Mechanisms of non-radiative energy transfer involving lanthanide ions revisited

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ARTICLE INFO

Article history:
Available online 5 September 2008

PACS:
31.70.Hq
33.70.Ca

Keywords:
Molecular orbital
Luminescence
Optical spectroscopy
Up-conversion
Rare-earths in glasses

ABSTRACT

In this work, the theoretical background of the Coulomb direct and exchange interactions in non-radiative energy transfer involving lanthanide ions is critically reviewed. Emphasis is given to the shielding effect produced by the filled 5s and 5p sub-shells of the lanthanide ion and the appropriate use of the so-called forced electric dipole intensity parameters of 4f–4f transitions, two aspects that have been often overlooked in the literature. An effective exchange hamiltonian, based on Mülliken-type approximations, and an expression for the resonant or quasi-resonant energy mismatch spectral overlap factor are proposed. Both cases of ion-to-ion and intramolecular energy transfer processes are discussed. Numerical estimates are compared with previous calculations, showing that order of magnitude differences appear. The analysis indicates that the donor–acceptor distance dependence of transfer rates by the exchange mechanism goes beyond the single exponential behavior adopted from Dexter’s approach.

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1. Introduction

Non-radiative energy transfer in the nanoscopic scale is a process of paramount importance to a great number of relevant phenomena in nature. A class of particularly interesting systems in which this process occurs consists of coordination compounds of lanthanide ions, usually trivalent europium and terbium ions, with organic ligands. The characteristic lanthanide ion luminescence (4f–4f luminescence) in these compounds is a consequence of the strong absorption in the UV region by one or more ligands, which then transfer energy non-radiatively to the lanthanide ion that subsequently emits in the visible (down-conversion of light). In this way, the emitting 4f level is in general populated much more efficiently than by direct excitation of the lanthanide ion excited levels. Thus, the 4f–4f luminescence intensity is the result of a balance between strong absorption by the ligands, ligand–lanthanide ion energy transfer rates, non-radiative decays and radiative emission rates involved. This phenomenon was first elucidated by Weissman in 1942 [1]. More recently, models describing the mechanisms of organic ligand–lanthanide ion energy transfer and 4f–4f emission quantum yields have been discussed in the literature [2].

In the case of inorganic materials (crystals and glasses) containing lanthanide ions, particularly noticeable was the discovery of sequential energy transfer between lanthanide ions, converting low energy photons into higher energy ones (up-conversion of light), by Auzel in 1966 [3,4]. This discovery allowed the comprehension of several non-linear processes in doped solid state structures and induced the prediction of new effects in these materials. The widely used up-conversion process has been the subject of intense scientific investigation and also technological applications that goes from the production of laser materials to the modeling of optical markers [5–8].

Even though the fundamentals of non-radiative energy transfer involving lanthanide ions are well established there are several aspects not yet firmly understood. The difficulties in dealing with factors such as the distribution of ions and statistical aspects of macroscopic energy transfer (concentration effects in the case of ion–ion energy transfer), coupled wavefunctions, 4f–4f transition intensities and energy overlap integrals are not the only ones. Distinguishing between the possible mechanisms governing the energy transfer is certainly a major problem. Luminescence quantum yields and the transient behavior of the luminescence in lanthanide ions compounds are strongly dependent on these factors when energy transfer is operative [9,10].

The present paper is focused on the theoretical background of the mechanisms of non-radiative energy transfer involving lanthanide ions, with emphasis on the electric multipolar and exchange mechanisms. The first aim is to call attention to certain aspects of crucial importance that are usually overlooked in the literature when pairwise transfer rates are evaluated. These aspects (the use of Judd–Ofelt intensity parameters and the inclusion of shielding factors) might lead to orders of magnitude differences in calculated transfer rates. The second goal is to propose, on the basis of a Mülliken-type approximation for two-center one-electron matrix elements [11,12], an effective exchange interaction hamiltonian

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doi:10.1016/j.jnoncrysol.2008.04.023
that may be used in the independent model systems, without needing to work with antisymmetrized wavefunctions. Within our purposes, the magnetic dipole–dipole wavefunctions [13,14], which might be of relevance when the selection rule on the total angular momentum is $\Delta l \leq 1$, particularly in centrosymmetric compounds, will not be considered. Finally, a formulation, based on Gaussian band shapes, is made for the energy overlap integral expressing the energy mismatch conditions in the transfer process.

