

Study of spectral intensities and bonding parameters of some Tm^{III} doped systems

R.S. VERMA and ARCHANA CHOUDHARY

Department of Chemistry, Government Dungar College, Bikaner (India)

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ABSTRACT

Electronic spectral studies of the saturated solutions of few amino acids, doped with Tm^{III} ions have been done. Spectral intensities were evaluated by using electronic spectra of the above solutions. Spectral intensities include oscillator strengths of various bands and Judd-Ofelt parameters (T_λ). The validity of Judd-Ofelt theory of $f \leftrightarrow f$ transitions has been established. The bonding parameters such as Sinha's covalency ($\delta\%$) covalency angular overlap (η) and mixing coefficient ($b^{1/2}$) have been determined. Covalency in metal ligand bond has been proved on the basis of bonding parameters. Peacock's relation ($p \propto \bar{\nu} T_2$) for hypersensitive transitions has been discussed for Tm^{III} doped systems. This relation is valid for some systems only.

Key words: Spectral intensities, Bonding parameters, Tm^{III} doped systems.

INTRODUCTION

Studies of the spectral properties and coordination chemistry of lanthanide chelates have been widely carried out because of their possible use as a laser materials^{1,2}.

The intensities of the solution spectra of most trivalent lanthanides have been interpreted by means of Judd-Ofelt theory the $f \leftrightarrow f$ transitions are assumed to be forced electric dipole in nature, occurring by the mixing of a higher energy configurations of opposite parity with $4f^N$ configuration via the odd term in crystal field expansion. The equation derived for the oscillator strength (P) of a transition between a ground state ($f^N \Psi_J$) and an excited state ($f^N \Psi_J'$) of the lanthanide ion in solutions is^{3,4}.

$$P = \sum T_\lambda \langle f^N \Psi_J | [U^{(\lambda)}] | f^N \Psi_J' \rangle^2 \quad \dots(1)$$

Where $\lambda = 2, 4, 6 \dots$ and

$\nu =$ the transition energy (expressed in wave numbers)

$\langle f^N \Psi_J | [U^{(\lambda)}] | f^N \Psi_J' \rangle^2$ are the reduced matrix elements of the unit tensor operators $U^{(\lambda)}$, connecting the initial and final states of the transition and T_λ parameters are generally called Judd-Ofelt intensity parameters. The value T_λ parameters have been computed by using partial and multiple regression method⁹⁻¹¹, where the values of reduced matrix elements have been taken from Carnall *et. al.*^{5,6}.

In the present study Tm^{III} ions have been doped with the saturated solution of various ligands in 50% ethanol (v/v). The saturated solutions have been prepared by dissolving various ligands (amino acids) which include L-Cystine, L-Leucine, L-Threonine, L-Proline, β -Alanine, L-Arginine and Aspartic acid in 50% ethanol. The solution spectra of each system has been recorded by using standard spectrophotometer (systronics-106). Judd-Ofelt parameters (T_2, T_4 and T_6) have been computed

by using spectral data. In the present study measurement was done in the range of 400-800nm region. In this region Tm^{III} ion show four peaks^{7,8} corresponding to



The transition ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ is regarded as hypersensitive and ${}^3\text{H}_6 \rightarrow {}^3\text{F}_3$ as pseudo hypersensitive transitions, the Peacock's relation ($p \propto T_2$) has been tried. This relation is valid for a few systems only.

MATERIAL AND METHODS

Tm Cl₃ · 6H₂O (99.9%) was obtained from fluka. All organic ligands were of AR grade (BDH) and spectra pure ethanol was used as solvent.

Preparation of saturated ligand solution

The saturated solution of amino acids were prepared in 50% ethanol at room temp 30°C (±2). This amino acids include β-Alanine, Arginine, L-Proline, L-Leucine, L-Threonine, Aspartic acid and L-Cystine, 0.1 gm of Tm Cl₃ · 6H₂O was added to 10ml of each saturated solution. In this way seven Tm^{III} doped systems were prepared.

