ELSEVIER

Chemical Physics 260 (2000) 401–414

Chemical Physics

www.elsevier.nl/locate/chemphys

Linear and convolution methods for the analysis of ground and excited state kinetics. Application to the monomer–excimer scheme

M.N. Berberan-Santos *, J.P.S. Farinha, J.M.G. Martinho

Centro de Química-Física Molecular, Instituto Superior Técnico, 1049-001 Lisboa, Portugal

Received 15 June 2000; in final form 1 August 2000

Abstract

A new linear method for the determination of the rate coefficients of complex first-order (or pseudo-first-order) mechanisms is presented and applied to simulated data. The errors associated with parameter recovery are compared with those of the traditional nonlinear least-squares method. Nonlinear methods based on convolution kinetics are also developed, and general convolution equations are obtained. Special attention is paid in both cases to excited state kinetics, where concentrations are usually known only up to a constant factor. The monomer–excimer kinetics is discussed in detail, explicit relations for parameter correlation being obtained. The influence of transient effects is also quantitatively discussed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

There are two distinct approaches to experimental data analysis. One, aprioristic, assumes a given mathematical model (that in kinetics results from a mechanism) and tries to fit the experimental results with theoretical laws containing unknown parameters. A second approach, more flexible and simpler, but at the same time less rich, assumes no particular model and merely uses empirical functions (e.g. sums of exponentials) to fit the results. This is typically the case in studies of exploratory nature, when no clear idea exists on the possible applicable model (or underlying mechanism), but may also be appropriate if a simple empirical description of the phenomenon suffices.

One of the main objectives of kinetic studies is the determination of the rate coefficients of the elementary steps of a given mechanism. These rate coefficients can be obtained from experimental data using both the differential and the integral methods [1–3]. It is generally accepted that the integral method has advantages over the differential method since the last one, being based on the numerical differentiation of the experimental curve, amplifies experimental error.

---

* Corresponding author. Tel.: +351-1-841-9219; fax: +351-21846-4455.

E-mail addresses: berberan@ist.utl.pt (M.N. Berberan-Santos), farinha@ist.utl.pt (J.P.S. Farinha), jgmartinho@alfa.ist.utl.pt (J.M.G. Martinho).

PII: S0301-0104(00)00274-3

Even if a given mechanism is compatible with experiment, it may not be the only one. Different mechanisms can produce identical time evolutions for the concentrations of some of the species involved (indistinguishability). Also, and assuming that the mechanism is known, the unambiguous assignment of precise values to individual rate coefficients may not be possible (unidentifiability). The aspects of distinguishability and identifiability have been addressed by several authors for first-order ground [4] and excited state [5,6] kinetics.

The aprioristic analysis of ground and excited state kinetic data is usually based on a nonlinear least-squares fit of the experimental curves, where time is the independent variable and the measured dependent variables are concentrations or quantities proportional to the concentrations. Sometimes the only available dependent variables are proportional, not to the concentration of a single species, but to a weighted sum of concentrations, rendering the analysis more delicate. This case will not be addressed here.

In this work, we present a new method for the analysis of ground state and excited state kinetics on the assumption that these are described by first-order mechanisms. In this method, the rate coefficients can be obtained from a linear least-squares fit, which allows the rigorous estimation of the errors associated with the parameters, and does not suffer from the parameter bias frequent in nonlinear fits [7]. Another unique advantage of the new method is that it avoids the computation of the theoretical time evolutions, which, even for moderately complex schemes, cannot be obtained in analytical form. We also derive general equations based on the convolution approach, that contain as particular cases some integral relations obtained previously [8].

Both treatments are applied to a reversible two-state kinetic reaction scheme that describes both the intramolecular and intermolecular excimer and exciplex formation processes [9] as well as intramolecular charge transfer state formation [10]. A detailed analysis of parameter correlation is carried out. The influence of transient effects (time-dependent rate coefficients) on parameter correlation removal is quantitatively discussed.

2. Linear method

2.1. Differential form

Consider a kinetic scheme involving species $X_1, X_2, \ldots, X_n$, and composed by elementary steps that are first-order or pseudo-first order. Besides interconversion, the species are produced at rates $I_i(t)$ $(i = 1, 2, \ldots, n)$, so that the governing rate equations are

$$\begin{aligned} \frac{\mathrm{d}C_1}{\mathrm{d}t} &= I_1(t) - k_{11}C_1 + k_{12}C_2 + \cdots, \\ \frac{\mathrm{d}C_2}{\mathrm{d}t} &= I_2(t) + k_{21}C_1 - k_{22}C_2 + \cdots, \end{aligned} \tag{1}$$

where C_i is the concentration of X_i, and the rate coefficient k_{ii} $(i = 1, 2, \ldots, n)$ is the sum of rate coefficients for all elementary decay paths of X_i (e.g., if X_i is an excited state species, $k_{ii} = \Gamma_i + \sum_{j, j\neq i} k_{ji}$ $(i = 1, 2, \ldots, n)$, where Γ_i is the intrinsic decay rate constant), and k_{ij} $(i \neq j)$ is the rate coefficient for the conversion $j \rightarrow i$. Unless explicitly stated, it is assumed throughout that all rate coefficients are time-independent.

Suppose all $C_i(t)$ and $I_i(t)$ curves $(i = 1, 2, \ldots, n)$ of Eq. (1) are known from experiment, at closely enough spaced times t_k $(k = 1, 2, \ldots, m; m \gg n)$. Then, Eq. (1) can be rewritten as

$$\begin{aligned} Y_1(t_k) &= I_1(t_k) - k_{11}C_1(t_k) + k_{12}C_2(t_k) + \cdots, \\ Y_2(t_k) &= I_2(t_k) + k_{21}C_1(t_k) - k_{22}C_2(t_k) + \cdots \quad (k = 1, 2, \ldots, m), \end{aligned} \tag{2}$$

where Y_i is the time derivative of C_i $(i = 1, 2, \ldots, n)$, numerically computed for time t_k. The problem of determining the rate constants k_{ij} is thus reduced to n linear least-squares fits according to Eq. (2), whereby the computed Y_i $(k_{i1}, k_{i2}, \ldots, k_{in})$, as given by Eqs. (1) and (2), are confronted to the Y_i numerically computed from the experimental data. As follows from Eq. (2), for a given Y_i to enter the least-squares fit it is not only necessary to know $C_i(t)$, but also the $C_j(t)$ of all X_j $(j \neq i)$ that react to give X_i.

This method of analysis, being based on the numerical differentiation, is not usually suited for the analysis of experimental (noisy) curves. The linear integral method discussed herein is to be preferred for that purpose.

