Absorption and Fluorescence Spectra of Europium(III) Compounds in Non-Aqueous Solutions

B. JEŻOWSKA-TRZEBIATOWSKA*, J. LEGENDZIEWICZ
Institute of Chemistry, University of Wrocław, Wrocław, Poland
and W. STRĘK
Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

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The absorption and fluorescence spectra of Eu(III) were investigated at room temperature in non-aqueous solutions. It was found that the intensity of hypersensitive bands is closely related to the molar refractivity of the solvent.

A possible mechanism of solvent effect on intensities of f–f transitions is discussed within the framework of Mason's polarizability mechanism.

Effect of solvent on fluorescence properties of Eu(III) was investigated and the mechanism of fluorescence quenching is also discussed.

Introduction

The spectroscopic properties of lanthanide complexes in solutions depend on the first coordination sphere of the lanthanide ion. The effect of the second coordination sphere is usually less essential. The solvent effect is relatively small for lanthanide ions in comparison with transition metal ions. The most prominent effect is manifested on hypersensitive transitions [1–5]. These transitions are strongly affected by solvent, both in absorption and in fluorescence spectra.

The structure of lanthanide complexes in solution is closely related to the specific chemical interaction between the lanthanide compounds dissolved and the solvent. From our recent results [3, 6] it follows that for perchlorate salts dissolved in different solvents the first coordination sphere of the lanthanide ion is formed by solvent molecules.

The problem of solvent effect on intensities of the lanthanide complexes has been investigated by many authors [1–11]. Recently we have shown that the intensity increase of hypersensitive bands in absorption spectra may be correlated to the molar refractivities of the solvents. A possible mechanism of solvent effect on intensities of f–f transitions may be explained within the framework of the polarizability mechanism [3, 4, 11]. In this paper we study the solvent effect on absorption and fluorescence spectra of europium perchlorates in non-aqueous solutions. The question of solvent effect on non-radiative decay is also discussed.

Experimental

The absorption spectra of europium perchlorate in non-aqueous solutions were measured on a Cary 14 spectrophotometer. The oscillator strengths were determined for all bands using ICH 30 integrating programme. The fluorescence spectra of Eu^{+3} ion solutions were excited by an argon laser ILA 120 (C. Zeiss, Jena) using a 488 nm line as an excitation, and were recorded by a GDM 1000 grating monochromator with a cooled photomultiplier M10 FD29 (C. Zeiss, Jena). The decay times were measured by means of a Boxar Integrator BCI 280 (Akademie der Wissenschaft der DDR), using a nitrogen laser as excitation.

Theory

The independent systems model [17] is a useful instrument for description of electronic relaxation in metal complexes. Within the framework of this model the total Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_{\mathrm{M}} + \mathcal{H}_{\mathrm{L}} + \mathcal{H}_{\mathrm{ML}} \tag{1}$$

where $\mathcal{H}_{\mathrm{M}}$ is the zero order electronic hamiltonian of free metal ion, $\mathcal{H}_{\mathrm{L}}$ is the zero order electronic hamiltonian linked with ligands and $\mathcal{H}_{\mathrm{ML}}$ is the interaction potential between metal ion and ligands,

$$\mathcal{H}_{\mathrm{ML}} = \sum_{L} \sum_{k_1 q_1} \sum_{k_2 q_2} \mathrm{T}^{(k_1+k_2)}_{-q_1-q_2}(L) D^{k_1}_{q_1}(M) D^{k_2}_{q_2}(L) \tag{2}$$

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*Author to whom correspondence should be addressed.

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with the operators for electric multiples as defined in [5].

The tensor $\mathrm{T}^{(k_1+k_2)}_{-q_1-q_2}(L)$ represents the geometric dependence of the metal–ligand interaction.

