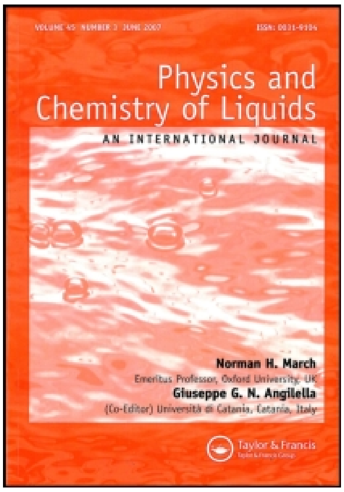

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Optical Properties of $Ho(NO_3)_3$ $6H_2O$: Organic Acid Complexes

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OPTICAL PROPERTIES OF $Ho(NO_3)_3\ 6H_2O$: ORGANIC ACID COMPLEXES

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Optical absorption studies have been carried out from the UV to NIR for Ho^{3+} ions (0.1 M%) mixed organic acids namely anthrolinic, benzoic, salicylic and pthalic acids. Spectral intensities of various observed bands of Ho^{3+} have neen affected very significantly depending upon the surrounding environment. We made a correlation between the intensity parameters and the spectral intensities quite clearly by the application of Judd-Ofelt theory. Of the various levels recorded, particularly the energy level $^5G_6 \leftarrow {}^5I_8$ has shown a distinctive phenomenon in its intensity magnitudes as a function of the host. We have also examined the bonding nature of the complexes, as ionic for Ho^{3+} in four different fluorescing organic acids.

KEY WORDS: Spectral intensities, complexes bonding nature.

INTRODUCTION

Over a period of one decade, we have made a detailed study on the electronic absorption spectra of Pr^{3+} and Nd^{3+} ions in various inorganic liquids. [1-7] Recently we have established the analysis of the spectral profiles of Sm^{3+} complexes in inorganic and organic media.[8,9] In the recent years, an important attention is being given to two different rare earth ions such as Ho^{3+} and Nd^{3+} as they display lasing properties.[10] Very recently, the fluorescence properties on Ho^{3+} doped anthrolinic benzoic, salicylic and pthalic acids were reported.[11] As a continuation to the fluorescence studies on the Ho^{3+} complexes reported earlier[11], we now present the analysis of the spectral intensities and radiative properties of Ho^{3+} doped organic acid complexes by the measurement of the absorption spectra form UV to NIR.

EXPERIMENTAL

The holmium complexes were prepared by dissolving 0.1 M% $Ho(NO_3)_3 6H_2O$ into the spectral pure liquids of anthrolinic, benzoic, salicylic and pthalic acids. The absorption spectral recordings of these holmium complexes were carried out from UV to NIR on two different spectrophotometers. By using a sodium vapour lamp, the refractive indices of four Ho^{3+} complexes were measured on a scientific refractometer.

RESULTS AND DISCUSSION

By following the standard procedures already reported in literature,[12,13] we assigned the measured bands with the necessary electronic transitions, as given below:

$$\begin{aligned} {}^5I_8 &\rightarrow {}^5I_{6,5,4} \\ &\rightarrow {}^5F_{5,4,3,2} \\ &\rightarrow {}^5G_{6,5,4,3,2} \\ &\rightarrow {}^3H_6 \\ &\rightarrow {}^3D_3 \end{aligned}$$

The observed energy levels with their energies (in cm^{-1}) are listed in Table 1. From this table, we have noticed that the energy states namely ${}^5G_{4,3}$ and ${}^3H_6$ could not be identified in anthrolinic acid, due to the fact of the more quenching property of this particular fluorescing organic acid as has been explained earlier.[11]

Spectral intensities

For the observed bands, the measurement of the spectral intensities was carried out from the expression:

$$f_{\text{expt.}} = 4.32 \times 10^{-9} \int \frac{A}{BC}\, d\nu$$

Where A = band absorbance value
B = pathlength of the cell (1 cm)
C = rare-earth ion concentration in the environmental and
$d\nu$ = band's width at half height.

The theoretical evaluation of spectral intensities was also made from the following two computational methods.

(i) Judd–Ofelt (f^{JO}_{cal}) method.[14,15]
(ii) Electric dipole-line strength ($f^{\text{em}}_{\text{cal}}$) method.[16]

i) Judd–Ofelt method According to the Judd–Ofelt theory, theoretical intensities of the bands could be obtained from the formulae

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

Table 1 The measured band energies (in cm^{-1}) of the various observed levels of $Ho(NO_3)_3\ 6H_2O$: Organic acid complexes.

