Spectral Intensities of Some Er^{3+} β-Diketonate Complexes

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The oscillator strengths of the absorption bands of Er^{3+} acetylacetonate, thenoyltrifluoroacetate, and dibenzoylmethide in methanol and dimethylformamide were determined and discussed in terms of the Judd-Ofelt's theory. It was possible to use the Judd-Ofelt parameters for the evaluation of the spectral intensities. The oscillator strength of the hypersensitive transition $^2H_{11/2}\leftarrow{}^4I_{15/2}$ of Er^{3+} complexes, $P(^2H_{11/2})$, was indicated by the $P(^2H_{11/2})\approx\tau_{2\mathrm{comp}}\,\nu_{\mathrm{comp}}\,\mathrm{U}(2)/2\mathrm{J}+1$ and it is demonstrated that "hypersensitivity" may be explained only by the τ_2 parameter of each complex, originating from the forced electric dipole transition.

The intensities of the solution spectra of the most lanthanoid(III) have been interpreted by the Judd-Ofelt's theory.[1,2] It should be noticed that the oscillator strengths of the certain transitions in lanthanoid(III) complexes are greater than those of the same transitions in the lanthanoid(III) aquo ions. These are known as "hypersensitive transitions"[3] and have hitherto been characterized by the selection rule $\Delta J\leqq 2$ and by relatively larger values of the matrix elements of $U^{(2)}$ in comparison with those of other transitions. However, no satisfactory explanation of hypersensitivity has yet been given. Some possible mechanisms involved in the appearance and the intensity of *f-f* transition have been reported, namely, (a) inhomogeneous dielectric,[3] (b) forced electric dipole transitions,[4] and (c) vibronic mechanism[5]+covalency.[6] In this paper, the Judd-Ofelt's theory was applied to the intensities of the spectra of some erbium(III)[7] β-diketonate complexes[8,9] in methanol and dimethylformamide(DMF).

Theoretical and Calculations

In Judd-Ofelt's theory, the *f-f* transitions (except those involving an allowed magnetic dipole mechanism) are assumed to be forced electric dipole in nature, occurring by the mixing of a higher energy configuration (or configurations) of opposite parity with the $4f^N$ configuration *via* the odd terms in the ligand field. The equation derived for the oscillator strengh (P) of a transition between a ground state $(f^N\phi_J|$ and an excited state $|f^N\phi'_{J'})$ of the lanthanoid(III) in solution is given by

$$P = \sum \tau_\lambda \nu \mathrm{U}(\lambda)/(2J+1) \qquad (1)$$
$$\lambda = 2,\ 4,\ 6$$
$$\mathrm{U}(\lambda) = (f^N\phi_J\| U^{(\lambda)} \| f^N\phi'_{J'})^2$$

where ν is the energy of the transition $\phi'_{J'}\leftarrow\phi_J$, *i. e.*, the baricentre of the absorption band in cm^{-1}, $\mathrm{U}(\lambda)$ is the reduced matrix elements of the unit tensor operators $U^{(\lambda)}$ concerning the initial and final states of the transition, and the τ_λ vaules are usually treated as empirical parameters in cm. Reduced matrix elements for all the lanthanoids(III) have been published.[10] By using the experimental oscillator strength P_{exp}, ν, and $\mathrm{U}(\lambda)$ values in Eq. (1) and carrying out an analysis by least-squares, an optimum set of three parameters, τ_λ, are obtained. The τ_λ parameters were, in turn, used to obtain "calculated oscillator strengths". The root-mean-square (rms) deviations between the calculated and experimental oscillator strengths were also calculated. All calculations were made with a FACOM 230-60 computer of Kyushu University.

