THE TIME EVOLUTION OF ENERGY DONOR INTENSITIES WHEN THERE IS A TRANSIENT TERM

J. C. CONTE
J. M. G. MARTINHO

Centro de Quimica Fisica Molecular
Complexo I
Instituto Superior Técnico
1000 LISBOA

When excimer forming molecules Y are dissolved in an inert solvent at appropriate molar concentration c_Y in the presence of another fluorescent species Z, molar concentration c_Z and the system is excited with electromagnetic radiation of intensity I_O (einstein $l^{-1}\ s^{-1}$) the reactions that can take place are well known [1].

If the excitation takes the form of a δ-pulse the differential equations that describe the time evolution of the monomer and the excimer intensities of the donor Y are easily obtained. For the case where the rate constants for energy transfer from the excited monomer of Y and excimer (k_{ZY}^{m} and k_{ZY}^{d} respectively) are both able to transfer its energy to the acceptor Z and are assumed to present a transient term [2], they have the general form

$$k = \frac{4\pi DN}{1000} R_{eff}\ [1 + \frac{R_{eff}}{\sqrt{\pi Dt}}] \qquad (1)$$

that is

$$k_{ZY}^{m} = k_{ZY}^{mo}\ [\ 1 + \frac{\sigma_m}{\sqrt{\pi Dt}}] = k_{ZY}^{mo} + At^{-1/2} \qquad (2)$$

$$k_{ZY}^{d} = k_{ZY}^{do}\ [1 + \frac{\sigma_d}{\sqrt{\pi Dt}}] + k_{ZY}^{do} + Bt^{-1/2} \qquad (3)$$

Then the general differential equations for the time evolution of monomer and excimer intensities when the solution is excited by a δ-pulse are

$$\frac{d}{dt}[M_Y^*] = k_{MDY}[D_Y^*] - k_{DMY}[M_Y^*]c_Y - k_{ZY}^{mo}[M_Y^*]c_Z - $$
$$- k_{MY}[M_Y^*] - At^{-1/2}[M_Y^*]c_Z \qquad (4)$$

$$\frac{d}{dt}[D_Y^*] = k_{DMY}[M_Y^*]c_Y - k_{MDY}[D_Y^*] - k_{ZY}^{do}[D_Y^*]c_Z - $$
$$- k_{DY}[D_Y^*] - Bt^{-1/2}[D_Y^*]c_Z \qquad (5)$$

The analysis of these equations is obviouly important since, as it is well known, accurate means of obtaining the time evolution of $[M_Y^*]$ and $[D_Y^*]$ are

available and also because they offer a means of studying the theories of the energy transfer, since they include the rate constants for this transfer in a form such as the different theories can be checked. Their complete integration, however, and to the present Author's knowledge, has not yet been achieved.

It is the purpose of this note to present the resolution of these equations in a particular case, as well as to the case where there is no acceptor in a novel way involving matricial calculus and to show how this can be extended to the general case. These considerations will be presented soon in future publications.

If we denote by x and y respectively, the concentrations of excited species $[M_Y^*]$ and $[D_Y^*]$ respectively we can write equations (4) and (5) above in the more appropriate form

$$\frac{d}{dt}x = A_x x + B_x y + C_x t^{-1/2} x \tag{6}$$

$$\frac{d}{dt}y = A_y y + B_y x + C_y t^{-1/2} y \tag{7}$$

where x and y are functions of t and A_x, B_x, C_x, A_y, B_y, C_y are independent of x, y and t.

