



Effect of Ca^{+2} , Mg^{+2} , and Sr^{+2} Codoped Ions on Electrostatic and Magnetic Interactions between the 4f-Electrons for Pr (III)-2AB Doped System

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Abstract Energy level of Pr (III) lanthanide ion with hetero cyclic aromatic N, S, O containing ligand i.e. Pr(III)-2AB system have been determined by absorption spectra in alcoholic: aqua (1:1) medium at 25°. By absorption spectra using Gaussian curve, half band width and expressing energy as Taylor series expansion to express the energy of j^{th} electronic energy level. The interactions have been expressed in terms of Slater-Condon (F_K), Lande Racah (E^K) and (ζ_{4f}) Parameters. Four assignments were made to justify these interaction Parameters. In this research paper we want to explore theoretically analysis of absorption spectra of (III) ion in alcoholic: aqua (1:1) medium. The values of parameters have been found as $F_2=307.068$ $F_4=39.1872$, $F_6=4.2933$, $E_1=4508.315$, $E_2=23.5856$, $E_3=455.8121$ & $\zeta_{4f}=710.7587$ for Pr (III)-2AB system.

Keywords Energy level, Interaction Parameters, absorption spectra and aromatic ligand

Introduction

After publication of Judd oflet theory (1,2), the value of various parameters like intensity, interaction and bonding parameters were computed with the help of various UV-Visible spectra of different lanthanide metal ions (3,4,5). 4f \leftrightarrow 4f transitions occur during absorption of UV-Visible and IR radiation for lanthanide ions. When there is electrostatic and magnetic interaction between the 4f-electrons The Energy level transition occurs due to magnetic and electrostatic interaction between 4f-electrons of lanthanides which can be calculated in terms of Slater-Condon (F_K), Lande (ζ_{4f}) and Racah (E^K) Parameters. Racah introduced a Taylor series expansion to solve energy levels (6,7,8). 4f-4f transitions of rare-earth lanthanide metal complexes in UV-Visible region are examined by various researchers (9-20). The inner structure of the lanthanide (III) complex can be revealed by examining the 4f-4f transition spectra recorded in various organic solvents, including S, O, and N donors were examined for Pr III systems (21-23). In the present study, diffuse spectra of Praseodymium complexes are studied. The energy levels of these elements can be expressed in terms of four parameters (F_2, F_4, F_6) and Lande's parameters.

Material and Methods

Pr (III) carbonate hydrate (alfa) and ligand 2-Amino Benzothiazole(2AB) were purchased from M/s Sita Trading Company. The solvents used in doped system are Ethyl Alcohol (AR 99.9%, Jiangsu-Hliaxi International Trade Co. Ltd., Made in China.



In the present study Pr (III) ions have been doped with the saturated solution of ligands in alcoholic: aqua (1:1) medium. The saturated solutions have been prepared by dissolving different ligands in alcoholic: aqua (1:1) medium. The saturated solution of ligand and metal Pr (III) ion 0.05M were prepared in solvents. The solution spectra of each system at room temperature in 1:3 ratio (Metal: Ligand) has been recorded by using standard UV-VIS spectrophotometer 3092.

Interactions can be expressed in terms of Slater-Condon (F_k), Lande (ζ_{4f}) and Racah (E^k) Parameters.

- (a) Slater- Condon- Lande Equation: The Slater- Condon F_2 , F_4 , & F_6 and Lande parameter or Spin-Orbit Coupling Constant (ζ_{4f}) may be evaluated by expressing energy as Taylor series expansion) may be used to express the energy of j^{th} electronic energy level(6,7,8) . In the first order approximation the energy E_j of a J-level is given by the following equation-

$$E_j(F_k, \zeta_{4f}) = E_{oj}(F_k^o, \zeta_{4f}^o) + \sum (\partial E_j / \partial F_k) \Delta F_k + (\partial E_j / \partial \zeta_{4f}) \Delta \zeta_{4f}$$

$$k = 2, 4, 6 \text{ ----- (1)}$$

$$E_{\text{obs}} = E_{oj} + (\partial E_j / \partial F_2) \Delta F_2 + (\partial E_j / \partial F_4) \Delta F_4 + (\partial E_j / \partial F_6) \Delta F_6 + (\partial E_j / \partial \zeta_{4f}) \Delta \zeta_{4f} \text{ ---}$$

$$\text{----- (2)}$$

$$E_{\text{obs}} - E_{oj} = (\partial E_j / \partial F_2) \Delta F_2 + (\partial E_j / \partial F_4) \Delta F_4 + (\partial E_j / \partial F_6) \Delta F_6 + (\partial E_j / \partial \zeta_{4f}) \Delta \zeta_{4f}$$

$$\text{----- (3)}$$

$$[(E_{\text{obs}} - E_{oj}) \div (\partial E_j / \partial F_2)] = \Delta F_2 + [(\partial E_j / \partial F_4) \div (\partial E_j / \partial F_2)] \Delta F_4 + [(\partial E_j / \partial F_6) \div (\partial E_j / \partial F_2)] \Delta F_6 + [(\partial E_j / \partial \zeta_{4f}) \div (\partial E_j / \partial F_2)] \Delta \zeta_{4f} \text{----- (4)}$$

