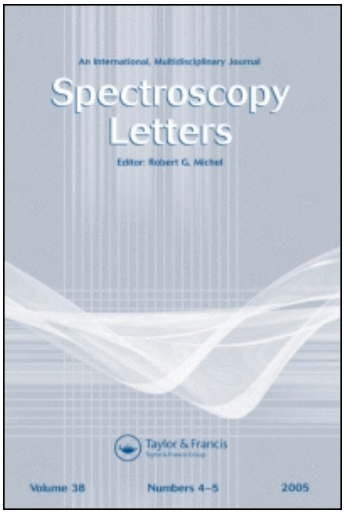

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Surana, S. S. L. , Mathur, R. C. and Tandon, S. P.(1978) 'The Intensities of f↔f Transitions and Bonding in Fluorinated Lanthanide β-Diketone Chelates', Spectroscopy Letters, 11: 6, 389 — 397
To link to this Article: DOI: 10.1080/00387017808067760
URL: http://dx.doi.org/10.1080/00387017808067760

SPECTROSCOPY LETTERS, 11(6), 389-397 (1978)

THE INTENSITIES OF f↔f TRANSITIONS AND BONDING IN FLUORINATED LANTHANIDE β-DIKETONE CHELATES

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Interest in the intensity of lanthanide f↔f spectra have begun nearly forty years ago, but most of the work was done after the publication of the theory of lanthanide intensity by Judd[1] and Ofelt[2] independently in 1962. Since then a number of lanthanide complexes having O-, N- or mixed donor ligands have been studied for the one reason or the other. Various β-diketone chelates were studied[3-7] for the reason that they proved to be good lasing materials. The present communication extends this study further to fluorinated β-diketone chelates of Pr^{3+} and Nd^{3+}, which gives useful information regarding interelectronic repulsion, spin-orbit interaction, nephelauxetic effect and bonding in these chelates.

The visible spectra of lanthanides arise[8] due to forbidden transitions within the ground $4f^N$ configuration. To the first approximation the energy level structure of $4f^N$ configuration may be considered to arise from the electrostatic and magnetic interactions between the 4f electrons. These interactions can be expressed in terms of Slater-Condon parameters F_K and Lande' parameter ζ_{4f}.

As a result of the complexation, contraction or expansion of wave functions occur, which is reflected by the changes in values of F_K and ζ_{4f} parameters with respect to the corresponding free ion

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values. This phenomenon is known as nephelauxetic effect[9], and can be expressed by the nephelauxetic ratio β defined as

$$\beta = F_K^c / F_K^f \qquad \ldots(1)$$

where c and f refer to the complex and free ion respectively.

If the degree of covalency ($b^{1/2}$) is defined as the amount of 4f-ligand mixing in the metal wave function, then the metal wave function can be written[10] as

$$\langle \phi_{4f}| = (1-b)^{1/2} \langle 4f| - b^{1/2} \langle \phi_{ligand}| \qquad \ldots(2)$$

On simplification of eq. (1) with the help of eq. (2), we get a relation between β and $b^{1/2}$, given by

$$b^{1/2} = \left[\frac{1}{2}(1 - \beta)\right]^{1/2} \qquad \ldots(3)$$

The +ve and -ve values of b for a complex correspond to covalent and ionic characters respectively.

The f↔f transitions are assumed to be forced-electric dipole in nature, occuring by the mixing of a higher energy configuration of opposite parity with the $4f^N$ configuration. The equation derived by Judd[1] and Ofelt[2] for the oscillator strength P of a transition between a ground state $\langle f^N \psi_J|$ and an excited state $|f^N \psi'_{J'}\rangle$ of the lanthanide ion in solution is

$$P = \sum_{\lambda=2,4,6} \nu T_\lambda \langle f^N \psi_J | U^{(\lambda)} | f^N \psi'_{J'} \rangle^2 \qquad \ldots(4)$$

T_λ values are usually treated as empirical parameters. These quantities are related to the radial wave functions of the states, the refractive index of the medium and the ligand field parameters which characterize the environmental field.

