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Solvent Effect on Intensities of *f–f* Transitions in Lanthanide(III) Complexes

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A general theory of the solvent effect on the intensities of *f–f* transitions of lanthanide complexes based on static and dynamic coupling between metal ion and ligands and solvent molecules is presented. New expressions are found correlating the intensity parameters τ_λ with physical characteristics of the solvent. It is shown that the solvent effect influences only in the parameter τ_2.

Key words: Lanthanide(III) complexes – Solvent effect

1. Introduction

Knowledge of the true absorption spectrum of trivalent lanthanide (Ln^{3+}) complexes in a given medium is necessary to obtain correctly the characteristics of the spectrum such as the position, intensity and shape of the bands. Also it can be helpful in studying the mechanism of intermolecular interaction.

The most useful method for the analysis of the intensities of the absorption bands of the trivalent lanthanide complexes is a theory developed by Judd [1] and Ofelt [2] in the early sixties. The general form of the equation obtained for the oscillator strength in this theory is expressed as a sum of three terms, each of which is given by an empirical parameter τ_λ multiplying the matrix element of a unit tensor operator, taken between the initial and final states.

As is well known, the *f–f* spectra of Ln^{3+} complexes show relatively weak dependence on the medium except for a certain transition obeying the selection rules $|\Delta J| \leqslant 2$, $|\Delta L| \leqslant 2$ and $\Delta S = 0$ and are for this reason called the hypersensitive transitions [3–4]. In general the dependence of τ_λ parameters on the medium is

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expressed through the refractive index n_ω under the assumption of an effective Lorentz field $E_{\text{eff}} = E(n_\omega^2 + 3)/3$ (ω is the frequency of the radiation field) in the calculation of oscillator strengths in solution. The experimental data [5–8] show that the τ_2 parameter is much more affected by the medium than are the τ_4 and τ_6 parameters.

Much experimental work has been done to investigate the solvent effect on the intensities of $f \to f$ transitions (see [5–8] and references therein). However, no theoretical work on this problem has been done.

The mechanism of the solute–solvent interaction and its effect on electronic spectra has been investigated by many authors.

The general theoretical model of the solvent effect on electric dipole transitions has been discussed particularly by Weigang [9]. His theory is based on an Onsager-reaction field in the framework of a dynamic coupling mechanism. This mechanism was recently applied to account for the intensity of hypersensitive transitions in non-centrosymmetric Ln^{3+} complexes [10] and centrosymmetric complexes (the vibronic mechanism of the electric dipole $f \to f$ transition) [11].

In this paper we propose a theory of solvent effect on the intensity of Ln^{3+} complexes. The model is based on dynamic (correlative) coupling between Coulombicly interacting non-overlapping chromophoric units.

2. Theoretical Model

The system under consideration consists of a lanthanide complex (metal ion and ligands) surrounded by solvent molecules, all randomly distributed. We take into account only pair interactions between metal ion and ligand, and metal ion and solvent molecules. The many-body interactions as well as the solvent effects on ligands are neglected. We assume also that all overlap integrals between interacting entities are equal to zero.

Within the framework of the dynamical coupling model [10] the perturbed wave-function to the first-order may be written as

$$\begin{aligned} |M_0L_0S_0) = |M_0L_0S_0\rangle &+ \sum_{k,l} (-E_k - E_l)^{-1} |M_kL_l\rangle\langle M_kL_l|V_{ML}|M_0L_0\rangle \\ &+ \sum_{k,m} (-E_k - E_m)^{-1} |M_kS_m\rangle\langle M_kS_m|V_{MS}|M_0S_0\rangle \end{aligned} \tag{1}$$

for the metal ground state, and

$$\begin{aligned} |M_aL_0S_0) = |M_aL_0S_0\rangle &+ \sum_{k,l} (E_a - E_k - E_l)^{-1} |M_kL_l\rangle\langle M_kL_l|V_{ML}|M_0L_0\rangle \\ &+ \sum_{k,m} (E_a - E_k - E_m)^{-1} |M_kS_m\rangle\langle M_kS_m|V_{MS}|M_aS_0\rangle \end{aligned} \tag{2}$$

for the metal excited state.

