



ENERGY TRANSFER IN TERNARY SYSTEMS: THE GENERAL EQUATIONS FOR NON-RADIATIVE TRANSFER UNDER STEADY-STATE CONDITIONS OF EXCITATION

J. C. CONTE

Núcleo de Química Física Molecular
Comissão de Estudos de Energia Nuclear (I.A.C.)
Instituto Superior Técnico
Lisboa-I

A general set of equations describing the non-radiative energy transfer process, under steady-state conditions of excitation, in a ternary system where all the molecules concerned are able to form excimers, is derived. It is shown the equations used by different authors can be obtained from the equations derived here. The problem of the transfer among excimer forming molecules where excimer formation has been neglected when the rate constants were evaluated is discussed. Some new particular cases and results are presented.

1 — INTRODUCTION

When a solution containing fluorescent molecules is excited with u. v. radiation of a given wavelength, the energy which reappears as light seldom has the same wavelength. This shows that some energy transfer processes have probably occurred. These energy transfer processes can be either intramolecular, the molecules which are initially excited undergoing non-radiative de-excitation processes before they emit, or intermolecular, if the light is emitted by a different molecule. The intermolecular process can be either radiative, if it involves the emission and reabsorption of photons, or non-radiative.

In recent years, considerable attention has been given to the non-radiative energy transfer process between molecules of different kind in solution (1) (2) (3). This problem, which has a bearing on scintillation studies (4) (5) (6), has its origin on the fact that it is experimentally found (7) (8) (9) that if a solution contains two fluorescent molecules X and Y, the first excited singlet state of Y being lower than that of X, it is possible to observe the fluorescence emission characteristic of Y, even when the optical density of X is much greater than that of Y, for the wavelength of the radiation used to excite the solutions. This shows that some of the initially excited X molecules are able to transfer their energy to Y molecules.

FÖRSTER'S theory resonance transfer (10) (11) has usually been invoked to describe this process, when it occurs non-radiatively. However, the rate constants for transfer, as found experimentally, are in most cases greater than those predicted by the theory (12) (13) (14). This has led to the suggestion (15) that energy migration among energy donor molecules and material diffusion of both energy donor and energy acceptor molecules can contribute to an increase of the transfer rates as compared with the theoretical predictions based only on Förster's theory. Accordingly, theoretical approaches have been presented, either introducing modifications into Förster's theory (16) (17) (14) or including into the diffusion equation the effect of energy migration (18) (19) (20) and Förster's resonance transfer (18) (21). In some cases, decay time measurements (22) (23) and the derivation of equations describing the variation of the emission inten-

sities with time following excitation by a flash (24) (25) have been used with advantage to assess the validity of the theory to be applied to each particular case, either coupled with steady state intensity measurements (24) (26) (27) or not (23) (28) (29). Experimentally, the systems used to study this problem have been, in most cases, only binary systems, in which only an energy donor and an energy acceptor are present (9) (21), although sometimes both are dissolved in a transparent solvent (12) (14). Ternary systems have been used in some cases, mainly in connection with scintillation studies, the solution being excited with ionizing radiation (30) (31) (32). For each case, the appropriate kinetic schemes were presented, and used as the basis for the analysis of the results, and ultimately for the evaluation of the transfer rate constants. Where any of the fluorescent molecules present in the system can form excimers, the kinetic scheme, and hence the analysis of the results, is more elaborated (33) (26) (34). However, if the consideration of excimers has any relation with the energy migration process, as it has been suggested in recent publications (35) (36) than the study of energy transfer processes involving excimer forming molecules may be of considerable interest. Furthermore, recently published work presents conflicting views on the contribution of excimers for the energy transfer process (35) (36) (37).

It is the purpose of this work to present a general kinetic scheme for the non-radiative energy transfer process under steady-state conditions of excitation in a ternary system where all the molecules concerned are able to form excimers. It will be shown that the equations used by different authors can be obtained from the general equations derived here. Since some studies have been presented involving excimer forming molecules, although excimer formation has been neglected in the analysis of the results, it will be shown what is the actual meaning of the constants evaluated using the simplified kinetic scheme in which excimer formation is not taken into account. The application of the general equations to some particular cases together with some experimental results obtained in this laboratory will be presented. The experimental techniques used for these studies have already been described in previous publications (38) (39).

2 — DERIVATION OF THE GENERAL EQUATIONS

2.1 — GENERAL CONSIDERATIONS

Let us consider a ternary system, containing a solvent X (molar concentration c_X) a primary solute Y (molar concentration c_Y) and a secondary solute Z (molar concentration c_Z). A «inert» solvent (transparent to the exciting radiation), may be added, in order to vary c_X , which, otherwise, is the concentration corresponding to X in pure liquid form. We shall consider the general case where X, Y and Z form excimers, due to the interaction between an excited molecule in its first excited singlet state and a molecule of the same kind in the ground state.

If the energies of the lowest excited monomer singlet states (E_1) decrease in the order $E_{1X} > E_{1Y} > E_{1Z}$, then when solvent molecules are excited they can transfer their energy to the primary solute molecules ($X \rightarrow Y$ transfer) and the latter can transfer their energy to the secondary solute molecules ($Y \rightarrow Z$ transfer). Direct $X \rightarrow Z$ transfer must also be taken into account (34) which means that the intensity of Z emission when X is excited will depend on the $X \rightarrow Z$ and $X \rightarrow Y \rightarrow Z$ transfer processes, occurring simultaneously. Since excimers are dissociated in the ground state, direct excitation to the excimer state (either due to direct absorption of the exciting light (40) or to non-radiative transfer (38) has not to be considered.

In the derivation of the general equations for the intensities of monomer and excimer emission of X, Y, Z, we shall assume that the solutions are excited, under steady state conditions of excitation, with ultraviolet radiation of intensity I_0 (expressed in Einstein. s^{-1}) and that, for the concentrations c_X , c_Y , c_Z used it is possible to consider separately the following cases of excitation:

- a) Z excitation — only secondary solute molecules (Z) are initially excited.
- b) Y excitation — only primary solute molecules (Y) are initially excited, direct absorption of the exciting radiation by Z being negligible.
- c) X excitation — only solvent molecules (X) are initially excited, direct absorption of the exciting radiation by either Y or Z being negligible.

Solvent excitation in cases *a*) and *b*) primary solute excitation in case *a*) does not need to be considered, if the first excited singlet states S_{1X} , S_{1Y} , S_{1Z} are well separated. We shall consider this to be the case. Radiative energy transfer will be neglected. Correction for this transfer as well as for any absorption by X in cases *a*) and *b*) and by Y in cases *a*) will be deferred to a later publication.

The reactions that can take place when the solutions are excited with light of the appropriate wavelength are indicated in table I. It is assumed that X and molecules have no quenching effect upon excited Z molecules and that X molecules do not quench excited Y and Z molecules.

2.2 — Z EXCITATION

When the solutions do not contain oxygen, only reactions 2 and 22 to 27 have to be considered, with $k_{OZ} = 1$. Under steady state conditions of excitation with u.v. radiation of intensity I_o^Z , the intensities of monomer (ξ_{MZ}) and excimer (ξ_{DZ}) secondary solute emission will be given by

$$\xi_{MZ} = \frac{c_{hZ}}{c_{hZ} + c_Z} q_{MZ} I_o^Z \quad (1)$$

$$\xi_{DZ} = \frac{c_Z}{c_{hZ} + c_Z} q_{DZ} I_o^Z \quad (2)$$

where

$$q_{MZ} = \frac{k_{fMZ}}{k_{fMZ} + k_{iMZ}} \equiv \frac{k_{fMZ}}{k_{MZ}} \quad (3)$$

and

$$q_{DZ} = \frac{k_{fDZ}}{k_{fDZ} + k_{iDZ}} \equiv \frac{k_{fDZ}}{k_{DZ}} \quad (4)$$

are the quantum efficiencies of monomer and excimer secondary solute emissions, respectively, and

$$c_{hZ} = \frac{k_{MZ} (k_{DZ} + k_{MDZ})}{k_{DZ} k_{DMZ}} \quad (5)$$

is the half-value concentration (14) for the monomer-excimer Z emission (i. e., the concentration c_Z

for which the quantum yield of monomer emission is half of the yield at infinite dilution and the quantum yield of excimer emission is half of the yield at infinite concentration).

