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Lifetime recovery for species participating in complex kinetics. Application to the reversible excimer

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A new method for the determination of intrinsic lifetimes of excited species participating in a complex mechanism is presented. This method is independent of the mechanism itself, and only requires that the interacting species maintain their identity and exist in a known number. The method is applied to the determination of the excimer lifetime of pyrene in cyclohexanol from 25 to 85 °C. An activation energy of 12 ± 1 kJ mol^{-1} is calculated from the reciprocal excimer lifetime Arrhenius plot.

1. Introduction

Determination of the intrinsic lifetimes of excited species participating in complex kinetics is often difficult, and indirect, because their decay law depends on the overall kinetics in a complicated manner. This problem exists for instance for monomer–excimer and exciplex kinetics in solution. Two different cases can be considered: intermolecular and intramolecular excimer (exciplex) formation. Assuming for the moment that only one excimer (exciplex) exists, the lifetimes to be determined are those of the monomer and of the excimer (exciplex). For intermolecular kinetics the monomer lifetime is easily obtained from a dilute solution where excimer formation is negligible. However, for intramolecular kinetics, the monomer lifetime is estimated by the use of a model compound [1], a procedure that is not always satisfactory because the chromophore of the model compound may not behave exactly as the chromophore in the bichromophoric compound, owing namely to chromophore–chromophore interactions [2]. Also the excimer (exciplex) lifetime for both the intermolecular and the intramolecular cases cannot be directly obtained from monomer or excimer decays, and is determined by assuming a kinetic model (usually Birks' kinetics [3]), where it can be related to the decay parameters. In cases where Birks' approach is not valid (time-dependence of the rate coefficients) it is difficult to evaluate with precision the excimer intrinsic lifetime and other methods of analysis should be used.

A similar situation exists for many other photophysical processes, e.g. TICT states formation kinetics [4], intramolecular energy [5] and electron transfer [6].

In this work, it is shown that by the right combination of experimental decays, it is in principle always possible to determine directly the intrinsic lifetimes of species participating in a given complex kinetic mechanism, without making any assumption about that mechanism except that the interacting species maintain their identity and that their number is known.

2. Method of data analysis

Consider a general kinetic mechanism, scheme 1, involving n excited species X_1, X_2, ..., X_n, whose in-

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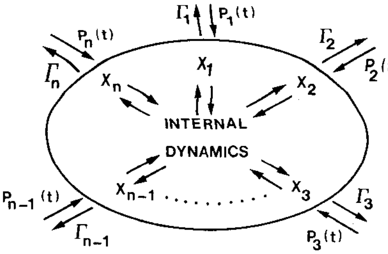

Scheme 1.

trinsic reciprocal lifetimes are $\Gamma_1, \Gamma_2, ..., \Gamma_n$. These species are externally produced (e.g. by light absorption) at time-dependent rates $P_1, P_2, ..., P_n$, and interconvert by unimolecular or pseudo-unimolecular processes ($X_i \to X_j$) with rate coefficients k_{ij} ($i, j=1, 2, ..., n$), that can be time-dependent or not. The macroscopic rate equations governing the kinetics are therefore

$$\frac{\mathrm{d}X_1}{\mathrm{d}t} = P_1 - \Gamma_1 X_1 - k_1 X_1 + k_{21} X_2 + ... + k_{n1} X_n ,$$

$$\frac{\mathrm{d}X_2}{\mathrm{d}t} = P_2 + k_{12} X_2 - \Gamma_2 X_2 - k_2 X_2 + k_{32} X_3 + ... + k_{n2} X_n ,$$

$$\vdots$$

$$\frac{\mathrm{d}X_n}{\mathrm{d}t} = P_n + k_{1n} X_1 + k_{2n} X_2 + ... - \Gamma_n X_n - k_n X_n , \qquad (1)$$

where $k_i = \sum_{j\neq i} k_{ij}$ and X_i denote the concentration of the ith species.

Summing all equations, one obtains

$$\frac{\mathrm{d}}{\mathrm{d}t}(X_1 + X_2 + ... + X_n) = P_1 + P_2 + ... + P_n - \Gamma_1 X_1 - \Gamma_2 X_2 - ... - \Gamma_n X_n , \qquad (2)$$

that is, internal dynamics, however complex, are eliminated. It is not difficult to give a physical interpretation of this result: the time evolution of the total number of excited species, regardless of their type, can only be a function of the external creation and death processes, that is of the P_i and of the Γ_i.

