451.
4. Newton, M. D.; Stanton, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2469.
5. Lüthi, H. P.; Almlöf, J. *Chem. Phys. Lett.* **1987**, *135*, 357.
6. Ozaki, M.; Takahashi, A. *Chem. Phys. Lett.* **1986**, *127*, 242.
7. Haddon, R. C.; Brus, E. L.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459.
8. Hale, P. D. *J. Am. Chem. Soc.* **1986**, *108*, 6087.
9. Sashi Satpathy *Chem. Phys. Lett.* **1986**, *130*, 545.
10. Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Stefan Loren; Hollander, F. J. *Science* **1991**, *252*, 312.
11. Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980.
12. Amié, D.; Trinajstip *J. Chem. Soc., Perkin Trans.* **1990**, *2*, 1595.
13. (a) Fagan, P. J.; Calabrese, J. C.; Brian Malone *Science* **1991**, *252*, 1160. (b) Cheng, P.-T.; Nyburg, S. C. *Can. J. Chem.* **1972**, *50*, 912.
14. Fagan, P. J.; Calabrese, J. C.; Brian Malone *J. Am. Chem. Soc.* **1991**, *113*, 9408.
15. Fann, Y. C.; Singh, D.; Jansen, S. A. *J. Phys. Chem.* **1992**, *96*, 5817.
16. (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *97*, 7240.
17. Hong, S. Y.; Marynick, D. S. *J. Chem. Phys.* **1992**, *96*, 5497.
18. Koga, N.; Morokuma, K. *Chem. Phys. Lett.* **1993**, *202*, 330.

Oscillator Strengths and Intensity Parameters of Ln(III) Complexes with 12-Crown-4 and 15-Crown-5 Ethers in Acetonitrile (Ln=Ho and Er)

Jun-Gill Kang*, **Soo-Kyung Yoon**, **Eun-Jeong Kim**, **Jong-Gu Kim**[†], **and Youn-Doo Kim**

Department of Chemistry, Chungnam National University, Taejeon 305-764, Korea
[†]*Radiochemistry Division, Korea Atomic Energy Research Institute, Taejeon 302-353, Korea*

Received November 23, 1994

The absorption spectra of holmium nitrate and erbium nitrate and the difference absorption spectra of their complexes with crown ethers were measured in acetonitrile. The crown ethers used in this study are 12-crown-4 and 15-crown-5. The oscillator strengths for the $4f \rightarrow 4f$ multiplet-to-multiplet transitions are empirically determined from the absorption spectra in combination with the difference spectra. The intensity parameters Ω_λ ($\lambda=2, 4, 6$) for the systems are also evaluated by applying the Judd-Ofelt theorem to the observed oscillator strengths. The values of the intensity parameters are compared and discussed to investigate the sensitivity of the intensity parameters to the ligand environment.

Introduction

Lanthanides have been expected to form stable complexes similarly to alkaline and alkaline earth metals because of the similarity of the chemical bonding and the ionic radii between the lanthanides and Na^+ or Ca^{2+} ions. A great works dealing with the complexation of trivalent lanthanide ions, Ln(III), with macrocyclic ligands, specially crown ethers and their derivatives, have been performed to elucidate thermodynamic and kinetic properties of lanthanide complexes.[1] From a combination of conductivity,[2] IR[3] and NMR studies,[4] solvent extraction[5~7] and fluorescence[4,8] the most of studies have deduced the stoichiometry and stability and the cation-selectivity of lanthanide complexes with several crown ethers. However, despite the vast number of papers on crown ether complexes, there are little information on the absorption properties of the lanthanide complexes.[9]

Lanthanide(III) ions with $4f^N5s^25p^6$ show very characteristic $4f \rightarrow 4f$ absorption spectra which correspond to transitions from the ground multiplet to the excited multiplet. These transitions are forbidden in principle by an electric dipole moment, but are partially allowed by the induced electric dipole moment. Judd[10] and Ofelt[11] individually derived significant theoretical expressions for the oscillator strength of the induced electric dipole moment, taking into account the crystal-field potential causing the mixing between the $4f$ orbital and another orbital with an opposite parity. On the basis of the intermediate coupling scheme, the Judd-Ofelt theorem for the oscillator strength of the transition from the initial ΨJ to the final $\Psi' J'$ state is expressed as

$$P_{ED}=\chi\left(\frac{8\pi^2 mc\bar{\nu}}{h}\right)\sum_{\lambda=2,4,6}\Omega_\lambda\langle f^N;\ \Psi J\|U^{(\lambda)}\|f^N;\ \Psi' J'\rangle^2(2J+1)^{-1} \tag{1}$$

where x is the Lorentz-field correction for the refractivity of the medium, m is the mass of an electron, and $\bar{\nu}$ is the transition energy given in cm^{-1}, $U^{(\lambda)}$ is an irreducible unit tensor operator of rank λ, and the bracket is the reduced

