more sensitivity towards symmetry changes[5,6,7] . Thus the ratio of T_4/T_6 (Judd-Ofelt parameters) may be used in determining the change in symmetry around lanthanide ion. T_4/T_6 values of 0.1 M Er^{+3}- 0.1 M Atropine Doped system have been found near about same but but this system gives negative values of T_4/T_6 at pH 3, Similarly 0.1 M Er^{+3}- 0.3 M Atropine Doped system gives negative values of T_4/T_6 at pH 4 & 6 .Since the negative values of judd-Ofelt parameters are insignificant hence only positive values of T_4/T_6 have been considered for change in symmetry around Er^{+3}ion. T_4/T_6 values for Er^{+3}– 0.2M Atropine doped system ranges 0.2439 to 0.9279 . In this M:L ratio we have been found noticeable effect of pH on Judd-Ofelt parameters . On the basis of T_4/T_6 parameters we may be classified arbitrarily in to the following groups –

Group	T_4/T_6 values	M:L Ratio & pH
A	0.2439 to 0.2852	1:2 at pH 4,5,6 & 1:3 at pH2,3,5

B	0.4489 to 0.6222	1:1 at pH 2,4,5,6
C	0.7566	1:2 at pH 3
D	0.9279	1:2 at pH 2

Each groups represents almost identical symmetry around Er^{+3} ion in solution at different pH . In this way we can say that effect of pH variation is clearly observed .The value of T_2 varies from 1.01×10^{-10} to 4.99×10^{-10}. According to K.Bukietynska[5] values of T_2 parameter change significantly as a function of ligand concentration .The value of T_4 varies from 0.049×10^{-10} to 1.33×10^{-10} and the value of T_6 varies from 0.77×10^{-10} to 4.31×10^{-10}.The variation in symmetry around Er^{+3} ion is represented by the variation in T_4/T_6 values .The value of T_4/T_6 is varies from 0.2263 to 0.9279 . Since negative value of Judd-Ofelt intensity parameters are insignificant, hence categorization of Er^{+3} doped system with respect to T_4/T_6 is done by using positive values only.

6. CONCLUSION The results reported in this study indicated that the small rms deviation (σ)for the $P_{cal.}$ and P_{obs} values suggest the validity of Judd-Ofelt theory for f-f transition in Er^{+3}- Atropine Doped systems at pH 2 to 6,different M:L ratio. Effect of pH and M:L concentration on the change in symmetry around Erbium ion in Er^{+3}-Atropine Doped systems have been measured on the basis of ratio of T_4/T_6 (Judd-Ofelt parameters).

7. ACKNOWLEDGEMENT Author is thankful to UGC, Bhopal for Financial assistance (Minor Research Project).

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