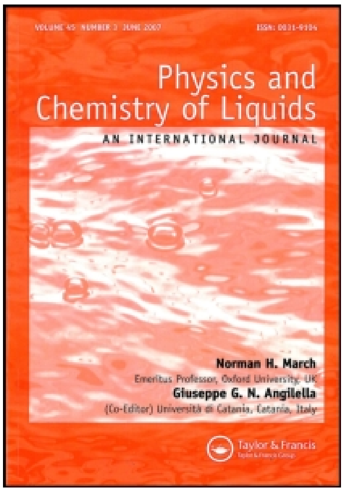
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

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

Spontaneous Transition Probabilities and Branching Ratios for the Excited States of Pr^3 in Acetylacetonate

Y. Subramanyam[a]; L. Rama Moorthy[a]; S. V. J. Lakshman[a]
[a] Spectroscopic and Chemical Physics Laboratories, Department of Physics, S. V. University, Tirupati, India

To cite this Article Subramanyam, Y. , Moorthy, L. Rama and Lakshman, S. V. J.(1988) 'Spontaneous Transition Probabilities and Branching Ratios for the Excited States of Pr^3 in Acetylacetonate', Physics and Chemistry of Liquids, 18: 2, 165 — 173

To link to this Article: DOI: 10.1080/00319108808078589

URL: http://dx.doi.org/10.1080/00319108808078589

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liq., 1988, Vol. 18, pp. 165-173
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Spontaneous Transition Probabilities and Branching Ratios for the Excited States of Pr^{3+} in Acetylacetonate

Y. SUBRAMANYAM, L. RAMA MOORTHY and S. V. J. LAKSHMAN

Spectroscopic and Chemical Physics Laboratories,
Department of Physics, S. V. University,
Tirupati—517 502, India.

(Received 13 October 1987)

UV-VIS absorption spectrum of Pr^{3+} in acetylacetonate chelate dissolved in five solvents, viz. (a) methanol, (b) ethanol, (c) DMF, (d) methanol + ethanol (1:3) and (e) DMF + solvent (d) (1:4) were recorded. From the observed spectral intensities of the bands, the three phenomenological Judd–Ofelt parameters Ω_2, Ω_4 and Ω_6 have been evaluated. Radiative transition probabilities (A), radiative relaxation rates (A_T), radiative lifetimes (T_R) and branching ratios (β_R) for the excited $^3P_1$, $^3P_0$ and $^1D_2$ levels were calculated and their usefulness for laser action is discussed.

Key Words: Radiative lifetimes, laser action, Judd-Ofelt parameters.

INTRODUCTION

In view of the potential laser action of rare earth chelates, many researchers[1–10] studied them in different organic solvents. The present paper reports the calculated radiative transition probabilities and branching ratios for the excited fluorescent levels of Pr^{3+} in acetylacetonate dissolved in certain organic solvents from the observed spectral intensities of the bands.

EXPERIMENTAL

Preparation of RE Chelates

Freeman and Crosby[11] reported details of the preparation of trisacetylacetonate chelates. Approximately 2g of praseodymium chloride (99.99%) was dissolved in 200 ml of distilled water. To this, 8 ml of redistilled acetylacetone was added. Concentrated ammonium hydroxide was added to this mixture drop by drop with vigorous stirring until precipitation of white microcrystalline chelate was complete. The precipitated chelate was collected by suction on a medium sintered glass filter funnel, washed with distilled water, air dried at room temperature and recrystallized from boiling acetone. Finally the recrystallized chelate was vacuum dried at room temperature for about 16 hours.

SPECTROSCOPIC MEASUREMENTS

For absorption measurements, the praseodymium acetylacetonate thus prepared was dissolved in five different solvents (a) methanol (MA), (b) ethanol (EA), (c) dimethyl formamide (DMF), (d) MA + EA (1:3) and (e) mixture of (c) and (d) by 4:1 in volume. All the solutions were prepared with a chelate concentration of 0.01 M just before its use.