Here

$$|M_k L_l S_m\rangle = |M_k\rangle |L_{l0}\rangle \cdots |L_{ul}\rangle \cdots |S_{l0}\rangle \cdots |S_{vm}\rangle \tag{3}$$

is the product of the zeroth-order wavefunctions representing the electronic states of the metal ion (M), ligands (L) and solvent molecules (S). Throughout this paper the index ul will refer to the lth excited state of the uth ligand and vm to the mth excited state of the vth solvent molecule. The ground states we will denote by the subscript zero. Now we assume that all ligands and also the solvent molecules are identical.

The V_{ML} and V_{MS} denote the electrostatic interaction potentials between metal ion and ligands and solvent molecules, respectively.

$$V_{ML} = \sum_{u} \sum_{l_1, l_2} \sum_{q_1, q_2} T^{(k_1+k_2)}_{-q_1-2}(L_u) D^{k_1}_{q_1}(M) D^{k_2}_{q_2}(L_u) \tag{4}$$

$$V_{MS} = \sum_{v} \sum_{l_1, l_3} \sum_{q_1, q_3} T^{(k_1+k_3)}_{-q_1-q_3}(S_v) D^{k_1}_{q_1}(M) D^{k_3}_{q_3}(S_v) \tag{5}$$

where the geometrical dependence of the interaction is given by the tensor

$$T^{(k_1+k_2)}_{-q_1-q_2}(L_u) = (-1)^{k_1+q_1+q_2} R_u^{-k_1+q_1+q_2} [B^{q_1,q_2}_{k_1,k_2}]^{1/2} C^{(k_1+k_2)}_{-q_1-q_2}(\Theta_u, \Phi_u) \tag{6}$$

with

$$[B^{q_1,q_2}_{k_1,k_2}] = \frac{(k_1 + k_2 + q_1 + q_2)!\,(k_1 + k_2 - q_1 - q_2)!}{(k_1 + q_1)!\,(k_1 - q_1)!\,(k_2 + q_2)!\,(k_2 - q_2)!} \tag{7}$$

The operator

$$D^{(k_1)}_{q_1}(M) = -\sum_i e r_i^{k_1} C^{(k_1)}_{q_1}(\Theta_i, \phi_i) \tag{8}$$

is restricted to the chromophoric electrons i on the metal ion labelled by i with coordinates (r_i, Θ_i, ϕ_i). A quite similar formula can be written for $D^{(k_2)}_{q_2}(L_u)$ and for $D^{(k_3)}_{q_3}(S_v)$ with the indexes j and k enumerating the electrons of ligand and solvent molecule, respectively. The position of the ligand L_u or solvent molecule S_v with respect to the metal ion is determined by the sets of coordinates (R_u, Θ_u, Φ_u) and $(R_v, \Theta_v. \Phi_v)$.

The operator $C^{(k_1)}_{q_1}(\Theta, \phi)$ is defined as

$$C^{(k_1)}_{q_1} = [4\pi/(2k_1 + 1)]^{1/2} Y_{k_1,q_1}(\Theta, \phi) \tag{9}$$

where $Y_{k_1,q_1}(\Theta, \phi)$ is a spherical harmonic of rank k_1. The electric dipole operator is chosen to be

$$\begin{aligned} D^1_q &= D^1_q(M) + D^1_q(L) + D^1_q(S) \\ &= -e\left[\sum_i r_i C^{(1)}_i(\Theta_i, \phi_i) + \sum_j r_j C^{(1)}_j(\Theta_j, \phi_j) + \sum_k r_k C^{(1)}_k(\Theta_k, \phi_k)\right]. \end{aligned} \tag{10}$$

