INTENSITIES OF 4f – 4f TRANSITIONS IN GLASS MATERIALS

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1. Introduction

Glass materials containing trivalent rare earth ions have been widely studied due to their potential applications as optical devices (lasers and fibers for optical amplifiers, among others)[1]. Moreover, these materials have a great advantage over crystalline systems since they can be in general easily prepared with high optical quality and in a large variety of chemical compositions.

The optical properties of these materials are directly related to the 4f–4f transitions in a $4f^N$ electronic configuration. In our days, the theoretical background for the rationalization of these intraconfigurational transitions, both radiative and non-radiative, is well established [2-12]. The standard Judd-Ofelt theory [2,3] has been used to evaluate absorption and emission cross-sections
in a great majority of works on these rare earth doped glasses, and the so-called intensity parameters $\Omega_\lambda$ ($\lambda = 2, 4$ and $6$) have been used to afford information on covalence, quality and mechanical properties of the medium [1]. Nevertheless, a certain number of problems still exist related to the application of the theory and to the interpretation of results obtained from it, particularly in the case of glasses, as one may note from the literature. Among these problems we may emphasize the systematic neglect of the dynamic coupling mechanism contributing to the $4f-4f$ intensities [5-9, 11].

We wish here to outline the main aspects of the above-mentioned theoretical background and to discuss briefly some rather problematic points concerning the use of the theory and the interpretation of results.

2. Some characteristics of the rare earth ions

2.1. The Hamiltonian for the free ion

The Hamiltonian, $H_{FI}$, for the rare earth free ion is composed by one part due to the central field, $H_0$, and several other interactions which are in general treated as perturbations. Among these interactions the interelectronic repulsion, $H_c$, and the spin-orbit interaction, $H_{so}$, are the most relevant.

$$H_{FI} = H_0 + H_c + H_{so} \quad (1)$$

The magnitudes of these interactions follow the order $H_0 > H_c > H_{so}$.

In the diagonalization procedure of the Hamiltonian $H_{FI}$ the spin-spin, spin-other-orbit and orbit-orbit interactions are in general of much less importance. Thus, in a first step, the eigenfunctions of $H_{FI}$ may be constructed from the eigenfunctions of the angular momentum operators $L^2$, $S^2$, $J^2$ and $J_Z$ where

- $L$ = total orbital angular momentum
- $S$ = total spin angular momentum
- $J$ = total angular momentum, $J = L + S$
- $J_Z = z$ component of $J$
with $L = \sum i \ell_i$ and $S = \sum i s_i$, $\ell$ and $s$ being mono-electronic orbital and spin angular momenta, respectively. The quantum number $J$ must satisfy the condition $|L - S| \leq J \leq L + S$. For rare earth ions an adequate scheme to represent a basis of eigenfunctions is the well-known L - S coupling scheme $|(4f^N)\varphi SLM J\rangle$. This notation implies that these eigenstates are pure $4f^N$ states, or, in other words, no configuration interaction (CI) via $H_{FI}$ is taken into account. CI effects, for each given case, have been considered without increasing the dimension of the matrix $[H_{FI}]$ through the use of effective operators acting within the $4f^N$ configuration.

In the construction of the eigenstates $|(4f^N)\varphi SLM J\rangle$ one frequently finds that they are not unambiguously defined by the quantum numbers $S$, $L$, $J$ and $M_J$. This problem can be solved by the use of group theory. Racah [13] has demonstrated that the irreducible representations of certain sub-groups of the GL$(4 \ell +2)$ continuous group may be used as quantum numbers to classify these eigenstates. This is due to the fact that they form bases for these irreducible representations. Thus, in the above scheme $\alpha$ represents the set of additional quantum numbers necessary to specify the eigenstate. A common procedure in the literature has been to diagonalize the Hamiltonian $H_{FI}$ on a basis formed by the above eigenstates. The usual form of $H_{FI}$ is [14]

$$H_{FI} = E_b (4f^N) + \sum_{k=0,1,2,3} E^k e_k + \zeta_{4f} \sum_i \ell_i \cdot \vec{s} + \text{CI contributions} \quad (2)$$

