A set of equations is derived which makes possible to study the radiative energy transfer process whereby the photons emitted by the energy donor are absorbed by the energy acceptor and so increase the efficiency of the overall energy transfer. It is shown that the coefficients describing the radiative transfer which appear in the expressions for the intensities of the energy donor and the energy acceptor are not the same, due to the fact that part of the fluorescence absorbed by the acceptor comes from radiation which is not detected as donor emission when there is no acceptor present. The general equations derived are applied to two particular cases commonly considered: measurements in reflection, where the fluorescence emission is observed from the same face of the absorption and measurements in transmission where the fluorescence emission is observed from the opposite face of the cell.

1. Introduction

It is well known [1,2] that in a binary liquid system containing two fluorescent molecules Y and Z it is possible to observe fluorescent emission from both species when the solution is excited with visible radiation of adequate energy, even when the optical density for absorption by one of the species is so low that it is valid to assume that all the excitation is absorbed by the other. This effect shows that an energy transfer process between an energy donor (which absorbs almost all the energy of excitation) and an energy acceptor is taking place.

This energy transfer process may be either radiative if photons are emitted by the energy donor and subsequently absorbed by the acceptor or nonradiative if it takes place without any emission followed by absorption.

That both processes may take place is widely accepted. The fact that radiative transfer is mainly important for solutions where the concentration of the energy acceptor is low and the quantum yield of the energy donor is high [3] has been used by several authors to choose the systems under study such as...
to avoid the corrections for radiative transfer. However this is not always possible and so it is necessary to distinguish between the two.

Except for a method based on the competition between the effect of quencher and the nonradiative energy transfer to the acceptor under study [4,5] the method that has been used implies the derivation of expressions describing the amount of energy that is emitted by the donor and absorbed by the acceptor in order to obtain, from the experimental results, the “corrected” energy transfer parameters, i.e. the quantities to be compared with the predictions of the theories for nonradiative energy transfer processes. These corrections depend on the geometrical conditions of observation and so different expressions have been presented by different authors. On the other hand the mathematical difficulties involved in the derivation of those expressions impose the use of approximations and so the different expressions are not always coincident.

It is the purpose of the present work to describe those corrections in a systematic way and to show how the expressions given by different authors can be compared. This is important since, as is known the agreement has not yet been reached as to what is the best description of the nonradiative energy transfer process [6].

2. The general case

Let us consider a binary liquid system where molecules Y (molar concentration $c_Y$) and molecules Z (molar concentration $c_Z$) are dissolved in an inert solvent (i.e. transparent to the exciting radiation). The solution is excited under stationary conditions, with monochromatic radiation (intensity $I_0$ Einstein $1^{-1}$ s$^{-1}$). At a first approximation it may be assumed that for the wavenumber of the exciting radiation ($\tilde{\nu}_{\text{exc}}$) the optical density of Y is such that all the energy is primarily absorbed by Y. This means that

$$\frac{\epsilon_Y(\tilde{\nu}_{\text{exc}})c_Y}{\epsilon_Y(\tilde{\nu}_{\text{exc}})c_Y + \epsilon_Z(\tilde{\nu}_{\text{exc}})c_Z} \approx 1, \quad (1)$$

$$\frac{\epsilon_Z(\tilde{\nu}_{\text{exc}})c_Z}{\epsilon_Y(\tilde{\nu}_{\text{exc}})c_Y + \epsilon_Z(\tilde{\nu}_{\text{exc}})c_Z} \approx 0, \quad (2)$$

where $\epsilon_Y(\tilde{\nu}_{\text{exc}})$ and $\epsilon_Z(\tilde{\nu}_{\text{exc}})$ are the molar extinction coefficients of Y and Z, respectively. Any emission from Z must be due, then, to an energy transfer from Y (the energy donor) to Z (the energy acceptor).

