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SPECTRAL STUDIES OF ND^{3+}: L-TRYPTOPHAN AMINO ACID COMPLEXES

ABSTRACT

Nd^{3+}:L-tryptophan amino acid complexes have been prepared with the molar concentrations of 0.1, 0.25, 0.5, 1.0 and 2.0 of $NdCl_3$. $6H_2O$.The optical absorption and ultrasonic studies have been recorded. Spectroscopic parameters such as Racah coefficients (E_1, E_2 and E_3), Slater-Condon (F_2, F_4, F_6), and Spin orbit (ξ_{4f}) parameters were computed. The intensity of $^4G_{5/2}$ level and Ω_2 increase with the increase in the concentration of Nd^{3+} ion. The radiative properties of these complexes lifetimes (τ_R), branching ratios (β) and absorption cross sections (σ_a) for certain lasing levels have been computed. The magnitudes of β of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ lasing transition are in the order of 0.62 for all the amino acid complexes which reflect its potential lasing transition.

Key words: Neodymium, L-tryptophan, Optical absorption, Radiative Parameters.

1. INTRODUCTION

The investigations in to the spectroscopic properties of Nd^{3+} ions in various types of glass environments are drawing attention due to their significant applications in the areas like laser, communication and medical technologies [1,2]. The studies on the energy transfer mechanism from one rare earth ion to another rare earth ion for selecting narrow useful emission lines [3] and the transfer of larger magnitudes of laser energies through interesting photonic fibres like HC-PCF [4] are vitalizing the significance of rare earth ions.

The rare earth based solid state materials as lasing materials have certain limitations like poor thermal management in their performance [5-6].The liquid environments as host materials can circumvent certain constraints like thermal behavior exhibited by crystals and glasses. Therefore lanthanide based organic acid complexes gained importance as host media for lasers, optic probes, labels for proteins and amino acids, LEDs and display devices[7-9]. In our earlier works we have attempted to study the lasing properties of Nd^{3+} ions in certain amino acids [10-13]. The present work reports the spectroscopic and ultrasonic properties of Nd^{3+}: L- tryptophan amino acid complexes in varied concentrations of Nd^{3+} ions. The lasing parameters such as lifetimes (τ_R), branching ratios (β) and absorption cross sections (σ_a) have been analyzed.

2. MATERIALS and METHODS

The L-tryptophan and $NdCl_3$ were obtained from Fluka and Indian Rare Earths Ltd. respectively. The neodymium complexes NTRYP 1-5 were prepared by dissolving $NdCl_3$ (0.1, 0.25, 0.5, 1.0, and 2.0 mol%) into spectral pure aqueous L-tryptophan solutions by heating at 90^0c for about 10 minutes and adjusting pH between 6-7 using dilute NaOH [14]. The optical absorption spectra in Vis region were recorded on Jasco spectrophotometer. The refractive indices of these amino acid complexes were determined using an Abbe refractometer.

3. RESULTS & DISCUSSION

The electronic spectra of Nd^{3+}: NTRYP 1-5 amino acid complexes were presented in Fig. 1. The observed absorption peaks were assigned to $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4F_{9/2}$, $^4G_{5/2}$, $^4G_{7/2}$, $^4G_{9/2}$, $^2K_{15/2}$, $^2D_{3/2}$, $^4G_{11/2}$, $^2P_{1/2}$, $^2D_{5/2}$, $^4D_{5/2}$ and $^4D_{7/2}$ electronic levels reported in literature [15,16].

The energy level diagram containing observed absorption and estimated emissions transitions of Nd^{3+}: NTRYP 1 amino acid complex is in Fig. 2. The Racah (E^K, where K = 1, 2, 3), spin-orbit (ξ_{4f}), configuration interaction (α, β, γ) parameters of NTRYP 1-5 amino acid complexes are evaluated by applying Taylor series expansion [15-17] and using the numerical values of zero-order energies and partial

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derivatives[18-20] and are collected in Table 1. From the table it is observed that the ratios of Racah parameters E^1/E^3 and E^2/E^3 are around 9.8 and 0.05 respectively which reflect the approximate values of hydrogenic ratios [21].