RESULTS AND DISCUSSIONS

The chelates of Pr^{3+} and Nd^{3+} with acetylacetone (AA), trifluoroacetylacetone (TFA) and hexafluoroacetylacetone (HFA) were

prepared by the usual methods[11,12]. The absorption measurements in the region 360-1000 nm were carried out with a Carl Zeiss VSU-2 Spectrophotometer using methanol as solvent. The experimental and calculated values of the energy levels and oscillator strengths of the absorption bands have been collected in Tables 1-4.

The Slator-Condon parameters F_2, F_4, F_6 and the Lande' ζ_{4f} parameter for the chelates under study were evaluated by expressing the energy as a Taylor series expansion by Wong's method[13] and have been collected in Table 5. In calculating these parameters the composite bands observed at ~ 12500 cm^{-1} and ~ 13450 cm^{-1} in case of Nd^{3+} chelates were not considered. In most of the cases F_K's and ζ_{4f} of lanthanide complexes exhibit a decrease from the values of the corresponding parameters of free ion, because on complexation expansion of the central metal ion orbital takes place.

The calculated F_K parameters were used to compute the nephelauxetic ratio β and the bonding parameter $b^{1/2}$, using relations (1) and (3).

The degree of covalency indicated by $b^{1/2}$ decreases in the order AA > TFA > HFA. The reduction in parameters with respect to the free ion parameters for Nd^{3+} chelates is less than that observed in case of Pr^{3+} chelates. It shows that the bonding due to 4f metal orbitals - ligand orbitals interaction is weaker in Nd^{3+} chelates than that in the corresponding Pr^{3+} chelates.

The intensity T_λ parameters were calculated from P_{exp} using eq. (4) by Carnall et. al.[14] method. The parameters have been collected in Table 5, along with the energy parameters. In case of Nd^{3+} chelates under study T_4/T_6 is nearly constant, whereas T_2 shows an appreciable change. With the increase in the oscillator strength of the hypersensitive band in the region 16500-18000 cm^{-1}, T_2 parameter shows a gradual increase. Pr^{3+} chelates under study do not show any such regularity in these parameters. The r.m.s. deviation obtained

Table 1. Energy values (in cm^{-1}) of bands of Nd^{3+}-chelates

Level	AA		TFA		HFA	
	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}
$^4I_{9/2}$	0	0	0	0	0	0
$^4F_{3/2}$	11440	11380	11364	11413	11481	11464
$^4F_{5/2}$, $^2H_{9/2}$	12384		12346		12398	
$^4F_{7/2}$, $^4S_{3/2}$	13333		13363		13385	
$^4F_{9/2}$	14605	14607	14590	14705	14640	14735
$^2H_{11/2}$	15805	15605	16000	15919	15873	15878
$^4G_{5/2}$	17167	17167	17232	17197	17226	17274
$^4G_{7/2}$	19007	18976	19084	19124	19139	19152
$^2G_{9/2}$	19418	19399	19531	19504	19531	19541
$^4G_{9/2}$	20852	20804	21008	21056	21031	21042
$^2D_{3/2}$	21060	20914	21097	21122	21242	21190
$^4G_{11/2}$	21505	21460	21598	21515	21710	21585
$^2P_{1/2}$	23250	23150	22970	22982	23118	23051
r.m.s.deviation	±74		±57		±56	