where $E_b$ is the energy of the baricenter of the $4f^N$ configuration (eigenvalue of the central field Hamiltonian). The second and third terms in the right-hand-side of this expression correspond to the interelectronic repulsion and spin-orbit interaction, respectively. The last term contains configuration interaction effects. Matrix elements of the components in eq.(2) are evaluated by irreducible tensor operator techniques [14-16]. The radial quantities in eq.(2), $E_k$ and $\zeta_{4f}$, the Racah and spin-orbit parameters, respectively, may in principle be calculated from ab initio methods (the $E^0$ parameter can be absorbed by $E_b$). However, they are in general treated as adjustable parameters for which the input data are the experimentally observed energies of the baricenters of the $J$ manifolds. The great advantage of this latter procedure is that, after diagonalization, one gets usually much more reliable free ion wavefunctions, which is essential to the evaluation of properties of rare earth ion doped materials.
2.2. The eigenfunctions in the intermediate coupling

Taking into account the fact that the interelectronic repulsion is not diagonal in the quantum number $\alpha$ and that the spin-orbit interaction is not diagonal in the quantum numbers $\varphi$, $S$ and $L$, these latter are no longer good quantum numbers. As a consequence, after diagonalization of $H_{FI}$ the eigenstates will be given by linear combinations of the states $\ket{(4f^N)\varphi SLJM_J}$, that is

$$\ket{(4f^N)\psi JM_J} = \sum_{\varphi SL} C(\varphi SL) \ket{(4f^N)\varphi SLJM_J}$$

(3)

with the condition

$$\sum_{\varphi SL} |C(\varphi SL)|^2 = 1$$

(4)

Eq. (3) expresses the so-called intermediate coupling scheme. The eigenstates given in this scheme, as mentioned before, are essential to describe the behavior of rare earth ions. A good example is the case of transitions between multiplets of different multiplicities, which otherwise can not be described. A typical case is illustrated by the transitions between the $^5D_J$ and $^7F_J$ multiplets of the Eu$^{3+}$ ion. Labeling a multiplet by the usual notation $^{2S+1}L_J$ is a mere indication of the dominant component in the summation in eq.(3). An interesting and useful aspect is that, since a chemical environment rather weakly affects the 4f orbitals, for each rare earth ion the eigenstates in the intermediate coupling scheme are essentially the same for different environments.

3. The ligand field

3.1. The usual form of the ligand field Hamiltonian

Even though weak, the interaction between 4f electrons and the chemical environment is responsible for the most interesting spectroscopic features of rare earth ions. The non-spherical even parity part of this interaction, responsible for the Stark splitting of 4f levels, is commonly written as
\[ H_{LF} = \sum_{k,q,i} B^k_q C^{(k)}_q (i) \]  

(5)

where the \( B^k_q \)'s (\( k = 2, 4 \) and \( 6 \)) are the so-called ligand field parameters of even rank and \( C^{(k)} \) is a Racah tensor operator of rank \( k \) [14-16]. The values of \( k \) are restricted by parity and triangularity rules for \( f \) orbitals [14]. The allowed values of \( q \) depend on the symmetry of the ligand field around the rare earth ion, and in this expression the index \( i \) run over the \( 4f \) electrons.

The Hamiltonian \( H_{LF} \) as given by eq.(5) is a one particle operator. A relevant point here is that the form of eq.(5) has a more general character than it might be supposed, in the sense that all one particle ligand field models lead to this form of \( H_{LF} \). Despite the fact that the \( B^k_q \)'s, for a given point symmetry, can be calculated from theoretical models, it has been a common practice to treat them also as adjustable parameters called phenomenological or experimental \( B^k_q \)'s. As for the case of the free ion radial parameters in eq.(2), the input data are the observed energies of the \( 4f \) levels under the action of the ligand field. The total Hamiltonian to be diagonalized is now

\[ H = H_{FI} + H_{LF} \]  

(6)

The ligand field interaction is also of fundamental importance to the case of \( 4f-4f \) transition intensities. These transitions are in principle electric dipole forbidden by Laporte’s rule. However, provided the site occupied by the rare earth ion does not present a center of inversion Laporte’s rule is relaxed due to odd parity terms in the ligand field Hamiltonian. The more general form of \( H_{LF} \) is actually

\[ H_{LF} = H_{LF}(\text{even}) + H_{LF}(\text{odd}) \]  

(7)

