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## ABSORPTION SPECTRA OF $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ALCOHOLIC COMPLEXES

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Band intensities and energies of  $\text{Nd}^{3+}$  ion in methyl, ethyl, isopropyl, butyl and amyl alcohols are studied. The lifetimes ( $\tau_R$ ) for certain fluorescing states of  $\text{Nd}^{3+}$  ion in all the five alcohols are reported. The second derivative spectra exhibited splittings for certain states of  $\text{Nd}^{3+}$  in five alcohols.

KEYWORDS: Neodymium complexes, band intensities.

### 1 INTRODUCTION

Vibrational spectra of polynuclear complexes of lanthanide nitrates have been analysed by Seminara<sup>1</sup>. Interligands charge transfer in lanthanide complexes have been characterised by Choppin<sup>2</sup>. Bunzli<sup>3</sup> has made a detailed study on the solvation of  $\text{Nd}^{3+}$  in various organic solvents. Magnetic properties of rare earth complexes have been studied by Urland<sup>4</sup>. Thermodynamic properties of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{KNO}_3$  have been investigated by Shevchu<sup>5</sup>. Vicentini and his coworkers have reported the lanthanide adducts spectra with several organic solvents<sup>6-8</sup>.

### 2 EXPERIMENTAL

The neodymium complexes were prepared by putting about 0.1 m% neodymium nitrate into the alcohols of methyl, ethyl, isopropyl, butyl and amyl. These five neodymium complexes have been used for recording the spectra. The UV-VIS spectra have been recorded from 920-320 nm on the UV-VIS spectrophotometer. In the same wavelength range, the second derivative spectra have also been recorded to obtain further clearer information about the energy-level structure. The measurement of refractive indices of these complexes have been made on a standard refractometer. By

using a microcomputer (DCM Spectrum 31) theoretical evaluation of spectral characteristic parameters has been carried out.

### 3 RESULTS AND DISCUSSION

#### 3.1 Band Energies

The spectral appearance of the  $\text{Nd}^{3+}$  in five different alcohols namely methyl(MA), ethyl(EA), isopropyl(IPA) butyl(BA) and amyl(AA) alcohols have revealed the presence of ten electronic states with  ${}^4\text{I}_{9/2}$  as the ground state. They are as follows:

$$\begin{aligned} {}^4\text{I}_{9/2} &\rightarrow {}^4\text{F}_{3/2}, {}^4\text{F}_{5/2}, {}^4\text{F}_{7/2} \text{ and } {}^4\text{F}_{9/2} \\ &\rightarrow {}^2\text{H}_{11/2} \\ &\rightarrow {}^4\text{G}_{5/2}, {}^4\text{G}_{7/2} \text{ and } {}^4\text{G}_{9/2} \\ &\rightarrow {}^2\text{D}_{3/2} \\ &\rightarrow {}^4\text{D}_{3/2} \end{aligned}$$

The experimental energies of these bands relating to the  $\text{Nd}^{3+}$  ion in five alcohols are presented in Table 1. The theoretical energies of these ten states have been obtained by using the conventional procedures<sup>9-11</sup> and are listed in Table 1. The rms deviation for the band energies is obtained from the relation.

$$\sigma = \left( \frac{\sum \Delta_i^2}{N} \right)^{1/2}$$

where  $\Delta_i$  is the difference in energy between the experimental and theoretical values,  $N$  is the number of states obtained in the present work. Table 1 shows that the rms deviation are found to be reasonably smaller and thus there exists a successful correlation between the experimental and calculated energy values. The relevant spectroscopic parameters namely Racah ( $E^1, E^2, E^3$ ), spin-orbit ( $\xi_{4f}$ ) configurational interaction ( $\alpha$ ) which characterise the band energies are evaluated by solving the  $4f^3$  energy matrices are given in Table 2. As the rms deviations (Table 1) for the band energies are found to be between  $\pm 17$  and  $\pm 51 \text{ cm}^{-1}$ , the computed parameters that are given in Table 2 are thus chosen as the best fit from the several trials made on the microcomputer. Table 2 also reveals that the following situation exists with regard to  $E^1$  and  $E^2$  values

$$E^1, E^2: \text{EA} > \text{MA} > \text{IPA} > \text{BA} > \text{AA}$$

On the other hand, the values of  $E^3, \xi_{4f}$  and  $\alpha$  are found to be at maximum in MA and the minimum in AA.

#### 3.2 Band Intensities

The squared reduced matrix elements required for theoretical evaluation of band intensities have been evaluated for  $\text{Nd}^{3+}$ : Methyl alcohol and are presented in Table 3. The experimental and calculated band intensities of  $\text{Nd}^{3+}$  ion in five alcohols are

**Table 1** Measured and calculated energies (in  $\text{cm}^{-1}$ ) of the observed levels for  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in various alcohols.