Where, E_j = Energy of j^{th} level

E_{oj} = Zero-order Energy of j^{th} level

ΔF_k = Small changes in the Slater-Condon parameters

$\Delta \zeta_{4f}$ = Small changes in the Lande parameters

$(\partial E_j / \partial F_k)$ = Partial derivatives with respect to F_k

$(\partial E_j / \partial \zeta_{4f})$ = Partial derivatives with respect to ζ_{4f}

The values of ΔF_k and $\Delta \zeta_{4f}$ may be evaluated using observed energy values (E_j), reported values of zero-order energies (E_{oj}) and partial derivatives $(\partial E_j / \partial F_k)$ and $(\partial E_j / \partial \zeta_{4f})$ by partial and multiple regression method (6, 25-26).

The values of Slater-Condon parameters (F_k) and Lande parameters (ζ_{4f}) are then evaluated using following equations-

$$F_k = F_k^o + \Delta F_k \text{----- (5)}$$

$$\zeta_{4f} = \zeta_{4f}^o + \Delta \zeta_{4f} \text{----- (6)}$$

Where, $\Delta F_k \ll F_k^o$, $\Delta \zeta_{4f} \ll \zeta_{4f}^o$ and F_k^o and ζ_{4f}^o are the zero -order values of Slater-Condon and spin-orbit interaction parameters as reported by Wong (6).

- (b) **Racah Parameters or Energy parameters (E^1 , E^2 and E^3):**

In the case of Pr metal the difficulty arises that the number of levels observed is just the same as the number of parameters evaluated so only two parameters have been computed. The radial Eigen function for Pr^{+3} has been assumed to be hydrogenic for which F_4 and F_6 can be evaluated in terms of F_2 . By assuming wave functions to be hydrogenic as E^k 's (racah parameters) are the linear combination of F_k 's, they may be calculated by using the



following relation the Racah parameters reduces to in case of Pr^{+3} complexes which have been evaluated using these equations (27,28).

$$E^1 = 14.6818F_2 \dots\dots\dots (7)$$

$$E^2 = 0.0768F_2 \dots\dots\dots (8)$$

$$E^3 = 1.4844 F_2 \dots\dots\dots (9)$$

(c) **R.M.S. Deviations (Energy)**: The energies E_j of the electronic states have been estimated by using the computed values of the parameters. For comparison between calculated (E_{cal}) and observed (E_{obs}) values of energy, the value of r.m.s. deviations (σ) have been computed by using the relations-

$$\sigma = \{\sum (E_{\text{cal}} - E_{\text{obs}}) / N\}^{1/2} \dots\dots\dots (10)$$

Where, N = Number of energy level fitted

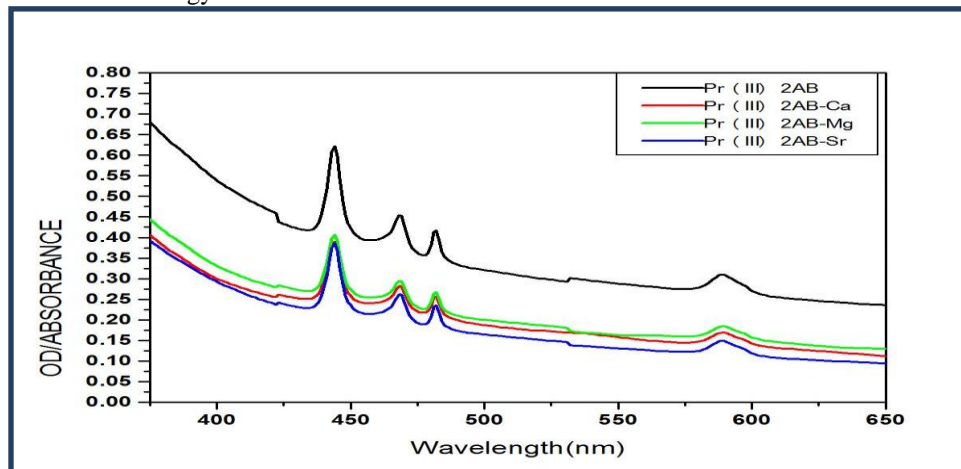


Figure 1: Comparative UV-Visible absorption spectra of Pr(III)-2AB system with codoping of $\text{Ca}^{+2}, \text{Mg}^{+2}, \text{Sr}^{+2}$ ion in alcoholic: aqua (1:1) medium