It is important to note that if the diagonalization of the total Hamiltonian \( H \) in eq.(6) is restricted to a basis formed by the states \( \left| (4f^N)\varphi_{\text{SLJM}} \right> \), due to parity selection rules the component \( H_{LF}(\text{odd}) \) will have no effect on the final results. This odd component is in general expressed as

\[ H_{LF}(\text{odd}) = \sum_{\ell,p,i} \gamma^\ell_p r^\ell_i \varphi_p (i) \]  

(8)
where \( r_i \) is the radial coordinate of the \( i \)-th electron and the \( \gamma_p \)'s \((t = 1, 3, 5 \text{ and } 7)\) are the so-called odd rank ligand field parameters. The values of \( t \) are restricted by parity and trian-
gularity rules involving \( f \), \( d \) and \( g \) orbitals \([2,3]\). Now the index \( i \), in principle, run over all electrons of the rare earth ion. As for the values of \( q \) in eq. (5), the allowed values of \( p \) depend on the symmetry around the rare earth ion. In the case of intensities the role of \( H_{LF} \text{(odd)} \) is to connect (mix) states belonging to electronic configurations of opposite parity. It follows that transitions between 4f levels become partially electric dipole allowed.

3.2. The ligand field and symmetry

As mentioned above, the values of \( q \) and \( p \) in eqs. (5) and (8), respectively, are restricted by the symmetry of the site occupied by the rare earth ion. Thus, for example, in a \( C_{4V} \) symmetry the allowed values are: \( k = 2, q = 0 ; k = 4, q = 0, \pm 4 ; k = 6, q = 0, \pm 4 ; t = 1, p = 0 ; t = 3, p = 0 ; t = 5, p = 0, \pm 4 ; t = 7, p = 0, \pm 4 \). This is a consequence of the fact that the ligand field parameters are actually a summation over the individual contributions from the surrounding atoms. Each individual contribution behaves as the spherical harmonics and the summation vanishes in a given symmetry for certain values of \( q \) and \( p \). A detailed work on this subject may be found in refs. [17] and [18].

One of the consequences of the action of \( H_{LF} \text{(even)} \) is that \( J \) is no longer a good quantum number. This produces the so-called \( J \)-mixing effect (a rather small effect due to the weak interaction between the 4f orbitals and the chemical environment), and as a result of the diagonalization of the total Hamiltonian \( H \) in eq. (6) the final eigenstates have the general form

\[
\left( 4f^N \right)^\Gamma = \sum_{\alpha,S,L,J,M,J_\alpha} A(\alpha,S,L,J,M,J_\alpha) \left| 4f^N\alpha SLJM_\alpha \right> \tag{9}
\]

with the condition

\[
\sum_{\varphi,S,L,J,M_\alpha} |A(\varphi,S,L,J,M_\alpha;\Gamma)|^2 = 1 \tag{10}
\]
Each eigenstate given by eq. (9) is now labeled by an irreducible representation, $\Gamma$, of the symmetry point group.

In the case of glasses, since there is a variety of different sites that can be occupied by the rare earth ion, we cannot talk about a well-defined set of ligand field parameters. The Stark splitting is in general not well determined in this case, which makes it difficult to define even an average set of ligand field parameters.

In figure 1 a schematic representation of the intraatomic and ligand field interactions discussed above is presented.

![Figure 1. Schematic representation and order of magnitude of the effects of the intra-atomic and ligand field interactions acting on a 4f$^N$ configuration.](image)

4. 4f - 4f intensities

4.1. Mechanisms of 4f - 4f intensities
The characteristic absorption and emission spectra of rare earth compounds in the visible, near ultra-violet and near infra-red is attributed to transitions between 4f levels due to the fact that they present sharp lines, mainly at low temperature, with oscillator strengths typically of the order of $10^{-6}$. These transitions are to first order electric dipole forbidden, but are allowed by the electric quadrupole, vibronic, magnetic dipole and forced electric dipole mechanisms. It has been noticed, since more than fifty years ago, that among these mechanisms only the magnetic dipole and forced electric dipole ones could account for the observed intensities [19]. The magnetic dipole character of the $^5D_0 \rightarrow ^7F_1$ transition of the Eu$^{3+}$ ion was demonstrated in 1939 by Deutschbein [20].