Recording of spectra

Each Tm^{III}-doped system was subjected to record solution in the range of 400-800 nm region. Solution spectra were recorded by using systronics-106 spectrophotometer. We have measured four peaks in the 400-800nm region corresponding to transitions from ${}^3\text{H}_6$ to ${}^1\text{G}_4$, ${}^3\text{F}_2$, ${}^3\text{F}_3$ & ${}^3\text{H}_4$ levels.

RESULTS AND DISCUSSION

Intensity parameters

The Juddo-Ofelt^{3,4} intensity parameters (T_2 , T_4 & T_6) have been computed by using "partial and multiple regression method⁹⁻¹¹, The value of oscillator strengths have been computed by using the relation¹².

$$P_{\text{obs}} = 4.6 \times 10^{-9} \times \epsilon_m \times \Delta\nu_{\lambda}^{-1} \quad \dots(2)$$

Where ϵ_m = molar extinction coefficient
= Half intensity band width

The solution spectra are analysed by resolving each band gaussian shaped curve, so as to enable, the evaluation of oscillator strength. The value of oscillator strength of each band is recalculated from the value of T_2 , T_4 & T_6 computed by using the relation^{3,4}.

$$P_{\text{cal}} = T_2 \bar{\nu} [U^{(2)}]^2 + T_4 \bar{\nu} [U^{(4)}]^2 + T_6 \bar{\nu} [U^{(6)}]^2 \dots(3)$$

The compound of oscillator strengths (P_{obs} & P_{cal}) along with energy of transitions have been tabulated in Table 1.

The oscillator strength of ${}^1\text{G}_4$ band varies from 2.07×10^{-6} to 3.55×10^{-6} . Oscillator strength of ${}^3\text{F}_2$ band various from 0.51×10^{-6} to 1.15×10^{-6} , oscillator strength of ${}^3\text{F}_3$ band varies from 7.62×10^{-6} to 9.49×10^{-6} . Oscillator strength of ${}^3\text{H}_4$ band varies from 6.21×10^{-6} to 7.82×10^{-6} .

The r.m.s derivation between P_{obs} & P_{cal} varies from 1.162×10^{-7} to 4.903×10^{-7} . The low values of r.m.s. deviations, showing the validity of Judd-ofelt theory for Tm^{III} doped systems.

The values of Juddo-ofelt parameters (T_2 , T_4 & T_6) have been tabulated in Table 2.

The value of T_2 parameters varies from 9.428×10^{-10} to 14.788×10^{-10} for the present system.

The values of T_4 varies from 10.37×10^{-10} to 14.121×10^{-10} and values of T_6 varies from 2.35×10^{-10} to 3.10×10^{-10} . The general sequence is

$T_4 > T_2 > T_6$ (for L-cystine, L-Leucine, L-threonine, L-Arginine, aspartic acid and for two amino acids (for L-proline & β-alanine)

$$T_4 > T_2 > T_6$$

It is well known fact that T_2 parameter show high sensitivity²⁻³ towards coordinations changes while T_4 & T_6 exhibit more sensitivity towards symmetry changes. Thus the ratio T_4/T_6 (Juddo-ofelt

Table 1: Computed values of Oscillator strengths and observed energy of various bands of Tm (III) doped systems