Experimental

The absorption measurements were carried out with a Hitachi EPS-2 spectrophotometer and a Jasco ORD/UV-5 recorder by scale expansion. The solvents used were "spec-pure" absolute methanol and DMF. The erbium(III) β-diketonate complexes do not dissociate in these two solvents. The erbium(III) acetylacetonate(AA), thenoyltrifluoroacetonate(TTA), and dibenzoyl methide(DBM) were prepared by using ordinary methods.[11–13] The absorption intensities were determined by measuring the area on the experimental absorption curves with planimeter, and the oscillator strengths were calculated by using the reduced Eq. (2)

$$P_{\mathrm{exp}} = 4.318\times10^{-9}\frac{9\eta}{(\eta^2+2)^2}\int\varepsilon(\nu)\mathrm{d}\nu \qquad (2)$$

where η in the refractive index of the solution and $\varepsilon(\nu)$ is the molar extinction coefficient at wave number ν. Refractive indices values of 1.32652 and 1.42817 were used for methanol and DMF, respectively, in calculation. These intensities were reproducible within $\pm0.2\times10^{-6}$ oscillator strength unit.

Results and Discussion

The experimental(P_{exp}) and calculated(P_{calc}) values of oscillator strengths of the absorption bands have been collected in Table 1—3. The τ_λ parameters are given in Table 4. The root-mean-square (rms) deviations obtained are very small in calculating four separated J'-bands ($^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, and $^4F_{7/2}$), containing only the hypersensitive $^2H_{11/2}$ band. As far as all four J'-bands are concerned, Judd-Ofelt's theory could be reasonably applied. But, the intensity of another hypersensitive transition $^4G_{11/2}\leftarrow{}^4I_{15/2}$ of Er(III) complex could not be adopted to the experimental oscillator strength, due to UV cut-off caused by intense absorption of the β-diketone ligands except acetylacetone, for calculation of the set of τ_λ parameters.

The results show that the effect of solvent and ligand on spectral intensity of Er(III) is very small for all the bands except for those in the region 18500—20000 cm^{-1}, which are known to be due to the hypersensitive transitions. Figure 1 shows the variation of the τ_λ parameters of Er(III) β-diketonate complexes in meth-

Table 1. Oscillator strengths of the absorption bands of Er^{3+} acetylacetonate

Spectral range (cm^{-1})	S′L′J′	Baricentre (cm^{-1})	ε_{max}	$P\times10^6$		
				Exptl	Calcd	Exptl-Calcd
(in MeOH)						
14500—16000	$^4F_{9/2}$	15420	2.5	2.26	2.00(2.24)$^{a)}$	0.26(0.02)
18000—18850	$^4S_{3/2}$	18665	2.5	0.88	0.72(0.69)$^{a)}$	0.16(0.19)
18850—20000	$^2H_{11/2}$	19450	29.5	30.35	55.01(30.35)$^{a)}$	−24.66(0)
20000—21200	$^4F_{7/2}$	20600	2.3	2.48	2.54(2.55)$^{a)}$	−0.06(−0.07)
21500—23000	$^4F_{5/2}$, $^4F_{3/2}$	22315	1.5	0.11	0.69	−0.58
23800—25100	$^2G_{9/2}$	24660	1.5	1.24	1.01	0.23
25100—26850	$^4G_{11/2}$	26340	98.5	110.17	96.05	14.12
26850—28400	$^4G_{9/2}$, $^2K_{15/2}$, $^2G_{7/2}$	27480	11.5	13.60		
					rms ±14.21(±0.20)	
(in DMF)						
14500—16000	$^4F_{9/2}$	15305	2.0	2.47	2.10(2.42)$^{a)}$	0.37(0.05)
18000—18500	$^4S_{3/2}$	18320	2.1	0.68	0.61(0.38)$^{a)}$	0.07(0.30)
18500—20000	$^2H_{11/2}$	19130	33.4	32.82	53.62(32.83)$^{a)}$	−20.79(0)
20000—21200	$^4F_{7/2}$	20470	1.9	1.74	2.30(1.85)$^{a)}$	−0.56(−0.11)
21500—23000	$^4F_{5/2}$, $^4F_{3/2}$	22070	0.8	0.71	0.58	0.13
23800—25100	$^2G_{9/2}$	24500	1.3	1.70	0.89	0.81
25100—26900	$^4G_{11/2}$	26390	92.4	106.99	95.30	11.69
26900—26400	$^4G_{9/2}$, $^2K_{15/2}$, $^2G_{7/2}$	27590	10.3	12.76		
					rms ±11.94(±0.32)	

a) Calculated values based on four J'-bands in parentheses.

