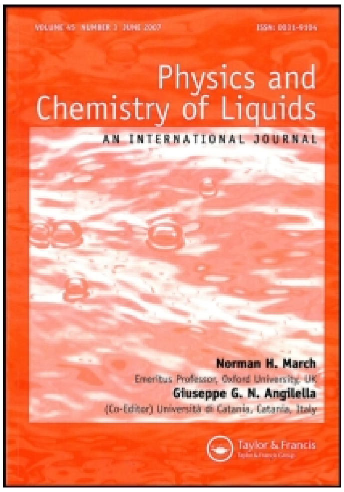

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Energy Levels and Band Intensities of Neodymium Organic Acid Complexes

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The optical absorption spectra of Nd^{3+} ion in glutamic, L-aspartic and maleic acids in UV-VIS and NIR regions have been recorded. From the spectral data thus obtained, various spectroscopic parameters are evaluated. The radiative lifetimes (τ_R) and branching ratios (β) for the excited states of Nd^{3+} ion in three acids have been computed. The relationship between the environment sensitive Judd-Ofelt parameter (Ω_2) and the intensities of hypersensitive level ($^4G_{5/2}$) is in good coincidence following the Judd–Ofelt theory.

Key Words: Branching ratio, radiative lifetime.

INTRODUCTION

Spectral studies of Nd^{3+} ion in mineral,[1–3] organic[4–8] and laser[9–10] liquids are available already in literature. In the present paper, we report the environmental effect on Nd^{3+} ion in three organic acids.

EXPERIMENTAL

One mol % of $NdCl_3$ is mixed in to the saturated solutions of glutamic, L-aspartic and maleic acids. The absorption spectra have been recorded in UV-VIS and NIR regions on Perkin-Elmer 551 and Carl-Zeiss Specord-61 spectrophotometers. The refractive indices of the three organic complexes were measured using PZO Warszawava 3275 refractometer. The intensities of the absorption bands are measured using area method following the expression.[11]

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

where ε is molar absorptivity and ν is the energy of the transition in wavenumber.

RESULTS AND DISCUSSION

Electronic Energy Levels

From the recorded spectra the energy levels have been assigned appropriately by following Dieke.[12] Using the partial derivatives[13] and adopting the least square fit analysis, the energy levels are fitted theoretically and are given in Table 1. The rms deviation is found to be reasonable. The Racah (E^k), spin-orbit (ξ_{4f}) and configurational interaction (α) parameters have been evaluated[8] and are given in Table 2.

Table 1 Experimental and calculated energylevels (in cm^{-1}) of Nd^{3+} acid complexes.

Terms from $^4I_{9/2}$	Nd^{3+}					
	Glutamic acid		L-aspartic acid		Maleic acid	
	E_{expt}	E_{calc}	E_{expt}	E_{calc}	E_{expt}	E_{calc}
$^4F_{3/2}$	11652	11531	11625	11500	11638	11621
$^4F_{5/2}$	12687	12672	12559	12440	12639	12625
$^4F_{7/2}$	13620	13712	13510	13564	13583	13684
$^4F_{9/2}$	14887	14877	14867	14913	14877	14941
$^2H_{11/2}$	16125	16195	16125	16056	—	...
$^4G_{5/2}$	17508	17433	17296	17165	17478	17459
$^4G_{7/2}$	19337	19311	19225	19102	19374	19362
$^4G_{9/2}$	19718	19766	19526	19577	19680	19771
$^4G_{11/2}$	21924	21847	21639	21690	21924	21849
$^2P_{1/2}$	23578	23540	23468	23439	23523	23511
$^4D_{5/2}$	28977	29056	28810	28676	29061	29093
rms deviation	$\pm$91.70		$\pm$126.31		$\pm$63.59	

Table 2 Spectroscopic parameters of Nd^{3+} organic complexes.

Parameter	Nd^{3+}		
	Glutamic acid	L-aspartic acid	Maleic acid
E^1 (cm^{-1})	4882.785	4845.168	4897.691
E^2 (cm^{-1})	25.545	26.047	25.548
E^3 (cm^{-1})	498.450	488.473	500.862
ξ_{4f} (cm^{-1})	892.096	913.980	887.269
α (cm^{-1})	1.896	0.640	4.021
$\Omega_2 \times 10^{20}$ cm^2	3.627	6.049	2.437
$\Omega_4 \times 10^{20}$ cm^2	2.169	0.109	3.466
$\Omega_6 \times 10^{20}$ cm^2	12.046	14.418	8.623
n	1.3410	1.3450	1.3485