Using (1) and (2) the dipole moment for the $|M_0L_0S_0) \rightarrow |M_aL_0S_0)$ transition can be expressed in the form

$$
\begin{aligned}
&(M_aL_0S_0|D_q^1|M_0L_0S_0) \\
&\quad = \langle M_aL_0S_0|D_q^1|M_0L_0S_0\rangle \\
&\qquad + \sum_{k,l,m} [\langle M_0L_0S_0|D_q^1|M_kL_lS_m\rangle\langle M_kL_lS_m|V_{ML} + V_{ML}|M_aL_0S_0\rangle \\
&\qquad\qquad \cdot(E_a - E_k - E_1 - E_m)^{-1} + \langle M_0L_0S_0|V_{ML} + V_{MS}|M_kL_lS_m\rangle \\
&\qquad\qquad \cdot\langle M_kL_lS_m|D_q^1|M_aL_0S_0\rangle(-E_k - E_l - E_m)^{-1}].
\end{aligned}
\tag{11}
$$

One can easily note that the first term in (11)

$$\langle M_aL_0S_0|D_q^1|M_0L_0S_0\rangle = \langle M_a|D_q^1(M)|M_0\rangle = 0$$

because the transition between the zeroth-order metal states is forbidden so that only next terms in Eq. (11) can give a non-vanishing zero-order contribution to the electric dipole transition moment in the system

$$
\begin{aligned}
&(M_0L_0S_0|D_q|M_aL_0S_0) \\
&\quad = \sum_{k\neq qa} [(E_a - E_k)^{-1}\langle M_0|D_q^1(M)|M_k\rangle \\
&\qquad\qquad \cdot(\langle M_kL_0|V_{ML}|M_aL_0\rangle + \langle M_kS_0|V_{MS}|M_aS_0\rangle) + (-E_k)^{-1} \\
&\qquad\qquad \cdot(\langle M_0L_0|V_{ML}|M_kL_0\rangle + \langle M_0S_0|V_{MS}|M_kS_0\rangle)\cdot\langle M_k|D_q^1(M)|M_a\rangle] \\
&\qquad + \sum_{l\neq a} [(E_a - E_1)^{-1}\langle L_0|D_q^1(L)|L_1\rangle\langle M_0L_1|V_{ML}|M_aL_0\rangle + (-E_a - E_1)^{-1} \\
&\qquad\qquad \cdot\langle M_aL_0|V_{ML}|M_aL_1\rangle\langle L_1|D_q^1(L)|L_0\rangle] \\
&\qquad + \sum_{m\neq a} [(E_a - E_m)^{-1}\langle S_0|D_q^1(S)|S_m\rangle\langle M_0S_m|V_{MS}|M_aS_0\rangle + (-E_a - E_m)^{-1} \\
&\qquad\qquad \cdot\langle M_0S_0|V_{MS}|M_aS_m\rangle\langle S_m|D_q^1(S)|S_0\rangle].
\end{aligned}
\tag{12}
$$

Eq. (12) is the basis of a general theory of the electronic $f \rightarrow f$ transition of Ln^{3+} ions. The first sum describes the "static mechanism" of the electronic transition in the metal ion linked with the static charge distribution on the ligands and solvent molecules. The next terms represent the "dynamic coupling mechanism" being the correlation between the transient electric moment induced in ligand and solvent molecules and the electronic transitions in the metal ion.

3. Method of Calculation

Judd [1] and Ofelt [2] assumed that the metal states $|M_k\rangle$ must arise from a configuration having opposite parity to force an electric dipole transition. Within the framework of a crystal field type theory it is usual to expand the potential $V = \langle L_0|V_{ML}|L_0\rangle$ in Eq. (12) as a series

