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Properties of the Energy Bands, Judd-Ofelt Parameters and the Fluorescence of Neodymium Chloride (NdCl$_3$) in Methanol, Iso-propanol and Butanol Solvents

Subrata Mitra · Samar Jana

Abstract Absorption bands of neodymium chloride (NdCl$_3$) dissolved in methanol, iso-propanol and butanol organic solvents at room temperature have been recorded in the ultraviolet–visible and near infrared regions between 190 and 1100 nm. Adopting a free-ion Hamiltonian we have calculated and assigned the energy multiplets of the $4f^3$ electronic configuration of the Nd^{3+} ion, and thereby the best-fit parameters are estimated. We have measured the oscillator strengths of the observed absorptions and using the experimentally measured oscillator strengths the three Judd-Ofelt intensity parameters Ω_2, Ω_4 and Ω_6 have been derived. Hence we have calculated the line strengths and the oscillator strengths for electric-dipole transitions. An intense fluorescence emission is found for $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition at 873 nm, upon excitation with 581 nm. The fluorescence characteristics are also investigated by evaluating the spontaneous transition probability (A), luminescence branching ratio (β), radiative lifetime (τ) and the stimulated emission cross section (σ).

Keywords Neodymium chloride (NdCl$_3$) · Energy bands · Judd-Ofelt analysis · Fluorescence characteristics

Introduction

Neodymium (Nd^{3+}) embedded complex host matrices like glasses and polymers have been an important arena of re-

search because of their more efficient output as far as their practical utilities are concerned in laser, luminescence and optical communication devices. Many of these complex matrices are organically modified and developed by following the alcohol method of synthesis. However, extensive investigations on the absorption and luminescence characteristics of trivalent Nd^{3+} in alcoholic solutions are hardly available, except a very few studies such as reported in Ref. [1–4]. Investigation on Nd^{3+} in various organic alcoholic solvents demand a striking interest for better understanding and explanation about the compatibility of the neodymium in these complex matrices, their synthesis, characterization and optical properties.

With this motivation, in this paper, we have reported a detailed investigation on the absorption and luminescence of 0.01 Molar concentration of NdCl$_3$ dissolved in methanol, iso-propanol and butanol non aqueous organic solvents at room temperature in the ultraviolet–visible and near infrared (NIR) regions between 190 and 1100 nm. Here we have presented the characteristics of the energy bands and calculated the energies theoretically by adopting a free-ion Hamiltonian of the $4f^3$ *electronic* configuration of the Nd^{3+} ion [5]. Thereby the best fit parameters are estimated. The Hamiltonian takes into account the Slater electrostatic repulsive interaction parameters (F^k, k=2,4,6), the spin-orbit coupling constant (ζ_{so}), Trees two-particle configuration interaction parameters (α, β, γ), and Judd's three-particle configuration interaction parameters (T^i, i=2,3,4, 6,7,8).

We have measured the experimental oscillator strength of the observed absorptions and utilizing the Judd-Ofelt theory [6, 7], the Judd-Ofelt intensity parameters (Ω_t, t=2,4,6) have been estimated by a least

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square fitting method. Thus the line strengths and the oscillator strengths for electric dipole transitions are calculated. Our calculation yields a very consistent result between the theoretical and the experimental values. An analysis of the fluorescence properties of $NdCl_3$ in those alcohols is also represented in this paper. We have determined the excitation band and hence recorded the fluorescence emission at 873 nm corresponding to $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. The important radiative parameters i.e., the spontaneous transition rate (A), fluorescence branching ratio (β), radiative lifetime (τ) and the stimulated emission cross-section (σ) have been derived by using the Judd-Ofelt intensity parameters.

Experimental

We had taken methanol $[CH_3OH]$, iso-propanol $[(CH_3)_2CHOH]$ and butanol $[CH_3(CH_2)_3OH]$ (Guaranteed Reagent grade, Merck, India) as the three organic solvents. The 0.01 M concentrations of $NdCl_3$ (here M stands for the Molar solution) samples were obtained by dissolving and mixing the anhydrous Neodymium chlorides ($NdCl_3$, Indian Rare Earth Ltd., purity 99.9 %) in the alcohols. Absorptions in the region 190–1100 nm were recorded at room temperature (300 K) in a double-beam UV-Visible Spectrometer (*Perkin Elmer, Model: Lambda 45*). During the experiment the $NdCl_3$ solution samples were kept in a quartz cuvette of path length 10 mm and the respective alcohol was taken as the reference. At room temperature we measured the fluorescence emission of 0.01 M of $NdCl_3$ mixed organic samples in a Spectrofluorometer (*Horiba Jobin Yvon, Model: FluoroMax-4P*). The excitation was provided by the 150 W ozone free Xenon arc lamp of the equipment. The excitation energy band was traced out first, then applying the excitations we recorded the fluorescence emission. In our experiment on excitation at 581 nm, we observed a strong emission at 873 nm due to $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition.