Let us consider the simple case where there is no acceptor. Then we are reduced to the well known case of the monomer-excimer equilibrium

$$\frac{d}{dt}x = A_x x + B_x y \tag{8}$$

$$\frac{d}{dt}y = A_y y + B_y x \tag{9}$$

Although the solution of these equations is well known [3] it is introduced here to present it in a different way as an introduction to the general case. If we define a vector

$$\mathbf{X} = \begin{bmatrix} x \\ y \end{bmatrix} \tag{10}$$

and the matrix

$$A = \begin{bmatrix} A_x & B_x \\ B_y & A_y \end{bmatrix} \tag{11}$$

The equations (8) and (9) above can be written in a matrix form as

$$\frac{d}{dt}\mathbf{X} = A\mathbf{X} \tag{12}$$

which can be easily integrated giving

$$\mathbf{X} = \mathrm{EXP}(At)\ \mathbf{X}_O \tag{13}$$

where EXP(At) is the exponential function and $\mathbf{X}_O$ is the vector $\mathbf{X}$ for the initial conditions at $t = 0$

$$\mathbf{X}_O = \begin{bmatrix} x_O \\ y_O \end{bmatrix} \tag{14}$$

Now it is known [4] that according to Sylvester's expansion theorem

$$\mathrm{EXP}(At) = \sum_{i=1}^{n} \mathrm{EXP}(\lambda_i t)\ F_i \tag{15}$$

with

$$F_i = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{A - \lambda_j I}{\lambda_i - \lambda_j} \tag{16}$$

where I is the unit matrix and λ_i the eigenvalues of the matrix A.

According to the usual notation the eigenvalues of A are

$$\lambda \pm = \frac{(A_x + A_y) + \sqrt{(A_x - A_y)^2 + 4B_x B_y}}{2} \tag{17}$$

and since they are intrinsically negative it is usual practice to define the quantities

$$\lambda_{1,2} = -\lambda \pm \tag{18}$$

then by substitution we may write

$$\mathrm{EXP}(At) = F_1\ \mathrm{EXP}(-\lambda_1 t) + F_2\ \mathrm{EXP}(-\lambda_2 t) \tag{19}$$

with

$$F_1 = \frac{A + \lambda_2 I}{\lambda_2 - \lambda_1} \qquad (20)$$

$$F_2 = \frac{A + \lambda_1 I}{\lambda_2 - \lambda_1} \qquad (21)$$

Now if we write down the matrices A and I we get

$$F_1 = \frac{1}{\lambda_2 - \lambda_1} \begin{bmatrix} A_x + \lambda_2 & B_x \\ B_y & A_y + \lambda_2 \end{bmatrix} \qquad (22)$$

$$F_2 = \frac{1}{\lambda_2 - \lambda_1} \begin{bmatrix} A_x + \lambda_1 & B_x \\ B_y & A_y + \lambda_1 \end{bmatrix} \qquad (23)$$

Since there is no excimer present for $t = 0$, we way write, from (14)

$$\begin{bmatrix} x \\ y \end{bmatrix} = EXP(At) \begin{bmatrix} x_O \\ 0 \end{bmatrix} \qquad (24)$$

and so, from (19) (22) (23) and (24)

$$x = x_O \frac{A_x + \lambda_2}{\lambda_2 - \lambda_1} EXP(-\lambda_1 t) - x_O \frac{A_x + \lambda_1}{\lambda_2 - \lambda_1} EXP(-\lambda_2 t) \qquad (25)$$

$$y = x_O \frac{B_y}{\lambda_2 - \lambda_1} \left[EXP(-\lambda_1 t) - EXP(-\lambda_2 t) \right] \qquad (26)$$

which is the known result [3].

It is precisely the elegance of the method and its formal simplicity that has offered indication that it could be applied with success to some other more complicated cases in the domain of the study of energy transfer measurements.
Let us consider, in fact, equations (6) (7) again and let us make the substitution

$$\tau = t^{1/2} \qquad (27)$$

and then

$$\frac{d}{d\tau} x = 2A_x \tau x + 2B_x \tau y + 2C_x x \qquad (28)$$

$$\frac{d}{d\tau} y = 2A_y \tau y + 2B_y \tau x + 2C_y y \qquad (29)$$

In the matrix form we have have now

$$\frac{d}{d\tau} \mathbf{X} = (2A\tau + 2C)\, \mathbf{X} \qquad (30)$$

where **X** is the vector (10), A the matrix (11) and C a new matrix defined as

$$C = \begin{bmatrix} C_x & 0 \\ 0 & C_y \end{bmatrix} \qquad (31)$$

The first and very important factor to note is that the matrices A and C do not commute. In fact

$$AC - CA = (C_x - C_y) \begin{bmatrix} 0 & -B_x \\ B_y & 0 \end{bmatrix} \qquad (32)$$