$$V = \sum_{t,p} A_{tp}D_p^{(t)} \tag{13}$$

where

$$D_p^{(t)} = \sum_i r_i^t C_p^{(t)}(\nu_i, \phi_i) \tag{14}$$

Utilizing Eqs. (4), (5) and (13) we can write (12) as

$$\begin{aligned}
D_{0a} = \sum_{t,p} \sum_{k \neq 0,a} & A_{tp}[(E_a - E_k)^{-1}\langle M_0|D_q(M)|M_k\rangle\langle M_k|D_p^{(t)}|M_a\rangle \\
& \qquad + (-E_k)^{-1}\langle M_0|D_p^{(t)}|M_k\rangle\langle M_k|D_q^1(M)|M_a\rangle] \qquad \text{(15a)} \\
& + \sum_v \sum_{k_1q_1} \sum_{k_3q_3} T_{-q_1-q_3}^{(k_1+k_3)}(S_v) \\
& \cdot[(E_a - E_k)^{-1}\langle M_0|D_q(M)|M_k\rangle\langle M_k|D_{q_1}^{(k_1)}|M_a\rangle \\
& \quad + (E_a - E_k)^{-1}\langle M_0|D_{q_1}^{(k_1)}|M_k\rangle\langle M_k|D_q^1(M)|M_a\rangle]\langle S_0|D_{q_1}^{(k_3)}|S_0\rangle \qquad \text{(15b)} \\
& + \sum_{k_1q_1} \sum_{k_2q_2} \sum_{l \neq a} [(E_a - E_1)^{-1}\langle L_0|D_q^1(L)|L_l\rangle\langle L_l|D_{q_2}^{(k_2)}|'L_0\rangle \\
& \qquad + (-E_a - E_l)^{-1}\langle L_0|D_{q_2}^{(k_2)}|L_l\rangle\langle L_l|D_q^1|L_0\rangle]\langle M_0|D_{q_1}^{(k_1)}|M_a\rangle \qquad \text{(15c)} \\
& + \sum_{k_1q_1} \sum_{k_3q_3} \sum_{m \neq a} [(E_a - E_m)^{-1}\langle S_0|D_q^1(S)|S_m\rangle\langle S_m|D_{q_3}^{(k_3)}|S_0\rangle \\
& \qquad + (-E_a - E_m)^{-1}\langle S_0|D_{q_3}^{(k_3)}|S_m\rangle\langle S_m|D_q^1(M)|S_0\rangle] \\
& \cdot\langle M_0|D_{q_1}^{(k_1)}|M_a\rangle. \qquad \text{(15d)}
\end{aligned}$$

The first part of the above Eq. (15a) is the basis of the Judd and Ofelt theory. In order to exploit this expression we introduce the average energy denominator $\Delta E \approx E_k \gg E_a$ [1, 2].

Taking the electronic states of the metal ion in the free ion approximation as a linear combination of Russell-Saunders coupled states $|f^N(M_a)JM\rangle$ and applying the closure theorem with respect to $|f^{N-1}d(M_k)J''M''\rangle$ states Eq. (15a) becomes

$$\begin{aligned}
D_{0a}^1(M) = e\sum_{p,t} \sum_{\lambda=2,4,6} & (-1)^{p+q} A_{tp}[\lambda]\Xi(t, \lambda) \\
& \cdot\begin{pmatrix} 1 & \lambda & t \\ q & -p-q & p \end{pmatrix}\begin{pmatrix} J & \lambda & J' \\ -M & -g-p & M' \end{pmatrix} \\
& \cdot\langle f^N(M_0)JM\|U_{-p-q}^{(\lambda)}\|f^N(M_a)J'M'\rangle
\end{aligned} \tag{16}$$

where

$$\begin{aligned}
\Xi(t, p) = 2\sum (-1)^{f+1}[f][l] & \begin{pmatrix} 1 & \lambda & t \\ f & l & f \end{pmatrix}\langle f\|C^{(1)}\|l\rangle\langle lC^{(t)}\|f\rangle \\
& \cdot\langle 4f^N|r|4f^{N-1}d\rangle\langle 4f^{N-1}d|r^t|4f^N\rangle(\Delta E)^{-1}.
\end{aligned} \tag{17}$$

The summation is made over all states $|4f^{N-1}d_kM_kJ''M''\rangle$. (:::) and {:::} means 3*j*- and 6*j*-symbols, respectively. Here the abbreviation $[\lambda] = 2\lambda + 1$ has been introduced.