Table 1: Computed value of energy interaction: Slater-Condon F_k (cm^{-1}), Spin-Orbit interaction Lande ζ_{4f} (cm^{-1}) Racah E^k (cm^{-1}) parameters and Hydrogenic Ratio (F_4/F_2), (F_6/F_2) and (E^1/E^3), (E^2/E^3) for Pr (III)-2AB system and Co-doping of $\text{Ca}^{+2}, \text{Mg}^{+2}$ and Sr^{+2} metal ions in Alc: Water (1:1) medium

S.N.	Complex Parameters	Pr (III)-2AB	Pr (III)-2AB Ca^{+2}	Pr (III)-2AB Mg^{+2}	Pr (III)-2AB Sr^{+2}
1	E_1	4508.315	4494.683	4522.68	4518.059
2	E_2	23.58284	23.51153	23.65799	23.63382
3	E_3	455.8121	454.4339	457.2645	456.7973
4	F_2	307.0683	306.1398	308.0467	307.732
5	F_4	39.1872	61.59273	42.35863	82.92903
6	F_6	4.2933	5.799821	4.528922	7.244155
7	ζ_{4f}	710.7587	751.133	704.9197	748.7798
8	%r ζ_{4f}	4.9721	-0.42588	5.752792	-0.11127
9	%r F_2	-2.56221	-2.25208	-2.88901	-2.78388
10	F_4/F_2	9.89073	9.89073	9.89073	9.89073
11	F_6/F_2	0.051738	0.051738	0.051738	0.051738
12	E_1/E_3	0.127617	0.201192	0.137507	0.269485
13	E_2/E_3	0.013981	0.018945	0.014702	0.02354

Table 2: Experimental and Calculated value of Energy (cm^{-1}) for various energy level of Pr(III)-2AB system and codoping of Ca^{+2} , Mg^{+2} and Sr^{+2} metal ions in Alcoholic: water (1:1) medium

S. No	Levels	Pr(III)-2AB		Pr(III)-2AB Ca^{+2}		Pr(III)-2AB Mg^{+2}		Pr(III)-2AB Sr^{+2}	
		E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}
1	$^3\text{P}_2$	22497.8	22497.19	22538	22547.91	22497.73	22497.19	22548.56	22547.91
2	$^3\text{P}_1$	21344.83	21344.72	21308.18	21321.96	21344.83	21344.72	21299.42	21299.25
3	$^3\text{P}_0$	20767.41	20768.43	2146.038	2072.539	20789.03	20790.02	20767.41	20768.43
4	$^1\text{D}_2$	16963.71	16963.53	16931.09	16963.53	16992.56	16992.35	16963.65	16963.53
5	r.m.s. (σ) dev. (\pm)	0.60		0.59		0.58		0.61	

Results and Discussion

Among F_2 , F_4 , F_6 and ζ_{4f} parameters, decrease has been observed with F_2 and ζ_{4f} parameters in comparison to free metal ion. This shows the expansion of 4f-orbital in the complex formation. These observations show that on complexation, central metal ion expands, which has expected to decrease the interelectronic repulsions and spin orbit interaction.

Trends in value /variations in value of Racah Parameters or Energy parameters (E^1 , E^2 and E^3) for various systems in alcoholic: aqua (1:1) medium

E_1 - Pr(III)2AB- Mg^{+2} > Pr(III)2AB - Sr^{+2} > Pr(III)2AB > Pr(III)2AB- Ca^{+2}

E_2 - Pr(III)2AB- Mg^{+2} > Pr(III)2AB - Sr^{+2} > Pr(III)2AB > Pr(III)2AB - Ca^{+2}

E_3 - Pr(III)2AB- Mg^{+2} > Pr(III)2AB - Sr^{+2} > Pr(III)2AB > Pr(III)2AB - Ca^{+2}

Trends in value /variations in value of Slater- Condon F_2 , F_4 , & F_6 parameters

F_2 - Pr(III)2AB- Mg^{+2} > Pr(III)2AB- Sr^{+2} > Pr(III)2AB > Pr(III)2AB- Ca^{+2}

F_4 - Pr(III)2AB- Sr^{+2} > Pr(III)2AB- Ca^{+2} > Pr(III)2AB- Mg^{+2} > Pr(III)2AB

Variations in value of Lande parameter or Spin-Orbit Coupling Constant (ζ_{4f}) Parameter

ζ_{4f} - Pr(III)2AB- Ca^{+2} > Pr(III)2AB- Sr^{+2} > Pr(III)2AB > Pr(III)2AB- Mg^{+2}

For Pr(III)2AB in alcoholic: aqua (1:1) medium system E_{cal} is same with respect to all transition and also after codoping of Mg^{+2} , E_{cal} remains same with respect to all transition, while in case of Pr(III)2AB- Ca^{+2} and Pr(III)2AB- Sr^{+2} E_{exp} is same E_{cal} is different. rms (σ) dev. (\pm) is very small as for all systems which is nearby same i.e. it vary from 0.58 to 0.61.

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