Energy levels from the ground $^5I_8$	*$Ho(NO_3)_3\ 6H_2O$*			
	Anthrolinic acid	*Benzoic acid*	*Salycilic acid*	*Pthalic acid*
$^5I_5$	8687	8656	8563	8625
$^5I_5$	11299	11236	11261	11299
$^5I_4$	14489	14447	14323	14184
$^5F_5$	15670	15670	15621	15670
$^5F_4$	18657	18762	18621	18727
$^5F_3$	20704	20747	20576	20704
$^5F_2$	21277	21276	21186	21231
$^5G_6$	22321	22321	22124	22321
$^5G_5$	24155	24038	23981	24096
$^5G_4$	—	25974	25907	25907
$^3H_6$	—	27778	27307	27855
$^5G_3$	—	—	28736	—
$^3D_3$	32154	32258	—	—

Where v is the energy (in cm^{-1}) of the band concerned and T_2, T_4 and T_6 are the Judd–Orfelt parameters $(U^2)^2$, $(U^4)^2$ and $(U^6)^2$ are the squared reduced matrix elements. The squared reduced matrix elements for various energy states that are used (Table 3) in the present work are the same as that of Ho^{3+} (aquo) published by Carnall and his co-workers.[17] Based on the suggestions made in literature by the several laser chemistry groups,[18,19] we too have not noticed any abnormal variations in the values of these squared reduced matrix elements with the change of environments surrounding the rare-earth ion. Therefore the same set of $|U^\lambda|^2$ values for

Table 2 Judd–Ofelt (T_2, T_4, T_6), refractive indices (n), intensity (Ω_2, Ω_4, Ω_6), nephelauxetic ($\bar{\beta}$) and bonding (δ) parameters for $Ho(NO_3)_3 6H_2O$: Organic acid complexes.

Parameters	*$Ho(NO_3)_3 6H_2O$*			
	Anthrolinic acid	*Benzoic acid*	*Salycilic acid*	*Pthalic acid*
$T_2 \times 10^9$ (cm^2)	0.353	0.125	0.125	0.053
$T_4 \times 10^9$ (cm^2)	0.085	0.688	0.477	0.468
$T_6 \times 10^9$ (cm^2)	0.608	0.602	0.626	0.539
n	1.339	1.337	1.337	1.337
$\Omega_2 \times 10^{20}$ (cm^2)	4.628	1.191	1.643	0.697
$\Omega_4 \times 10^{20}$ (cm^2)	1.116	9.040	6.273	6.146
$\Omega_6 \times 10^{20}$ (cm^2)	7.978	7.908	8.228	7.086
$\bar{\beta}$	1.000154	1.002339	1.000884	1.006651
δ	−0.015397	−0.233363	−0.088419	−0.660777

Table 3 The squared reduced matrix elements $(\psi J|U^{\lambda}|^2\psi' J')^2$ for various states of HO^{3+} (aquo) used in the present work for evaluating the theoretical intensities and electric dipole linestrengths.

Energy levels from the ground state $^5I_8$	ν (cm^{-1})	$\lvert U^2\rvert^2$	$\lvert U^4\rvert^2$	$\lvert U^6\rvert^2$
$^5I_6$	8580	0.0084	0.0386	0.6921
$^5I_5$	11120	0	0.0100	0.0936
$^5F_4$	13300	0	0	0.0077
$^5F_5$	15500	0	0.04250	0.5687
$^5F_4$	18500	0	0.2392	0.7071
$^5F_3$	20600	0	0	0.3460
$^5F_2$	21100	0	0	0.1921
$^5G_6$	22100	1.5201	0.8410	0.1411
$^5G_5$	23950	0	0.5338	0.0002
$^5G_4$	25800	0	0.0315	0.0359
$^3H_6$	27700	0.2155	0.1179	0.0028
$^5G_3$	28800	0	0	0.0133
$^3D_3$	33200	0	0	0.0030

various energy levels of Ho^{3+} (aquo) have been used in our present calculations as well. By substituting the experimental values for f_{cal} and also by using the listed data in Table 4, the values of Judd–Ofelt parameters (T_2, T_4 and T_6) have been computed by performing a least-squares fit procedure. And the computed values of f_{cal} are presented in Table 5 along-with experimental $f_{\text{expt.}}$ values. The values of Judd–Ofelt (T_2, T_4, T_6), refractive indices (n) of holmium complexes are tabulated in Table 2.

Table 4 The evaluated values of electric dipole linestrengths ($S_{\text{ed}} \times 10^{20}$) for computing the theoretical spectral intensities ($f^{\text{ed}}_{\text{cal}} \times 10^6$) of the energy levels of $Ho(NO_3)_3\ 6H_2O$: Organic acid complexes.