The bonding parameter for all these complexes are evaluated using the following expression [22,23] and are given in the Table 1.

$$\text{Bonding parameter } (\delta) = \frac{(1-\bar{\beta})}{\bar{\beta}} \qquad (1)$$

Where $\bar{\beta} = \nu_a/\nu_b$ and ν_a and ν_b are the energies of corresponding transitions in the amino acid complexes and aquo ions respectively. The negative values obtained for all these complexes indicate ionic nature.

The oscillator strengths f_{expt} were measured for the absorption levels using area method from the following equation [24].

$$f_{expt} = 4.318 \times 10^{-9} \int \varepsilon(\upsilon)\, d\upsilon \qquad (4)$$

Where $\varepsilon(\upsilon)$ is the molar extinction coefficient . The squared reduced matrix elements reported in literature [24] were employed in the evaluation theoretical intensities of the electronic levels following least square fit method. The Judd-Ofelt intensity parameters (Ω_λ, $\lambda = 2, 4, 6$) were evaluated from the following equation [23] and are given in Table 2.

$$\Omega_\lambda = [\, 3h\,(2J+1)/8\pi^2\, mc\, \chi\,] \;X\; T_\lambda \qquad (5)$$

The variation in tendency of Ω_λ in all the five complexes observed are observed to be as follows:

$$\Omega_2 > \Omega_4 > \Omega_6$$

It is worthwhile to note that the magnitudes of the environment sensitive Ω_2 parameter and vibration dependant parameter Ω_6 exhibit maximum and minimum values in all the five complexes under study. The spectroscopic quality factor ($\Omega_4/\ \Omega_6$) observed for all the amino acid complexes exhibit least values. This is a favorable feature for an important $^4F_{3/2} \rightarrow {}^4I_{11/2}$ lasing transition of neodymium complexes.

Certain transitions of RE ions in different environments exhibit increased in their intensities in the absorption spectra [25,26]. They are labeled as hypersensitive transitions and they obey the following selection rule

$$\mathbf{\Delta J \leq 2}$$
$$\mathbf{\Delta L \leq 2}$$
$$\mathbf{\Delta S \leq 2}$$

The intensity of the observed hypersensitive transition $^4G_{5/2} \rightarrow {}^4I_{9/2}$ of Nd^{3+} : NTRYP1-5 located in the middle visible region (Fig 3) increases with the increase in the concentration of neodymium in the amino acid complexes [9, 26]. This indicates that there is increment in asymmetry due to the field around the rare earth ion [9, 26, 27].

The radiative transition probabilities (A), electric dipole line strengths (S_{ed}) , fluorescence branching ratios (β_R) and absorption cross sections (σ_a) for certain lasing levels of Nd^{3+}:amino acid complexes have been evaluated using the equations mentioned below [10,20,30].

The radiative transition probabilities (A) is given by

$$A\,(SLJ,S'L'J') = \frac{64\,\pi 4\,\nu 2}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n^2} S_{ed} + n^3 S_{md}\right] \qquad (11)$$

The electric dipole line strength (S_{ed}) is given by

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$$S_{ed} = e^2 \sum_{\lambda=2,4,6} |\langle (S\ L\ J \| U^{\lambda} \| S'L'J') \rangle|^2 \quad (12)$$

The radiative lifetime (τ_R) for $^4F_{3/2}$ state is calculated from the following equation

$$\tau_R = \sum_J A[(^4F_{3/2}):(^4I_J)]^{-1} \quad (13)$$

The fluorescence branching ratios (β_R) can be calculated from the transition probabilities using the following equation [24]:

$$\beta_R\ (^4F_{3/2}):(^4I_J) = A[(^4F_{3/2}):(^4I_J)] / \sum A[(^4F_{3/2}):(^4I_J)] \quad (14)$$

The absorption cross sections (σ_a) are evaluated for certain lasing transitions

$$\sigma_a = \frac{\lambda_P^2}{8\pi c n^2} A(a_j, b_j) \quad (15)$$

The computed values of radiative lifetimes for certain lasing transitions in all the Nd^{3+}: amino acid complexes are presented in Table 4. It is interesting to note that the magnitudes of lifetimes of the transitions show similar trend in NTRYP 1-4 amino acid solutions. This may probably be due to the orderly imposition of NTRYO1-4 amino acid complex environments for the systems under study.