When the solutions contain oxygen at concentration $[O_2]$, reactions 32 and 33 from table I must also be considered. Defining the quantities

$$\gamma'_{MZ} = \frac{k'_{MZ}}{k_{MZ}} \quad (6)$$

$$\gamma'_{DZ} = \frac{k'_{DZ}}{k_{DZ}} \quad (7)$$

$$\gamma'_{MDZ} = \frac{k'_{DZ}}{k_{DZ} + k_{MDZ}} \quad (8)$$

it is easy to see that under the same conditions of excitation the intensities of monomer (ξ'_{MZ}) and excimer (ξ'_{DZ}) secondary solute emission are given by

$$\xi'_{MZ} = \frac{c'_{hZ}}{c'_{hZ} + c_Z} q'_{MZ} I_o^Z \quad (9)$$

$$\xi'_{DZ} = \frac{c_Z}{c'_{hZ} + c_Z} q'_{DZ} I_o^Z \quad (10)$$

where the quantum efficiencies of monomer (q'_{MZ}) and excimer (q'_{DZ}) emission are

$$q'_{MZ} = \frac{q_{MZ}}{1 + \gamma'_{MZ} [O_2]} \quad (11)$$

$$q'_{DZ} = \frac{q_{DZ}}{1 + \gamma'_{DZ} [O_2]} \quad (12)$$

and the half-value concentration c'_{hZ} is now

$$c'_{hZ} = c_{hZ} \frac{1 + \gamma'_{MZ} [O_2]}{1 + \gamma'_{DZ} [O_2]} (1 + \gamma'_{MDZ} [O_2]) \quad (13)$$

Obviously these equations can be applied if the solutions contain a quenching agent other than oxygen, provided the quenching effect can be described by reactions similar to 32 and 33.

2.3 — Y EXCITATION

For deoxygenated solutions, reactions 2 and 14 to 27 of table I must now be taken into account,

Table I

Reaction	Rate (s ⁻¹)	Process
(1) $M_X \rightarrow M_X^*$	k_{OX}	solvent (X) excitation
(2) $M_Y \rightarrow M_Y^*$	k_{OY}	primary solute (Y) excitation
(3) $M_Z \rightarrow M_Z^*$	k_{OZ}	secondary solute (Z) excitation
(4) $M_X^* \rightarrow M_X + h\nu_{MX}$	k_{fMX}	monomer emission (X)
(5) $M_X^* \rightarrow M_X$	k_{iMX}	monomer intramolecular radiationless deactivation (X)
(6) $M_X^* + M_X \rightarrow D_X^*$	$k_{DMX}c_X$	excimer formation (X)
(7) $M_X^* \rightarrow M_X^* + M_X$	k_{MDX}	excimer dissociation (X)
(8) $D_X^* \rightarrow M_X + M_X + h\nu_{DX}$	k_{fDX}	excimer emission (X)
(9) $D_X^* \rightarrow M_X + M_X$	k_{iDX}	excimer intramolecular radiationless deactivation (X)
(10) $M_X^* + M_Y \rightarrow M_X + M_Y^*$	$k_{YX}^m c_Y$	X \rightarrow Y transfer (from the solvent monomer)
(11) $D_X^* + M_Y \rightarrow M_X + M_X + M_Y^*$	$k_{YX}^d c_Y$	X \rightarrow Y transfer (from the solvent excimer)
(12) $M_X^* + M_Z \rightarrow M_X + M_Z^*$	$k_{ZX}^m c_Z$	X \rightarrow Z transfer (from the solvent monomer)
(13) $D_X^* + M_Z \rightarrow M_X + M_X + M_Z^*$	$k_{ZX}^d c_Z$	X \rightarrow Z transfer (from the solvent excimer)
(14) $M_Y^* \rightarrow M_Y + h\nu_{MY}$	k_{fMY}	monomer emission (Y)
(15) $M_Y^* \rightarrow M_Y$	k_{iMY}	monomer intramolecular radiationless deactivation (Y)
(16) $M_Y^* + M_Y \rightarrow D_Y^*$	$k_{DMY}c_Y$	excimer formation (Y)
(17) $D_Y^* \rightarrow M_Y^* + M_Y$	k_{MDY}	excimer dissociation (Y)
(18) $D_Y^* \rightarrow M_Y + M_Y + h\nu_{DY}$	k_{fDY}	excimer emission (Y)
(19) $D_Y^* \rightarrow M_Y + M_Y$	k_{iDY}	excimer intramolecular radiationless deactivation (Y)
(20) $M_Y^* + M_Z \rightarrow M_Y + M_Z$	$k_{ZY}^m c_Z$	Y \rightarrow Z transfer (from the primary solute monomer)
(21) $D_Y^* + M_Z \rightarrow M_Y + M_Y + M_Z^*$	$k_{ZY}^d c_Z$	Y \rightarrow Z transfer (from the primary monomer excimer)
(22) $M_Z^* \rightarrow M_Z + h\nu_{MZ}$	k_{fMZ}	monomer emission (Z)
(23) $M_Z^* \rightarrow M_Z$	k_{iMZ}	monomer intramolecular radiationless deactivation (Z)
(24) $M_Z^* + M_Z \rightarrow D_Z^*$	$k_{DMZ}c_Z$	excimer formation (Z)
(25) $D_Z^* \rightarrow M_Z^* + M_Z$	k_{MDZ}	excimer dissociation (Z)
(26) $D_Z^* \rightarrow M_Z + M_Z + h\nu_{DZ}$	k_{fDZ}	excimer emission (Z)
(27) $D_Z^* \rightarrow M_Z + M_Z$	k_{iDZ}	excimer intramolecular radiationless deactivation (Z)
(28) $M_X^* + [O_2] \rightarrow M_X$	k'_{MX}	monomer oxygen quenching (X)
(29) $D_X^* + [O_2] \rightarrow M_X + M_X$	k'_{DX}	excimer oxygen quenching (X)
(30) $M_Y^* + [O_2] \rightarrow M_Y$	k'_{MY}	monomer oxygen quenching (Y)
(31) $D_Y^* + [O_2] \rightarrow M_Y + M_Y$	k'_{DY}	excimer oxygen quenching (Y)
(32) $M_Z^* + [O_2] \rightarrow M_Z$	k'_{MZ}	monomer oxygen quenching (Z)
(33) $D_Z^* + [O_2] \rightarrow M_Z + M_Z$	k'_{DZ}	excimer oxygen quenching (Z)

with $k_{oY} = 1$. Under steady state conditions of excitation with u.v. radiation of intensity I_o^Y , the intensities of monomer (η_{MY}) and excimer (η_{DY}) primary solute emission, and monomer (η_{MZ}) and excimer (η_{DZ}) secondary solute emission will be given by

$$\eta_{MY} = \frac{\Gamma_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} q_{MY} I_o^Y \quad (14)$$

$$\eta_{DY} = \frac{c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} q_{oY} I_o^Y \quad (15)$$

$$\eta_{MZ} = \frac{\sigma_{ZY}^m c_Z \Gamma_Y + \sigma_{ZY}^d c_Z c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \frac{c_{hZ}}{c_{hZ} + c_Z} q_{MZ} I_o^Y \quad (16)$$

$$\eta_{DZ} = \frac{\sigma_{ZY}^m c_Z \Gamma_Y + \sigma_{ZY}^d c_Z c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \frac{c_Z}{c_{hZ} + c_Z} q_{DZ} I_o^Y \quad (17)$$

where

$$q_{MY} = \frac{k_{fMY}}{k_{fMY} + k_{iMY}} \equiv \frac{k_{fMY}}{k_{MY}} \quad (18)$$

$$q_{DY} = \frac{k_{fDY}}{k_{fDY} + k_{iDY}} \equiv \frac{k_{fDY}}{k_{DY}} \quad (19)$$

are the quantum efficiencies of monomer and excimer primary solute emissions, respectively,

$$\sigma_{ZY}^m = \frac{k_{ZY}^m}{k_{MY}} \quad (20)$$

$$\sigma_{ZY}^d = \frac{k_{ZY}^d}{k_{DY}} \quad (21)$$

are the «Stern-Volmer constants» for the monomer and excimer $Y \rightarrow Z$ transfer, respectively, and

$$\Gamma_Y = c_{hY} (1 + \gamma_Y \sigma_{ZY}^d c_Z) \quad (22)$$

where

$$c_{hY} = \frac{k_{MY}(k_{DY} + k_{MDY})}{k_{DY} k_{DMY}} \quad (23)$$

is the half-value concentration for monomer-excimer Y emission and

$$\gamma_Y = \frac{k_{DY}}{k_{DY} + k_{MDY}} \quad (24)$$

Comparing equations 1, 2, 16 and 17 it is easily seen that the quantity

$$F_{ZY} = \frac{\sigma_{ZY}^m c_Z \Gamma_Y + \sigma_{ZY}^d c_Z c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \quad (25)$$

represents the fraction of excited Y molecules (either monomer or excimer) which transfer their energy to Z. Then it may be called the energy transfer coefficient for $Y \rightarrow Z$ transfer.