2. The case of ion-to-ion energy transfer

2.1. The interaction hamiltonian

The electrons in the 4f sub-shell of a lanthanide ion are strongly shielded by the filled 5s and 5p sub-shells, leading to rather weak interactions between the ion and its environment. It is also conceivable that the Coulomb interaction between two electronic clouds becomes somehow modified by the optically inactive medium connecting the donor and acceptor species. For donor–acceptor distances where the multipolar interactions dominate (large distances) such effect is usually taken into account through the dielectric constant of the medium ($\varepsilon$) by simply multiplying the Coulomb hamiltonian by $1/\varepsilon$. For distances where the exchange interaction is the dominant one (short distances) this effect can be considered by working with lanthanide ion 4f wavefunctions appropriately modified by the weak interaction with the chemical environment. For both distance ranges this effect is not expected to change figures within order of magnitude calculations, and will not be explicitly taken into account for our purposes.

In contrast, the shielding factors produced by the filled 5s and 5p sub-shells may lead to significant changes in calculated transfer rates. Thus, they will be explicitly considered. We anticipate the fact that this shielding effect applies when for the donor–acceptor pair antisymmetrized wavefunctions are not used in the evaluation of matrix elements, or in other words, when matrix elements do not depend explicitly on the donor–acceptor overlap integrals. Otherwise, the same physical effect risks to be counted twice. This is due to the fact that the overlap integrals naturally incorporate this shielding.

The interaction hamiltonian between the electronic clouds of a donor ($D$) and an acceptor ($A$), indicated in Fig. 1, can be separated in two parts according to:

$$H = H_C + H_{ex} = \sum_{ij} \frac{e^2}{r_{ij}} - \sum_{ij} \frac{e^2}{r_{ij}} P_{ij},$$

where $H_C$ represents the direct Coulomb interaction and $H_{ex}$ the exchange interaction. In this expression, the indices $i$ and $j$ run over donor and acceptor electrons, respectively, and $P_{ij}$ is the exchange operator, given by [15]:

$$P_{ij} = \frac{1}{2} \hat{s}_i \cdot \hat{s}_j,$$

where $\hat{s}_i$ and $\hat{s}_j$ are the spin operators of electrons $i$ and $j$.

Evaluation of the exchange interaction matrix elements is in general a task of enormous complexity [15]. The convenience of using the exchange hamiltonian in the form of the second term on the right-hand side of Eq. (1) depends on the nature of donor and acceptor species and how wavefunctions are treated. Important aspects may be elegantly clarified by the used of second quantization methods together with irreducible tensor operator techniques. In this procedure the Coulomb interaction between the two electronic clouds is written as [16]:

$$H = \sum_{i,j,k} a_i^* d_i^* \left( \xi_i \eta_j \left[ \frac{e^2}{r_{12}} \right] d_j a_i + \sum_{\Delta k} a_i^* d_i^* \left( \xi_i \eta_j \left[ \frac{e^2}{r_{12}} \right] \xi_j \right) a_i d_j \right),$$

(3)

In this expression $a^*$ and $a$ are creation and annihilation operators, respectively, for electrons of the acceptor ion, while $d^*$ and $d$ are creation and annihilation operators of electrons of the donor ion. In the case of ion-to-ion energy transfer, Greek letters stand for one-electron 4f wavefunctions (spin–orbitals). The first and second terms on the right-hand side correspond, respectively, to the direct Coulomb and exchange interactions.

The common practice is to expand the two-electron interaction ($e^2/r_{12}$) in terms of Racah’s irreducible spherical tensor operators, $C^{(k)}(\Omega)$, by using the bipolar expansion [17]. This leads to:

$$\frac{e^2}{r_{12}} = e^2 \sum_{k_1 k_2} \sum_{q_1 q_2} (-1)^k \left[ \frac{2k_1 + 2k_2 + 1}{(2k_1 + 1)(2k_2 + 1)} \right]^{\frac{1}{2}} \left( q_1 \ v_{\Omega q_2} \ q_2 \ v_{\Omega q_1} \right)$$

$$\times \frac{C^{(k_1 + k_2)}(\Omega)}{R_{12}^{C_{12}}} r_{12}^{C_{12}} C^{(k_1)}(\Omega_1) \times r_{22}^{C_{22}} C^{(k_2)}(\Omega_2)(1 - \sigma_k)(1 - \sigma_k),$$