$$^2H_{11/2} > {}^4G_{7/2} > {}^4F_{3/2} > {}^4F_{9/2} > {}^4F_{5/2} > {}^4G_{5/2} > {}^4G_{9/2}$$

The NTRYP 5 shows a slightly different tendency in the magnitudes of its lifetimes for lasing levels as shown:

$$^2H_{11/2} > {}^4G_{7/2} \approx {}^4F_{3/2} > {}^4F_{9/2} > {}^4F_{5/2} > {}^4G_{5/2} > {}^4G_{9/2}$$

The potential lasing transitions $^4F_{3/2} \rightarrow {}^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ depend only upon the ratio Ω_4/Ω_6 known as the spectroscopic quality factor, since Ω_2 does not contribute to the intensity as the magnitude of $\|U^2\|^2$ is zero for these transitions. The $\Omega_4 < \Omega_6$ condition [32] favors the potentiality of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ lasing transition. For all investigated amino acid complexes this condition is well satisfied yielding the values comparable to those reported for other host media [32]. The radiative lifetimes (τ_R) and branching ratios (β_R) for $^4F_{3/2} \rightarrow {}^4I_J$ (J = 13/2, 11/2 and 9/2) transitions of these amino acid complexes (Table 5) are comparable to those reported in the literature [23, 25, 32]. The energy level diagram for estimated lasing transitions and the magnitudes of branching ratios of $^4F_{3/2} \rightarrow {}^4I_J$ (J = 13/2, 11/2 and 9/2) are presented in Fig. 2. The branching ratios β_R obtained for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition are in the order of 0.62 for all the amino acids of the present study indicates its good lasing potency.

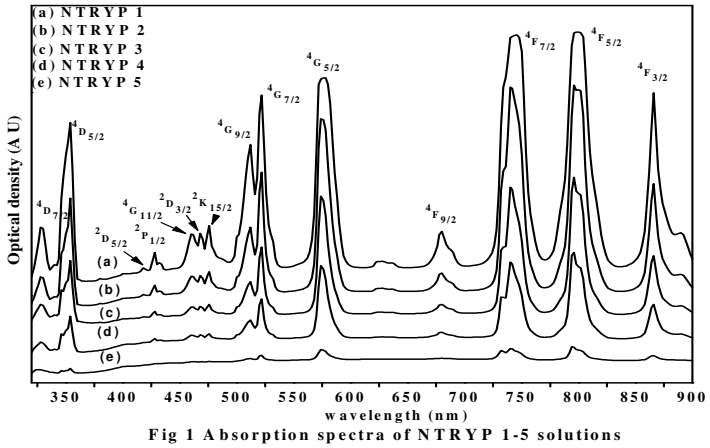

Fig 1 Absorption spectra of NTRYP 1-5 solutions

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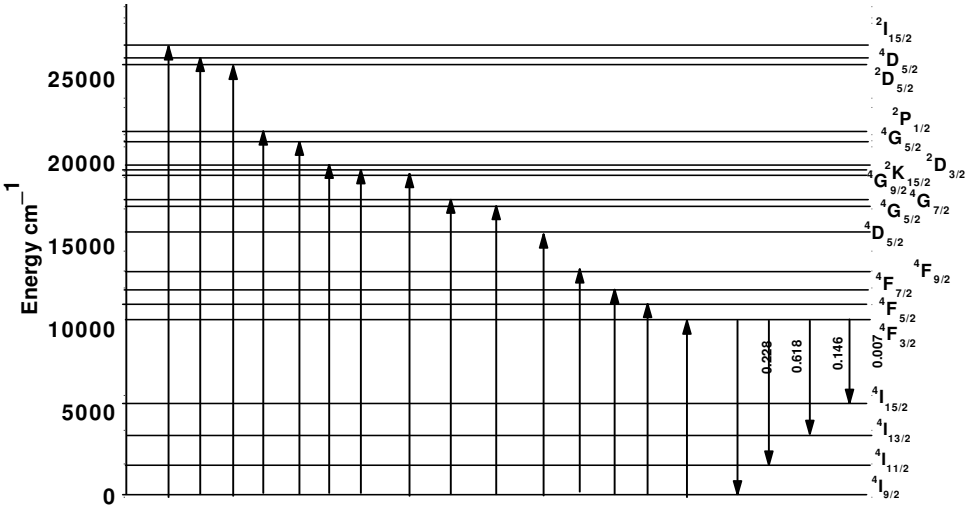

Fig 2. The energy level diagram of observed absorption and estimated emission transitions of Nd^{3+}:NTRYP1 amino acid.