Let us assume that the operator

$$R = R_1 + R_2 \tag{3}$$

is a composite operator inducing the one-electron transition in the system. Here R_1 is subjected to metal ions and R_2 to ligands. In the presence of metal– ligand interaction, relaxation between different electronic terms is caused by the composite perturbation

$$\mathcal{H}' = R + \mathcal{H}_{\mathrm{ML}} \tag{4}$$

The transition moment for the operator $\mathcal{H}'$ may be written as

$$\begin{aligned}
&\langle M_{\mathrm{a}}L_0|\mathcal{H}'|M_{\mathrm{b}}L_0\rangle \\
&\quad = (M_{\mathrm{a}}L_0|R_1|M_{\mathrm{b}}L_0) + && \text{(5a)}\\
&\quad + (M_{\mathrm{a}}L_0|\mathcal{H}_{\mathrm{ML}}|M_{\mathrm{b}}L_0) + && \text{(5b)}\\
&\quad + \sum_k [(-E_{\mathrm{a}} - E_k)^{-1}(M_{\mathrm{a}}L_0|R_1|M_kL_0)(M_kL_0|\mathcal{H}_{\mathrm{ML}}|M_{\mathrm{b}}L_0) + \\
&\quad + (E_{\mathrm{b}} - E_k)^{-1}(M_{\mathrm{a}}L_0|\mathcal{H}_{\mathrm{ML}}|M_kL_0)(M_kL_0|R_1|M_{\mathrm{b}}L_0)] + && \text{(5c)}\\
&\quad + \sum_l [(E_{\mathrm{a}} - E_{\mathrm{b}} - E_l)^{-1}(M_{\mathrm{a}}L_0|R_2|M_{\mathrm{a}}L_l)(M_{\mathrm{a}}L_l|\mathcal{H}_{\mathrm{ML}}|M_{\mathrm{b}}L_0) + \\
&\quad + (-E_l)^{-1}(M_{\mathrm{a}}L_0|\mathcal{H}_{\mathrm{ML}}|M_{\mathrm{b}}L_l)(M_{\mathrm{b}}L_l|R_2|M_{\mathrm{b}}L_0)] && \text{(5d)}
\end{aligned}$$

Eqn. (5) is a basis for description of electronic relaxation in metal complexes. The term (5c) describes the static contribution to relaxation linked with the unperturbed ligands. The term (5d) linked with the perturbed ligands describes the dynamic contribution.

Radiative Transitions

In our description of electric dipole transitions in metal complexes we identify the operator R with the electric dipole operator D^1_q

$$R \equiv D^1_q = D^1_q(M) + D^1_q(L) = -e\left[\sum_i r_i C^1_q(\theta_i, \phi_i) + \sum_j r_j C^1_q(\theta_j, \phi_j)\right] \tag{6}$$

Here i, j refer to electrons of the metal and ligands, respectively.

Assuming that in eqn. (5c)

$$V_{\mathrm{c}} = (L_0|\mathcal{H}_{\mathrm{ML}}|L_0) = \sum_{tp} A_{tp}D^t_p \tag{7}$$

defines the static crystal field, where A_{tp} are the crystal field parameters and

$$D^t_p = \sum_i r^t_i C^t_p(\theta_i, \phi_i) \tag{8}$$

and substituting eqns. (6) and (7) into eqn. (5), we get for the static transition dipole moment

$$(D^1_{\mathrm{ab}})_{\mathrm{s}} = \sum_t \sum_p \sum_k A_{tp}[(E_{\mathrm{a}} - E_k)^{-1}(M_{\mathrm{a}}|D^1_{q_1}|M_k)(M_k|D^t_p|M_{\mathrm{b}}) + (E_{\mathrm{b}} - E_k)^{-1}(M_{\mathrm{a}}|D^t_p|M_k)(M_k|D^1_{q_1}|M_{\mathrm{b}})] \tag{9}$$

