



## Absorption Spectra of Praseodymium with Amino Acid

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Available online at: [www.isca.in](http://www.isca.in)

Received 20<sup>th</sup> March 2013, revised 29<sup>th</sup> March 2013, accepted 25<sup>th</sup> April 2013

### Abstract

The electronic absorption spectra of ternary complex i.e praseodymium as rare earth metal, amino acid histidine as primary ligand and propane 1,3-diol as secondary ligand in ratio 1:1:2 were recorded in visible region (360-620 nm) in different solvents i.e water (18.01), methanol(32.04), ethanol(46.07) and acetic acid(60.05). Various energies and intensities of all the transitions were calculated using Judd-Ofelt relation and are perfectly matches with observed value. Low rms deviation confirms the formation of complex.

**Keywords:** UV-Vis. Spectra, rare earth metals, amino acid, Judd-Ofelt parameters, intensity parameters.

### Introduction

Too much work has taken place on rare earth complex during past so many years, with oxygen donor liquids<sup>1-4</sup>. These rare earth metal i.e. Neodymium and Praseodymium have been considered as important lasing material due to narrow line width and weak crystal field interaction. Most of the  $f \leftrightarrow f$  transitions in rare earths are found to be weak in comparison to pseudo-hypersensitive transition in case of Praseodymium. The intensity too changes fast in case of pseudo-hypersensitive transition<sup>5-6</sup>. In this paper we report the electronic Spectra of Praseodymium complex with Histidine and Propane 1,3-diol in ratio 1:1:2. All intensity and energy parameters were calculated using the theories available with us.

### Material and Methods

The complex of  $\text{Pr}^{3+}$ (praseodymium chloride, Histidine and propane 1,3-diol) was prepared<sup>7-8</sup> and the chemicals used were of AR grade and metals 99.9%. Pure obtained from Indian Rare earth Ltd. The complex was prepared in molar ratio 1:1:2. The spectra were recorded in visible region (360-620 nm) on model uv-2601 spectrophotometer (Rayleigh analytical instrument corp.) in the laboratory.

$$E_j(F_k, \zeta_{4f}) = E_{0j}(F_k^0, \zeta_{4f}^0) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f} \quad (1)$$

**Energy levels:** The energy levels for various transitions were evaluated theoretically by using relation.

The observed energy (have been converted into wave numbers) as well as calculated values of energy levels using above equation for  $\text{Pr}^{3+}$  complex in different solvents has been collected in table-1.

The calculated values of Slater-Condon parameters  $F_2, F_4$  and  $F_6$ , Racah parameters  $E^1, E^2, E^3$ , Lande's parameters  $\zeta_{4f}$ , nephelauxetic ratio  $\beta$ , and bonding parameters  $b^{1/2}$  have been collected in table 2.

$$b^{1/2} = \left[ \frac{1 - \beta}{2} \right]^{1/2} \quad (2)$$

The relation for nephelauxetic ratio  $\beta$  and degree of covalency  $b^{1/2}$  is given by

The value of Nephelauxetic<sup>10</sup> ratio has been obtained using relation  $\beta = F_2^c / F_2^f$  where subscript c and f refer to complex and free ion.

The small variation in bonding parameter suggests that the coordination environment around the praseodymium ion does not change significantly when the ligands are changed. The amino acid co-ordinate through carboxylic oxygen only, where as nitrogen remains unaffected.

**Intensity Parameter:** Oscillator strength of each transition has been calculation using the formula.

$$P_{\text{exp}} = 4.6 \times 10^{-9} \times \epsilon_m \times \Delta \nu_{1/2} \quad (3)$$

$\epsilon_m$  and  $\Delta \nu_{1/2}$  are the molecular extinction coefficient and half band width respectively.

The theoretical value of oscillator strength has been derived using Judd-ofelt relation.

$$P_{\text{theoretical}} = \sum_{\lambda=2,4,6} T_{\lambda} \langle \int \psi_j | U^{\lambda} | f^N \psi^1_f \rangle^2 \quad (2)$$

Where various symbols have their usual meaning.

**Table-1**  
**Observed and calculation values of energy levels for Pr<sup>3+</sup> complex in different solvents**

Levels	Water		Methanol		Ethanol		Acetic Acid	
	Cal. cm <sup>-1</sup>	Obs. cm <sup>-1</sup>	Cal. cm <sup>-1</sup>	Obs. cm <sup>-1</sup>	Cal. cm <sup>-1</sup>	Obs. cm <sup>-1</sup>	Cal. cm <sup>-1</sup>	Obs. cm <sup>-1</sup>
<sup>3</sup> P <sub>2</sub>	22418.51	22522.52	22335.51	22471.91	22335.51	22471.91	22317.67	22471.91
<sup>3</sup> P <sub>1</sub>	21244.29	21367.52	21173.56	21276.59	21173.56	21276.59	21161.88	21276.59
<sup>3</sup> P <sub>0</sub>	20747.51	20746.88	20702.33	20703.93	20702.33	20703.93	20702.04	20703.93
<sup>1</sup> D <sub>2</sub>	17127.18	16977.92	17077.08	16920.47	17077.08	16920.47	17067.78	16891.89
rms deviation	109.8667		115.9212		115.9212		130.2775	