The coefficient of spontaneous emission between two manifolds $J$ and $J'$, due to the magnetic dipole mechanism, is given by

$$A_{J,J'} = \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} n^3 S_{md}$$

where the magnetic dipole line strength $S_{md}$ (in units of e$^2$, where $e$ is the electronic charge = -4.8·10$^{-10}$ e.s.u.), is

$$S_{md} = \frac{\hbar^2}{4m_e c^2} \left| \langle (4f^N)\psi' J' \rangle (L + 2S) \langle (4f^N)\psi J \rangle \right|^2 \frac{1}{2J + 1}$$

In the above equations $\omega$ is the angular frequency of the transition $J \rightarrow J'(= 2\pi c \sigma$, $\sigma$ being the transition energy in cm$^{-1}$), $n$ is the index of refraction of the medium and the angular momentum operators $L$ and $S$ are in units of. The eigenstates in eq.(12) are given in the intermediate coupling scheme. Most of the 4f - 4f transitions in the rare earth series cannot be accounted for by the magnetic dipole mechanism, not only because the predicted oscillator strengths are in general smaller than $10^{-6}$ but also due to the restrictive selection rules on the $J$ quantum number ($\Delta J = 0$, $\pm 1$), as far as $J$ is considered a good quantum number.

The forced electric dipole mechanism was treated in detail for the first time in 1962 by Judd [2] and Ofelt [3] through the powerful technique of irreducible tensor operators [14-16]. Two years later it was proposed by Jorgensen and Judd [21] that an additional mechanism of 4f - 4f transitions, originally referred to as the pseudoquadrupolar mechanism due to inhomogeneities of
the dielectric constant, could be as operative as, or, for some transitions, even more relevant than the forced electric dipole one. These two mechanisms will be briefly described in the next two sub-sections.

4.2. The Judd - Ofelt theory

The electric dipole strength, $S_{ed}$ (in units of $e^2$), of a transition between two states $\phi$ and $\phi'$ is given by

$$S_{ed} = \left| \langle \phi' | \sum_i \vec{r}_i | \phi \rangle \right|^2 \quad (13)$$

If the states $\phi$ and $\phi'$ are pure $4f^N$ states, as those given by eqs.(3) and (9), than by parity selection rule (Laporte’s rule) the dipole strength $S_{ed}$ is identically null. However, provided there is no center of inversion in the site occupied by the rare earth ion, this selection rule is relaxed by the odd component of the ligand field Hamiltonian, $H_{LF}(\text{odd})$, which mixes states of opposite parity electronic configurations. Thus, since $H_{LF}(\text{odd})$ is a one particle operator, the configurations that can be mixed with the ground $4f^N$ configuration are those of the type $4f^{N-1}nd$, $4f^{N-1}ng$ ($n \geq 5$) and $n'd^{d+1}4f^{N+1}$ ($d = 2$, $n' = 3$ and 4, corresponding to core excitations). In the standard Judd-Ofelt theory the initial step is to consider this mixing through perturbation theory up to first order in the wavefunctions. If we take the perturbation on the eigenstates given by eq.(9), then we may write

$$|\phi\rangle = |(4f^N)\Gamma\rangle + \sum_{B\beta} \frac{\langle B\beta | H_{LF}(\text{odd}) | (4f^N)\Gamma\rangle}{E(\Gamma) - E(B\beta)} |B\beta\rangle \quad (14)$$

where $B$ designates an opposite parity excited configuration and $\beta$ its states. The state $|\phi'\rangle$ has a similar expression. The matrix element in eq.(13), abbreviated as $\bar{\mu}_{ed}$, is consequently given by
An interesting order of magnitude estimate can be made from eq.(15). For an electric dipole allowed transition the oscillator strength can be as high as 1. For rare earth ions the ligand field interaction is typically of the order of $100 \text{ cm}^{-1}$ and the interconfigurational energy differences for the lowest opposite parity excited configuration ($4f^{N-1}5d$) is typically of the order of $10^5 \text{ cm}^{-1}$. This gives a factor of $10^{-3}$ in eq.(15), which squared leads to the typical order of magnitude of $4f$ - $4f$ oscillator strengths ($10^{-6}$).