This mechanism is well known and with respect to the lanthanide ions was applied to description of intensities of f–f transitions by Judd [12] and Ofelt [13]. The dynamic component of the transition dipole moment given by eqn. (5d) may be rewritten in the form

$$\begin{aligned}
(D^1_{\mathrm{ab}}) = &\sum_l \sum_{k_1k_2} \sum_{q_1q_2} \mathrm{T}^{(k_1+k_2)}_{-q_1-q_2}(R_l, \Theta_l, \Phi_l)(M_{\mathrm{a}}|D^{k_1}_{q_1}|M_{\mathrm{b}}) \times \\
&\times \left\{\sum_l [(E_{\mathrm{a}} - E_{\mathrm{b}} - E_l)^{-1}(L_0|D^1_{q_2}|L_l)(L_l|D^{k_2}_{q_2}|L_0) + (-E_l)^{-1}(L_0|D^{k_2}_{q_2}|L_l)(L_l|D^1_{q_2}|L_0)]\right\}
\end{aligned} \tag{10}$$

Assuming that the leading contribution in the multipolar interaction (2) is connected with the dipole ligand transitions $k_2 = 1$, an expression defines

$$\alpha_{q_2 q} = \sum_{l} [(E_\mathrm{a} - E_\mathrm{b} - E_l)^{-1} (L_0|D^1_q|L_l)(L_l|D^1_{q_2}|L_0) + (-E_l)^{-1} (L_0|D^1_{q_2}|L_l)(L_l|D^1_q|L_0)]$$

the $q_2 q$-th component of the ligand polarizability measured at the frequency of metal ion transition ν_ab.

For lanthanide complexes we may rewrite eqn. (10) substituting $k_1 \to \lambda$ and $q_1 \to p$ as follows

$$(D^1_\mathrm{ab})_q = \sum_{l} \sum_{p q_2} \mathrm{T}^{(\lambda+1)}_{-p-q_2}(L)(M_\mathrm{a}|D^\lambda_p|M_\mathrm{b})\,\alpha_{q_2 p}(L) \tag{12}$$

where

$$(M_\mathrm{a}|D^\lambda_p|M_\mathrm{b}) = \langle f^\mathrm{n} JM|D^\lambda_p|f^\mathrm{n} J'M'\rangle = \langle f||C^\lambda||f\rangle\langle 4f|r^\lambda|4f\rangle\langle f^\mathrm{n} JM|U^\lambda_p|f^\mathrm{n} J'M'\rangle \tag{13}$$

with $\lambda = 2, 4, 6$.

The final expression for oscillator strength (assuming that ligands are isotropic) is given by

$$P_\mathrm{ab} = \frac{8\pi^2 mc\sigma}{3h} [J]^{-1}(1-\sigma_2)^2 \sum_{\lambda=2,4,6} [\lambda]^{-1}\langle J||U^\lambda||J\rangle^2 \langle f||C^\lambda||f\rangle^2 \langle 4f|r^\lambda|4f\rangle^2 \times$$
$$\times \left| \sum_{p,q} \sum_{L} \mathrm{T}^{\lambda+1}_{-p-q}(L)\,\bar{\alpha}(L) \right|^2 \tag{14}$$

where $[\lambda] = 2\lambda + 1$ and $[J] = 2J + 1$. The factor $(1 - \sigma_2)^2$ has been introduced after Judd [14] in order to take into account screening of quadrupole fields by the outer shells of rare earth ions.

Non-Radiative Transitions

In our description of non-radiative f–f transitions in lanthanide complexes we identify the perturbation operator R with the vibronic interaction potential

$$R = \mathcal{H}_\mathrm{NR} = \sum_{\nu} \frac{\partial V_\mathrm{ML}}{\partial Q_\nu} Q_\nu \tag{15}$$

where Q_ν represents the normal coordinates of the system. The matrix element for the operator $\mathcal{H}'$ associated with the non-radiative transition $|M_\mathrm{a}L_0) \rightsquigarrow |M_\mathrm{b}L_0)$ is given as

