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Non-linear least-squares and chemical kinetics. An improved method to analyse monomer-excimer decay data

J.P.S. Farinha [a], J.M.G. Martinho [a] and Lionello Pogliani [b]

[a] *Centro de Quimica-Fisica Molecular, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal*
[b] *Dipartimento di Chimica, Universitá della Calabria, 87030 Rende (CS), Italy*

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The least squares fitting of experimental results with a non-linear model can result in a serious loss of accuracy in the model parameters estimation if the statistical nature of the method is not correctly considered. This occurs when the experimental data is fitted to a set of functional parameters that depend in the model parameters to be estimated in the end. A realistic example can be found in the two state model of monomer-excimer kinetics. The decay curves of the monomer and excimer are a sum and a difference of two exponentials, respectively. It is usual to fit the experimental decays in order to obtain the pre-exponential factors and decay constants, thus using a reparametrization that is non-linear with respect to the model parameters. This procedure is thoroughly discussed and a new method to analyse the decay curves that circumvents the problem of reparametrization is presented. The proposed method yields improved results with less than 7% bias in the recovered rate constants. Monte Carlo simulations have been performed in order to obtain confidence intervals for the fitting and model parameters.

1. Introduction

The evaluation of adjustable parameters from both linear and non-linear regression analysis have been extensively discussed [1,2,4]. In general an independent variable y can be expressed in terms of the variables x_i $(i = 1, \dots, m)$ and a set of model parameters p_j $(j = 1, \dots, n)$. The most simple case occurs when a linear relationship can be established between y (subject to random errors) and the parameters p_j, being the variables x_i considered exact. In this case analytical expressions can be obtained for the parameters in terms of the variables y and x_i, being the variances and covariances of the parameters obtained in a closed form.

In the most general case of a non-linear relationship between y and the parameters p_j, iterative methods must be used to obtain the best estimate of the parameters. In this case it is common to fit the results to a set of parameters q_l $(l = 1, \dots, n')$ that are functions of the model parameters, $q_l = g(p_j)$. When the model parameters are non-linear functions of the fitted parameters, the results are biased, with an eccentricity that depends in the variances, covariances and other functions of the fitting quantities. To solve the problem, the bias on the model parameters has to be deduced from the errors in the fitting parameters. However, these errors can not be derived by parametric statistics owing to the linear approximation involved in the non-linear least-squares analysis [2]. This problem of reparametrization is usually not considered, although significative errors can be introduced in the calculation of the model parameters.

In this paper the non-linear least-squares methodology is applied to a system where reparametrization is currently used. We chose the monomer-excimer kinetics of a well known excimer forming system, pyrene in hydrocarbon solvent [3]. The monomer decays as a sum of two exponentials and the excimer as a difference of the same exponentials. The parameters that are usually fitted (the lifetimes and the pre-exponential values) are complicated functions of the rate parameters. The attempt to fit simulated decays directly to the model parameters resulted in problems of convergence caused by errors introduced in the numerical calculations. Nevertheless, using simulated decay curves and Monte Carlo methods we show that the rate constants can be accurately calculated once the lifetimes are obtained with good precision from the excimer fit, and its values are maintained in the monomer decay curve fit.

2. Non-linear least-squares fitting

Consider a model depending on an independent variable $\boldsymbol{x}$ (x_i: $i = 1, \ldots, m$) and n parameters $\boldsymbol{p}$ (p_j: $j = 1, \ldots, n$) with values initially unknown. To each value of $\boldsymbol{x}$ corresponds a value of $\boldsymbol{y}^{\text{cal}}$ (y_i^{cal}: $i = 1, \ldots, m$) given by the function f,

$$\boldsymbol{y}^{\text{cal}} = f(\boldsymbol{p}, \boldsymbol{x}). \tag{1}$$

If one value of a measured property $\boldsymbol{y}^{\text{obs}}$ (y_i^{obs}: $i = 1, \ldots, m$) is related to each value of $\boldsymbol{x}$ (considered exact) then

$$\boldsymbol{y}^{\text{obs}} = \boldsymbol{y}^{\text{cal}} + \boldsymbol{e}, \tag{2}$$

where $\boldsymbol{e}$ (e_i: $i = 1, \ldots, m$) are the random errors associated with the experimental measurement of $\boldsymbol{y}^{\text{obs}}$.

