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A study of covalency of Erbium and Neodymium ternary complexes in Alanine and Urea

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Abstract: *The element of the first series that is from Cerium to Lutetium ($_{58}$Ce to $_{71}$ Lu), which form a part of the sixth period are called lanthanides. These fourteen elements form 4f inner transition series. They are heavy metals. Their Laser properties were demonstrated in early sixties by Whan and Crossby. In this study two rare-earth Neodymium and Erbium have been taken. Due to electrostatic and magnetic interactions, there exist energy levels associated with rare-earth element. The energy levels of these elements can be expressed in terms of four parameters (F_2,F_4,F_6) and Landes parameter. By taking their spectra, we know position of energy levels. Both Neodymium and Erbium complexes are studied in solvent form. Ten peaks are observed for Neodymium and eight peaks are observed for Erbium in visible region. Due to complexation some of the absorption bands are modified and become more intense. These bands are due to hypersensitive transitions known as hypersensitive bands. Occurrence of these bands is explained by Judd.*

Key-Words: *Neodymium, Erbium, Alanine, Urea and hypersensitive transitions*

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I. INTRODUCTION

For finding the natural frequency of lanthanides, absorption and luminescence spectroscopy are useful, either in solution or in glasses form, rare-earth complexes show lines. These bands are due to incomplete 4f shell, electronic to electronic transitions. These energy states are calculated by the diagonalization of complete matrices developed by Slater and Condon. But calculation is done by this method is applicable only for the configuration not more than f^2.Racah introduced a simpler method based on Taylor series expansion to solve these energy levels.

All f-f transitions of rare-earth complexes in visible region are studied by various coworkers [1-19]. The solution spectra of rare-earth Neodymium and Erbium have been studied. In case of rare-earth complexes, electric field which is produced by the distortion of the tri-positive ions by the surrounding atmosphere is weak as compare to rigid crystals.

The different modes by which electronic transitions are

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

In case of rare earth complexes observed intensities of spectral lines 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.

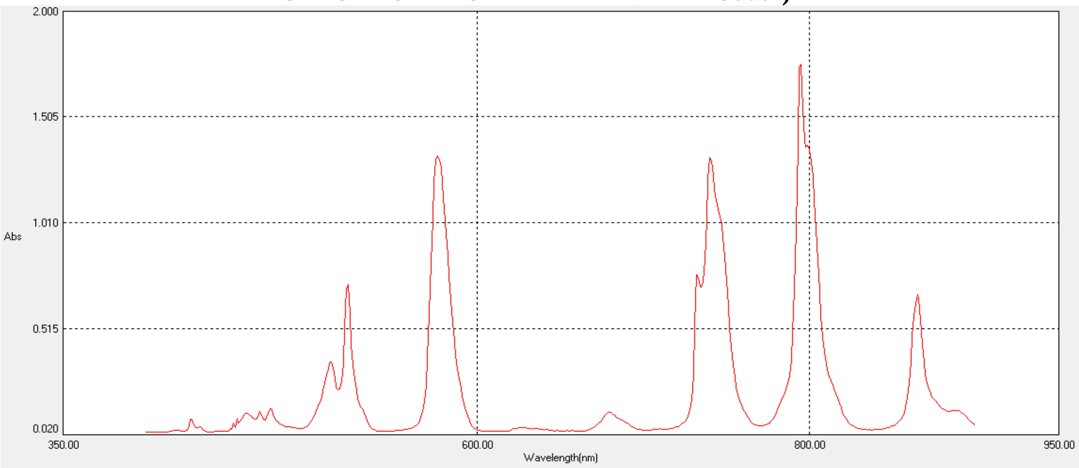
Oscillator strength corresponding to these transitions can be expressed in terms of three T_λ parameters. According to Judd, T_λ parameters have contribution due to both parts, radial as well as perturbing configurations. The electronic and spin orbit interactions yield energy levels parameters that deviate much from the observed energy levels.

Experimental

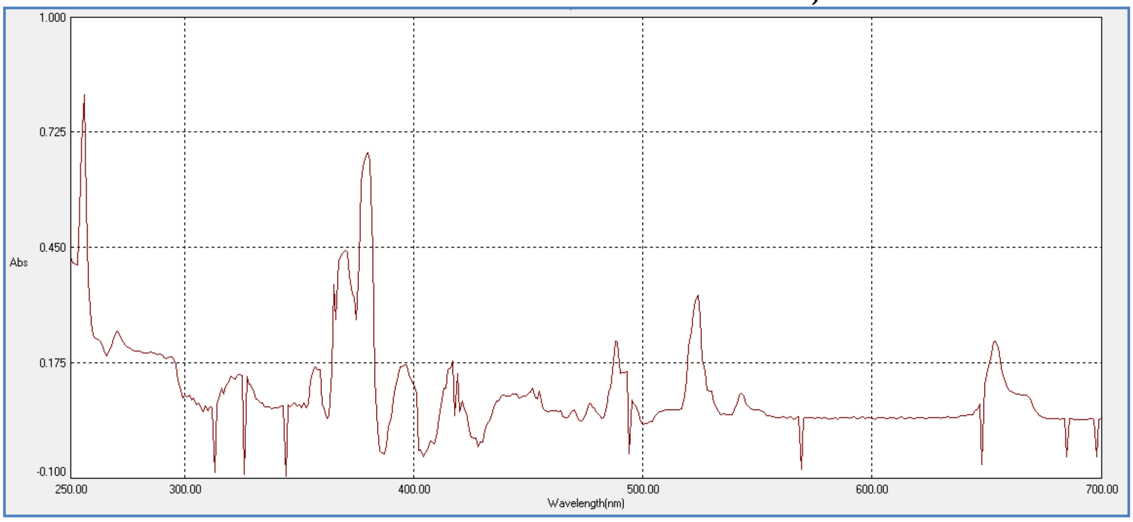
Two Rare-earth Neodymium and Erbium are taken. Their solutions are prepared by taking Alanine, as primary ligand and Urea as secondary ligand. Their ternary complexes are studied in solvent form. The calculated energy levels corresponding to different peaks of Neodymium and Erbium Complexes are compared with the experimentally observed values. These energy level values change due to either change in ligands or change in solvents.