Transition from $^4I_{9/2}$	Methyl alcohol		Ethyl alcohol		Isopropyl alcohol		Butyl alcohol		Amyl alcohol	
	$E_{\text{expt}}$	$E_{\text{calc}}$	$E_{\text{expt}}$	$E_{\text{calc}}$	$E_{\text{expt}}$	$E_{\text{calc}}$	$E_{\text{expt}}$	$E_{\text{calc}}$	$E_{\text{expt}}$	$E_{\text{calc}}$
$^4D_{3/2}$	28977	29037	28894	28960	28810	28872	28894	28880	28563	28647
$^2D_{3/2}$	22020	21987	22045	22013	21972	21930	21900	21900	21828	21807
$^4G_{9/2}$	19955	19854	19797	19764	19757	19831	19680	19678	19641	19615
$^4G_{7/2}$	19393	19380	19375	19309	19337	19241	19225	19239	19189	19187
$^4G_{5/2}$	17539	17520	17508	17466	17417	17417	17417	17426	17387	17285
$^2H_{11/2}$	16229	16255	16177	16219	16073	16137	16125	16116	16125	16129
$^4F_{9/2}$	14966	15060	14944	14997	14877	14951	14899	14923	14910	14910
$^4F_{7/2}$	13723	13706	13676	13651	13639	13623	13648	13616	13676	13638
$^4F_{5/2}$	12671	12659	12623	12623	12623	12617	12639	12628	12671	12692
$^4F_{3/2}$	11652	11657	11611	11635	11598	11621	11611	11637	11638	11631
rms deviation	$\pm 50$		$\pm 42$		$\pm 51$		$\pm 17$		$\pm 45$	

**Table 2** Values of Racah ( $E^1, E^2, E_3$ ), spin-orbit ( $\xi_{4f}$ ), configurational interaction ( $\alpha$ ), Judd-Ofelt ( $T_i$ ), refractive index ( $n$ ) and intensity ( $\Omega_i$ ) Parameters for  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in various alcohols.

Parameter	Methyl alcohol	Ethyl alcohol	Isopropyl alcohol	Butyl alcohol	Amyl alcohol
$E^1$	5032.17	5048.63	5013.23	4998.92	4917.04
$E^2$	27.92	28.08	27.84	27.37	26.30
$E^3$	502.65	500.88	498.72	498.90	490.84
$\xi_{4f}$	912.62	900.93	894.70	882.34	888.92
$\alpha$	5.917	5.134	3.75	2.74	-2.73
$T_2 \times 10^9$	1.440	0.992	1.575	1.353	1.305
$T_4 \times 10^9$	0.816	0.609	0.607	0.593	0.763
$T_6 \times 10^9$	1.680	1.745	1.737	1.544	1.619
$n$	1.338	1.369	1.380	1.403	1.406
$\Omega_2 \times 10^{20}$	11.122	8.836	1.580	9.998	9.624
$\Omega_4 \times 10^{20}$	6.307	5.425	4.561	4.382	5.632
$\Omega_6 \times 10^{20}$	12.977	15.542	13.045	11.414	11.940

**Table 3** Squared reduced matrix elements  $(\psi J | U^{\lambda} | \psi' J')^2$  for the observed levels of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ : Methyl alcohol.

Transition from $^4I_{9/2}$	$ U^2 ^2$	$ U^4 ^2$	$ U_6 ^2$
$^4D_{3/2}$	0	0.19212	0.01633
$^2D_{3/2}$	0	0.01407	0.00002
$^4G_{9/2}$	0.00291	0.04127	0.02308
$^4G_{7/2}$	0.08737	0.23674	0.07886
$^4G_{5/2}$	0.89547	0.41615	0.03459
$^2H_{11/2}$	0.00118	0.00198	0.02008
$^4F_{9/2}$	0.00045	0.00680	0.05793
$^4F_{7/2}$	0.00167	0.03697	0.42825
$^4F_{5/2}$	0.00094	0.23950	0.39484
$^4F_{3/2}$	0	0.22989	0.05223

listed in Table 4. Table 4 reveals that the hypersensitive transition ( $^4I_{9/2} \rightarrow ^4G_{5/2}$ ) has the maximum intensity which follows the selection rule

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

The intensity of this transition is well monitored by  $T_2$  and  $\|U^2\|^2$  parameters. The other two parameters namely  $T_4$  and  $T_6$  will be supplemental to  $T_2$  parameter in explaining the variations in the intensity values of the hypersensitive transition. With regard to the intensities of other remaining bands, all the three ( $T_i$ ) parameters will influence the changes. The dependance of  $f_{\text{cal}}$  (hypersensitive transition) on the Judd-Ofelt  $T_2$  parameter is shown below for the complexes under study.

Parameters	MA	EA	IPA	BA	AA
$f_{\text{cal}} (\times 10^6)$	29.597	21.057	31.577	26.335	26.821
$T_2 (\times 10^9)$	1.440	0.992	1.675	1.353	1.305

**Table 4** Measured and computed spectral intensities ( $f \times 10^6$ ) of the observed levels for  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in various alcohols.