2.2. Integral form

The integrated form of Eq. (1) admits an entirely equivalent approach; integrating both sides with respect to time, one obtains,

$$\begin{aligned} C_1(t) &= C_1(0) + \int_0^t I_1(u)\mathrm{d}u - k_{11}\int_0^t C_1(u)\mathrm{d}u + k_{12}\int_0^t C_2(u)\mathrm{d}u + \cdots, \\ C_2(t) &= C_2(0) + \int_0^t I_2(u)\mathrm{d}u + k_{21}\int_0^t C_1(u)\mathrm{d}u - k_{22}\int_0^t C_2(u)\mathrm{d}u + \cdots \end{aligned} \tag{3}$$

and the problem of determining the rate constants k_{ij} is again reduced to n linear least-squares fits according to Eq. (4),

$$\begin{aligned} C_1(t_k) &= C_1(0) + J_1(t_k) - k_{11}Z_1(t_k) + k_{12}Z_2(t_k) + \cdots, \\ C_2(t_k) &= C_2(0) + J_2(t_k) + k_{21}Z_1(t_k) - k_{22}Z_2(t_k) + \cdots, \end{aligned} \tag{4}$$

where $J_i(t_k) = \int_0^{t_k} I_i(u)\mathrm{d}u$ and $Z_i(t_k) = \int_0^{t_k} C_i(u)\mathrm{d}u$, all integrations being performed numerically. Without loss of generality, it may be supposed that $C_i(0) = C_i(0^-) = 0$ $(i = 1, 2, \ldots, n)$, the initial concentrations $C_i(0) = C_i(0^+)$ being incorporated in the production term J_i. As before, for a given C_i to enter the least-squares fit it is not only necessary to know $Z_i(t)$, but also the $Z_j(t)$ of all X_j $(j \neq i)$ that react to produce X_i.

For future reference, we remark here that both methods also hold in the more general case of elementary steps of any order.

Considering again Eqs. (2) and (4), there are generally n^2 unknowns and the same number of parameters, and the problem is determined. A special case, applicable to ground-state kinetics, is that where $k_{ii} = \sum_{j,j\neq i} k_{ji}$ $(i = 1, 2, \ldots, n)$, the number of independent unknowns being reduced to $(n^2 - n)$. In such a case a joint least-squares (global analysis) of all equations is justified.

2.3. When the concentrations are known only up to a constant factor

Consider now that all concentrations and production rates are known from experiment but for a constant, unknown factor, as is the case in most excited-state studies, including fluorescence decay measurements. In this case

$$I_i = a_i P_i, \qquad C_i = b_i D_i, \tag{5}$$

where a_i and b_i are the unknown factors and P_i and D_i are the experimental production rates and observables, respectively $(i = 1, 2, \ldots, n)$. Eq. (1) can then be rewritten as

$$\begin{aligned}\frac{\mathrm{d}D_1}{\mathrm{d}t} &= \alpha_1 P_1 - \beta_{11} D_1 + \beta_{12} D_2 + \cdots,\\ \frac{\mathrm{d}D_2}{\mathrm{d}t} &= \alpha_2 P_2 + \beta_{21} D_1 - \beta_{22} D_2 + \cdots,\end{aligned} \tag{6}$$

where $\alpha_i = a_i/b_i$ and $\beta_{ij} = b_j k_{ij}/b_i$. The fitting Eq. (2) thus become

$$\begin{aligned}Y_1(t_k) &= \alpha_1 P_1(t_k) - \beta_{11} D_1(t_k) + \beta_{12} D_2(t_k) + \cdots,\\ Y_2(t_k) &= \alpha_2 P_2(t_k) + \beta_{21} D_1(t_k) - \beta_{22} D_2(t_k) + \cdots \quad (k = 1, 2, \ldots, m),\end{aligned} \tag{7}$$

where Y_i now stands for the numerical time derivative of the observable D_i. In each equation, there are $n+1$ coefficients that can in principle be determined. Since there are n equations, the total number of coefficients is $n(n+1)$. On the other hand, the number of unknowns is higher, $n^2 + 2n$. In this way, n out of $n^2 + 2n$ parameters must be determined independently. As before, a special case, applicable to ground-state kinetics, is that where $k_{ii} = \sum_{j,j\neq i} k_{ji}$ $(i = 1, 2, \ldots, n)$, the number of independent unknowns being $n^2 + n$, and all parameters can thus be obtained from experiment. A joint fit (global analysis) of all equations is again justified.

If some of the production rates are zero, there is again a reduction in the number of parameters. For instance, if only one production rate is nonzero, the number of unknowns is $n^2 + n + 1$, and only one extra relation is needed.

The same reasoning applies to the integrated equations: Instead of Eqs. (3) and (4) we have

$$\begin{aligned}D_1 &= \alpha_1 J_1 - \beta_{11} Z_1 + \beta_{12} Z_2 + \cdots,\\ D_2 &= \alpha_2 J_2 + \beta_{21} Z_1 - \beta_{22} Z_2 + \cdots,\end{aligned} \tag{8}$$

where now $J_i(t) = \int_0^t P_i(u)\mathrm{d}u$ and $Z_i(t) = \int_0^t D_i(u)\mathrm{d}u$. Again $\alpha_i = a_i/b_i$ and $\beta_{ij} = b_j k_{ij}/b_i$ and thus, the previous conclusions regarding the number of parameters and equations are also valid here.

2.4. Advantages and limitations of the linear method

The proposed method of kinetic data analysis has two great advantages. Firstly, it is linear in the parameters, thus allowing a straightforward parameter and parameter uncertainty evaluation. For the evaluation of the latter, it should be generally valid to assume that the errors of the dependent (Y_i or C_i) variable are independent of the errors of the dependent variables (C_i or Z_i). This is completely justified if the temporal dependence of the measurement errors is of the white-noise type; in such a situation, the error of the time-derivative Y_i or of the time-integral Z_i will be uncorrelated with the error of the concentration itself, C_i. It is also of course assumed that the errors of the dependent variables are uncorrelated. Secondly, contrary to the usual approaches, it does not require the computation of the theoretical time evolutions, which, even for moderately complex schemes, cannot be obtained in analytical form.

The major limitation of the proposed method stems from the fact that, in most cases of interest, not all relevant concentrations C_i are known, or, if so, not for the sufficiently small time steps required for the accurate numerical differentiations or integrations used by the least-squares fitting according to Eqs. (2) and (4).