The Newton algorithm of non-linear estimation is based on successive approximations: Firstly the function f is expanded as a Taylor series about an initial value $\boldsymbol{p}^{\text{ini}}$ of the parameter vector. Then, keeping only the first term of the series and replacing the differential $\mathrm{d}p_j$ by the finite increment Δp_j, we obtain

$$y_i^{\text{cal}} = y_i^{\text{ini}} + \sum_{j=1}^{n} \left(\frac{\partial y_i^{\text{cal}}}{\partial p_j^{\text{ini}}} \right) \Delta p_j \tag{3}$$

that can be rewritten into the following compact form:

$$\boldsymbol{y}^{\text{cal}} = \boldsymbol{y}^{\text{ini}} + \boldsymbol{J} \Delta \boldsymbol{p}, \tag{3$'$}$$

where $y_i^{\text{ini}} = f(\boldsymbol{p}^{\text{ini}}, x_i)$. This is a good approximation of the function f in the limit of small Δp_j, i.e., for $y_i^{\text{cal}} \approx y_i^{\text{ini}}$.

A vector $\boldsymbol{r}$ (r_i: $i = 1, \ldots, m$) of residuals is defined as $\boldsymbol{r} = \boldsymbol{y}^{\text{obs}} - \boldsymbol{y}^{\text{cal}}$. Using the expression (3′) for $\boldsymbol{y}^{\text{cal}}$ we obtain $\boldsymbol{r} = \Delta\boldsymbol{y} - \boldsymbol{J}\Delta\boldsymbol{p}$, where $\Delta\boldsymbol{y} = \boldsymbol{y}^{\text{obs}} - \boldsymbol{y}^{\text{ini}}$ and $\boldsymbol{J}$ is the Jacobian matrix with elements $J_{ij} = \partial y_i^{\text{cal}} / \partial p_j^{\text{ini}}$.

The function S to be minimised is defined as the sum of weighted squares of the residuals,

$$S = \sum_{h=1}^{m} \sum_{k=1}^{m} r_h W_{hk} r_k = \boldsymbol{r}^{\text{T}} \boldsymbol{W} \boldsymbol{r}, \tag{4}$$

where $\boldsymbol{r}^{\text{T}}$ is the transpose of the vector of the residuals and $\boldsymbol{W}$ is a weight matrix. The matrix $\boldsymbol{W}$ is here, as often, taken to be the inverse of the variance-covariance matrix $\boldsymbol{M}$ of elements

$$M_{ij} = \begin{cases} \text{cov}\left(y_i^{\text{obs}}, y_j^{\text{obs}}\right), & i \neq j, \\ \text{var}\left(y_i^{\text{obs}}\right), & i = j. \end{cases} \tag{5}$$

The stationary points of the function S are obtained from the system of m equations

$$\frac{\partial S}{\partial p_k} = \sum_{t=1}^{m} \sum_{u=1}^{m} \left[\left(\frac{\partial r_t}{\partial p_k} \right) W_{tu} r_u + r_t W_{tu} \left(\frac{\partial r_u}{\partial p_k} \right) \right] = 0 \quad (k = 1, \ldots, m), \tag{6}$$

which can be written as a matrix product

$$\boldsymbol{J}^{\text{T}} \boldsymbol{W} \boldsymbol{J} \Delta\boldsymbol{p} = \boldsymbol{J}^{\text{T}} \boldsymbol{W} \Delta\boldsymbol{y}. \tag{7}$$

For non-linear equations the set of normal equation (7) can only be solved iteratively. The initial parameter values ($\boldsymbol{p}^{\text{ini}}$) are estimated, and the subsequent corrections $\Delta\boldsymbol{p}$ are calculated. The process is repeated for new values of $\boldsymbol{p} \leftarrow (\boldsymbol{p} + \Delta\boldsymbol{p})$ until a convergence criterion is achieved.