When the solution contains oxygen, reactions 30 to 33 from table I must also be taken into account. By analogy with 6, 7 and 8 we may define

$$\chi'_{MY} = \frac{k'_{MY}}{k_{MY}} \quad (26)$$

$$\chi'_{DY} = \frac{k'_{DY}}{k_{DY}} \quad (27)$$

$$\chi'_{MDY} = \frac{k'_{DY}}{k_{DY} + k_{MDY}} \quad (28)$$

The intensities of monomer (η'_{MY}) and excimer (η'_{DY}) primary solute emission and of monomer (η'_{MZ}) and excimer (η'_{DZ}) secondary solute emission are given by

$$\eta'_{MY} = \frac{\Gamma_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} q'_{MY} I_o^Y \quad (29)$$

$$\eta'_{DY} = \frac{c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} q'_{DY} I_o^Y \quad (30)$$

$$\eta'_{MZ} = \frac{\sigma'_{ZY}c_Z\Gamma'_Y + \sigma'_{ZY}c_Zc_Y}{(1 + \sigma'_{ZY}c_Z)\Gamma'_Y + (1 + \sigma'_{ZY}c_Z)c_Y} \cdot \frac{c'_{hZ}}{c'_{hZ} + c_Z} q'_{MZ}I_o^Y \quad (31)$$

$$\eta'_{DY} = \frac{\sigma'_{ZY}c_Z\Gamma'_Y + \sigma'_{ZY}c_Zc_Y}{(1 + \sigma'_{ZY}c_Z)\Gamma'_Y + (1 + \sigma'_{ZY}c_Z)c_Y} \cdot \frac{c_Z}{c'_{hZ} + c_Z} q'_{DZ}I_o^Y \quad (32)$$

where

$$\sigma'_{ZY} = \frac{\sigma_{ZY}^m}{1 + \chi'_{MY}[O_2]} \quad (33)$$

$$\sigma'_{ZY} = \frac{\sigma_{ZY}^d}{1 + \chi'_{DY}[O_2]} \quad (34)$$

are the Stern-Volmer constants for monomer and excimer $Y \rightarrow Z$ transfer, respectively.

$$q_{MY} = \frac{q_{MY}}{1 + \chi'_{MY}[O_2]} \quad (35)$$

$$q'_{DY} = \frac{q_{DY}}{1 + \chi'_{DY}[O_2]} \quad (36)$$

are the quantum efficiencies of monomer and excimer primary solute emissions in the presence of

oxygen, respectively, and

$$\Gamma'_Y = c'_{hY}(1 + \gamma'_Y\sigma'_{ZY}c_Z) \quad (37)$$

with

$$c'_{hY} = c_{hY} \frac{1 + \chi'_{MY}[O_2]}{1 + \chi'_{DY}[O_2]} (1 + \chi'_{MDY}[O_2]) \quad (38)$$

$$\gamma'_Y = \gamma_Y \frac{1 + \chi'_{DY}[O_2]}{1 + \chi'_{MDY}[O_2]} \quad (39)$$

The energy transfer coefficient for $Y \rightarrow Z$ transfer in the presence of oxygen will be given by

$$F_{YZ} = \frac{\sigma'_{ZY}c_Z\Gamma'_Y + \sigma'_{ZY}c_Zc_Y}{1 + \sigma'_{ZY}c_Z\Gamma'_Y + (1 + \sigma'_{ZY}c_Z)c_Y} \quad (40)$$

2.4 — X EXCITATION

If we consider now that the solution is excited with u.v. radiation of intensity I_o^X , and that there is no oxygen present, reactions 1 and 4 to 27 in Table I must be considered, with $k_{oX} = 1$. Then a steady state analysis leads to the following expressions for the intensities of monomer (ξ_{MX}) and excimer (ξ_{DX}) solvent emission, monomer (ξ_{MY}) and excimer (ξ_{DY}) primary solute emission, monomer (ξ_{MZ}) and excimer (ξ_{DZ}) secondary solute emission

$$\xi_{MX} = \frac{\Gamma_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)\Gamma_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} q_{MX}I_o^Y \quad (41)$$

$$\xi_{DX} = \frac{c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)\Gamma_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} q_{DX}I_o^X \quad (42)$$

$$\xi_{MY} = \frac{\sigma'_{YX}c_Y\Gamma_X + \sigma'_{YX}c_Yc_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)\Gamma_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} \times \frac{\Gamma_Y}{(1 + \sigma'_{ZY}c_Z)\Gamma_Y + (1 + \sigma'_{ZY}c_Z)c_Y} q_{MY}I_o^X \quad (43)$$

$$\zeta_{DY} = \frac{\sigma_{YX}^m c_Y \Gamma_X + \sigma_{YX}^d c_Y c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \times \frac{c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} q_{DY} I_O^X \quad (44)$$

$$\zeta_{MZ} = \frac{\sigma_{YX}^m c_Y \Gamma_X + \sigma_{YX}^d c_Y c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \times \frac{\sigma_{ZY}^m c_Z \Gamma_Y + \sigma_{ZY}^d c_Z c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \\ + \frac{c_{hZ}}{c_{hZ} + c_Z} q_{MZ} I_O^X + \frac{\sigma_{ZX}^m c_Z \Gamma_X + \sigma_{ZX}^d c_Z c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \frac{c_{hZ}}{c_{hZ} + c_Z} q_{MZ} I_O^Y \quad (45)$$

$$\zeta_{DZ} = \frac{\sigma_{YX}^m c_Y \Gamma_X + \sigma_{YX}^d c_Y c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \times \frac{\sigma_{ZY}^m c_Z \Gamma_Y + \sigma_{ZY}^d c_Z c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \\ + \frac{c_Z}{c_{hZ} + c_Z} q_{DZ} I_O^X + \frac{\sigma_{ZX}^m c_Z \Gamma_X + \sigma_{ZX}^d c_Z c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \frac{c_Z}{c_{hZ} + c_Z} q_{DZ} I_O^Y \quad (46)$$

where

$$q_{MX} = \frac{k_{fMX}}{k_{fMX} + k_{iMX}} \equiv \frac{k_{fDX}}{k_{MX}} \quad (47)$$

and

$$q_{DX} = \frac{k_{fDX}}{k_{fDX} + k_{iDX}} \equiv \frac{k_{fDX}}{k_{DX}} \quad (48)$$

are the quantum efficiencies of monomer and excimer solvent emissions, respectively,

$$\sigma_{YX}^m = \frac{k_{YX}^m}{k_{MX}} \quad (49)$$

$$\sigma_{YX}^d = \frac{k_{YX}^d}{k_{DX}} \quad (50)$$

are the Ster-Volmer constants for the monomer and excimer $X \rightarrow Y$ transfer, respectively,

$$\sigma_{ZX}^m = \frac{k_{ZX}^m}{k_{MX}} \quad (51)$$

$$\sigma_{ZX}^d = \frac{k_{ZX}^d}{k_{DX}} \quad (52)$$

are the Stern-Volmer constants for the monomer and excimer $X \rightarrow Z$ transfer, respectively, and

$$\Gamma_X = c_{hX} [1 + \gamma_X (\sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z)] \quad (53)$$

where

$$c_{hX} = \frac{k_{MX}(k_{DX} + k_{MDX})}{k_{DX} k_{DMX}} \quad (54)$$

is the half-value concentration for monomer and excimer X emission, and

$$\gamma_X = \frac{k_{DX}}{k_{DX} + k_{MDX}} \quad (55)$$

An inspection to the equations 45 and 46 shows that the fraction of excited solvent molecules that transfer their energy to primary solute (i.e. the energy transfer coefficient for $X \rightarrow Z$ transfer) is given by

$$F_{YX} = \frac{\sigma_{YX}^m c_Y \Gamma_X + \sigma_{YX}^d c_Y c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \quad (56)$$

while the energy transfer coefficient for direct $X \rightarrow Z$ transfer is

$$F_{ZX} = \frac{\sigma_{ZX}^m c_Z \Gamma_X + \sigma_{ZX}^d c_Z c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \quad (57)$$