All reagents used in this study are taken of standard purity. In this work all chemicals are taken from C.D.H Company. The complexes are synthesized by taking Amino-acid that is Alanine as primary ligand and Urea as secondary Ligand, mixed in1:1:2 molar ratio .The solution is stirred for half an hour with magnetic stirrer method The formation of complex is also checked by infrared spectra in Chemistry lab of S.P.C Government College, Ajmer . The absorption spectra of the complexes are recorded with UV-VIS Spectrophotometer LABINDA 3000$^+$. Peaks of these absorption spectra are recorded in between 400nm to 800nm.

SPECTRA OF NEODYMIUM, ALANINE AND UREA (AS OBSERVRD WITH UV-SPECTROPHTOMETER LABINDA 3000$^+$)



SPECTRA OF ERBIUM, ALANINE AND UREA (AS OBSERVRD WITH UV-SPECTROPHTOMETER LABINDA 3000$^+$)



Parameters

Some parameters are calculated after taking its absorption spectra. These parameters are, Slater-Condon Parameters, Lande parameter, Bonding parameter , Oscillator Strength,Judd-Ofelt parameters and Omega parameters

The electronic transitions within f^n configuration will arise due to

1) Electric –dipole 2)Magnetic- dipole 3)Electric quadrupole

Formula for calculation of Oscillator Strength is

$$P=4.6\ x10^{-9}\ x\ \varepsilon_{max}\ x\ \Delta\nu_{1/2}$$

Where ε_{max} = Molar Extinction Coefficient $\Delta\nu_{1/2}$=Half Band Width

From the Spectrum, Half Band Width

ε_{max} = 1/ C x L (Log I_0/I) = 1/ C x L (Optical Density)

C=Concentration of the Solution. L= Thickness of Cell in cm

The values of reduced matrix elements are collected from W.T. Carnall [19]. The parameter $b^{1/2}$ is measurements of types of bonding is calculated by the given formula

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

The effect of complexation on the free ions is the red shift of electronic transitions. The red shift is due to the expansion of metal orbital radius, resulting in the decrease of the inter-electronic repulsion parameters. This effect is known as Nephelauxetic effect [17]. This effect is usually expressed in term of β $\beta = F^c_k / F^f_k$

Where c=complex state f =free ion state

$\delta = (1-\beta) / \beta$, Where δ is a bonding parameter.

1) If δ is positive then there is covalent bonding between metal and ligands.
2) If δ is negative then there is ionic bonding between metal and ligands.

Table-1 - Showing Observed and Calculated Energy Levels of Nd:Al:U

Levels	$^4F_{3/2}$	$^4F5_{/2}$	$^4F_{7/2}$	$^4F_{9/2}$	$^4G_{5/2}$	$^4G_{7/2}$	$^4G_{9/2}$	$^2G_{9/2}$	$^4G_{11/2}$	$^2P_{1/2}$
Observed energy	11560.7	2594.76	13513.51	14727.54	17361.11	19157.08	19531.25	21052.63	21691.97	23419.2
Calculated energy	11561.76	12574.59	13410.89	14795.81	17396.22	19190.08	19579.04	21021.22	21676.69	23417.24
Change in energy	-1.06347	19.860	102.6	-68.26	-35.11	-33.01	-47.7	31.4	15.28	1.962

ENERGY PARAMETERS
E1 : 5116.125 **E2** : 26.45488 **E3** : 496.0764
E1 / E3: 10.31318 **E2 / E3** : 5.332824E-02

F PARAMETERS
F2 : 341.8098 **F4** : 47.5493 **F6** : 5.561712
Zeta4F : 873.9931
F4 / F2 : .1391104 **F6 / F2** : 1.627136E-02 **rms Deviation** : 46.27774
Nephelauxetic Ratio : 1.032159
Bonding Parameter : .1268051

Table-2 - Showing Observed and Calculated Oscillator Strength (OS) of Nd:Al:U ($x10^6$)