If this transfer is purely nonradiative, i.e., if the photons emitted by Y are not absorbed by Z, the intensities of Y emission observed at the wavenumber $\tilde{\nu}_{\text{em}}$ will be

$$I_Y(\tilde{\nu}_{\text{em}}, \tilde{\nu}_{\text{exc}}) = S(\tilde{\nu}_{\text{em}}, \tilde{\nu}_{\text{exc}})I_0(\tilde{\nu}_{\text{exc}})(1 - f_{\text{NR}, Y}^{N})q_Y. \quad (3)$$
where \( f_{ZY}^{NR} \) is the nonradiative energy transfer coefficient, defined as the fraction of excited Y molecules that transfer its energy to Z, \( q_Y \) is the quantum efficiency of the Y emission and \( S(\tilde{\nu}_{em}, \tilde{\nu}_{exc}) \) takes into account the solid angle of detection, the spectral form of the emission as well as the sensitivity of the detector for the wavenumber at which the emission is observed.

If it is the emission from Z (at wavenumber \( \tilde{\nu}_{em}^Z \)) that is detected, the following expression for the fluorescence intensity will apply

\[
I_Z(\tilde{\nu}_{em}^Z, \tilde{\nu}_{exc}) = S(\tilde{\nu}_{em}^Z, \tilde{\nu}_{exc}) I_0(\tilde{\nu}_{exc}) f_{ZY}^{NR} q_Z. \tag{4}
\]

where \( q_Z \) is the quantum efficiency of the Z emission, the factor \( S \) being different from the above because the emission is different.

If by analogy with \( f_{ZY}^{NR} \) we define a radiative energy transfer coefficient \( f_{ZY}^R \) as the fraction of excited Y molecules emitting at wavenumber \( \tilde{\nu}_{em}^Y \) that transfer its energy radiatively to Z, i.e. by emission from Y and subsequent absorption by Z, it seems logical to use the following expression for the intensity of the Y emission

\[
I_Y(\tilde{\nu}_{em}^Y, \tilde{\nu}_{exc}) = S(\tilde{\nu}_{em}^Y, \tilde{\nu}_{exc}) I_0(\tilde{\nu}_{exc}) (1 - f_{ZY}^{NR}) \left[ 1 - f_{ZY}^R(\tilde{\nu}_{em}^Y) \right] q_Y. \tag{5}
\]

On the other hand, the emission from Z will include, under the same assumptions, the contribution from the nonradiative transfer as well as the contribution from the radiative transfer, and so it seems possible to write

\[
I_Z(\tilde{\nu}_{em}^Z, \tilde{\nu}_{exc}) = S(\tilde{\nu}_{em}^Z, \tilde{\nu}_{exc}) I_0(\tilde{\nu}_{exc}) \left[ f_{ZY}^{NR} + f_{ZY}^R(\tilde{\nu}_{em}^Y) \right] q_Y. \tag{6}
\]

As a matter of fact, Z molecules will absorb radiation emitted from Y at different wavenumbers. This justifies (6), in which \( f_{ZY}^R \) refers to all of \( \tilde{\nu}_{em}^Y \) and so is different from \( f_{ZY}^R(\tilde{\nu}_{em}^Y) \) appearing in (5). The total number of photons from Y absorbed by Z will be converted into Z emission which will then be detected. The corresponding increase in the intensity relative to the case where there is no radiative transfer will obviously depend on the sensitivity of the detecting system for the particular wavenumber of the emitted radiation, the quantum efficiencies \( q_Z \) and \( q_Y \) for Z and Y emissions, the spectral overlap between the emission from Y and Z absorption and the solid angle of detection \([7,8]\). The mathematical complexity of the expressions involved on the description of this process justifies Birks' [9] assertion that "trivial" is an unfortunate choice of adjective for the radiative energy transfer process.

From these relationships others can be derived in which the shape of the emission or solid angle effects are explicitly considered. They have been used by a number of authors \([10-12]\) to assess the corrections for radiative transfer.