Transition from $^4I_{9/2}$	Methyl alcohol		Ethyl alcohol		Isopropyl alcohol		Butyl alcohol		Amyl alcohol	
	$f_{\text{expt}}$	$f_{\text{calc}}$	$f_{\text{expt}}$	$f_{\text{calc}}$	$f_{\text{expt}}$	$f_{\text{calc}}$	$f_{\text{expt}}$	$f_{\text{calc}}$	$f_{\text{expt}}$	$f_{\text{calc}}$
$^4D_{3/2}$	7.096	5.341	6.908	4.206	7.344	4.179	6.034	4.021	7.206	4.947
$^2D_{3/2}$	0.318	0.253	0.355	0.190	0.233	0.188	0.289	0.185	0.372	0.235
$^4D_{9/2}$	—	1.530	—	1.552	—	1.383	—	1.261	—	1.428
$^4G_{7/2}$	11.166	8.759	9.404	7.143	9.378	8.260	8.637	7.315	10.839	8.108
$^4G_{5/2}$	29.385	29.597	20.832	21.057	31.479	31.577	26.218	26.335	26.578	26.821
$^2H_{11/2}$	0.105	0.601	0.064	0.605	0.122	0.611	0.113	0.544	0.247	0.753
$^4F_{9/2}$	0.540	1.549	0.574	1.579	0.239	1.569	0.547	1.402	0.877	1.484
$^4F_{7/2}$	10.470	10.332	11.852	10.555	11.062	10.491	9.601	0.360	10.698	9.900
$^4F_{5/2}$	10.793	10.901	9.155	10.555	10.095	10.514	9.356	9.521	9.534	10.434
$^4F_{3/2}$	1.492	3.210	1.662	2.685	1.389	2.671	1.306	2.520	1.613	3.027

From this table it is observed that the hypersensitive level ( ${}^4G_{5/2}$ ) intensities are found to be reasonably high in isopropyl alcohol (IPA) and much smaller in ethyl alcohol (EA). From Table 2 it is noted that Judd-Ofelt ( $T_\lambda$ ) parameters are found to be in the following order for the five  $Nd^{3+}$  complexes.

$$T_6 > T_2 > T_4$$

Similar observations have earlier been made for  $Nd^{3+}$  in inorganic hosts too<sup>9-10</sup>. Since the change of environments around the rare earth ion influence the variation in band intensities and a little amount of shift in the energy level structure, the values of eigenvectors of the states remain more or less the same. As a result of this there will not be much change in the values of  $\|U^\lambda\|^2$  of  $Nd^{3+}$  complexes.

In Table 4, there are certain disagreements exist between the measured and theoretical intensities. The reasons, for the above inconsistent correlations are explained as follows. The calculated ' $f$ ' is more dependent on Judd-Ofelt ( $T_\lambda$ ) and  $\|U^\lambda\|^2$  values as explained earlier<sup>9</sup>. As these  $\|U^\lambda\|^2$  values are very lightly influenced (in case of certain states) by the environments, there could be a situation for an unsatisfactory agreement between the theory and experimental values. The band intensity of  ${}^4G_{9/2}$  could not be measured experimentally in all the hosts, however the theoretical values are evaluated and presented in Table 3.

### 3.3 Radiative Lifetimes ( $\tau_R$ )

The lifetimes of the fluorescent states have been determined through the theoretical approach by using the Judd-Ofelt parameters (Table 2). For  $Nd^{3+}$ , there are about eight states identified as electronic excited states. Of them, one state is believed to be a radiative transition and the other seven are called non-radiative transitions,<sup>11</sup> they are as follows:

$$\begin{aligned} \text{Radiative transition:} & \quad {}^4F_{3/2} \\ \text{Non-radiative transitions:} & \quad {}^4F_{5/2}, {}^4F_{9/2}, \\ & \quad {}^2H_{11/2}, \\ & \quad {}^4G_{5/2}, {}^4G_{7/2}, {}^4G_{9/2} \\ & \quad {}^4D_{3/2} \end{aligned}$$

For the above eight fluorescing states and their next power lying follow up states, the values of squared reduced matrix elements  $\|U^\lambda\|^2$  for  $Nd^{3+}$ : methyl alcohol have been computed and listed in Table 5. By using the data given in Tables 2 and 5, the computed numerical values of electric dipole ( $S_{ed}$ ), magnetic dipoles ( $S_{md}$ ), transition probability ( $A$ ) and relaxation rate ( $A_T$ ) are presented in Table 6. The reciprocal value of  $A_T$  gives us the lifetime ( $\tau_R$  in  $\mu s$ ) of the fluorescing state. The theoretically predicted  $\tau_R$  values for the eight excited states of five  $Nd^{3+}$  complexes are summarised in Table 7. From this table, it is noted that the fluorescing state  ${}^2H_{11/2}$  has the maximum and the minimum for  ${}^4D_{3/2}$ . The following is the order in which the lifetime values  $\tau_R$  (in  $\mu s$ ) vary from host to host.

$${}^2H_{11/2} > {}^4F_{3/2} > {}^4F_{9/2} > {}^4F_{5/2} > {}^4G_{9/2} > {}^4G_{7/2} > {}^4G_{5/2} > {}^4D_{3/2}$$

**Table 5** Squared reduced matrix elements ( $\psi J \| U^\lambda \| \psi' J' \rangle^2$  for the fluorescent levels ( $^4F_{3/2, 5/2, 9/2}$ ,  $^2H_{11/2}$ ,  $^4G_{5/2, 7/2, 9/2}$  &  $^4D_{3/2}$ ) and other low-lying levels of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O: *Methyl alcohol*.