It is precisely the fact that A and C do not commute that prevents us to integrate equation (30) as if it was a linear differential equation. However its simple form opens way to a simple treatment based in a series expansion and also as a infinit product which will be the subject of future publications.
From the foregoing considerations there is however one case where the complete integration is possible. It is obviously seen from (32) that A and C commute if

$$C_x = C_y = C_o \qquad (33)$$

Then we may write, from (30)

$$\mathbf{X} = EXP(A\tau^2 + 2C\tau)\mathbf{X}_O \qquad (34)$$

The reason why this is possible is that since A and C commute [5] we may write

$$EXP(A\tau^2 + 2C\tau) = EXP(A\tau^2).\, EXP(2C\tau) \qquad (35)$$

It will be left to future publications the full discussion of this case as well as the general cases. An example will be however given here to show how the solution (34) can be developed. For this it is necessary to use the expansion

$$\mathrm{EXP}(P) = \sum_{k=0}^{\infty} \frac{P^k}{k!} \tag{36}$$

Then if we use (36) we may write

$$\mathbf{X} = \mathrm{EXP}(At + 2Ct^{1/2})\ \mathbf{X}_O \tag{37}$$

with

$$\mathrm{EXP}(At + 2Ct^{1/2}) = \sum_{k=0}^{\infty} \frac{(At + 2Ct^{1/2})^k}{k!} \tag{38}$$

an expression which is valid for any square matrix [4] although (37) is only valid if A and C commute. Now although the evaluation of (38) is straightforward it is rather cumbersome since it involves successive powers of the matrices A and C. We will present another way of dealing with the problem which can easily be tackled by the usual calculator processes.

We denote by $\lambda_{\pm}$ (t) the eigenvalues of the matrix $A(t) = At + 2Ct^{1/2}$ and define the quantities

$$\lambda_{1,2}(t) = -\lambda_{\pm}\ (t)$$

It must be stressed that although the quantities $\lambda_{\pm}(t)$ are similar to (18) they are not the same. They include the factor t as well as C_x and C_y in the present case.

If S and S^{-1} are the matrices that can lead $A(t)$ to the diagonal form

$$A'(t) = S^{-1} A(t) S = \begin{bmatrix} -\lambda_1(t) & 0 \\ 0 & -\lambda_2(t) \end{bmatrix} \tag{39}$$

i.e.

$$A(t) = S \begin{bmatrix} -\lambda_1(t) & 0 \\ 0 & -\lambda_2(t) \end{bmatrix} S^{-1} \tag{40}$$

Now from

$$\mathrm{EXP}(At) = \sum_{k=0}^{\infty} \frac{[A(t)]^k}{k!}$$

$$= \sum_{k=0}^{\infty} \frac{1}{k!} \left\{ S \begin{bmatrix} -\lambda_1(t) & 0 \\ 0 & -\lambda_2(t) \end{bmatrix} S^{-1} \right\}^k$$

$$= \sum_{k=0}^{\infty} \frac{1}{k!}\ S \begin{bmatrix} -\lambda_1(t) & 0 \\ 0 & -\lambda_2(t) \end{bmatrix}^k S^{-1}$$

$$= S \begin{bmatrix} \sum_{k=0}^{\infty} \frac{[-\lambda_1(t)]^k}{k!} & 0 \\ 0 & \sum_{k=0}^{\infty} \frac{[-\lambda_2(t)]^k}{k!} \end{bmatrix} S^{-1}$$

$$= S \begin{bmatrix} \mathrm{EXP}(-\lambda_1(t)) & 0 \\ 0 & \mathrm{EXP}(-\lambda_2(t)) \end{bmatrix} S^{-1} \tag{41}$$