Nevertheless, in some special situations experimental data of good quality and closely spaced in time may be available for all species involved. This is for instance the case for monomer–excimer kinetics studied by the single-photon timing technique when monomer and excimer are spectrally well separated, as with pyrene [8,11]. The discussed approach should be of interest here. This kinetic scheme is discussed in detail in Section 4.

3. Convolution form

The rate equations can be written in an integrated form more general than Eq. (3). Consider again Eq. (1), rewritten as

$$\begin{aligned}\frac{dC_1}{dt} &= I_1(t) - \alpha_1 k_{11} C_1 - (1-\alpha_1)k_{11}C_1 + k_{12}C_2 + \cdots,\\ \frac{dC_2}{dt} &= I_2(t) + k_{21}C_1 - \alpha_2 k_{22}C_2 - (1-\alpha_2)k_{22}C_2 + \cdots,\end{aligned} \tag{9}$$

where $\alpha_1, \alpha_2, \ldots$ are parameters taking arbitrary values between 0 and 1. Eq. (9) can be written as

$$\begin{aligned}\frac{dC_1}{dt} + \alpha_1 k_{11}C_1 &= I_1(t) - (1-\alpha_1)k_{11}C_1 + k_{12}C_2 + \cdots,\\ \frac{dC_2}{dt} + \alpha_2 k_{22}C_2 &= I_2(t) + k_{21}C_1 - (1-\alpha_2)k_{22}C_2 + \cdots.\end{aligned} \tag{10}$$

Taking Laplace transforms on both sides, one obtains

$$\begin{aligned}(s+\alpha_1 k_{11})\overline{C}_1 &= \overline{I}_1 - (1-\alpha_1)k_{11}\overline{C}_1 + k_{12}\overline{C}_2 + \cdots,\\ (s+\alpha_2 k_{22})\overline{C}_2 &= \overline{I}_2 + k_{21}\overline{C}_1 - (1-\alpha_2)k_{22}\overline{C}_2 + \cdots,\end{aligned} \tag{11}$$

or

$$\begin{aligned}\overline{C}_1 &= \frac{\overline{I}_1}{s+\alpha_1 k_{11}} - \frac{(1-\alpha_1)k_{11}\overline{C}_1}{s+\alpha_1 k_{11}} + \frac{k_{12}\overline{C}_2}{s+\alpha_1 k_{11}} + \cdots,\\ \overline{C}_2 &= \frac{\overline{I}_2}{s+\alpha_2 k_{22}} + \frac{k_{21}\overline{C}_1}{s+\alpha_2 k_{22}} - \frac{(1-\alpha_2)k_{22}\overline{C}_2}{s+\alpha_2 k_{22}} + \cdots\end{aligned} \tag{12}$$

and finally, performing the inverse Laplace transformation,

$$\begin{aligned}C_1 &= [I_1 - (1-\alpha_1)k_{11}C_1 + k_{12}C_2 + \cdots] \otimes \exp(-\alpha_1 k_{11} t),\\ C_2 &= [I_2 + k_{21}C_1 - (1-\alpha_2)k_{22}C_2 + \cdots] \otimes \exp(-\alpha_2 k_{22} t),\end{aligned} \tag{13}$$

where $\otimes$ stands for convolution, the convolution between two functions $f(t)$ and $g(t)$ being another function $h(t) = \int_0^t f(u)g(t-u)du = f \otimes g = g \otimes f$. Eq. (13) reduce to Eq. (3) if $\alpha_1 = \alpha_2 = \ldots = 0$.

If k_{ii} is a sum of rate coefficients, as mentioned in Section 2,

$$k_{ii} = \Gamma_i + \sum_{j,j\neq i} k_{ji} \quad (i = 1,2,\ldots,n). \tag{14}$$

Eq. (13) admits a further generalization, because one can write,

$$k_{ii} = [\alpha_i + (1-\alpha_i)]\Gamma_i + \sum_{j,j\neq i}[\beta_{ji} + (1-\beta_{ji})]k_{ij} \quad (i = 1,2,\ldots,n), \tag{15}$$

where α_i and β_{ji} are again parameters taking arbitrary values between 0 and 1. Eq. (13) become

$$\begin{aligned} C_1 &= \left\{ I_1 - \left[(1-\alpha_1)\Gamma_1 + \sum_{j,j\neq 1} (1-\beta_{j1}) k_{j1} \right] C_1 + k_{12} C_2 + \cdots \right\} \otimes \exp\left[-\left(\alpha_1 \Gamma_1 + \sum_{j,j\neq 1} \beta_{j1} k_{j1} \right) t \right], \\ C_2 &= \left\{ I_2 + k_{21} C_1 - \left[(1-\alpha_2)\Gamma_2 + \sum_{j,j\neq 2} (1-\beta_{j2}) k_{j2} \right] C_2 + \cdots \right\} \otimes \exp\left[-\left(\alpha_2 \Gamma_2 + \sum_{j,j\neq 2} \beta_{j2} k_{j2} \right) t \right]. \end{aligned} \tag{16}$$

The importance of the α_i and β_{ij} coefficients will now be discussed in connection with a particular kinetic scheme.

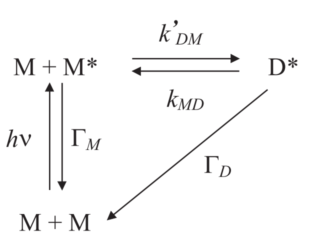
4. Application to monomer–excimer kinetics

4.1. Usual method

Consider a two-state kinetic model that describe the excimer/exciplex kinetics (Scheme 1). The usual approach to this problem consists of a nonlinear least-squares fit of monomer and excimer theoretical decays to the experimental ones. This amounts to two double exponential fits whose common decay constants are [9]

$$\Gamma_{1,2} = -\frac{1}{2}\left\{ (X+Y) \mp \left[(Y-X)^2 + 4k_{\mathrm{DM}}k_{\mathrm{MD}} \right]^{1/2} \right\}, \quad X = \Gamma_{\mathrm{M}} + k_{\mathrm{DM}};\ Y = \Gamma_{\mathrm{D}} + k_{\mathrm{MD}}, \tag{17}$$

