

Spectral Studies of Pr^{3+} in Different Solvents

A.H. QUSTI* and A.G.M. AL-SEHEMI**

*Department of Chemistry, King Abdulaziz University,
Jeddah, Saudi Arabia

**Department of Science, Teacher's College, Abha, Saudi Arabia

ABSTRACT. Absorption spectra of Pr^{3+} ion in water (deionized), heavy water, dimethylsulphoxide, hexadeutrodijmethylsulphoxide, was studied in the UV-Vis. and near IR regions. Judd-Ofelt (T_2, T_4, T_6), Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3), and spin-orbit (ζ_4) parameters of Pr^{3+} in the aforementioned media are evaluated. The values of nephelauxetic ratio (β), Sinha's parameter ($\delta\%$) and the bonding parameters ($b^{1/2}$) are also discussed.

Introduction

Since 1962 when the Judd-Ofelt theory was published^[1,2], the spectroscopic properties of tripositive rare-earth ions have been studied extensively, both experimentally and theoretically^[3-10]. Carnal *et al.*^[11] correlated the experimental and theoretical intensities of the solutions bands of Pr^{3+} in the ethyl acetate. Surana *et al.*^[12] have studied the absorption spectrum of Pr^{3+} in haloacetate solution. Lakshman and Buddhudu^[13] reported the Slater-Condon, configuration, spin-orbit, nephelauxetic, bonding, and Judd-Ofelt parameters of Pr^{3+} in the acetates of Praseodymium, Magnesium, Calcium, and Cadmium complexes. Moreover, Buddhudu and Babu^[14] reported the Racah and Judd-Ofelt parameters for Pr^{3+} ion in methyl, butyl, isopropyl and amyl alcohols. In general, semiempirical calculations based on the Judd-Ofelt theory were not satisfactory for the Pr^{3+} ion^[14,15]. In these studies, high root-mean-square deviations of the oscillator strengths and negative values of T_2 are reported. In this work, various spectroscopic parameters have been evaluated from the UV-Vis. bands of Pr^{3+} in different solution media.

Theory

1. Experimental Oscillator Strength

The experimental oscillator strength (P_{exp}) of a band is obtained by

$$P_{\text{exp}} = 4.18 \times 10^{-9} \int_{\nu_1} \epsilon(\nu) d\nu \quad (1)$$

where $\int \epsilon(\nu) d\nu$ is the area under the corresponding band, $\epsilon(\nu)$ is the molar extinction coefficient defined by :

$$\epsilon = \frac{\ell}{C} \log \frac{I_0}{I} \quad (2)$$

where C is the molar concentration, ℓ is the light path length in (cm), and $\log I_0/I$ is the optical density.

2. Judd-Ofelt Parameters

According to the Judd-Ofelt theory^[1,2] the oscillator strength of an induced electric dipole transition is given by :

$$P_{ed} = \nu \sum_{\lambda=2,4,6} T_{\lambda} (\psi_i J \| U^{\lambda} \| \psi_f J)^2 \quad (3)$$

where ν is the energy of a $\psi_i \rightarrow \psi_f$ transition, expressed in cm^{-1} , T_{λ} are the Judd-Ofelt parameters (T_2, T_4, T_6), and $(\psi_i J \| U^{\lambda} \| \psi_f J)^2$ are the squares of the reduced matrix elements of the unit tensor operator U^{λ} . Using experimental oscillator strength of the observed bands and the corresponding squared reduced matrix elements, a number of linear equations equal to the number of observed bands are formed. Employing a least square fit method, the intensity parameters T_2, T_4 , and T_6 are evaluated. These parameters are then used in equation (3) to calculate the so-called calculated oscillator strength (P_{cal}).

The root-mean-square deviation (r.m.s.) are calculated using formula :

$$rms = \left[\frac{\sum (\Delta J)^2}{N} \right]^{\frac{1}{2}} \quad (4)$$

where ΔJ is the deviation of the J^{th} -levels and N is the number of fitted levels.