Transitions	$\ U^2\ ^2$	$\ U^4\ ^2$	$\ U^6\ ^2$	Transitions	$\ U^2\ ^2$	$\ U^4\ ^2$	$\ U^6\ ^2$
$^4F_{3/2} \rightarrow ^4I_{15/2}$	0	0	0.03049	$^4G_{7/2} \rightarrow ^2H_{9/2}$	0.00956	0.00700	0.04899
$^4I_{13/2}$	0	0	0.20473	$^4F_{3/2}$	0.16289	0.11967	0
$^4I_{11/2}$	0	0.14166	0.41294	$^4I_{15/2}$	0	0.02599	0.01255
$^4I_{9/2}$	0	0.22989	0.05223	$^4I_{13/2}$	0	0.25536	0.08103
$^4F_{5/2} \rightarrow ^2H_{9/2}$	0.00696	0.02815	0.00186	$^4I_{11/3}$	0.86846	0.15737	0.00387
$^4F_{3/2}$	0.05127	0.05062	0	$^4I_{9/2}$	0.08737	0.23674	0.07886
$^4I_{15/2}$	0	0	0.23155	$^4G_{9/2} \rightarrow ^2K_{13/2}$	0.02137	0.08858	0.14144
$^4I_{13/2}$	0	0.17914	0.40013	$^4G_{7/2}$	0.00005	0.10380	0.05613
$^4I_{11/2}$	0	0.16911	0.03630	$^4G_{5/2}$	0.00021	0.04579	0.23214
$^4I_{9/2}$	0.00094	0.23950	0.39484	$^2G_{7/2}$	0.04231	0.01012	0.08025
$^4F_{9/2} \rightarrow ^4F_{7/2}$	0.03397	0.11864	0.02914	$^2H_{11/2}$	0.01189	0.00854	0.37918
$^4S_{3/2}$	0	0.00048	0.00192	$^4F_{9/2}$	0.15820	0.03479	0.21691
$^4F_{5/2}$	0.00540	0.04381	0.07785	$^4F_{7/2}$	0.23731	0.03440	0.14919
$^2H_{9/2}$	0.06497	0.00061	0.13785	$^4S_{3/2}$	0	0.16519	0.00042
$^4F_{3/2}$	0	0.01266	0.10688	$^4F_{5/2}$	0.10458	0.10158	0.00396
$^4I_{15/2}$	0	0.54159	0.46011	$^2H_{9/2}$	0.00067	0.00079	0.15416
$^4I_{13/2}$	0.00935	0.20948	0.52360	$^4F_{3/2}$	0	0.02209	0.04978
$^4I_{11/2}$	0.00055	0.02968	0.38272	$^4I_{15/2}$	0	0.05302	0.26399
$^4I_{9/2}$	0.00045	0.00680	0.05793	$^4I_{13/2}$	0.61658	0.31090	0.04945
$^2H_{11/2} \rightarrow ^4F_{9/2}$	0.07066	0.02790	0.06529	$^4I_{11/2}$	0.09851	0.26325	0.01753
$^4F_{7/2}$	0.00252	0.00006	0.17148	$^4I_{9/2}$	0.00291	0.04127	0.02308
$^4S_{3/2}$	0	0.03627	0.00012	$^4D_{3/2} \rightarrow ^2P_{3/2}$	0.04796	0	0
$^4F_{5/2}$	0	0.00012	0.02207	$^2D_{5/2}$	0.01531	0.00256	0
$^2H_{9/2}$	0.07266	0.00615	0.09862	$^2P_{1/2}$	0.00038	0	0
$^4F_{3/2}$	0	0.00204	0.00049	$^4G_{11/2}$	0	0.00262	0.20569
$^4I_{15/2}$	0.09709	0.05203	0.00021	$^2D_{3/2}$	0.03459	0	0
$^4I_{13/2}$	0.00280	0.01147	0.00061	$^2K_{15/2}$	0	0	0.00035
$^4I_{11/2}$	0.00427	0.00021	0.00550	$^2G_{9/2}$	0	0.00257	0.05196
$^4I_{9/2}$	0.00118	0.00198	0.02008	$^2P_{3/2}$	0.04796	0	0
$^4G_{5/2} \rightarrow ^2G_{7/2}$	0.00688	0.17259	0.00003	$^2D_{5/2}$	0.01531	0.00256	0
$^2H_{11/2}$	0	0.00045	0.01163	$^2P_{1/2}$	0.00038	0	0
$^4F_{9/2}$	0.00009	0.01068	0.07645	$^4G_{11/2}$	0	0.00262	0.20569
$^4F_{7/2}$	0.02191	0.05997	0.17791	$^2D_{3/2}$	0.03459	0	0
$^4S_{3/2}$	0.00467	0.19857	0	$^2K_{15/2}$	0	0	0.00035
$^4F_{5/2}$	0.26596	0.13885	0	$^2G_{9/2}$	0	0.00257	0.05196
$^2H_{9/2}$	0.00422	0.00319	0.03846	$^4G_{9/2}$	0	0.00233	0.07355
$^4F_{3/2}$	0.47207	0.01708	0	$^2K_{13/2}$	0	0	0.00100
$^4I_{15/2}$	0	0	0.00442	$^4G_{7/2}$	0.24665	0.00343	0
$^4I_{13/2}$	0	0.03470	0.04739	$^4G_{5/2}$	0.17008	0.00069	0
$^4I_{11/2}$	0	0.29034	0.09678	$^2G_{7/2}$	0.15151	0.01244	0
$^4I_{9/2}$	0.89547	0.41615	0.03349	$^2H_{11/2}$	0	0.04085	0.01035
$^4G_{7/2} \rightarrow ^4G_{5/2}$	0.00419	0.38400	0.07589	$^4D_{3/2} \rightarrow ^4F_{9/2}$	0	0.17805	0.00248
$^2G_{7/2}$	0.00063	0.01126	0.02235	$^4F_{7/2}$	0.24549	0.06892	0
$^2H_{11/2}$	0	0.02194	0.04375	$^4S_{3/2}$	0.15642	0	0
$^4F_{9/2}$	0.03661	0.08504	0.28835	$^4F_{5/2}$	0.05742	0.19898	0
$^4F_{7/2}$	0.26678	0.10369	0.00033	$^2H_{9/2}$	0	0.02015	0.00605
$^4S_{3/2}$	0.00042	0.16535	0	$^4F_{3/2}$	0.14720	0	0
$^4F_{5/2}$	0.41940	0.00921	0.14311	$^4I_{15/2}$	0	0	0.00821
				$^4I_{13/2}$	0	0	0.02695
				$^4I_{11/2}$	0	0.27543	0.00689
				$^4I_{9/2}$	0	0.19212	0.01633

