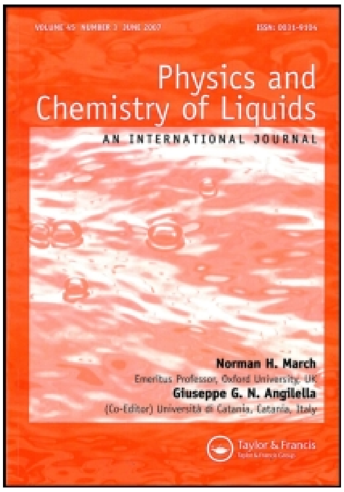

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Energy Level Structure-Band Intensities of $Pr(NO_3)_3 6\,H_2O$: Organic Acids

A. Suresh Kumar[a]; S. Buddhudu[a]
[a] Spectroscopic Laboratories, Department of Physics, S.V. University, Tirupati, India

To cite this Article Kumar, A. Suresh and Buddhudu, S.(1986) 'Energy Level Structure-Band Intensities of $Pr(NO_3)_3 6\,H_2O$: Organic Acids', Physics and Chemistry of Liquids, 16: 2, 147 — 151
To link to this Article: DOI: 10.1080/00319108608078512
URL: http://dx.doi.org/10.1080/00319108608078512

Phys. Chem. Liq., 1986, Vol. 16, pp. 147-152
0031-9104/86/1602-0147$18.50/0

Printed in the United Kingdom

Energy Level Structure-Band Intensities of $Pr(NO_3)_3 6H_2O$: Organic Acids

A. SURESH KUMAR and S. BUDDHUDU

Spectroscopic Laboratories, Department of Physics, S.V. University, Tirupati–517 502, India.

(*Received April 14, 1986*)

Analysis of the spectra of Praseodymium nitrate mixed with organic complexes such as Glutamic, L Aspartic and Maleic acids has been carried out from UV to NIR regions. About six energy levels for Pr^{3+} in all the three hosts have been measured and assigned to the appropriate electronic transitions. By applying the Judd-Ofelt theory, the absorption band intensities and lifetimes of the electronic states $^3P_{1,0}$ and $^1D_2$ have been computed theoretically.

INTRODUCTION

A significant contribution on the spectra of Rare earths, has been made in various inorganic acid media.[1–4] The effects of environments on the hypersensitive transitions of lanthanides have been carried out in certain organic compounds by Choppin *et al.*[5] In the present paper, the authors report the details of energy levels, spectral oscillator strengths of the observed bands of $Pr(NO_3)_3 6H_2O$ in three organic acid complexes.

EXPERIMENTAL STUDIES

The Rare earth chemicals with 99.99% purity were obtained from M/s Rare earth India Ltd., Udyogmandal, India. The Praseodymium complexes were prepared by adding 0.1 M% of $Pr(NO_3)_3 6H_2O$ into the organic liquids such as Glutamic, L Aspartic and Maleic acids. These three solutions were used in recording the absorption spectra from UV-VIS and NIR regions on Perkin-Elmer and Carl-Zeiss spectrophotometers respectively. The refractive indices of solutions were measured on a Warszawava 3275 refractometer.

RESULTS AND DISCUSSION

From the recorded UV-VIS, NIR spectra of Pr^{3+} :Glutamic, L Aspartic and Maleic acids, about six bands have been measured and assigned to the transitions as follows

$$^3H_4 \rightarrow {}^3P_2, {}^3P_1, {}^3P_0, {}^1D_2, {}^3F_4 \text{ and } {}^3F_3$$

As has been carried out by Lakshman and Buddhudu[6] the theoretical energies of the bands has been computed on a micro computer. Both the theoretical and measured energies of the bands are presented in Table I. This table reveals a good correlation between the measured and computed energies. The r.m.s. deviations[7] appear to be reasonably low, as seen from this table.

The various computed energy level parameters known as[8] Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3), configurational interaction (α, β) and spin-orbit (ξ_{4f}) for these three Pr^{3+} organic complexes are given in Table II.