Results and Discussion

Absorption and the Observed Energy Bands

Absorption of 0.01 M concentration of $NdCl_3$ in methanol, iso-propanol and butanol organic solvents are recorded in the ultraviolet (UV)-visible and near infrared (NIR) regions between 300 and 900 nm and these are represented in Figs. 1, 2, and 3.

Figure 1 shows the spectra in the 300–400 nm region. Here we observe very weak band for transition from the ground
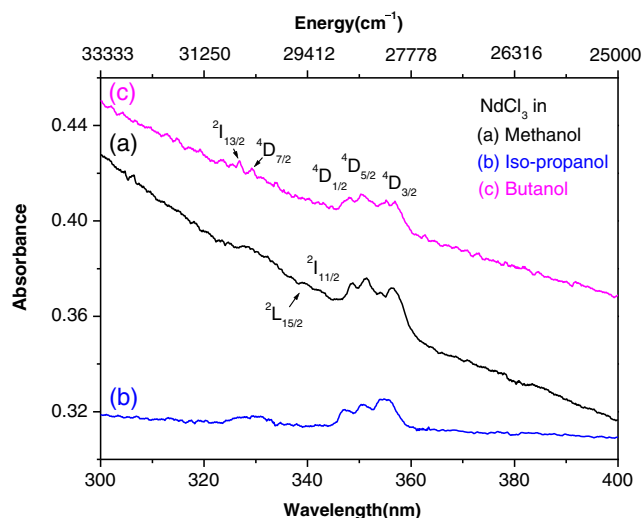

Fig. 1 Absorption of 0.01 M concentration of $NdCl_3$ dissolved in methanol, iso-propanol and butanol organic solvents respectively, in 300–400 nm region

state $^4I_{9/2}$ to the excited $^2I_{13/2}$ level at 327.4 nm (30,544 cm^{-1}) and 326.9 nm (30,590 cm^{-1}) in methanol and butanol respectively. The band $^4D_{7/2}$ also arises faintly at 328.9 nm (30,404 cm^{-1}) and 329.4 nm (30,358 cm^{-1}) for iso-propanol and butanol. Other two very weak bands $^2L_{15/2}$ and $^2I_{11/2}$ have been detected at 339 nm (29,499 cm^{-1}) and 341.6 nm (29,274 cm^{-1}) in methanol only. The $^4I_{9/2} \rightarrow {}^4D_{1/2}$ transition at 348.7 nm (28,678 cm^{-1}), 347.2 nm (28,802 cm^{-1}) and 348 nm (28,736 cm^{-1}), and $^4D_{5/2}$ energy bands at 351.4 nm (28,458 cm^{-1}), 350.8 nm (28,506 cm^{-1}) and 350.5 nm (28,531 cm^{-1}) are comparatively clear in methanol,
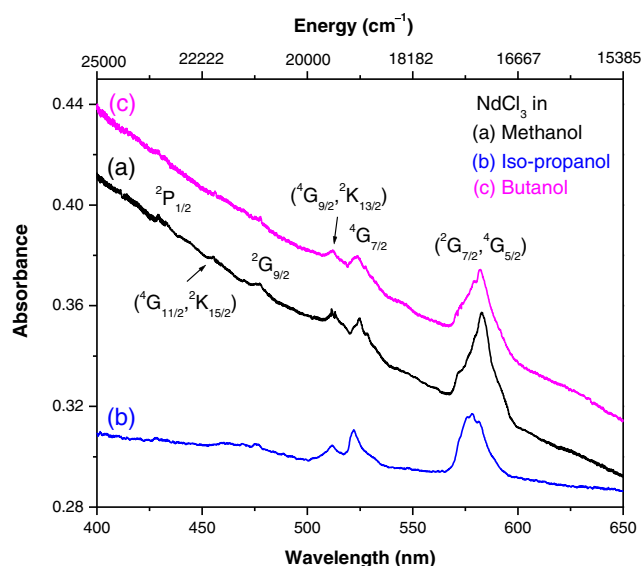

