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Environmental sensitivity of pseudo quadrupolar transition ($^3H_4 \rightarrow {}^3P_2$) for pr (III) complexes with quinoline derivatives in doped system

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Abstract
The intensities of $4f$-$4f$ transitions of lanthanide ion are little affected by environment [1-3]. Which is measured by Oscillator strength. The bands having oscillator strength ~10^{-5} and found much sensitive to the ligands & solvents are called hypersensitive transitions. The Judd-Oflet parameters and thermodynamic parameters [4, 5] were carried out for some *f-f* transitions specially on pseudo quadrupolar or Hypersensitive transitions for Pr(III) complexes with (2-Hydroxy quinoline, 8-Hydroxyquinoline, and 8-Aminoquinoline) in alcoholic (Et-OH) as well as micellar medium.

Keywords: pr (III), quinoline derivatives, oscillator strength, work function, pseudo quadrupolar

Introduction
Study about Hypersensitive transitions has been carried out by Karraker [6-7] particularly for Nd (III), Ho (III) and Er (III) complexes of β-diketone having 6, 7 and 8 coordination number. The Hypersensitive or pseudo quadrupolar transitions obey the selection rule I ΔJ I ≤ 2. The term on Hypersensitive refer to the transitions which show a relatively large variability in the magnitude of oscillator strength caused by the eigen perturbation [8-11]. In our case hypersensitive transitions for Pr (III) $^3H_4 \rightarrow {}^3P_2$ the Hyper sensitive transitions show a significant Red shift. The higher values of P and T_λ parameters of salt solutions in comparison to Pr (III) aqueous solutions show an involvement of 4f-orbital of Pr (III) ion. In the past year change in magnitude of oscillator strength of hypersensitive transition was successfully used to determine the stability constant as a function of ligand contraction.

Material and Method
Praseodymium chloride of 99.9% was purchased from Ms. Indian Earth limited and ligand were synthesized in our laboratory. The solvents used in doped system are Ethyl Alcohol (AR 99.9%, Jiangsu-Hliaxi International Trade Co. Ltd., Made in China) and Triton-X-100(100 CMC solution, Loba Chemia Pvt.Ltd., Mumbai, India).The saturated solution of ligand and metals Pr(III) ion 0.05 M were prepared in different solvents (Triton X-100 of 100 CMC (1.8 x 10^{-2} M, Sodium Dodecyl sulphate, (SDS) of 75 CMC (0.05 M), and Hexadecyl Trimethyl Ammonium Bromide, (HTAB) of 100 CMC (9.2 x 10^{-2}M) is used for preparing saturated solution of ligand and metal. Absorption spectra of each solution at room temperature in 1:3 ratio (Metal: Ligand) were recorded on UV Visible Double Beam Spectrophotometer (UV-5704-SS) upgraded with resolution and expansion of scale in the region 190nm to 1100nm at green chemistry research center (GCRC).

Methods
Oscillator strength was calculated as a function of hyper sensitive transition. Judd-Oflet theory [4-5] predicts that the intensity of f-f transitions arises principally from forced electric dipole mechanism. Thus, the electric dipole oscillator strength (P) is expressed as the product of T_λ (λ=2, 4, 6) parameters and appropriate transition matrix element $U^{(\lambda)}$ at frequency of transition J-J' the intensity of an absorption band is measured by Oscillator strength, which is directly proportional to area under the absorption curve.

$$P = 4.315 \text{ X } 10^{-9} \int \varepsilon \, d\nu \quad (1)$$

Here, ε_{max} = Molar Absorptivity or molar extinction Coefficient
The equation may be expressed in terms half band width

$$P_{obs} \approx 4.6 \text{ X } 10^{-9} \text{ X } \varepsilon_{max} \, \Delta\nu^{1/2} \quad (2)$$

$$P_{cal} = T_2 \nu [U^{(2)}]^2 + T_4 \nu [U^{(4)}]^2 + T_6 \nu [U^{(6)}]^2 \quad (3)$$

Where $[U^{(2)}]^2$, $[U^{(4)}]^2$, $[U^{(6)}]^2$ are matrix elements [12-13]
For hypersensitive transitions, oscillator strength (P) is found directly proportional to νT_6. This linear correlation has been proposed by R. D. Peacock [14].