---

*To whom correspondence should be addressed.

matrix element of $U^{(\lambda)}$. In the equation, the Ω_λ quantities (λ=2, 4, 6), called as the Judd-Ofelt intensity parameter, are phenomenologically determined from the observed oscillator strengths. Upon the complexation of lanthanide ions with the ligands, the oscillator strengths of the $4f\rightarrow 4f$ transitions are changed only slightly in most case, but certain transitions exhibit a strong sensitivity to the ligand environment. Such transitions have been labelled hypersensitive. Among the three intensity parameters, the Ω_2 has drawn a special attention, related to the peculiar sensitivity to the environment.

Up to date, any papers dealing with oscillator strength and intensity parameter of the lanthanide(III) complexes with these crown ethers have not been reported. A few papers have reported the quantitative experimental-evidence for hypersensitivity in complexes of Pr(III) with 18-crown-6 (18C6) and of Eu(III) with 15C5 and B15C5 (benzo-15-crown-5).[8] In this study we first performed the measurement of absorption and the difference absorption spectra for acetonitrile solutions of complexes of holmium nitrate and of erbium nitrate with crown ethers. Ho(III) and Er(III) ions are known to exhibit the hypersensitive behavior in accessible UV-visible spectral region. Specially, the $^5I_8\rightarrow{}^5G_6$ transition of Ho(III) and the $^4I_{15/2}\rightarrow{}^2H_{11/2}$ and $^4I_{15/2}\rightarrow{}^4G_{11/2}$ transitions of Er(III) are of interest, having large value of the reduced matrix element of $U^{(2)}$. The crown ethers(CEs) used in this study are 12C4 and 15C5. Under a strongly coordinating anion like NO_3^- the lanthanides are known to form the unsolvated 1 : 1, 3 : 2 or 4 : 3 complexes with 12C4 and 15C5 depending on the relative sizes between the lanthanide ion and crown ether.[3] The main purpose of this paper is to investigate oscillator strengths and the Judd-Ofelt intensity parameters of the acetonitrile solutions containning various mole ratios of holmium nitrate and erbium nitrate to 12C4 or 15C5. We also demonstrate the possibility of deducing the stoichiometry of Ho(III) and Er(III) complexes with 12C4 and 15C5 from the oscillator strength and the intensity parameter.

Experimentals

$Ho(NO_3)_3\cdot 6H_2O$ (99.99%) and $Er(NO_3)_3\cdot 6H_2O$ (99.99%) were purchased from Johnson Matthey and used without further purification. 12-crown-4 (98%+) and 15-crown-5 (98%+) were purchased from Aldrich and used without further purification. Acetonitrile (99.8%+) was purchased from Merck and used without further purification. All spectroscopic measurements were carried out on actonitrile solutions in which the concentration of Ho(III) or Er(III) were held at 1.0×10^{-2} M. Seven samples were prepared, in which the mole ratio of [Ln^{3+}] to [CE] were 1 : 0.5, 1 : 0.67, 1 : 0.75, 1 : 1, 1 : 1.5, 1 : 2 and 1 : 3. Absorption and difference absorption spectra were recorded on a Carry 3 spectrophotometer with the samples contained in 4 cm quartz cells.

The oscillator strength defined as Eq. (1) can be expressed in terms of the measured intensity of the absorption band in acetonitrile.

$$P_{obs}=4.32\times 10^{-9}\int\varepsilon(\bar{\nu})d\,\bar{\nu} \qquad (2)$$

where ε is the molar absorption coefficient at the transition energy $\bar{\nu}$ and the integral