**Table-2**  
**Computed value of Slater- Condon parameters and Lande's parameters β and b<sup>1/2</sup> for Pr<sup>3+</sup> complex in different solvents**

	Water	Methanol	Ethanol	Acetic Acid
F <sub>2</sub> (cm <sup>-1</sup> )	310.8394	310.5313	310.5313	310.6765
F <sub>4</sub> (cm <sup>-1</sup> )	42.9113	42.8688	42.8688	42.8888
F <sub>6</sub> (cm <sup>-1</sup> )	4.6967	4.6921	4.6921	4.6943
ζ <sub>4f</sub> (cm <sup>-1</sup> )	691.5265	679.1609	679.1609	673.6628
E <sup>1</sup> (cm <sup>-1</sup> )	4563.682	4559.158	4559.158	4561.29
E <sup>2</sup> (cm <sup>-1</sup> )	23.8724	23.8488	23.8488	23.8599
E <sup>3</sup> (cm <sup>-1</sup> )	461.4101	460.9526	460.9526	461.1682
F <sub>4</sub> /F <sub>2</sub>	0.13805	0.13805	0.13805	0.13805
F <sub>6</sub> /F <sub>2</sub>	0.01511	0.01511	0.01511	0.01511
E <sup>1</sup> /E <sup>3</sup>	9.8907	9.8907	9.8907	9.8907
E <sup>2</sup> /E <sup>3</sup>	5.1738E-02	5.1738E-02	5.1738E-02	5.1738E-02
β	0.9650	0.9641	0.9641	0.9645
b <sup>1/2</sup>	0.1321	0.1339	0.1339	0.1331

Free ion Pr<sup>3+</sup> F<sub>2</sub> = 322.09

**Table-3**  
**Observed and calculated value of Oscillator strength for Pr<sup>3+</sup> complex in different solvents.**

Levels	water		Methanol		Ethanol		Acetic Acid	
	Cal. x10 <sup>-6</sup>	Obs x10 <sup>-6</sup>	Cal. x10 <sup>-6</sup>	Obs. x10 <sup>-6</sup>	Cal. x10 <sup>-6</sup>	Obs. x10 <sup>-6</sup>	Cal. x10 <sup>-6</sup>	Obs. x10 <sup>-6</sup>
<sup>3</sup> P <sub>2</sub>	10.5971	9.7662	10.7414	10.0572	6.6104	6.0075	8.7555	8.3693
<sup>3</sup> P <sub>1</sub>	4.4782	3.6900	4.0039	3.3561	2.4731	1.9022	3.6931	3.3274
<sup>3</sup> P <sub>0</sub>	2.3783	1.6130	2.4605	1.8301	1.8065	1.2510	1.9138	1.5580
<sup>1</sup> D <sub>2</sub>	3.0213	2.3950	2.9286	2.4134	1.7251	1.2711	2.5032	2.2129
rms deviation	7.5656E-07		6.2264E-07		5.4871E-07		3.5140E-07	

**Table-4**  
**Compute value of T<sub>λ</sub> – parameters and T<sub>4</sub> / T<sub>6</sub> for Pr<sup>3+</sup> complex in different solvents**

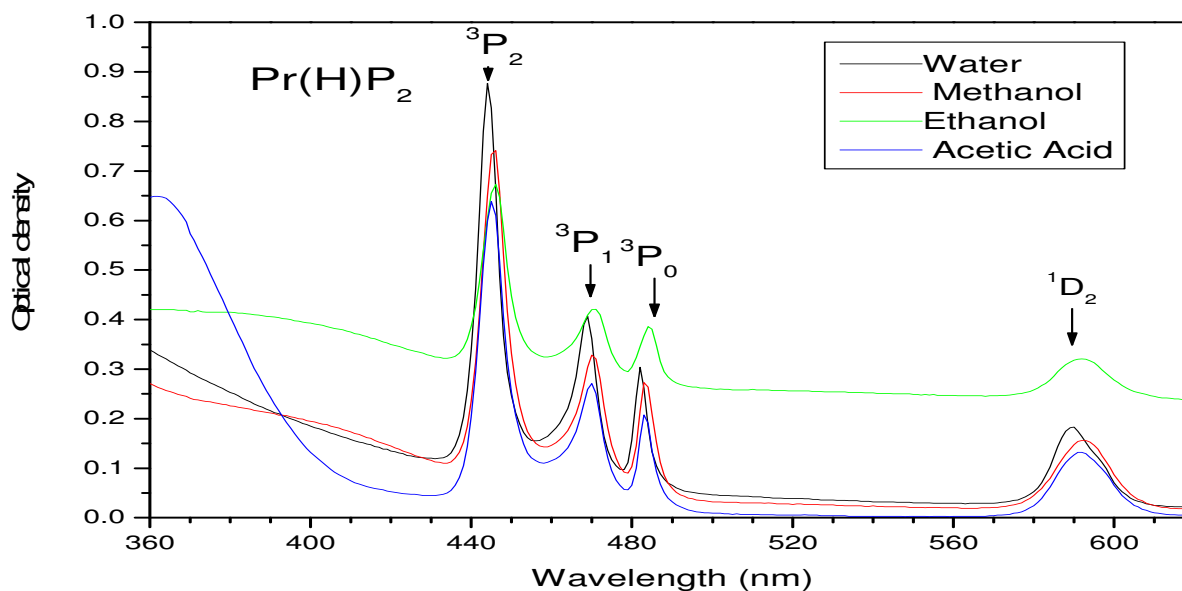
	Water	Methanol	Ethanol	Acetic Acid
T <sub>2</sub> x 10 <sup>10</sup>	-17.9722	-48.0520	-48.0945	-11.5107
T <sub>4</sub> x 10 <sup>10</sup>	6.6340	6.8774	5.0495	5.3495
T <sub>6</sub> x 10 <sup>10</sup>	32.9518	33.4389	20.3607	27.3253
T <sub>4</sub> / T <sub>6</sub>	0.2013	0.2056	0.2480	0.1957