Levels	$^4F_{3/2}$	$^4F5_{/2}$	$^4F_{7/2}$	$^4F_{9/2}$	$^4G_{5/2}$	$^4G_{7/2}$	$^4G_{9/2}$	$^2G_{9/2}$	$^4G_{11/2}$	$^2P_{1/2}$
Observed OS	1.346	2.3	1.78	0.106	3.38	1.94	0.51	0.341	0.4	0.177
Calculated OS	1.310	2.40	1.66	0.197	3.374	1.439	0.747	0.367	0.079	0.402
Change in P	0.035	-0.10	0.118	-0.09	0.006	0.500	-0.23	-0.026	0.32	-0.23

INTENSITY PARAMETERS
T2 : -9.448552E-05 **T4** : 4.570911E-04 **T6** : 1.554134E-04
T4 / T6 : 2.941131
rms Deviation : .2224793
Refractive Index : 1.37

OMEGA PARAMETERS
OMEGA2 : -7.14518E-15 **OMEGA4** : 3.45661E-14 **OMEGA6** : 1.17526E-14

Table-3 - Showing Observed and Calculated Energy Levels of Er:Al:U

Levels	$4I_{9/2}$	$^4S_{3/2}$	$^2H_{11/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$	$^2H_{9/2}$	$^4G_{11/2}$	$4G_{9/2}$
Observed energy	15290.52	18416.20	19083.96	20491.18	22123.80	22522.52	24691.13	26315.78	27932.96
Calculated energy	15319.54	18280.7	19410.02	20550.49	22095.45	22482.27	24632.4	26620.1	27693.41
Change in energy	-29.023	135.50	-56.054	-59.30	28.34	40.25	58.72	-304.32	239.55

ENERGY PARAMETERS
E1 : 1419.283 **E2** : 4.829614 **E3** : -222.057
E1 / E3 : -6.391528 **E2 / E3** : -2.174944E-02
F PARAMETERS
F2 : -7.921631 **F4** : -1.25707 **F6** : 6.802421

Zeta4F : -3.613403
F4 / F2 : .1586883
F6 / F2 : -.8587147
rms Deviation : 142.1014
Nephelauxetic Ratio : -1.793523E-02
Bonding Parameter : .7134197

Table-4- Showing Observed and Calculated Oscillator Strength (OS) of Er:Al:U ($x10^6$)

Levels	$4I_{9/2}$	$^4S_{3/2}$	$^2H_{11/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$	$^2H_{9/2}$	$^4G_{11/2}$
Observed OS	1.027	0.586	1.94	1.42	0.431	0.382	0.844	6.374
Calculated OS	1.135	0.524	2.34	1.748	0.666	0.410	0.770	6.25

INTENSITY PARAMETERS
T2 : 1.572679E-04 **T4** : 1.814551E-05 **T6** : 1.338741E-04
T4 / T6 : .1355416
rms Deviation : .2121908
OMEGA PARAMETERS
OMEGA2: 1.181157E-14 **OMEGA4:** 1.362815E-15 **OMEGA6**: 1.005459E-14

II. Results and Discussion

Forbidden Transitions are responsible for the Visible and near Infra-red spectra of Neodymium and Erbium ternary complexes. Neodymium and Erbium belongs to lanthanides series.

Ternary complexes of Neodymium and Erbium with Alanine act as primary ligands and Urea as secondary ligands are studied in the molar ratio 1:1:2.Their spectra are studied in solution form by the UV – Spectrophotometer Labinda 3000^+.

Slater-Condon parameters and Landes parameter are specified by the electronic energy levels. Observed energy levels corresponding to different peaks of Neodymium and Erbium complexes are nearly same as calculated value. Hence R.M.S deviation is small which confirms the formation of complex. On complexation the value of Slater-Condon and Lande's parameters decreases. The ratio of F_4/F_2 for Neodymium compexes is 0.139 and for Erbium complexes is 0.158.

Bonding in rare-earth complexes is weaker than in the 3d complexes. Bonding parameter $b^{1/2}$ expresses bonding strength of rare-earth complexes. In case of rare-earth complexes value of $b^{1/2}$ is small as compared to 3d complexes. This suggests that 4f orbitals are slightly involved in bonding for the rare-earth complexes.

It has been observed from the calculation that bond strength for Neodymium is less than that of Erbium complexes. According to this, as atomic number of metal ion increases, contraction of 4f orbitals increases. By knowing the value of F_2, Nephelauxetic ratio and bonding parameters are calculated. It has been observed that if ligands are same and solvent is same then as atomic number increases, covalency increases. It also increases with increase in number of amino-acids for same rare-earth.

Hypersensitivity is not described by T_2 parameter alone but it is expressed in ratio of T_4/T_2 and T_6/T_2 .Oscillator strength of different peaks can be expressed in terms of T_2, T_4, T_6 parameters. For Neodymium ratio of T_4/T_2 is 2.45 and for Erbium ratio of T_4/T_2 is 0.135.

III. Conclusion

In case of Nd(III) bonding parameter is not real therefore its ternary complexes will make ionic bonding with other ligands. But for Erbium bonding parameter is positive and high which indicates strong covalency. On complexation intensity of peaks are not changes too much but their absorbance changes.

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