Energy levels from the ground $^5I_8$	$Ho(NO_3)_3\ 6H_2O$			
	Anthrolinic acid	*Benzoic acid*	*Salycilic acid*	*Pthalic acid*
$^5I_6$	5.603	5.832	5.950	5.147
$^5I_5$	0.757	0.830	0.832	0.724
$^5I_4$	0.064	0.061	0.063	0.546
$^5F_5$	5.011	8.339	7.346	6.641
$^5F_4$	5.908	7.754	7.319	6.480
$^5F_3$	2.760	2.736	2.847	2.451
$^5F_2$	1.533	1.519	1.581	1.361
$^5G_6$	9.099	10.528	8.934	7.227
$^5G_5$	0.587	4.827	3.350	3.282
$^5G_4$	0.317	0.568	0.493	0.276
$^3H_6$	1.151	1.129	1.116	0.894
$^5G_4$	0.106	0.105	0.109	0.094
$^3D_3$	0.023	0.023	0.024	0.021

Table 5 The measured ($f_{expt} \times 10^6$), Judd–Ofelt (f^{JO}_{cal}) and electric dipole method ($f^{ed}_{cal} \times 10^6$) spectral intensities for $Ho(NO_3)_3 6H_2O$: Organic acid complexes.

Energy levels from the ground state $^5I_8$	$Ho(NO_3)_3\,6H_2O$											
	Anthrolinic acid			*Benzoic acid*			*Salycilic acid*			*Pthalic acid*		
	f_{expt}	f^{JO}_{cal}	f^{ed}_{cal}	f_{expt}	f^{JO}_{cal}	f^{ed}_{cal}	f_{expt}	f^{JO}_{cal}	f^{ed}_{cal}	f_{expt}	f^{JO}_{cal}	f^{ed}_{cal}
$^5I_6$	3.100	3.664	3.664	3.330	3.809	3.809	3.380	3.804	3.814	2.980	3.360	3.360
$^5I_5$	0.224	0.652	0.652	0.110	0.719	0.712	0.143	0.715	0.715	0.109	0.622	0.621
$^5I_4$	0.60	0.063	0.063	0.060	0.062	0.062	0.060	0.064	0.064	0.060	0.055	0.055
$^5F_5$	6.259	5.983	5.980	7.879	9.998	9.938	7.394	8.737	8.733	6.847	7.921	7.912
$^5F_4$	13.087	8.396	8.392	12.882	11.648	11.062	10.533	10.375	10.369	8.744	9.234	9.230
$^5F_3$	5.526	4.353	4.351	2.268	4.362	4.316	5.443	4.460	4.457	6.443	3.862	3.860
$^5F_2$	4.156	2.464	2.464	8.769	2.440	2.440	6.690	2.537	2.537	4.679	2.185	2.185
$^5G_6$	15.444	15.672	15.464	17.789	17.896	17.896	14.985	15.045	15.038	12.238	12.274	12.269
$^5G_5$	5.335	4.099	4.099	10.039	8.827	8.822	7.490	6.115	6.113	7.516	6.107	6.015
$^5G_4$	—	0.633	0.633	—	1.117	1.117	—	0.969	0.969	—	0.880	0.880
$^3H_6$	—	2.427	2.427	—	2.831	2.831	—	2.352	2.352	—	1.884	1.884
$^5G_3$	—	0.233	0.233	—	0.231	0.231	—	0.231	0.231	—	0.207	0.207
$^3D_3$	—	0.061	0.061	—	0.060	0.060	—	0.063	0.063	—	0.054	0.054

From the data in Table 2, we have noted the following trends.

Anthrolinic acid: $T_6 > T_2 > T_4$
Benzoic acid: $T_4 > T_6 > T_2$
Salicylic acid: $T_6 > T_4 > T_2$
Pthalic acid: $T_6 > T_4 > T_2$

ii Electric dipole linestrengths method The theoretical oscillator—strength (f_{cal}) could be evaluated from the following expression:

$$f_{\text{cal}} = f^{\text{ed}} + f^{\text{md}}$$

According to our computer analysis, the magnitudes of f_{md} appear to be very smaller compared with the f^{ed} values, therefore the factor $f^{\text{md}}_{\text{cal}}$ has now been ignored following the results reported by Tandon.[20] Now we have the following form of an expression for $f^{\text{ed}}_{\text{cal}}$

$$f_{\text{cal}} = f^{\text{ed}}_{\text{cal}} = \frac{8\pi^2 mc\nu}{3he^2(2J+1)} \frac{(n^2+2)^2}{9n} S_{\text{ed}}$$

