The effect of radiative transport on fluorescence emission

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A model for radiative transport of electronic excitation energy in solution is presented and applied to the time-resolved and steady-state fluorescence of DPA (9, 10-diphenylanthracene) in benzene. The model predicts a nonexponential and wavelength-dependent decay at high concentrations, in agreement with experimental results. Recovered parameters, along with the time-resolved emission spectrum, are interpreted on the basis of a progression of the excitation with time farther into the cell, after the excitation pulse.

I. INTRODUCTION

It is well known that atomic and molecular fluorescence (spectra and decays) is affected by radiative transport, i.e., consecutive reabsorption events by atoms or molecules of the same species.[1,2] This phenomenon is the more noticeable, the larger the spectral overlap between absorption and fluorescence. It also depends on the cell size and shape, sample concentration, and detection geometry.

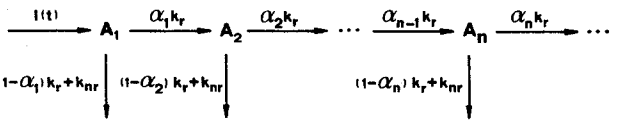
A complete treatment, taking into account all these aspects is not available at present, and seems to be a formidable task. A simpler approach, along the lines of Kilin and Rozman's work[3] is nevertheless possible without almost any loss of generality. This is however achieved at the expense of introducing unknown parameters, whose exact evaluation cannot be done on theoretical grounds, excpet for special cases. These parameters are, in principle, obtainable from experiment.

In this work, a model for radiative transport is presented and applied to the study of steady-state and time-resolved emissions of the fluorescence standard 9, 10-diphenylanthracene (DPA) in benzene solution. This compound does not exhibit excimer formation or concentration quenching of its fluorescence, due to steric hindrance by the phenyl groups,[1] and is therefore ideal for our purposes. In Sec. II the model for radiative transfer is presented, and its limitations outlined. It is also shown how the Birks model is retrieved, in the particular case of equal absorption probabilities for emissions of any order. In Sec. IV the stationary-state and time-resolved emissions of DPA in benzene are presented, the experimental conditions being described in Sec. III. In Sec. V the presented model is applied to the experimental results, and its adequacy discussed. The main conclusions are summarized at the end. In particular, it is found that all results agree with the picture of a progressively deeper penetration of excitation, following a delta pulse, as time evolves.

The present model encompasses the widely used Birks model[1,4] and accounts for the emission wavelength dependence of the fluorescence decay, as observed in solution[5] and in molecular crystals.[6] The Birks model is found to be inadequate for a quantitative study.

II. THE MODEL

Consider the following kinetic scheme:



where A_1 is A excited by the incoming beam of light at the excitation wavelength, A_2 is A indirectly excited by reabsorption of photons emitted by A_1 molecules, etc., k_r the radiative rate constant, k_{nr} the nonradiative rate constant and the parameter α_n is the average probability of absorption for a photon emitted by a nth-generation molecule A_n. This probability is the result of an average over space directions and wavelength. Consider first the absorption probability $\alpha'_n(\lambda)$ which is an average over orientations for a single emission wavelength,

$$\alpha'_n(\lambda) = \int \alpha''_n(\Omega,\lambda)\,d\Omega, \tag{1}$$

where $\alpha''_n(\Omega,\lambda)$ is the absorption probability for a certain wavelength and direction. Note that $\alpha''_n(\Omega,\lambda)$—and hence $\alpha'_n(\lambda)$—should depend on n owing to the different spacial distributions of the A_n within the cell.[7] Note also that these probabilities depend on the excitation wavelength, because the distribution of primarily excited molecules A_1 directly relates with the beam penetration through the Lambert–Beer law.