$$\langle M_\mathrm{a}L_0|\mathcal{H}'|M_\mathrm{b}L_0\rangle$$
$$= \langle M_\mathrm{a}L_0|\mathcal{H}_\mathrm{NR}|M_\mathrm{b}L_0\rangle + \tag{16a}$$
$$+ \langle M_\mathrm{a}L_0|V_\mathrm{ML}|M_\mathrm{b}L_0\rangle + \tag{16b}$$
$$+ \sum_{k} [(-E_\mathrm{a} - E_k)^{-1}\langle M_\mathrm{a}L_0|\mathcal{H}_\mathrm{NR}|M_kL_0\rangle\langle M_kL_0|V_\mathrm{ML}|M_\mathrm{b}L_0\rangle +$$
$$+ (E_\mathrm{b} - E_k)^{-1}\langle M_\mathrm{a}L_0|V_\mathrm{ML}|M_kL_0\rangle\langle M_kL_0|\mathcal{H}_\mathrm{NR}|M_\mathrm{b}L_0\rangle] + \tag{16c}$$
$$+ \sum_{l} [(E_\mathrm{a} - E_\mathrm{b} - E_l)^{-1}\langle M_\mathrm{a}L_l|\mathcal{H}_\mathrm{NR}|M_\mathrm{a}L_l\rangle\langle M_\mathrm{a}L_l|V_\mathrm{ML}|M_\mathrm{b}L_0\rangle +$$
$$+ (E_l)^{-1}\langle M_\mathrm{a}L_l|V_\mathrm{ML}|M_\mathrm{b}L_l\rangle\langle M_\mathrm{b}L_l|\mathcal{H}_\mathrm{NR}|M_\mathrm{b}L_0\rangle] \tag{16d}$$

The terms (16a) and (16b) represent the first and the second order static contributions to the non-radiative transitions respectively. The next term (16c) represents the dynamic mechanism of non-radiative transitions in metal complexes.

According to the transitions density localization criterion the static mechanism is associated with the metal bond involving vibrations, whereas the dynamic mechanism is combined with the internal ligand vibrations as promoting and accepting modes. The expression for non-radiative rate constant may be written as [5]

$$k_{ab} = \frac{2\pi}{\hbar} \sum_{\nu} I^{\nu}_{ab} F^{\nu}_{ab} \tag{17}$$

where I^{ν}_{ab} and F^{ν}_{ab} are the electronic and vibrational factors respectively.

The Electronic Factors

For the first order static mechanism; $\nu = \xi$

$$I^{\xi}_{ab} = \sum_{\lambda=2,4,6} \eta_{\lambda\xi} \langle f^n(M_a)J' \| U^{\lambda} \| f^n(M_b)J \rangle^2 (2J+1)^{-1} \tag{18}$$

where

$$\eta_{\lambda\xi} = \sum_{p} \left(\frac{\partial A_{tp}}{\partial Q_{\nu}}\right)^2 \langle f^n | r^{\lambda} | f^n \rangle^2 \langle f \| C^{\lambda} \| f \rangle^2, \tag{19}$$

for the second order static mechanism; $\nu = \zeta$

$$I^{\zeta}_{ab} = \sum_{\lambda=2,4,6} \eta_{\lambda\zeta} \langle f^n(M_a)J' \| U^{\lambda} \| f^n(M_b)J \rangle^2 (2J+1)^{-1} \tag{20}$$

where

$$\eta_{\lambda\zeta} = (2\lambda+1) \sum_{tp} \sum_{t'p'} A_{tp} \left(\frac{\partial A_{t'p'}}{\partial Q\zeta}\right) \Xi^2(t,t',\lambda)(2t+1)^{-1}(2t'+1)^{-1} \tag{21}$$

for the dynamic mechanism; $\nu = \eta$

$$I^{\eta}_{ab} = \sum_{\lambda=2,4,6} \eta_{\lambda\eta} \langle f^n(M_a)J' \| U^{\lambda} \| f^n(M_b)J \rangle^2 (2J+1)^{-1} \tag{22}$$

where

$$\eta_{\lambda\eta} = \left| \sum_{L} \sum_{tp} \sum_{k_2 q_2} \mathrm{T}^{k_2+t}_{-q_2-p}(L)\, \alpha^{k_2 t}_{q_2 p} (\partial A_{tp}/\partial Q_{\eta}) \right|^2 \tag{23}$$

with

$$\eta_{\lambda\eta} = \tfrac{1}{3} [\lambda]^{-1} \left[\sum_{pt} (A_{tp})^2 \Xi^2(t,\lambda)(2t+1)^{-1} + \langle f \| C^{\lambda} \| f \rangle^2 \langle f | r^{\lambda} | 4f \rangle^2 \right] \tag{24}$$