Table 2. Oscillator strengths of the absorption bands of Er^{3+} thenoyltrifluoroacetonate

Spectral range (cm^{-1})	S′L′J′	Baricentre (cm^{-1})	ε_{max}	$P\times10^6$		
				Exptl	Calcd	Exptl-Calcd
(in MeOH)						
14500—16000	$^4F_{9/2}$	15360	4.0	2.37	2.41	−0.04
18000—18700	$^4S_{3/2}$	18525	3.3	0.63	0.89	0.26
18700—20000	$^2H_{11/2}$	19220	46.7	39.40	39.40	0
20000—21200	$^4F_{7/2}$	20585	5.2	3.23	3.12	0.11
					rms	±0.29
(in DMF)						
14500—16000	$^4F_{9/2}$	15240	1.8	2.98	2.98	0
18000—18550	$^4S_{3/2}$	18320	1.4	0.68	0.68	0
18550—19900	$^2H_{11/2}$	19120	46.0	39.97	39.97	0
19900—21200	$^4F_{7/2}$	20470	3.5	2.82	2.82	0
					rms	±0.003

Table 3. Oscillator strengths of the absorption bands of Er^{3+} dibenzoylmethide

Spectral range (cm^{-1})	S′L′J′	Baricentre (cm^{-1})	ε_{max}	$P\times10^6$		
				Exptl	Calcd	Exptl-Calcd
(in MeOH)						
14500—16000	$^4F_{9/2}$	15360	2.5	2.74	2.79	−0.05
18000—18700	$^4S_{3/2}$	18485	2.0	0.73	1.09	−0.36
18700—20000	$^2H_{11/2}$	19240	52.0	48.01	48.01	0
20000—21200	$^4F_{7/2}$	20600	4.2	3.90	3.76	0.14
					rms	±0.39
(in DMF)						
14500—16000	$^4F_{9/2}$	15270	1.8	2.38	2.34	0.04
18000—18500	$^4S_{3/2}$	18335	2.3	1.19	0.90	0.29
18550—19800	$^2H_{11/2}$	19130	53.0	51.88	51.88	0
19800—21100	$^4F_{7/2}$	20475	4.0	3.06	3.17	−0.11
					rms	±0.31

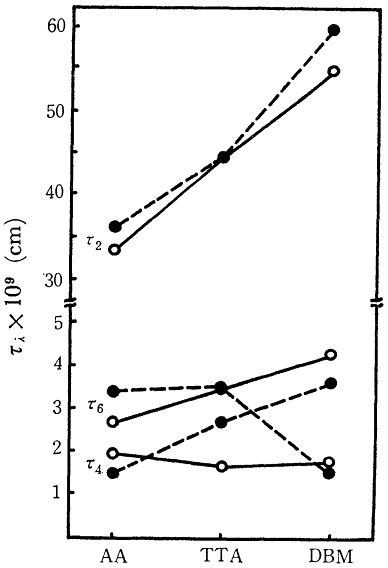

Fig. 1. Plot of the τ_λ parameters for Er(III) β-diketonates; —○— in MeOH, --●-- in DMF.

Table 4. Values of Judd-Ofelt's parameters for Er(III) β-diketonates in MeOH and DMF

		$\tau_\lambda \times 10^9$ (cm) MeOH	DMF
AA	τ_2	33.55±0.36	36.36±0.59
	τ_4	2.01±0.52	3.43±0.87
	τ_6	2.69±0.30	1.51±0.50
TTA	τ_2	44.60±0.52	44.57±0.01
	τ_4	1.69±0.76	3.51±0.01
	τ_6	3.47±0.43	2.70±0.01
DBM	τ_2	54.46±0.70	59.57±0.57
	τ_4	1.76±1.03	1.50±0.83
	τ_6	4.25±0.59	3.57±0.47
Aquo[14]	τ_2	1.70±0.15	
	τ_4	2.40±0.22	
	τ_6	2.31±0.12	