Eq. (2) is easily integrated by means of Laplace transforms to yield (see Appendix)

$$\sum_i \left(X_i \otimes \prod_{j\neq i} \exp(-\Gamma_j t) \right) = \left(\sum_i P_i \right) \otimes \exp(-\Gamma_1 t) \otimes \exp(-\Gamma_2 t) \otimes ... \otimes \exp(-\Gamma_n t) , \qquad (3)$$

where $\otimes$ stands for convolution. This equation constitutes the basis of the method of data analysis: X_i is, apart from a multiplication factor a_i the experimental decay of the ith species, $X_i = a_i F_i$ and the P_i are also supposedly known (e.g. exciting pulse shape) again apart from a multiplicative constant b_i, $P_i = b_i I_i$. Parameters to be determined are therefore the reciprocal lifetimes, $\Gamma_1, \Gamma_2, ..., \Gamma_n$ and the linear coefficients a_i and b_i,

$$\sum_i \left(a_i F_i \otimes \prod_{j\neq i} \exp(-\Gamma_j t) \right) = \left(\sum_i b_i I_i \right) \otimes \exp(-\Gamma_1 t) \otimes \exp(-\Gamma_2 t) \otimes ... \otimes \exp(-\Gamma_n t) . \qquad (4)$$

3. Experimental

Fluorescence spectra were recorded on a Spex Fluorolog 2 spectrofluorimeter. The fluorescence decay curves were obtained by the single photon counting technique. The excitation source used was a mode-locked Nd:YAG laser (Coherent model 76-s) frequency-doubled by a KTP crystal to synchronously pump rhodamine 6G in a cavity dumped dye laser (Coherent model 701-3). Pulses of ≈10 ps fwhm, obtained at 620 nm, were frequency-doubled by a KTP crystal to obtain UV pulses at 310 nm for use as excitation source. The repetition rate is selected by a Cavity Dumper (Coherent model 7220) attached to the end of the dye laser. The fluorescence was detected by a Hamamatsu R1564U-01 MCP photomultiplier whose output, after being discriminated (Tennelec TC454), was used as the start signal of the time-to-amplitude converter (TAC). The stop signal was obtained from a Hamamatsu S2840 high speed Pin silicon photodiode exposed to the residual fundamental beam of the dye laser.

Pyrene was zone refined (one hundred steps) and cyclohexanol (spectrograde, Kodak) was used as received. A dilute solution ($[\mathrm{Py}] = 1.0 \times 10^{-6}$ M) and two concentrated ones ($[\mathrm{Py}] = 1.0 \times 10^{-2}$ M and $[\mathrm{Py}] = 8.9 \times 10^{-2}$ M) were prepared and degassed by the freeze–pump–thaw technique. The pyrene monomer fluorescence decay curves were observed at 376 nm and the excimer decays at 520 nm (front face viewing for the concentrated solutions and 90° viewing for the dilute one) with at least 2000 counts in the most populated of 1024 channels. When analyzing the fluorescence decay curves a lamp function [7] was recovered from the single exponential decay of a dilute solution of 2,5-diphenyloxazole (PPO) in cyclohexane ($\tau = 1.37$ ns).

4. Application to intermolecular excimer kinetics: pyrene in cyclohexanol

For intermolecular excimer kinetics, two species are assumed: monomer (M) and excimer (D), of which only the former is externally produced by pulse $P = b_1 I$. Eq. (4) reduces to

$$a_1 I_M(t)\otimes\exp(-\Gamma_2 t)+a_2 I_D\otimes\exp(-\Gamma_1 t) = b_1 I\otimes\exp(-\Gamma_1 t)\otimes\exp(-\Gamma_2 t)\,, \tag{5}$$

where $I_M(t)$ and $I_D(t)$ are the monomer and excimer decay curves. Performing the convolution on the right-hand side of eq. (5) we obtain

$$\alpha_1 I_M(t)\otimes\exp(-\Gamma_2 t)+\alpha_2 I_D(t)\otimes\exp(-\Gamma_1 t) = I\otimes[\exp(-\Gamma_1 t)-\exp(-\Gamma_2 t)]\,, \tag{6}$$

where $\alpha_1 = (\Gamma_2-\Gamma_1)a_1/b_1$ and $\alpha_2 = (\Gamma_2-\Gamma_1)a_2/b_1$. Four fitting parameters thus exist: α_1, α_2, Γ_1 and the sought-for Γ_2. Note that two asymmetric equations are also possible in an alternative form of eq. (6) [8],

$$\alpha_1 I_M(t)+\alpha_1(\Gamma_1-\Gamma_2)I_M(t)\otimes\exp(-\Gamma_2 t)+\alpha_2 I_D(t) = I\otimes\exp(-\Gamma_2 t)\,, \tag{7}$$

$$\alpha_1 I_M(t)+\alpha_2 I_D(t)+\alpha_2(\Gamma_2-\Gamma_1)I_D(t)\otimes\exp(-\Gamma_1 t) = I\otimes\exp(-\Gamma_1 t)\,. \tag{8}$$