Intensity Parameters

Intensities of the absorption levels of Nd^{3+} ion in three acids have been measured using area method. The theoretically evaluated[11] intensities of the levels are listed in Table 3. A reasonable rms deviation is observed. Following Ramesh Babu *et al.*,[8] Judd–Ofelt intensity parameters have been derived and are presented in Table 2. The trend in variation of Ω_λ parameters of Nd^{3+} ion in three acids are as follows:

Ω_2: L-aspartic acid > Glutamic acid > Maleic acid

Ω_4: Maleic acid > Glutamic acid > L-aspartic acid

Ω_6: L-aspartic acid > Glutamic acid > Maleic acid

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

Terms from $^4I_{9/2}$	Nd^{3+}					
	Glutamic acid		L-aspartic acid		Maleic 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} ($\times 10^6$)
$^4F_{3/2}$	3.997	4.603	0.600	0.965	0.601	0.965
$^4F_{5/2}$	12.702	10.773	4.398	5.389	4.396	5.389
$^4F_{7/2}$	11.543	15.029	3.827	3.148	3.827	3.148
$^4F_{9/2}$	1.544	1.120	—	—	—	—
$^4G_{5/2}$	25.038	25.036	5.609	6.588	5.609	6.588
$^4D_{5/2}$	3.309	3.072	—	—	0.645	0.945
rms deviation	± 2.339		± 2.407		± 2.797	

Table 4 Intensities of hypersensitive level ($^4G_{5/2}$) and Judd–Ofelt intensity parameter (Ω_2) of Nd^{3+} organic acid complexes.

	Nd^{3+}		
	Glutamic acid	L-aspartic acid	Maleic acid
$\Omega_2 \times 10^{20}$ cm^2	3.627	6.049	2.437
f_{expt} ($\times 10^6$)	10.712	13.886	9.169

It is also noted that the environment sensitive (Ω_2)[14] and vibronic dependant (Ω_6)[15] parameters exhibit maximum and minimum values both in L-aspartic and Maleic acids.

Hypersensitive Transitions

Transitions which are sensitive to the host environment are called the hypersensitive transitions. They obey the following selection rule.

$$\Delta J \leq 2, \quad \Delta L \leq 2 \quad \text{and} \quad \Delta S \leq 0$$

For Nd^{3+} ion $^4I_{9/2} \rightarrow {}^4G_{5/2}$ is the hypersensitive transition.[16] Table 4 represents the Ω_2 values and intensities of $^4G_{5/2}$ level of Nd^{3+} ion in three acids. From this Table it is evident that Ω_2 increases with the increase in intensity of $^4G_{5/2}$ level verifying the validity of the Judd–Ofelt theory.[15]

Radiative Lifetimes and Branching Ratios

The radiative lifetimes 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 acids have been computed[8] and are presented in Table 5. The variational trend of the energy levels of Nd^{3+} ion in three acids are stated as follows:

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

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

It is noted that $^2H_{11/2}$ and $^4G_{5/2}$ excited states of Nd^{3+} ion yield maximum and minimum values for their lifetimes in all the three acid media.

Lasing potency defining parameter namely branching ratio[14] and radiative lifetimes (τ_R) for $^4F_{3/2} \rightarrow {}^4I_J$ ($J = 9/2, 11/2, 13/2$) lasing lines

Table 5 Computed radiative lifetimes (τ_R) (in μs) for the fluorescent levels of Nd^{3+} organic acid complexes.

Level	Nd^{3+}		
	Glutamic acid	L-aspartic acid	Maleic acid
$^4F_{3/2}$	333	316	392
$^4F_{5/2}$	273	249	334
$^4F_{9/2}$	276	244	352
$^2H_{11/2}$	4958	3833	5501
$^4G_{5/2}$	132	106	138
$^4G_{7/2}$	155	225	153
$^4G_{9/2}$	195	143	183

Table 6 Radiative lifetimes (τ_R) (in μs) and branching ratios (β) of lasing levels of Nd^{3+} organic acid complexes.

Transition	Nd^{3+}			
	Parameter	Glutamic acid	L-aspartic acid	Maleic acid
$^4F_{3/2} \rightarrow {}^4I_{13/2}$	τ_R (μs)	2554	2116	3510
	β	0.124	0.142	0.106
$^4F_{3/2} \rightarrow {}^4I_{11/2}$	τ_R (μs)	479	415	622
	β	0.565	0.612	0.519
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	τ_R (μs)	333	316	392
	β	0.305	0.239	0.369

are shown in Table 6. The variational trend of both β and τ_R of these three levels in three organic complexes are as shown below:

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

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

This situation explains that $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition exhibits maximum lasing potency (β) in all the three organic complexes studied.

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