The $\Delta\boldsymbol{p}$ values should be calculated so that convergence is achieved in each step. One of the most used procedures is based on the Marquardt algorithm [5]. This provides a way to rotate the vector $\Delta\boldsymbol{p}$, calculated for the direction of local steepest descent, so that maximum convergence is achieved for each iteration [1,2,5,6]. For sufficiently good initial estimates of the parameters, the process converges giving the best statistical estimate of the parameters.

Parametric statistics can provide the errors and correlation coefficients of the parameters. To calculate these errors, the expression for $\boldsymbol{r}$ is substituted in the normal equations to yield $\boldsymbol{p} = \boldsymbol{T}\boldsymbol{y}^{\text{obs}} - \boldsymbol{a}$, where $\boldsymbol{T} = (\boldsymbol{J}^{\text{T}}\boldsymbol{W}\boldsymbol{J})^{-1}\boldsymbol{J}^{\text{T}}\boldsymbol{W}$ and $\boldsymbol{a} = \boldsymbol{T}\boldsymbol{y}^{\text{ini}} - \boldsymbol{p}^{\text{ini}}$. As the vector $\boldsymbol{a}$ does not have experimental error, the variance-covariance matrix of the parameters is $\boldsymbol{P} = \boldsymbol{T}\boldsymbol{M}\boldsymbol{T}^{\text{T}}$ [2], where $\boldsymbol{M} = \boldsymbol{W}^{-1}$ is the variance-covariance matrix of the experimental values $\boldsymbol{y}^{\text{obs}}$ and $\boldsymbol{T}^{\text{T}}$ is the transpose of matrix $\boldsymbol{T}$. This expression simplifies to $\boldsymbol{P} = (\boldsymbol{J}^{\text{T}}\boldsymbol{W}\boldsymbol{J})^{-1}$ which contains the information on the parameter errors (variances) and correlation between parameters (covariances).

However, for non-linear least squares fitting the errors and correlation coefficients calculated by parametric statistics are, in a statistical sense, biased. The bias arises from neglecting the terms of order higher than the first in the Taylor series expansion of the function f (equation (3)). As a consequence it is impossible to obtain reliable parameter errors and correlation coefficients using parametric statistics.

Other problems arise when a reparametrization of the equation is done. In this case the model parameters, p_j $(j = 1, \ldots, n)$, are not fitted directly: the fitted parameters $q_l = g(p_j)$ $(l = 1, \ldots, n')$ are obtained and the model parameters calculated from $p_j = g^{-1}(q_l)$. If the number of fitted parameters (n') is larger than the number of model parameters (n) the dimension of the problem is altered. That is, $n' - n$ of the system constraints are not considered, which results in a chi-square surface with $n' - n$ more dimensions. The consequences in the fitting are unpredictable and the model parameters obtained will be meaningless.

Even if the number of parameters is not changed in the reparametrization, the values of the model parameters are very difficult to obtain accurately. Indeed, the values of the fitted parameters $\boldsymbol{q}$, are the statistical expectations of the parameter estimators $[\hat{q}_j]$ $(j = 1, \ldots, n)$ taken from a sample with N observations:

$$q_j = \mathrm{E}[\hat{q}_j] = \frac{1}{N} \sum_{i=1}^{N} (\hat{q}_j)_i. \tag{8}$$