These equations are more apropriate for the evaluation of the reciprocal monomer and excimer lifetimes, Γ_1 and Γ_2, respectively. While these equations still contain four fitting parameters only one is nonlinear (Γ_2 in eq. (7) and Γ_1 in eq. (8)). For the fitting, eqs. (7) and (8) were rewritten as

$$I_M(t) = (\Gamma_2-\Gamma_1)I_M(t)\otimes\exp(-\Gamma_2 t) + C_1 I\otimes\exp(-\Gamma_2 t)+C_2 I_D(t)\,, \tag{9}$$

$$I_M(t) = C_1(\Gamma_2-\Gamma_1)I_D(t)\otimes\exp(-\Gamma_1 t) + C_2 I\otimes\exp(-\Gamma_1 t)+C_1 I_D(t)\,. \tag{10}$$

These forms were used to fit the experimental decays of pyrene monomer and excimer in cyclohexanol, recorded from room temperature (25°C) up to 85°C.

Fig. 1 shows the monomer decay curve of a pyrene solution ($[\mathrm{Py}] = 10^{-2}$ M) in cyclohexanol at 35°C, fitted with expression (9), fixing Γ_1 to the value determined from the single exponential decay of the dilute solution at the same temperature. The fit is reasonable as judged by the χ^2, the residuals and the autocorrelation of the residuals.

The Arrhenius plots of the reciprocal lifetimes of the excimer and the monomer are linear (fig. 2), with activation energies of 3.3 and 12.1 kJ mol^{-1} for the monomer and excimer, respectively. Excimer lifetimes obtained from the two concentrated solutions agree very closely, with an average deviation of 4%.

In fig. 2 the values of $\tau_M = 1/\Gamma_1$ obtained from the fit of the monomer and excimer decay curves to eq. (10) are also shown. The $\tau_M = 1/\Gamma_1$ values are very close to those determined from the decays of the dilute solution, and the corresponding pre-exponential factors of both fits agree very well, confirming the adequacy of the method of analysis.

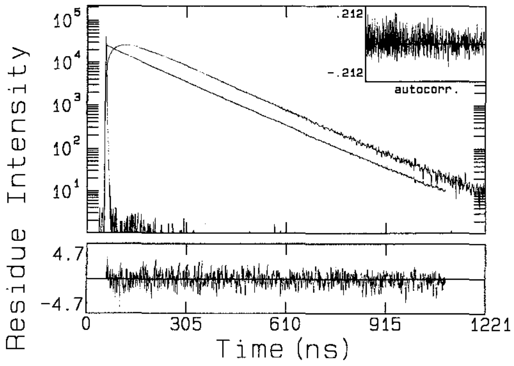

Fig. 1. Fluorescence decay curves of the reference compound collected at 376 nm and of the 10^{-2} M solution of pyrene in cyclohexanol at 35°C, collected at 376 nm (monomer) and 520 nm (excimer). The monomer decay is fitted with eq. (9), fixing Γ_1 to the value obtained for a dilute solution (10^{-6} M) in the same solvent at the same temperature.

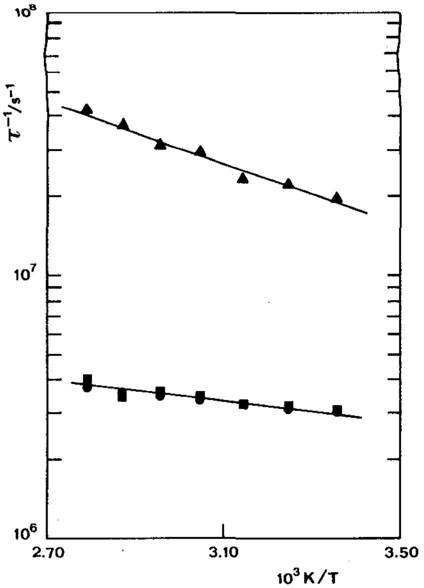

Fig. 2. Arrhenius plot of $1/\tau_M = \Gamma_1$ and $1/\tau_D = \Gamma_2$, as obtained from the 10^{-6} M solution ($1/\tau_M$ (●)) or from the 10^{-2} M solution ($1/\tau_M$ (■); $1/\tau_D$ (▲)).