(4)

In this expansion it has been assumed that $r_1$ and $r_2$ are smaller than $R$. The quantity in ( ) is a 3-j symbol and the quantities $(1 - \sigma_k)$ are the shielding factors (also known as Sternheimer factors [18]) due to the filled 5s and 5p sub-shells in both donor and acceptor ions. From a comparison between ligand field models, for lanthanide compounds, as given by the Simple Overlap Model [19] and by the Crude Electrostatic Approximation, it has been argued that the shielding factors may be conveniently expressed in terms of the radial overlap integral, $\rho$, between the 4f sub-shell and the valence shell of a ligating atom in the first coordination sphere of the lanthanide ion, by the following relation [20]:

$$(1 - \sigma_k) = \rho(2\beta)^{k+1},$$

(5)

where $\beta$ is a number very close to 1. A typical value of the overlap $\rho$ in lanthanide compounds is 0.05. Thus, for instance, for $k = 2, 4$ and $6 \left( 1 - \sigma_k \right)$ from Eq. (5) takes the values 0.4, 1.6 and 6.4, respectively. These values and their trend agree fairly well with theoretical calculations of Sternheimer factors for lanthanide ions. It should be clear that Eq. (5) should be regarded as a rather observational relationship.

2.2. Wavefunctions

In the Russell–Saunders coupling the lanthanide free ion wavefunctions are taken in the angular momentum representation as $(4f)^n\psi_{SMJ}$, where the total angular momentum $J = L + S$ and $\psi$ represents additional quantum numbers necessary to unambiguously define the wavefunction. Taking into account the fact that the intra-ion Coulomb repulsion is not diagonal in the quantum number $\phi$ and that the spin–orbit interaction is not diagonal in the quantum numbers $\phi$, $S$ and $L$, these latter are no longer good
quantum numbers. As a consequence, after diagonalization of the free ion hamiltonian the free ion eigenstates are given by linear combinations of the wavefunctions \( |4f^n \psi_{5l}M_j \rangle \), that is:
\[
|4f^n \psi_{5l}M_j \rangle = \sum_{s,S,L} C(s,SLI) |4f^n \psi_{5l}SJM_j \rangle
\]
with the following condition:
\[
\sum_{S,L} |C(s,SLI)|^2 = 1.
\]

Eq. (6) expresses the so-called intermediate coupling scheme. The eigenstates given in this scheme are essential to describe the behavior of lanthanide ions. A good example is the case of transitions between multiplets of different multiplicities, which otherwise cannot 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. (6). An interesting and useful aspect is that, since the chemical environment weakly affects the 4f orbitals, for each lanthanide ion the eigenstates in the intermediate coupling scheme are essentially the same for different environments. However, the weak nonspherical part of the ligand field hamiltonian is responsible for effects of crucial importance in the spectroscopy of lanthanide ions, as J-level splitting, J-mixing (the quantum number \( J \) slightly deviates from a good quantum number) and the mixing of electronic configurations of opposite parities, relaxing Laporte’s rule. This latter effect is in the origin of the forced electric dipole contribution to the 4f–4f intensities, as described by the Judd–Ofelt theory [21,22].

The independent systems model is fairly adequate to the case of non-radiative energy transfer between two interacting lanthanide ions. According to this model the initial and final two-centers states of the lanthanide ion-pair, \( |\Phi \rangle \) and \( |\Phi' \rangle \), respectively, are given by
\[
|\Phi \rangle = |D^+ \rangle |A^* \rangle = |D A^* \rangle
\]
and
\[
|\Phi' \rangle = |D \rangle |A^* \rangle = |D A^* \rangle,
\]
where the donor and acceptor states, \( |D \rangle \) and \( |A \rangle \), respectively, are given in the intermediate coupling scheme (Eq. (6)). The asterisk indicates excited states. The situation is schematically shown in Fig. 2.