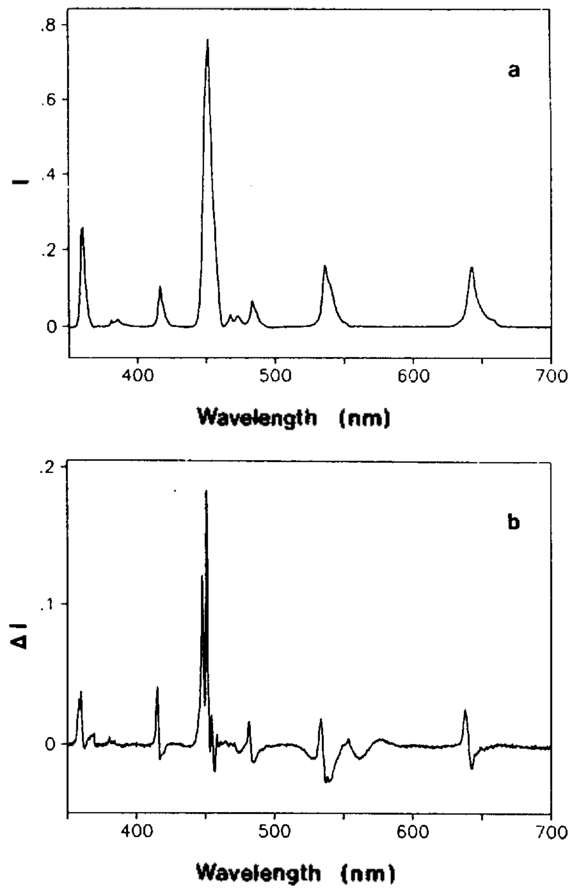

Figure 1. Absorption spectrum of holmium nitrate (a) and difference absorption spectrum of the 1 : 1 Ho(III) : 12C4 mixture (b) in acetonitrile.

$$I=\int\varepsilon(\bar{\nu})d\,\bar{\nu} \qquad (3)$$

corresponds to the area of the absorption band for a certain transition. The combination of Eqs. (1) and (2) can express the integration over the entire $\Psi J\rightarrow\Psi' J'$ absorption band as:

$$I(\Phi' J')=2.98\times 10^{19}\bar{\nu}(2J+1)^{-1} \times\sum_{\lambda=2,4,6}\Omega_\lambda[f^N;\ \Psi J\|U^{(\lambda)}\|f^N;\ \Psi' J'\rangle^2 \qquad (4)$$

The difference absorption spectrum can be defined as the difference between the absorbance of the complex and that of the free ion in solvent as follows:

$$\Delta I=I(\text{complex})-I(\text{free ion}) \qquad (5)$$

The resolution and the integration of the observed band were made by running the commercialized LC software (Galactic Industries Corp., USA) in a PC computer for the observed data.

Results and Discussion

The absorption spectra of holmium nitrate and erbium nitrate in acetonitrile were measured in the near UV-visible wavelength-range. Figures 1(a) and 2(a) show the absorption spectra of the two solution, respectively. The observed absorption bands of holmium nitrate and erbium nitrate were

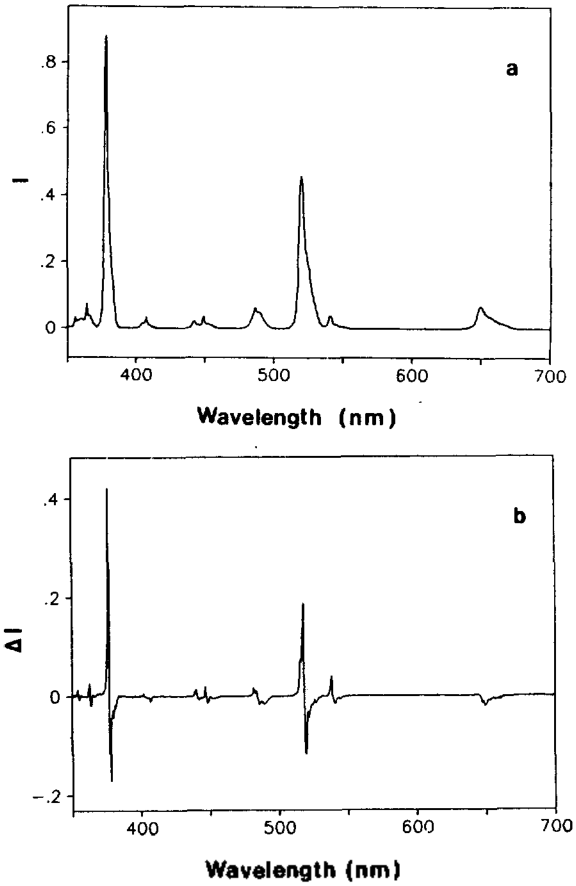

Figure 2. Absorption spectrum of erbium nitrate (a) and difference absorption spectrum of the 1 : 1 Er(III) : 12C4 mixture (b) in acetonitrile.

Table 1. Transition regions and matrix elements of $U^{(\lambda)}$ for Ho (III) used in the intensity analysis

Transition region			$\langle\|U^{(\lambda)}\|\rangle^2$		
Label	Transition	$\bar{\nu}$ (cm^{-1})	$\lambda=2$	$\lambda=4$	$\lambda=6$
(*a*)	$^5I_8\rightarrow{}^5F_5$	15,570	0	0.425	0.569
(*b*)	$^5I_8\rightarrow{}^5S_2+{}^5F_4$	18,670	0	0.239	0.934
(*c*)	$^5I_8\rightarrow{}^5F_3$	20,700	0	0	0.346
(*d*)	$^5I_8\rightarrow{}^5F_2+{}^3K_8$	21,270	0.02	0.033	0.350
(*e*)	$^5I_8\rightarrow{}^5G_6$	22,160	1.520	0.841	0.141
(*f*)	$^5I_8\rightarrow{}^5G_5+{}^3G_5$	24,020	0	0.534	0
(*g*)	$^5I_8\rightarrow{}^5G_4+{}^3K_7$	26,080	0.010	0.036	0.080
(*h*)	$^5I_8\rightarrow{}^5G_5+{}^3H_5+{}^3H_6$	27,780	0.220	0.197	0.164

identified in terms of the term symbol according to the energy-level diagram eported by Carnal *et al.*[12] and are listed in Tables 1 and 2, respectively.