Thus the overall energy transfer coefficient for $X \rightarrow Z$ transfer which includes the direct transfer and the two-step $X \rightarrow Y \rightarrow Z$ transfer will be

$$F_{ZYX} = F_{YX}F_{ZY} + F_{ZX} \quad (58)$$

When the solution contains oxygen, reactions 28 to 33 from table I must also be taken into account. Then the intensities of monomer (ξ'_{MX}) and excimer (ξ'_{DX}) solvent emission, monomer (ξ'_{MY}) and excimer (ξ'_{DY}) primary solute emission, monomer (ξ'_{MZ}) and excimer (ξ'_{DZ}) secondary solute emission are given by

$$\xi'_{MX} = \frac{I'_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} q'_{MX}I_0^X \quad (59)$$

$$\xi'_{DX} = \frac{c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} q'_{DX}I_0^X \quad (60)$$

$$\begin{aligned} \xi'_{MY} &= \frac{\sigma'_{YX}c_Y I'_X + \sigma'_{YX}c_Y c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZY}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} \times \\ &\times \frac{I'_Y}{(1 + \sigma'_{ZY}c_Z)I'_Y + (1 + \sigma'_{ZY}c_Z)c_Y} q'_{MY}I_0^X \end{aligned} \quad (61)$$

$$\begin{aligned} \xi'_{DY} &= \frac{\sigma'_{YX}c_Y I'_X + \sigma'_{YX}c_Y c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} \times \\ &\times \frac{c_Y}{(1 + \sigma'_{ZX}c_Z)c_Y + (1 + \sigma'_{ZY}c_Z)c_Y} q'_{DY}I_0^X \end{aligned} \quad (62)$$

$$\begin{aligned} \xi'_{MZ} &= \frac{\sigma'_{YX}c_Y I'_X + \sigma'_{YX}c_Y c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} \times \frac{\sigma'_{ZY}c_Z I'_Y + \sigma'_{ZY}c_Z c_Y}{(1 + \sigma'_{ZY}c_Z)I'_Y + (1 + \sigma'_{ZY}c_Z)c_Y} \\ &\times \frac{c'_{hZ}}{c'_{hZ} + c_Z} q'_{MZ}I_0^X + \frac{\sigma'_{ZY}c_Z I'_X + \sigma'_{ZY}c_Z c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} \times \frac{c'_{hZ}}{c'_{hZ} + c_Y} q'_{MZ}I_0^X \end{aligned} \quad (63)$$

$$\begin{aligned} \xi'_{DZ} &= \frac{\sigma'_{YX}c_Y I'_X + \sigma'_{YX}c_Y c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} \times \frac{\sigma'_{ZY}c_Z I'_Y + \sigma'_{ZY}c_Z c_Y}{(1 + \sigma'_{ZY}c_Z)I'_Y + (1 + \sigma'_{ZY}c_Z)c_Y} \\ &\times \frac{c_Z}{c'_{hZ} + c_Z} q'_{DZ}I_0^X + \frac{\sigma'_{ZY}c_Z I'_X + \sigma'_{ZY}c_Z c_X}{(1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)I'_X + (1 + \sigma'_{YX}c_Y + \sigma'_{ZX}c_Z)c_X} \times \frac{c_Z}{c'_{hZ} + c_Y} q'_{DZ}I_0^X \end{aligned} \quad (64)$$

where

$$\sigma'_{YX} = \frac{\sigma_{YX}^m}{1 + \chi'_{MX}[O_2]} \quad (65)$$

and

$$\sigma'_{YX}^d = \frac{\sigma_{YX}^d}{1 + \chi'_{DX}[O_2]} \quad (66)$$

are the Stern-Volmer constants for monomer and excimer $X \rightarrow Y$ transfer in the presence of oxygen, respectively,

$$\sigma'_{ZX} = \frac{\sigma_{ZX}^m}{1 + \chi'_{MX}[O_2]} \quad (67)$$

and

$$\sigma_{ZX}^d = \frac{\sigma_{ZX}^d}{1 + \gamma'_{DX}[O_2]} \quad (68)$$

are the Stern-Volmer constants for monomer and excimer $X \rightarrow Z$ transfer in the presence of oxygen, respectively,

$$q'_{MX} = \frac{q_{MX}}{1 + \gamma'_{MX}[O_2]} \quad (69)$$

and

$$q'_{DX} = \frac{q_{DX}}{1 + \gamma'_{DX}[O_2]} \quad (70)$$

are the quantum efficiencies of monomer and excimer emissions,

$$\Gamma'_X = c'_{hX} [1 + \gamma'_X (\sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z)] \quad (71)$$

$$c'_{hX} = c_{hX} \frac{1 + \gamma'_{MX}[O_2]}{1 + \gamma'_{DX}[O_2]} (1 + \gamma'_{MDX}[O_2]) \quad (72)$$

$$\gamma'_X = \gamma_X \frac{1 + \gamma'_{DX}[O_2]}{1 + \gamma'_{MDX}[O_2]} \quad (73)$$

In all these equations,

$$\gamma'_{MX} = \frac{k'_{MX}}{k_{MX}} \quad (74)$$

$$\gamma'_{DX} = \frac{k'_{DX}}{k_{DX}} \quad (75)$$

$$\gamma'_{MDX} = \frac{k'_{DX}}{k'_{DX} + k_{MDX}} \quad (76)$$

The energy transfer coefficient F'_{YX} for the $X \rightarrow Y$ transfer, the energy transfer coefficient F'_{ZX} for the direct $X \rightarrow Z$ transfer and the overall energy transfer coefficient F'_{ZYX} for the $X \rightarrow Z$ transfer are now given by

$$F'_{YX} = \frac{\sigma_{YX}^m c_Y \Gamma'_X + \sigma_{YX}^d c_Y c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma'_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \quad (77)$$

$$F'_{ZX} = \frac{\sigma_{ZX}^m c_Z \Gamma'_X + \sigma_{ZX}^d c_Z c_X}{(1 + \sigma_{YX}^m c_Y + \sigma_{ZX}^m c_Z) \Gamma'_X + (1 + \sigma_{YX}^d c_Y + \sigma_{ZX}^d c_Z) c_X} \quad (78)$$

$$F'_{ZYX} = F'_{YX} F'_{ZY} + F_{ZX} \quad (79)$$

3 — DISCUSSION

3.1 — BINARY SYSTEMS WHERE THE ENERGY DONOR DOES NOT FORM EXCIMERS

In a liquid system, and under steady state conditions of excitation, the Stern-Volmer constants for energy transfer are easily obtained from the variations of the donor intensities with the acceptor concentration, provided the donor does not form excimers. In fact, let us consider the case of a ternary system (XYZ) where Y does not form excimers, and let us assume that only Y molecules are ini-

tially excited. For deoxygenated solutions, equations 14 to 25 are now to be applied. The fact that Y does not form excimers can be introduced in the general equations through the condition

$$c_{hY} \gg c_Y \quad (80)$$

Then, since $q_D = 0$ and $\sigma_{ZY}^d = 0$, equations 14 and 22 give

$$\gamma_{MY} = \frac{1}{1 + \sigma_{ZY}^m c_Z} q_{MY} I_0^Y \quad (81)$$

and so

$$\frac{1}{\tau_{MY}} = \frac{1}{I_O^Y} (1 + \sigma_{ZY}^m c_Z) \quad (82)$$

The ratio between the slope and the intercept of this straight line gives the value of σ_{ZY}^m . Knowing k_{MY} (i.e., the reciprocal of the Y decay time is the absence of Z) it is then possible to evaluate k_{ZY}^m from equation 20.

Equations 81 and 28 have been used by a number of authors (13) (42). The contribution of radiative transfer from Y to Z, which may be quite important (43) must be taken into account before the equations are applied. Alternatively, the effect of radiative transfer may be included into the equations 12 (44) with the advantage that the variation of donor intensities with the wavelength of emission (due to the variation of the extinction coefficient of the acceptor molecules) offers a means of a more reliable correction for the radiative transfer (45) (46).

The variation of the acceptor intensities with acceptor concentration can also be used to obtain the transfer rate constants when the donor does not form excimers. For simplicity, let us assume that the acceptor Z does not form excimers. As before, we can use the general equations with

$$c_{hZ} \gg c_Z \quad (83)$$

For deoxygenated solutions, equation 16 gives

$$\tau_{MZ} = \frac{\sigma_{ZY}^m c_Z}{1 + \sigma_{ZY}^m c_Z} q_{MZ} I_O^Y \quad (84)$$

The energy transfer coefficient is then (cf. equation 15)

$$F_{ZY} = \frac{\sigma_{ZY}^m c_Z}{1 + \sigma_{ZY}^m c_Z} \quad (85)$$

Assuming that radiative transfer is unimportant, the energy transfer coefficient is best evaluated by comparing the intensities observed when the donor is excited and transfers its energy to the acceptor with the intensities observed when only the acceptor is excited. It is obvious from equations 16 and 1 that

$$F_{ZY} = \frac{\tau_{MZ}}{\tau_{MZ}} \frac{I_O^Z}{I_O^Y} \quad (86)$$

An integrating solution (47) can be used to obtain I_O^Z/I_O^Y and hence F_{ZY} is easily evaluated. In a practical case, solutions containing only the acceptor can be used integrating solutions (48) with the advantage that any effect of concentration emission is readily accounted for, if η_{MZ} and ξ_{MZ} are measured for the same concentration c_Z . In fact, equations 1 and 16 can be adapted to the case where concentration quenching (49) of Z emission occurs, if we define

$$\tau_Z = \frac{1}{c_{hZ}} \quad (87)$$

as the quenching constant. Then,

$$\tau_{MZ} = F_{YZ} \frac{q_Z}{1 + \tau_Z c_Z} I_O^Z \quad (88)$$

$$\tau_{MZ} = \frac{q_Z}{1 + \tau_Z c_Z} I_O^Z \quad (89)$$

from which equation 86 is again obtained.