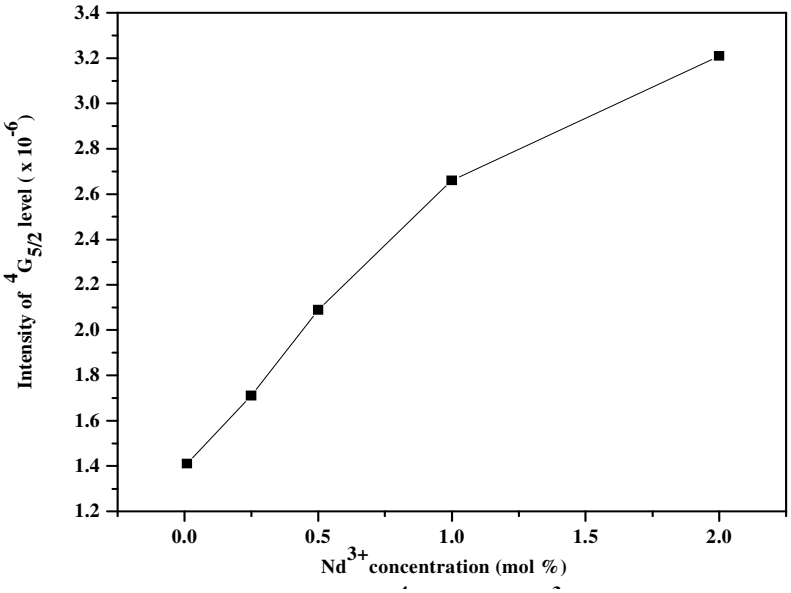

Fig 3. Variation of intensities of $^4G_{5/2}$ level of Nd^{3+}:NTRYP1-5 amino acids.

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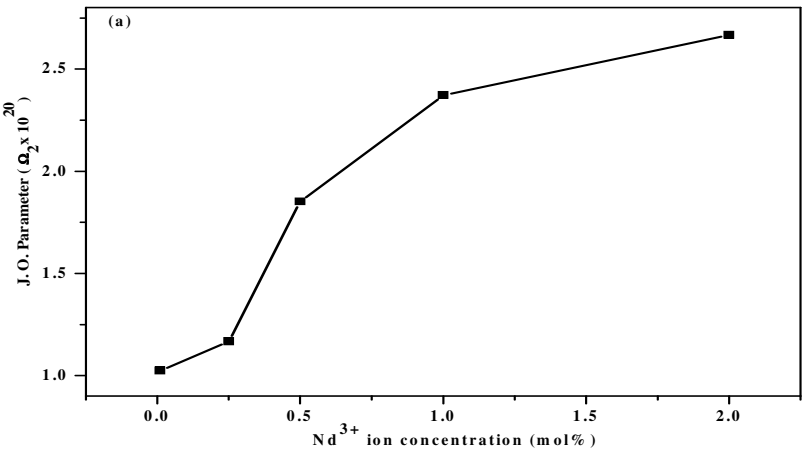

Fig 4. Variation of J.O Parameter with concentration of Nd^{3+}:NTRYP1-5 amino acids.