The difference absorption spectra of Ho(III) and Er(III) ions were measured as a function of concentration of crown ether in acetonitrile solution to investigate the effect of crown ether on the transition probability. Figures 1(b) and 2(b) show the difference absorption spectra of the 1 : 1 Ho (III) : CE and Er(III) : CE in acetonitrile, respectively.

Table 2. Transition regions and matrix elements of $U^{(\lambda)}$ for Er(III) used in the intensity analysis

Transition region			$\langle\|U^{(\lambda)}\|\rangle^2$		
Label	Transition	$\bar{\nu}$(cm^{-1})	$\lambda=2$	$\lambda=4$	$\lambda=6$
(*a*)	$^4I_{15/2}\rightarrow{}^4F_{9/2}$	15,400	0	0.535	0.462
(*b*)	$^4I_{15/2}\rightarrow{}^4S_{3/2}$	18,520	0	0	0.221
(*c*)	$^4I_{15/2}\rightarrow{}^2H_{11/2}$	19,250	0.713	0.413	0.093
(*d*)	$^4I_{15/2}\rightarrow{}^4F_{7/2}$	20,520	0	0.147	0.627
(*e*)	$^4I_{15/2}\rightarrow{}^4F_{5/2}+{}^4F_{3/2}$	22,470	0	0	0.340
(*f*)	$^4I_{15/2}\rightarrow({}^2G+{}^4F+{}^2H)_{9/2}$	24,570	0	0.019	0.226
(*g*)	$^4I_{15/2}\rightarrow{}^2G_{11/2}$	26,480	0.918	0.526	0.117
(*h*)	$^4I_{15/2}\rightarrow{}^4G_{9/2}+{}^2K_{15/2}$	27,830	0.022	0.246	0.199

Table 3. Areas of the difference absorption bands for the various mole ratio of Ho(III) to crown ether in acetonitrile (unit is mol^{-1}cm^{-1})

Transition	ΔI						
	1:0.5	1:0.67	1:0.75	1:1	1:1.5	1:2	1:3
12-crown-4							
(*a*)	0.442	0.301	0.753	0.360	0.782	−0.334	0.568
(*b*)	2.483	−2.479	−1.941	−3.273	−2.418	−4.608	−2.346
(*c*)	0.290	3.431	−1.838	−1.778	−2.256	−3.471	−2.007
(*d*)	−0.360	−0.703	−0.815	−0.681	−1.045	−1.171	−1.421
(*e*)	9.145	11.78	13.35	15.12	24.58	20.29	13.90
(*f*)	0.740	0.764	0.952	0.949	1.391	1.710	1.325
(*g*)	0.164	0.196	0.224	0.282	0.169	−0.039	−0.244
(*h*)	2.069	2.400	2.718	3.389	3.738	2.628	2.275
15-crown-5							
(*a*)	−2.943	−1.154	−2.544	−3.60	−4.40	−2.740	−4.919
(*b*)	−2.507	−1.848	−3.504	−2.374	−4.745	−4.691	−4.668
(*c*)	0.047	0.387	−0.092	0.225	−0.241	−0.289	−0.180
(*d*)	−0.341	−0.742	−0.720	−0.824	−0.481	−1.130	−0.823
(*e*)	23.98	20.03	22.61	23.72	21.63	18.57	23.66
(*f*)	0.299	0.506	0.286	0.351	−0.132	0.164	−0.031
(*g*)	0.087	0.434	0.457	0.166	0.383	0.250	0.241
(*h*)	2.552	2.434	2.674	2.841	2.438	2.043	3.225

For the 1 : 1 Ho(III) : CE solution, among the observed bands the transition, $^5I_8\rightarrow{}^5G_6$, labelled as (e) draws a special attention since the characteristic feature of the difference spectrum is found in this electronic transition. The spectrum shows that as Ho(III) becomes under the enviornment of crown ether, the absorbance of this transition increases. For the 1 : 1 Er(III) : CE solution, the similar feature is found in the transitions, $^4I_{15/2}\rightarrow{}^2H_{11/2}$ and $^4I_{15/2}\rightarrow{}^2G_{11/2}$, labelled as (c) and (g), respectively. It can be seen from Table 1 and 2 that the matrix element of $U^{(2)}$ for these transitions are very large, compared with the others. Accordingly, these transitions can be monitored to characterize the complexation of Ho(III) and Er(III) with crown ethers.