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**Table 6** The electric ( $S_{ed} \times 10^{22}$ ), magnetic ( $S_{md} \times 10^{22}$ ) dipole line strengths, transition probabilities ( $A$  in  $\text{sec}^{-1}$ ) and relaxation ratio ( $A_T$  in  $\text{sec}^{-1}$ ) for the fluorescent levels ( $^4F_{3/2, 5/2, 9/2}$ ,  $^2H_{11/2}$ ,  $^4G_{5/2, 7/2, 9/2}$  &  $^4D_{3/2}$ ) of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in various alcohols.

Transitions $SLJ \rightarrow SL'J'$	Methyl alcohol			Ethyl alcohol			Isopropyl alcohol			Butyl alcohol			Amyl alcohol		
	$S_{ed}$	$S_{md}$	$A$	$S_{ed}$	$S_{md}$	$A$	$S_{ed}$	$S_{md}$	$A$	$S_{ed}$	$S_{md}$	$A$	$S_{ed}$	$S_{md}$	$A$
$^4F_{3/2} \rightarrow ^4I_{15/2}$	39	0	23.90	47	0	31.57	39	0	27.58	34	0	26.82	36	0	27.51
$^4I_{13/2}$	255	0	435.81	318	0	564.78	267	0	488.35	233	0	462.88	244	0	479.89
$^4I_{11/2}$	625	0	2123.10	718	0	2609.30	603	0	2243.90	533	0	2116.50	572	0	2270.90
$^4I_{9/2}$	212	0	1258.80	205	0	1292.80	172	0	1108.40	160	0	1084.70	191	0	1303.70
	$A_T$		3841	$A_T$		4498	$A_T$		3868	$A_T$		3690	$A_T$		4082
$^4F_{5/2} \rightarrow ^2H_{9/2}$	27	0	0	24	0	0	24	0	0	21	0	0	24	0	0
$^4F_{3/2}$	88	33.98	0.41	72	33.89	0.96	87	33.89	0.41	73	34.02	0.36	77	33.36	0.39
$^4I_{15/2}$	300	0	209.14	359	0	272.25	302	0	236.49	264	0	226.15	276	0	234.56
$^4I_{13/2}$	632	0	1033.60	719	0	1261.10	603	0	1087.20	535	0	1034.20	578	0	1116.70
$^4I_{11/2}$	153	0	479.33	148	0	491.02	124	0	421.73	115	0	414.99	138	0	499.76
$^4I_{9/2}$	664	0	3426.90	744	0	4056.90	625	0	5211.20	556	0	3248.90	607	0	3574.30
	$A_T$		5149	$A_T$		6081	$A_T$		6957	$A_T$		4924	$A_T$		5425
$^4F_{9/2} \rightarrow ^4F_{7/2}$	150	28.31	0.50	139	28.31	0.53	134	28.43	0.51	119	28.27	0.46	134	28.71	0.52
$^4S_{3/2}$	2	0	0.01	3	0	0.04	2	0	0.01	2	0	0.01	2	0	0.01
$^4F_{5/2}$	134	0	2.21	149	0	2.54	128	0	2.16	113	0	1.94	122	0	2.16
$^2H_{9/2}$	251	16.23	7.87	271	16.54	7.87	261	16.23	8.34	222	16.16	7.00	227	16.03	7.36
$^4F_{3/2}$	146	0	7.97	172	0	9.66	145	0	8.07	127	0	7.15	134	0	7.83
$^4I_{15/2}$	938	0	943.32	1008	0	1089.92	847	0	936.29	762	0	904.05	854	0	1013.80
$^4I_{13/2}$	822	0	1596.70	935	0	1936.80	790	0	1667.90	698	0	1564.50	752	0	1692.20
$^4I_{11/2}$	516	0.15	1694.00	611	0.12	2125.60	513	0.14	1815.50	450	0.14	1675.60	474	0.14	1778.90
$^4I_{9/2}$	79	0.12	401.54	94	0.09	497.00	79	0.09	425.39	69	0.09	390.40	73	0.09	416.89
	$A_T$		4655	$A_T$		5669	$A_T$		4864	$A_T$		4551	$A_T$		4119