where $k_{\mathrm{DM}} = k'_{\mathrm{DM}}[\mathrm{M}]$ is a pseudo-unimolecular rate constant, and [M] is the ground state concentration of monomer. As is well-known [4,5,9], unless Γ_{M} is known from a separate experiment, the individual rate constants cannot be obtained from the pair of fitted lifetimes and from the experimental ratio of the pre-exponential factors of the monomer decay curve. The method was improved by Boens and Ameloot et al. that developed a global (compartmental) analysis of fluorescence decays recorded at several excitation and emission wavelengths [12]. This allowed the determination of the rate coefficients and the species associated excitation and emission spectra. Nevertheless, owing to limitations of the nonlinear least-square procedure, the precise evaluation of the parameters uncertainties is in itself difficult. In addition, the rate coefficients can be biased due to the nonlinearity between the rate coefficients and the fitted parameters [7]. Simulated monomer and excimer decay curves, with added synthetic noise, were generated as previously described [7], using as input values the experimental rate constants for the pyrene monomer and excimer in cyclohexane at room temperature [13], $\Gamma_{\mathrm{M}} = 2.25 \times 10^6\ \mathrm{s}^{-1}$, $\Gamma_{\mathrm{D}} = 1.55 \times 10^7\ \mathrm{s}^{-1}$, $k_{\mathrm{DM}} = 6.7 \times 10^6\ \mathrm{s}^{-1}$ and $k_{\mathrm{MD}} = 6.5 \times 10^6\ \mathrm{s}^{-1}$, and a concentration of 1.0×10^{-3} M. From the analysis of the simulated decays by the usual method (using a double exponential fit of the monomer decay curve), a set of kinetic parameters was



Scheme 1. Monomer–excimer kinetics.

Table 1
Values of the parameters obtained from the fit of a simulated pyrene monomer decay by the nonlinear least-squares method[a]

	Input value	Recovered value	Bias (%)
k_{DM} (s^{-1})	6.7×10^6	6.8×10^6	2
k_{MD} (s^{-1})	6.5×10^6	7.2×10^6	11
τ_D (ns)	64.5	62	4

[a] Percent bias relative to the input parameter values. $\tau_M = 444$ ns is assumed to be known from an independent experiment.

obtained. These are in general biased with respect to the input values, owing to the nonlinear nature of the fitting procedure, as can be seen in Table 1 [7].

4.2. Linear method

Application of the equations of Section 2 (linear method) to the monomer–excimer (or exciplex) mechanism shown in Scheme 1 is immediate. From the rate equations,

$$\begin{aligned}\frac{d[M^*]}{dt} &= I(t) - \Gamma_M[M^*] - k_{DM}[M^*] + k_{MD}[D^*],\\ \frac{d[D^*]}{dt} &= -\Gamma_D[D^*] - k_{MD}[D^*] + k_{DM}[M^*],\end{aligned} \tag{18}$$

one obtains the differential form. From the single photon timing experiments, the impulse function $L(t)$, and the monomer $I_M(t)$ and excimer $I_D(t)$ decays are related with the production rate $I(t)$, and the monomer, $[M^*](t)$, and the excimer $[D^*](t)$, by

$$I(t) = aL(t), \qquad [M^*](t) = b_M I_M(t), \qquad [D^*](t) = b_D I_D(t), \tag{19}$$

where a, b_M and b_D are unknown parameters, the differential form of the linear method becomes

$$\begin{aligned}\frac{dI_M}{dt} &= \alpha L - (\Gamma_M + k_{DM})I_M + \beta_{MD} I_D,\\ \frac{dI_D}{dt} &= -(\Gamma_D + k_{MD})I_D + \beta_{DM} I_M,\end{aligned} \tag{20}$$

where

$$\alpha = \frac{a}{b_M}, \qquad \beta_{MD} = \frac{b_D}{b_M} k_{MD}, \qquad \beta_{DM} = \frac{b_M}{b_D} k_{DM}. \tag{21}$$

A fit according to Eq. (20) yields therefore in principle the following constants: $\Gamma_M + k_{DM}$, $\Gamma_D + k_{MD}$, and $\beta_{MD}\beta_{DM} = k_{MD}k_{DM}$. The number of parameters obtainable from a single experiment is thus inferior by one to the number of unknowns. The extra relation needed can be obtained either from a steady-state experiment or, in the case of an intermolecular excimer, by studying two or more concentrations under the same conditions [4,5].

The analogous integral method discussed in Section 2 yields

$$\begin{aligned}[M^*] &= \int_0^t I(u)du - (\Gamma_M + k_{DM})\int_0^t [M^*](u)du + k_{MD}\int_0^t [D^*](u)du,\\ [D^*] &= -(\Gamma_D + k_{MD})\int_0^t [D^*](u)du + k_{DM}\int_0^t [M^*](u)du\end{aligned} \tag{22}$$

and, given Eq. (19),

$$\begin{aligned} I_{\mathrm{M}} &= \alpha \int_0^t L(u)\mathrm{d}u - (\Gamma_{\mathrm{M}} + k_{\mathrm{DM}}) \int_0^t I_{\mathrm{M}}(u)\mathrm{d}u + \beta_{\mathrm{MD}} \int_0^t I_{\mathrm{D}}(u)\mathrm{d}u, \\ I_{\mathrm{D}} &= -(\Gamma_{\mathrm{D}} + k_{\mathrm{MD}}) \int_0^t I_{\mathrm{D}}(u)\mathrm{d}u + \beta_{\mathrm{DM}} \int_0^t I_{\mathrm{M}}(u)\mathrm{d}u, \end{aligned} \tag{23}$$

where the parameters retain the meanings given in Eq. (21). A fit according to Eq. (23) yields again the constants: $\Gamma_{\mathrm{M}} + k_{\mathrm{DM}}$, $\Gamma_{\mathrm{D}} + k_{\mathrm{MD}}$, and $\beta_{\mathrm{MD}}\beta_{\mathrm{DM}} = k_{\mathrm{MD}}k_{\mathrm{DM}}$. As previously mentioned, the linear integral method is better suited for the analysis of noisy data than the differential one.

Analysis of simulated pyrene decay curves using the integral method yield parameter values exactly coincident with the input parameters (given in Table 1), when Γ_{M} is supposed to be known (in experimental studies this parameter can usually be obtained from independent measurements). This method also has the advantage of allowing a straightforward estimation of the uncertainty of the recovered parameters, in contrast to the usual nonlinear method.