Fig. 2 Absorption band observed in the visible region 400–650 nm for $NdCl_3$ mixed (*a*) methanol (*b*) iso-propanol and (*c*) butanol respectively
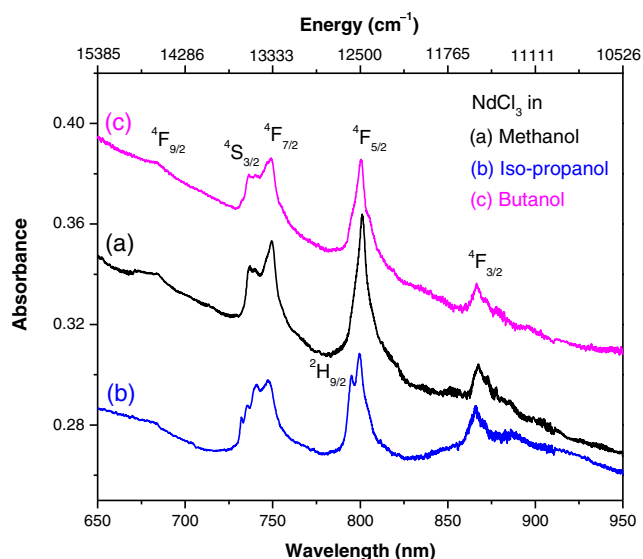
Fig. 3 Experimental absorption spectra between 650 and 950 nm region of NdCl$_3$ in methanol, iso-propanol and butanol solutions respectively

iso-propanol and butanol, respectively. The appearance of $^4D_{3/2}$ is prominent with a broad bandwidth for methanol, iso-propanol and butanol respectively around 354.1 nm (28, 241 cm^{-1}), 354 nm (28,249 cm^{-1}) and 355.2 nm (28,153 cm^{-1}).

The absorption in the visible region 400–650 nm is depicted in Fig. 2. Here transition from the ground level $^4I_{9/2}$ to the following $^{2S+1}L_J$ levels: $^2P_{1/2}$, $^2K_{15/2}$, $^4G_{11/2}$, ($^2D_{3/2}+^2P_{3/2}$), $^2G_{9/2}$, $^2K_{13/2}$ and $^4G_{9/2}$ appear very weakly. But the other absorption band $^4G_{7/2}$ shows reasonably clear peak. Amongst all the bands in this region, the $^4I_{9/2}\rightarrow^4G_{5/2}$ transition occurs with a strong intensity and it is overlapped by a less intense transition $^4I_{9/2}\rightarrow^2G_{7/2}$. Thereby absorption having broad bandwidth is observed at 582.7 nm (17,161 cm^{-1}), 581.5 nm (17,197 cm^{-1}) and 582.1 nm (17,179 cm^{-1}) in methanol, iso-propanol and butanol respectively. This $^4I_{9/2}\rightarrow^4G_{5/2}$ transition known as the hypersensitive transition of Neodymium is sensitive to the coordinating ligand environment [1, 4, 8].

The strongest absorption bands are observed between 650 to 950 nm region which is represented in Fig. 3. Here the weak energy band $^4F_{9/2}$ appears at 683.8 nm (14,624 cm^{-1}), 683.8 nm (14,624 cm^{-1}) and 683.3 nm (14,635 cm^{-1}) in methanol, iso-propanol and butanol, respectively. The $^4S_{3/2}$ and $^4F_{7/2}$ bands are overlapped and the peaks are observed around 737 nm (13, 569 cm^{-1}), 735.6 nm (13,594 cm^{-1}), 736.4 nm (13, 580 cm^{-1}), and 749.4 nm (13,344 cm^{-1}), 747.3 nm (13,382 cm^{-1}) and 749.1 nm (13,349 cm^{-1}) respectively for the three samples. The most intense band with a narrow FWHM arises for $^4I_{9/2}\rightarrow^4F_{5/2}$ transition at 801.1 nm (12,483 cm^{-1}), 799.5 nm (12,508 cm^{-1}) and

800.5 nm (12,492 cm^{-1}) respectively. In the methanol, iso-propanol and butanol samples the $^4F_{3/2}$ band occur at 867.3 nm (11,530 cm cm^{-1}), 865.8 nm (11,550 cm^{-1}) and 866.4 nm (11,542 cm^{-1}) respectively.

The observed energy multiplets and the theoretically calculated energies for methanol, iso-propanol and butanol samples are given in Table 1.

The Calculated Free-Ion Energies and the Parameters

The energy bands which are observed in the ultraviolet, visible and near infra-red regions have occurred due to the transition between $4f^3$ and $4f^3$ configuration of the Nd^{3+} ion in the organic alcohol solutions. In the trivalent lanthanides the free-ion is only slightly perturbed by the electrostatic field of the ligands of the solution matrix. In solution spectra the ligand field components (i.e., the so-called ligand field splitting) are usually not resolved and therefore the observed absorption bands can only be characterized in terms of the free-ion levels [8]. We have calculated the energy levels theoretically by fitting the baricenter of the observed multiplets. For the $4f^3$ electronic configuration of the Nd^{3+} ion, we have constructed a parametric free-ion Hamiltonian [5]:

$$H_{free-ion} = \sum_{k=2,4,6} F^k f_k + \sum_{i=1}^{n} \varsigma_{so} l_i.s_i + \alpha L(L+1) + \beta G(G_2)$$
$$+ \gamma F(R_7) + \sum_{j=2,3,4,6,7,8} T^j t_j \qquad (1)$$

The Hamiltonian adopts the Slater electrostatic repulsive interaction parameters (F^2, F^4, F^6), the spin-orbit coupling constant ζ_{so}, Trees two-particle configuration interaction parameters (α, β, γ), and Judd's three-particle configuration interaction parameters (T^2, T^3, T^4, T^6, T^7, T^8).