${}^2\text{H}_{11/2} \rightarrow {}^4\text{F}_{9/2}$	180	3.34	0.09	175	3.86	0.10	186	3.62	0.07	157	3.72	0.08	161	3.67	0.08
${}^4\text{F}_{7/2}$	225	0	2.23	268	0	2.90	226	0	2.31	198	0	2.07	207	0	2.18
${}^4\text{S}_{3/2}$	23	0	2.90	19	0	0.26	16	0	0.20	16	0	0.20	20	0	0.24
${}^4\text{F}_{5/2}$	28	0	0.92	34	0	1.18	28	0	0.95	25	0	0.86	26	0	0.91
${}^2\text{H}_{9/2}$	212	15.22	11.50	220	15.15	12.27	222	15.25	11.44	187	15.33	10.52	191	15.42	10.89
${}^4\text{F}_{3/2}$	2	0	0.14	2	0	0.16	2	0	0.13	2	0	0.12	2	0	0.15
${}^4\text{I}_{15/2}$	141	0	150.35	114	0	131.88	146	0	170.55	120	0	150.47	123	0	153.98
${}^4\text{I}_{13/2}$	182	1.06	359.87	18	1.04	38.55	16	1.03	38.15	14	0.98	36.05	16	1.01	39.99
${}^4\text{I}_{11/2}$	12	0.29	38.76	12	0.29	43.94	12	0.28	44.76	10	0.28	40.01	10	0.28	40.87
${}^4\text{I}_{9/2}$	28	0	137.98	33	0	170.24	28	0	147.20	24	0	134.64	26	0	142.85
	$A_T$		704		$A_T$	401		$A_T$	415		$A_T$	375		$A_T$	392
${}^4\text{G}_{5/2} \rightarrow {}^2\text{G}_{7/2}$	116	8.59	0.08	99	8.67	0.07	534	8.58	0.38	82	8.82	0.05	103	10.27	0.02
${}^2\text{H}_{11/2}$	15	0	0.30	18	0	0.37	15	0	0.33	13	0	0.32	14	0	0.26
${}^4\text{F}_{9/2}$	106	0	5.31	124	0	6.73	104	0	5.75	92	0	5.52	97	0	4.86
${}^4\text{F}_{7/2}$	285	0.21	44.99	319	0.20	53.59	279	0.20	47.26	244	0.18	43.88	260	0.21	41.43
${}^4\text{S}_{3/2}$	130	0	23.22	111	0	21.03	96	0	18.04	91	0	18.12	116	0	19.65
${}^4\text{F}_{5/2}$	383	0.02	115.38	310	0.01	98.91	397	0.01	127.58	326	0.01	110.72	334	0.01	103.63
${}^2\text{H}_{9/2}$	56	0	22.37	65	0	26.65	56	0	23.82	49	0	21.43	51	0	20.70
${}^4\text{F}_{15/2}$	641	0.02	350.97	426	0.02	244.94	601	0.02	347.56	479	0.01	289.91	463	0.02	263.15
${}^4\text{I}_{15/2}$	6	0	21.62	6	0	27.83	6	0	23.88	5	0	22.51	6	0	22.58
${}^4\text{I}_{13/2}$	83	0	526.37	92	0	62.33	77	0	533.48	69	0	508.10	76	0	540.42
${}^4\text{I}_{11/2}$	309	0	2990.02	308	0	3166.70	258	0	2705.70	237	0	2633.40	279	0	3016.80
${}^4\text{I}_{9/2}$	1303	0	17696.00	1070	0	15610.00	1361	0	20154.00	1117	0	17407.00	1137	0	17401.00
	$A_T$		22069		$A_T$	19880		$A_T$	23987		$A_T$	21060		$A_T$	21434

(continued)

**Table 6** The electric ( $S_{ed} \times 10^{22}$ ), magnetic ( $S_{md} \times 10^{22}$ ) dipole line strengths, transition probabilities (A in  $\text{sec}^{-1}$ ) and relaxation ratio ( $A_T$  in  $\text{sec}^{-1}$ ) for the fluorescent levels ( ${}^4F_{3/2, 5/2, 7/2, 9/2}$ ,  ${}^2H_{11/2}$ ,  ${}^4G_{5/2, 7/2, 9/2}$  &  ${}^4D_{3/2}$ ) of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in various alcohols. (continued)