4.3. Convolution form

Consider now the equations applicable to the monomer–excimer Scheme 1, that follow from Eq. (16)

$$\begin{aligned} [\mathrm{M}^*] &= \{I_1 - [(1-\alpha_{\mathrm{M}})\Gamma_{\mathrm{M}} + (1-\beta_{\mathrm{DM}})k_{\mathrm{DM}}][\mathrm{M}^*] + k_{\mathrm{MD}}[\mathrm{D}^*]\} \otimes \exp[-(\alpha_{\mathrm{M}}\Gamma_{\mathrm{M}} + \beta_{\mathrm{DM}}k_{\mathrm{DM}})t], \\ [\mathrm{D}^*] &= \{k_{\mathrm{DM}}[\mathrm{M}^*] - [(1-\alpha_{\mathrm{D}})\Gamma_{\mathrm{D}} + (1-\beta_{\mathrm{MD}})k_{\mathrm{MD}}][\mathrm{D}^*]\} \otimes \exp[-(\alpha_{\mathrm{D}}\Gamma_{\mathrm{D}} + \beta_{\mathrm{MD}}k_{\mathrm{MD}})t]. \end{aligned} \tag{24}$$

It is seen from these equations that a fit of the type

$$\begin{aligned} [\mathrm{M}^*] &= (I + a[\mathrm{M}^*] + b[\mathrm{D}^*]) \otimes \exp(ct), \\ [\mathrm{D}^*] &= (d[\mathrm{M}^*] + e[\mathrm{D}^*]) \otimes \exp(ft), \end{aligned} \tag{25}$$

allows the determination of the four rate constants, because

$$\begin{aligned} -(a+c) &= \Gamma_{\mathrm{M}} + k_{\mathrm{DM}}, \\ -(e+f) &= \Gamma_{\mathrm{D}} + k_{\mathrm{MD}}, \\ b &= k_{\mathrm{MD}}, \\ d &= k_{\mathrm{DM}}. \end{aligned} \tag{26}$$

From Eq. (26) we can see that there are perfect correlations between the fitting parameter pairs (a, c) and (e, f).

Considering again Eq. (24), one may fix beforehand the values of some or of all the arbitrary parameters α_{M}, α_{D}, β_{DM} and β_{MD}, so as to alter the general form of Eq. (25). There are first the following possibilities, where a single correlation remains:

(i) $a = 0 \Longleftrightarrow \alpha_{\mathrm{M}} = \beta_{\mathrm{DM}} = 1$; ($e$ and f correlated).
(ii) $c = 0 \Longleftrightarrow \alpha_{\mathrm{M}} = \beta_{\mathrm{DM}} = 0$; ($e$ and f correlated).
(iii) $e = 0 \Longleftrightarrow \alpha_{\mathrm{D}} = \beta_{\mathrm{MD}} = 1$; ($a$ and c correlated).
(iv) $f = 0 \Longleftrightarrow \alpha_{\mathrm{D}} = \beta_{\mathrm{MD}} = 0$; ($a$ and c correlated).

One may also consider the following combinations, for which the fitting parameters are no longer correlated:

(v) $a = 0$ and $e = 0$.
(vi) $a = 0$ and $f = 0$.
(vii) $c = 0$ and $e = 0$.
(viii) $c = 0$ and $f = 0$.

In all cases the four rate constants can be recovered from the appropriate fit (the last one corresponds to the linear form discussed in Section 2).

We now consider the experimental situation corresponding to single photon timing, i.e., for which only the quantities given by Eq. (19) are known from experiment. One has, instead of Eq. (24),

$$\begin{aligned} I_{\mathrm{M}} &= \{\alpha L - [(1-\alpha_{\mathrm{M}})\Gamma_{\mathrm{M}} + (1-\beta_{\mathrm{DM}})k_{\mathrm{DM}}]I_{\mathrm{M}} + \gamma_{\mathrm{MD}} I_{\mathrm{D}}\} \otimes \exp[-(\alpha_{\mathrm{M}}\Gamma_{\mathrm{M}} + \beta_{\mathrm{DM}}k_{\mathrm{DM}})t], \\ I_{\mathrm{D}} &= \{\gamma_{\mathrm{DM}} I_{\mathrm{M}} - [(1-\alpha_{\mathrm{D}})\Gamma_{\mathrm{D}} + (1-\beta_{\mathrm{MD}})k_{\mathrm{MD}}]I_{\mathrm{D}}\} \otimes \exp[-(\alpha_{\mathrm{D}}\Gamma_{\mathrm{D}} + \beta_{\mathrm{MD}}k_{\mathrm{MD}})t], \end{aligned} \tag{27}$$

where

$$\alpha = \frac{a}{b_{\mathrm{M}}}, \qquad \gamma_{\mathrm{MD}} = \frac{b_{\mathrm{D}}}{b_{\mathrm{M}}} k_{\mathrm{MD}}, \qquad \gamma_{\mathrm{DM}} = \frac{b_{\mathrm{M}}}{b_{\mathrm{D}}} k_{\mathrm{DM}} \tag{28}$$

In this way, instead of Eq. (25) one has

$$\begin{aligned} I_{\mathrm{M}} &= (\alpha L + aI_{\mathrm{M}} + bI_{\mathrm{D}}) \otimes \exp(ct), \\ I_{\mathrm{D}} &= (dI_{\mathrm{M}} + eI_{\mathrm{D}}) \otimes \exp(ft), \end{aligned} \tag{29}$$

where

$$\begin{aligned} -(a+c) &= \Gamma_{\mathrm{M}} + k_{\mathrm{DM}}, \\ -(e+f) &= \Gamma_{\mathrm{D}} + k_{\mathrm{MD}}, \\ bd &= k_{\mathrm{MD}} k_{\mathrm{DM}}. \end{aligned} \tag{30}$$

In this way, and as before, not all parameters can be determined from a single concentration. Again, there are perfect correlation relations between the fitting parameter pairs (a, c) and (e, f), and if one fixes beforehand the values of some of the arbitrary parameters α_{M}, α_{D}, β_{DM} and β_{MD} in Eq. (27), the general form of Eq. (29) is altered. For the following possibilities, a single correlation remains:

(i) $a = 0 \Longleftrightarrow \alpha_{\mathrm{M}} = \beta_{\mathrm{DM}} = 1$; ($e$ and f correlated).
(ii) $c = 0 \Longleftrightarrow \alpha_{\mathrm{M}} = \beta_{\mathrm{DM}} = 0$; ($e$ and f correlated).
(iii) $e = 0 \Longleftrightarrow \alpha_{\mathrm{D}} = \beta_{\mathrm{MD}} = 1$; ($a$ and c correlated).
(iv) $f = 0 \Longleftrightarrow \alpha_{\mathrm{D}} = \beta_{\mathrm{MD}} = 0$; ($a$ and c correlated).

But in the combinations

(v) $a = 0$ and $e = 0$,
(vi) $a = 0$ and $f = 0$,
(vii) $c = 0$ and $e = 0$,
(viii) $c = 0$ and $f = 0$,

the fitting parameters are no longer correlated and all four rate constants can be recovered from the appropriate fit (the last one corresponds to the linear form Eq. (23)). Fig. 1 shows several plots of the reduced chi-squared χ^2 (a common goodness-of-fit criterion), as a function of the parameter c, for fixed values of the parameter a obtained from the analysis of simulated monomer decay curves (same conditions as for Table 1). As predicted from Eqs. (29) and (30) the minimum value of χ^2 occurs when $\Gamma_{\mathrm{M}} + k_{\mathrm{DM}} = -(a+c)$. Then, only when Γ_{M} or k_{DM} are fixed beforehand, can the other parameter be recovered from the fit.