Table 2. Oscillator strengths ($P \times 10^6$) of Nd^{3+}-chelates

Spectral region	AA		TFA		HFA	
	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}
11000-12000	2.05	1.94	2.27	2.14	3.23	2.58
12000-13000	8.96	9.26	10.30	10.80	12.00	12.91
13000-14000	11.00	10.95	13.30	12.92	16.00	15.34
14000-15000	0.72	0.82	0.95	0.96	1.80	1.15
15500-16500	0.31	0.22	0.41	0.26	0.60	0.31
16500-18000	33.45	33.55	38.10	38.13	47.00	47.00
18500-19200	4.50	4.34	5.71	4.93	6.35	5.98
19200-20500	1.33	1.63	1.63	1.88	1.81	2.24
20500-21100	0.25	0.52	0.39	0.61	0.27	0.72
21100-21500	1.30	0.18	1.84	0.19	1.56	0.23
21500-22000	0.35	0.26	0.47	0.30	0.58	0.36
22000-24000	0.46	0.38	0.56	0.40	0.49	0.48
r.m.s.deviation	$\pm 3.60 \times 10^{-7}$		$\pm 5.70 \times 10^{-7}$		$\pm 6.13 \times 10^{-7}$	

Table 3. Energy values (in cm^{-1}) of bands of Pr^{3+}-chelates

Level	AA		TFA		HFA	
	E_{exp}	E_{cal}	E_{exp}	E_{cal}	E_{exp}	E_{cal}
$^1D_2$	16806	16803	16920	17129	16920	17144
$^3P_0$	20242	20241	20661	20708	20747	20796
$^3P_1$	20833	20747	21231	21310	21322	21319
$^3P_2$	22123	21945	22523	22511	22472	22478
r.m.s.deviation	±99		±114		±114	

Table 4. Oscillator strengths ($P \times 10^6$) of Pr^{3+}-chelates

Level	AA		TFA		HFA	
	P_{exp}	P_{cal}	P_{exp}	P_{cal}	P_{exp}	P_{cal}
$^1D_2$	2.90	2.89	6.09	6.09	5.07	5.07
$^3P_0$	4.51	6.62	4.31	5.36	3.57	4.63
$^3P_1$	7.05	6.77	6.53	5.44	5.80	4.70
$^3P_2$	9.12	8.66	19.64	19.64	16.70	16.70
r.m.s. deviation	$\pm 1.72 \times 10^{-6}$		$\pm 0.75 \times 10^{-6}$		$\pm 0.76 \times 10^{-6}$	

Table 5. Energy, Bonding and Intensity Parameters of Nd^{3+} and Pr^{3+}-chelates

	F_2	F_4	F_6	ζ_{4f}	β	$b^{1/2}$	$T_2 \times 10^6$	$T_4 \times 10^6$	$T_6 \times 10^6$
(A) Nd^{3+}-chelates									
AA	324.26	48.65	4.95	872.30	0.9791	0.1020	16.49	4.50	12.12
TFA	327.98	50.17	5.16	873.80	0.9904	0.0693	18.84	4.77	14.41
HFA	330.87	49.46	5.20	874.70	0.9991	0.0210	23.36	5.70	17.14
aquo[16]	-	-	-	-	-	-	2.97	4.32	4.18
free ion[14]	331.16	50.71	5.15	884.00	-	-	-	-	-
(B) Pr^{3+}-chelates									
AA	303.50	41.90	4.57	695.90	0.9423	0.1700	7.40	2.05	2.62
TFA	308.24	42.54	4.65	729.17	0.9570	0.1466	7.93	1.50	6.03
HFA	310.79	42.89	4.69	691.81	0.9649	0.1324	4.01	1.29	5.14
aquo[17]	-	-	-	-	-	-	4.26	1.66	2.70
free ion[14]	322.09	44.46	4.87	741.00	-	-	-	-	-

for Pr^{3+} chelates is also high as compared to that obtained for the corresponding Nd^{3+} chelates. Also the values of T_2 required to obtain the best fit are in some cases[15] negative and consequently are meaningless in terms of theory, since by definition $T_\lambda > 0$. These observations suggest that the intensity theory of Judd-Ofelt in the present form is not applicable to Pr^{3+} chelates.

ACKNOWLEDGEMENTS

The authors are grateful to the Council of Scientific and Industrial Research, India and to Prof. A.N.Nigam, Head, Department of Physics, University of Jodhpur, Jodhpur for providing the necessary facilities.

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Received 1-16-78

Accepted 4- 4-78