There is however an important fact that seems to have been overlooked in most of the papers published on this subject. Except in the case where all the light emitted by either Y or Z is collected the effect of the radiative transfer on
the emission intensity from Y due to absorption by Z is not described by the
same “energy transfer coefficient” as that describing the effect of this absorp-
tion upon the Z emission. This results from the fact that since Y emits in all
directions, some Y radiation not previously (in the absence of radiative
transfer) detected can be absorbed and then, because Z emission is also
emitted in all directions, is detected as Z emission.

In the following discussion two particular cases will be presented in which
these points will be clarified. In future publications experimental results for
both cases will be presented.

3. Measurements in reflection

Let us consider the experimental arrangement depicted in fig. 1. The excit-
ing radiation enters the cell containing the binary system Y, Z with an
incidence angle \( \alpha \). It will be assumed that the depth of penetration is \( x \). The
exciting radiation is then converted into Y radiation which is emitted in all
directions. However from the point of view of the detecting system it will be
assumed that the detectable radiation can be assimilated to a light ray leaving
the cell at an angle \( \beta \) after following an optical path \( y \). Obviously either \( y \) or \( \beta \)
represent average values, whose introduction has the advantage of making
calculations easier. In this sense it is also possible to define a coordinate \( z \) such
\[
z = x \sin \alpha = y \sin \beta.
\]  

The amount of radiation absorbed by Y in the interval \((x, x + dx)\) when Y
and Z are present at concentrations \( c_Y \) and \( c_Z \) is
\[
dI_Y(r_{exc}^z, x, x + dx) = \mu_Y(r_{exc}^z)c_YI_0(r_{exc}^z)\exp\left\{-\left[\mu_Y(r_{exc}^z)c_Y + \mu_Z(r_{exc}^z)c_Z\right]x\right\} dx.
\]  

Fig. 1. Measurements in reflection.
where the use of the molar absorptivities
\[ \mu_Y(\tilde{r}_{\text{exc}}) = 2.303 \epsilon_Y(\tilde{r}_{\text{exc}}), \]
\[ \mu_Z(\tilde{r}_{\text{exc}}) = 2.303 \epsilon_Z(\tilde{r}_{\text{exc}}), \]
is more advisable than the use of the molar extinctions coefficients \( \epsilon_Y \) and \( \epsilon_Z \) because the integrations are easier to perform in terms of exponentials than in terms of decadic coefficients.

The amount of radiation emitted by \( Y \) and detected at wavenumber \( \tilde{r}_{\text{em}} \) in the absence of radiative transfer and corresponding to the radiation absorbed in the interval \((x, x + dx)\) is
\[ dI_Y(\tilde{r}_{\text{exc}}, \tilde{r}_{\text{em}}; x, x + dx) = S(\tilde{r}_{\text{exc}}, \tilde{r}_{\text{em}}) \mu_Y(\tilde{r}_{\text{exc}}) I_0(\tilde{r}_{\text{exc}}) \]
\[ \times \Phi_Y \exp \left\{ - \left[ \mu_Y(\tilde{r}_{\text{exc}}) c_Y + \mu_Z(\tilde{r}_{\text{exc}}) c_Z \right] x \right\} \exp \left\{ - \mu_Z(\tilde{r}_{\text{em}}) c_Z y \right\} dx. \] (9)

To obtain the total amount of radiation from \( Y \) we have to integrate for all values of \( x \) and \( y \). Assuming that \( \beta \) is constant, which means that \( \beta \) represents the mean value of all the values of \( \beta \) corresponding to the different depths of penetration we may use (7) and evaluate the integral with the variable \( z \)
\[ I_Y(\tilde{r}_{\text{exc}}, \tilde{r}_{\text{em}}, \delta) = S(\tilde{r}_{\text{exc}}, \tilde{r}_{\text{em}}) \mu_Y(\tilde{r}_{\text{exc}}) c_Y I_0(\tilde{r}_{\text{exc}}) \]
\[ \times \Phi_Y \frac{1}{\sin \alpha} \int_0^\delta \sin \alpha \exp \left\{ - \frac{1}{\sin \alpha} \left[ \mu_Y(\tilde{r}_{\text{exc}}) c_Y + \mu_Z(\tilde{r}_{\text{exc}}) c_Z \right] \beta + \mu_Z(\tilde{r}_{\text{em}}) c_Z \alpha \right\} dz \] (11)

\( \delta \) being the optical path for the exciting radiation.