Absorption spectra of five solutions were recorded in the wavelength region 400 to 620 nm on a Perkin-Elmer 551 spectrophotometer. Refractive indices (n) of these solutions were measured at different wavelengths of mercury by minimum deviation method using hallow glass prism and a spectrometer. The variation of refractive index (n) with wavelength (λ in Å) could be fitted to the following formula in the case of the chelates studied[12]

$$n = 1.3124 + \frac{81.9124}{\lambda(\text{Å}) - 744.023} \tag{1}$$

The spectral intensities were determined by measuring the area under the absorption curves using the weight method. The oscillator strengths of the bands were calculated using the relation

$$f_{\text{expt}} = 4.32 \times 10^{-9} \int \varepsilon(v)\, dv \tag{2}$$

where $\varepsilon(v)$ is the molar extinction coefficient at wavenumber v.

RESULTS AND ANALYSIS

Energy Levels

UV-VIS absorption spectra recorded for Pr^{3+} in acetylacetonate chelate complex in the five different organic solvents are shown in Figure 1. Only four bands could be observed in all the complexes studied. They are $^1D_2$, $^3P_0$, $^3P_1$ and $^3P_2$. The energy levels of lanthanides arise due to the electrostatic and spin-orbit interactions between the $4f^n$ electrons. Since in the present work, only four bands are observed, F_4 and F_6 parameters are fixed in terms of F_2 assuming radial wavefunctions to be hydrogenic and using the following expressions[13]

$$F_4 = 0.138\ F_2$$
$$F_6 = 0.0151\ F_2$$

Introducing these Slater-Condon (F_k) parameters in Racah (E^k) parameters we obtain

$$E^1 = 14.68\ F_2$$
$$E^2 = 0.077\ F_2$$

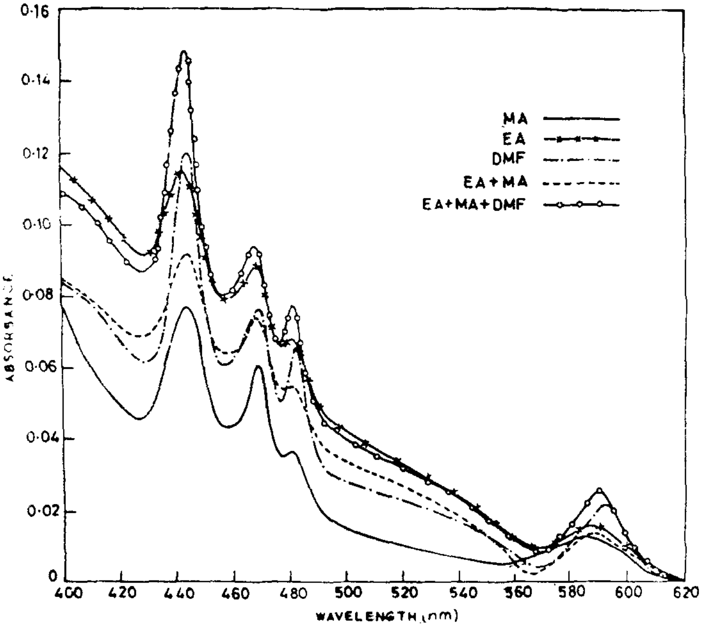


Figure 1 Absorption spectra of Pr^{3+} in Acetyl Acetonate in different organic solvents.

and

$$E^3 = 1.48\ F_2$$

From the expressions of Dieke[13]

$$F_2 = 12.4\,(Z - 34)$$

where $Z = 59$ for praseodymium, the value of F_2 is first evaluated and thus E^1, E^2 and E^3 are calculated. The f^2 configuration energy matrices[14] are solved with these E^1, E^2 and E^3 and aquo ion ξ value of 750 cm^{-1}. The matrices are again solved with the same E^k but $\xi = 751$ cm^{-1}. The difference of the latter and former values gives the partial derivative $dE/d\xi$ for each state. The energy of the state in the former case is E_{0J} (zero order energy). These values are given in Table 1. Substituting the observed band energy (E_J), zero-order energy (E_{0J}) and the partial derivative ($dE_J/d\xi$) in Eq. 3,

$$E_J = E_{0J} + \frac{dE}{d\xi}\,\Delta\xi \tag{3}$$

the $\Delta\xi$ value is calculated for each band. The average for the four observed bands is determined. From the average $\Delta\xi$ value thus determined in the five complexes, the spin-orbit interaction parameter (ξ) for Pr^{3+} in each of the complexes has been calculated using the relation

$$\xi = \xi^0 + \Delta\xi \tag{4}$$

where ξ^0 is aquo ion value of 750 cm^{-1}. Eigenvalues and eigenvectors have been evaluated by solving the energy matrices for $f^2(Pr^{3+})$ configurations[14] using spectrum 31 micro computer. Observed and calculated energies along with the spin-orbit interaction (ξ) parameters are presented in Table 2.