$$K^{/} = P_{obs} / \nu_{obs} x T_6 \quad (4)$$

Thermodynamic parameters may also support covalency in metal-ligand interaction in addition to spectral parameters for hypersensitive transitions [15-19].

$$\text{Thermodynamic Efficiency Of transition (TET)} = \frac{\text{Work Function for transition}}{\text{Energy absorbed for transition}} \quad (5)$$

By using thermodynamic relation-

$$A = E - TS \text{ and } S = K \ln P_{obs}$$

Following relation may be obtained-

$$A = E - KT \ln P_{obs}$$

Where,
A = Work function (cm^{-1})
E = Energy absorbed for hypersensitive transition (cm^{-1})
K = Boltzmann Constant = 0.6945 cm^{-1}
T = Absolute Temperature
P_{obs} = Oscillator strength of transition
S= Absolute energy

Table 1: Observed and calculated values of thermodynamic parameters of Hypersensitive ($^3H_4 \rightarrow {}^3P_2$) Transition for Pr (III) doped system in ETOH medium

$^3H_4 \rightarrow {}^3P_2$	Energy (CM^{-1})		Oscillatorstrength		Workfunction(CM^{-1})		TET		Peacock const.
COMPLEXES	E_{Obs}	E_{cal}	$P_{obs}x10^6$	$P_{CAL}x10^6$	A_{Obs}	A_{Cal}	TET_{Obs}	TET_{Cal}	K`
Pr(III)-2HQ	22522.52	22523.07	14.627	27.386	22438.58	22443.85	0.996273	0.996483	0.1248
Pr(III)-8HQ	23337.22	23334.724	29.371	193.952	23258.53	23270.27	0.996628	0.997238	0.0553
Pr(III)-8AQ	22246.94	22249.191	5.306	10.191	22155.35	22162.50	0.995883	0.996104	0.1560

Table 2: Observed and calculated values of thermodynamic parameters of Hypersensitive Transition for Pr (III) doped system in TX-100 medium

$^3H_4 \rightarrow {}^3P_2$	Energy(CM^{-1})		Oscillatorstrength		Workfunction(CM^{-1})		TET		Peacock const.
COMPLEXES	E_{Obs}	E_{cal}	$P_{obs}x10^6$	$P_{CAL}x10^6$	A_{Obs}	A_{Cal}	TET_{Obs}	TET_{Cal}	K`
Pr(III)-2HQ	22446.6	22447.187	12.019	12.019	22363.05	22361.76	0.996278	0.996194	0.1746
Pr(III)-8HQ	23337.22	23334.891	51.401	50.864	23262.75	23260.34	0.996809	0.996805	0.1376
Pr(III)-8AQ	23337.22	23374.838	43.742	43.662	23261.54	23299.14	0.996757	0.996762	0.1364

Table 3: Observed and calculated values of thermodynamic parameters of Hypersensitive ($^3H_4 \rightarrow 3P_2$) Transition for Pr (III) doped system in HTAB medium

$^3H_4 \rightarrow {}^3P_2$	Energy(CM^{-1})		Oscillatorstrength		Workfunction(CM^{-1})		TET		Peacock const.
COMPLEXES	E_{Obs}	E_{cal}	$P_{obs}x10^6$	$P_{CAL}x10^6$	A_{Obs}	A_{Cal}	TET_{Obs}	TET_{Cal}	K`
Pr(III)-2HQ	22522.5	22523.012	0.207	17.696	22441.17	22440.50	0.996389	0.996337	0.1593
Pr(III)-8HQ	23577.12	23553.943	66.844	60.684	23504.63	23480.73	0.996926	0.996892	0.1500
Pr(III)-8AQ	22522.2	22523.231	14.042	12.107	22437.95	22437.86	0.996259	0.99621	0.1580

Table 4: Observed and calculated values of thermodynamic parameters of Hypersensitive ($^3H_4 \rightarrow {}^3P_2$) Transition for Pr (III) doped system in SDS medium