This result shows that it is possible to evaluate the energy transfer coefficients F_{ZY} even when Z does not form excimers, provided we use the ratios η_{MZ}/ξ_{MZ} or η_{DZ}/ξ_{DZ} to obtain equation 86. In any case, if direct absorption by Z is not negligible, an expression for F_{ZY} is easily derived (50) which includes the fraction of the exciting radiation initially absorbed by Y and Z.

From the values of the energy transfer coefficients F_{ZY} obtained by any of these methods, the Stern-Volmer rate constants σ_{ZY}^m can be found from the linear relationship

$$\frac{c_Z}{F_{ZY}} = \frac{1}{\sigma_{ZY}^m} + c_Z \quad (90)$$

As before, from the knowledge of σ_{ZY}^m and k_{MY} , the rate constant k_{ZY}^m is evaluated.

These equations have been used by several authors (48) (51) although some criticisms to this method can be made (2) since the corrections for radiative transfer are more difficult to evaluate.

For oxygenated solutions, equations similar to those above can be derived, from the general equations 6 to 13 and 26 to 40. The fact that Y does not form excimers is introduced in the general equation by considering

$$c'_{hY} \gg c_Y \quad (91)$$

Since $q'_D = 0$ and $\sigma'_{ZY} = 0$, we get

$$\eta'_{MY} = \frac{1}{1 + \sigma'_{ZY} c_Z} q'_{MY} I_O^Y \quad (92)$$

$$\frac{1}{\eta'_{MY}} = \frac{1}{q'_{MY} I_O^Y} (1 + \sigma'_{ZY} c_Z I) \quad (93)$$

The energy transfer coefficient is now

$$F'_{ZY} = \frac{\eta'_{MZ}}{\zeta'_{MZ}} \frac{I_O^Z}{I_O^Y} \quad (94)$$

this relationship being valid even where there is concentration quenching or when Z forms excimers. In the latter case we have also

$$F'_{ZY} = \frac{\eta'_{DZ}}{\zeta'_{DZ}} \frac{I_O^Z}{I_O^Y} \quad (95)$$

the energy transfer coefficient F'_{ZY} being related to the Stern-Volmer constant σ'_{ZY} through

$$F'_{ZY} = \frac{\sigma'_{ZY} c_Z}{1 + \sigma'_{ZY} c_Z} \quad (96)$$

from which

$$\frac{c_Z}{F'_{ZY}} = \frac{1}{\sigma'_{ZY}} + c_Z \quad (97)$$

From the values of σ'^m obtained by any of these methods, it is possible to evaluate the energy transfer rate constant, if the decay time of the donor emission is known. From equations 33, 20 and 26

$$\sigma'_{ZY} = \frac{k'_{ZY}}{k_{MY}} \frac{1}{1 + \chi'_{MY} [O_2]} = \frac{k'_{ZY}}{k_{MY} + k'_{MY} [O_2]} \quad (98)$$

where $k_{MY} + k'_{MY} [O_2]$ is the reciprocal of the donor decay time in the absence of acceptor (but with oxygen present). On the other hand, if σ'_{ZY} and σ'^m_{ZY} are evaluated, it is possible to obtain the oxygen quenching rate constant for the donor emission,

$$\frac{\sigma'^m_{ZY}}{\sigma'_{ZY}} - 1 = \chi'_{MY} [O_2] \quad (99)$$

provided k_{MY} and the oxygen concentration are known and we make use of equation 26. Obviously, if instead of oxygen, another quenching agent is used, the quenching constant can be easily obtained once the energy transfer coefficients for $Y \rightarrow Z$ transfer for various quencher concentrations are evaluated. It is easy to see that by analogy with 99

$$\frac{\sigma'^m_{ZY}}{\sigma'_{QZY}} - 1 = \frac{k'_{QMY}}{k_{MY}} [Q] \quad (100)$$

where σ'^m_{QMY} is the Stern-Volmer constant for the $Y \rightarrow Z$ transfer for the solution containing the quenching agent Q at concentration [Q] and k'_{QMY} is the quenching constant for the donor emission. Here again the quenching constant can be evaluated from the knowledge of energy transfer coefficients for various quencher concentrations but it is also possible to obtain directly k'_{YZ} if the decay time of the donor in the presence of quencher is known.

These equations have been used mainly when the donor intensity is too low to be measured accurately, either due to its low quantum yield or to the fact that the transfer coefficient is high. The use of quenchers has also been used either to evaluate the Stern-Volmer rate constants (52) or to obtain the quenching constants (53) mainly when the donor emission intensities are low (it is worth noting that, regardless of the transfer efficiency, the donor emission intensity is proportional to the donor quantum efficiency, while the acceptor emission intensity is proportional to the quantum yield of acceptor emission, which is usually higher).

3.2 — BINARY SYSTEMS WHERE THE ENERGY DONOR FORMS EXCIMERS

In the study of the energy transfer processes in liquid systems, it has been common practice to use the energy donor as a solvent (e.g. benzene and alkylbenzenes and liquid naphthalene derivatives), in which a suitable solute (e.g. an oxazole derivative) is dissolved. Most of the work done on these systems has been analysed neglecting any excimer formation among the energy donor molecules. The equations for this case are easily obtained from the general equations derived before. In fact let us

consider a binary system XY and let us assume that neither X nor Y form excimers. As before, these conditions may be introduced with the conditions

$$c_{hX} \gg c_X \quad c_{hY} \gg c_Y \quad (101)$$

Since no secondary solute is present, $c_Z = 0$. Then, from equation 43 we get

$$\zeta_{MY} = \frac{\sigma_{YX}^m c_Y}{1 + \sigma_{YX}^m c_Y} q_{MY} I_0^X \quad (102)$$

which is obviously similar to equation 84, the energy transfer coefficient for the X → Y transfer being now (cfr. equation 85)

$$F_{YX} = \frac{\sigma_{YX}^m c_Y}{1 + \sigma_{YX}^m c_Z} \quad (103)$$

The Stern-Volmer rate constant σ_{XY}^m is readily obtained from

$$\frac{c_Y}{F_{YX}} = \frac{1}{\sigma_{YX}^m} + c_Y \quad (104)$$

and the rate constant for the X → Y transfer is then calculated from

$$\sigma_{YX}^m = k_{YX}^m \tau_X^0 \quad (105)$$

where τ_X^0 is the decay time of the solvent molecules in the absence of solute. Obviously, if the solvent does not form excimers $\tau_X^0 = 1/k_{MX}$ and we get equation 49.

These equations have been used by a number of authors (48) (28) (50) and the fact that c_Y/F_{YX} plotted against c_Y gives a straight line has been considered as a proof that this simplified kinetic scheme, which does not consider any excimer formation among solvent molecules, is valid. Nevertheless, and in contrast with some measurements in ternary systems, under conditions of primary solute excitation (51), the rate constants for energy transfer calculate from equation 105 were found to be greater than those predicted from Forster's theory of resonance transfer. This has lead to the assumption that material diffusion, energy migration among excited molecules or both processes might be responsible for the increased rates of energy transfer as mentioned in the introduction. The presence of an energy migration effect raises however the ques-

tion of a possible dependence of the energy transfer rate constant on the donor concentration. It is unfortunate that only a few studies have been presented on this (48) (54) (55).

The fact that solvent molecules may form excimers has only recently (33) (56) (36) been considered in the analysis of the energy transfer process. This is however quite important because most of the molecules which have been used as solvents do in fact form excimers. Since excimer formation depends on the concentration, it is obvious that any studies on the effect of solvent concentration (which are essential for the understanding of the energy migration processes) must take excimer formation into account. It may be argued that if excimer formation is relevant for the energy transfer then the linear relationship 105 should not be valid, since it is based on a very simplified kinetic scheme. However, it is easily seen from the general equations derived before, that this is not the case, provided the rate constants which can be evaluated from the simplified equations are regarded as «average rate constants». In fact, for benzene and naphthalene derivatives, which, as mentioned before, are the most commonly used solvents, the rate constants for excimer formation and dissociation are very fast compared with the constants for monomer and excimer deactivation (57) (58). This means that

$$k_{MDX} k_{DMX} c_X \gg k_{DX} k_{MX} \quad (106)$$

Then, from equations (54) and (55)

$$c_{hX} \approx \frac{k_{MX} k_{MDX}}{k_{DX} k_{DMX}} \quad (107)$$

$$\gamma_X \approx \frac{k_{DX}}{k_{MDX}} \ll 1 \quad (108)$$

If it is also assumed that

$$\gamma_X \sigma_{YX}^d c_Y \ll 1 \quad (109)$$

then, from equation 43 and remembering that in the case under consideration $c_Z = 0$ and Y is assumed not to form excimers, it is seen that

$$\zeta_{MY} = \frac{\sigma_{YX}^m c_Y c_{hX} + \sigma_{YX}^d c_Y c_X}{(1 + \sigma_{YX}^m c_Y) c_{hX} + (1 + \sigma_{YX}^d c_Y) c_X} q_{MY} I_0^X \quad (110)$$

and the energy transfer coefficient F_{YX} (equation 56) becomes

$$F_{YX} = \frac{\sigma_{YX}^m c_Y c_{hX} + \sigma_{YX}^d c_Y c_X}{(1 + \sigma_{YX}^m c_Y) c_{hX} + (1 + \sigma_{YX}^d c_Y) c_X} \quad (111)$$