2.3. Matrix elements

It has been agreed that in the expansion in Eq. (4) the relevant components, for lanthanide ions, correspond to \( k_1 \) and \( k_2 \leq 2 \). The term for \( k_1 = k_2 = 0 \) is the isotropic contribution. In this case, the expansion in Eq. (4) reduces to a constant term equal to \((e^2/R)\). Thus, the hamiltonian in Eq. (3) takes the following form:
\[
H^{(0)} = \frac{e^2}{R} \sum_{\ell,\ell',\ell''} \left( 1 - \sigma_0 \right)^2 d^\ell_d d_{\ell'}^\ell d_{\ell''}^\ell + S_{\ell_1} S_{\ell_2} a_{\ell_1}^\ell d_{\ell_2}^\ell d_{\ell_3}^\ell.
\]
where the quantities \( S_{\ell_1} \) are the overlap integrals between the 4f orbitals of donor and acceptor ions. The first term in the sum reduces to \( N_D N_A \), where \( N \) represents the number of 4f electrons [16]. Note that shielding does not appear in the exchange term since, as mentioned before, they are naturally incorporated in the overlap integrals \( S_{\ell_1} \). Using the relation \( a_d d_e + d_e a_d = 0 \), Eq. (10) is written as
\[
H^{(0)} = \frac{e^2}{R} \left( 1 - \sigma_0 \right)^2 N_D N_A - \sum_{\ell,\ell',\ell''} S_{\ell_1} S_{\ell_2} a_{\ell_1}^\ell d_{\ell_2}^\ell d_{\ell_3}^\ell\right).
\]

The first term on the right-hand side of the above equation, obviously, will not contribute to the energy transfer process. It may be noted that approximating all the \( S_{\ell_1} \) integrals to an average value \( \bar{S} \) is an unreliable assumption, since by using the relation for 4f electrons
\[
\sum_{\ell,\ell',\ell''} c_{\ell_1} c_{\ell_2} = -\sqrt{2} U^{(0)},
\]
where \( U^{(0)} \) is a unit tensor operator [16], matrix elements become zero, once the tensor operator \( U^{(0)} \) is a constant. However, the overlap integrals \( S_{\ell_1} \) may be separated as a product of radial and angular parts. Thus, the second term on the right-hand side of Eq. (11) is directly proportional to the square of the radial overlap integral \( 4f_D|4f_A| \).

For \( k_1 (or \, k_2) = 0 \) and \( k_2 (or \, k_1) \neq 0 \) it is not difficult to see from Eq. (3) that the direct Coulomb interaction will contribute with zero matrix elements, while the exchange hamiltonian will contribute with a term linear in the overlap integrals. This linearity is, however, apparent, since the two-center matrix elements of the operators with \( k_2 (or \, k_1) \neq 0 \), for instance \( \langle \eta_2 | r^{2} \psi_{4f}^{(0)} | \eta_2 \rangle \), somehow depend on the 4f–4f overlap and are also strongly dependent on the distance \( R \). For the sake of illustration, in the case of a dipole-type two-center matrix element \( \langle k_2 (or \, k_1) = 1 \rangle \) if one crudely uses a Mülliken–type approximation [11,12], then:
\[
\langle \eta_2 | r^{2} \psi^{(0)} | \eta_2 \rangle \approx \frac{1}{2} R \langle \eta_2 | \eta_2 \rangle
\]
and the dependence on the 4f–4f overlap becomes explicit. Actually, the exchange interaction will depend on structures of the type:
\[
p_{4f}^{(k_1)}(\xi, \eta) p_{4f}^{(k_2)}(\eta, \lambda) a_{\ell_1}^\ell d_{\ell_2}^\ell a_{\ell_3}^\ell d_{\ell_4}^\ell,
\]
where the quantities \( p_{4f}^{(k_1)} \) and \( p_{4f}^{(k_2)} \) may be interpreted as the multipole moments of the overlap region, formed by the small overlap between the donor and acceptor electronic clouds. If order of magnitude estimates are envisaged, it is tempting enough to use a Mülliken-type approximation and write
\[
\langle DA^* | H_{Ex} | DA \rangle \approx \frac{e^2}{R} (4f_{DA^*})^2.
\]

Transfer rates would then depend on the fourth power of the 4f–4f radial overlap. Obviously, in this very crude approximation, the important selection rules on the \( \psi \) and \( J \) quantum numbers do not appear. An alternative is to use the following matrix element for the exchange interaction:
\[
\langle DA^* | H_{Ex} | DA \rangle \approx - (4f_{DA^*})^2 \langle DA^* | \sum_{ij} \left( \frac{1}{2} + 2S_i \cdot S_j \right) \frac{e^2}{r_{ij}} | DA \rangle,
\]
where the non-antisymmetrized wavefunctions are given by Eqs. (8) and (9).
This analysis has indicated that the distance dependence of the exchange mechanism actually goes beyond the single exponential behavior, as it has been adopted from Dexter’s formulation [23].