$^3H_4 \rightarrow {}^3P_2$	Energy(CM^{-1})		Oscillatorstrength		Workfunction(CM^{-1})		TET		Peacock const.
COMPLEXES	E_{Obs}	E_{cal}	$P_{obs}x10^6$	$P_{CAL}x10^6$	A_{Obs}	A_{Cal}	TET_{Obs}	TET_{Cal}	K`
Pr(III)-2HQ	22471.9	22472.4	9.534	7.515	22384.73	22383.43	0.996121	0.996041	0.1728
Pr(III)-8HQ	23310.02	23307.836	65.296	59.064	23237.36	23234.42	0.996883	0.99685	0.1505
Pr(III)-8AQ	22197.5	22199.021	11.660	6.911	22111.85	22109.42	0.996141	0.995964	0.2298

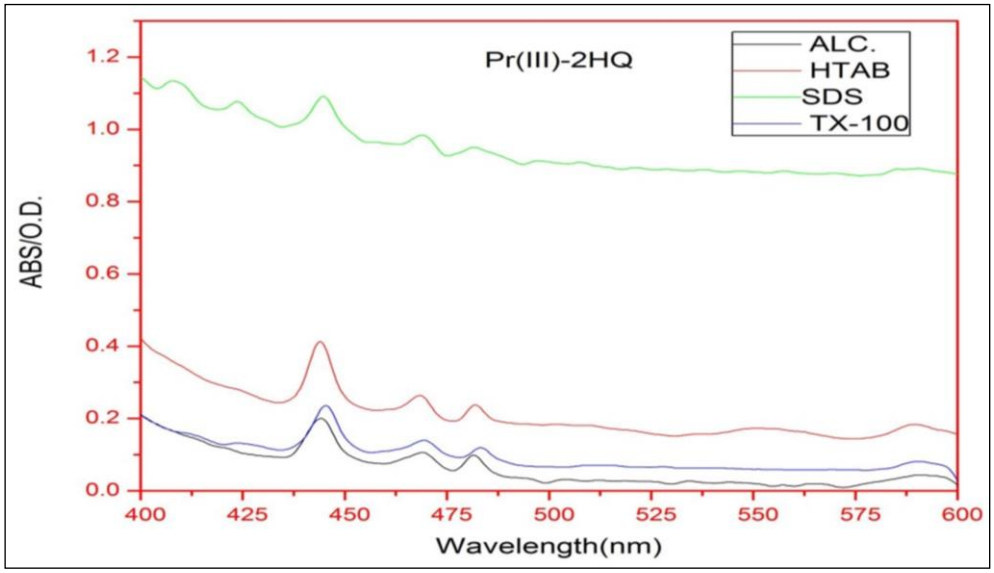

Fig 1: Variation of optical density with wavelength for Pr (III)-2HQ complex in different solvent

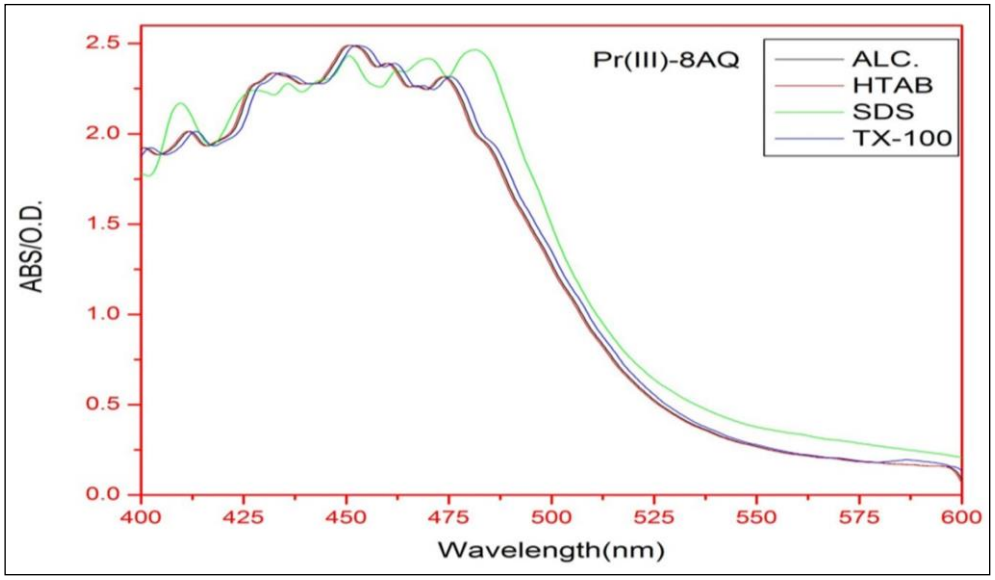

Fig 2: Variation of optical density with wavelength for Pr (III)-8AQ complex in different solvent