In eqn. (23) the $\alpha^{k_2 t}_{q_2 p}$ is the $(q_2 p)$ component of the $k_2 + t$ rank tensor of the electric hyperpolarizability of the ligand at a frequency of electronic transition. The vibrational factor in weak coupling approximation may be written in a well known form of the energy gap law [15]

$$F^{\nu}_{ab} = \frac{\hbar}{2M_{\nu}\omega_{\nu}} (n^0_{\nu}+1) A^{\nu}_1 \exp\left[-\gamma^{\nu}_1 \frac{\Delta E - \hbar\omega_{\nu}}{\hbar\omega_{\nu}}\right] \tag{25}$$

where A^{ν}_1 and γ^{ν}_1 are the constants defined in ref. 5.

Results and Discussion

The room temperature spectra of europium perchlorate absorptions of the hypersensitive band $^7F_0 \rightarrow {}^5D_2$ in different solutions are shown in Fig. 1. The oscillator strengths of that band are listed in Table I [7]. From eqn. (14) describing the intensity of hypersensitive bands and lanthanide complexes the oscillator strength in the case of identical ligands is proportional to the ligand polarizability

$$P_{ab} \propto [\bar{\alpha}(L)]^2 \tag{26}$$

Since for dissolved europium perchlorate compound the first coordination sphere of europium ion is formed by solvent ligands, we can correlate the variation of oscillator strengths of the hypersensitive band

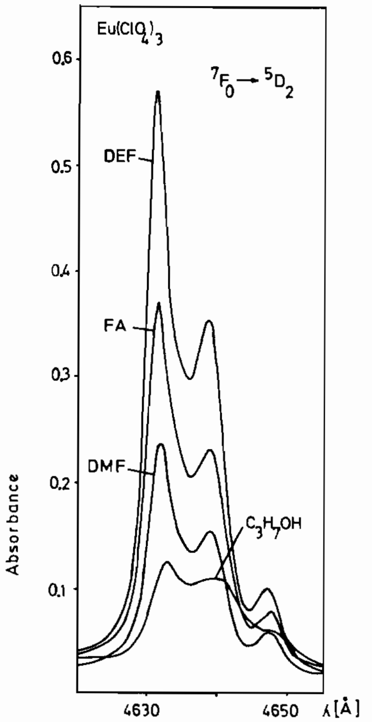

Fig. 1. Behaviour of hypersensitive bond $^7F_0 \rightarrow {}^5D_2$ for $Eu(ClO_4)_3$ in various solvents at 300 K.

$^7F_0 \rightarrow {}^5D_2$ in various solutions against the polarizabilities of solvent molecules. Some information about the polarizabilities of solvent molecules can be obtained from the mean molar refractivities of solvents by a simple relation

$$\bar{\alpha} = 0.3964\ 10^{-24} R_\infty \quad \text{(in units of cm}^{-3}\text{)}$$

where R_∞ is the mean molar refractivity in the infinite wavelength limit,

$$R_\nu = \frac{n_\nu^2 - 1}{n_\nu^2 + 2} \frac{M}{d} \qquad (27)$$

with M as molecular weight, d as density and n_ν as refractive index at the wavelength ν.

The values of mean molar refractivities are listed in Table I [7]. In Fig. 2 is shown a correlation of the measured values of square roots of oscillator strengths $P^{1/2}$ and the mean molar refractivities of the solutions.

TABLE I. Oscillator Strengths of $^7F_0 \rightarrow {}^5D_2$ Transition for $Eu(ClO_4)_3$ in Solutions [7].