3. Slater-Condon Parameters

To a first approximation, the energy E_J of the J -th levels may be expressed in terms^[13] of change in parameters by a Taylor-series expansion :

$$E_J = E_{0J} + \sum_{\kappa=2,4,6} \frac{dE_J}{dF_{\kappa}} \Delta F_{\kappa} + \frac{dE_J}{d\xi_{4f}} \Delta \xi_{4f} \quad (5)$$

where E_{0J} is the zero-order energy, (dE_J / d_{κ}) and $(dF_J / d\xi_{4f})$ are the partial derivatives. The values of the zero-order energy and the partial derivatives are taken from

tables of Wong.^[16] Employing a least-squares fit method, correction factors ΔF_2 , ΔF_4 , ΔF_6 and $\Delta \xi_{4f}$ are obtained. The Slater-Condon (F_2 , F_4 , F_6) and the spin-orbit (ξ_{4f}) parameters are obtained from the relations.^[13]

$$\begin{aligned}\Delta F_2 &= F_2 - F_2^0 \\ \Delta F_4 &= F_4 - F_4^0 \\ \Delta F_6 &= F_6 - F_6^0 \\ \Delta \xi_{4f} &= \xi_{4f} - \xi_{4f}^0\end{aligned}\quad (6)$$

where F_2^0 , F_4^0 , F_6^0 and ξ_{4f}^0 are the zero-order parameters.

4. The Racah Parameters

The Racah parameters (E^1 , E^2 , E^3) are defined^[17,18] by :

$$\begin{aligned}E^1 &= (70F_2 + 231F_4 + 2002F_6) / 9 \\ E^2 &= (F_2 + 3F_4 + 7F_6) / 9 \\ E^3 &= (5F_2 + 6F_4 - 91F_6) / 3\end{aligned}\quad (7)$$

5. Nephelauxetic, Sinha and Bonding Parameters

The nephelauxetic effect observed in the spectra of rare-earths complexes is revealed by shifts in absorption bands toward lower energies. These red-shifts of spectral bands of 4f-complexes compared to those of the respective aquas, are may be due to : a reduction in electronic parameters in the 4f-complexes, splitting of bands, and their hypersensitivity.^[19] The average nephelauxetic ratio (β) is given^[13] by :

$$\beta = \frac{1}{n} \sum \frac{\nu_c}{\nu_a}\quad (8)$$

where ν_c and ν_a are the wavenumber in cm^{-1} of 4f-4f band in complex, and aqueous solutions, respectively and n is the number of observed bands. The nephelauxetic ratio (β) is related to the covalency parameter bonding parameter ($\delta\%$)^[20] by :

$$\delta \% = \frac{(1 - \beta)}{\beta} \times 100\quad (9)$$

The bonding parameter ($b^{1/2}$) is given^[17] by :

$$b^{1/2} = \left[\frac{1}{2} (1 - \beta) \right]^{1/2}\quad (10)$$

Less than one value of β and positive values of $\delta\%$ and $b^{1/2}$ indicate that the bonding in complex is more covalent in nature than in aqueous solution.

Experimental

Material used in this study are :

$Pr(NO_3)_3 \cdot 5H_2O$ 99.9% (Fluka), $PrCl_3 \cdot 6H_2O$ 99.9% (Aldrich), D_2O , $(CH_3)_2SO$, $(CD_3)_2SO$, and CH_3COOH (BDH).

All the UV-VIS absorption spectral bands of Pr^{3+} were recorded with Shimadzu UV-260 spectrophotometer. Optical cells of pathlength of 10 mm were recorded at 25°C.

Results and Discussion

The UV-Vis. absorption bands of Pr^{3+} in H_2O (deionized), D_2O , $(\text{CH}_3)_2\text{SO}$, $(\text{CD}_3)_2\text{SO}$, and CH_3COOH , were recorded at 25°C. The four bands observed in the UV-Vis. regions are due to the $4f-4f$ transitions: ${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1$ (${}^1\text{I}_6$) and ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$. These bands are shown in Fig. 1. In this figure, the absorption bands of Pr^{3+} in $(\text{CD}_3)_2\text{SO}$ and D_2O are shown in (a) and (b) respectively. The two spectra are similar except that the shoulder of the ${}^3\text{H}_4 \rightarrow {}^1\text{D}_2$ band in D_2O is on the right side while the shoulder of the same band in $(\text{CD}_3)_2\text{SO}$ is on left side.