The average probability of absorption is then given by

$$\alpha_n = \int \alpha'_n(\lambda) f_n(\lambda)\,d\lambda, \tag{2}$$

where $f_n(\lambda)$ is the normalized emission of A_n. It is reasonable to assume that all excited molecules, irrespective of n, have the same emission $f(\lambda)$. This implies a fast relaxation in the excited state, prior to emission. Excitation wavelength dependent emission is known to occur when ground state conformers are locked in a rigid matrix.[8] In fluid media this will hardly be the case. The overlap between emission and absorption spectra may also be due to absorption hot bands, and in this situation the emission spectrum will be the same

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for all n, as long as thermal equilibrium is reached in the excited state.

For delta pulse excitation, the time evolution of the initially excited molecules is

$$A_1 = A_0 \exp\left(-\frac{t}{\tau_0}\right) = A_0 \rho(t), \tag{3}$$

where A_0 is the initial number of primarily excited A molecules, τ_0 is the molecular fluorescence lifetime of A, and $\rho(t)$ is the normalized decay. Part of the emitted light is absorbed in the cell creating new excited molecules (see Scheme I) by a pulse $\alpha_1 k_r A_1$. The time evolution of these new excited molecules is given by a convolution integral[9]

$$A_2 = A_0 \alpha_1 k_r \rho \otimes \rho = A_0 \alpha_1 k_r t \exp\left(-\frac{t}{\tau_0}\right), \tag{4}$$

where $\otimes$ denotes convolution. Repeated application of this procedure yields

$$A_n = A_0 \alpha_1 \alpha_2 \cdots \alpha_{n-1} \frac{(k_r t)^{n-1}}{(n-1)!} \exp\left(-\frac{t}{\tau_0}\right). \tag{5}$$

Defining

$$a_{n-1} = \prod_{i=1}^{n-1} \alpha_i \quad (a_0 = 1.0). \tag{6}$$

Equation (5) becomes

$$A_n = A_0 a_{n-1} \frac{(k_r t)^{n-1}}{(n-1)!} \exp\left(-\frac{t}{\tau_0}\right). \tag{7}$$

The intensity due to the A_n observed in a certain direction and solid angle I_n depends not only on the number of the A_n but also on the probability of photon escape within that solid angle,

$$I_n(\lambda,t) = G_n S_n(\lambda) k_r A_n(t), \tag{8}$$

where G_n is a geometric factor accounting for the solid angle of observation and also for "dilution effects" due to emission from different regions of the cell and $S_n(\lambda)$ is the escape probability for photons of wavelength λ in the observation direction,

$$S_n(\lambda) = \int [1 - \alpha_n''(\lambda,\Omega)] g(\Omega) d\Omega, \tag{9}$$

where $g(\Omega)$ defines the angle of observation. The dilution effects can be minimized by probing the emission at distances from the cell large compared with its width. In this way, $G_n = G$ and the decay law for delta pulse excitation

$$I(\lambda,t) = \sum_{n=1}^{\infty} I_n(\lambda,t) \tag{10}$$

can be written as

$$I(\lambda,t) = G k_r A_0 \exp\left(-\frac{t}{\tau_0}\right) \sum_{n=1}^{\infty} S_n(\lambda) a_{n-1} \frac{(k_r t)^{n-1}}{(n-1)!}. \tag{11}$$

When all the α_n are equal (to α, say) one has $a_{n-1} = \alpha^{n-1}$ and $S_n(\lambda) = S(\lambda)$, hence

$$I(\lambda,t) = G k_r A_0 S(\lambda) \exp\left(-\frac{t}{\tau}\right), \tag{12}$$

where

$$\tau = \frac{\tau_0}{1 - \alpha\Phi}, \tag{13}$$

Φ being the molecular fluorescence quantum yield $\Phi = k_r \tau_0$. Equation (13) is the well known Birks formula.[1,4] However, Eq. (11) shows that the decay is wavelength dependent and cannot, in general, be reduced to a single exponential, even in the red part of the emission, where $S_n(\lambda) = 1$.