The difference absorption spectra of 0.010 M Ho(III) or Er(III) acetonitrile solution containing various mole ratios of 12C4 or 15C5 were measured. The evaluated area of the

Table 4. Areas of the difference absorption bands for the various mole ratio of Er(III) to crown ether in acetonitrile (unit is $mol^{-1}cm^{-1}$)

Transition	ΔI						
	1:0.5	1:0.67	1:0.75	1:1	1:1.5	1:2	1:3
12-crown-4							
(a)	−2.477	−2.706	−2.772	−3.505	−5.036	−5.550	−3.437
(b)	0.390	0.566	0.553	0.776	0.603	0.957	0.544
(c)	2.222	2.568	3.407	3.663	0.121	4.668	2.690
(d)	−1.195	−1.837	−1.612	−2.139	−2.940	−3.713	−1.847
(e)	0.275	0.292	0.510	0.390	0.376	0.582	0.339
(f)	−0.697	−0.604	−0.640	−0.680	−1.023	−0.912	−0.565
(g)	2.584	0.678	0.793	1.571	−4.978	0.241	0.315
(h)	0.117	0.017	0.039	0.101	0.050	0.078	−0.043
15-crown-5							
(a)	−0.876	−1.385	−1.441	−1.451	−1.653	−1.683	−1.628
(b)	0.155	0.248	0.444	0.508	0.543	0.730	0.390
(c)	2.230	1.646	1.908	1.998	0.599	1.400	0.845
(d)	−0.785	−0.687	−0.809	−1.000	−0.836	−1.630	−0.647
(e)	−0.316	−0.467	−0.166	−0.363	−0.348	−0.525	−0.254
(f)	−0.244	−0.284	−0.148	−0.184	−0.325	−0.290	−0.156
(g)	5.916	6.067	6.212	5.920	10.22	3.000	8.391
(h)	0.775	0.706	0.634	0.558	0.620	0.528	0.570

difference absorption bands, ΔI, are listed in Tables 3 and 4. For Ho(III) coordinating with crown ethers, as expected, the relatively large increase in oscillator strength can be found in the transition *(e)*. In the case of the transitions labelled as *(a)*, *(b)* and *(f)*, although the matrix elements of $U^{(4)}$ or $U^{(6)}$ are somewhat large, the increase in ΔI did not appear at all. For Ho(III) : 12C4 mixture, the largest increment of ΔI is found in the 1 : 1.5 solution, among the observed solutions containing various mole ratios of 12C4. For Ho(III) : 15C5 mixture, the similar increment is found in the 1 : 0.5, 1 : 1 and 1 : 3 Ho(III) : 15C5 solutions. For Er(III), the appreciable increase in ΔI can be found in the transitions *(c)* and *(g)*. The relative increment of these transitions differs from 12C4 to 15C5. 12C4 causes the ${}^4I_{15/2}\rightarrow{}^2H_{11/2}$ transition to be more sensitive to the environment of coordination, while for 15C5 the ${}^4I_{15/2}\rightarrow{}^2G_{11/2}$ transition becomes more effective than the other. The largest increment of ΔI is found in the 1 : 2 Er(III) : 12C4 from the transition *(c)* and in the 1 : 1.5 Er(III) : 15C5 from the transition *(g)*.

The three Judd-Ofelt intensity parameters were obtained from the empirically determined oscillator strengths by the multiple regression method, in which the Ω_2, Ω_4 and Ω_6 quantities were treated as adjustable parameters. The three parameters yielding the optimal fit for holmium nitrate and Ho(III) : CE mixtures in acetonitrile are listed in Table 5 and those for erbium nitrate and Er(III) : CE mixtures are listed in Table 6. The small root-mean-square deviations appeared in the Ω_2 parameters. It may arise from the fact that the large oscillator strengths of the observed transitions are strongly determined by the matrix elements of $U^{(2)}$.

The ratios of Ω_λ (complex) to Ω_λ (free) have been considered to discuss the stoichiometry and the relative binding ability of crown ether. As listed in Tables 5 and 6, although the increase in Ω_2 resulted from the complexation with crown ether is not large, one can find that Ω_2 is more sensitive to the coordination environment than Ω_4 and Ω_6. Clearly, It is recognized that Ω_2 is a parameter exhibiting the relative coordination-abilities of 12C4 and 15C5. Among the Ho(III) : 12C4 mixtures, the 1 : 1.5 ratio gives rise to the largest increment in Ω_2 when Ho(III) is complexed by 12C4. It suggests that the 2 : 3 complex may be formed as the major species.