This equation can be written in the form

$$F_{YX} = \frac{A_{YX} c_Y}{1 + A_{YX} c_Y} \quad (112)$$

where

$$A_{YX} = \frac{\sigma_{YX}^m c_{hX} + \sigma_{YX}^d c_X}{c_{hX} + c_X} \quad (113)$$

is independent of c_Y . Then the linear relationship

$$\frac{c_Y}{F_{YX}} = \frac{1}{A_{YX}} + c_Y \quad (114)$$

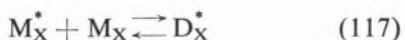
is to be expected (and found experimentally), even when excimer formation in the solvent is taken into account. If we use the approximated value c_{hX} (equation 107) we get

$$A_{YX} = \frac{\sigma_{YX}^m k_{MX} k_{MDX} + \sigma_{YX}^d k_{DX} k_{DMX} c_X}{k_{MX} k_{MDX} + k_{DX} k_{DMX} c_X} \quad (115)$$

If we introduce now the quantity

$$K_e = \frac{k_{DMX}}{k_{MDX}} \quad (116)$$

which divided by c_Y represents the equilibrium constant (57) for the equilibrated reaction



it is seen that, using also equations 20 and 21

$$A_{YX} = \frac{k_{YX}^m + K_e c_X k_{YX}^d}{1 + K_e c_X} \times \frac{1 + K_e c_X}{k_{MX} + K_e c_X k_{DX}} \quad (118)$$

On the other hand, under conditions 106, both monomer and excimer decay with the same decay time (59).

$$\tau_X = \frac{1 + K_e c_X}{k_{MX} + K_e c_X k_{DX}} \quad (119)$$

If we define an «average transfer rate constant»

$$\bar{k}_{YX} = \frac{k_{YX}^m + K_e c_X k_{YX}^d}{1 + K_e c_X} \quad (120)$$

and an «average rate constant for donor deactivation»

$$\bar{k}_X = \frac{k_{MX} + K_e c_X k_{DX}}{1 + K_e c_X} = \frac{1}{\tau_X} \quad (121)$$

we may write

$$A_{YX} = \frac{\bar{k}_{YX}}{\bar{k}_X} \quad (122)$$

This result shows that the Stern-Volmer constant A_{YX} can still be given by the product of an energy transfer rate constant and a decay time. Since this decay time represents the actual decay of the energy donor for zero concentration of the acceptor, the published values of the energy transfer rate constants from donors obeying condition 106 do in fact represent the average rate constants for transfer as given by 120.

Obvioulsy, if

$$k_{YX}^m = k_{YX}^d = k_{YX} \quad (123)$$

we get

$$\bar{k}_{YX} = k_{YX} \quad (124)$$

which is the approximation used in the analysis of some binary systems where the energy donor molecules form excimers under conditions 106.

For oxygenated solutions, similar equations can be derived. In particular, the ratio between the average Stern-Volmer constants A_{YX} (for deoxygenated solutions) and A'_{YX} (for solutions containing oxygen) are related with an «average rate constant for oxy-

gen quenching \bar{k}'_X through an equation similar to (99) (60)

$$\frac{A_{YX}}{A'_{YX}} - 1 = \bar{k}'_X \tau_X [O_2] \quad (125)$$

where

$$\bar{k}'_X = \frac{k_{MX} + K_e c_X k'_{DX}}{1 + K_e c_X} \quad (126)$$

Only under the condition $k'_{MX} \simeq k'_{DX}$ (56) the value \bar{k}'_X would represent a true rate constant for oxygen quenching.

It has been suggested (35) that the energy migration among solvent molecules is due to successive excimer formations and dissociations. Under these conditions, the energy transfer rate constant is diffusion-migration controlled and conditions 123 can then be used into 120 in order to obtain a «true rate constant» that depends on the diffusion and migration coefficients and on the radii of solvent and solute molecules (39).

In the general case where no assumptions are made about the mechanism of energy migration, the experimentally measured energy transfer coefficients F_{YX} (and the average Stern-Volmer rate constants that can be obtained from the F_{YX} values) would involve both monomer and excimer Stern-Volmer constants σ_{YX}^m and σ_{YX}^m . Decay time measurements coupled with steady state intensity measurements have been used recently (26) (27) to obtain these constants, although this method may be open to some criticisms, if the average distribution of excited species is different under steady state conditions of excitation and under flash excitation (61).

3.3—A SPECIAL CASE OF ENERGY TRANSFER IN BINARY SYSTEMS

In order to study the effect of excimer formation upon energy migration, a different approach is in progress at this laboratory. The system pyrene—9,10 diphenylanthracene (DPA) in benzene solutions has been chosen for a detailed study, since it offers the interesting property that the energy of the first excited singlet state of the acceptor (DPA) is lower than the first excited singlet state of the donor (pyrene) but higher than the energy of the pyrene excimer. Hence only pyrene monomer can transfer to DPA. Since pyrene excimers do not exist in the

ground state, there is no transfer from DPA to the pyrene excimer (38). If we consider the case where only pyrene is excited and transfers to DPA, which does not exhibit excimer formation (62) then for deoxygenated solutions equation 15 gives

$$\eta_{DY} = \frac{c_Y}{(c_Y + c_{hY}) + c_{hY} \sigma_{ZY}^m c_Z} q_{DY} I_0^Y \quad (127)$$

since $\sigma_{ZY}^d = 0$ as stated above. For solutions containing oxygen, equation 30 yields

$$\eta'_{DY} = \frac{c_Y}{(c_Y + c_{hY}) + c_{hY} \sigma_{ZY}^m c_Z} q_{DY} I_0^Y \quad (128)$$

From these equations, and using the intensities $\eta(\lambda_{DY})$ and $\eta'(\lambda_{DY})$ measured at a fixed wavelength of emission for the excimer, which avoids the need of knowing the correcting factor $S(\lambda_{DY})$ for the monochromator-photomultiplier detector system (38), the following relationships are easily obtained

$$\frac{1}{\eta(\lambda_{DY})} = \frac{1}{q_{DY} I_0^Y S(\lambda_{DY}) c_Y} [(c_Y + c_{hY}) + c_{hY} \sigma_{ZY}^m c_Z] \quad (129)$$

$$\frac{1}{\eta'(\lambda_{DY})} = \frac{1}{q'_{DY} I_0^Y S(\lambda_{DY}) c_Y} [(c_Y + c'_{hY}) + c'_{hY} \sigma_{ZY}^m c_Z] \quad (130)$$

Figures 1 to 6 give the emission spectra of deoxygenated solutions of pyrene (from Fluka) and DPA (from Fluka) in benzene (Merck, p.a.), for a fixed pyrene concentration ($c_Y = 0.02$ mole. l^{-1}) and different DPA concentration (63). The dotted lines represent the decomposition of the total emission spectra into the pyrene excimer and DPA emissions, obtained through statistical analysis. It is seen that DPA emissions is located between pyrene monomer and excimer emissions, which shows that only pyrene monomer can transfer its energy to DPA. Pyrene monomer and excimer intensities decrease with increasing DPA concentration c_Z , while DPA emission intensity increases, although for all cases pyrene optical density is greater than the optical density of DPA, thus showing that in fact there is transfer from the initially excited pyrene molecules to DPA molecules. Similar results were obtained with the same solutions containing dissolved oxygen.

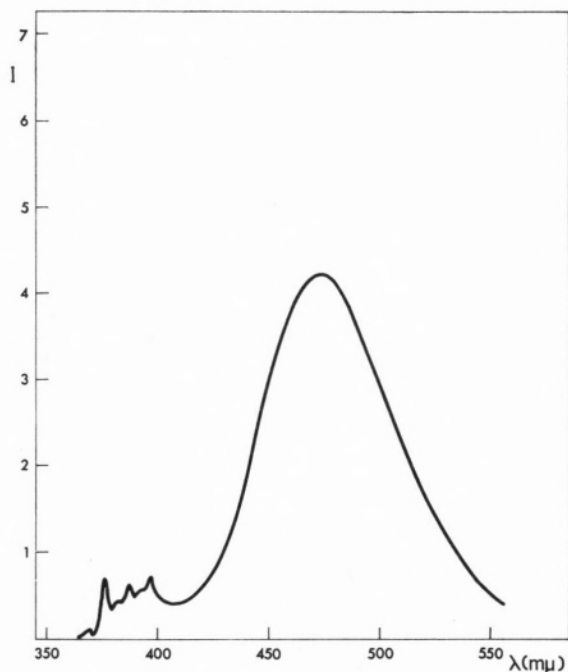


Fig. 1 — Emission spectrum of deoxygenated pyrene solutions in benzene. Pyrene concentration $c_y = 0.02$ mole. l^{-1} .