The summation over B and $\beta$ in eq.(15) reminds the possibility of using a closure procedure, and indeed this is the next step in the Judd - Ofelt treatment. This summation becomes much more treatable if one assumes that the intraconfigurational energy differences are much smaller than the energy differences between the baricenters of the ground and excited configurations, or, in other words, if one assumes that $E(\Gamma) - E(B\beta) \cong E(\Gamma') - E(B\beta) \cong E_b(4f^N) - E_b(B) = \Delta E(B)$. The main point now is to use the following relation involving two irreducible tensor operators $X_q(i) = \sum x_q(i)$ and $Z_q(i) = \sum z_q(i)$ [2,3]

$$
\sum_{\beta} \left[ \langle (4f^N)\Gamma' | \sum_{i} \tilde{r}_i | B\beta \rangle | B\beta | H_{\text{ef}}(\text{odd}) | (4f^N)\Gamma \rangle \right] \frac{1}{E(\Gamma) - E(B\beta)} + \sum_{\beta} \left[ \langle (4f^N)\Gamma' | H_{\text{ef}}(\text{odd}) | B\beta \rangle \sum_{i} \tilde{r}_i | (4f^N)\Gamma \rangle \right] \frac{1}{E(\Gamma') - E(B\beta)}
$$

(15)

In this equation the quantities in ( ) and { } are 3-j and 6-j symbols, respectively [14-16]. The monoelectronic reduced matrix elements involving $x^{(k)}$ and $z^{(k)}$ contain the radial part corresponding to these operators, and $U^{(\lambda)}$ is an irreducible unit tensor operator [14-16]. In the case of core excitations ($\ell = d, n = 3$ and 4 ) a minus sign appears in the right-hand-side of eq.(16).
In our case the ranks k and k' are equal to 1 (from the dipole operator) and t (from $H_{LF}$(odd)), respectively. Thus, it may be shown that the only difference between the two terms in the right-hand-side of eq.(15) is in the 3-j symbols which are related by

$$\begin{pmatrix} t & 1 & \lambda \\ p & q & -Q \end{pmatrix} = (-1)^{t+1+\lambda} \begin{pmatrix} 1 & t & \lambda \\ p & q & -Q \end{pmatrix}$$

Since t is odd only even values of $\lambda$ will lead to nonvanishing values of $\mu_{ed}$. From the triangularity rules for the 6-j symbol in eq.(16) one has $\lambda \leq 2f$, i.e., $\leq 6$. The unit tensor operator $U^{(0)}$ is a scalar and cannot contribute to transition probabilities. Therefore, the operative values of $\lambda$ are 2, 4 and 6.

The matrix element $\mu_{ed}$ may then be put in the form

$$\mu_{ed} = \sum_{\lambda,t,Q,p,q} (-1)^{Q}(2\lambda+1) \begin{pmatrix} 1 & t & \lambda \\ p & q & -Q \end{pmatrix} B_{\lambda t p}^{ed} \left\langle (4f^N)\Gamma' \right| U_Q^{(\lambda)} \left| (4f^N)\Gamma \right\rangle \vec{e}_q^*$$

(17)

where the spherical unit vectors satisfy the condition $\vec{e}_q^* \cdot \vec{e}_q = \delta_{qq'}$, and the quantities $B_{\lambda t p}^{ed}$ are given by

$$B_{\lambda t p}^{ed} = \Xi(t,\lambda)\gamma_p^t$$

(18)

where

$$\Xi(t,\lambda) = 2\sum_{n,\ell} \begin{pmatrix} f & 1 & \ell \\ t & f & \lambda \end{pmatrix} \langle f\|C^{(\ell)}\|f\rangle \langle \ell\|C^{(\ell)}\|f\rangle \langle 4f|r|n\ell\rangle \langle n\ell|r'|4f\rangle \frac{1}{\Delta E(n\ell)} (19)$$

If one is not interested on transition intensities between Stark levels ( $\Gamma, \Gamma'$ ) but rather on integrated intensities between J and J' manifolds, to a first approximation J – mixing effects may be neglected and the $4f^N$ eigenstates in eq.(17) may be replaced the eigenstates in the intermediate coupling scheme defined in eq.(3). Thus, the total electric dipole strength is a sum over $M_J$ and $M_{J'}$ divided by $2J+1$, which assumes that the components of the initial J manifold are equally
thermally populated. Using the Wigner-Eckart theorem and the orthogonality relation between \(3-j\) symbols, it may be easily shown that the total electric dipole strength in eq. (13) is then given by

\[
S_{ed} = \frac{1}{2J+1} \sum_{\lambda=2,4,6} \Omega_{\lambda}^{ed} \left( \langle 4f^N | \psi' J' \| U^{(\lambda)} \| (4f^N) | \psi J \rangle \right)^2
\]