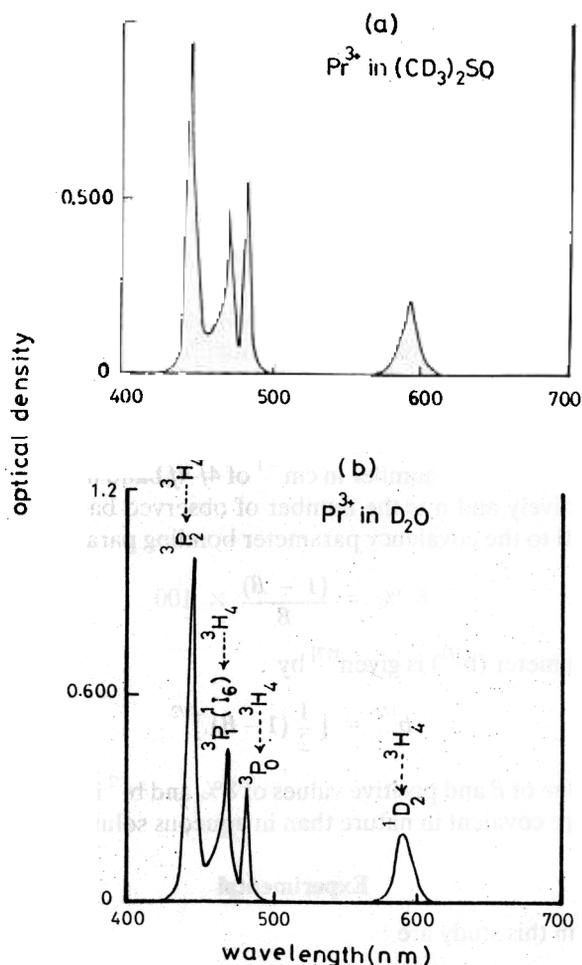


FIG. 1. Absorption spectra of Pr^{3+} at room temperature in: (a) $(\text{CD}_3)_2\text{SO}$, (b) D_2O .

1. Experimental and Calculated Oscillator Strengths

Experimental oscillator strength (P_{exp}) were obtained using equation (1). The area under the observed curves $[\int \epsilon(\nu) d\nu]$ were determined by weighing method or by a computer program. The results observed from both methods are nearly identical. We determined empirical values for the T_{λ} parameters and use them in equation (3), to determine calculated oscillator strengths (P_{cal}). For each observed band the values of P_{exp} and ν are substituted together with corresponding squared reduced matrix element in equation (3). The values of the square reduced matrix elements used to calculate P_{cal} of Pr^{3+} in D_2O and deionized H_2O , were those of Pr^{3+} (aqua) reported by Carnall. Those used to calculate P_{cal} for Pr^{3+} bands in $(\text{CH}_3)_2\text{SO}$, $(\text{CD}_3)_2\text{SO}$ and CH_3COOH were those of Pr^{3+} in methyl alcohol reported by Buddhudu^[14]. The values of the square reduced matrix elements of a given lanthanide (Ln^{3+}) are nearly the same in organic and aqueous media. Buddhudu and Babu^[14] have calculated these elements for Pr^{3+} in methyl alcohol and have used the same values to calculate P_{cal} in ethyl, butyl, isopropyl and amylalcohols.

Experimental and calculated oscillator strengths of Pr^{3+} bands in H_2O (deionized), D_2O , $(\text{CH}_3)_2\text{SO}$, $(\text{CD}_3)_2\text{SO}$ and CH_3COOH are listed in Table 1.

TABLE 1. Experimental and calculated intensities ($P \times 10^6$) for the observed levels for the Pr^{3+} ion in various media.

		Pr^{3+} in									
Terms $^3\text{H}_4 \rightarrow$	H_2O		D_2O		$(\text{CH}_3)_2\text{SO}$		$(\text{CD}_3)_2\text{SO}$		CH_3COOH		
	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}	
$^3\text{P}_2$	19.4	19.0	19.5	19.1	14.9	14.7	17.2	16.8	14.1	13.8	
$^3\text{P}_1(^1\text{I}_0)$	6.51	6.08	9.03	8.66	7.69	7.49	10.2	10.0	4.72	4.10	
$^3\text{P}_0$	2.85	3.38	3.26	3.71	4.02	4.27	5.12	5.33	1.54	1.94	
$^1\text{D}_2$	3.48	5.17	4.05	5.73	3.36	4.17	4.22	5.01	2.63	3.90	
r.m.s. $\times 10^{-7}$	8.67		8.49		4.17		3.99		6.51		