This has to be considered when evaluating the function g^{-1} to obtain the model parameters from the fitting parameters. The values of $\boldsymbol{p}$ should be obtained from the expectation value of the function of the fitting parameter estimators $\boldsymbol{p} = \mathrm{E}[g^{-1}(\hat{\boldsymbol{q}})]$. In the non-linear case a “mixture factor” ξ_q arises comprising variances, covariances or other functions of the parameter estimators

$$\boldsymbol{p} = \mathrm{E}\big[g^{-1}(\hat{\boldsymbol{q}})\big] = g^{-1}\big(\mathrm{E}[\hat{\boldsymbol{q}}]\big) + \xi_q, \tag{9}$$

where $\xi_q = 0$ when the model parameters are linear functions of the fitted parameters.

So, it is generally incorrect to fit results with functions of the model parameters, unless the same number of fitting and model parameters is used, and the factor ξ_q is correctly considered.

3. The monomer–excimer kinetics

The kinetics of excimer formation can be described by the two-state model shown in figure 1. Upon excitation, the ground-state monomer M is promoted to an excited electronic state M*, with intrinsic lifetime $\tau_{\mathrm{M}} = 1/\Gamma_{\mathrm{M}}$. Upon the encounter of an excited monomer with a ground-state species M an excimer can be formed by a bimolecular reaction with rate coefficient k'_{DM}. A pseudo-first-order parameter $k_{\mathrm{DM}} = k'_{\mathrm{DM}}[\mathrm{M}]$ can be considered since in the usual experimental conditions $[\mathrm{M}] > [\mathrm{M}^*]$. Once formed the excimer can dissociate with rate coefficient k_{MD} to reform the excited plus ground-state monomer or decay to give two ground state monomer with intrinsic lifetime $\tau_D = 1/\Gamma_D$. From now on "monomer" will stand for the excited monomer M^*.

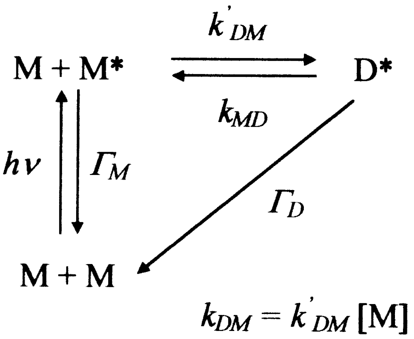

Figure 1. Kinetic scheme of excimer formation.

If the excitation is produced by a δ-pulse of light, the concentration of excited species is given by [3]

$$[M^*] = a_1^M \times \exp(\lambda_1 t) + a_2^M \times \exp(\lambda_2 t), \tag{10}$$

$$[D^*] = a_1^D \times \exp(\lambda_1 t) + a_2^D \times \exp(\lambda_2 t), \quad (a_1^D = -a_2^D), \tag{11}$$

where the decay constants and pre-exponential factors are ($i = 1, 2$)

$$\lambda_i = \frac{-(X+Y) + (-1)^{i+1} \times \sqrt{(Y-X)^2 + 4k_{MD}k_{DM}}}{2}, \tag{12}$$

$$a_i^M = (-1)^i \frac{\lambda_i + Y}{\lambda_2 - \lambda_1}, \qquad a^D = -\frac{k_{DM}}{\lambda_2 - \lambda_1}, \tag{13}$$

and

$$X = k_{DM} + \Gamma_M, \qquad Y = k_{MD} + \Gamma_D. \tag{14}$$

The non-linear fit of the monomer decay curve allow the calculation of the parameters a_1^M/a_2^M, $\lambda_1 = -1/\tau_1$ and $\lambda_2 = -1/\tau_2$. The rate coefficients are commonly obtained from the expressions

$$k_{DM} = -(\lambda_1 + \lambda_2 + \Gamma_M + Y), \tag{15}$$

$$\Gamma_D = \frac{\lambda_1 \times \lambda_2 + \Gamma_M \times Y}{k_{MD}}, \tag{16}$$

$$k_{MD} = Y - \Gamma_D, \tag{17}$$

where the parameter Y (equation (16)) is given by

$$Y = -\frac{a_1^M/a_2^M \times \lambda_2 + \lambda_1}{a_1^M/a_2^M + 1} \tag{18}$$

and $\tau_M = 1/\Gamma_M$ is the intrinsic lifetime of the monomer species, known from an independent measurement (e.g., from a very diluted pyrene solution).