Implicit in the above derivation is the assumption of a negligible time for light propagation. Given that the speed of light is ~ 30 cm ns^{-1}, this is justified when using normal cells (< 1 cm) and for lifetimes in the nanosecond range. Two other approximations made were the neglect of nonradiative transport and of molecular diffusion. In fact, nonradiative transfer may well be operating parallel to radiative transfer, since it also depends on an overlap integral between fluorescence and absorption spectra. Nonradiative transport affects some properties of the outcoming radiation, notably its polarization.[10] However, the decay law (and steady-state emission) is not changed by nonradiative transport,[11] neither are to an appreciable extent the spacial distributions of the A_n. This can be shown by considering the diffusion coefficient for excitation migration[12]

$$\Lambda = 2.19 \frac{R_0^6}{\tau_0} n^{4/3}, \tag{14}$$

where R_0 is the critical Förster transfer distance by a dipole–dipole mechanism and n is the number density. Using the calculated value of R_0 for DPA–DPA transfer in benzene (28 Å) we obtain for the most concentrated solution of DPA ($c = 5.0 \times 10^{-2}$ M) a migration coefficient of 1.4×10^{-5} cm^2 s^{-1}. Thus, the spread of the excitation after 100 ns is only 2.9×10^{-6} cm. A similar result is obtained when considering molecular diffusion ($D \sim 10^{-5}$ cm^2 s^{-1} in fluid solvents). Although for short times the excitation motion is not strictly diffusive[13] this approximate equation suffices for our purposes of an order of magnitude calculation.

III. EXPERIMENTAL

Solutions of 9, 10-diphenylanthracene (DPA) (Koch–Light, scintillation grade) in Benzene (Merck Uvasol) were degassed by the freeze–pump–thaw technique (4 cycles at 10^{-5} Torr).

Fluorescence spectra were recorded with a Perkin–Elmer MPF3 spectrofluorimeter coupled to a Digital PDP 11/23 computer. For all samples the excitation wavelength was 337 nm. The measurements were done using front-face geometry except for [DPA] $= 1.0 \times 10^{-6}$ M, where right-angle geometry was used. The spectra were corrected using the instrumental response at each wavelength as described elsewhere.[14]

Fluorescence decay curves were measured using the single-photon counting technique with an apparatus described elsewhere.[14] The excitation wavelength was 337 nm and alternate measurements (10^3 counts at the maximum per cycle) of the pulse profile and sample emission were done until 3×10^4 counts at the maximum were reached. The "wavelength shift" of the system essentially due to the color effect of the photomultiplier was evaluated from the best fits to a single exponential of the fluorescence decays of DPA solu-

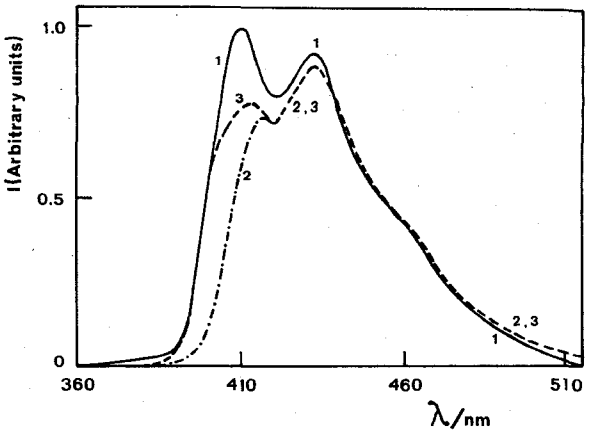

FIG. 1. Fluorescence spectra of DPA in benzene. (1) [DPA] = 1.0×10^{-6} M; (2) [DPA] = 5.0×10^{-2} M; (3) Curve 2 corrected for reabsorption using Eq. (15).

tion (1.0×10^{-6} M) in benzene measured at several emission wavelengths within the range of interest. The decays were analyzed on a PDP 11/73 computer using two programs. One is based on the modulation functions method[15] allowing data analysis with a sum of up to three exponentials (Sandbox for Digital PDP 11 and Vax 780). The other program fits the data to a function consisting on the product of an exponential by a polynomial of the nth degree in time, using linear regression analysis. The measurements were made using 0.5 mm slits in the entrance and exit of the excitation and emission monochromators and a visible cutoff filter in the excitation beam to avoid spurious scattered light on the fluorescence decay. The fluorescent measurements (steady state and time resolved) were performed at 25.0 ± 0.5 °C.