**Table-5**  
**Refractive index value observed for Complex Pr<sup>3+</sup> in different solvents**

Complex	Solvent	Refractive index
Pr(H)P <sub>2</sub>	water	1.352
	Methanol	1.354
	Ethanol	1.371
	Acetic Acid	1.389

**Table-6**  
**Observed value of omega parameters complex Pr<sup>3+</sup> in different solvents**

	Water	Methanol	Ethanol	Acetic Acid
$\Omega_2 \times 10^{20}$	-12.3821	-33.0613	-32.7106	-7.7322
$\Omega_4 \times 10^{20}$	4.5705	4.7319	3.4343	3.5935
$\Omega_6 \times 10^{20}$	22.7025	23.0070	13.8480	18.3557



**Figure-1**  
**Variation of optical density with wavelength for Pr<sup>3+</sup> complex in different solvent**

## Results and Discussion

The experimentally observed value of oscillator strength for Pr<sup>3+</sup> complex along with their calculated value has been shown in table-3. The value of T<sub>2</sub>, T<sub>4</sub> and T<sub>6</sub> parameter was computed using Judd-Ofelt relation<sup>11</sup> by partial multiple regression method and has been collected in table-4. The value of reduced matrix elements was collected from Carnall et al<sup>12</sup>.

From table 2- We have calculated the value of Slater-Condon parameters F<sub>2</sub> in different solvent and the value matches with free ion value. In Table 3- We have reported the calculated value of Oscillator strength for Pr<sup>3+</sup> complex in different solvents which is in good agreement with observed value.

From table-4 we have observed that value of T<sub>4</sub> and T<sub>6</sub> remain nearly invariant. Where the value of T<sub>2</sub> which is sensitive to the environment of metal ion is negative which has no physical significance.

The value in parenthesis indicates the corresponding molecular weight of different solvent.

Four peaks have been observed in case of Pr<sup>3+</sup> complex. Also in case of Pr<sup>3+</sup> complex we have pseudo-hypersensitive transition (<sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub>), not much shifting of peak even when the solvents were changed.

The value of oscillator strength observed is maximum /highest among all transitions in all solvents for pseudo-hypersensitive transition.

## Conclusion

High value of rms deviation in case of Pr<sup>3+</sup> complex supports the assumption of 4f – wave function to be hydrogenic<sup>9</sup>. From table-1. We find that the value of energy levels calculated for

Praseodymium matches with observed value which clearly indicates that the formation of complex is perfect.

The decreases in value of  $F_2$  from that of free ion may support the complexation. This decrease is bit more in case of  $Pr^{3+}$ , which shows that on complexation the contraction of 4f- orbital is reduced with the increase in atomic number of metal ion.

The  $\beta$  value for  $Pr^{3+}$  complex  $< 1.0$  shows that complex is covalent in nature.

In table-4 we have observed the ratio  $T_4/T_6 < 1.0$  in each solvent. The complex under study has ratio ( $T_4/T_6$ ) lies between 0.20-0.24 supporting that they have oxygen / nitrogen –donor liquids.

The value of refractive index have also been obtained which are in order Water – 1.352, Methanol- 1.354, Ethanol- 1.371 , Acetic Acid- 1.389. Which are in the increasing order of molecular weight of the solvents.

Another intensity parameters i.e omega parameters too were calculated and have been reported in table- 6. Here we find that like  $T_2$  parameters the values of  $\Omega_2$  is negative and that of  $\Omega_4$  and  $\Omega_6$  parameters are positive. The ratio of  $T_4/T_6$  and that  $\Omega_4/\Omega_6$  is exactly constant showing the perfect match.

### Acknowledgement

One of the author Shri Kishan Ujjwal thanks University Grants Commission, New Delhi (India) for awarding a Rajiv Gandhi National Fellowship.

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