(20)

where

\[
\Omega_{\lambda}^{ed} = (2\lambda + 1) \sum_{t,p} \left| B_{\lambda,1p}^{ed} \right|^2 \frac{2t + 1}{2t + 1}
\]

(21)

An alternative way of performing the summation in eq. (15) has been used through the average energy denominator method introduced by Bebb and Gold [22]. The advantage is that one has to deal with a single average energy difference in eq. (15). It has been shown that the predicted values of the so-called intensity parameters \(B_{\lambda,1p}^{ed}\) and \(\Omega_{\lambda}^{ed}\) are very similar to those given by the standard Judd-Ofelt treatment [9]. The coefficient of spontaneous emission taking into account both the forced electric dipole and magnetic dipole mechanisms is then given by

\[
A_{1f} = \frac{4e^2 \omega^3}{3hc^3} \left[ \frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right]
\]

(22)

It should be noted, however, that the above equation is valid as far as \(J\) – mixing is neglected, otherwise a cross term between the electric dipole and magnetic dipole transition moments may appear. The corresponding expression for the oscillator strength may be obtained from the relation

\[
P_{f,J} = \frac{2J+1}{2J'+1} \frac{m_e c^3}{2\omega^2 e^2 n^2} A_{1f}
\]

(23)

4.3. The dynamic coupling
This mechanism was originally proposed by Jorgensen and Judd [21] in an attempt to explain the uncommon intensity variation of certain 4f - 4f transitions denominated hypersensitive transitions. A simplified visualization of this mechanism is shown in figure 2.

\[
\text{TOTAL FIELD} = \vec{E}_i + \sum_j \vec{E}_{dc}(j)
\]

**Figure 2.** A pictorial representation of the dynamic coupling.

The incident radiation field induces oscillating dipoles in the surrounding atoms and, as a consequence, an additional oscillating electric field is produced. This electric field, being produced close to the rare earth ion, has large local gradients and may induce 4f - 4f transitions with oscillator strengths of the order of, or even greater than $10^{-6}$. To a first approximation the induced oscillating dipoles depend on the isotropic dipolar polarizabilities of the surrounding atoms, as indicated in fig. 2. The interaction energy with the 4f electrons, $H_{dc}$, is given by
\[ H_{DC} = e \sum_{i,j} \bar{\mu}_j \cdot \frac{(\vec{r}_i - \vec{R}_j)}{|\vec{r}_i - \vec{R}_j|^3} \] (24)

which must be added to the interaction, with the incident field, that leads to the forced electric dipole mechanism. When expanded in terms of irreducible tensor operators [14], the even rank components of \( H_{DC} \) lead to a transition moment (in units of e) that has exactly the same form as the transition moment given in eq. (17), that is

\[ \bar{\mu}_{DC} = \sum_{\lambda,i,Q,p,q} (-1)^Q (2\lambda + 1)^{t} \left( \lambda \right) B^{DC}_{\lambda t p} \langle (4f^N) \Gamma' | U^{(\lambda)}_Q | (4f^N) \Gamma \rangle \bar{\bar{e}}_q * \] (25)

where

\[ B^{DC}_{\lambda t p} = - \left[ \frac{(\lambda + 1)(2\lambda + 3)}{(2\lambda + 1)} \right]^{1/2} \left( 4f^t \frac{1}{4f} \langle 1 - \sigma_\lambda \rangle \langle \mathbf{f} \rangle \frac{\mathbf{C}^{(\lambda)} \mathbf{f} \rangle \Gamma^{*}_p \delta_{t,\lambda+1} \right] \] (26)

and

\[ \Gamma^{*}_p = \left( \frac{4\pi}{2t + 1} \right)^{1/2} \sum_{R^{t+1}_j} \frac{\alpha_j}{R^{t+1}_j} Y^*_p (\Omega_j) \] (27)

\( Y^*_p \) being a spherical harmonic and \((1 - \sigma_\lambda)\) in eq. (26) is a shielding factor due to the 5s and 5p filled sub-shells of the rare earth ion [9]. The total intensity parameter is now \( B_{\lambda t p} = B^{ed}_{\lambda t p} + B^{DC}_{\lambda t p} \), which is the quantity to be used in eq. (21) to obtain the total \( \Omega_\lambda \) parameters.