5. Discussion

The method of analysis allows the evaluation of intrinsic lifetimes of the excited species involved in a complex mechanism with the only assumptions that, although interacting, both species retain their identity, and their number is assumed to be known. This was experimentally confirmed by the analysis of monomer–excimer kinetics of pyrene in cyclohexanol. The activation energy of the monomer lifetime found is due to the intersystem-crossing process [9]. The excimer lifetime activation energy was previously attributed to the internal conversion process, owing to molecular motion that distorts the symmetrical parallel sandwich excimer configuration and leads to increased intermolecular vibrational interaction [10]. However, at high viscosities (low temperatures) ($\eta > 4.7$ cP) [10] this motion is subject to viscous constraint and the excimer lifetime should attain a plateau [10]. At variance with these results we observe that the excimer lifetime varies with temperature for viscosities much higher than 4.7 cP (the viscosity of cyclohexanol is 52 cP at 25°C and 3.2 cP at 85°C). Recently, Van der Auweraer et al. [11] examined the temperature dependence of the radiative rate constant of TICT states and exciplexes to obtain activation energies of 100–600 cm^{-1} attributed to vibrational activation, since the radiative transition from the equilibrium excited state is highly forbidden. This is also the case for the pyrene excimer and the variation of the radiative rate constant of the excimer with temperature could explain the observed trend of the pyrene excimer lifetime. Further work is however required to confirm this.

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Appendix

Laplace transforming eq. (2) one obtains, after rearrangement,

$$\sum_i (s+\Gamma_i)\bar{X}_i = \sum_i X_i(0) + \sum_i \bar{P}_i . \qquad (A.1)$$

But $X_i(0)=0$ for all i (species are created by the P_i). Dividing by $\prod_j (s+\Gamma_j)$, eq. (A.1) becomes

$$\sum_i \frac{\bar{X}_i}{\prod_{j\neq i}(s+\Gamma_j)} = \frac{\sum_i \bar{P}_i}{\prod_i (s+\Gamma_j)} \qquad (A.2)$$

or

$$\sum_i \left(\bar{X}_i \prod_{j\neq i} \frac{1}{s+\Gamma_j} \right) = \sum_i P_i \prod_j \frac{1}{s+\Gamma_j} , \qquad (A.3)$$

and, by Laplace inversion, eq. (3) is obtained.

References

[1] K.A. Zachariasse, R. Busse, G. Duveneck and W. Kühnle, J. Photochem. 28 (1985) 237.
[2] A.L. Maçanita, J. Magalhães, A. Dias, H. Teles and E. Iglesias, J. Chem. Soc. Faraday Trans. 86 (1990) 4011.
[3] J.B. Birks, Rept. Progr. Phys. 38 (1975) 903.
[4] E. Lippert, W. Rettig, V. Bonačić-Koutecký, F. Heisel and J.A. Miehé, Advan. Chem. Phys. 61 (1987) 1;
K. Rotkiewicz and G. Köhler, J. Luminescence. 37 (1987) 219.

[5] J. Mugnier, B. Valeur and E. Gratton, Chem. Phys. Letters 119 (1985) 217;
S. Hassoon, H. Lustig, M.B. Rubin and S. Speiser, J. Phys. Chem. 88 (1984) 6367;
H. Oevering, J.W. Verhoeven, M.N. Paddon-Row, E. Cotsaris and N.S. Hush, Chem. Phys. Letters 143 (1988) 488.
[6] A.M. Oliver, D.C. Craig, M.N. Paddon-Row, J. Kroon and K.W. Verhoeven, Chem. Phys. Letters 150 (1988) 366.
[7] D.R. James, D.R. Demmer, R.E. Verall and R.P. Steer, Rev. Sci. Instr. 54 (1983) 1121.
[8] M.N. Berberan-Santos and J.M.G. Martinho, J. Chem. Phys. 95 (1991) 1817.
[9] B. Stevens, M.F. Thomaz and J. Jones, J. Chem. Phys. 46 (1967) 405;
H. Hirano and T. Azumi, Chem. Phys. Letters 86 (1982) 102.
[10] J.B. Birks, A.J.H. Alwattar and M.D. Lumb, Chem. Phys. Letters 11 (1971) 89.
[11] M. Van der Auweraer, Z.R. Grabowski and W. Rettig, J. Phys. Chem. 95 (1991) 2083.