This procedure can lead to incorrect results since the rate coefficients are obtained from non-linear expressions of the fitting parameters and it is impossible to calculate the factors ξ_q $(q = k_{\mathrm{MD}}, k_{\mathrm{DM}}, \Gamma_{\mathrm{D}})$.

To overcome this problem the monomer decay should be fitted directly in terms of the rate constants. However, this procedure is extremely time consuming as compared to the usual methods and leads to unexpected convergence problems, owing to the complex dependence of the monomer decay parameters on the fitting parameters and the random errors in recovering the pre-exponential factors. Then, we develop a strategy using both the monomer and excimer decay curves, that minimizes the variances and covariances in the fitted decay parameters, thus reducing the values of ξ_q $(q = k_{\mathrm{MD}}, k_{\mathrm{DM}}, \Gamma_{\mathrm{D}})$. The decay constants λ_1 and λ_2, are recovered with good accuracy from the fit of the excimer decay curve equation (11). Then, the λ_1 and λ_2 values are constrained in the monomer fit to obtain the $a_1^{\mathrm{M}}/a_2^{\mathrm{M}}$ parameter. The rate coefficients are then calculated by equations (15)–(18) following the classic procedure.

4. Simulated decays

The experimental monomer and excimer decay curves are usually obtained by the single photon timing technique. The decay curves are recovered as histograms of the fluorescence intensity (proportional to the excited monomer or excimer concentration) *versus* time. The fluorescence intensities are subject to random errors that obey Poisson statistics. The simulated decays are calculated as a convolution product of an experimental response function to the expressions (10) or (11) for the monomer or the excimer, respectively. The number of counts, $I_r^0(i)$ $(r = \mathrm{M}, \mathrm{D})$, in each channel i was adjusted, using the pre-exponential factors of the decays, to give 20000 counts in the most populated channel. In each channel of the histogram of the decay curves Poisson synthetic noise was added according to the following procedure: for channels with less than 100 counts, Poisson noise was generated using the inverse transformation algorithm with standard deviation $\sqrt{I_r^0(i)}$ [7]. For the other channels (with more than 100 counts) the central limit theorem is applicable and therefore normally distributed noise with standard deviation $\sqrt{I_r^0(i)}$ and mean $I_r^0(i)$ was added. This was done by generating a normally distributed random variable with mean zero and one standard deviation (X_i) using the polar variation of the Box–Mueller algorithm [7]. Since $(I_r(i) - I_r^0(i))/\sqrt{I_r^0(i)}$ is normally distributed with mean zero and a standard deviation one, it follows that

$$I_r(i) = I_r^0(i) + X_i\sqrt{I_r^0(i)}. \tag{19}$$

In order to calculate the variances, covariances and confidence intervals of the fitted parameters by the Monte Carlo method [1,7], 200 decays were independently simulated for each set of parameters. The decays were then analysed by the usual free fit of monomer decay curves and by the constrained fit, where the lifetimes obtained from the free fit of the excimer were fixed in the monomer decay curve analysis. Within the range of 200 to 400 simulations, the statistical parameters do not change.

The confidence intervals can be calculated by two different procedures. Assuming that the recovered parameter values are normally distributed, their confidence intervals at 95% probability are equal to two times the standard deviation [2]. On the other end, the Monte Carlo method allows one to calculate the confidence intervals without assuming a distribution. The values of each parameter are sorted in numerical order and the upper and lower 2.5% are eliminated from the list. This procedure automatically accounts for the errors (variances) and correlations between the parameters (covariances).