$\langle 4f^N|r^t|4f^{N-1}d\rangle$ is the radial integral of the single-electron wave functions.

4. Electric Dipole Transitions

To calculate the electric dipole transition of Ln^{3+} complexes in a solvent we can note that only the first two parts of Eq. (15) are responsible for this process.

The solvent contribution to the oscillator strength is included through Eq. (15b). We assume here that the Coulombic interaction between metal ion and solvent V_{MS} is dipole–dipole in nature and put $k_1 = k_2 = 1$. The oscillator strength of an electric dipole transition from $|f^N(M_0)JM\rangle$ to $|f^N(M_a)J'M'\rangle$ is given by

$$P_{0a} = \chi\left(\frac{8^2 mc\sigma}{he^2}\right)|\langle M_0|D_q|M_a\rangle|^2 \tag{18}$$

where m is the electron mass, h is Planck's constant, c is the velocity of light, σ is the energy of the transition in cm^{-1} and χ is the Lorentz field correction for the refractivity of the medium. Taking into account (15a, b), (16), and condition $k_1 = k_2 = 1$ we express (18) as

$$P_{0a} = \left[\frac{8\pi^2 mc\sigma}{h}\right]\Bigg[\sum_{p,t}\sum_{\lambda=2,4,6}(-1)^{p+q}\overline{A}_{tp}\Xi(t,\lambda)\begin{pmatrix}1 & \lambda & t\\ q & -p-q & p\end{pmatrix} \cdot\langle f^N(M_0)JM|U^{(\lambda)}_{-p-q}|f^N(M_a)J'M'\rangle\Bigg]^2 \tag{19}$$

where now a new effective parameter $\overline{A}_{tp}$ is:

$$\overline{A}_{tp} = A_{tp} + \delta_{t,1}\sum_{q_3 v} T^{1+t}_{-p-q_3}(v)\mu_{q_3}(S_v). \tag{20}$$

Here the delta function indicates that the medium effect is limited only to the values of A_{tp} with $t = 1$.

$$\mu_{q_3}(S_v) = \langle S_0|D^1_{q_3}|S_0\rangle$$

denotes the q_3th component of the permanent dipole moment of S_vth solvent molecule. It is convenient in the analysis of $f \to f$ transitions to write the oscillator strength in the form proposed by Judd [1]

$$P_{0a} = \sum_{\lambda=2,4,6}\bar{\tau}_\lambda\sigma|\langle f^N(M_0)J\|U^{(\lambda)}\|f^N(M_a)J'\rangle|^2 \tag{21}$$

where

$$\bar{\tau}_\lambda = \chi\left[\frac{8\pi^2 mc}{3h}\right][\lambda]\sum_{q,t}|\overline{A}_{tp}|^2\Xi^2(t,\lambda)(2t+1)^{-1} \tag{22}$$

Eqs. (21, 22) provide explicit expressions to calculate the solvent effect on the intensity of $f \to f$ transitions. The effect manifests itself mainly through the effective parameter $\overline{A}_{tp}$. From the 3-j triangle conditions for $\begin{pmatrix}1 & \lambda & t\\ q & -p-q & q\end{pmatrix}$ with $t = 1$ results that $\lambda = 2$. Then the medium effect is linked only with one parameter $\bar{\tau}_2$.

The dependence τ_2 on the medium expressed by $\overline{A}_{1p}$ (Eq. (25)) may be calculated under the assumption that the orientations and positions of all molecules involved are known. In principle this could be done rigorously only for molecular systems with fixed structure. In practice the problem is very complex and therefore we use an approximate empirical method relating the average value of $\sum_v T^2_{-q-q_3}(v)\mu(S_v)$ to macroscopic parameters characterizing the medium.

