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OPTICAL ABSORPTION SPECTRA OF Nd^{3+} IONS IN ORGANIC ACIDS

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Various spectroscopic parameters of Nd^{3+} ion in malic, α-ketoglutamic and tartaric acids have been evaluated from the measured spectral data. Judd-Ofelt intensity parameters (Ω_λ) have been derived from the band intensities. Relationship between the Judd-Ofelt intensity parameter (Ω_2) and intensitities of hypersensitive level ($^4G_{5/2}$) of Nd^{3+} ion in three acids are satisfactorily explained. Radiative lifetimes (T_R) and branching ratios (β) have been determined theoretically for certain excited states of Nd^{3+} ions in three organic acids.

Key Words : Energy Levels; Judd-Ofelt Intensity Parameters; Lifetimes; Branching Ratios

INTRODUCTION

SPECTRAL studies on Nd^{3+} ion in certain organic acid complexes have been carried out by several workers in the recent past.[1–8] In the present paper, the authors report the spectroscopic parameters for Nd^{3+} ions in malic, α-ketoglutamic and tartaric acids.

EXPERIMENTAL STUDIES

Neodymium acid complexes were prepared by dissolving one mol% of $Nd(NO_3)_3\,6H_2O$ into the saturated solutions of malic, α-ketoglutamic and tartaric acids. Absorption spectra of neodymium organic acid complexes have been recorded on Perkin-Elmer 551 (UV-VIS) and Carl-Zeiss Specord-61 (NIR) spectrophotometers. The refractive indices of these organic acids were measured using PZO warszawava 3275 refractometer.

RESULTS AND DISCUSSION

Electronic Energy Levels

For the measured absorption spectra, the assignments of the electronic energy states of Nd^{3+} organic acids have been made by following the procedures of

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Dieke.[7] From the observed band positions using the least-square fit method, the energy levels have been theoretically evaluated[8] and are presented in Table I. The rms deviation obtained is reasonably low. The Racah (E^k), spin-orbit (ξ_{4f}), configurational interaction (α) parameters have been obtained using the expressions given by Lakshman and Jayasankar[9] and that are given in Table II.

TABLE I

Experimental and calculated energy levels (in cm^{-1}) of Nd^{+3} acid complexes

Terms from $^4I_{9/2}$	Nd^{+3}					
	Malic acid		α-ketoglutamic acid		Tartaric acid	
	E_{expt}	E_{calc}	E_{expt}	E_{calc}	E_{expt}	E_{calc}
$^4F_{3/2}$	11625	11614	11571	11607	11625	11720
$^4F_{5/2}$	12689	12641	12559	12554	12623	12530
$^4F_{7/2}$	13602	13655	13639	13678	13583	13562
$^4F_{9/2}$	14877	14932	14723	14603	14921	15101
$^2H_{11/2}$	16125	16133	15996	15992	16125	16114
$^4G_{5/2}$	17478	17388	17487	17489	17478	17443
$^4G_{7/2}$	19300	19285	19225	19176	19300	19256
$^4G_{9/2}$	19680	19720	19790	19694	19757	19715
$^4G_{11/2}$	21828	21772	21639	21634	21876	21944
$^2P_{1/2}$	23523	23487	23413	23432	24624	24701
$^4D_{5/2}$	28893	28971	—	—	—	—
rms deviation	±64.21		±64.29		±114.99	

TABLE II

Spectroscopic parameters of Nd^{3+} organic complexes

Parameters	Nd^{3+}		
	Malic acid	α-ketoglutamic acid	Tartaric acid
E^1 (cm^{-1})	4874.100	4938.454	5411.890
E^2 (cm^{-1})	25.125	25.672	33.978
E^3 (cm^{-1})	497.198	504.662	514.996
ϵ_{4f} (cm^{-1})	885.006	833.698	869.489
α (cm^{-1})	1.549	5.323	13.227
$\Omega_2 \times 10^{20}$ cm^2	6.647	0.809	2.338
$\Omega_4 \times 10^{20}$ cm^2	10.836	0.240	0.994
$\Omega_6 \times 10^{20}$ cm^2	10.108	3.902	7.448
n	1.3460	1.3455	1.3650

Spectral Intensities

The intensity of an absorption band is measured by its oscillator strength, which is directly proportional to the area under the curve. The oscillator

strength (f) can be expressed in terms of the molar absorptivity (ϵ), the energy of the transition in wavenumber (ν) by the relation[10]

$$f = 4.32 \times 10^{-9} \int \epsilon (\nu)\, d\nu$$

In the evaluation of the integral part namely $\int \epsilon (\nu)\, d\nu$ normally one of the following three methods is in practice :-

1. Half width method
2. Area method
3. Weight method

In the present study, the authors could comfortably make use of the area method, as there has been a good accuracy in the measurement. From the integrated intensities of the absorption bands, three Judd-Ofelt intensities (Ω_2, Ω_4, Ω_6) parameters are computed[4] and that are given in Table II. The theoretically evaluated intensities of the bands are given in Table III. The rms deviations thus obtained are in acceptable magnitude. From Table III, it is observed that the variation in the trend of the Judd-Ofelt intensity parameters are as follows :—

$$\Omega_{2,4,6} = \text{Malic acid} > \text{Tartaric acid} > \alpha\text{-ketoglutamic acid}$$

TABLE III

Experimental and calculated intensities for the energy levels of Nd^{3+} acid complexes