Here the given characteristic factors are

m = mass of an electron
c = velocity of light
e = charge of an electron
h = Planck's constant
n = refractive index of the complex
ν = energy of the transition (cm^{-1}) concerned
S_{ed} = electric–dipole line strength, which is defined through the Judd–Ofelt parameters as explained below:

$$S_{\text{ed}} = \Omega_2 |U^2|^2 + \Omega_4 |U^4|^2 + \Omega_6 |U^6|^2$$

The intensity parameters, that are obtained from the equation

$$\Omega_\lambda = \left[1.0845 \times 10^{11} \frac{(n^2+2)^2}{9n}\right]^{-1} (2J+1) T_\lambda$$

The evaluated intensity (Ω_λ) parameters for the ion in four different hosts are given in Table 2. The electric-dipole linestrength (S_{ed}) values for the various observed bands are given in Table 4. Thus the values of $f^{\text{ed}}_{\text{cal}}$ for all the observed states have been calculated and presented in Table 5 along with the values of $f_{\text{expt.}}$ and $f^{\text{JO}}_{\text{cal}}$. Our results that are shown in this table reveal that the values of $f^{\text{ed}}_{\text{cal}}$ and f_{cal} are much identical. These two are in turn found to be in good comparison with the experimental intensities as we see in Table 5.

Hypersensitive Transition

The spectral intensity of an hypersensitive transition is highly monitored by the Judd–Ofelt T_2 parameter followed by two other factors T_6 and T_4. For Ho^{3+} ion $^5I_8 \rightarrow {}^5G_6$ will be the hypersensitive level which exhibits a special kind of absorption intensity variation, by fulfilling the selection rules:[22,23]

$$\Delta J \leq 2, \Delta L \leq 2, \Delta S = 0$$

Accordingly, from Table 2 it is now observed that the term $^5G_6$ has revealed a larger intensity value compared to the other remaining transitions of the holmium complexes as shown in Table 5. Apart form this fact, from Table 3, we have also observed that $^5G_6$ transition state has a higher value for its squared reduced matrix element $\|U^2\|^2$, compared to any other transition of the ion. It is now understood that the hypersensitive level intensity is influenced by the change of the environment, Judd–Ofelt parameter (T_2) and also the $\|U^2\|^2$ value. The relationship between the intensity of the hypersensitive transition ($^5I_8 \rightarrow {}^5G_6$) and the Judd–Ofelt ($T_2$) parameter and its dependence on the change of environment around the ion is clearly shown in Table 6.

Bonding nature of the complexes

By following the theoretical procedures reported earlier by several chemists,[22–26] we too have estimated the magnitudes of the nephelauxetic ratio from

$$\beta = \nu_c/\nu_a$$

here, the energy term ν_c, ν_a represent the band energies in cm^{-1} for the complex and aquo ion respectively. The nephlauxetic ratio parameter was determined for each of the measured transitions and thus evaluated the average ($\bar{\beta}$) nephelauxetic ratio parameter with which the bonding parameter (δ) was obtained from the following equation.

$$\delta = \left[\frac{(1-\bar{\beta})}{\bar{\beta}}\right]100$$

Table 6 The relationship between the hypersensitive intensity (f^{JO}_{cal}) $^5I_8$ $^5G_6$) and the Judd–Ofelt (T_2), intensity (Ω_2) parameters for $Ho(NO_3)_3$ $6H_2O$: Organic acid complexes.

Parameters	*Pthalic acid*	*Salycilic acid*	*Anthrolinic acid*	*Benzoic acid*
$^5I_8 \rightarrow {}^5G_6(f^{JO}_{cal} \times 10^6)$	12.274	15.045	15.672	17.896
$T_2 \times 10^9$ (cm^2)	0.053	0.125	0.353	†
$\Omega_2 \times 10^{20}$ (cm^2)	0.697	1.643	4.628	†

† Since T_4 and T_6 in Benzoic acid have larger values (Table 2) compared to T_2 the hypersensitive transition intensity in this host particular depends on all the three Judd-Ofelt parameters.

The average values of $\bar{\beta}$ are presented in Table 2 for the Ho^{3+} complexes. Since the bonding parameter (δ) takes a negative sign for all the four complexes as we look in Table 2, it is expected that bonding nature of the complexes could be ionic. Similar results for different rare earths mixed inorganic hosts were previously reported in literature.[24–27] The following is the ionic nature trend for Ho^{3+} in four different fluorescing organic liquids.

Anthrolinic acid > Salysilic acid > Benzoic acid > Pthalic acid.

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