We have incorporated all the interactions in the Hamiltonian by a computer programme. The free-ion parameters are obtained by utilizing the peak of the observed energy bands. In our calculatiom we have diagonalized the free-ion Hamiltonian within the 364 Russell-Saunders basis sets |τSLJM$_J$> of the $4f^3$ electronic configuration of the Nd^{3+} ion. The eigen values give the corresponding energy levels. The energy baricenters are identified and assigned by recognizing the components of the respective eigen functions. The baricenter energies (i.e., the free-ion centroid energy for each J multiplet) are optimized by varying the parameters. We then fitted the eigenvalues of the Hamiltonian to the observed energies. Minimizing the sum of the squared differences between the experimental and

Table 1 The observed and the calculated energy levels, and their differences for NdCl$_3$ in alcohol solvents

Multiplets	NdCl$_3$ + methanol			NdCl$_3$ + iso-propanol			NdCl$_3$ + butanol		
	Obs. (cm^{-1})	Cal. (cm^{-1})	Diff. (cm^{-1})	Obs. (cm^{-1})	Cal. (cm^{-1})	Diff. (cm^{-1})	Obs. (cm^{-1})	Cal. (cm^{-1})	Diff. (cm^{-1})
$^4I_{9/2}$	–	0		–	0		–	0	
$^4I_{11/2}$	–	1816		–	1839		–	1827	
$^4I_{13/2}$	–	3757		–	3804		–	3780	
$^4I_{15/2}$	–	5782		–	5851		–	5816	
$^4F_{3/2}$	11530	11458	72	11550	11461	89	11542	11427	115
$^4F_{5/2}$	12483	12487	4	12508	12505	3	12492	12466	26
$^2H_{9/2}(2)$	–	12489		12579	12520	59	–	12508	
$^4F_{7/2}$	13344	13442	98	13382	13471	89	13349	13430	81
$^4S_{3/2}$	13569	13599	30	13594	13634	40	13580	13587	07
$^4F_{9/2}$	14624	14643	19	14624	14692	68	14635	14646	11
$^2H_{11/2}(2)$	–	15636		–	15708		–	15678	
$^4G_{5/2}$	17161	17188	27	17197	17168	29	17179	17129	50
$^2G_{7/2}(1) + {}^4G_{7/2}$	17259	17199	60	17289	17227	62	17259	17205	54
$^4G_{7/2}$	19048	18959	89	19153	18987	166	19102	18948	154
$^4G_{9/2}$	19486	19396	90	–	19427		–	19380	
$^2K_{13/2}$	19550	19698	148	19547	19732	185	19535	19707	172
$^2G_{9/2}(1,2)$	20951	20879	72	21053	20958	95	20934	20913	21
$^2D_{3/2}(1) + {}^2P_{3/2}$	21286	21213	73	21331	21245	86	–	21159	
$^4G_{11/2}$	–	21404		–	21439		–	21377	
$^2K_{15/2}$	–	21624		–	21677		–	21639	
$^2P_{1/2}$	23310	23377	67	23375	23420	45	23305	23346	41
$^2D_{5/2}(1)$	–	24238		–	24301		–	24219	
$^2P_{3/2} + {}^2D_{3/2}(1)$	–	25970		–	26053		–	25934	
$^4D_{3/2}$	28074			28193			28019		
	28241	28388	147	28249	28364	115	28153	28307	154
$^4D_{5/2}$	28458	28468	10	28506	28440	66	28531	28380	151
$^4D_{1/2}$	28678	28733	55	28802	28720	90	28736	28649	87
$^2I_{11/2}$	29274	29345	71	–	29369		–	29293	
$^2L_{15/2}$	29499	29669	170	–	29698		–	29598	
$^4D_{7/2}$	–	30363		30404	30360	44	30358	30282	76
$^2I_{13/2}$	30544	30642	98	–	30688		30590	30608	18
$^2L_{17/2}$	–	31112		–	31152		–	31043	
$^2H_{9/2}(1)$	–	33249		–	33277		–	33152	
$^2D_{3/2}(2)$	–	34176		–	34204		–	34140	
$^2D_{5/2}(2)$	–	34495		–	34524		–	34409	
$^2H_{11/2}(1)$	–	34563		–	34614		–	34479	
$^2F_{5/2}(2,1)$	–	39466		–	39529		–	39383	
$^2F_{7/2}(2,1)$	–	40739		–	40802		–	40647	
$^2G_{9/2}(2,1)$	–	48482		–	48468		–	48329	
$^2G_{7/2}(2,1)$	–	49344		–	49337		–	49194	
$^2F_{7/2}(1,2)$	–	68304		–	68355		–	68153	
$^2F_{5/2}(1,2)$	–	69271		–	69321		–	69113	

calculated energy levels the best values of the free-ion parameters are estimated, alike to that of our earlier work on Praseodymium samples [9, 10].

