OPTICAL ABSORPTION SPECTRA OF TERNARY COMPLEX OF PRASEODYMIUM IN DIFFERENT ENVIRONMENT

ANUP KUMAR GUPTA

*Department of Physics, Jai Narain Vyas University
 Jodhpur, Rajasthan, India 342005
 anupgupta58@gmail.com*

SHRI KISHAN UJJWAL²

*Department of Physics, Jai Narain Vyas University
 Jodhpur, Rajasthan, India 342005
 s.k.ujjwal@gmail.com*

The optical absorption spectra of complex of Praseodymium in different solvents i.e water, Methanol, Ethanol & Acetic Acid have been recorded in visible region (360-620 nm for Pr^{3+}) using amino acid as primary ligand and diol as secondary ligand. The value of energies & intensities of various transitions have been calculated using Judd-Ofelt relation is in good agreement with experimental result. The study of complex found it to be covalent in nature. The spectra in visible region have been recorded on model uv-2601 Rayleigh analytical instrument corp.

Keywords: Rare earth metals, Amino acid, Optical absorption Spectroscopy, Judd-Ofelt parameters.

1. Introduction

Lot of work has been done on rare earth complex with oxygen ligands¹⁻⁵. It is considered as important lasing material due to narrow line width & weak crystal field interaction. Most $f \leftrightarrow f$ transitions in rare earths are found to be weak in comparison to one which are called as hypersensitive transition⁶⁻⁷. The intensity of hypersensitive transition changes with change of environment of metal ion in different complex⁸. Various intensity parameters i.e Judd-Ofelt parameters (T_2 , T_4 , T_6), bonding parameters $b^{1/2}$, of complex, energy parameters (F_2 , F_4 , F_6) & covalency of complex have been calculated & discussed as well.

2. Experimental Details

The complex of Pr^{3+} (Praseodymium chloride, proline & propane 1,3-dio) was prepared⁹ & the chemicals used was of AR grade & metals 99.9%. Pure (Indian Rare earth Ltd.) were used. The complex was prepared in molar ratio 1:2:1. The visible spectra was recorded on model uv-2601 spectrophotometer (Rayleigh analytical instrument corp.) in

the laboratory. Praseodymium ternary complex ML_2L' with amino acid proline as primary ligand & propane-1,3 diol as secondary ligand were prepared following Whan & Cross by.

3. Evaluation of Parameters

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

Energy levels:- The energy levels for various transition 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 Pr^{3+} complex in different solvents has been collected in table-1. rms deviation calculated & observed value is very low which actually supports the validity of relation. Some high value of rms deviation in case of Pr^{3+} complex supports the assumption of 4f – wave function to be hydrogenic¹⁰. 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 value of rms deviation is very small.

The calculated values of Slater-Condon parameters F_2 , F_4 & F_6 , Racah parameters E^1 , E^2 , E^3 , Lande's parameters ζ_{4f} , nephelauxetic ratio β , & bonding parameters $b^{1/2}$ have been collected in table 2. 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 reduced¹¹ with the increase in atomic number of metal ion.

The relation for nephelauxetic ratio β & degree of covalency $b^{1/2}$ is given by

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

The value of Nephelauxetic¹¹ ratio has been obtained using relation $\beta = F_2^c / F_2^f$ where subscript c & f refer to complex & free ion. The β value for Pr^{3+} complex < 1.0 shows that complex is covalent in nature. Also with change of metal i.e as the atomic number of metal ion increases the covalency decreases.

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

$$P_{exp} = 4.6 \times 10^{-9} \times \epsilon_m \times \Delta \nu_{1/2}$$

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

Table 1:- observed & calculation values of energy levels for Pr^{3+} complex in different solvents.

Levels	water		Methanol		Ethanol		Acetic Acid	
	Cal. cm^{-1}	Obs. cm^{-1}	Cal. cm^{-1}	Obs. cm^{-1}	Cal. cm^{-1}	Obs. cm^{-1}	Cal. cm^{-1}	Obs. cm^{-1}
$^3\text{P}_2$	22406.76	22522	22342.42	22471	22337.93	22471	22353.13	22471
$^3\text{P}_1$	21252.49	21367	21194.27	21321	21197.97	21321	21185.44	21321
$^3\text{P}_0$	20789.78	20790	20745.71	20746	20763.37	20764	20703.54	20703
$^1\text{D}_2$	17127.66	16977	17087.41	16920	17087.83	16920	17086.42	16920
rms deviation	110.7805		123.1064		123.5031		122.4382	

Table 2:- Computed value of Slater- Condon parameters & Lande's parameters β & $b^{1/2}$ for Pr^{3+} complex in different solvents.