In this study, it is found that the experimental oscillator strengths of the observed transitions decrease in the order :

$$^3\text{P}_2 : \text{D}_2\text{O} > \text{H}_2\text{O} > (\text{CD}_3)_2\text{SO} > (\text{CH}_3)_2\text{SO} > \text{CH}_3\text{COOH}$$

$$^3\text{P}_1 : (\text{CD}_3)_2\text{SO} > \text{D}_2\text{O} > (\text{CH}_3)_2\text{SO} > \text{H}_2\text{O} > \text{CH}_3\text{COOH}$$

$$^3\text{P}_0 : (\text{CD}_3)_2\text{SO} > (\text{CH}_3)_2\text{SO} > \text{D}_2\text{O} > \text{H}_2\text{O} > \text{CH}_3\text{COOH}$$

$$^1\text{D}_2 : (\text{CD}_3)_2\text{SO} > \text{D}_2\text{O} > \text{H}_2\text{O} > (\text{CH}_3)_2\text{SO} > \text{CH}_3\text{COOH}$$

The r.m.s. values shown in Table 1 were calculated according to equation (4). These values are lower than those reported for Pr^{3+} in laser liquids^[6], on the other

hand they are little higher than those reported for Pr^{3+} in acetate complexes solutions^[14] in which seven bands were observed.

2. Judd-Ofelt Parameters

Using P_{exp} for P_{ed} , the values of T_2 , T_4 and T_6 parameters were evaluated using equation (3), by a least square fit program. The values of these parameters together with other spectroscopic parameters are presented in Table 2. Our results show that T_2 has negative values for Pr^{3+} in H_2O (deionized), $(\text{CH}_3)_2\text{SO}$ and CH_3COOH . Negative values of T_2 have been also reported for Pr^{3+} in $\text{CD}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, amylalcohol, and $\text{ZrCl}_4\text{-POCl}_3$. This behaviour may be due one or more of the following. Strong f - d mixing, poor resolution method of the overlapped 3P -bands, small number of observed or fitted lines, or due to using incorrect values of the reduced matrix elements of Pr^{3+} or due to other reasons.

TABLE 2. Slater-Condon (F_2 , F_4 and F_6) Racah (E^1 , E^2 and E^3), spin-orbit (ξ_{4f}), Judd-Ofelt (T_2 , T_4 and T_6) parameters and hydrogenic ratio F_4/F_2 and F_6/F_2 Pr^{3+} ion in various media at room temperature.

Parameters	Pr^{3+} in				
	H_2O	D_2O	$(\text{CH}_3)_2\text{SO}$	$(\text{CD}_3)_2\text{SO}$	CH_3COOH
F_2	316.2	316.1	314.5	314.6	314.1
F_4	60.86	55.90	63.63	63.34	62.07
F_6	5.698	5.366	5.833	5.818	5.738
E^1	5289	5087	5377	5367	5312
E^2	19.28	20.66	18.27	18.36	18.67
E^3	475.8	475.9	474.4	474.5	473.5
F_4/F_2	0.192	0.177	0.202	0.201	0.198
F_6/F_2	0.018	0.017	0.019	0.018	0.018
ξ_{4f}	743.9	741.1	735.9	735.6	760.5
$T_2 \times 10^9$	-7.228	3.486	-2.337	1.622	-2.014
$T_4 \times 10^9$	0.942	1.036	1.196	1.499	0.542
$T_6 \times 10^9$	5.975	5.975	4.524	5.142	4.384

3. Other Spectroscopic Parameters

The calculated energies of Pr^{3+} ion in various media have been evaluated according to equation (5) by a least squares fit method. The values of E_{exp} of observed levels and the values of E_{exp} and E_{cal} of Pr^{3+} in different solvents are given in Table 3. The extremely low r.m.s. values indicate excellent agreements between the experimental and calculated energies. The Slater-Condon (F_2 , F_4), spin-orbit (ξ_{4f}),

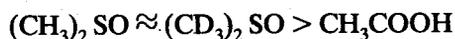
Racah (E^1, E^2, E^3) parameters and the hydrogenic ratio F_4/F_2 and F_6/F_2 were calculated and are shown in Table 2.