Several interesting aspects may be discussed on the forced electric dipole and dynamic coupling mechanisms. An analysis from typical values of the quantities that appear in eqs. (18) and (26) indicates that these two mechanisms contribute to the total transition moment with opposite signs [11]. Both the odd rank ligand field parameters, \( \gamma^t_p \), and the polarizability
dependent quantities $\Gamma_p^t$ contain in general the same type of sum over the surrounding atoms. Therefore, they carry out the same symmetry information. The only difference is that $\Gamma_p^t$ does not depend on the spherical harmonic of rank 1 ($\gamma_p^1$) as it may be noted from the Kronecker’s delta in eq. (26). As the site occupied by the rare earth ion becomes more symmetric, the lower rank $\gamma_p^1$ and $\Gamma_p^t$ tend to vanish more rapidly than the higher rank ones, or in a more general way, the former quantities are more sensitive to changes in symmetry than the latter ones, though the higher rank $\gamma_p^1$ and $\Gamma_p^t$ are more sensitive to changes in distances. This goes in the correct sense towards the rationalization of the so-called hypersensitive transitions, which are in general those transitions dominated by the effective operator $\Omega_2 \mathbf{U}^{(2)}$. However, it has been observed that symmetry alone cannot account for the enormous variation sometimes observed in the intensities of these transitions for different chemical environments. Theoretical estimates have shown that the dynamic coupling contribution is able to account for this enormous intensity variation through the polarizabilities of the surrounding atoms, or groups of atoms. Thus, for example, in going from the gaseous compound NdF$_3$ to gaseous NdI$_3$ there is a change in polarizability, from the ion F$^-$ to the ion I$^-$, of almost one order of magnitude. This might produce a change of almost two orders of magnitude in the intensities dominated by $\Omega_2 \mathbf{U}^{(2)}$. Abnormal changes in the intensities dominated by $\Omega_4 \mathbf{U}^{(4)}$ and $\Omega_6 \mathbf{U}^{(6)}$ may not occur since for these cases the considerable increase in the distance Nd – X (X = F and I) may compensate for the increase in the polarizability values.

A point that should be stressed here is that, in contrast to a common procedure found in the literature in the case of rare earth doped glasses, the dynamic coupling mechanism cannot in any circumstance be neglected. When the $\Omega_\lambda$ intensity parameters are determined phenomenologically from experimental intensities, the forced electric dipole and dynamic coupling mechanisms are absorbed simultaneously and cannot be distinguished. Thus, when treating energy transfer processes between rare earth ions one should keep in mind that in the dipole-dipole or dipole-quadrupole expressions for the transfer rates the $\Omega_\lambda$’s which appear refer only to the forced electric dipole contribution, that is, $\Omega^{ed}_\lambda$. This is one of the reasons that motivate theoretical calculations of the individual $B^{ed}_{\lambda,1p}$ and $B^{DC}_{\lambda,1p}$ contributions. These theoretical calculations turn out to be an enormous problem, in vitreous materials, due to the large variety of different site symmetries occupied by the rare earth ion, unless a model system with a statistically well defined distribution
of site symmetry types is available. In this case the $\Omega_\lambda$ parameters represent average values over all types of sites.

5. Intensity parameters in vitreous materials

One of the effects of a distribution of different symmetry sites occupied by the rare earth ion is to produce the inhomogeneous line broadening. The Stark levels overlap in such a way that, in most cases, even the fluorescence line-narrowing technique cannot help to identify a particular site occupied by the rare earth ion. Figure 3 shows the emission spectrum of the Eu$^{3+}$ ion in fluoroborate glasses [23], where this effect can be clearly noted, particularly in the $^5D_0 \rightarrow ^7F_2$ hypersensitive transition at $\sim 612$ nm.

![Figure 3. Luminescence spectrum of the Eu$^{3+}$ ion, in the presence (a) and in the absence (b) of silver particles, in a fluoroborate glass.](image)