For $k_1$ and/or $k_2 = 1$, in the direct Coulomb Hamiltonian, it is necessary to invoke the mixing of opposite parity electronic configurations through the odd components of the ligand field Hamiltonian, as in the Judd–Ofelt theory of 4f–4f intensities [21,22]. This parity admixture relaxes Laporte’s rule and produces matrix elements that are competitive with those parity allowed for $k_1$ and $k_2 = 2$. These $k_1$ and $k_2$ combinations lead to the exchange, dipole–dipole, dipole–quadrupole and quadrupole–quadrupole contributions to the transfer rates. For the dipole–dipole and dipole–quadrupole contributions one is involved with Judd–Ofelt matrix elements of the type [21]:

$$
|A\rangle r^{(2)} |\psi_{q}^{(1)} \rangle = \frac{2}{\mathbb{E}_{2}-\mathbb{E}_{0}} \sum_{J_1} \sum_{J_2} \sum_{\lambda_{1}} \sum_{\lambda_{2}} \left( -1 \right)^{\lambda_{1}} (2K + 1) \times \left[ \langle 4f | r | n \rangle \langle n | r | 4f \rangle \langle f | C^{(1)} | \ell \rangle \langle \ell | C^{(1)} | f \rangle \times \left( \frac{t}{p} \frac{1}{q} \frac{1}{\rho} \right) \right]
\times \langle \psi_{\lambda_{1}}^{(1)} | U^{(2)} | \psi_{\lambda_{2}}^{(1)} \rangle,
(17)
$$

where $(n, \ell)$ indicates excited configurations with opposite parity to the 4f$^6$ one and with average energies $\mathbb{E}_{0}$. The $\gamma_{pq}$ are the so-called odd rank ligand field parameters that appear in the expression for the ligand field Hamiltonian:

$$
H_{L}(\text{odd}) = \sum_{t} \gamma_{t}^{(1)} r^{(2)} (\Omega_{t}).
(18)
$$

For lanthanides $t = 1, 3, 5$ and 7, and $K = 2, 4$ and 6. In Eq. (17) $\langle 4f | r | n \rangle$ is a radial integral, $\langle f | C^{(1)} | \ell \rangle$ is a one-electron reduced matrix element and {} is a 6-$f$ symbol.

For $k_1$ and/or $k_2 = 2$ the matrix element involved is:

$$
|A\rangle r^{(2)} |\psi_{q}^{(1)} \rangle = \langle 4f | r | 4f \rangle \langle f | C^{(2)} | f \rangle \langle f | C^{(1)} | \ell \rangle \langle \ell | C^{(1)} | f \rangle \times 
\left( \frac{t}{p} \frac{1}{q} \frac{1}{\rho} \right) \times
\langle \psi_{\lambda_{1}}^{(1)} | U^{(2)} | \psi_{\lambda_{2}}^{(1)} \rangle,
(19)
$$

where we have used the Wigner–Eckart theorem, with the eigenstates given in the intermediate coupling scheme (Eq. (6)).

From the above matrix elements, as far as $J$ is considered as a good quantum number, the following selection rule is derived:

$$
|J' - J| = \kappa \leq |J' + J|,
(20)
$$

where $\kappa$ stands for $k_1$, $k_2$ or $K$.

2.4. Energy transfer rates

In the independent systems model, according to Fermi’s golden rule, energy transfer rates between a donor and an acceptor ion may be expressed as:

$$
W_{IF} = \frac{2\pi}{h} | \langle DA' | H | DA \rangle |^2 F,
(21)
$$

where the temperature dependent factor $F$ contains a sum over Franck–Condron factors and the appropriate energy mismatch conditions (donor–acceptor spectral overlap).