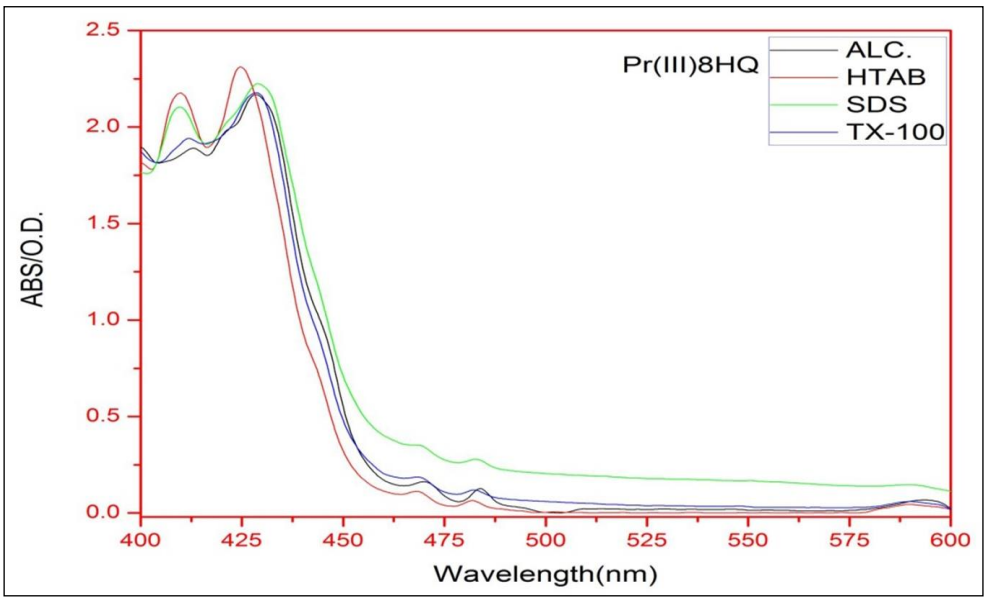

Fig 3: Variation of optical density with wavelength for Pr (III)-8HQ complex in different solvent

Results and Discussion

The computed values of the thermodynamic parameters (for hypersensitive transition) from the spectroscopic data have been tabulated in (Table-1 –IV). This clearly shows a significant change in the oscillator strength of *f-f* transition particularly for $^3H_4 \rightarrow {}^3P_2$ transition of Pr (III) ion. Comparative absorption spectra of Pr (III)-complexes in alcoholic and micellar medium [20-23] (Fig.1 to 3) clearly shows a significant enhancement in the oscillator strength of *f-f* transition. From data it is evident that Pr (III)-8HQ complex show maximum variation [24-28] in all parameters in all solvent rather than Pr (III)-2HQ and Pr (III)-8AQ

- Thermodynamic parameter for Pr (III)-8HQ vary in the following manner in different medium

Observed oscillator strength (P_{obs}) - HTAB >SDS >TX-100>EtOH
Work Function for transition (A_{obs}) - HTAB > TX-100> SDS > EtOH
Thermo dynamic Efficiency of Transition - HTAB =SDS> TX-100> EtOH

Conclusion

The significance of thermodynamic parameters is that there are more covalent character or metal-ligand interaction between Pr (III)-8HQ complex in HTAB micellar medium. Pseudo quadrupolar transitions or hypersensitive transition) for Pr (III) ion is more sensitive towards 8-Hydroxy quinoline. The microscopic behavior with respect to TET for Pr (III) doped systems is same for different ligands with respect to different solvent. Peacock constant is also nearby same for all ligands in HTAB micellar medium which prove Judd-Oflet theory.

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