5. Combined monomer and excimer

5.1. Linear method

Consider the starting rate equations, Eq. (18). Addition of these two equations termwise leads to a simpler equation, that does not contain the cross terms [14],

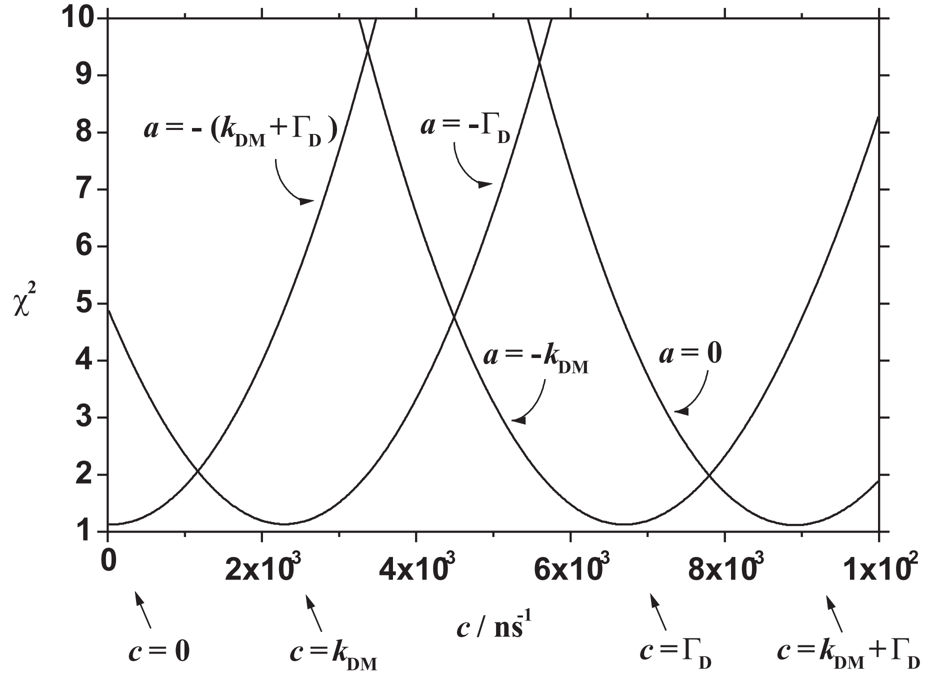


Fig. 1. Plot of the reduced chi-squared χ^2 as a function of the parameter c, obtained for fixed values of the parameter a. Simulated monomer decay curves were analyzed with Eq. (29). As predicted from Eqs. (29) and (30), the minimum value of χ^2 occurs when $\Gamma_M + k_{DM} = -(a + c)$. Then, only when either Γ_M or k_{DM} are fixed beforehand, can the other parameter be recovered from the fit.

$$\frac{d[M^*]}{dt} + \frac{d[D^*]}{dt} = I(t) - \Gamma_M[M^*] - \Gamma_D[D^*]. \tag{31}$$

A fit of the type discussed in Section 2, with $[M^*] + [D^*]$ either in the differential or in the integral form, allows the direct evaluation of Γ_D and Γ_M. If however only the impulse function $L(t)$, and the monomer $I_M(t)$ and excimer $I_D(t)$ decays are known, Eq. (31) becomes

$$b_M \frac{dI_M}{dt} + b_D \frac{dI_D}{dt} = aL(t) - b_M \Gamma_M I_M - b_D \Gamma_D I_D. \tag{32}$$

From the point of view of fitting, one can rewrite Eq. (32) as

$$\frac{dI_D}{dt} = AL + BI_M + CI_D + D\frac{dI_M}{dt}, \tag{33}$$

where A, B, C and D are fitting parameters.

Consider now a general linear combination of the time derivatives of $[M^*]$ and $[D^*]$, where the cross terms necessarily appear,

$$\frac{d[M^*]}{dt} + (1 + \delta)\frac{d[D^*]}{dt} = I - (\delta k_{DM} + \Gamma_M)[M^*] + (\delta k_{MD} - \Gamma_D)[D^*]. \tag{34}$$

In terms of the single photon timing observables, Eq. (34) becomes,

$$\frac{\mathrm{d}I_\mathrm{D}}{\mathrm{d}t} = \frac{a}{(1+\delta)b_\mathrm{D}}L - \frac{b_\mathrm{M}}{(1+\delta)b_\mathrm{D}}\left\{(\delta k_\mathrm{DM} + \Gamma_\mathrm{M})I_\mathrm{M} + \frac{\mathrm{d}I_\mathrm{M}}{\mathrm{d}t}\right\} + \frac{1}{(1+\delta)}(\delta k_\mathrm{MD} - \Gamma_\mathrm{D})I_\mathrm{D}, \tag{35}$$

which has the same form as Eq. (33) and therefore the simultaneous determination of Γ_D and Γ_M is impossible. However, if Γ_M, for instance, is known, the ambiguity disappears because the fitting equation may be written as

$$\frac{\mathrm{d}I_\mathrm{D}}{\mathrm{d}t} = AL + B\left(\Gamma_\mathrm{M}I_\mathrm{M} + \frac{\mathrm{d}I_\mathrm{M}}{\mathrm{d}t}\right) + CI_\mathrm{D}, \tag{36}$$

where $C = -\Gamma_\mathrm{D}$, and Γ_D can be determined.

5.2. *Convolution form*

It is also possible to obtain integral relations between $[\mathrm{M}^*]$ and $[\mathrm{D}^*]$ that do not contain the rate constants for interconversion k_DM and k_MD [7,10].