5. Results and discussion

Fluorescence decay curves of pyrene monomer and excimer were simulated using the rate constants, at room temperature in cyclohexane, found by Birks [3]: $\Gamma_{\mathrm{M}} = 2.25 \times 10^6\ \mathrm{s}^{-1}$, $\Gamma_{\mathrm{D}} = 1.55 \times 10^7\ \mathrm{s}^{-1}$, $k_{\mathrm{DM}} = 6.7 \times 10^6\ \mathrm{s}^{-1}$ and $k_{\mathrm{MD}} = 6.5 \times 10^6\ \mathrm{s}^{-1}$, for a concentration of 1.0×10^{-3} M. The corresponding fitting parameters calculated from equations (12)–(13) and (14) are $\lambda_1 = -6.20 \times 10^{-6}\ \mathrm{s}^{-1}$, $\lambda_2 = -2.48 \times 10^{-7}\ \mathrm{s}^{-1}$ and $a_1^{\mathrm{M}}/a_2^{\mathrm{M}} = 5.74$ and $Y = 2.20 \times 10^7\ \mathrm{s}^{-1}$.

The simulated decays were analysed using a free double exponential fit of the monomer decay curves (classical procedure) and the constrained fit of the monomer decay, with lifetimes obtained from the excimer decay curve analysis.

The analysis of the excimer decay curves allows the calculation of the symmetric variance-covariance matrix of the decay parameters (table 1).

The confidence intervals calculated by the two methods described above coincide, thus indicating a normal distribution of parameter values. The expected values and the 95% probability intervals obtained for the parameters as well as the bias in percentages are shown in table 2.

These results show that λ_1 and λ_2 are recovered practically without error from the fit of the excimer decay curves because these are described by a difference of two

Table 1
Variance-covariance matrixes (M_{ij}) of the decay parameters obtained from the free fit of the pyrene monomer and excimer decay curves.

Monomer	$a_1^{\mathrm{M}}/a_2^{\mathrm{M}}$	τ_1(ns)	τ_2(ns)
$a_1^{\mathrm{M}}/a_2^{\mathrm{M}}$	1.26×10^{-5}	4.69×10^{-4}	3.99×10^{-4}
τ_1(ns)		1.53	1.24×10^{1}
τ_2(ns)			3.27×10^{-2}
Excimer	$a_1^{\mathrm{E}}/a_2^{\mathrm{E}}$	τ_1(ns)	τ_2(ns)
$a_1^{\mathrm{E}}/a_2^{\mathrm{E}}$	1.32×10^{-7}	1.16×10^{-5}	-5.2×10^{-6}
τ_1(ns)		8.38×10^{-3}	-7.33×10^{-3}
τ_2(ns)			1.41×10^{-2}

Table 2
Simulated and obtained values of the monomer and excimer decay parameters of pyrene and percent bias (ξ_{q_i}/q_i) of the parameters.

Monomer	simulated	estimated	bias
$a_1^{\mathrm{M}}/a_2^{\mathrm{M}}$	0.174	0.167 ± 0.007	4%
τ_1(ns)	40.4	38 ± 2	6%
τ_2(ns)	161.4	161.4 ± 0.4	0%
Excimer	**simulated**	**estimated**	**bias**
$a_1^{\mathrm{E}}/a_2^{\mathrm{E}}$	-1	-1.0001 ± 0.0009	0%
τ_1(ns)	40.4	40.5 ± 0.2	0%
τ_2(ns)	161.4	161.4 ± 0.2	0%

Table 3
Variance-covariance matrix (M_{ij}) for the model parameters obtained from the free and constrained fits of the pyrene monomer decay.