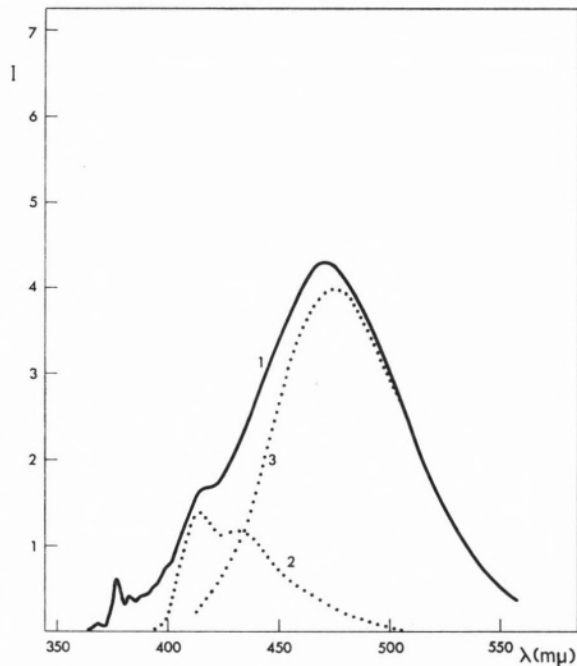


Fig. 3 — Emission spectrum of deoxygenated pyrene and DPA solutions in benzene. Pyrene concentration $c_y = 0.02$ mole. l^{-1} ; DPA concentration $c_z = 0.393 \times 10^{-3}$ mole. l^{-1} .
(1): Full emission spectrum; (2): DPA emission; (3): pyrene excimer emission.

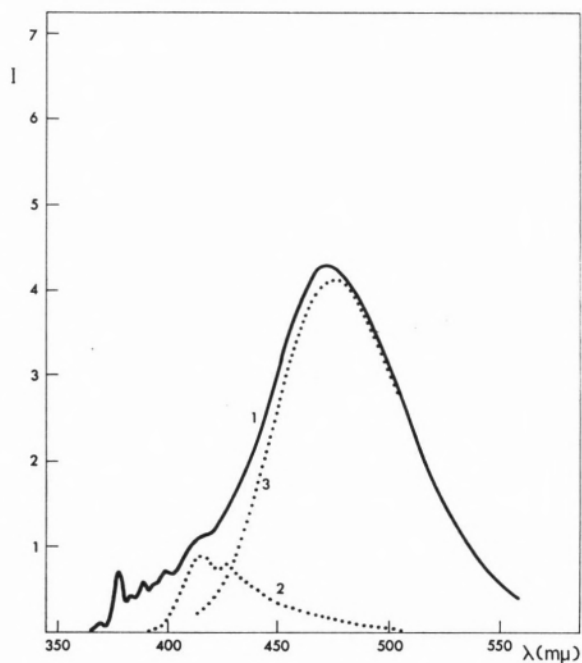


Fig. 2 — Emission spectrum of deoxygenated pyrene and DPA solutions in benzene. Pyrene concentration $c_y = 0.02$ mole. l^{-1} ; DPA concentration $c_z = 0.193 \times 10^{-3}$ mole. l^{-1} .
(1): Full emission spectrum; (2): DPA emission; (3): pyrene excimer emission.

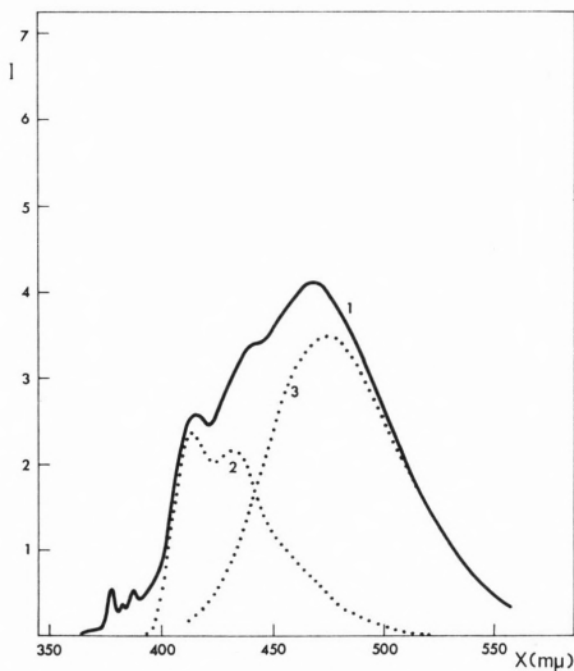


Fig. 4 — Emission spectrum of deoxygenated pyrene and DPA solutions in benzene. Pyrene concentration $c_y = 0.02$ mole. l^{-1} ; DPA concentration $c_z = 0.787 \times 10^{-3}$ mole. l^{-1} .
(1): Full emission spectrum; (2): DPA emission; (3): pyrene excimer emission.

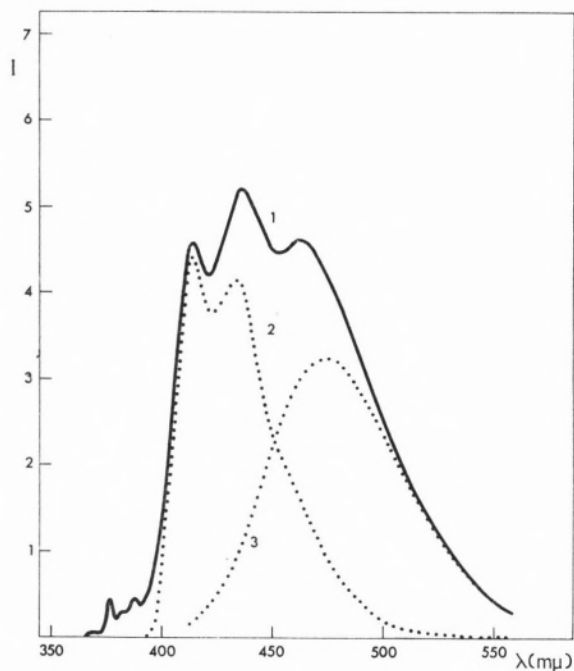


Fig. 5 — Emission spectrum of deoxygenated pyrene and DPA solutions in benzene. Pyrene concentration $c_y = 0.02$ mole. l^{-1} ; DPA concentration $c_z = 1.574 \times 10^{-3}$ mole. l^{-1} . (1): Full emission spectrum; (2): DPA emission; (3): pyrene excimer emission.

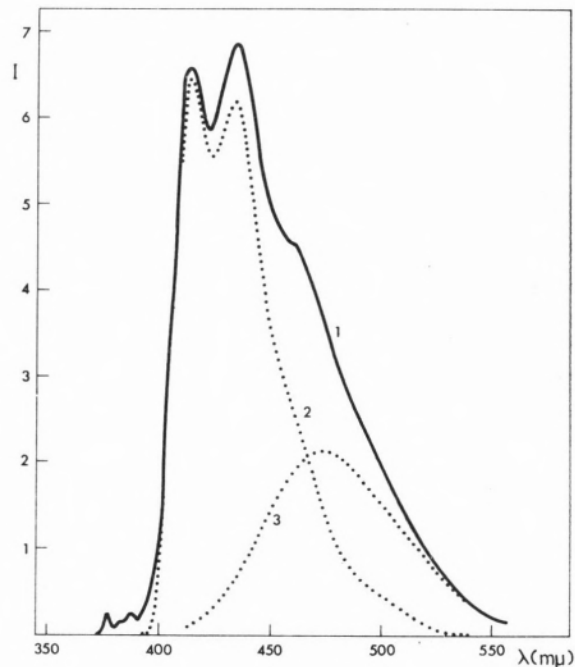


Fig. 6 — Emission spectrum of deoxygenated pyrene and DPA solutions in benzene. Pyrene concentration $c_y = 0.02$ mole. l^{-1} ; DPA concentration $c_z = 3.148 \times 10^{-3}$ mole. l^{-1} . (1): Full emission spectrum; (2): DPA emission; (3): pyrene excimer emission.