TABLE I

Experimental and calculated energies of $Pr(NO_3)_3 6H_2O$ in Organic complexes

Levels from $^3H_4$	Pr^{3+} Glutamic acid E_{expt} cm^{-1}	Glutamic acid E_{calc} cm^{-1}	L Aspartic acid E_{expt} cm^{-1}	L Aspartic acid E_{calc} cm^{-1}	Maleic acid E_{expt} cm^{-1}	Maleic acid E_{calc} cm^{-1}
$^3P_2$	22669	22635	22593	22571	22618	22604
$^3P_1$	21453	21426	21407	21370	21407	21405
$^3P_0$	20784	20762	20741	20729	20784	20779
$^1D_2$	17002	17003	17002	17001	17060	17052
$^3F_4$	6850	6840	6850	6853	6850	6825
$^3F_3$	6150	6171	6200	6223	6100	6183
r.m.s. Deviation	±22.03		±18.33		±36.06	

TABLE II

The values of Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3), Configurational interaction (α, β), spin-orbit (ξ_{4f}), Judd-Ofelt (T_2, T_4, T_6), Intensity (Ω_2, Ω_4, Ω_6) parameters and refractive indices (n) for $Pr(NO_3)_3 6H_2O$: Organic acids

	Pr^{3+}		
Parameters	Glutamic Acid	L Aspartic Acid	Maleic Acid
F_2 (cm^{-1})	320.75	319.36	323.25
F_4 (cm^{-1})	54.67	54.69	56.03
F_6 (cm^{-1})	5.32	5.37	5.47
E^1 (cm^{-1})	5081.32	5082.15	5171.61
E^2 (cm^{-1})	21.55	21.43	21.46
E^3 (cm^{-1})	482.55	478.76	485.09
ξ_{4f} (cm^{-1})	775.21	763.63	760.36
α(cm^{-1})	11.32	15.04	9.37
β(cm^{-1})	−667.20	−773.94	−776.56
T_2 (10^{-9})	19.81154	14.90761	18.79331
T_4 (10^{-9})	0.91022	0.72785	0.68623
T_6 (10^{-9})	5.06384	5.71630	3.90647
Ω_2 (10^{-20})	114.56	103.52	130.02
Ω_4 (10^{-20})	6.46	5.05	4.75
Ω_6 (10^{-20})	34.60	39.69	27.03
n	1.3400	1.3400	1.3455

The experimental band intensities (f_{expt}) are calculated from the following relation

$$f_{expt} = 4.32 \times 10^{-9} \int \varepsilon \delta \nu$$

where ε is the extinction coefficient and $\delta \nu$ is the band width at half height of the band. Buddhudu *et al.*[9] have given the method of evaluation of these two (ε, $\delta \nu$) parameters in their recent article.[9] In the same article, the method of evaluation of theoretical intensities (f_{cal}) has also been given. Both the experimental and calculated intensities of the observed bands for the complexes took up in this paper are tabulated in Table III. While calculating the theoretical "f" values, a set of three intensity characterizing parameters namely Judd-Ofelt (T_2, T_4, T_6) and intensity (Ω_2, Ω_4, Ω_6) have been obtained. They are also accommodated in Table II. By using the Judd-Ofelt[10,11] parameters an attempt has been made by the authors to predict the lifetime values of the fluorescent levels $^3P_1$, $^3P_0$ and $^1D_2$ of Pr^{3+}:Organic complexes from their absorption measurements. Similar such attempts have earlier been made for other Rare earth elements Tm^{3+}, Er^{3+}, Nd^{3+}.[12–14]

TABLE III

The measured and computed intensities for observed bands of $Pr(NO_3)_3 6H_2O$: Organic acids