	Water	Methanol	Ethanol	Acetic Acid
$\text{F}_2 (\text{cm}^{-1})$	311.8876	311.4458	311.88	310.4087
$\text{F}_4 (\text{cm}^{-1})$	43.0560	42.9951	43.0550	42.8519
$\text{F}_6 (\text{cm}^{-1})$	4.7126	4.7059	4.7125	4.6902
$\zeta_{4f} (\text{cm}^{-1})$	675.1093	668.2482	661.5235	684.3126
$\text{E}^1 (\text{cm}^{-1})$	4579.071	4572.586	4578.960	4557.358
$\text{E}^2 (\text{cm}^{-1})$	23.9529	23.9190	23.9523	23.8393
$\text{E}^3 (\text{cm}^{-1})$	462.9659	462.3102	462.9547	460.7707
F_4/F_2	0.13805	0.13805	0.13805	0.13805
F_6/F_2	0.01511	0.01511	0.01511	0.01511
E^1/E^3	9.8907	9.8907	9.8907	9.8907
E^2/E^3	5.1738E-02	5.1738E-02	5.1738E-02	5.1738E-02
β	0.9683	0.9669	0.9683	0.9637
$b^{1/2}$	0.1258	0.1285	0.1258	0.1346

Free ion Pr^{3+} $\text{F}_2 = 322.09$

Table 3:- Observed & calculated value of Oscillator strength for Pr^{3+} complex in different solvents.

Levels	water		Methanol		Ethanol		Acetic Acid	
	Cal. $\times 10^{-6}$	Obs $\times 10^{-6}$	Cal. $\times 10^{-6}$	Obs. $\times 10^{-6}$	Cal. $\times 10^{-6}$	Obs. $\times 10^{-6}$	Cal. $\times 10^{-6}$	Obs. $\times 10^{-6}$
$^3\text{P}_2$	12.1094	11.6616	10.0297	9.0269	10.3771	9.7665	10.4947	9.6195
$^3\text{P}_1$	5.7303	5.3054	5.4870	4.5356	5.1004	4.5210	4.6715	3.8410
$^3\text{P}_0$	2.5817	2.1691	2.8772	1.9514	2.6492	2.0855	3.2640	2.4576
$^1\text{D}_2$	3.6214	3.2842	2.9652	2.2102	3.0286	2.5688	2.7950	2.1360

Table 4:- Compute value of T_λ – parameters & T_4 / T_6 for Pr^{3+} complex in different solvents.

	Water	Methanol	Ethanol	Acetic Acid
$T_2 \times 10^{10}$	19.1646	5.6524	-2.0128	-64.9014
$T_4 \times 10^{10}$	7.2166	8.0259	7.3901	9.1238
$T_6 \times 10^{10}$	37.8427	30.7960	32.107	32.0301
T_4 / T_6	0.1907	0.2606	0.2301	0.2848
rms deviation	4.0780E-07	9.1353E-07	5.5632E-07	7.9695E-07

Table 5:- Refractive index value observed for Complex Pr^{3+} in different solvents.

Complex	Solvent	Refractive index
$\text{Pr}(\text{P})_2\text{P}$	water	1.356
	Methanol	1.374
	Ethanol	1.382
	Acetic Acid	1.392

Table 6:- Observed value of omega parameters complex Pr^{3+} in different solvents.

	Water	Methanol	Ethanol	Acetic Acid
$\Omega_2 \times 10^{20}$	13.1681	3.8365	-1.3586	-43.5066
$\Omega_4 \times 10^{20}$	4.9586	5.4474	4.9884	6.1161
$\Omega_6 \times 10^{20}$	2.6001	20.9023	21.6726	21.4714
Goodness of the fit	0.0375	0.1834	0.0673	0.1363

In **Fig. 1** We have show the variation of optical density with wavelength in all solvents for Pr^{3+} complex in visible region (360-620 nm). In figs 2-5. A variation of optical density with wavelength in infrared region (1000-2000 nm) have been shown for different solvents i.e water, methanol, ethanol, acetic acid.