To evaluate transfer rates in the intermediate coupling scheme, the common practice is to carry out a sum over the $M$ quantum numbers weighted by the degeneracies of the donor and acceptor initial states, $1/(2J_{D} + 1)$ and $1/(2J_{A} + 1)$. Kushida has then derived the following expressions, without including shielding, for the dipole–dipole (d–d), dipole–quadrupole (d–q) and quadrupole–quadrupole (q–q) mechanisms of energy transfer [24]:

$$
W_{d–d} = \frac{1}{h} \sum_{\Lambda} \langle \frac{1}{4} \frac{1}{\mathbb{E}_{2} - \mathbb{E}_{0}} \frac{1}{(2J_{D} + 1)} \frac{1}{(2J_{A} + 1)} \exp \left( \frac{1}{4} \frac{\Lambda}{\mathbb{E}_{2} - \mathbb{E}_{0}} \right)^{2} \ln 2 \right]^{2} \ln 2 \right]
(27)
$$

where $\gamma_{\text{rep}}$ represents band width at half-height and $\Lambda$ is the difference between the donor and acceptor transition energies involved in the transfer process. Eq. (27) has been successfully used in the case of energy transfer between molecular units of a polymeric chain in a hybrid material [27]. In this way, the temperature dependence and phonon-assistance to the transfer rates are taken into account in an implicit effective fashion. Recently, a detailed

$$
W_{q–q} = \frac{1}{h} \sum_{\Lambda} \langle \frac{1}{4} \frac{1}{\mathbb{E}_{2} - \mathbb{E}_{0}} \frac{1}{(2J_{D} + 1)} \frac{1}{(2J_{A} + 1)} \exp \left( \frac{1}{4} \frac{\Lambda}{\mathbb{E}_{2} - \mathbb{E}_{0}} \right)^{2} \ln 2 \right]^{2} \ln 2 \right]
(27)
$$

where $\gamma_{\text{rep}}$ represents band width at half-height and $\Lambda$ is the difference between the donor and acceptor transition energies involved in the transfer process. Eq. (27) has been successfully used in the case of energy transfer between molecular units of a polymeric chain in a hybrid material [27]. In this way, the temperature dependence and phonon-assistance to the transfer rates are taken into account in an implicit effective fashion. Recently, a detailed
theoretical analysis of the factor $F$ has been performed for the case of intramolecular energy transfer involving ligand-to-metal charge transfer states in luminescence thermal quenching effects [28]. Typical values of $F$ for a lanthanide ion-pair are in the range of $10^{12}$–$10^{13}$ erg$^{-1}$.

3. The case of ion–ligand intramolecular energy transfer

In this case the energy transfer process involves donor and acceptor species with completely different characteristics. Despite the fact that this problem has been experimentally elucidated in the 1940s [1], only in the last decade theoretical approaches have appeared [2]. This gap might be partially attributed to the computational difficulties involved.

In organic ligands, once the spin–orbit interaction is very small the spin is to a large extent a good quantum number, and the molecular states have well defined multiplicities. They are either singlets or triplets, with the ground state being a singlet. Under this circumstance it is not difficult to conclude that the isotropic contribution (1 = 1, 2, 4 and 6, for the direct Coulomb interaction, and $k_1 = 1$ and $k_2 = 0$ for the exchange interaction). The results are as follows:

$$W_{d-m} = \frac{S_1}{\|G\|} \frac{2\pi e^2}{h} \sum_{\gamma} \gamma_{\gamma}(\psi_{\gamma}^\ast \|U^K\|\psi_{\gamma})^2 F$$  \hspace{1cm} (28)

for the dipole–m¿ultipole contributions, $k_2 = K = 2, 4$ and $6$, where

$$\gamma_{\gamma} = \langle K + 1 \rangle \left( \frac{e^2}{R_{\gamma}} \right)^2 \|U^K\| \|\psi_{\gamma}\|^2 (1 - \sigma_\gamma)^2$$ \hspace{1cm} (29)

with $\gamma_{\gamma} \ll \gamma_4 \ll \gamma_2$ and

$$W_{d-d} = \frac{S_1 (1 - \sigma_1)}{\|G\|} \frac{2\pi e^2}{h} \sum_{\gamma_2} \sum_{\gamma_4} \gamma_{\gamma_2}(\psi_{\gamma_2}^\ast \|U^K\|\psi_{\gamma_4})^2 F$$ \hspace{1cm} (30)

for the dipole–dipole contribution ($k_2 = 1$). If an exchange interaction matrix element of the type given by Eq. (16) is used, one gets:

$$W_{ex} = \frac{(4f^4 L^4)}{\|J\|} \frac{8\pi e^2}{3h} \left( \psi_{\gamma_2}^\ast \|S\| \psi_{\gamma_4} \right)^2$$

$$\times \sum_{m} \left( \phi \left( \sum_{j} \mu_z(j) \phi_j \right) \phi_j^\ast \right)^2 F.$$ \hspace{1cm} (31)

