

A Study of Co-ordination Geometry of Neodymium and Praseodymium

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ABSTRACT

In case of rare earth complexes, absorption spectra of Neodymium and diffuse reflectance of Praseodymium were studied. Observed intensities of spectral lines in case of rare-earths are too large and cannot be explained on the basis of magnetic dipole and electric quadrupole interactions. Induced electric dipole transitions are mainly responsible for the occurrence of these lines. Induced electric dipole transition is strongest in three. Hypersensitive transitions obey the selection rule of quadrupole transitions and therefore known as Pseudo-quadrupole transitions. Various parameters like Slater-Condon, Nephelauxetic ratio are calculated. On the basis of these parameters their co-ordinate geometry are studied.

Key-words- Praseodymium, Neodymium, Quadruple Interactions and Nephelauxetic Ratio

INTRODUCTION

In this work spectra of Neodymium and Praseodymium are studied[1-18]. Absorption spectra of Neodymium and diffuse reflectance spectra are studied. The ternary complexes of rare-earth metal in different environments play an important role in various biological systems to photonic devices. Their electronic spectra have been studied by various Researchers[1-24]. Judd and Ofelt theory gave a clear explanation of oscillator strength of induced transitions in rare-earth ternary complexes.

The effective part of Hamiltonian for $4f^n$ Configuration consists of three types of interactions i.e. electrostatic, magnetic and configuration interaction.

$$H_{\text{eff}} = H_e + H_m + H_c$$

$$H_e = \sum_{i < j}^N \frac{e^2}{r_{ij}}$$

Where, summation runs for all the electrons of configuration.

$$E_e = \sum_{K=0}^6 f_K F^K$$

Where, f_k represents angular part of the interaction and value of K is even. F^k are Slater-Condon parameters.

A pure electrostatic model is not sufficient to explain all the interactions and there exists another type of interaction known as magnetic interaction. The magnetic interaction is divided into four parts.

- 1) Spin-Orbit interaction
- 2) Spin-Spin interaction
- 3) Spin-Other Orbit interaction
- 4) Orbit-Orbit interaction

The chemical bond for rare-earth complex is considered to be ionic because of their inert gas electronic configuration. It is due to well shielding of 4f orbitals. But experimentally, covalency is also observed for some rare-earth complexes[21-24].

Hypersensitivity is due to charge transfer in transitions in lanthanides complexes due to which intensity and energy of levels changes. According to dynamics coupling model, dipoles are induced by the charge distribution of f-f transitions. In this, f electrons polarises the ligands and ligands polarises the lanthanide ion. T_2 parameter alone cannot explain hypersensitivity but the relative magnitude of T_2 with respect to T_4 and with respect to T_6 . These three Judd-Ofelt parameters (T_2 , T_4 , T_6) are related to the radial part of the $4f^n$ configuration.

EXPERIMENTAL DETAIL

Complex of Neodymium, Glycine and Urea is prepared in the molar ratio 1:1:2 in the solvent form. Its absorption spectra were recorded. Complex of Praseodymium, Glycine and propylenediamine is also prepared in the molar ratio 1:1:2. Their diffuse spectrum was also recorded. All rare-earth and all other reagent are of standard purity.

OBSERVATION

TABLE-1 Energy Levels of Neodymium: Glycine: Urea in molar ratio 1:1:2

Levels	Observed energy	Calculated Energy	Delta E
$^4F_{3/2}$	11560.70	11537.65	23.04
$^4F_{5/2}$	12578.61	12579.31	-0.698
$^4F_{7/2}$	13513.51	13410.11	103.40
$^4F_{9/2}$	14749.26	14789.17	-39.90
$^4G_{5/2}$	17361.11	17383.33	-22.22
$^4G_{7/2}$	19157.08	19188.87	-31.19
$^4G_{9/2}$	19531.25	19603.41	-72.16
$^2G_{9/2}$	21052.63	21021.75	30.88
$^4G_{11/2}$	21691.97	21708.01	-16.04
$^2P_{1/2}$	23094.68	23101.43	-6.74
rms deviation			45.54

Neodymium: Glycine: Urea

Energy parameters

E_1 : 4995.222,

E_2 : 25.13588,

E_3 : 495.5675

E_1 / E_3 : 10.0798,

E_2 / E_3 : 5.072141E-02

F parameters;