Fig. 1 Variation of optical density with wavelength for Pr^{3+} complex in different solvent.

Fig. 2 A variation of optical density with wavelength in infrared region for water solvent.

Fig. 3 A variation of optical density with wavelength in infrared region for methanol solvent.

Fig. 4 A variation of optical density with wavelength in infrared region for ethanol solvent.

Fig. 5 A variation of optical density with wavelength in infrared region for acetic acid solvent.

4. Results and Discussion

The experimentally observed value of oscillator strength for Pr^{3+} complex along with their calculated value have been shown in Table 3. The value of F_2 , F_4 & F_6 parameters were computed using Judd-Ofelt relation¹² by partial multiple regression method & have been collected in table-2. The value of reduced matrix elements were collected from Carnall et al¹³.

From Table 2- We have calculated the value of Slater-Condon parameters F_2 in different solvents & the value matches with free ion value. In Table 3- We have reported the calculated value of Oscillator strength for Pr^{3+} complex in different solvents which is in good agreement with observed value.

From table-4 we have observed that value of T_4 & T_6 remain nearly invariant. It has been observed that the value of T_2 changes linearly with molecular weight of amino acid. In case of Pr^{3+} complex T_2 is negative which has no physical significance. From above table we observe that the ratio of T_4/T_6 is low in Pr^{3+} complex. The complex under study has a ratio (T_4/T_6) lies between 0.19-0.28 supporting that they have oxygen / nitrogen donor liquids. Also in table-4 We have reported T_λ parameters low value of rms deviation confirms the formation of complex. Four peaks have been observed in case of Pr^{3+} complex. Also in case of Pr^{3+} complex we have pseudo- hypersensitive transition ($^3\text{H}_4 \rightarrow ^3\text{P}_2$), not much shifting of peak even when the solvents were changed. The difference of energy value between observed & calculated is very small supports the formation of complex well. The value of refractive index have also been obtained which are in order.

Water – 1.356, Methanol- 1.374, Ethanol- 1.382, Acetic Acid- 1.392

In Table-5. We have reported the value of refractive index for Pr^{3+} complex which is in the increasing order as is the increasing order of molecular weight of the solvents. In Table-6. We have reported the value of omega parameters for Pr^{3+} in different solvents.

For Pr^{3+} the value of oscillator strength is max. for pseudo- hypersensitive transition. The variation of wave length with optical density for Pr^{3+} complex has been shown in graph in visible region. We have also shown the Infra-red spectra in range 1000-2000 nm for Pr^{3+} complex in graph in all solvents, observed is almost same in all solvents. Both the complex have been show in single graph in different solvent indicating that peaks are almost in same position but intensity is changing.

Acknowledgment

One of the author Shri Kishan Ujjwal thanks UGC, New Delhi for awarding Rajiv Gandhi National Fellowship.

References

1. R D Peacock, Struct & Bonding (Germany). **22**, 83(1975)
2. S P Tandon & P C Mehta , J.Chem Phys. (USA),**52** , 4313(1970)
3. D G Karakker ,J.inorg & Nucl chem (GB),**33**, 3713 (1971)
4. Y K Sharma,SSL Surana,R P Dubedi,Mat.Sci.Engg.B,**119**,131 (2005)
5. Y K Sharma,SSL Surana,Optical Materials,**29**,598 (2007)
6. W Streak, Theor Chim Acta (Berlin), **52**, 45 (1979).
7. M P Bhutra & Anup K.Gupta, Ind. J. Pure & Appl Phys **20**,954 (1982)
8. B R Judd,Phys Rev.(USA),**127** , 750 (1962)
9. G S Ofelt, J. Chem Phys.(USA),**37**, 511 (1962)
10. S N Mishra,G K Joshi,M P Bhutra,Ind.Journal of chem sci. **21**, 275 (1982)
11. S P Tandon, R C Govil, Spectroscopic letters (USA),**6**, 125 (1973)
12. Cyril H Goulden, Method of statistical analysis (Asia Publishing House, Bombay,1964).
13. W T Carnall, P R Fields & B G Wybourne , J Chem .Phys (USA) **42**, 3797 (1965)
14. R E Whan & C A Crossby, J.Mole.Spec. (USA), **8**, 315 (1962)