In the program we set the electrostatic interaction between 4f electrons determined by Racah parameters E^i (i=1, 2, 3), and thereby the electrostatic Slater

Table 2 The best fit parameters for the free-ion Hamiltonian of the Nd^{3+} ion in alcohols

Parameters	Values (cm^{-1})		
	Methanol	Iso-propanol	Butanol
E^1	5097	5105	5090
E^2	21.63	21.59	21.31
E^3	487	486	485.1
F^2	72573.70	72526.98	72179.09
F^4	59868.13	59998.24	60249.99
F^6	38960.12	39176.83	38882.05
ζ_{SO}	858	868	863
α	10	10	10.1
β	−470	−490	−485
γ	405	400	403
T^2	211	211	211
T^3	41	41	41
T^4	73	73	73
T^6	−119	−119	−119
T^7	267	267	267
T^8	314	314	314

parameters F^k (k=2, 4, 6), are obtained as follows [11, 12]:

$$F_2 = \frac{1}{42}\left(E^1 + 143E^2 + 11E^3\right) \tag{2a}$$

$$F_4 = \frac{1}{77}\left(E^1 - 130E^2 + 4E^3\right) \tag{2b}$$

$$F_6 = \frac{1}{462}\left(E^1 + 35E^2 - 7E^3\right) \tag{2c}$$

$$F^2 = 225F_2, \quad F^4 = 1089F_4 \text{ and } F^6 = 7361.64F_6 \tag{2d}$$

Table 1 represents the experimental, calculated energy levels and their differences, and the best fit free-ion parameters are enlisted in Table 2.

Experimental and Calculated Oscillator Strengths, and the Judd-Ofelt Parameters

The experimental oscillator strengths indicate the measures of intensities of the absorption bands. We have measured the oscillator strengths of experimentally observed absorptions of various multiplets of the $4f^3$ electronic configuration of the Nd^{3+} ions, which have occurred in the ultraviolet, visible and the near infrared (NIR) regions due to the transitions from the ground state $^4I_{9/2}$.

For a given absorption band the experimentally measured oscillator strength (f_{expt}) is determined by [13, 14]:

$$f_{exp} = \frac{2303mc^2}{N_A\pi e^2}\int\varepsilon(\upsilon)d\upsilon \tag{3a}$$

$$= 4.318 \times 10^{-9}\int\varepsilon(\upsilon)d\upsilon \tag{3b}$$

In this equation m and e represent the mass and the charge of the electron, respectively, c is the velocity of light, N_A is the Avogadro's number, and $\varepsilon(\nu)$ is the molar absorption (i.e., molar extinction) coefficient (per molar concentration per path length (centimeter)) of the band at the energy ν (cm^{-1}). The area under the absorption band is denoted by the term $\int\varepsilon(\upsilon)d\upsilon$ and these are obtained by integrating the corresponding observed absorption bands as shown in Figs. 1, 2, and 3. Hence using Eq. (3b) the experimental oscillator strengths have been measured.

Following the Judd-Ofelt theory [6, 7], the oscillator strength $f_{JJ'}$ of electric-dipole 4f-4f transition of trivalent rare

Table 3 The experimental (f_{exp}) and calculated oscillator strength (f_{cal}), the ratio f_{cal}/f_{exp}, the electric-dipole line strength (S_{ed}) and the root-mean square deviation (δ_{rms}) for $NdCl_3$ in Methanol

Level	Band range (cm^{-1})	Energy (cm^{-1})	f_{exp} ($\times 10^{-6}$)	f_{cal} ($\times 10^{-6}$)	Residual	f_{cal}/f_{exp}	S_{ed} ($\times 10^{-20}$ cm^2)
$^4F_{3/2}$	11402–11617	11530	0.668	1.000	0.332	1.497	0.674
$^4F_{5/2} + {}^2H_{9/2}$	12240–12820	12483	3.750	3.264	0.486	0.870	2.032
$^4F_{7/2} + {}^4S_{3/2}$	13210–13695	13453	3.231	3.427	0.196	1.061	1.980
$^4G_{5/2} + {}^2G_{7/2}$	16779–17668	17224	7.950	7.904	0.046	0.994	3.567
$^4G_{7/2}$	18868–19231	19048	0.822	1.536	0.714	1.869	0.627
$^4G_{9/2} + {}^2K_{13/2}$	19342–19755	19549	0.484	0.920	0.436	1.901	0.366
$^4D_{3/2+5/2+1/2}$	27855–28902	28379	4.796	4.680	0.116	0.976	1.282