In the case of the Ho(III) : 15C5 mixture, the 1 : 0.5, 1 : 1 and 1 : 3 mixtures show almost similar values of the Ω_2 (complex)/Ω_2 (free) ratio. The 2 : 1, 1 : 1 and 1 : 3 complexes

Table 5. The Judd-Ofelt intensity parameters of the Ho(III) system calculated from experimental data

Complex	$\Omega_\lambda\times10^{21}$ (cm^2)			Ω_λ (complex)/Ω_λ (free)		
	λ=2	λ=4	λ=6	λ=2	λ=4	λ=6
Ho(III)	1.726 (±0.228)	0.742 (±0.357)	0.884 (±0.242)			
Ho(III) : 12C4						
1 : 0.5	1.868 (±0.242)	0.770 (±0.357)	0.827 (±0.242)	1.08	1.04	0.94
1 : 0.67	1.911 (±0.242)	0.784 (±0.357)	0.813 (±0.242)	1.11	1.06	0.92
1 : 0.75	1.925 (±0.242)	0.799 (±0.371)	0.813 (±0.257)	1.12	1.08	0.92
1 : 1	1.968 (±0.242)	0.799 (±0.371)	0.784 (±0.242)	1.14	1.08	0.89
1 : 1.5	2.111 (±0.257)	0.827 (±0.385)	0.784 (±0.257)	1.22	1.12	0.89
1 : 2	2.039 (±0.257)	0.827 (±0.371)	0.713 (±0.257)	1.18	1.12	0.81
1 : 3	1.925 (±0.257)	0.813 (±0.371)	0.784 (±0.257)	1.12	1.10	0.89
Ho(III) : 15C5						
1 : 0.5	2.154 (±0.214)	0.713 (±0.328)	0.799 (±0.214)	1.25	0.96	0.90
1 : 0.67	2.068 (±0.228)	0.742 (±0.342)	0.813 (±0.228)	1.20	1.00	0.92
1 : 0.75	2.125 (±0.228)	0.727 (±0.328)	0.770 (±0.228)	1.23	0.98	0.87
1 : 1	2.154 (±0.214)	0.713 (±0.314)	0.784 (±0.214)	1.25	1.00	0.89
1 : 1.5	2.139 (±0.214)	0.685 (±0.314)	0.742 (±0.214)	1.24	0.92	0.84
1 : 2	2.068 (±0.228)	0.727 (±0.342)	0.742 (±0.228)	1.20	0.98	0.84
1 : 3	2.168 (±0.200)	0.685 (±0.299)	0.742 (±0.200)	1.26	0.92	0.84

Table 6. The Judd-Ofelt intensity parameters of the Er(III) system calculated from experimental data

complex	$\Omega_\lambda \times 10^{21}$ (cm^2)			Ω_λ (complex)/Ω_λ (free)		
	$\lambda=2$	$\lambda=4$	$\lambda=6$	$\lambda=2$	$\lambda=4$	$\lambda=6$
Er(III)	1.678 (±0.456)	0.618 (±0.765)	0.389 (±0.443)			
Er(III) : 12C4						
1 : 0.5	1.785 (±0.470)	0.524 (±0.779)	0.376 (±0.456)	1.06	0.85	0.97
1 : 0.67	1.772 (±0.497)	0.524 (±0.081)	0.362 (±0.470)	1.06	0.85	0.93
1 : 0.75	1.785 (±0.497)	0.510 (±0.832)	0.362 (±0.483)	1.06	0.83	0.93
1 : 1	1.812 (±0.497)	0.483 (±0.819)	0.362 (±0.483)	1.08	0.78	0.93
1 : 1.5	1.691 (±0.497)	0.443 (±0.819)	0.336 (±0.483)	1.01	0.72	0.86
1 : 2	1.839 (±0.523)	0.416 (±0.872)	0.336 (±0.510)	1.10	0.67	0.86
1 : 3	1.785 (±0.497)	0.483 (±0.819)	0.362 (±0.470)	1.06	0.78	0.93
Er(III) : 15C5						
1 : 0.5	1.799 (±0.443)	0.617 (±0.725)	0.362 (±0.430)	1.07	1.00	0.93
1 : 0.67	1.799 (±0.430)	0.604 (±0.711)	0.362 (±0.416)	1.07	0.98	0.93
1 : 0.75	1.812 (±0.430)	0.591 (±0.711)	0.376 (±0.416)	1.08	0.96	0.97
1 : 1	1.812 (±0.443)	0.591 (±0.725)	0.362 (±0.416)	1.08	0.96	0.93
1 : 1.5	1.879 (±0.389)	0.577 (±0.644)	0.362 (±0.376)	1.12	0.93	0.93
1 : 2	1.758 (±0.456)	0.591 (±0.752)	0.349 (±0.430)	1.05	0.96	0.90
1 : 3	1.852 (±0.040)	0.577 (±0.658)	0.376 (±0.376)	1.10	0.93	0.97