As already mentioned above the $\Omega_\lambda$ intensity parameters in vitreous materials correspond to statistical average values over all sites, and these values, determined experimentally, incorporate both the forced electric dipole and dynamic coupling contributions. The dependence with the polarizabilities of the neighboring ions confers to the latter mechanism a stronger dependence with the nature of the chemical environment (for the sake of comparison, in a 100% ionic model of the
ligand field interaction the charge on the fluorine and chlorine ions, for example, is $-1$, in units of the electronic charge, while their dipolar isotropic polarizabilities are, respectively, $1 \text{ A}^3$ and $\sim 3 \text{ A}^3$. This may account for the hypersensitive behavior of certain $4f - 4f$ transitions, those which are in general dominated by $\Omega_2 \text{U}^{(2)}$. A correlation has been noted in the sense that compounds expected to have a higher degree of covalence tend to present higher values of $\Omega_2$ [1], suggesting that in these cases the dynamic coupling mechanism dominates. This correlation can be clearly seen from the $\Omega_2$ values collected in table 1 of ref.[1], where the oxides and chalkogenides present higher values for this intensity parameter than the fluorides. Another correlation has also been noted between the $\Omega_4$ and $\Omega_6$ parameters and the amplitudes of localized vibrational modes involving the rare earth ion [1], giving an indication of the rigidity of the material. It is, however, rather difficult to rationalize this correlation in terms of the quantities that appear in eqs.(18) and (26).

An interesting and controversial case of intensity parameters is the $\text{Pr}^{3+}$ ion. In many compounds with $\text{Pr}^{3+}$ it is found that the phenomenological $\Omega_2$ parameter is negative, which, from the definition of the $\Omega_2$ (eq.(21)), is not acceptable. It has been argued [4] that for this ion the lowest opposite parity excited configuration, $4f5d$, is too close($\sim 50000 \text{ cm}^{-1}$) to the ground configuration($4f^2$), invalidating the approximation made on the energy denominators in eq.(15). There are different ways in which corrections could be introduced. One is to take the $4f^N$ wavefunctions up to higher than first order in perturbation theory [7]. Another one is, for example, to make appropriate expansions on the inverse of the energy differences in eq.(15) as it has been done in ref.[24]. In either way one finds that the odd rank effective operators $\Omega_\lambda^e \text{U}^{(\lambda)}(\lambda = 1, 3, 5)$ may be of significance when $\Delta E(5d)$ is small, as in the case of the $\text{Pr}^{3+}$ ion. However, one should keep in mind that even in this case, depending on the chemical environment, the dynamic coupling mechanism may dominate, which would make more difficult to evaluate precisely the effect of the odd rank effective operators. There are evidences in the case of the isoelectronic ion $\text{U}^{4+}(5f^2)$, found by F.Auzel [25], indicating a rather independent behavior of the $5f - 5f$ transition intensities with the position of the $5f6d$ opposite parity excited levels, suggesting a dominance of the dynamic coupling mechanism. Another aspect on $\text{Pr}^{3+}$ compounds concerns the statistical procedure which is usually adopted to extract the $\Omega_\lambda$ intensity parameters from experimental oscillator strengths (least-squares method). It is possible that in this case the set of linear equations is particularly sensitive to very small variations, within experimental errors, in the
oscillator strengths. A method in which branching ratios are included in the least-squares procedure has been proposed by Quimby and Miniscalco [26], and a method in which the standard deviation for each individual oscillator strength is introduced in the minimization procedure has been used by Goldner and Auzel [27], both leading to reliable intensity parameters.

6. Concluding remarks

Some very basic aspects of the theory of 4f – 4f transition intensities applied to vitreous materials have been discussed above. The characteristics of the intra-atomic rare earth free ion and ligand field interactions, as well as the formalisms of the forced electric dipole and dynamic coupling mechanisms of 4f – 4f intensities, have been outlined. One of the main points was to call attention to the contribution from the dynamic coupling mechanism to the intensities, a point that has been commonly overlooked in the literature of rare earth doped glass materials. Not taking into account this mechanism is equivalent to assume that the phenomenological $\Omega$ intensity parameters coincide with $\Omega^\text{ed}$, corresponding to the forced electric dipole contribution alone. This would be a clear misinterpretation of the theory. From the theoretical expressions given in eqs. (18) and (26) it is possible to rationalize the correlation between $\Omega_2$ and covalence, as discussed in ref.[1]. However, the same is not evident concerning the correlation between $\Omega_4$ and $\Omega_6$ and the rigidity of the medium. The case of the Pr$^{3+}$ ion has been briefly discussed under the light of the forced electric dipole and dynamic coupling mechanisms, and attention has been called to the fact that, for this ion, statistical problems may arise when determining phenomenological intensity parameters from experimental oscillator strengths.

References


[25]. F. Auzel, private communication.