Diffuse Reflectance Spectrum of Some Pr^{3+} Complexes

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Diffuse reflectance spectra of eight Pr^{3+} complexes in the visible region have been recorded for the first time. From them, values of Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3) interelectronic repulsion, and Landé (ζ_{4f}) parameters have been computed. The decrease in F_2 values of the complexes as compared to the free ion is greatest among all the parameters. The bonding parameter $b^{\frac{1}{2}}$ has been computed from the observed nephelauxetic ratio. The relative variation of covalent bonding in the complexes has been discussed.

Introduction

The diffuse reflectance spectra of some 3d complexes [1–7] and other compounds [8–11] has been studied recently. But in the case of 4f complexes no such studies have been reported. The absorption spectra of these complexes have been widely studied [12–19] either in solutions or in rare earth doped crystals. In the former, the effect of the solvent, and in the later the crystal forces affect the spectrum of the complex. The diffuse reflectance is expected to give an unmodified spectrum which is analogous to the absorption spectrum due to the complex alone. Consequently, the present investigations on Pr^{3+} complexes were carried out. This article reports the values of Slater-Condon (F_k), Racah (E^k), Landé (ζ_{4f}) and bonding ($b^{1/2}$) parameters and electronic states computed from these parameters in the case of eight Pr^{3+} complexes.

I. Experimental and Results

Diffuse reflectance from the samples has been measured with a Hilger's UVISPEK spectrophotometer fitted with an annular ring type of diffuse reflectance attachment. Lithium fluoride has been used as reference standard for the reasons described in earlier [5] communications. The praseodymium oxide, chloride and sulphate under study were of spectrograde. The Pr^{3+} complexes of acetylacetone (A), benzoylacetone (BA), thenoyltrifluoroacetone (TFA), ethyl-1-methylacetoacetate (E-1-MA) and ethylacetoacetate (EA) were synthesised using the method described by Whan and coworkers [20, 21] starting with $PrCl_3$ of spectrograde. The reagents used were of A.R. grade.

The observed and calculated energy levels have been given in Table 1.

II. Parameters

The forbidden transitions within the ground $4f^2$ configuration give rise [19] to the visible and near

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infrared spectrum of Pr^{3+}. The energy level structure of $4f^2$ configuration to a first approximation may be considered to arise from electrostatic and magnetic interactions between the 4f electrons. The electrostatic interaction (E_e) and Slater-Condon (F_k) parameters are related [19] by

$$E_e = \sum_{k=0}^{6} f^k F_k = \sum_{k=0}^{6} f_k F^k \qquad (1)$$

where f^k is the angular coefficient and F_k is given by

$$F_k = D_k^{-1} \int_0^\infty \int_0^\infty r_<^k / r_>^{k+1} R^2(r_1) R_2(r_2) \, dr_1 \, dr_2 \qquad (2)$$

where the subscripts 1 and 2 refer to electron 1 and 2, respectively, R is the 4f radial function, $r_<$ denotes the radius of the electron near the nucleus, $r_>$ denotes the radius of more distant electrons, D_k's denote the denominators whose values are given in CONDON and SHORTLEY's book [22]. In Eq. (1) k is even and the f_k's are coefficients of the linear combination and represent the angular part of the interaction. The Racah parameters, E^k's, as shown below, are linear combinations of the F_k's,

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

The spin orbit interaction is an important magnetic interaction. Its energy E_{so} is given by

$$E_{so} = A_{so}\,\zeta_{4f} \qquad (4)$$

where A_{so} represents the angular part and ζ_{4f} the radial integral, known as Landé parameter.

The nephelauxetic ratio β is given by [23]

$$\beta = F_k^c / F_k^f \qquad (5)$$

where F_k^c and F_k^f refer to the complex and free ion respectively. The bonding parameter $b^{1/2}$ is given [24] by

$$b^{1/2} = [\tfrac{1}{2}(1-\beta)]^{1/2}\,. \qquad (6)$$

III. Evaluation of Parameters and Energy Levels

Since the transitions to all the expected levels have not been observed in the present case, it is not possible to evaluate all the F_k and ζ_{4f} parameters simultaneously by the method of least squares fit to energy levels. It has been shown earlier [15, 19] that in this case the radial eigenfunctions may be reasonably assumed to be hydrogenic. Under this assumption the ratios of the F_k's for 4f electrons are

$$F_4/F_2 = 0.13805\,, \qquad F_6/F_2 = 0.01511\,. \qquad (7)$$

The parameters F_2 and ζ_{4f} can be evaluated [25] by expressing the energy of the levels as a Taylor series expansion