Solvent	Concentration	$P \times 10^8$	Molar refractivity R
1. CH_3OH	0.2123	4.25	8.23
2. C_2H_5OH	0.2253	3.61	12.93
3. C_3H_7OH	0.2019	5.97	17.48
4. DMSO	0.2044	6.06	20.16
5. FA	0.3795	10.35	10.63
	0.2040	10.70	
6. DEF	0.4550	13.60	29.01
	0.2235	13.79	
7. MFA	0.4244	9.67	15.27
	0.1003	9.66	
8. DMF	0.3438	12.96	19.86
	0.1090	13.12	

It is seen that most of the experimental points are located alongside the straight line, confirming the approximate formula. Some discrepancy can be observed for amide solutions which in general exhibit a higher intensity of the hypersensitive band [1–3, 5, 11]. Similar relations have been reported for Nd(III), Ho(III) and Er(III) (see Fig. 3) [11]. The fluorescence spectra of europium perchlorates in different solvents are shown in Fig. 4 [1, 7]. We have noticed that in spite of the fact that the intensity of total fluorescence varies in a different manner throughout the series of alcohols and amides, the relative intensity of the hypersensitive fluorescence band $^5D_0 \rightarrow {}^7F_2$ generally increases with an increasing solvent molar refractivity in the same order as in an absorption spectrum. In Table II we have listed the values of the branching ratio of fluorescence from the $^5D_0$ level to the $^7F_2$ and $^7F_3$ terms, respectively. The transition $^5D_0 \rightarrow {}^7F_3$ is forbidden by selection rules for electric and magnetic dipole, and to a lesser extent is affected by solvent. The correlation between the square root of the fluorescence branching ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_3)$ and the mean molar refractivity of solution is given in Fig. 5 [7]. The intensity of the hypersensitive fluorescence transition $^5D_0 \rightarrow {}^7F_2$ behaves in the same way as in the absorption spectrum. Quite similar observations were originally reported by

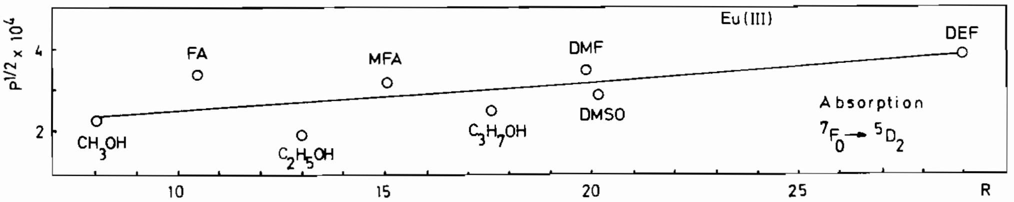

Fig. 2. The dependence of the square root strengths of hypersensitive transition $^7F_0 \rightarrow {}^5D_2$ on molar refractivity [2].

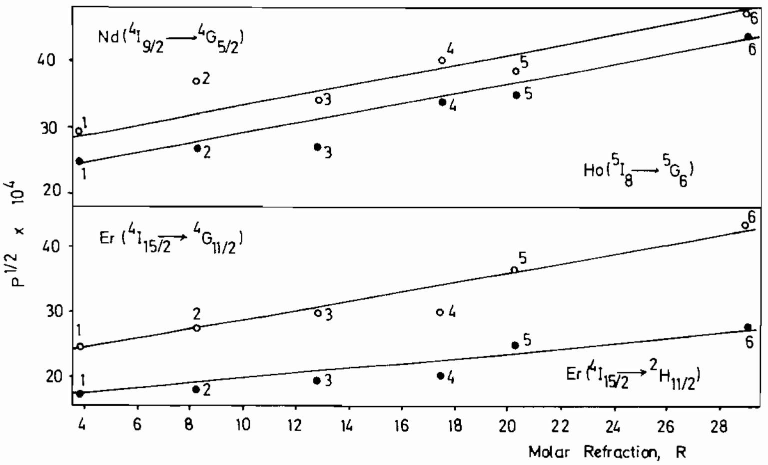

Fig. 3. The dependence of the square root strengths of hypersensitive transitions
$^4I_{9/2} \rightarrow {}^4G_{5/2}$ (Nd^{+3}) $(^4I_{15/2} \rightarrow {}^4G_{11/2})$
$(^5I_8 \rightarrow {}^5G_6)$ (Ho^{+3}) $(^4I_{15/2} \rightarrow {}^2H_{11/2})$ } Er^{+3}
on molar refractivity.