The result is easily obtained as
\[ I_Y(\tilde{r}_{\text{exc}}, \tilde{r}_{\text{em}}, \delta) = S(\tilde{r}_{\text{exc}}, \tilde{r}_{\text{em}}) I_0(\tilde{r}_{\text{exc}}) \Phi_Y \]
\[ \times \mu_Y(\tilde{r}_{\text{exc}}) c_Y \sin \beta \]
\[ \left[ \frac{\mu_Y(\tilde{r}_{\text{exc}}) c_Y + \mu_Z(\tilde{r}_{\text{exc}}) c_Z}{\sin \beta} + \mu_Z(\tilde{r}_{\text{em}}) c_Z \frac{\sin \alpha}{\sin \beta} \right] \left[ 1 - \exp \left\{ - \frac{1}{\sin \beta} \left[ \mu_Y(\tilde{r}_{\text{exc}}) c_Y + \mu_Z(\tilde{r}_{\text{exc}}) c_Z \sin \beta + \mu_Z(\tilde{r}_{\text{em}}) c_Z \sin \alpha \frac{\sin \alpha}{\sin \beta} \right] \frac{1}{\sin \beta} \right\} \right]. \] (12)
If almost all the radiation is absorbed in a very small thickness of the solution (concentrated solutions) we can assume that at a first approximation the exponential term is zero. Then

\[ I_\gamma(Y; \tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}}) = S(\tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}}; \alpha, \beta) \Phi(Q_{ZY}(\alpha, \beta; \tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}})), \]  

(13)

where

\[ Q_{ZY}(\alpha, \beta; \tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}}) = \frac{\mu_Y(\tilde{v}_{\text{exc}})c_Y \sin \beta}{[\mu_Y(\tilde{v}_{\text{exc}})c_Y + \mu_Z(\tilde{v}_{\text{exc}})c_Z] \sin \beta + \mu_Z(\tilde{v}_{\text{em}})c_Z \sin \alpha} \]  

(14)

is the correcting factor for the radiative energy transfer.

In the case where there is no absorption by Z of the radiation emitted by Y the factor \( Q_{ZY} \) reduces to

\[ Q_{ZY}(\alpha, \beta; \tilde{v}_{\text{exc}}) = \frac{\mu_Y(\tilde{v}_{\text{exc}})c_Y}{\mu_Y(\tilde{v}_{\text{exc}})c_Y + \mu_Z(\tilde{v}_{\text{exc}})c_Z}. \]  

(15)

which represents the fraction of Y molecules that absorb the exciting radiation (cf. eq. (1)). This important results shows that the factor \( Q_{ZY} \) given by (14) includes the effect of radiative energy transfer as well as the effect of absorption of the exciting radiation by Z. We could think that the true correcting factor for the radiative energy transfer only would be

\[ Q_{ZY}(\alpha, \beta; \tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}}) = Q_{ZY}(\alpha, \beta; \tilde{v}_{\text{exc}}), \]

(16)

The problem now is to decide what coefficient to use to correct the experimentally measured values of the Y emission intensity for the radiative energy transfer.