$$\begin{aligned} E_j(F_2, \zeta_{4f}) = E_{0j}(F_2^0, \zeta_{4f}^0) &+ (\partial E_j / \partial F_2)\,\Delta F_2 \\ &+ (\partial E_j / \partial \zeta_{4f})\,\Delta \zeta_{4f} \qquad (8) \end{aligned}$$

where E_j is the energy of the j-th level and E_{0j} is the zero order energy of the j level. Using the values [26] $F_2^0 = 305.0$ and $\zeta_{4f}^0 = 730.5\ \text{cm}^{-1}$ and carrying out a least squares fit to the observed levels, the values of F_2 and ζ_{4f} have been evaluated. Using Eqs. (3) and (7) the values of other F_k's and E^k's have been calculated.

The β and $b^{1/2}$ values have been calculated using Eqs. (5) and (6) respectively. The computed values of various parameters have been collected in Table 2.

The energy levels have been computed from the refined set of F_k and ζ_{4f} parameters.

IV. Discussion

Energy Levels

A comparison of the observed and calculated values of energy levels (Table 1) show that the average deviation is 36 to 97. The r.m.s. deviation 46 to 126 indicates good results even though the radial eigenfunctions have been assumed to be hydrogenic.

Interelectronic Repulsion and Magnetic Interaction Parameters

The interelectronic repulsion, F_k and E^k, and Landé ζ_{4f} parameters exhibit a decrease from the values of the corresponding parameters of Pr^{3+} "free" ion (Table 2). This is due to the decrease in interelectronic repulsion and spin-orbit interaction due to expansion of the central metal ion orbital on complexation.

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Table 1. Energy level assignments of Pr^{3+} complexes.

Levels	$PrCl_3$		$Pr_2(SO_4)_3$		Tris-E-1-MA		Tris-BA	
	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}
$^1D_2$	16 949	215	17 035	75	16 806	230	16 750	122
$^3P_0$	20 746	0	20 618	61	20 618	0	20 408	66
$^3P_1$	21 276	14	21 276	−66	21 052	55	20 920	−44
$^3P_2$	22 472	18	22 472	−66	22 371	−89	22 123	−114
Average deviation		62		67		94		87
r m s deviation		108		67		126		92

Levels	Pr_2O_3		Tris-EA		Tris-A		Tris-TFA	
	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}	E_{exp} cm^{-1}	$E_{cal}-E_{exp}$ cm^{-1}
$^1D_2$	16 949	121	16 806	235	16 806	−3	16 750	10
$^3P_0$	20 618	−17	20 576	−6	20 242	−1	20 120	65
$^3P_1$	21 276	−129	21 186	−81	20 833	−86	20 618	66
$^3P_2$	22 472	−119	22 321	−15	22 123	−178	21 881	−1
Average deviation		97		84		67		36
r m s deviation		107		124		99		46

Table 2. Computed values of various parameters of Pr^{3+} complexes.

Complex	F_2 Cm^{-1}	F_4 Cm^{-1}	F_6 Cm^{-1}	ζ_{4f} Cm^{-1}	E^1 Cm^{-1}	E^2 Cm^{-1}	E^3 Cm^{-1}	β	$b^{1/2}$
Free ion	322.1[27]	44.46	4.867	741.0	4729	24.75	478.13	—	—
$PrCl_3$	310.2	42.82	4.687	714.4	4464	23.84	460.47	0.9635	0.135
$Pr_2(SO_4)_3$	309.4	42.71	4.675	708.4	4453	23.77	459.28	0.9606	0.140
Tris-ethyl-1-methyl acetoacetate	309.1	42.67	4.671	687.7	4448	23.75	458.82	0.9596	0.142
Tris-benzoylacetonate	308.2	42.55	4.657	645.5	4436	23.68	457.50	0.9568	0.147
Pr_2O_3	308.1	42.53	4.655	715.3	4434	23.66	457.36	0.9565	0.147
Tris-ethylacetoacetate	307.8	42.49	4.651	710.1	4430	23.65	456.90	0.9556	0.149
Tris-acetylacetonate	303.5	41.90	4.586	695.9	4366	23.32	450.52	0.9423	0.170
Tris-thenoyltri-fluoroacetonate	302.8	41.80	4.575	692.4	4358	23.27	449.49	0.9408	0.172

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Nephelauxetic Ratio and Bonding

In Table 2 the Pr^{3+} complexes have been arranged in decreasing order of nephelauxetic ratio and increasing order of bonding parameter $b^{1/2}$. The $b^{1/2}$ values are positive indicating covalent bonding. Among the complexes the covalent bonding is least in chloride and maximum in TFA complex.

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