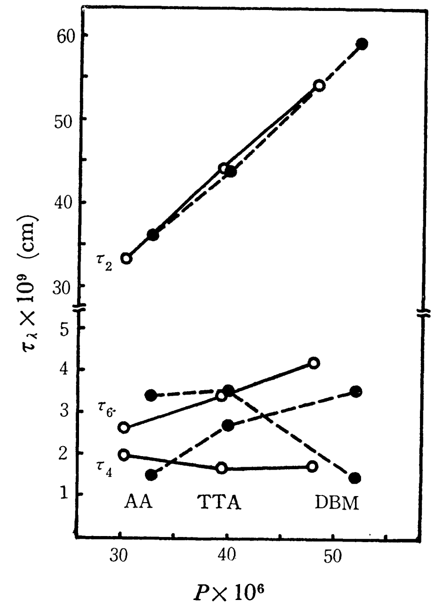

Fig. 2. Plot of the τ_λ parameters *vs.* the oscillator strength of the hypersensitive transition of ${}^2H_{11/2} \leftarrow {}^4I_{15/2}$ for Er(III) β-diketonates; —○— in MeOH, --●-- in DMF.

anol and DMF. The τ_2 parameter in the complex, $\tau_{2\mathrm{comp}}$, is the most sensitive to the environment, with marked differences in relative magnitudes of other τ_λ. (Refer to Table 4). The ratios of the experimental intensities ($P_{\mathrm{comp}}/P_{\mathrm{aquo}}$) at each J′-band and those of the calculated τ_λ parameters ($\tau_{\lambda\mathrm{comp}}/\tau_{\lambda\mathrm{aquo}}$) of Er(III) β-diketonate complexes are shown in Table 5. Table 5 seems to indicate that in the case of hypersensitive transition, the increase in the intensity is due to the solvent or ligand, and that it may be correlated with the marked increase in the value of τ_2 parameter.[6–7] This is shown more clearly in Fig. 2, by plotting of τ_λ values of the complexes *vs.* oscillator strength of the hypersensitive band (${}^2H_{11/2}$) in the complexes. It may be pointed out that approximately τ_2 value of complex is linear to the intensity of the hypersensitive

Table 5. Values of ratios of the (observed) oscillator strengths and the (calculated) τ_λ parameters of Er(III) complexes to Er(III) aquo ion

Er(III)	S′L′J′	AA MeOH	AA DMF	TTA MeOH	TTA DMF	DBM MeOH	DBM DMF
$\frac{P_{\mathrm{comp}}}{P_{\mathrm{aquo}}}$	${}^4F_{9/2}$	1.00	1.10	1.05	1.32	1.22	1.06
	${}^4S_{3/2}$	1.33	1.03	0.95	1.03	1.11	1.80
	${}^2H_{11/2}$	10.50	11.36	13.63	13.83	16.61	17.95
	${}^4F_{7/2}$	1.09	0.77	1.42	1.24	1.72	1.35
$\frac{\tau_{\lambda\mathrm{comp}}}{\tau_{\lambda\mathrm{aquo}}}$	λ						
	2	19.74	21.39	26.24	26.22	32.04	35.04
	4	0.84	1.43	0.70	1.46	0.73	0.63
	6	1.16	0.65	1.50	1.17	1.84	1.55
$\frac{P(2)_{\mathrm{comp}}}{\sum P(\lambda)_{\mathrm{comp}}}({}^2H_{11/2})$ $\lambda=2, 4, 6$		0.96	0.94	0.97	0.95	0.97	0.98

band. The values in the last row of Table 5 are those of

$$\frac{P(2)_{\mathrm{comp}}}{\sum P(\lambda)_{\mathrm{comp}}},$$
$$\lambda = 2, 4, 6$$

$$\{P(\lambda) = \tau_{\lambda}\nu \mathrm{U}(\lambda)/2J+1,\ P = \sum P(\lambda)\}$$
$$\lambda = 2, 4, 6$$

and this term expresses clearly contribution of τ_2 value to the intensity of the observed hypersensitive band($^2H_{11/2}$). Thus, it is concluded that $P(^2H_{11/2} \leftarrow {}^4I_{15/2})$ is approximately equal to the value of $\tau_{2\mathrm{comp}}\nu_{\mathrm{comp}}\mathrm{U}(2)/2J+1$.

Therefore, this fact seems to support the result that the intensities of hypersensitive transitions are characterized by the magnitude of the τ_2 parameter, in three parameters of the Judd-Ofelt's theory.

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