The experimental values \( I_Y \) are affected by the absorption from Z. Hence the correcting factor to be used is (14) and the value of the energy donor intensity corrected for both the radiative energy transfer and absorption by Z will be given by

\[ I_Y(\tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}}) = I_Y(Y; \tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}}) \frac{a(\tilde{v}_{\text{exc}}) + a'(\tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}})}{a(\tilde{v}_{\text{exc}})}. \]

(17)

where

\[ a(\tilde{v}_{\text{exc}}) = \mu_Y(\tilde{v}_{\text{exc}})c_Y \sin \beta, \]  

(18)

\[ a'(\tilde{v}_{\text{exc}}, \tilde{v}_{\text{em}}) = \left[ \mu_Z(\tilde{v}_{\text{exc}}) \sin \beta + \mu_Z(\tilde{v}_{\text{em}}) \sin \alpha \right] c_Z. \]  

(19)
The correcting factor (14) depends on the wavenumber of the Y emission, as would be expected. We can make use of this fact to obtain the nonradiative energy transfer coefficient. In fact, in the absence of energy acceptor the intensity of Y emission for a given wavenumber $\tilde{v}_{em}$ is

$$I_Y^0(\tilde{v}_{exc}, \tilde{v}_{em}) = S(\tilde{v}_{exc}, \tilde{v}_{em}) I_0(\tilde{v}_{exc}) \Phi_Y^0,$$

(20)

the factor $S$ being the same as that appearing in (13) if the concentration $c_Y$ is such that all the exciting radiation is absorbed in a small thickness of the solution (which incidently conforms with the assumption made to obtain (13). Hence

$$\frac{I_Y^0(\tilde{v}_{exc}, \tilde{v}_{em})}{I_Y^0(\tilde{v}_{exc}, \tilde{v}_{em})} = \frac{\Phi_Y}{\Phi_Y^0} \frac{a(\tilde{v}_{exc})}{a(\tilde{v}_{exc}) + a'(\tilde{v}_{exc}, \tilde{v}_{em})}.$$

(21)

This shows that if one plots $I_Y^0/I_Y^0$ versus $a/(a + a')$ for various wavenumbers of emission, a straight line will be obtained whose slope is $\Phi_Y/\Phi_Y^0$. Now it is known [2,13] that if Y does not form excimers

$$\Phi_Y/\Phi_Y^0 = 1 - f^\text{NR}_Y,$$

(22)

which shows that $f^\text{NR}_Y$ can easily be obtained from the measurement of the intensities of the Y emission for different wavenumbers of emission.

To the knowledge of the authors of the present work a systematic analysis of these equations has not yet been presented. However some of these equations have already been used by a number of authors. The use of the intensities observed for different wavenumbers of emission has been reported by Feitelson [14] and Kinka et al. [15] and as a particular case Marinari and Saltiel [16] proposed a method based on the use of two different wavelengths. Other contributions refer to different experimental arrangements and so different forms of (14) and (16) have been proposed [17-19].

### 4. Measurements in transmission

Let us now consider the case where the radiation emitted either by Y or by Z is detected from the face of the cell containing the solution opposite to that receiving the exciting radiation (measurements in transmission). We shall assume that the exciting beam of radiation will remain parallel when going through the solution. The radiation absorbed will be emitted as fluorescence of Y and fluorescence of Z in all directions. However we will neglect any solid angle effects and we will assume that the beam of fluorescence radiation is also parallel, and that 50% goes in the "positive" direction (towards the detector) while the remaining 50% goes in the "negative" direction (away from the detecting system) as depicted in the fig. 2.
In the absence of radiative energy transfer and for the case where almost all the exciting radiation is absorbed by Y, the detected intensities for Y and Z emission will be given, respectively, by

\[
I_Y = I_{Y,0} A_Y q_Y (1 - f_{ZY}^{NR}),
\]

\[
I_Z = I_{Z,0} A_Z q_Z f_{ZY}^{NR},
\]

where the factors \( A \) take into account the different sensitivities of the detecting system as well as the spectral distribution of the emission for each type of molecule and the particular wavenumber considered.