Table 7. Experimental and calculated oscillator strengths for the Ho(III) systems in acetonitrile

Transition	1 : 1.5 Ho(III) : 12C4		1 : 1 Ho(III) : 15C5	
	P_{exptl}	P_{fit}	P_{exptl}	P_{fit}
${}^5I_8 \rightarrow {}^5F_5$	1.570	0.941	1.381	0.884
${}^5I_8 \rightarrow {}^5S_2 + {}^5F_4$	1.284	1.315	1.286	1.277
${}^5I_8 \rightarrow {}^5F_3$	0.177	0.425	0.284	0.425
${}^5I_8 \rightarrow {}^5F_2 + {}^3K_8$	0.165	0.558	0.174	0.553
${}^5I_8 \rightarrow {}^5G_6$	6.768	6.737	6.731	6.685
${}^5I_8 \rightarrow {}^5G_5 + {}^3G_5$	0.521	0.803	0.476	0.693
${}^5I_8 \rightarrow {}^5G_4 + {}^3K_7$	0.397	0.207	0.397	0.200
${}^5I_8 \rightarrow {}^5G_5 + {}^3H_5 + {}^3H_6$	1.350	1.570	1.311	1.542

Table 8. Experimental and calculated oscillator strengths for the Er(III) systems in acetonitrile

Transition	1 : 2 Er(III) : 12C4		2 : 3 Er(III) : 15C5	
	P_{exptl}	P_{fit}	P_{exptl}	P_{fit}
${}^4I_{15/2} \rightarrow {}^4F_{9/2}$	0.534	0.632	0.703	0.590
${}^4I_{15/2} \rightarrow {}^4S_{3/2}$	0.168	0.128	0.151	0.119
${}^4I_{15/2} \rightarrow {}^2H_{11/2}$	3.455	2.304	3.322	2.497
${}^4I_{15/2} \rightarrow {}^4F_{7/2}$	0.380	0.553	0.504	0.515
${}^4I_{15/2} \rightarrow {}^4F_{5/2} + {}^4F_{3/2}$	0.300	0.239	0.259	0.223
${}^4I_{15/2} \rightarrow ({}^2G + {}^4F + {}^2H)_{9/2}$	0.117	0.197	0.142	0.184
${}^4I_{15/2} \rightarrow {}^2G_{11/2}$	3.536	4.071	3.967	4.413
${}^4I_{15/2} \rightarrow {}^4G_{9/2} + {}^2K_{15/2}$	0.409	0.596	0.432	0.572

could be formed together as major species. In the case of Er(III), the 1 : 2 complex for 12C4 and the 2 : 3 complex for 15C5 complex are formed as the major species.

In the case of NO_3^- anion, various Ln(III) : CE ratios have been reported for the 1 : 1 complex with 12C4, the 1 : 1 and 4 : 3 complexes with 15C5 and the 1 : 1 and 4 : 3 complexes with 18C6 as major formations in solid state. In solution state, more various complexes of lanthanide could be formed. Successful analysis has not been reported for the complex of lanthanide with macrocylic ligands in solution state. The structures of the 2 : 3 and 1 : 2 12C4 or 15C5 complexes can be assumed to be a sandwitch type. It has been argued that even if the complexes of lanthanide are the 1 : 1 12C4 or 15C5, the crown ether does not encapsulate the lanthanide ion in its cavity. According to the reported X-ray analysis of the $Ln(NO_3)_3$-12C4 or −15C5 in solid state,[13] the crown ether is coordinated as a tetra- or pentadentate ligand on one side of Ln(III) ion and the three bidentate nitrates are bonded on the other side. For the 2 : 1 and 1 : 3 complexes, 12C4 or 15C5 may not be coordinated directly to Ho(III) and Er(III). The coordinating abilities of 12C4 and 15C5 are not strong enough to induce the hypersensitivity in absorbing transitions of Ho(III) and Er(III). It could be due to the high coordination number of lanthanide. If the coordination number of Ho(III) or Er(III) is larger than 10, the lanthanide ions may be not only be coordinated by the bidentate NO_3^- anion but also strongly solvated by acetonitrile. Consequently, the relative small space for the coordinating of oxygen atoms of crown ether may make the nondirectional bond preferable. However, although the increment of the Ω_2 is not large, the comparison of the Ω_2 of the complex suggests that the 15C5 could form more stable complex than the 12C4 for a given lanthanide ion.