Following McRae [12] we define the electrostatic field due to the permanent dipole moment of the solvent molecules acting on solute molecules as

$$E^u_s = -\left\langle \sum_v T^2_{-q-q_3}(v)\mu(S_v) \right\rangle \tag{23}$$

where $\langle \cdots \rangle$ indicates the Boltzmann averaging over all orientations of molecules, which can be identified with the Onsager reaction field R [13] assuming that the averaging is equivalent to replacing the solvent molecules by a homogeneous dielectric. For spherical molecules $|E^u_s|^2 = 3|R|^2$ and for rod-like molecules $|E^u_s| = R^2$ [12].

For isotropic solute molecule [12]

$$R = \frac{2\mu_u}{a^3}\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right) \tag{24}$$

where D is the static dielectric constant and n the solvent refractive index extrapolated to zero frequency, μ_u is the dipole moment for solute molecule and a denotes the radius of the Onsager cavity.

Thus the $\bar{\tau}_2$ parameter characterizing the solvent effect on the intensity of $f \to f$ transitions can be written as

$$\bar{\tau}_2 = \left(\frac{8\tau^2 mc\sigma}{h}\right)\left|\sum_{p,t}\left[A_{tp} + \delta_{t,l}\frac{2\mu_u}{a^3}\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right)\right]\right|^2 \Xi^2(t,2)\cdot(2t+1)^{-1}. \tag{25}$$

5. Hypersensitive Transitions

The $f \to f$ transitions with the selection rule $|\Delta J| \leqslant 2$ show a relatively stronger sensitivity to the medium appearing in the intensity changes and frequency shifts. It was shown by Peacock *et al.* [10] that the dynamic coupling mechanism represented by Eqs. (15c, d) is responsible for the oscillator strengths of hypersensitive transitions. Within the framework of this theory Eq. (15d) describes the solvent contribution for hypersensitive transitions.

The transition moment

$$\begin{aligned}\langle M_0|D^{(k_1)}_{q_1}|M_a\rangle &= \langle f^N(M_0)JM|D^{(k_1)}_{q_1}|f^N(M_a)J'M'\rangle \\ &= \langle f|C^{(k_1)}|f\rangle\langle 4f|r^{k_1}|4f\rangle\langle f^N(M_0)JM|U^{(k_1)}_{q_1}|f^N(M_a)J'M'\rangle\end{aligned} \tag{26}$$

Here $\langle f|C^{(k_1)}|f\rangle = 7\begin{pmatrix}3 & k_1 & 3\\ 0 & 0 & 0\end{pmatrix}$ then $1 \leqslant k_1 \leqslant 6$ and next

$$\begin{aligned}&\langle f^N(M_0)JM|U^{(k_1)}_{q_1}|f^N(M_a)J'M'\rangle \\ &\quad = \begin{pmatrix}J & k_1 & J'\\ -M & -q_1 & M'\end{pmatrix}\langle f^N(M_0)J\|U^{(k_1)}\|f^N(M_a)J'\rangle.\end{aligned} \tag{27}$$

The 3-j triangle condition implies $k_1 \leqslant |J' - J|$. Since the dipole $f \to f$ transitions with $k_1 = 1$ are forbidden then the lowest order non-vanishing term ($k_1 = 2$) is an electric quadrupole transition corresponding to the hypersensitive transitions restricted to $|\Delta J| \leqslant 2$.

One can note that the magnitudes in square brackets appearing in (15c, d)

$$\alpha_{qq_2}(L) = \sum_l [(E_a - E_l)^{-1}\langle L_0|D_q^1|L_l\rangle\langle L_l|D_{q_2}^1|L_0\rangle \\ + (-E_a - E_l)^{-1}\langle L_0|D_{q_2}^1|L_1\rangle\langle L_1|D_q^1|L_0\rangle], \tag{28}$$

$$\alpha_{qq_3}(S) = \sum_m [(E_a - E_m)^{-1}\langle S_0|D_q^1|S_m\rangle\langle S_m|D_{q_3}^1|S_0\rangle \\ + (-E_a - E_m)^{-1}\langle S_0|D_{q_3}^1|S_m\rangle\langle S_m|D_q^1|S_0\rangle] \tag{29}$$

define the qq_2th and qq_3th tensor components of the electric dipole polarizability at the frequency $\nu_{0a} = (E_a - E_0)/h$ for ligand and solvent molecules respectively.