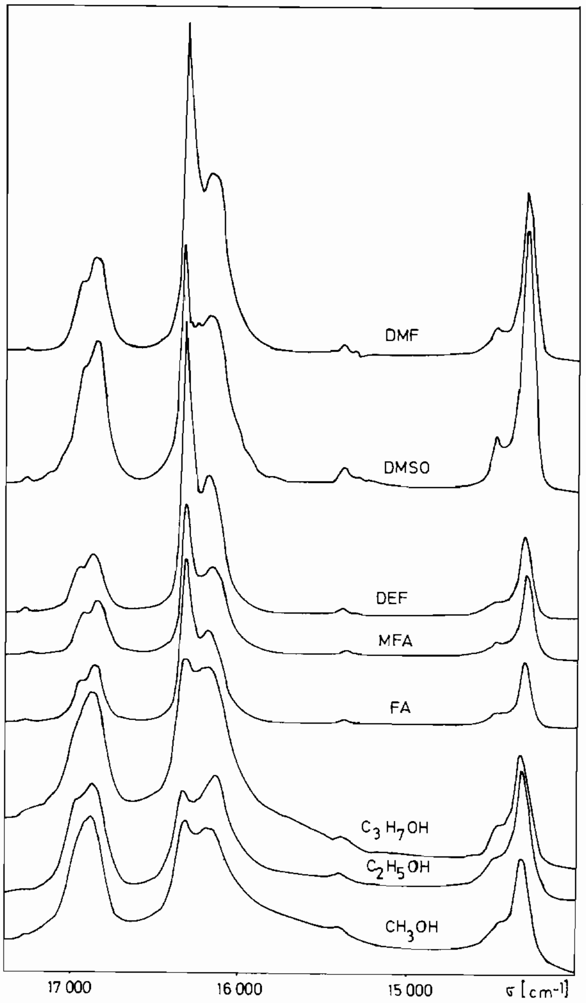

Fig. 4. Behaviour of fluorescence transition $^5D_0 \rightarrow {}^7F_J$ for Eu(ClO$_4$)$_3$ in various solvents at 300 K.

TABLE II. The Comparison of the Lifetimes of the $^5D_0$ Level of Eu(ClO$_4$)$_3$ and the Fluorescent Ratios of Integral Intensities from the $^5D_0$ Level into the $^7F_2$ and $^7F_3$ Levels of Different Solvents.

Solvent	τ (μS)	K_{NR} (s^{-1})	$\dfrac{A^I(^5D_0 \rightarrow {}^7F_2)}{A(^5D_0 \rightarrow {}^7F_3)}$
1. CH_3OH	200	5000	22.0
2. C_2H_5OH [7]	230*	4300	9.2
3. C_3H_7OH [7]	180*	5500	23.5
4. DMSO	1300	769	22.0
5. FA	580	1724	40.6
6. DEF	1100	909	59.4
7. MFA	600	1666	38.6
8. DMF	1150	869	39.9

*Decay times observed were not pure exponential curves.

Haas and Stein [9] for solvent effect on fluorescence spectra of europium compounds.

The fluorescence lifetimes of europium perchlorate, measured at room temperature, are listed in Table II. The longest lifetime was measured for DMSO solution while the shortest was for propanol solution. The results obtained indicate that the solvent-dependence of the fluorescence lifetime of Eu(III) ion is more complex in comparison with the solvent effect on the intensity of hypersensitive transitions.