F_2 : 334.307,

F_4 : 48.17958,

F_6 : 5.207804

Zeta4F: 881.0516,

F_4 / F_2 : .1441178

F_6 / F_2 : 1.557791E-02

R.m.s Deviation: 45.54791 ,

Nephelauxetic Ratio: 1.009503

Bonding Parameter 6.893115E-02

Table-2 Oscillator Strength of Nd:G:U

Levels	ObservedX10 ⁶	Calculatedx10 ⁶
⁴ F _{3/2}	1.46	1.18
⁴ F _{5/2}	1.73	1.80
⁴ F _{7/2}	1.288	0.947
⁴ F _{9/2}	.237	0.133
⁴ G _{5/2}	2.89	2.69
⁴ G _{7/2}	1.86	1.26
⁴ G _{9/2}	.78	.627
² G _{9/2}	.417	.325
⁴ G _{11/2}	.472	6.28E-2
² P _{1/2}	.36	0.371

INTENSITY PARAMETERS

T2: -1.101834E-04,

T4: 4.303919E-04,

T6: 7.712616E-04

T4 / T6 0.5580362

r.m.s Deviation : .2836167

Refractive Index: 1.37

Table3 Energy Levels of Praseodymium:Glycine: Propylenediamine in molar ratio 1:1:2

Levels	Observed energy	Calculated Energy	Delta E
¹ D ₂	16807	16985.95	-178.95
³ P ₀	20576	20576.85	-0.849
³ p ₁	21186	21037.1	148.89
³ P ₂	22321	22197.5	123.5

ENERGY PARAMETERS

E1 : 4535.05,

E2 : 23.72269,

E3 : 458.5152

E1 / E3 : 9.89073,

E2 / E3 : 5.173808E-02

F PARAMETERS

F2 : 308.8892,

F4 : 42.64216,

F6 : 4.667316

Zeta4F : 673.778,

F4 / F2 : .13805,

F6 / F2 : .01511

rms Deviation : 131.7647**Nephelauxetic Ratio** : .9590152**Bonding Parameter (b 1/2)**: .1431517**Table-4 Oscillator Strength**

Levels	ObservedX10 ⁶	Calculatedx10 ⁶	Difference
¹ D ₂	0.87	1.08	-0.219
³ P ₀	1.79	2.05	-0.268
³ p ₁	1.81	2.08	-0.276
³ P ₂	4.41	4.70	-0.291

INTENSITY PARAMETERS

T₂ : -6.852577E-03, T₄ : 5.789368E-04, T₆ : 1.399705E-03
 T₄ / T₆ : 0.4136135

rms Deviation : .2651946, Refractive Index : 1.38

Result and Discussion

In Neodymium complex ten peaks are observed but for Praseodymium four peaks are observed. The value of R.M.S. deviation for Neodymium complex is smaller as compared to Praseodymium complex. This indicates that Neodymium has greater tendency to form complexes as compared to Praseodymium.

Judd–Ofelt Theory is quite useful for intensity measurements of lanthanide's ternary complexes. Intensity of various transitions is expressed in terms of T_λ and Ω_λ parameters. This theory is most suitable to characterize the intensities of forced electric dipole transitions between the 4f states of rare-earth (III) ions. Since the absorption and emission probabilities for an ion matrix combination are expressed as set of three Judd-Ofelt parameters. The Judd-Ofelt intensity parameters are calculated by knowing the oscillator strength of various peaks. T₂ parameter is function of ligand concentration only. It changes with the change in concentration. With organic solvents parameter T₂ changes significantly because these solvents have high coordinating power in comparison to water. T₄/T₆ refers to symmetry around the metal ion. In case of Neodymium hypersensitive band is at a 577nm and in case of Praseodymium it is at 448nm.

CONCLUSION

In case of Neodymium Nephelauxetic ratio is greater is one. It is 1.009503 which is greater than one. Therefore Bonding Parameter is 6.893115E-02. Hence in case of Neodymium bonding is Ionic.

For Praseodymium Nephelauxetic Ratio is 0.9590152. It is slightly less than one. Bonding Parameter (b 1/2) is 0.1431517. Therefore Praseodymium complex is Slightly Covalent.

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