Repeating now the procedure applied in Eqs. (9)–(13), but starting with Eq. (31), one obtains, after rearrangement,

$$\begin{aligned}(\Gamma_\mathrm{M} - \alpha_2\Gamma_\mathrm{D})[\mathrm{M}^*] \otimes \exp(-\alpha_2\Gamma_\mathrm{D}t) + (\alpha_1\Gamma_\mathrm{M} - \Gamma_\mathrm{D})[\mathrm{D}^*] \otimes \exp(-\alpha_1\Gamma_\mathrm{M}t)\\ = I \otimes [\exp(-\alpha_2\Gamma_\mathrm{D}t) - \exp(-\alpha_1\Gamma_\mathrm{M}t)] + (1-\alpha_1)\Gamma_\mathrm{M}[\mathrm{M}^*] \otimes \exp(-\alpha_1\Gamma_\mathrm{M}t) - (1-\alpha_2)\Gamma_\mathrm{D}[\mathrm{D}^*]\\ \otimes \exp(-\alpha_2\Gamma_\mathrm{D}t),\end{aligned} \tag{37}$$

where α_1 and α_2 are again parameters taking values between 0 and 1. The equations previously derived in Refs. [8,11] can be obtained from Eq. (37) as particular cases:

(i) If $\alpha_1 = \alpha_2 = 1$,

$$(\Gamma_\mathrm{M} - \Gamma_\mathrm{D})\{[\mathrm{M}^*] \otimes \exp(-\Gamma_\mathrm{D}t) + [\mathrm{D}^*] \otimes \exp(-\Gamma_\mathrm{M}t)\} = I \otimes [\exp(-\Gamma_\mathrm{D}t) - \exp(-\Gamma_\mathrm{M}t)]. \tag{38}$$

(ii) If $\alpha_1 = 0$ and $\alpha_2 = 1$,

$$(\Gamma_\mathrm{M} - \Gamma_\mathrm{D})[\mathrm{M}^*] \otimes \exp(-\Gamma_\mathrm{D}t) - \Gamma_\mathrm{D}[\mathrm{D}^*] \otimes 1 = I \otimes [\exp(-\Gamma_\mathrm{D}t) - 1] + \Gamma_\mathrm{M}[\mathrm{M}^*] \otimes 1, \tag{39}$$

whose differentiation gives

$$[\mathrm{M}^*] + [\mathrm{D}^*] + (\Gamma_\mathrm{M} - \Gamma_\mathrm{D})[\mathrm{M}^*] \otimes \exp(-\Gamma_\mathrm{D}t) = I \otimes \exp(-\Gamma_\mathrm{D}t). \tag{40}$$

(iii) If $\alpha_1 = 1$ and $\alpha_2 = 0$,

$$\Gamma_\mathrm{M}[\mathrm{M}^*] \otimes 1 + (\Gamma_\mathrm{M} - \Gamma_\mathrm{D})[\mathrm{D}^*] \otimes \exp(-\Gamma_\mathrm{M}t) = I \otimes [1 - \exp(-\Gamma_\mathrm{M}t)] - \Gamma_\mathrm{D}[\mathrm{D}^*] \otimes 1, \tag{41}$$

whose differentiation gives

$$[\mathrm{M}^*] + [\mathrm{D}^*] + (\Gamma_\mathrm{D} - \Gamma_\mathrm{M})[\mathrm{D}^*] \otimes \exp(-\Gamma_\mathrm{M}t) = I \otimes \exp(-\Gamma_\mathrm{M}t). \tag{42}$$

One thus sees that fits of the types

$$[\mathrm{M}^*] + [\mathrm{D}^*] = (a[\mathrm{M}^*] + I) \otimes \exp(bt)$$

and

$$[\mathrm{M}^*] + [\mathrm{D}^*] = (c[\mathrm{D}^*] + I) \otimes \exp(dt), \tag{43}$$

where *a*, *b*, *c* and *d* are the fitting parameters, allow the determination of Γ_M and Γ_D. Also, Eq. (38), rewritten as

$$[\mathrm{D}^*] \otimes \exp(-\Gamma_\mathrm{M} t) = aI \otimes [\exp(-\Gamma_\mathrm{D} t) - \exp(-\Gamma_\mathrm{M} t)] - [\mathrm{M}^*] \otimes \exp(-\Gamma_\mathrm{D} t) \quad a = \frac{1}{\Gamma_\mathrm{M} - \Gamma_\mathrm{D}} \tag{44}$$

should allow the determination of Γ_D, provided Γ_M is known.

It is of interest to note that Eqs. (40) and (42) are particular cases of a more general relation obtained from the memberwise addition of Eq. (24) or Eq. (25), imposing the equality of the arguments of the two exponentials, and yielding

$$[\mathrm{M}^*] + [\mathrm{D}^*] = I \otimes \exp(-\alpha t) + (\alpha - \Gamma_\mathrm{M})[\mathrm{M}^*] \otimes \exp(-\alpha t) + (\alpha - \Gamma_\mathrm{D})[\mathrm{D}^*] \otimes \exp(-\alpha t), \tag{45}$$

where α, common argument of the exponentials, is

$$\alpha = \alpha_\mathrm{M}\Gamma_\mathrm{M} + \beta_\mathrm{DM}k_\mathrm{DM} = \alpha_\mathrm{D}\Gamma_\mathrm{D} + \beta_\mathrm{MD}k_\mathrm{MD} \tag{46}$$

and α_M, α_D, β_MD and β_DM are parameters taking values between 0 and 1 (see Eq. (24)). Consideration of the same relations in terms of the single-photon timing observables (L, I_M and I_D) leads to the conclusions reached in Section 5.1. In fact,

$$\begin{aligned}[\mathrm{M}^*] + (1+\delta)[\mathrm{D}^*] = {} & aL \otimes \exp(-\alpha t) + (\alpha - \Gamma_\mathrm{M} + \delta k_\mathrm{DM})[\mathrm{M}^*] \otimes \exp(-\alpha t) \\ & + [(\alpha - \Gamma_\mathrm{D}) - \delta(\Gamma_\mathrm{D} + k_\mathrm{MD} - \alpha)][\mathrm{D}^*] \otimes \exp(-\alpha t)\end{aligned} \tag{47}$$

and if one attempts to fit I_M and I_D according to Eq. (43), the following correlations are obtained where δ is usually unknown:

$$\alpha = \Gamma_\mathrm{D} + \frac{\delta}{1+\delta}k_\mathrm{MD}, \tag{48}$$

$$\alpha = \Gamma_\mathrm{M} - \delta k_\mathrm{DM}. \tag{49}$$

Simultaneous determination of Γ_M and Γ_D demands therefore that additional information be used, either from steady-state measurements or from other decays obtained at different concentrations (which is possible for intermolecular processes only). Nevertheless, if one of the parameters is known from experiment, the other can be evaluated using the above relations [8,11].