In these equations $S_0$ is the dipole strength of the ligand transition involved in energy transfer process and $G$ is the degeneracy of the ligand initial state. In Eq. (31) $s_m (m = -1, 0, 1)$ is the spherical component of the spin operator of electron $j$ in the ligand, $\mu_z$ is the $z$-component of its dipole operator and $S$ is the total spin operator of the lanthanide ion. Typical values of the squared matrix element of the coupled dipole and spin operators in Eq. (31) are in the range $10^{-34}$–$10^{-35}$ (e.s.u.)$^2$ cm$^2$. This coupled operator breaks down the usual selection rules in the singlet–singlet and singlet–triplet matrix elements.

Eqs. (30) and (31) differ from the ones obtained in the original treatment of intramolecular energy transfer in lanthanide compounds [2]. In the first case, in the previous works the shielding factor $(1 - \sigma_1)$ has been overlooked. In the second case, the ion–ligand overlap has been considered through the shielding factor $(1 - \sigma_0)$ squared. However, the analysis developed in the above sections indicates that the correct form should involve $(4f^4 L^4)$ in place of $(1 - \sigma_0)^2$. This difference introduces a change of approximately three orders of magnitude in the calculated transfer rates by the exchange mechanism. Nevertheless, estimated ligand-to-ion energy transfer rates by this mechanism are still very fast, assuming values much higher than the typical intraconfigurational 4f–4f decay rates (radiative and non-radiative). This guarantees the validity of the overall conclusions reached in the previous works on the theoretical emission quantum yields of trivalent europium coordination compounds [2].

4. Numerical estimates

4.1. The ion–ion case

The aim here is to illustrate the critical aspects discussed in the previous sections, particularly the effect of shielding on the electric multipolar interaction and the overlap dependence of the exchange interaction, and to check their reliability in the evaluation of energy transfer rates. For the ion–ion case we have chosen a pair of trivalent ytterbium ions separated by a distance $R$. Even though in this case $4f^1$, as mentioned previously, the magnetic dipole–dipole interaction will not be taken into account. Fig. 3 shows the radial overlap integral between the 4f orbitals of the two ions as a function of $R$. This overlap, $S_{4f}$, has been calculated from the following expression:

$$S_{4f} = (4f^4 |4f_{\lambda})^2 = \sum_{\gamma \delta} S_{4f}.$$

where Greek letters now stand for the one-electron quantum number $m_l$ in the Slater-type spin-orbitals $|4f_{m_l}m_m>$. The calculations have been carried out with the ZINDO program.

The dipole–dipole, dipole–quadrupole and quadrupole–quadrupole transfer rates were calculated from Eqs. (5), (22), (23) and (24). The oscillator strength of the $4f^{10}2^2F_{7/2}$ to $4f^{10}2^2F_{5/2}$ transition in the Yb$^{3+}$ ion has the typical value of $3 \times 10^{-4}$. The parity allowed magnetic dipole contribution to this oscillator strength can be readily estimated to be $1.2 \times 10^{-6}$. If we assume that half of the remaining oscillator strength value is due to the forced electric dipole mech-

![Fig. 3. 4f-4f radial overlap integral, as a function of the distance $R$, calculated from Eq. (32). The individual overlap $S_\lambda$ have been calculated from the ZINDO program with Slater-type spin-orbitals.](image-url)
anism and the other half is due to the dynamic coupling mechanism, then we get $\sum \Omega_k \langle \psi^f \mid | \mathbf{J}^F \rangle \mid \psi \rangle \sim 1 \times 10^{-20}$ cm$^2$ [6]. The radial integral $(R^2) \sim 2 \times 10^{-17}$ cm$^2$, and the band width at half-height of the $^5\text{F}_{7/2} \rightarrow ^5\text{F}_{5/2}$ transition is typically of the order of $400$ cm$^{-1}$. The transfer rate due to the exchange mechanism was estimated from the crude approximation given in Eq. (15). The results are collected in Table 1 for $R = 3.0, 3.5$ and $4.0$ Å.