If there is radiative energy transfer from Y to Z this means that a fraction of the light emitted by Y will be absorbed by Z. The decrease in the observed intensity of the Y emission will depend on the number of Z molecules placed between the point of emission and the detecting system. However the increase in the intensity of the Z emission will correspond not only to this increase but also to the radiation emitted by Y in the “negative” direction, absorbed by Z and then emitted as Z emission in the “positive” direction. If we define an energy transfer coefficient \( a_{ZY}^+ \) for the “positive” direction and another energy transfer coefficient \( a_{ZY}^- \) for the “negative” direction the following relationships will apply

\[
I_Y^+ = 0.5 I_{Y,0} A_Y q_Y (1 - f_{ZY}^{NR}) \left[ 1 - a_{ZY}^+ \left( \tilde{r}_{exc}, \tilde{r}_{em} \right) \right],
\]

\[
I_Z^+ = 0.5 I_{Z,0} A_Z q_Z f_{ZY}^{NR} + 0.5 I_{Y,0} A_Y q_Y (1 - f_{ZY}^{NR}) a_{ZY}^+ \left( \tilde{r}_{exc} \right) \times 0.5 q_Z,
\]

\[
I_Y^- = 0.5 I_{Y,0} A_Y q_Y (1 - f_{ZY}^{NR}) \left[ 1 - a_{ZY}^- \left( \tilde{r}_{exc}, \tilde{r}_{em} \right) \right],
\]

\[
I_Z^- = 0.5 I_{Z,0} A_Z q_Z f_{ZY}^{NR} + 0.5 I_{Y,0} A_Y q_Y (1 - f_{ZY}^{NR}) a_{ZY}^- \left( \tilde{r}_{exc} \right) \times 0.5 q_Z.
\]

It must be noted that, as pointed out in sect. 2, the coefficient \( a_{ZY}^- \) which appears in \( I_Z^- \) is not the same as that appearing in \( I_Y^+ \). In the former case it is rather an average value since it is the complete overlap between Y emission and Z absorption that contributes to the overall energy transfer. In \( I_Y^+ \) the
reduction in intensity refers only to the wavenumber $\tilde{\nu}_{em}$ for which $I^I_Y$ is measured.

However, if instead of considering the radiation emitted by either Y or Z for a particular wavenumber we consider the total emission spectrum, we may use the average values and a fortiori an "integrated" $A$

$$I^I_Y(\tilde{\nu}_{exc}) = 0.5A_Y I_0(\tilde{\nu}_{exc})(1 - f_{zY}^{NR})q_Y\left[1 - a_{zY}(\tilde{\nu}_{exc})\right],$$  \hspace{1cm} (27)

$$I^I_Z(\tilde{\nu}_{exc}) = 0.5I_0(\tilde{\nu}_{exc})f_{zY}^{NR}q_Z$$

$$+ 0.25I_0(\tilde{\nu}_{exc})q_Y(1 - f_{zY}^{NR})a_{zY}(\tilde{\nu}_{exc})q_Z$$

$$+ 0.25I_0(\tilde{\nu}_{exc})q_Y(1 - f_{zY}^{NR})a_{zY}(\tilde{\nu}_{exc})q_ZA_Z.$$  \hspace{1cm} (28)

If it is possible to make

$$a_{zY}(\tilde{\nu}_{exc}) = a_{zY}(\tilde{\nu}_{exc}) = a_{zY},$$  \hspace{1cm} (29)

we may write

$$I^I_Y(\tilde{\nu}_{exc}) = 0.5A_Y I_0(\tilde{\nu}_{exc})(1 - f_{zY}^{NR})q_Y(1 - a_{zY}),$$  \hspace{1cm} (30)

$$I^I_Z(\tilde{\nu}_{exc}) = 0.5A_Z I_0(\tilde{\nu}_{exc})q_Z\left[f_{zY}^{NR} + (1 - f_{zY}^{NR})a_{zY}q_Y\right],$$  \hspace{1cm} (31)

which are the relationships presented by Birks [11]. However, as it is shown later the values of $a_{zY}$ and $a_{zY}$ depend on the optical path of the radiation and then are not likely to be equal.