S. No	Tm(III) Doped systems	¹ G ₄ band			³ F ₂ band			³ F ₃ band			³ H ₄ band			r.m.s. derivation σ(±)
		E _{obs}	P _{obs}	P _{cal}	E _{obs}	P _{obs}	P _{cal}	E _{obs}	P _{obs}	P _{cal}	E _{obs}	P _{obs}	P _{cal}	
1.	L-Cystine	21276	2.661	3.120	15082	0.591	0.914	14493	8.200	8.513	12658	6.405	6.678	3.149×10 ⁻⁷
2.	L-Lucine	21186	2.070	2.690	15105	0.768	1.208	14471	8.098	8.521	12626	6.210	6.579	4.725×10 ⁻⁷
3.	L-Proline	21367	2.513	2.840	15128	0.738	0.968	14492	7.628	7.850	12626	6.288	6.481	2.481×10 ⁻⁷
4.	L-Threonine	21276	3.558	3.318	15082	1.150	0.987	14430	9.660	9.496	12626	6.900	6.757	1.833×10 ⁻⁷
5.	β-Alanine	21276	3.246	3.400	15105	0.886	0.992	14450	8.200	8.304	12626	7.820	7.911	1.162×10 ⁻⁷
6.	Arginine	21276	2.956	3.601	15082	0.517	0.972	14492	8.870	9.308	12658	7.360	7.743	1.903×10 ⁻⁷
7.	Aspartic acid	21186	2.628	3.187	15060	0.683	1.079	14450	8.831	9.212	12626	6.702	7.035	4.28×10 ⁻⁷
8.	Tm ³⁺ aqua ion	21367	-	-	15105	-	-	14492	-	-	12674	-	-	-

Table 2: Computed values of Judd-ofelt intensity parameters and bonding parameters of Tm (III) - doped systems

S. No.	Tm (III) doped	T ₂ ×10 ⁻¹⁰	T ₄ ×10 ⁻¹⁰	T ₆ ×10 ⁻¹⁰	T ₄ /T ₂	T ₄ /T ₆	Nephelauxetic ratio β	Sinha's covalency δ%	Mixing coefficient b ^{1/2}	Covalency angular overlap "η"
1.	L-Cystine	10.682	12.317	2.350	1.1526	5.240	0.9987	0.1301	0.0254	0.0006
2.	L-Lucine	9.428	10.370	3.100	1.0999	3.345	0.9962	0.3814	0.0435	0.0019
3.	L-Proline	10.582	10.527	2.480	0.9947	4.244	0.9962	0.3814	0.0435	0.0019
4.	L-Threonine	9.771	14.121	2.512	1.4451	5.260	0.9962	0.3814	0.0435	0.0019
5.	β-Alanine	14.788	11.393	2.546	0.7703	4.473	0.9962	0.3814	0.0435	0.0019
6.	Arginine	13.245	13.659	2.498	1.0312	5.467	0.9987	0.1301	0.0254	0.0006
7.	Aspartic acid	10.659	12.770	2.776	1.1980	4.600	0.9962	0.3814	0.0435	0.0019

parameter ratio) may be used for determining the change in symmetry around lanthanide ion. In the same way T_4/T_2 ratio may be used for knowing the variation in coordination number around lanthanide ion in doped systems or in complexes. These parameters, however, do not give and information regarding absolute value of symmetry or coordinations number.

The value of T_4/T_2 varies from 0.7703 to 1.4451 and the value of T_4/T_6 varies from 3.345 to 5.620. These value represent very slight change in coordination number & symmetry around Tm^{III} ion in doped systems. As per the value of T_4/T_6 and T_4/T_2 , Tm^{III} doped systems may be classified arbitrarily into the following groups:-

	T_4/T_2 value	Systems
Group A	0.7703-1.1000	(L-Arginine, β -Alanine, L-proline & L-Leucine)
Group B	1.1000-1.5000	(L-Cystine, L-Threonine)

	T_4/T_2 value	Systems
Group A	3.345-4.6000	(L-Leucine, L-Proline Aspartic acid β -alanine)
Group B	5.240-5.620	(L-Cystine, L-Threonine, L-Arginine)

Each group represents almost the same symmetry and coordination number around Tm^{III} ion.

Nephelauxetic ratio (β) and bonding parameters

The effect of complexation on the free ion is the red shift of the electronic transitions¹⁴⁻¹⁵.