$\delta_{rms} = 0.524 \times 10^{-6}$

Table 4   NdCl$_3$ dissolved in iso-propanol solvent

Level	Band range (cm^{-1})	Energy (cm^{-1})	f_{exp} (×10^{-6})	f_{cal} (×10^{-6})	Residual	f_{cal}/f_{exp}	S$_{ed}$ (×10^{-20} cm^2)
$^4F_{3/2}$	11406–11641	11550	0.637	0.809	0.172	1.270	0.527
$^4F_{5/2} + {}^2H_{9/2}$	12240–12739	12490	2.926	3.370	0.444	1.152	2.030
$^4F_{7/2} + {}^4S_{3/2}$	12958–13824	13391	4.333	3.891	0.442	0.898	2.187
$^4G_{5/2} + {}^2G_{7/2}$	16667–17699	17183	4.919	4.880	0.039	0.992	2.137
$^4G_{7/2}$	18904–19342	19153	0.764	1.209	0.445	1.582	0.475
$^4G_{9/2} + {}^2K_{13/2}$	19342–19724	19533	0.293	0.871	0.578	2.973	0.336
$^4D_{3/2+5/2+1/2}$	27778–29070	28424	3.714	3.495	0.219	0.941	0.925

$\delta_{rms} = 0.501 \times 10^{-6}$

earth ions between the initial J and final J' multiplet is expressed as: [15–19]:

$$f_{JJ'} = \frac{8\pi^2 mc\upsilon\chi}{3h(2J+1)} \sum_{t=2,4,6} \Omega_t \langle f^N(\alpha, S, L)J \| U^t \| f^N(\alpha', S', L')J' \rangle^2 \quad (4)$$

We have the relation between line strength $S_{ed}{}^{cal}$ and the oscillator strength $f_{JJ'}{}^{cal}$ for each electric dipole transition:

$$f_{JJ'}{}^{cal} = \frac{8\pi^2 mc\upsilon\chi}{3h(2J+1)} S_{ed}{}^{cal}(J, J') \quad (5)$$

In the above equations m, c and h represent the mass of electron, the velocity of light, and the Planck constant, respectively. $\chi = [(n^2+2)^2/(9n)]$ where n is the refractive index, and υ is the frequency in cm^{-1}. Here we have the refractive indices 1.329, 1.377 and 1.399 for methanol, iso-propanol and butanol samples respectively. In this equation Ω_t ($t=2, 4, 6$) are the Judd-Ofelt intensity parameters, f^N are the wave functions for the $4f^3$ electronic configuration of the Nd^{3+} ion, J and J' denote the total angular momentum of initial and final states, (α S, L) define all other quantum numbers needed to specify the states, and the elements $\| U^t \|$ represent the reduced matrix elements of the tensor operators U^t. The calculation has been carried out by using the matrix elements $\| U^t \|$ for Nd^{3+} in aqueous solution as reported by W.T. Carnall et al. [8].

The Judd-Ofelt intensity parameters Ω_t have been evaluated by using the experimentally measured oscillator strengths, with the adoption of the least square fitting procedure [20]. Thereby we have calculated the line strengths and the oscillator strengths for electric-dipole transitions. The estimated root mean square deviation (δ_{rms}) expressed as:

$$\delta_{rms} = \left[\frac{\sum_{i=1}^{N} \left(f^i_{expt} - f^i_{cal} \right)^2}{N-3} \right]^{\frac{1}{2}} \quad (6)$$

where N is the number of the levels fitted, indicates the quality of fitting.

Tables 3, 4, and 5 summarize the experimental (f_{expt}) and calculated (f_{cal}) oscillator strengths, the electric-dipole line strengths (S_{ed}) for the absorption bands of NdCl$_3$ in methanol, iso-propanol and butanol alcoholic solutions respectively. The residuals (i.e., the absolute difference between the calculated and the observed oscillator strengths), their ratios and the root mean square deviations (δ_{rms}) are also shown. The three Judd-Ofelt intensity parameters Ω_t and the spectroscopic quality factors i.e., the ratio [Ω_4/Ω_6] are represented in Table 6. Our calculation indicates a very good agreement between the experimental and the calculated values of the oscillator strengths for all