Transitions SLJ	Methyl alcohol			Ethyl alcohol			Isopropyl alcohol			Butyl alcohol			Amyl alcohol		
	$S_{ed}$	A	$S_{md}$	$S_{ed}$	A	$S_{md}$	$S_{ed}$	A	$S_{md}$	$S_{ed}$	A	$S_{md}$	A	$S_{ed}$	$S_{md}$
${}^4G_{7/2} \rightarrow {}^4G_{5/2}$	345	38.64	3.44	330	38.59	3.39	279	38.69	2.92	259	38.46	2.78	310	36.98	3.63
${}^2G_{7/2}$	36	0.31	0.86	41	0.32	1.00	35	0.32	0.86	31	0.34	0.75	33	0.37	0.70
${}^2H_{11/2}$	70	0	6.50	79	0	7.61	67	0	6.63	59	0	6.24	64	0	6.24
${}^4F_{9/2}$	468	0.01	74.56	526	0.01	88.67	461	0.01	78.40	403	0.01	72.88	392	0.01	66.07
${}^4F_{7/2}$	363	0.79	123.40	292	0.65	104.93	383	0.64	138.04	312	0.63	117.95	315	0.76	113.23
${}^4S_{3/2}$	104	0	38.77	90	0	34.94	75	0	29.31	72	0	29.39	93	0	34.89
${}^4F_{5/2}$	658	0.34	357.36	598	0.33	341.38	647	0.33	370.63	423	0.33	253.90	579	0.41	334.86
${}^2H_{9/2}$	78	0.13	62.69	88	0.13	60.94	79	0.13	55.52	68	0.12	49.55	71	0.10	50.06
${}^4F_{3/2}$	257	0	220.97	209	0	185.92	260	0	234.46	216	0	202.29	225	0	205.28
${}^4I_{15/2}$	32	0	139.17	33	0	152.97	28	0	130.93	25	0	127.59	29	0	143.68
${}^4I_{13/2}$	266	0	1786	264	0	1886.80	222	0	1611.5	204	0	1573.9	240	0	1822.00
${}^4I_{11/2}$	1070	0	10532.00	858	0	8945.30	1169	0	12365.00	941	0	10505.00	929	0	10245.00
${}^4I_{9/2}$	348	0	4735.20	328	0	4699.40	320	0	4656.10	281	0	4282.50	311	0	4712.90
	$A_T$	18018		$A_T$	16513		$A_T$	19680		$A_T$	17224		$A_T$	17732	
${}^4G_{9/2} \rightarrow {}^2K_{13/2}$	263	0	0.16	286	0	0.16	251	0	0.18	221	0	0.18	239	0	0.42
${}^4G_{7/2}$	138	16.32	0.01	143	14.01	0.01	120	13.81	0.01	109	13.88	0.01	125	15.84	0.02
${}^4G_{5/2}$	330	0	4.45	385	0	5.29	323	0	4.39	285	0	3.92	303	0	5.02
${}^2G_{7/2}$	157	24.36	5.57	167	24.36	6.01	162	24.32	5.87	138	24.49	5.04	142	25.80	4.96
${}^2H_{11/2}$	509	0.20	51.32	602	0.20	62.46	512	0.21	54.71	447	0.19	50.37	467	0.08	51.44
${}^4F_{9/2}$	479	6.81	80.61	495	6.74	87.55	497	6.77	88.45	421	6.52	79.32	430	5.85	79.18
${}^4F_{7/2}$	479	0.45	160.10	460	0.45	161.21	508	0.46	178.52	422	0.47	154.92	425	0.39	153.93
${}^4S_{3/2}$	104	0	37.88	90	0	34.06	75	0	28.43	72	0	28.45	93	0	35.10
${}^4F_{5/2}$	185	0	96.15	153	0	83.35	183	0	99.40	153	0	87.08	162	0	9.15
${}^2H_{9/2}$	201	1.54	127.78	240	1.54	156.98	202	1.54	134.09	176	1.54	120.82	185	1.56	125.81
${}^4F_{3/2}$	78	0	12.73	89	0	74.34	75	0	62.50	66	0	57.53	71	0	62.25
${}^4I_{15/2}$	376	0	140.22	439	0	1745.10	368	0	1490.50	323	0	1396.20	345	0	1479.00
${}^4I_{13/2}$	946	0	5488.10	790	0	4864.60	982	0	6137.20	809	0	5361.10	827	0	5463.70
${}^4I_{11/2}$	298	0.64	2516.00	257	0.04	2290.90	266	0.04	2410.90	233	0.04	2226.50	264	0.04	2513.40
${}^4I_{9/2}$	59	0.01	684.10	60	0.01	740.08	52	0.01	647.99	47	0.01	611.59	53	0.01	868.37
	$A_T$	9405		$A_T$	10312		$A_T$	11343		$A_T$	10178		$A_T$	10943	

${}^2D_{3/2} \rightarrow {}^2P_{3/2}$	53	0	3.55	42	0	2.96	60	0	4.41	47	0	3.96	46	0	3.01
${}^2D_{5/2}$	18	0.07	12.85	15	0.06	10.94	20	0.06	15.16	16	0.07	12.45	16	0.10	10.49
${}^2P_{1/2}$	1	0.31	0.57	1	0.31	0.51	1	0.31	0.64	1	0.33	0.62	1	0.37	0.60
${}^4G_{11/2}$	268	0	347.39	321	0	453.01	269	0	387.39	235	0	362.84	247	0	358.65
${}^2D_{3/2}$	38	0.06	67.96	30	0.07	55.96	43	0.06	81.60	34	0.04	67.90	33	0.03	61.36
${}^2K_{15/2}$	1	0	0.88	1	0	2.34	1	0	0.99	1	0	0.93	1	0	0.97
${}^2G_{9/2}$	69	0	132.92	82	0	171.07	68	0	146.38	60	0	135.93	63	0	131.32
${}^4G_{9/2}$	96	0	303.10	115	0	388.85	97	0	332.00	84	0	306.21	89	0	300.17
${}^2K_{13/2}$	1	0	5.11	2	0	6.48	1	0	5.64	1	0	5.22	1	0	5.48
${}^4G_{7/2}$	276	0	1089.70	219	0	834.96	311	0	1202.40	248	0	1005.60	239	0	927.54
${}^4G_{5/2}$	189	0	1079.20	150	0	913.29	214	0	1314.90	170	0	1993.50	164	0	1030.50
${}^2G_{7/2}$	176	0	1180.90	140	0	1001.40	196	0	1417.90	156	0	1176.30	152	0	1074.90
${}^2H_{11/2}$	39	0	359.82	38	0	372.68	32	0	319.75	29	0	311.52	35	0	351.05
${}^4F_{9/2}$	115	0	1242.82	100	0	1153.60	84	0	982.68	80	0	992.71	103	0	1202.40
${}^4F_{7/2}$	316	0	4396.10	254	0	3761.90	340	0	5089.40	275	0	4328.90	275	0	4121.70
${}^4S_{3/2}$	173	0.01	2494.70	138	0.01	2105.90	196	0.01	3021.60	156	0.01	2518.30	150	0.01	2290.20
${}^4F_{5/2}$	189	0.01	3149.60	158	0.01	2806.6	162	0.01	2912.30	144	0.01	2711.50	167	0.01	3009.10
${}^2H_{9/2}$	20	0	372.09	20	0	388.29	17	0	331.38	15	0	318.23	18	0	360.85
${}^4F_{3/2}$	163	0	3300.80	130	0	2779.20	185	0	3896.4	147	0	3323.5	141	0	3085.10
${}^4I_{15/2}$	10	0	483.56	12	0	619.61	10	0	529.08	9	0	491.59	9	0	497.94
${}^4I_{13/2}$	34	0	2076.30	41	0	2652.10	35	0	2261.80	30	0	2092.9	32	0	2129.8
${}^4I_{11/2}$	182	0	13774.00	160	0	12834.00	134	0	10955.00	128	0	11024.00	163	0	13678.00
${}^4I_{9/2}$	142	0	13237.00	129	0	12780.00	108	0	10892.00	102	0	10798.00	127	0	13147.00
		$A_T$	49110		$A_T$	46095		$A_T$	46220		$A_T$	43083		$A_T$	47778