Table 1 Computed zero-order energies (E_{0J}) and the partial derivatives $dE_J/d\xi$ for $^1D_2$, $^3P_0$, $^3P_1$ and $^3P_2$ levels in f^2 configuration. ($E^1 = 4550.39$, $E^2 = 23.83$, $E^3 = 460.26$)

Term	E_{0J} (cm^{-1})	$dE_J/d\xi$
$^1D_2$	17264.0	3.02
$^3P_0$	20830.0	1.91
$^3P_1$	21457.0	3.07
$^3P_2$	22711.0	5.28

Table 2 Observed (E_{obs}) and calculated (E_{cal}) energies (cm^{-1}) of the absorption bands of Pr^{3+} in acetylacetonate dissolved in different organic solvents. ($E^1 = 4550.39$, $E^2 = 23.83$, $E^3 = 460.26$)

	Acetylacetonate of praseodymium(III) in									
	MA		EA		DMF		(MA + EA)		(MA + EA) + DMF	
Transition from $^3H_4$	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
$^1D_2$	17089	17138	17002	17104	16873	17068	17002	17112	16944	17121
$^3P_0$	20763	20750	20720	20728	20720	20706	20763	20734	20784	20739
$^3P_1$	21316	21329	21293	21294	21316	21258	21339	21303	21362	21311
$^3P_2$	22542	22493	22542	22431	22491	22368	22491	22446	22542	22461
σ	±36		±75		±119		±63		±103	
ξ	708.4		696.9		685.1		699.8		742.6	

σ–R.M.S. Deviation
ξ–Spin orbit parameter

MA: Methyl alcohol, EA: Ethyl alcohol, DMF: Dimethyl formamide.

Spectral Intensities and Radiative Lifetimes

Measured oscillator strengths (f) of the observed spectral lines of Pr^{3+} in acetylacetonate in five different organic solvents are presented in Table 3. The equation for the oscillator strength of a transition between the ground state (ψJ) and an excited state ($\psi' J'$) of the lanthanide ion is given by Kirby and Palmer[15]

$$f_{\text{expt}} = f_{\text{ed}} = \chi\left[\frac{8\pi^2 mc}{3h(2J+1)}\right]\nu \sum_{\lambda=2,4,6} \Omega_\lambda(\psi J\|U^\lambda\|\psi' J')^2 \tag{5}$$

where f_{ed} is the electric dipole linestrength of the transition between the ground (ψJ) and upper ($\psi' J'$) states, Ω_λ is the Judd-Ofelt parameter, $\|U^\lambda\|$ is the transition matrix element, ν is the energy of the band in cm^{-1}, $\chi = (n^2+2)^2/9n$ is the Lorentz field factor which is a function of the refractive index of the bulk medium and J is the total angular momentum of the grand level, which for Pr^{3+} is 4. The other symbols have their usual significance. $\|U^\lambda\|^2$ values are first calculated for the intermediate coupling scheme.[16] Substituting the appropriate values,

Table 3 Measured (f_{expt}) and calculated (f_{cal}) oscillator strengths (× 10^6) of the absorption spectral lines of Pr^{3+} in acetylacetonate dissolved in different organic solvents along with the Judd–Ofelt intensity parameters (Ω_λ).

	Pr^{3+} acetylacetonate in														
	MA			EA			DMF			MA + EA			(MA + EA) + DMF		
Terms	f_{expt}	f_{cal}	f ratio w.r.t. $^3P_0$	f_{expt}	f_{cal}	f ratio w.r.t. $^3P_0$	f_{expt}	f_{cal}	f ratio w.r.t. $^3P_0$	f_{expt}	f_{cal}	f ratio w.r.t. $^3P_0$	f_{expt}	f_{cal}	f ratio w.r.t. $^3P_0$
$^1D_2$	0.367	0.367	3.6	0.314	0.314	3.4	0.461	0.461	1.9	0.392	0.392	6.2	0.520	0.520	2.5
$^3P_0$	0.103	0.214	1.0	0.093	0.191	1.0	0.246	0.330	1.0	0.063	0.163	1.0	0.204	0.308	1.0
$^3P_1$	0.330	0.215	3.2	0.293	0.192	3.2	0.420	0.335	1.7	0.270	0.166	4.3	0.422	0.311	2.1
$^3P_2$	0.969	0.969	9.4	0.781	0.781	8.4	1.313	1.313	5.3	0.687	0.687	10.9	1.547	1.547	7.6
σ		±0.082			±0.070			±0.059			±0.072			±0.076	
$\Omega_2 \times 10^{20}$		= 6.675			7.474			8.970			16.074			6.112	
$\Omega_4 \times 10^{20}$		= 0.415			0.362			0.655			0.313			0.489	
$\Omega_6 \times 10^{20}$		= 2.128			1.652			2.874			1.470			3.332	
n		= 1.329			1.363			1.299			1.354			1.369	

