

To study Nephelauxetic Ratio of Praseodymium in Different Environments

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Abstract

The observed spectra of tripositive lanthanides ions can be explained by considering the transitions between the energy states of the $4f^n$ configurations energy. These energy states can be calculated by diagonalization of complete matrices. The absorbing spectra of highly absorbing amorphous materials which may be insoluble in solvents can be studied by technique of diffuse reflectance. In diffuse reflectance a well collimated incident beam is equally distributed in all directions after reflection from the metal surface. Various parameters Slater-Condon, Racah parameters are calculated. On the basis of which Nephelauxetic ratio of different complexes are calculated.

Key-Words-Slater-Condon parameters, Nephelauxetic ratio, Lanthanides and Diffuse Spectra

INTRODUCTION

To explain diffuse reflectance, its theory is classified into two parts.

- 1) Differential Equation Method
- 2) Statistical Method

The observed absorption spectra appears due to f-f transitions in case of tripositive lanthanides ions having configurations $[Xe] 4f^n$. These bands are due to incomplete 4f shell, electronic to electronic transitions. In free ion, only magnetic transitions are allowed but on complexation, electric dipole transitions are induced as Ligand field mixes odd parity configuration to the rare-earth configuration. Transitions occurs in lanthanides are due to induced electric dipoles. Some transitions are due to electric as well as magnetic dipole. Energy states are calculated by the diagonalization of complete matrices developed by Slater and Condon. But calculation done by this method is applicable only for the configuration not more than f^2 . Racah introduced a Taylor series expansion to solve energy levels.

When there is formation of complex, the repulsion decreases. It causes a red shift of bands as compared to the bands of free ions. This is known as Nephelauxetic effect. f-f transitions of rare-earth complexes in visible region are studied by various researchers[1-12]. In the present study, diffuse spectra of Praseodymium complexes are studied. In case of rare-earth complexes, electric field which is produced by the distortion of the tripositive ions by the surrounding atmosphere is weak as compare to rigid crystals. Due to electrostatic and magnetic interactions, there exist energy levels associated with rare-earth elements. The energy levels of these elements can be expressed in terms of four parameters (F_2, F_4, F_6) and Lande's parameter. By taking their spectra, we know position of energy levels. The different modes by which electronic transitions take place are

1. Electric dipole,
2. Magnetic dipole,
3. Electric Quadrupole

EXPERIMENTAL DETAILS

In this study Praseodymium is of 99-99% pure . Praseodymium, aminoacids(Alanine and Cystine) and all solvents used are of CDH company. Complex of praseodymium is ML_2L' . An alcoholic solution of lanthanides chloride was mixed with alcoholic solution of ligand in the molar ratio 1:2:1. The reaction was completed by adding ammonia drop wise. Continuous stirring was done till the complexes are precipitated out.

THEORY

Rare-earth metals in different environments play an important role in various biological systems to photonic devices and also wide applications in operational amplifiers, fibre lasers, communication and display devices. The free ion electronics spectra of rare-earths undergo modifications when they are placed in different lattice sites either in crystal or in solutions and their electronic spectra have been studied by various Researchers. Judd and Ofelt theory gave a clear explanation of oscillator strength of induced transitions in rare-earth ternary complexes.

Change in environment of rare-earth ions sometimes doesn't change the position of energy levels too much. This causes only a slight change in various parameters. It is very difficult to solve these parameters using method of diagonalisation because in some cases number of levels are higher than number of parameters. Various parameters like Slater-Condon, Lande's and Racah (Energy level parameter) on complexation as compared to free ion reveals, that on complexation there is change in symmetry around the metal ion, types of bonding between metal and ligands. On complexation, there is very small change in F parameters and Lande's parameter. After formation of complex these two parameters decrease slightly. The decrease in value of Lande's parameter is more than Slater-Condon parameters. This signifies that ligands affect spin-orbit coupling more than the electrostatic repulsion.

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. On complexation, there is expansion of 4f orbital's which can be expressed in terms of Nephelauxetic Ratio (β).

$$\beta = F_k^c / F_k^f$$

$$\text{Bonding parameter is } b^{1/2} = [(1 - \beta) / 2]^{1/2}$$

$$\delta = (1 - \beta) / \beta$$

RESULTS

Table-1 Energy Levels of Praseodymium: Alanine: Ethyl Alcohol

Levels	Energy Observed	Calculated	Delta E
¹ D ₂	17036	17136.04	-100.03
³ P ₀	20747	20746.06	0.929
³ P ₁	21322	21255.1	66.9
³ P ₂	22522	22436.01	85.99

ENERGY PARAMETERS

E1 : 4561.027

E2 : 23.85858

E3 : 461.1416

E1 / E3 : 9.89073

E2 / E3 : 5.173808E-02

F PARAMETERS

F2 : 310.6586

F4 : 42.88642

F6 : 4.694051

Zeta4F : 697.4348

F4 / F2 : .13805

F6 / F2 : .01511

rms Deviation : 73.95833

Nephelauxetic Ratio : .9645085

Bonding Parameter (b 1/2): 0.1332132

Table-2 Energy Levels of Praseodymium: Cysteine: Ethyl Alcohol

Levels	Energy Observed	Calculated	Delta E
¹ D ₂	17094	17155.5	-61.49
³ P ₀	20747	20742.65	4.34
³ P ₁	21276	21278.79	-2.79
³ P ₂	22573	22474.53	98.47

ENERGY PARAMETERS

E1 : 4555.095
 E2 : 23.82755
 E3 : 460.5418
 E1 / E3 : 9.89073
 E2 / E3 : 5.173808E-02

F PARAMETERS

F2 : 310.2545
 F4 : 42.83064
 F6 : 4.687946
 Zeta4F : 710.5221
 F4 / F2 : .13805
 F6 / F2 : .01511

rms Deviation : 58.10707
 Nephelauxetic Ratio : .9632541
 Bonding Parameter (b 1/2): .1355469

When there is formation of ternary complexes of Praseodymium then red shift occurs. On complexation, there is very small change in F parameters and Lande's parameter. After formation of complex these two parameters decrease slightly. The decrease in value of Lande's parameter is more than Slater-Condon parameters. This signifies that ligands affect spin-orbit coupling more than the electrostatic repulsion. Columbic and spin-orbit parameter decreases and there is expansion of the central metal ion on complexation. According to Carnall and Ryan Nephelauxetic ratio increases.

In case of praseodymium, Alanine and Ethyl Alcohol RMS deviation is higher than the RMS deviation of praseodymium, Cysteine and Ethyl Alcohol. Therefore complex of Praseodymium with Cysteine is more stable than with Alanine. Nephelauxetic ratio in first complex is 0.9645085 but for second complex is .9632541. This is nearly equal to one but slightly less than one. Hence bonding parameters are real for these complexes. Therefore bonding is Covalent.

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