**Table 7** The radiative lifetimes ( $\tau_R$ ) in  $\mu\text{s}$  for the fluorescent level ( ${}^4\text{F}_{3/2, 5/2, 9/2}$ ,  ${}^2\text{H}_{11/2}$ ,  ${}^4\text{G}_{5/2, 7/2, 9/2}$  &  ${}^4\text{D}_{3/2}$ ) of  $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  in various alcohols.

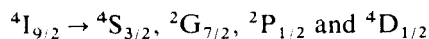
Fluorescent levels	Methyl alcohol	Ethyl alcohol	Isopropyl alcohol	Butyl alcohol	Amyl alcohol
${}^4\text{F}_{3/2}$	260.3	222.3	258.5	270.9	244.9
${}^4\text{F}_{5/2}$	194.1	164.4	143.7	203.1	184.3
${}^4\text{F}_{9/2}$	214.8	176.4	205.5	219.7	203.2
${}^2\text{H}_{11/2}$	1418.8	2490.5	2404.8	2666.2	2549.8
${}^4\text{G}_{5/2}$	45.3	50.3	41.6	47.4	46.6
${}^4\text{G}_{7/2}$	55.4	60.5	50.8	58.1	56.3
${}^4\text{G}_{9/2}$	106.3	96.9	88.1	98.2	91.4
${}^4\text{D}_{3/2}$	20.5	21.6	22.1	23.2	20.9

The following situation has also been noted from Table 7:

$$\begin{aligned} \tau_R (\mu\text{s}): {}^4\text{F}_{3/2}: & \text{BA} > \text{MA} > \text{IPA} > \text{AA} > \text{EA} \\ {}^4\text{F}_{5/2}: & \text{BA} > \text{MA} > \text{AA} > \text{EA} > \text{IPA} \\ {}^4\text{F}_{9/2}: & \text{BA} > \text{MA} > \text{IPA} > \text{AA} > \text{EA} \\ {}^2\text{H}_{11/2}: & \text{BA} > \text{AA} > \text{EA} > \text{IPA} > \text{MA} \\ {}^4\text{G}_{5/2}: & \text{EA} > \text{BA} > \text{AA} > \text{MA} > \text{IPA} \\ \tau_R (\mu\text{s}): {}^4\text{G}_{7/2}: & \text{EA} > \text{BA} > \text{AA} > \text{MA} > \text{IPA} \\ {}^4\text{G}_{9/2}: & \text{MA} > \text{BA} > \text{EA} > \text{AA} > \text{IPA} \\ {}^4\text{D}_{3/2}: & \text{BA} > \text{IPA} > \text{EA} > \text{AA} > \text{MA} \end{aligned}$$

### 3.4 Second Derivative Spectra

The following four electronic states which could not be recorded in the normal spectra of  $\text{Nd}^{3+}$  complexes, are now found to exist in the second derivative spectra. The measured energies of these four new states are presented in Table 7.



Thus the second derivative spectra of these  $\text{Nd}^{3+}$  complexes have revealed altogether fourteen energy states.

**Table 8** The measured energies of certain bands revealed by the second derivative spectra, which have not been noticed in the normal spectra of  $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  in various alcohols.

Transitions from ${}^4\text{I}_{9/2}$	Methyl alcohol	Ethyl alcohol	Isopropyl alcohol	Butyl alcohol	Amyl alcohol
${}^4\text{S}_{3/2}$	13620	13620	13583	13546	13620
${}^2\text{G}_{7/2}$	21361	21316	21453	21316	21361
${}^2\text{P}_{1/2}$	23578	23467	23522	23467	23412
${}^4\text{D}_{1/2}$	29403	29317	29146	29274	29146

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