One may note the great difference with respect to the transfer rates (d–d, d–q and q–q) estimated without the shielding effect (values are given in parentheses). This difference is considerably accentuated for the dipole–dipole transfer rate. It is also noticeable that $\mathbf{L}^0$ for a distance $R > 4$ Å this transfer rate is totally negligible. Another interesting point is that overall the quadrupole–quadrupole mechanism dominates. For a distance $R = 3.0$ Å one finds $W_{d-d} = 3.2 \times 10^{-4}$, $W_{d-q} = 17 s^{-1}$ and $W_{q-q} = 1.6 \times 10^{-4}$ s$^{-1}$.

### Table 1

<table>
<thead>
<tr>
<th>$r$ (Å)</th>
<th>$W_{d-d}$</th>
<th>$W_{d-q}$</th>
<th>$W_{q-q}$</th>
<th>$W_{d-q}$ ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>$4.4 \times 10^4$</td>
<td>$2.6 \times 10^7$</td>
<td>$2.8 \times 10^7$</td>
<td>$2.9 \times 10^7$</td>
</tr>
<tr>
<td>3.5</td>
<td>$1.7 \times 10^4$</td>
<td>$7.5 \times 10^6$</td>
<td>$6.0 \times 10^6$</td>
<td>$1.0 \times 10^6$</td>
</tr>
<tr>
<td>4.0</td>
<td>$8.0 \times 10^4$</td>
<td>$2.6 \times 10^6$</td>
<td>$1.6 \times 10^6$</td>
<td>$55$</td>
</tr>
</tbody>
</table>

The values in parentheses correspond to the transfer rates without the shielding factors.

5. Concluding remarks

In lanthanide doped materials (crystals and glasses), when non-radiative energy transfer is operative, several situations that depend on the concentrations of donor and acceptor ions may occur. These situations have been discussed in the literature [9,10]. In general, the kinetics of the energy transfer process is conveniently treated by an appropriate system of rate equations and one is often involved with average energy transfer rates of the following form:

$$\langle W_{E T} \rangle = \int_{R_0}^{\infty} W_{E T}(R) G(R) / (4\pi R^2) \, dR,$$

where $G(R)$ is a donor (or acceptor) concentration dependent statistical function. Thus, knowing the dependence of $W_{E T}$ on the distance $R$, or knowing the relevant energy transfer mechanisms, is a point of crucial importance in describing the transfer kinetics. In this respect, the theoretical apparatus described in the above sections is certainly useful.

Not only is the functional dependence of $W_{E T}$ on $R$ of relevance but also its magnitude, particularly when the different mechanisms are competitive. One is then involved with estimates, as accurate as possible, of donor–acceptor distances, 4f radial integrals, forced electric dipole intensity parameters, shielding factors and 4f–4f donor–acceptor overlap integrals. In this context some points have been critically emphasized. The use of experimental $\Omega_k$ intensity parameters in Eqs. (22) and (23) would be an erroneous procedure, and the shielding effect due to the filled 5s and 5p sub-shells cannot be neglected in the direct Coulomb interaction when non-antisymmetrized wavefunctions for the donor–acceptor pair are used in the evaluation of matrix elements. In the case of the exchange interaction, the distance dependence of energy transfer rates goes beyond the one usually taken from Dexter’s formulation. Order of magnitude estimates suggest that the exchange mechanism becomes irrelevant for ion–ion distances larger than $4$ Å. We have proposed that more precise estimates of this mechanism, including selection rules, can be obtained from the effective exchange hamiltonian defined by the matrix element in Eq. (16).

This hamiltonian was used in the case of intramolecular energy transfer (ion–ligand transfer). Large differences in the calculated transfer rates with respect to previous calculations appear. However, since the transfer rates are still much higher than the intra-configuration 4f–4f decay rates, these differences will not change the overall conclusions previously obtained on emission quantum yields.

### Acknowledgements

The author is grateful to the CNPq (Brazilian Agency) and the IMMC and RENAMI (National Projects) for the support. He is also grateful to Mr Renaldo T. de Moura Jr. for the valuable help with the calculations of the 4f–4f radial overlaps.

### References