For the major mole-ratio mixtures of Ho(III) and Er(III) with 12C4 or 15C5 in acetonitrile, experimental and fitted oscillator strengths are compared to testify the Judd-Ofelt theorem. As listed in Tables 7 and 8, the very good agreements between the experimental and the calculated oscillator strengths were found in the transitions having the large matrix elements of $U^{(2)}$. For the other transitions some deviations are arisen from the relative small matrix elements of $U^{(\lambda)}$. Although crown ether may not give rise to the strong crystal-field perturbation, the $^5I_8\rightarrow{}^5G_6$ transition of Ho(III) and the $^4I_{15/2}\rightarrow{}^2H_{11/2}$ and $^4I_{15/2}\rightarrow{}^2G_{11/2}$ transitions of Er(III) can prove their senstivities to the coordination environment of the crown ether. If the polyether reducing the symmetry of Ln(III) lower than 12C4 or 15C5 is used as the ligand, the qualitative informations on the stability of complexes of Ho(III) and Er(III) can be obtained through the more hypersensitive of the transitions to the environment of the coordination.

Conclusion

The Judd-Ofelt intensity parameters Ω_λ ($\lambda=2$, 4, 6) for Ho(III) and Er(III) complexes with 12-crown-4 and 15-crown-5 ethers have been determined to demonstrate the sensitivity of these parameters to the coordination environment. Among the three Ω_λ parameters, the Ω_2 is the most sensitive to minor changes in the ligand. The sensitivity of Ω_2 to the coordination environment appears from the matrix element of $U^{(2)}$ which is only determined from the electronic states in the ground and excited states of free ion. Although $U^{(4)}$ and/or $U^{(6)}$ matrix elements are large for the transitions, e.g., $^5I_8\rightarrow{}^5F_5$, $^5I_8\rightarrow{}^5S_2+{}^5F_4$ and $^5I_8\rightarrow{}^5G_5+{}^3G_5$ for Ho(III), and $^4I_{15/2}\rightarrow{}^4F_{9/2}$ and $^4I_{15/2}\rightarrow{}^4F_{7/2}$ for Er(III), Ω_4 and Ω_6 were found to be insensitive to ligand effect.

The Ω_2 (complex)/Ω_2 (free) ratios were used to discuss the stoichiometry of the complex and the ligand effect. Compared with the cases of tridentate ligands such as oxydiacetate, dipicolinate, methyiminodiacetate, etc.,[14] 12C4 and 15C5 do not give rise to the hypersensitivity in the transitions having the large matrix elements of $U^{(2)}$ for Ho(III) and Er(III). In acetonitrile the lanthanide ions could be strongly solvated and coordinated by a bidentate NO_3^- anion. Under a such circumstance the lanthanide ions may be indirectly coordinated with oxygen atoms of crown ethers. This phenomena can be also assumed from the fact that the saturation of ΔI were not observed with increasing the concentration of crown ether. It can be assumed that the oscillator strength of the Ln(III) : CE solution could be affected by the dynamic coupling of the solvated lanthanoide nitrate with oxygen atoms of crown.

Furthermore, we are carrying out the extensive study on the Ln(III) complexes with macrocyclic ligands causing the low symmetry. It may allow us to present the sensitivity of the intensity parameters to ligand effects in detail.

Acknowledgment. This work was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1993.

References

1. Adachi, G.-Y.; Hirashima, Y. *Cation Binding by Macrocycles;* Inoue, Y.; Gokel, G. W., Ed.; Marcel Dekker: New York and Basel, **1990**; pp 701-741.
2. Massaux, J.; Desreux, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 2967.
3. Bunzli, J.-C. G.; Wessner, D.; Oanh, H. T. T. *Inorg. Chim. Acta* **1979**, *32*, L33.
4. Simon, J. D.; Moomaw, W. R.; Ceckler, T. M. *J. Phys. Chem.* **1985**, *89*, 5659.
5. Tsay, L.-M.; Shih, J.-S.; Wu, S.-C. *Analyst.* **1983**, *108*, 1108.
6. Aly, H. F.; Khalifa, S. M.; Navratil, J. D.; Saba, M. T. *Sovent Extr. Ion Exch.* **1985**, *3*, 623.
7. Nakagawa, K; Okada, S.; Inoue, Y.; Tai, A; Hakushi, T. *Anal. Chem.* **1988**, *60*, 2527.
8. Bunzli, J.-C. G.; Giorgetti, A. *Inorg. Chim. Acta* **1985**, *110*, 225.
9. Seminara, A.; Musumeci, A. *Inorg. Chim. Acta* **1980**, *39*, 9.
10. Judd, B. R. *Phys. Rev.* **1962**, *127*, 750.
11. Ofelt, G. S. *J. Chem. Phys.* **1962**, *37*, 511.
12. Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4424.
13. see references given in Table 1 of Ref. 1.
14. Stephens, E. M.; Davis, S.; Reid, M. F.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 4607; Devlin, M. T.; Stephens, E. M.; Richardson, F. S.; Van Cott, T. C.; Davis, S. A. *Inorg. Chem.* **1987**, *26*, 1204.