Table 5   NdCl$_3$ in butanol solution

Level	Band range (cm^{-1})	Energy (cm^{-1})	f_{exp} (×10^{-6})	f_{cal} (×10^{-6})	Residual	f_{cal}/f_{exp}	S$_{ed}$ (×10^{-20} cm^2)
$^4F_{3/2}$	11417–11620	11542	0.612	0.701	0.089	1.145	0.450
$^4F_{5/2} + {}^2H_{9/2}$	12323–12687	12505	2.355	2.187	0.168	0.929	1.296
$^4F_{7/2} + {}^4S_{3/2}$	13235–13708	13472	2.178	2.235	0.057	1.026	1.229
$^4G_{5/2} + {}^2G_{7/2}$	16787–17637	17212	6.471	6.449	0.022	0.997	2.777
$^4G_{7/2}$	18893–19268	19102	0.776	1.128	0.352	1.454	0.438
$^4G_{9/2} + {}^2K_{13/2}$	19350–19716	19533	0.457	0.634	0.177	1.387	0.241
$^4D_{3/2+5/2+1/2}$	27840–28994	28392	3.372	3.319	0.053	0.984	0.866

$\delta_{rms} = 0.222 \times 10^{-6}$

Table 6 The Judd-Ofelt intensity parameters Ω_t (t=2, 4, 6) along with the spectroscopic quality factor (Ω_4/Ω_6) in NdCl$_3$ mixed alcohol solutions

Sample	Ω_2 ($\times 10^{-20}$ cm^2)	Ω_4 ($\times 10^{-20}$ cm^2)	Ω_6 ($\times 10^{-20}$ cm^2)	Ω_4/Ω_6
NdCl$_3$ in methanol	2.088	2.260	2.844	0.795
NdCl$_3$ in iso-propanol	1.039	1.531	3.209	0.477
NdCl$_3$ in butanol	1.790	1.542	1.756	0.878

the absorption bands in the three samples. Again for methanol and iso-propanol we find that $\Omega_2 < \Omega_4 < \Omega_6$. But in the butanol the value of Ω_4 is slightly smaller than the others.

Fluorescence Properties

We recorded the fluorescence emission using various excitation energies. Figure 4 depicts the excitation energy band for the emission around 873 nm and it indicates the intense excitation energy at 581 nm. Upon excitation with 581 nm, a strong emission is observed for $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition at 873.5 nm, 872.6 nm and 873.2 nm respectively, in methanol, iso-propanol and butanol samples. The fluorescence emission spectra in the near infrared region between 840 and 900 nm region in 0.01 M of NdCl$_3$ mixed methanol, iso-propanol and butanol solutions at room temperature is shown in Fig. 5. The intensities are plotted in counts per second (cps) unit.

The fluorescence of NdCl$_3$ in organic alcoholic solvents have been characterized by evaluating the probability of spontaneous transition (A), fluorescence branching ratio (β), radiative lifetime (τ) and the stimulated emission cross-section (σ). Utilizing the Judd-Ofelt parameters all these radiative parameters have been derived.
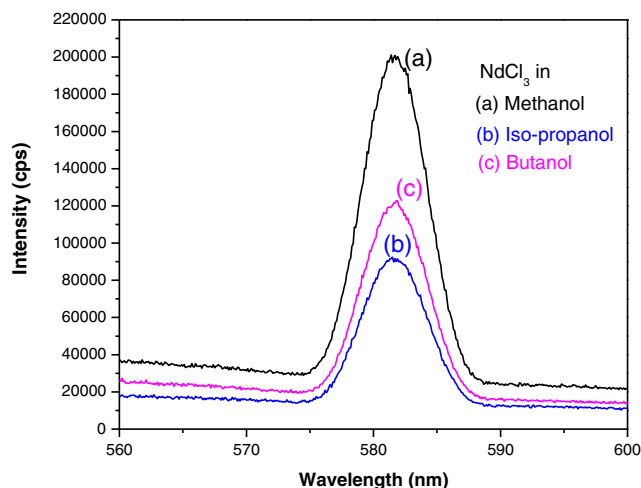
The radiative transition rate (i.e., the spontaneous emission probability) for the electric dipole transition from an excited state (J) to a lower state (J') is expressed by the following equation [14, 21, 22]:

$$A_{JJ'} = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \times \frac{n(n^2+2)^2}{9} \sum_{t=2,4,6} \Omega_t \left\langle f^N(\alpha,S,L)J \| U^t \| f^N(\alpha',S',L')J' \right\rangle^2 \tag{7}$$

We have the radiative lifetime of the excited state:

$$\tau_{rad} = \frac{1}{\sum A_{JJ'}} \tag{8}$$

The fluorescence branching ratio β of transition from initial manifold $|$ (S,L) J > to lower levels $|$ (S',L') J' > is written as [21, 22]:

$$\beta_{JJ'} = \frac{A_{JJ'}}{\sum A_{JJ'}} = A_{JJ'}\tau_{rad} \tag{9}$$

Within the available range in the Spectrofluorometer equipment of our laboratory, it has been possible to record the $^4F_{3/2} \rightarrow ^4I_{9/2}$ fluorescence emission only. Thereby we have measured the branching ratio β_{mes} from the area under the emission band and the radiative lifetimes have been estimated by using these β_{mes} values.