6. Transient effects

The only case where Eq. (32) can be used for the simultaneous determination of Γ_D and Γ_M is when transient effects are present (i.e., the rate coefficient k_DM is time-dependent). In such a case, the general linear combination contains a time-dependent coefficient

$$\frac{\mathrm{d}I_\mathrm{D}}{\mathrm{d}t} = \frac{a}{(1+\delta)b_\mathrm{D}}L - \frac{b_\mathrm{M}}{(1+\delta)b_\mathrm{D}}\left\{(\delta k_\mathrm{DM}(t) + \Gamma_\mathrm{M})I_\mathrm{M} + \frac{\mathrm{d}I_\mathrm{M}}{\mathrm{d}t}\right\} + \frac{1}{(1+\delta)}(\delta k_\mathrm{MD} - \Gamma_\mathrm{D})I_\mathrm{D} \tag{50}$$

and is therefore of the form

$$\frac{\mathrm{d}I_\mathrm{D}}{\mathrm{d}t} = AL + B(t)I_\mathrm{M} + CI_\mathrm{D} + D\frac{\mathrm{d}I_\mathrm{M}}{\mathrm{d}t}. \tag{51}$$

In this situation only when the two time derivatives are appropriately weighted, does the time-dependence of coefficient B disappear, and Eq. (33), with constant coefficients, is valid. Then, the fit with Eq. (33) automatically yields the $\delta = 0$ solution.

Table 2
Values of the parameters obtained from the fit of simulated pyrene monomer and excimer decays with Eq. (47)

D (nm^2 ns^{-1})	Γ_M (ns^{-1})	Bias (%)	Γ_D (ns^{-1})	Bias (%)	χ^2
10^{-2}	3.0×10^{-3}	30	1.7×10^{-3}	6	1.1
10^{-3}	2.3×10^{-3}	0	1.6×10^{-3}	0	1.1

The same conclusion is valid for an analysis carried out according to the linear integral method or according to the convolution relations. Considering Eq. (47) for instance, it is seen that for $\delta \neq 0$ a time-dependent coefficient arises. But a fit using constant coefficients automatically ensures that $\delta = 0$.

The above considerations imply that if a significant time-dependence of k_{DM} exists, the deviations between fitting function and experimental decay will be important for $\delta \neq 0$ and the solution for $\delta = 0$ is obtained. Indeed, simulated decay curves for irreversible monomer–excimer kinetics show that the simultaneous recovery of both parameters (Γ_M and Γ_D) is strongly dependent on the magnitude of the transient term. In most of the cases of excimer formation in nonviscous solvents the importance of the transient effect is minor and only visible for the initial times of decay so that Γ_M and Γ_D cannot be obtained simultaneously. Analysis of simulated data was carried out in order to quantify this aspect. Monomer and excimer decay curves with added synthetic noise were simulated as before [7], using the mechanism previously proposed for excimer formation [8,11], where diffusion is described by the Smoluchowski equation and the effect of reversibility (excimer dissociation during its lifetime) is negligible. The curves were simulated with $\Gamma_M = 2.25 \times 10^6$ s^{-1} and $\Gamma_D = 1.55 \times 10^7$ s^{-1}, a pyrene concentration of 5×10^{-2} M, and diffusion coefficients of either $D = 10^{-2}$ nm^2 ns^{-1} or $D = 10^{-3}$ nm^2 ns^{-1} . After convolution with an experimental excitation profile, Poisson noise was added [7] and the curves were analysed with Eq. (47). Some results are presented in Table 2. For the higher diffusion coefficient ($D = 10^{-2}$ nm^2 ns^{-1}) the time dependence of k_{DM} is not important enough to force a fit with $\delta = 0$ and the precision of parameter recovery is poor. On the other hand, for the curves simulated with the smaller coefficient ($D = 10^{-3}$ nm^2 ns^{-1}), diffusion of the pyrene molecules is slower and the transient effects are large enough to force $\delta = 0$ in Eq. (47). In this case it is possible to recover the Γ_M and Γ_D parameters with good precision, without assumptions as to the nature of k_{DM} and k_{MD}.

Molski and Boens [15] have given theoretical support to the method of recovery proposed by Berberan-Santos et al. [8,11] for Γ_M and Γ_D. In this section we showed the explicit effect of this aspect on the fit, and examined realistic cases to determine the extent to which transient effects must exist for the recovery to be effective.

7. Conclusions

A new linear method for the determination of the rate coefficients of ground and excited-state complex first-order (or pseudo-first-order) mechanisms was presented and applied to simulated data. Nonlinear methods based on convolution kinetics were also developed, and the general Eq. (16) were obtained. Excited-state kinetics, where concentrations are usually known only up to a constant factor, was discussed in detail, in connection with monomer–excimer kinetics. In particular, explicit relations between parameters (parameter correlation) were obtained and discussed. Removal of this correlation through the influence of transient effects was also quantitatively discussed.

References

[1] K.J. Laidler, Chemical Kinetics, third ed., Harper and Row, New York, 1987.
[2] J.I. Steinfeld, J.S. Francisco, W.L. Hase, Chemical Kinetics and Dynamics, second ed., Prentice-Hall, New Jersey, 1999.

[3] C. Steel, K.R. Naqvi, J. Phys. Chem. 95 (1991) 10713.
[4] S. Vadja, H. Rabitz, J. Phys. Chem. 92 (1988) 701.
[5] M. Ameloot, N. Boens, R. Andriessen, V. Van den Bergh, F.C. De Schryver, J. Phys. Chem. 95 (1991) 2041.
[6] K. Sienicki, G. Durocher, J. Photochem. Photobiol. A: Chem. 63 (1992) 279.
[7] J.P.S. Farinha, J.M.G. Martinho, L. Pogliani, J. Math. Chem. 21 (1997) 131.
[8] M.N. Berberan-Santos, J.P. Farinha, J.M.G. Martinho, J. Duhamel, M.A. Winnik, Chem. Phys. Lett. 189 (1992) 328.
[9] J.B. Birks, Photophysics of Aromatic Molecules, Wiley, New York, 1970.
[10] E. Lippert, W. Rettig, V. Bonacic-Koutecky, F. Heisel, J.A. Miehé, Adv. Chem. Phys. 61 (1987) 1.
[11] J.M.G. Martinho, J.P. Farinha, M.N. Berberan-Santos, J. Duhamel, M.A. Winnik, J. Chem. Phys. 96 (1992) 8143.
[12] L.V. Dommelen, N. Boens, F.C. De Schryver, M. Ameloot, J. Phys. Chem. 99 (1995) 8959 and references therein.
[13] J.B. Birks, Rep. Prog. Phys. 38 (1975) 903.
[14] M.N. Berberan-Santos, J.M.G. Martinho, Chem. Phys. 164 (1992) 259.
[15] A. Molski, N. Boens, J. Chem. Phys. 110 (1999) 1628 and references therein.