IV. RESULTS

A. Fluorescence spectra

The fluorescence spectra of DPA solutions of concentrations 1.0×10^{-6} M and 5.0×10^{-2} M in benzene, normalized at 450 nm, are presented in Fig. 1. The fluorescence spectra for the concentrated solution has lower intensities in the blue region of the spectrum due to reabsorption. As part of the absorbed light is reemitted,the global intensity increases with concentration. This increase in intensity is not visible due to the normalization procedure.

Several authors[16(a),16(b)] obtained good agreement between the corrected intensities in the blue region of the spectrum with the molecular fluorescence intensities considering that the absorption factors $S_n(\lambda)$ are independent of the order of absorption and equal to $S(\lambda)$ given by Eq. (15). Assuming an exponential distribution of the initially excited molecules, given by the Lambert–Beer law, they obtain,[16]

$$S(\lambda)=\frac{\mu(\lambda_{\rm exc})\sin\beta}{\mu(\lambda_{\rm exc})\sin\beta+\mu(\lambda_{\rm em})\sin\alpha}\,\frac{\left\{1-\exp\left[-\delta c\,\dfrac{\mu(\lambda_{\rm exc})\sin\beta+\mu(\lambda_{\rm em})\sin\alpha}{\sin\beta}\right]\right\}}{\{1-\exp[-\delta c\mu(\lambda_{\rm exc})]\}}, \tag{15}$$

where $\mu(\lambda)$ is the molar absorption coefficient at wavelength λ ($\mu=2.303\,\epsilon$ and ϵ the molar extinction coefficient), c the concentration, δ the penetration depth of the excitation beam in the sample, and the angles α and β are related to the angles α', β' that, respectively, the excitation beam and the emission beam make with the face of the cell, by the Snell refraction law

$$\frac{\cos\alpha'}{\cos\alpha}=\frac{\cos\beta'}{\cos\beta}=n, \tag{16}$$

where n is the refractive index of the solvent.

Figure 1 shows the corrected spectrum of the 5.0×10^{-2} M DPA solution obtained dividing the fluorescence intensities by $S(\lambda)$. The corrected intensities do not match the intensities of the diluted solution, showing that, for this concentration, the simple formula (15) is inaccurate. However deviations become smaller for lower concentrations and for sufficiently diluted solutions expression (15) gives accurate correcting factors.[16(a),16(b)]

B. Fluorescence decays

The fluorescence decay of DPA in benzene at low concentration (1.0×10^{-6} M) can be fitted with a single exponential irrespective to the emission wavelength (400–450 nm). The measured lifetime at 25 °C is $\tau_0=7.1(4)$ ns, in agreement with the published value.[17] The increase of DPA concentration induces three effects: (i) The fluorescence lifetime increases, (ii) it becomes dependent on the emission wavelength, and (iii) the fluorescence decays gradually deviate from single exponentiality (see Fig. 2).

When the DPA concentration is 1.0×10^{-3} M the decays are still almost single exponential but τ_0 increases from 7.1 to 8.0 ns at $\lambda_{\rm em}=400$ nm and to 8.6 ns at $\lambda_{\rm em}=450$ nm. At [DPA] = 1.0×10^{-2} M slight deviations from single exponential are observed (an improvement of the fit is obtained with a sum of two exponentials) and the lifetime increases further to 8.2 ns at $\lambda_{\rm em}=400$ nm and to 9.6 ns at $\lambda_{\rm em}=450$ nm. Finally, the fluorescence decays of the 5.0×10^{-2} M solution in benzene can only be fitted with a sum of two or three exponentials.