It goes beyond the scope of the present note to develop more fully these considerations. It may be added at this stage however that the matrices S(and S^{-1}) are easily obtained from the eigenvalues of $A(t)$. If we consider the eigenvalue equation

$$A\mathbf{U}_{\pm} = \lambda_{\pm}\mathbf{U}_{\pm} \tag{42}$$

in the form

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} 1 \\ \alpha_{\pm} \end{bmatrix} = \lambda_{\pm} \begin{bmatrix} 1 \\ \alpha_{\pm} \end{bmatrix} \tag{43}$$

it will be found that

$$S = \begin{bmatrix} 1 & 1 \\ \alpha_+ & \alpha_- \end{bmatrix} \tag{44}$$

$$S^{-1} = \frac{1}{\alpha_- - \alpha_+} \begin{bmatrix} \alpha_- & -1 \\ -\alpha_+ & +1 \end{bmatrix} \tag{45}$$

Important relationships as

$$a_{11}-\lambda_{\pm} \quad =-a_{12}\alpha_{\pm} \tag{46}$$

$$a_{21}-\alpha_{\pm}\lambda_{\pm} \;=-a_{22}\lambda_{\pm} \tag{47}$$

are easily derived which can be used to obtain S and S^{-1} from the (also easily obtained) eigenvalues of the matrix A(t).

Then

$$\alpha_{\pm} = \frac{\lambda_{\pm}-a_{11}}{a_{12}} \tag{48}$$

By substituion into (44) and (45) and then into (40) the expression for EXP(At) is obtained. Then

$$\mathbf{X} = \begin{bmatrix} x \\ y \end{bmatrix} = \mathrm{EXP}(At) \begin{bmatrix} x_o \\ 0 \end{bmatrix} \tag{49}$$

Finally we get the solution

$$x = x_o[F_1\,\mathrm{EXP}(-\lambda_1 t)-F_2\,\mathrm{EXP}(-\lambda_2 t)]\,\mathrm{EXP}(2C_o t^{1/2}) \tag{50}$$

$$y = x_o F_3[\mathrm{EXP}(-\lambda_1 t)-\mathrm{EXP}(-\lambda_2 t)]\,\mathrm{EXP}(2C_o t^{1/2}) \tag{51}$$

which obviously reduces to (25) and (26) when $c_Z = 0$ and is the solution of (28) and (29) under conditions (33).

Numerical applications will be left to future publications.

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REFERENCES

[1] J. C. Conte, *Rev. Port. Quím.*, **11**, 169(1969).
[2] W. R. Ware, T. L. Nemzek, *Chem. Phys. Letters*, **23**, 557 (1973)
[3] J. B. Birks, «Photophysics of Aromatic Molecules», Wiley — Interscience (1970), page 304.
[4] B. P. Lathi — «Signals, Systems and Controls», Intext Educational Publ., N. Y. (1974), page 501.
[5] T. Apostol, «Calculus», vol. I, Blaisdell Publ. Co., London, 1967.

ABSTRACT

The equations which give the time variation of the fluorescence emission intensities of an excimeric energy donor are analysed in the case where a transient term for the energy transfer rate constants has to be considered. A matricial method is proposed to solve the differential equations. A particular case is studied where a rigorous solution is achieved.

RESUMO

Evolução no tempo das intensidades de um doador de energia quando há um termo transiente

Analisam-se as equações que traduzem a variação no tempo da intensidade de emissão de fluorescência de um doador excimérico de energia no caso de haver necessidade de considerar que as constantes de transferência contêm termos transientes. Propõe-se um método Matricial para a resolução das respectivas equações diferenciais. No caso considerado o método conduz a uma solução rigorosa.