Parameter	NTRYP 1	NTRYP 2	NTRYP 3	NTRYP 4	NTRYP 5
E^1 (cm^{-1})	4739	4739	4739	4739	4739
E^2 (cm^{-1})	25.65	25.94	24.94	24.79	24.82
E^3 (cm^{-1})	484.1	482.4	482.4	484.8	484.7
ξ_{4f} (cm^{-1})	927.2	924.8	924.9	914.9	917.1
$\alpha(cm^{-1})$	-1.398	-2.126	-2.126	-0.707	-0.664
$\beta(cm^{-1})$	99.27	99.55	99.55	44.16	38.39
$\gamma(cm^{-1})$	1578	1548	1548	1595	1588
F_2 (cm^{-1})	326.9	324.1	324.1	324.2	324.2
$F_4(cm^{-1})$	43.37	44.50	44.50	44.87	44.83
F_6 (cm^{-1})	4.867	4.839	4.839	4.792	4.795
E^1/E^3	9.790	9.825	9.825	9.776	9.778
E^2/E^3	0.053	0.052	0.052	0.051	0.051
B	1.002	1.001	1.001	1.001	1.002
Δ	-0.002	-0.001	-0.001	-0.001	-0.002

Table 1. Spectroscopic parameters of Nd^{3+}; NTRYP 1-5 amino acids.

Solutions/ parameter	NTRYP 1	NTRYP 2	NTRYP 3	NTRYP 4	NTRYP 5
Ω_2	1.023	1.167	1.852	2.372	2.667
Ω_2	0.126	0.935	0.015	0.015	0.012
Ω_2	8.059	5.865	8.465	10.348	10.348
Ω_4 / Ω_6	0.016	0.159	0.002	0.001	0.001
$\Omega_2 + \Omega_4 + \Omega_6$	9.208	7.967	10.331	12.735	15.373

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Table 2: Judd -Ofelt intensity parameters (Ω_λ, λ=2,4,6) (10^{-20} cm^2) of Nd^{3+}: NTRYP 1-5 amino acids.

Lasing level	NTRYP 1	NTRYP 2	NTRYP 3	NTRYP 4	NTRYP 5
$^4G_{9/2}$	150	186	147	120	94
$^4G_{7/2}$	858	954	781	630	422
$^4G_{5/2}$	393	375	315	252	155
$^2H_{11/2}$	10017	12069	9457	7668	5417
$^4F_{9/2}$	446	674	480	395	330
$^4F_{5/2}$	439	636	473	389	315
$^4F_{3/2}$	626	883	675	556	441

Table 3. Computed radiative lifetime (in µs) of certain lasing levels of Nd^{3+} : NTRYP 1-5 amino acids.

Transition		NTRYP 1			NTRYP 2			NTRYP 3			NTRYP 4			NTRYP 5		
		τ_R	β	σ_a	τ_R	β	σ_a	τ_R	β	σ_a	τ_R	β	σ_a	τ_R	β	σ_a
$^4F_{3/2}$	$^4I_{13/2}$	3603	0.17	3.51	5746	0.15	2.31	3862	0.17	3.39	3177	0.17	4013	2774	0.15	4.47
	$^4I_{11/2}$	747	0.66	8.74	1144	0.62	6.04	802	0.67	8.41	660	0.67	10.25	558	0.63	11.52
	$^4I_{9/2}$	626	0.16	1.47	883	0.23	1.54	675	0.16	1.38	556	0.16	1.68	441	0.21	2.67

Table 4. Radiative lifetime (τ_R in µs) Branching rations (β) and integrated absorption cross sections (σ_a x 10^{-18} cm^{-1}) of certain lasing transitions of Nd^{3+}: NTRYP 1-5 amino acids.

CONCLUSIONS

The optical studies on Nd^{3+}: NTRYP 1-5 amino acid complexes are studied. The ionic bonding is observed in these complexes. The ratios of Racah parameters E^1/E^3 and E^2/E^3 are found to be around 9.8 and 0.05 which do not show much deviation from the hydrogenic ratios. The trend in the variation of Judd-Ofelt parameters in all the complexes are in the order of $\Omega_2 > \Omega_4 > \Omega_6$. The magnitudes of environment sensitive Ω_2 parameter and intensities of $^4G_{5/2}$ hypersensitive levels increase with the increase in the Nd^{3+} ion concentration. A favorable trend of less than unity in the values of spectroscopic quality factor (Ω_4/Ω_6) is observed in all the complexes. The magnitudes of branching ratios of the potential $^4F_{3/2} \rightarrow {}^4I_{11/2}$ lasing transition observed in all the amino acids are around 0.62. The Judd-Ofelt intensity parameter Ω_2 decrease with the increase in the Nd^{3+} ion concentration reflecting the orderly imposition of NTRY1-5 amino acid environments.

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