Fig. 4 The excitation energy band for NdCl$_3$ in alcohol solvents by setting for an emission around 874 nm
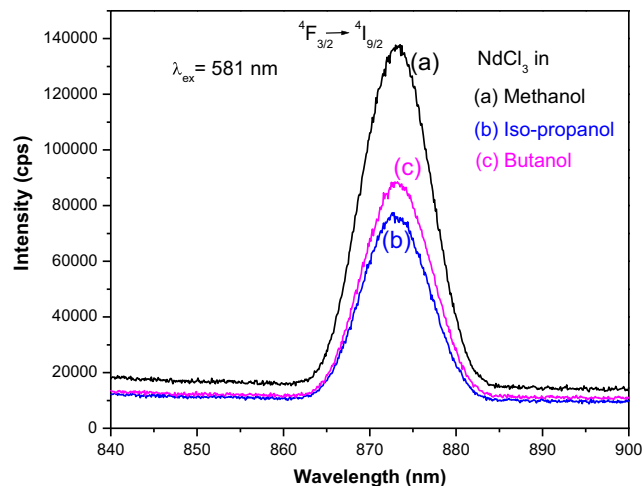

Fig. 5 Fluorescence emission observed between 840 and 900 nm region for $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition in NdCl$_3$ mixed (*a*) methanol (*b*) iso-propanol and (*c*) butanol respectively

Table 7 The spontaneous transition rate (A), fluorescence branching ratio (β), radiative lifetime (τ) and the stimulated emission cross-section (σ) corresponding to $^4F_{3/2} \to {}^4I_{9/2}$ fluorescence emission of $NdCl_3$ in alcohol solvents

Sample	Wavelength λ_p (nm)	$\Delta\lambda_{eff}$ (nm)	A_R (s⁻¹)	β	τ_{rad} (μs)	σ_e (×10⁻²⁰ cm²)
$NdCl_3$ in methanol	873.5	9.707	383	0.120	313	1.725
$NdCl_3$ in iso-propanol	872.6	9.510	333	0.064	192	1.420
$NdCl_3$ in butanol	873.2	9.648	298	0.075	252	1.217

The stimulated emission cross-section (σ_e) of the transition is evaluated from the observed fluorescence emission band according to equation [22]:

$$\sigma_e(JJ') = \frac{\lambda_P^4}{8\pi c n^2 \Delta\lambda_{eff}} A_{JJ'} \qquad (10)$$

here λ_P denotes the wavelength of the emission peak and $\Delta\lambda_{eff}$ the effective bandwidth of the transition is given by [22, 23]:

$$\Delta\lambda_{eff} = \frac{\int I(\lambda)d\lambda}{I_{peak}} \qquad (11)$$

In this equation I_{peak} is the intensity at the peak of the emission band. We have measured the $\Delta\lambda_{eff}$ values as 9.707, 9.510 and 9.648 nm for $NdCl_3$ in methanol, iso-propanol and butanol solvents respectively.

Table 7 summarizes the spontaneous transition rates (A), fluorescence branching ratios (β), radiative lifetimes (τ) and the stimulated emission cross-sections (σ). The radiative lifetimes (τ) are obtained in the orders of microsecond (1 μs=10^{-6} s). Here we note that for $^4F_{3/2} \to {}^4I_{9/2}$ emission the estimated values of the radiative parameters are consistent and comparable to that of other alike hosts [16].

Conclusion

Our work elucidates the characteristics of the absorption bands, energy multiplets, free-ion parameters, oscillator strengths, Judd-Ofelt parameters and fluorescence of $NdCl_3$ in various alcohol organic solvents. The calculated energies are best fitted with the observed energy bands. Utilizing the Judd-Ofelt theory we have calculated the oscillator strengths of the absorptions having smallest values in the root mean square deviations. A comparison indicates that the calculated oscillator strengths are in good agreement with the experimentally measured values. The Judd-Ofelt parameters and the spectroscopic quality factors are estimated. Our calculation reveals that in methanol and iso-propanol solvents

$\Omega_2 < \Omega_4 < \Omega_6$, and in butanol the value of Ω_4 is slightly smaller than the others. The spectroscopic quality factors are consistent for the three solvents.

We have obtained a strong fluorescence emission for $^4F_{3/2} \to {}^4I_{9/2}$ transition at 873.5, 872.6 and 873.2 nm respectively, in methanol, iso-propanol and butanol samples and hence several important radiative parameters are estimated.

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