Actually, under the approximations already referred to it is easy to evaluate these quantities. Assuming that all radiation is absorbed by Y, ($\mu_Z(\tilde{\nu}_{exc}) \approx 0$), the intensity of Y emission which is detected from the radiation absorbed in the interval $(x, x + dx)$ is (see fig. 2)

$$dI^I_Y(\tilde{\nu}_{em}, x, x + dx) = A(\tilde{\nu}_{em}) \times 0.5I_0(\tilde{\nu}_{exc})\mu_Y(\tilde{\nu}_{exc})c_Y$$

$$\times \exp\left\{ - (\mu_Y(\tilde{\nu}_{exc})c_Y)x \right\}(1 - f_{zY}^{NR})q_Y dx$$

$$\times \left[1 - \int_0^{f_{zY}^{NR}} \mu_Z(\tilde{\nu}_{em})c_Z \exp\left\{ - \mu_Z(\tilde{\nu}_{em})c_Z y \right\} dy \right].$$  \hspace{1cm} (32)

Now to obtain the intensity of Y emission detected we have to integrate (32) from 0 to $l$.

$$I^I_Y(\tilde{\nu}_{em}) = 0.5I_0(\tilde{\nu}_{exc})A(\tilde{\nu}_{em})(1 - f_{zY}^{NR})q_Y\frac{\mu_Y(\tilde{\nu}_{exc})c_Y}{\mu_Y(\tilde{\nu}_{exc})c_Y - \mu_Z(\tilde{\nu}_{em})c_Z}$$

$$\times \exp\left\{ - \mu_Z(\tilde{\nu}_{em})c_Zl \right\}\left[1 - \exp\left\{ - (\mu_Y(\tilde{\nu}_{exc})c_Y - \mu_Z(\tilde{\nu}_{em})c_Z)l \right\}\right].$$  \hspace{1cm} (33)
then
\[
a_{ZY}(\tilde{r}_{exc}, \tilde{r}_{em}) = 1 - \frac{\mu_Y(\tilde{r}_{exc})c_Y \exp\{ - \mu_Z(\tilde{r}_{em})c_Z \}}{\mu_Y(\tilde{r}_{exc})c_Y - \mu_Z(\tilde{r}_{em})c_Z}
\times \left[ 1 - \exp\{ - (\mu_Y(\tilde{r}_{exc})c_Y - \mu_Z(\tilde{r}_{em})c_Z)l \} \right].
\] (34)

To obtain the coefficient for the radiative transfer in the “positive” direction corresponding to all the wavenumbers of Y emission it is necessary to integrate over all emission. Since there is no analytical dependence on wavenumber for the molar absorptivity the integration must be carried out numerically. To avoid the use of a cumbersome expression we may define a mean value in terms of the molecular intensities \( F_Y(\tilde{r}_{em}) \)

\[
\mu_Z = \frac{\int_Y F_Y(\tilde{r}_{em}) \mu_Z(\tilde{r}_{em}) \, d\tilde{r}_{em}}{\int_Y F_Y(\tilde{r}_{em}) \, d\tilde{r}_{em}}.
\] (35)

Then
\[
a_{ZY}^+(\tilde{r}_{exc}) = 1 - \frac{\mu_Y(\tilde{r}_{exc})c_Y}{\mu_Y(\tilde{r}_{exc})c_Y - \mu_Zc_Z}
\exp\{ - \mu_Zc_Zl \}
\times \left[ 1 - \exp\{ - (\mu_Y(\tilde{r}_{exc})c_Y - \mu_Zc_Z)l \} \right].
\] (36)