σ–R.M.S. Deviation: MA: Methyl alcohol, EA: Ethyl alcohol, DMF: Dimethyl formamide.

four equations were formed for the four bands namely $^1D_2$, $^3P_0$, $^3P_1$ and $^3P_2$ as follows:

$$f(^1D_2) = 0.1205 \times 10^{11}\,\nu[\Omega_2(0.0026) + \Omega_4(0.0170) + \Omega_6(0.0520)]$$
$$f(^3P_0) = 0.1205 \times 10^{11}\,\nu[\Omega_2(0) + \Omega_4(0.1728) + \Omega_6(0)]$$
$$f(^3P_1) = 0.1205 \times 10^{11}\,\nu[\Omega_2(0) + \Omega_4(0.1707) + \Omega_6(0)]$$
$$f(^3P_2) = 0.1205 \times 10^{11}\,\nu[\Omega_2(0) + \Omega_4(0.0362) + \Omega_6(0)]$$

The three phenomenological parameters Ω_2, Ω_4 and Ω_6 were evaluated by the least squares fit analysis and are presented in Table 3, along with the calculated oscillator strengths. Small r.m.s. deviations support the applications of Judd–Ofelt theory.[17,18]

Electric dipole linestrengths (S_{ed}), magnetic dipole linestrengths (S_{md}), radiative transition probabilities $A(\psi J)$, radiative lifetimes (T_R) and the branching ratios (β_R) have been theoretically evaluated using the procedure followed by Lakshman and Rama Moorthy.[19] Radiative lifetimes and the branching ratios thus evaluated for the excited $^3P_0$, $^3P_1$ and $^1D_2$ levels of Pr^{3+} in acetylacetonate chelate in different solvents are presented in Tables 4 and 5 respectively.

DISCUSSION

From Table 3, it can be noted that the intensities of the observed spectral lines are slightly increased in DMF and MA + EA + DMF solvents compared to other organic solvents and the intensity ratios of $^1D_2$, $^3P_1$ and $^3P_2$ w.r.t. $^3P_0$ are high in MA, EA and (MA + EA) and low in DMF and MA + EA + DMF solvents. The order of the three phenomenological parameters Ω_2, Ω_4 and Ω_6 derived from the oscillator strengths applying J–O theory are $\Omega_2 > \Omega_6 > \Omega_4$ in all the five chelate complexes studied. The theoretically estimated radiative lifetimes (T_R) of the $^3P_1$, $^3P_0$ and $^1D_2$ levels of Pr^{3+} in acetylacetonate in five organic solvents are in the following order (Table 4).

$$^3P_1(T_R)\colon MA > EA > (MA + EA) + DMF) > DMF > MA + EA$$
$$^3P_0(T_R)\colon MA > (MA + EA) + DMF) > EA > DMF > MA + EA$$
$$^1D_2(T_R)\colon MA > (MA + EA) + DMF) > EA > DMF > MA + EA$$

Usually the branching ratios are high for potential laser transitions.[20] It is therefore predicted from Table 5 that the transitions $^3P_1 \rightarrow {}^3F_3$, $^3P_0 \rightarrow {}^3F_2$ and $^1D_2 \rightarrow {}^3F_4$ which have high (β_R) values are the most potential laser transitions.

Table 4 Radiative lifetimes (T_R) for the excited $^3P_1$, $^3P_0$ and $^1D_2$ levels of Pr^{3+} in acetylacetonate in five organic solvents.

States	MA T_R (μ sec)	EA T_R (μ sec)	DMF T_R (μ sec)	MA + EA T_R (μ sec)	MA + EA + DMF T_R (μ sec)
$^3P_1$	79	67	58	34	63
$^3P_0$	70	62	55	31	64
$^1D_2$	413	362	340	178	393

Table 5 Theoretically computed branching ratios (β_R) for the excited flourescent levels of Pr^{3+} in acetylacetonate in different organic solvents.