Free fit	Y(s^{-1})	k_{DM}(s^{-1})	k_{MD}(s^{-1})	τ_{D}(ns)
Y(s^{-1})	5.42×10^{-7}	8.51×10^{1}	3.42×10^{2}	-7.60×10^{-4}
k_{DM}(s^{-1})		1.66×10^{10}	5.90×10^{10}	-9.97×10^{4}
k_{MD}(s^{-1})			2.25×10^{11}	-4.48×10^{5}
τ_{D}(ns)				1.21
Constrained fit	**Y(s^{-1})**	**k_{DM}(s^{-1})**	**k_{MD}(s^{-1})**	**τ_{D}(ns)**
Y(s^{-1})	0	0	0	3.43×10^{-30}
k_{DM}(s^{-1})		1.95×10^{9}	2.76×10^{9}	1.47×10^{4}
k_{MD}(s^{-1})			4.54×10^{9}	1.90×10^{4}
τ_{D}(ns)				0.121

exponentials with a ratio of pre-exponential factors equal to one. Using the same procedure to fit the monomer decay curves, we obtain results with much higher associated errors (tables 1, 2). In this case, the bias of the obtained values for the decay parameters is not zero as for the excimer, but it should be noted that it is always covered by the confidence intervals.

The monomer decay parameters alone can be used to recover the model parameters, whose variances, covariances, confidence intervals and bias are obtained by the same procedure as before (tables 3 and 4). The parameter Y was included in the tables for comparison with the proposed analysis method. In the calculation of the rate constants the value of $\tau_{\mathrm{M}} = 444.44$ ns was used. This value can be obtained from the single exponential decay of pyrene in cyclohexane dilute solutions.

The bias in the model parameters are meaningful and for τ_{D}, the simulated value is not even contained in the confidence interval. The confidence intervals calculated by the Monte Carlo method and assuming a normal distribution give identical results and therefore the parameter distribution is almost normal.

From the results presented so far the conclusion may be drawn that the decay

Table 4
Values of the model parameters obtained from the free and constrained fits of the pyrene monomer decay. Percent bias (ξ_{q_i}/q_i) relative to the simulated parameter values.

		Free fit		Constrained fit	
	simulated	estimated	bias	estimated	bias
$Y(\mathrm{s}^{-1})$	2.2×10^{-2}	$(2.3 \pm 0.1) \times 10^{-2}$	6%	2.2×10^{-2}	0%
$k_{\mathrm{DM}}(\mathrm{s}^{-1})$	6.7×10^{7}	$(6.8 \pm 0.2) \times 10^{6}$	2%	$(6.66 \pm 0.09) \times 10^{6}$	1%
$k_{\mathrm{MD}}(\mathrm{s}^{-1})$	6.5×10^{7}	$(7.2 \pm 0.9) \times 10^{6}$	11%	$(6.4 \pm 0.1) \times 10^{6}$	1%
$\tau_{\mathrm{D}}(\mathrm{ns})$	64.5	62 ± 2	4%	64.5	0%

parameters τ_1 and τ_2 should be obtained from the excimer decay and not from the monomer decay. To calculate the three model parameters, another decay parameter (Y) is needed that has to be taken from the monomer decay analysis. To evaluate this new method of analysis, τ_1 and τ_2 were obtained from the excimer decay and constrained into the corresponding monomer decay, both simulated with independent random numbers (tables 3, 4).

In the case of pyrene monomer-excimer analysis, the proposed method provide much better results than the analysis of only the monomer decay. This is not surprising since the possible correlation between the parameters on the free monomer fit is attenuated or even suppressed if the decay values obtained from an independent measurement analysis (the excimer decay curve) are constrained in the monomer fit.

6. Conclusions

The statistical nature of least square fitting must always be considered whenever this method is to be applied to non-linear problems. The monomer-excimer rate constants recovered from simulated monomer decay curves have significant errors, that result essentially from errors related to the correlation between the fitting parameters. This can be avoided using the decay constants calculated from the excimer decay curve in the constrained monomer decay curve analysis. The proposed method is as easy to implement as the classical one but significantly improves the accuracy of the rate constants.

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