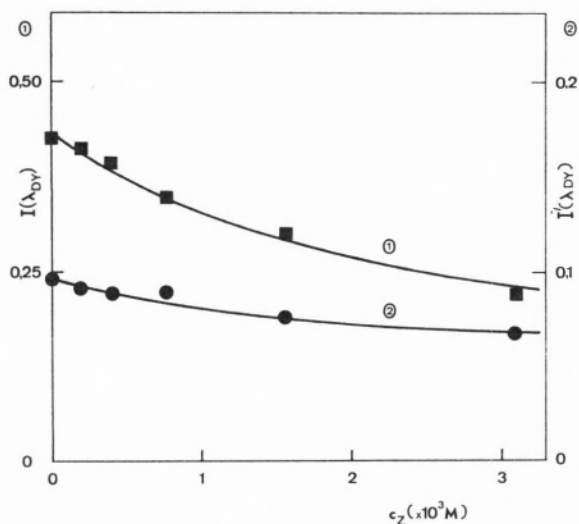


Fig. 7 — Variation of pyrene excimer intensity $I(\lambda_{DY})$ (for deoxygenated solutions—curve 1) and $I'(\lambda_{DY})$ (for air-equilibrated solutions—curve 2) obtained at $\lambda_{DY} = 473$ mμ, with DPA concentration c_z .

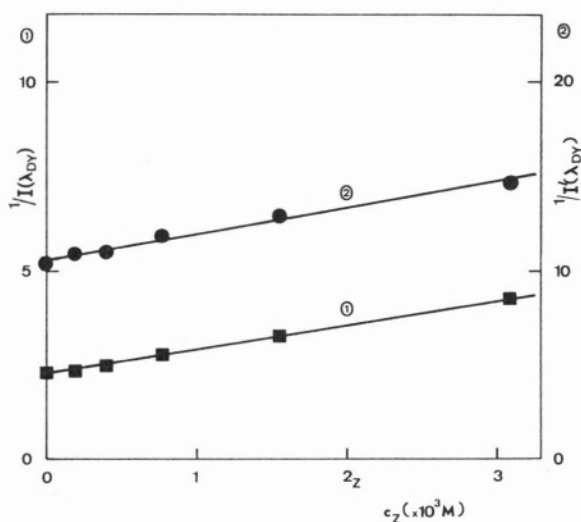


Fig. 8 — Variation of the reciprocals of pyrene excimer intensity $1/I(\lambda_{DY})$ (for deoxygenated solutions—curve 1) and $1/I'(\lambda_{DY})$ (for air-equilibrated solutions—curve 2) obtained at $\lambda_{DY} \approx 473$ mμ, with DPA concentration, c_z .

Figure 7 gives the variation of pyrene excimer intensity with DPA concentration (measured at $\lambda_{DY} \simeq 473 \text{ m}\mu$) for both deoxygenated ($\eta(\lambda_{DY})$) and oxygenated ($\eta'(\lambda_{DY})$) solutions. Figure 8 gives the reciprocals of these intensities plotted against DPA concentration c_Z .

The linear relationships 129 and 130 are well verified. From the ratios between the slopes and intercepts and according to these equations it is obtained

$$\frac{c_{hY}}{c_Y + c_{hY}} \sigma_{ZY}^m = 277 \text{ mole} \cdot \text{l}^{-1} \quad (131)$$

$$\frac{c'_{hY}}{c_Y + c'_{hY}} \sigma_{ZY}^m = 132 \text{ mole} \cdot \text{l}^{-1} \quad (132)$$

Taking the values $c'_{hY} = 12 \times 10^{-3} \text{ mole} \cdot \text{l}^{-1}$, $c_{hY} = 11 \times 10^{-4} \text{ mole} \cdot \text{l}^{-1}$ (38) and since $c_Y = 0.02 \text{ mole} \cdot \text{l}^{-1}$ one obtains $\sigma_{ZY}^m = 5286 \text{ mole} \cdot \text{l}^{-1}$, $\sigma_{ZY}'^m = 352 \text{ mole} \cdot \text{l}^{-1}$. Now from equation (33)

$$\frac{\sigma_{ZY}^m}{\sigma_{ZY}'^m} = 1 + \chi'_{MY}[O_2] \quad (133)$$

and hence

$$1 + \chi'_{MY}[O_2] = 15 \quad (134)$$

To verify these results, it is only necessary to know the decay times of pyrene monomer emission τ_{MY} (for deoxygenated solutions) and τ'_{MY} (for solutions containing oxygen). In fact

$$\frac{\tau_{MY}}{\tau'_{MY}} = \frac{k_{MY} + k'_{MY}[O_2]}{k_{MY}} = 1 + \chi'_{MY}[O_2] \quad (135)$$

Now $\tau_{MY} = 465 \times 10^{-9} \text{ s}$ (64), $\tau'_{MY} = 22.1 \times 10^{-9} \text{ s}$ (65) from which we obtain $\tau_{MY}/\tau'_{MY} = 21$, the difference to the above value 15 being probably due to differences in oxygen concentration. It is to note that the value $\tau_{MY} = 300 \times 10^{-9} \text{ s}$ for pyrene decay time has been reported (66). Using this value one obtains $\tau_{MY}/\tau'_{MY} = 13$.

On the other hand, the straight lines in figure 9 seem to indicate that equations 129 and 130 describe well the experimental results, and hence seem to prove the validity the partial kinetic scheme from which they were derived.

Obviously, the variation of τ_{YX}^m and τ'_{YX} with c_X will give important information about the effect of the energy donor concentration, and in particular the excimer concentration on the energy migration process. Work is currently in progress at this laboratory on this problem.

3.4 — TERNARY SYSTEMS

The case of ternary system is obviously of interest although the analysis of the results is much more complicated, mainly because radiative transfer from the primary solute Y to the secondary solute Z is usually significant. Work is currently in progress at this laboratory on the ternary system Benzene + 2,5-diphenyloxazole (PPO) + 2,2'-p-phenylene-bis-(5-phenyloxazole) (POPOP). It has been shown (34) that under benzene excitation both benzene and PPO transfer their energy to POPOP, the energy transfer coefficient for the overall transfer being dependent on the rate constants for the transfer from benzene to PPO and POPOP obtained from the measurements in the binary systems benzene + PPO and benzene + POPOP (39). This shows the validity of the general equations derived before, and in particular equations 45 and 63. This result has been obtained by comparison between the intensities of POPOP emission measured under conditions of PPO excitation and benzene excitation, with the advantage that the contribution of radiative transfer from PPO to POPOP does not affect the conclusions. In fact, since POPOP does not form excimers, equations 14, 15 and 16 describing the case of PPO excitation, can be written in the form

$$\tau_{MY} = \varphi_{ZY}^m q_{MY} I_O^Y \quad (136)$$

$$\tau_{DY} = \varphi_{ZY}^d q_{DY} I_O^Y \quad (137)$$

$$\tau_{MZ} = F_{ZY} q_{MZ} I_O^Y \quad (138)$$

where

$$\varphi_{ZY}^m = \frac{\Gamma_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \quad (139)$$

$$\varphi_{ZY}^d = \frac{c_Y}{(1 + \sigma_{ZY}^m c_Z) \Gamma_Y + (1 + \sigma_{ZY}^d c_Z) c_Y} \quad (140)$$

and F_{ZY} is given by 29. Similar relations can be written for solutions containing oxygen. On the other hand, under benzene excitation, and for the same system, equations 43, 44, 45, 56 and 57 give

$$\zeta_{MY} = F_{YX} \zeta_{ZY}^m q_{MY} I_O^X \quad (141)$$

$$\zeta_{DY} = F_{YX} \zeta_{ZY}^d q_{DY} I_O^X \quad (142)$$

$$\zeta_{MZ} = (F_{YX} F_{ZY} + F_{ZX}) q_{MZ} I_O^X \quad (143)$$

with similar equations for oxygenated solutions. Defining the quantity

$$\Delta Z = \zeta_{MZ} - r_{MZ} \frac{\zeta_{MY}}{r_{MY}} \quad (144)$$

and remembering that condition 106 holds, since benzene is the solvent

$$I_X^* = c_{0X}$$

it is easily seen that

$$\Delta Z = \frac{\bar{k}_{ZX}}{\bar{k}_X + \bar{k}_{YX} c_Y + \bar{k}_{ZX} c_Z} q_Z I_O^X \quad (145)$$

which does not depend on the radiative transfer from PPO and POPOP, as discussed elsewhere (34). The use of the corresponding equations for solutions containing oxygen gives a similar expression for $\Delta'Z$. The knowledge of \bar{k}_{ZX}/\bar{k}_X and \bar{k}_{ZX}/\bar{k}_X obtained from measurements with the binary systems (XY) and (XZ) can then be used to verify the experimentally found values for ΔZ and $\Delta'Z$ and thus to verify the general kinetic scheme from which it was derived.

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