This red shift of the bands is due to the expansion of the central metal orbital radius, resulting in the decrease in interelectronic repulsion parameters.

The phenomenon is called nephelauxetic effect. This effect is measured in terms of nephelauxetic ration (β) and is given by

$$\beta = \bar{\nu} \text{ system} / \bar{\nu} \text{ aqua} \quad \dots(4)$$

In the present study, we have observed red shift for all the spectral bands measured.

The following bonding parameters may be computed by using the nephelauxetic ration (β).

Sinha's covalency parameter ($\delta\%$)

$$\delta = \frac{1-\beta}{\beta} \times 100$$

Covalency angular overlap parameter (η)

$$\eta = \left(\frac{1-\beta^{1/2}}{\beta^{3/2}} \right)$$

Mixing coefficient or covalency factor ($b^{3/2}$)

$$b^{3/2} = \left(\frac{1-\beta}{2} \right)^{3/2}$$

Table 3: Validity of Peacock's relation ($p \propto T_2$) for Tm^{3+} doped system

S. No.	Tm^{3+} - doped systems	$P_{obs} \times 10^6$ (for band 3H_4 cm^{-1})	Energy of 3H_4 band (cm^{-1})	$T_2 \times 10^{10}$	$\nu T_2 \times 10^{10}$	$k = \frac{P_{obs}}{\nu T_2}$
1.	L-Cystine	6.405	12658	12.317	155908.58	0.4108
2.	L-Leucine	6.210	12626	10.370	130931.62	0.4742
3.	L-Threonine	6.900	12626	14.121	178291.74	0.3870
4.	L-Proline	6.288	12626	10.527	132913.90	0.4730
5.	β -Alanine	7.820	12626	11.393	143848.01	0.5436
6.	Arginine	7.360	12658	13.659	172895.62	0.4256
7.	Aspartic acid	5.913	12642	12.770	161438.34	0.3662

The computed values of nephelauxetic ratio (β) and various bonding parameters ($\delta\%$, η and $b^{3/2}$) have been tabulated in Table 3.

The value of β varies from 0.9962-0.0254. Sinha's covalency parameter ($\delta\%$) varies from 0.3814% to 0.1301% and covalency angular parameter (η) varies from 0.0019 to 0.0006, showing very slight (partial) covalency in metal-ligand linkage.

The trend in the following parameters or covalency in L-Leucine \approx L-Proline = β -alanine-Aspartic acid and L-Threonine > L-cystine \approx L-Arginine.

Thus, five amino acids show stronger covalent character in metal=ligand bond. Only two amino acids, viz., L-cystine & L-Arginine, show weaker covalent interaction with Tm^{III} ion.

Hyper sensitive transitions

Certain transitions, called hypersensitive exhibit a relatively strong sensitivity to the environment around the metal ion.

Jorgensen & Judd¹⁶ have concluded from a detailed study that the transitions following the selection rules $\Delta J \leq 2$, $\Delta L \leq 2$ and $\Delta S = 0$, should be considered in this category.

From Tm^{III} ion, the transition ${}^3H_6 \rightarrow {}^3H_4$ is regarded as hypersensitive. For hypersensitive transition, the oscillator strength is directly proportional to T_2 , as proposed by R.D. Peacock^{2,15}. Hence the proportionality constant ($k = P_{obs} / \nu T_2$) should be constant.

A perusal of data reported in Table 3 reveals that the value of k is almost constant for the present systems only β -alanine and Aspartic acid show larger deviations.

Pseudo hypersensitive transitions

Certain transitions¹⁷⁻¹⁹, which do not obey selection rule for hypersensitive transition but show larger sensitivity to ligand and environment are called pseudo hypersensitive.

In case of Tm^{III} doped system, the transition ${}^3H_6 \rightarrow {}^3F_3$ is regarded as Pseudo-hypersensitive transition. In most of the amino acid systems the oscillator strength of this transition is considerably higher than the oscillator strength of hypersensitive transition.

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