TABLE 3. Experimental and calculated energies of the levels for Pr^{3+} ion in various media at room temperature.

Pr ³⁺ in										
Terms ³ H ₄ →	H ₂ O		D ₂ O		(CH ₃) ₂ SO		(CD ₃) ₂ SO		CH ₃ COOH	
	E _{exp.}	E _{cal.}	E _{exp.}	E _{cal.}	E _{exp.}	E _{cal.}	E _{exp.}	E _{cal.}	E _{exp.}	E _{cal.}
¹ S ₀	–	52830	–	51040	–	53560	–	53470	–	53080
³ P ₂	22522	22522	22520	22520	22411	22411	22410	22410	22502	22502
¹ I ₆	–	22020	–	21730	–	22070	–	22060	–	22050
³ P ₁	21340	21340	21350	21350	21240	21240	21240	21240	21304	21304
³ P ₀	20755	20755	20760	20760	20678	20678	20680	20680	20687	20687
¹ D ₂	16966	16966	16970	16670	16829	16829	16840	16840	16892	16892
¹ G ₄	–	10840	–	10270	–	11110	–	11070	–	11070
³ F ₂	–	4787	–	4802	–	4757	–	4757	–	4776
³ F ₃	–	6161	–	6170	–	6115	–	6115	–	6185
³ S ₄	–	7088	–	6922	–	7141	–	7132	–	7164
³ H ₆	–	4221	–	4220	–	4165	–	4164	–	4312
³ H ₅	–	2040	–	2048	–	2007	–	2007	–	2085
³ H ₄	–	0	–	0	–	0	–	0	–	0
r.m.s.	0.184		0.198		0.252		0.252		0.115	

4. Nephelauxetic Effect

The nephelauxetic ratio (β), covalency ($\delta\%$), and bonding ($b^{1/2}$) parameters of Pr^{3+} in $(CH_3)_2SO$, $(CD_3)_2SO$ and CH_3COOH , are shown in Table 4. All the values of β are less than one and all the values of $\delta\%$ and $b^{1/2}$ are positive. These results indicate more covalent nature of bonding between Pr^{3+} and the ligand in complexes. The high value of β and the small values of $\delta\%$ and $b^{1/2}$ in CH_3COOH suggest small participation of the 4f orbitals of Pr^{3+} in bonding. Table 4 also shows, that the $\delta\%$ and $b^{1/2}$ parameters are in the order :



This order seems to be credible because increase of acidity of the solvent shifts the system to less covalent nature since $b^{1/2}$ decreased.

TABLE 4. Nephelauxetic effect for Pr³⁺ ion in various media.

Parameters	Pr ³⁺ ion in:		
	(CH ₃) ₂ SO	(CD ₃) ₂ SO	CH ₃ COOH
β	0.9947	0.9948	0.9974
δ (%)	0.5328	0.5227	0.2607
$b^{1/2}$	0.0364	0.0361	0.0255

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دراسات طيفية لأيون Pr^{3+} في مذيبات مختلفة

عبد الله حسين قستي* و عبد الله غدران السهيمي**

*قسم الكيمياء ، كلية العلوم ، جامعة الملك عبد العزيز ، جدة ، المملكة العربية السعودية ؛
و **قسم العلوم ، كلية المعلمين بأبها ، المملكة العربية السعودية

المستخلص . تم بعون الله تعالى دراسة طيف الامتصاص لأيون Pr^{3+} في H_2O (في الحالة الحرة) ، D_2O ، $(CD_3)_2SO$ ، $(CH_3)_2SO$ ، CH_3COOH وذلك في المنطقة المرئية - فوق البنفسجية (UV-Vis.) والقريبة من تحت الحمراء (IR) . ولقد تم تعيين قيم المتغيرات (البارامترات) الطيفية (T_2, T_4, T_6) ، (F_2, F_4, F_6) ، (E^1, E^2, E^3) و ξ_{4f} ، في المذيبات السابقة الذكر . كما تم مناقشة متغيرات الربط $\beta, \delta, \beta, \delta, \beta$.