The same expression can obviously be obtained if we consider the value of the intensity of the emission from Z. Assuming that all radiation is absorbed by Y, the intensity of Z emission which is detected as a result of transfer from Y molecules absorbing the exciting radiation in the interval \((x, x + dx)\)

\[
dI_Z(\tilde{r}_{em}, x, x + dx) = 0.5I_0(\tilde{r}_{exc})A(\tilde{r}_{em})q_Zf_{ZY}^{NR}
+ 0.5I_0(\tilde{r}_{exc})A(\tilde{r}_{em})q_Z\left[ 0.5(1 - f_{ZY}^{NR}) \right.
\times \mu_Y(\tilde{r}_{exc})c_Y \exp\{ - \mu_Y(\tilde{r}_{exc})c_Yx \} \int_0^{x} \mu_Zc_Z \exp( - \mu_Zc_Zy ) \, dy \, dx
\left. + 0.5(1 - f_{ZY}^{NR})q_Y\mu_Y(\tilde{r}_{exc})c_Y \exp\{ - \mu_Y(\tilde{r}_{exc})c_Yx \}
\times \left[ \int_0^x \mu_Zc_Z \exp( - \mu_Zc_Zy ) \, dy \right] \, dx \right].
\] (37)

The expression for the total intensity can be found if we integrate the variable \(x\) between 0 and \(l\). Then it is easy to obtain

\[
a_{ZY}^+ = 1 - \frac{\mu_Y(\tilde{r}_{exc})c_Y}{\mu_Y(\tilde{r}_{exc})c_Y - \mu_Zc_Z}
\exp\{ - \mu_Zc_Zl \}
\times \left[ 1 - \exp\{ - (\mu_Y(\tilde{r}_{exc})c_Y - \mu_Zc_Z)l \} \right].
\] (38)
\[ a_{ZY} = 1 - \frac{\mu_Y(\tilde{r}_{exc})c_Y}{\mu_Y(\tilde{r}_{exc})c_Y + \tilde{\mu}_Z c_Z} \left[ 1 - \exp\left\{ - \left( \mu_Y(\tilde{r}_{exc})c_Y + \tilde{\mu}_Z c_Z \right)l \right\} \right], \]  

which is in agreement with (36) and shows, once again, that the contribution for the radiative transfer that appears in the expression for the intensity of the Y emission is not the same as that appearing in the expression giving the emission from the acceptor.

5. Conclusions

For two different cases expressions have been deduced that describe the effect of radiative transfer on the fluorescence intensities of either the energy donor or the energy acceptor. It is obviously possible to generalize these equations to other cases but the complexities involved are quite evident from the equations presented in this work. It is worth noting that for some cases the corrections may be more important than it has been assumed in a number of published papers. This is easily proved if calculations are made based on the relationships presented here. It is the belief of the present authors that some of the results already published for nonradiative energy transfer efficiencies must be re-evaluated, namely those obtained under conditions where the contribution of radiative transfer is large and the analysis is based on the emission from the energy acceptor.

When the energy donor is an excimer-forming molecule it may be necessary to define an energy transfer coefficient for radiative transfer from the monomer and another for the excimer, since the overlap integral between the emission from these species and the absorption from the acceptor is different.

If on the other hand dilute solutions are used, it will be the definition of optical paths that becomes difficult. And then the integrations that are necessary to obtain the radiative energy transfer will be quite cumbersome. For concentrated solutions the problem may be further complicated if energy migration among the energy donor molecules takes place. An interesting contribution from Lavorel [20] demonstrates this fact.

It may be argued that here again, if one wants to study the nonradiative energy transfer process the best way would be to study the cases where the radiative transfer is unimportant. It is the belief of the present authors that this is seldom the case. Even for samples with a very small thickness the contribution of radiative transfer may be large, mainly if the quantum yield of the energy donor is high and the concentration of its energy acceptor is large (since the amount absorbed will be large too).

If the first aspect depends on the system chosen, the use of high concentrations may be necessary to obtain high transfer efficiencies. All this means that for some important cases it will actually be necessary to correct for the radiative energy transfer.
In future publications it will be shown how these corrections can be applied to specific cases.

References


Note added in proof

The expressions derived here do not take into account the effect of refractive index. This will be included in future publications.