Terms from $^4I_{9/2}$	Nd^{3+}					
	Malic acid		α-ketoglutamic acid		Tartaric acid	
	f_{expt} ($\times 10^6$)	f_{calc} ($\times 10^6$)	f_{expt} ($\times 10^6$)	f_{calc} ($\times 10^6$)	f_{expt} ($\times 10^6$)	f_{calc} ($\times 10^6$)
$^4F_{3/2}$	1.096	1.735	1.459	1.210	1.452	1.916
$^4F_{5/2}$	8.829	8.829	8.194	9.569	7.028	7.043
$^4F_{7/2}$	8.482	5.068	8.044	5.847	7.671	7.790
$^4F_{9/2}$	1.171	1.162	—	—	—	—
$^4G_{5/2}$	10.712	10.708	13.886	13.902	9.169	9.167
$^4D_{5/2}$	1.760	1.544	1.356	1.345	1.761	1.493
	rms deviation ± 2.009		± 2.017		± 1.195	

It is also noted that the environment sensitive (Ω_2)[11] and vibrionic dependent (Ω_6)[12] parameters exhibit the highest and the lowest values in Malic and α-ketoglutamic acids.

Hypersensitive Transitions

Transitions, where intensities are particularly sensitive to the host and follow the selection rule

$$\Delta J \leqslant 2, \qquad \Delta L \leqslant 2 \qquad \text{and } \Delta S \leqslant 0$$

For Nd^{3+} ion $^4I_{9/2} \rightarrow {}^4G_{5/2}$ is the hypersensitive transition.[13] The environment sensitive (Ω_2) parameter and the intensities of hypersensitive $^4G_{5/2}$ level connected to the present work are given in Table IV. From this Table, it is observed that Ω_2 increases with increase in the intensity of $^4G_{5/2}$ level which is in accordance with the Judd-Ofelt theory.[12]

TABLE IV

Intensities of hppersensitive level ($^4G_{5/2}$) and Judd-Ofelt intensity parameter (Ω_2) of Nd^{3+} organic acid complex

	Nd^{3+}		
	Malic acid	α-ketoglutamic acid	Tartaric acid
$\Omega_2 \times 10^{20}$	6.647	0.809	2.338
f_{expt} ($\times 10^6$)	5.038	2.297	5.609

Radiative Lifetimes and Branching Ratios

The radiative lifetimes (T_R) for the excited states $^4F_{3/2, 5/2, 9/2}$, $^2H_{11/2}$, $^4G_{5/2, 7/2, 9/2}$ of Nd^{3+} ion in three organic acids are evaluated[10] and presented in Table V. Depending upon the lifetimes values, the following trend has been noted by the authors in three different acid media :

TABLE V

Computed radiative lifetimes (T_R) (in μs) for the fluorescent levels of Nd^{3+} organic acid complexes

	Nd^{3+}		
Level	Malic acid	α-ketoglutamic acid	Tartaric acid
$^4F_{3/2}$	180	1115	563
$^4F_{5/2}$	216	892	457
$^4F_{9/2}$	247	881	458
$^2H_{11/2}$	2749	14008	7617
$^4G_{5/2}$	62	572	28
$^4G_{7/2}$	122	675	261
$^4C_{9/2}$	77	26	312

Nd^{3+} (malic acid) : $^2H_{11/2} > {}^4F_{9/2} > {}^4F_{5/2} > {}^4F_{3/2} > {}^4G_{7/2} > {}^4G_{9/2} > {}^4G_{5/2}$

Nd^{3+} (α-ketogluta-mic acid) : $^2H_{11/2} > {}^4F_{3/2} > {}^4F_{5/2} > {}^4F_{9/2} > {}^4G_{7/2} > {}^4G_{5/2} > {}^4G_{9/2}$

$$Nd^{3+} \text{ (tartaric acid : } {}^2H_{11/2} > {}^4F_{5/2} > {}^4F_{9/2} > {}^4F_{5/2} > {}^4G_{9/2} > {}^4G_{7/2} > {}^4G_{5/2}$$

Of these seven excited states, only $^2H_{11/2}$ has the maximum value in all hosts, compared to the other remaining states of the ion studied.

Branching ratio (β) is a parameter which characterizes the lasing potency of a particular transition.[11,14] The lifetimes and branching ratios for $^4F_{3/2} \rightarrow {}^4I_J$ (J = 9/2, 11/2, 13/2) transition in three acids are listed in Table VI. From this table, it is observed tnat the below-mentioned situation exists pertaining to the lasing lifetime values which are given in micro seconds (μs).

TABLE VI

Radiative lifetimes (T_R) (in μs) and branching ratios (β) of lasing levels of Nd^{3+} organic acid complexes

Transition	Parameter	Nd^{3+}		
		Malic acid	α-ketoglutamic acid	Tartaric acid
$^4F_{3/2} \rightarrow {}^4I_{13/2}$	T_R (μs)	3010	7808	4171
	β	0.056	0.136	0.128
$^4F_{3/2} \rightarrow {}^4I_{11/2}$	T_R (μs)	460	1510	791
	β	0.330	0.596	0.576
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	T_R (μs)	180	1115	563
	β	0.610	0.262	0.289

$$T_R : {}^4F_{3/2} \rightarrow {}^4I_{13/2} > {}^4F_{3/2} \rightarrow {}^4I_{11/2} > {}^4F_{3/2} \rightarrow {}^4I_{9/2}$$

With regard to the branching ratios (β), there has been a different order as mentioned below:

$$\beta : {}^4F_{3/2} \rightarrow {}^4I_{11/2} > {}^4F_{3/2} \rightarrow {}^4I_{9/2} > {}^4F_{3/2} \rightarrow {}^4I_{13/2}$$

In all the hosts studied, the most efficient lasing transition thus identified is $^4F_{3/2} \rightarrow {}^4I_{11/2}$, depending upon the branching ratio value.

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