Levels from $^3H_4$	Pr^{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} ($\times 10^6$)
$^3P_2$	16.42	16.42	16.24	16.24	12.65	12.65
$^3P_1$	5.07	3.32	4.46	2.65	4.03	2.50
$^3P_0$	1.56	3.25	0.87	2.60	0.99	2.46
$^1D_2$	5.65	5.65	5.93	5.93	4.54	4.54
r.m.s. Deviation	$\pm 1.22 \times 10^{-6}$		$\pm 1.25 \times 10^{-6}$		$\pm 1.06 \times 10^{-6}$	

CONCLUSIONS

The results presented in Tables I, III reveal a strong correlation between the measured and computed energies and intensities of bands $^3P_0$, $^3P_1$, $^3P_0$, $^1D_2$, $^3F_4$ and $^3F_3$ from the ground state $^3H_4$. Thus the validity of least-squares fit method and Judd-Ofelt theory has been tested. Since the values of band intensities of $^3F_{4,3}$ are appearing to be negligible compared to the other four levels, they have not been included in Table III. As suggested by Choppin *et al.*[5] the effects of the environments on the intensities of hypersensitive transitions ($^3H_4 \rightarrow {}^3P_2, {}^1D_2$) have been understood from Table III. The influence of Judd-Ofelt (T_2, T_4, T_6), intensity (Ω_2, Ω_4, Ω_6) parameters has been verified in predicting the lifetimes of the fluorescent levels, as is seen in Table IV. The lifetimes of the levels are found to be in the following manner in all the hosts studied

$$^3P_0 > {}^1D_2 > {}^3P_1$$

TABLE IV

The Predicted lifetimes of fluorescent levels of $Pr(NO_3)_3 6H_2O$: Organic complexes

Lifetimes (μs)	Pr^{3+}		
	Glutamic acid	L Aspartic acid	Maleic acid
$^3P_1$	11.66	11.10	9.81
$^3P_0$	305.64	335.11	398.01
$^1D_2$	70.51	76.04	64.11

The following trends have also been observed

$T_R(\mu s)$ $^3P_1$ Glutamic > L Aspartic > Maleic
$^3P_0$ Maleic > L Aspartic > Glutamic
$^1D_2$ L Aspartic > Glutamic > Maleic

Acknowledgement

The authors express their grateful thanks to Prof. S. V. J. Lakshman for his cooperation and necessary help in the present work.

References

1. N. S. Poluektov, *Zh. Neorg. Khim.*, **27** **(9)**, 2232 (1982).
2. G. Liu, *Gao. Mua. Kua.*, **4** **(1)**, 8, (1983).
3. V. Ramesh Babu, S. V. J. Lakshman and S. Buddhudu, *Bull. Pure & Appl. Sciences*, **4D** **(1&2)**, 33 (1985).
4. C. Krishna Murthy, and S. Buddhudu, *Ind. J. Phys.*, **60A**, 1 (1986).
5. G. R. Choppin, *Coord. Chem. Rev.*, **18**, 199 (1976).
6. S. V. J. Lakshman and S. Buddhudu, *J. Quant. Spec. & Radiat. Transf.*, **27** **(5)**, 531 (1982).
7. S. V. J. Lakshman and S. Buddhudu, *Acta Physica Hungarica*, **54** **(3-4)**, 231 (1983).
8. W. T. Carnall, J. P. Hessler, P. J. Wagner, *J. Chem. Phys.*, **82**, 2152 (1978).
9. S. Buddhudu, S. V. J. Lakshman and V. Ramesh Babu, *J. Quant. Spec. & Radiat. Transf.*, **33**, 657 (1985).
10. B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).
11. G. S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).
12. M. J. Weber, T. E. Varitmos, and B. H. Matsinger, *Phys. Rev. B*, **8**, 47 (1973).
13. S. Buddhudu, S. V. J. Lakshman and V. Ramesh Babu, *Proc. INSA*, **51A** **(4)**, 746 (1985).
14. S. Buddhudu, C. Krishna Murthy and L. R. Moorthy, *Mat. Sci. Engg. (UK)*, **72** **(2)**, L-31 (1985).