SLJ	S'L'J'	MA β_R	EA β_R	DMF β_R	MA + EA β_R	(MA + EA) + DMF β_R
(1)	(2)	(3)	(4)	(5)	(6)	(7)
$^3P_1$	$^1D_2$	0.001	0.001	0.001	0.002	0.001
	$^1G_4$	0.004	0.003	0.007	0.001	0.004
	$^3F_4$	0.013	0.010	0.014	0.004	0.013
	$^3F_3$	0.542	0.552	0.507	0.584	0.502
	$^3F_2$	0.324	0.330	0.300	0.353	0.257
	$^3H_6$	0.054	0.027	0.052	0.017	0.074
	$^3H_5$	0.034	0.055	0.089	0.029	0.120
	$^3H_4$	0.028	0.022	0.030	0.009	0.028
$^3P_0$	$^1D_2$	0	0	0	0	0
	$^1G_4$	0.005	0.004	0.006	0.002	0.006
	$^3F_4$	0.012	0.010	0.014	0.004	0.014
	$^3F_2$	0.838	0.889	0.824	0.944	0.780
	$^3H_6$	0.076	0.040	0.077	0.025	0.159
	$^3H_4$	0.069	0.056	0.079	0.024	0.081
$^1D_2$	$^1G_4$	0.103	0.109	0.116	0.108	0.093
	$^3F_4$	0.727	0.760	0.738	0.783	0.697
	$^3F_3$	0.036	0.036	0.036	0.037	0.035
	$^3F_2$	0.028	0.026	0.028	0.024	0.028
	$^3H_6$	0.011	0.008	0.012	0.002	0.010
	$^3H_5$	0	0	0	0	0
	$^3H_4$	0.060	0.060	0.045	0.045	0.136

Acknowledgements

One of the authors (LR) is grateful to the Council of Scientific and Industrial Research, New Delhi, India, for financial support in the form of Research Associateship.

References

1. G. A. Crosby and M. Kasha, *Spectrochim. Acta.*, **10**, 377 (1958).
2. G. A. Crosby, R. E. Whan and R. M. Alire, *J. Chem. Phys.*, **34**, 743 (1961).
3. G. A. Crosby, R. E. Whan and J. J. Freeman, *J. Chem. Phys.*, **36**, 2493 (1962).

4. R. E. Whan and G. A. Crosby, *J. Mol. Spectrosc.*, **8**, 315 (1962).
5. A. Lempicki and H. Samelson, *Phys. Lett.*, **4**, 133 (1963).
6. N. E. Wolf and R. J. Pressley, *Appl. Phys. Lett.*, **2**, 152 (1963).
7. E. J. Schmitichek, *Appl. Phys. Lett.*, **3**, 117 (1963).
8. A. P. B. Sinha, *Spectroscopy in Inorganic Chemistry* (Academic Press, New York, 1971).
9. T. Isobe and S. Misumi, *Bull. Chem. Soc. Japan*, **47**, 281 (1974).
10. H. Samelson, A. Lempicki, V. A. Brophy and C. Breecher, *J. Chem. Phys.*, **40**, 2547 (1974).
11. J. J. Freeman and G. A. Crosby, *J. Phys. Chem.*, **67**, 2717 (1963).
12. M. P. Rich, *Appl. Optics.*, **5**, 1966 (1966).
13. G. H. Dieke, *Spectra and Energy Levels of Rare Earths Ions in Crystals.* (Interscience Publishers, John Wiley & Sons, New York, 1968).
14. L. Rama Moorthy, Ph.D. thesis entitled "Spectroscopic Investigations of Pr^{3+}, Nd^{3+}, Er^{3+} and Tm^{3+} Ions in PCl_3:$SnCl_4$ Laser Liquid," S. V. University, Tirupati (1983).
15. A. F. Kirby and R. A. Palmer, *Inorg. Chem.*, **20**, 4219 (1981).
16. W. T. Carnall, P. R. Fields and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).
17. B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).
18. G. S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).
19. S. V. J. Lakshman and L. Rama Moorthy, *Materials Letters*, **4**, 39 (1985).
20. R. Reisfeld and C. K. Jorgensen, *Lasers and Excited States of Rare Earths* (Springer, Berlin, 1977).