Further, for simplicity of calculation we assume that the ligand and solvent molecules are isotropic entities so that the sums over the components of the polarizability tensors will be reduced to a single term replaced by the mean values of polarizabilities for ligand $\bar{\alpha}(L)$ and solvent molecules $\bar{\alpha}(S)$, respectively.

Utilizing (26, 27) and definitions (28) and (29) we can express the oscillator strength for hypersensitive transitions in the form

$$P_{0a} = \chi\left(\frac{4mc\sigma}{3h}\right)\bar{\tau}_2|\langle f^N(M_0)J\|U^{(2)}\|f^N(M_a)J'\rangle|^2(2J + 1)^{-1} \tag{30}$$

where

$$\bar{\tau}_2 = |\langle 4f|r^2|4f\rangle|^2|\langle f\|C^{(2)}\|f\rangle|^2\left[\sum_L T^{(3)}_{-q-q_2}(L)\bar{\alpha}(L) + \sum_v T^{(3)}_{-q-q_3}(S_v)\bar{\alpha}(S_v)\right]^2. \tag{31}$$

The dependence of hypersensitive transitions on the medium is expressed by a simple formula through the parameter $\bar{\tau}_2$. That parameter differs from the one calculated [10] for a free lanthanide complex by the term

$$\sum_{q,q_3} T^{(3)}_{-q-q_3}(S_v)\alpha(S_v).$$

This term may be approximated as was done in the former section by the use of the reaction field model [9]

$$\sum_{q,q_3}\sum_v T^{(3)}_{-q-q_3}(S_v)\bar{\alpha}(S_v) = \frac{2\mu_u}{a^3}\left(\frac{n^2 - 1}{n^2 + 2}\right). \tag{32}$$

The mean molar refractivity at the frequency ω of the radiation field is $R_\omega = (n_\omega^2 - 1/n_\omega^2 + 2)(M/d)$, where M = molar weight, d density and n_ω, the refractivity index at the frequency ω. Therefore the root square of $\bar{\tau}_2$ (the parameter for hypersensitive transitions) should be proportional to the mean molar refractivity.

6. Conclusions

In this paper we presented the theory of solvent effects on intensities of $f \rightarrow f$ transitions in lanthanide complexes. The general formula for intensity parameters $\bar{\tau}_\lambda$ including solvent effects were developed for the case of dipole and hypersensitive transitions under the assumption of dipole–dipole solute–solvent interactions. It was shown that the solvent effect is included only in one parameter $\bar{\tau}_2$. However, a mechanism of solvent effects on the $\bar{\tau}_2$ parameter is substantially different in the two cases. For dipole transitions it depends on the permanent dipole moment of the solvent while for hypersensitive transitions it depends on the polarizabilities of the solvent molecules. In practice it may be difficult to use Eqs. (22) and (31) for absolute calculation of the τ_2 parameter for an isolated complex owing to the tensor $T^{(3)}_{-q-q_3}(S_v)$ representing the geometrical dependence of the solute–solvent interaction. Nevertheless, some quantitative features can be obtained applying the approximated expressions within the framework reaction field method.

The present treatment is capable of generalization (the vibronic contribution to the electric dipole oscillator, higher order solute–solvent interactions) and, hopefully may provide a basis for further experimental and theoretical investigations.

In conclusion we should like to point out that the intensity analysis of $f \rightarrow f$ transitions in lanthanide complexes, through the possibility of a precise determination of the $\bar{\tau}_\lambda$ parameter, may be a helpful method in the investigation of intermolecular interactions in liquids.

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