The decay of the $^5D_0$ level is mainly governed by non-radiative transitions [16]. For instance, the radiative decay times which can be estimated from the Judd–Ofelt calculation are usually higher by one or two orders of magnitude than are the measured decay times. According to the theory of non-radiative

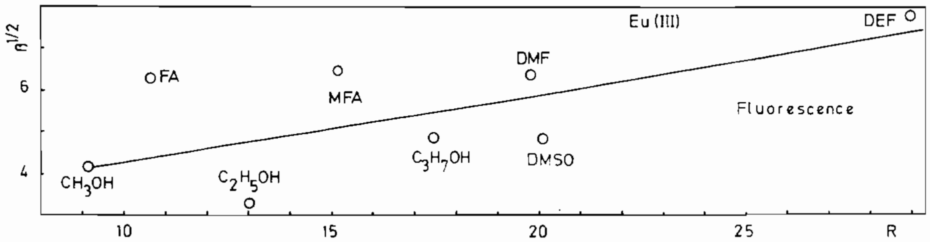

Fig. 5. The dependence of the square root of fluorescence branching ratio $\frac{I(^5D_0 \rightarrow {}^7F_2)}{I(^5D_0 \rightarrow {}^7F_3)}$ on molar refractivity.

transitions in lanthanide complexes presented briefly in the former chapter, the vibrational factor in rough approximation is controlled by energy gap dependence and maximum energy frequency of solvent. For europium ions the energy gap remains practically unchanged under the solvent effect, so that the highest energy vibrations should be taken into account in any discussion of non-radiative transitions. As known for lanthanide ions the maximum frequency modes promote radiationless transitions [16]. In fact the shortest lifetimes were found for alcohols where promoting modes are connected with the OH vibrations (~3600 cm^{-1}).

For amides the shortest lifetimes of Eu(III) ions were measured in the MFA and FA solutions where the maximum frequency modes are combined with the NH vibrations (~3450 cm^{-1}). However the lifetimes measured for these solutions are much higher than could result from the maximum frequency rule. We suppose that this follows from the localization of maximum energy modes with respect to the Eu(III) ion. It is well rationalized within the framework of theory of radiationless transitions in lanthanide complexes.

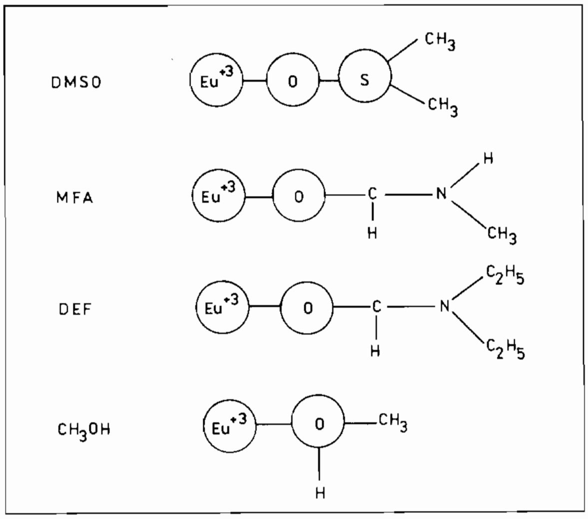

Fig. 6. Representation of the bonds in the DMSO alcohols and amides in the first solvation sphere.

In Fig. 6 is shown a schematic representation of the bonds in the first coordination sphere of the studied systems. It is important to note that in alcohols and amides the decay rates may be correlated with the magnitudes of the respective intensities of hypersensitive bands, suggesting that the polarizability mechanism operates also for non-radiative transitions. This conclusion is easily understood in view of the expression (23) for the electronic factor in the dynamic coupling mechanism, which is responsible for the process in metal complexes.

In summary, the results presented indicate that the polarizability mechanism plays an important role both in radiative and in non-radiative transitions.

We hope this work will lead to a new approach in the studies of solvent effects on the spectroscopic properties of lanthanide ions in solution.

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