The mean fluorescence lifetime $\bar{\tau}$ presented in Table I, was calculated from

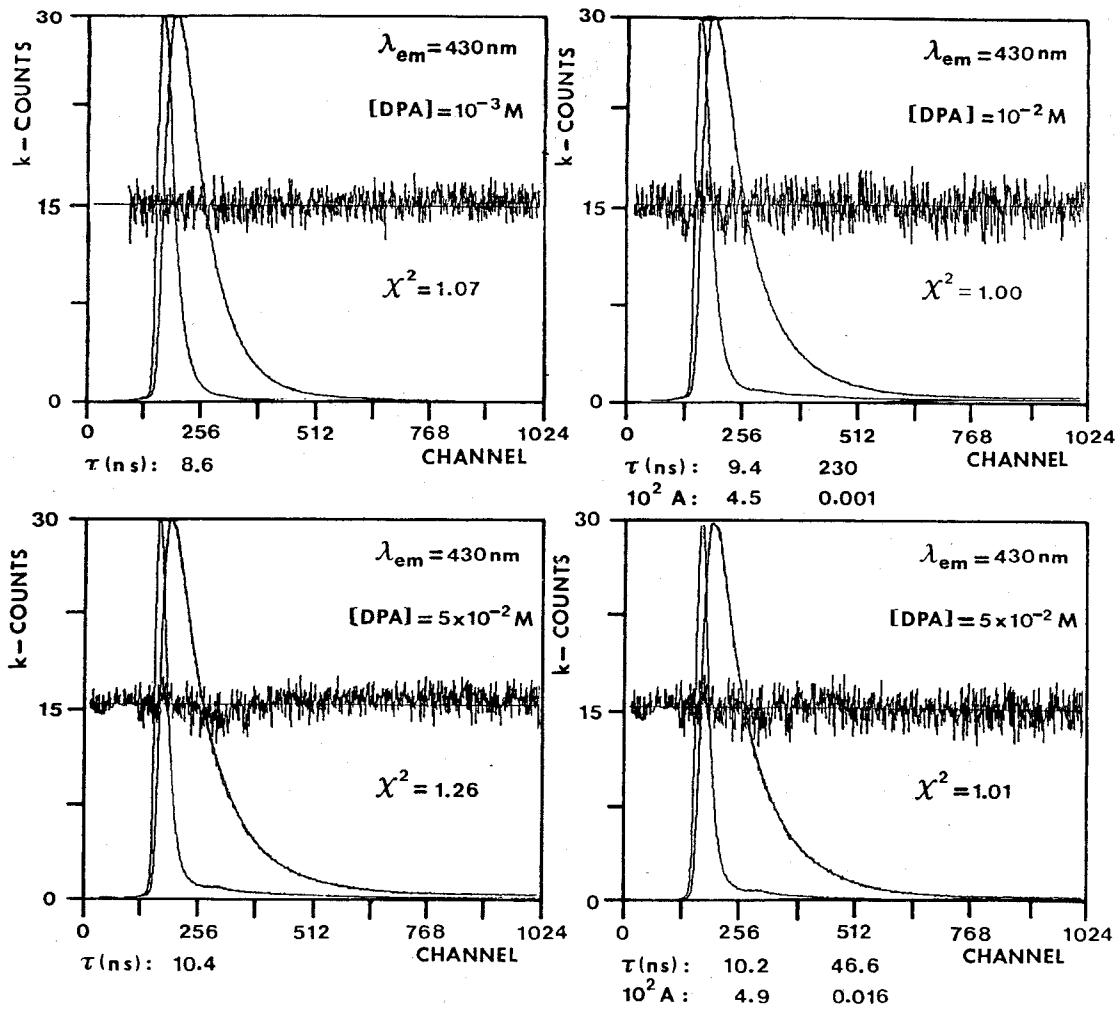

FIG. 2. Fluorescence decay curves of DPA solutions analyzed with a sum of exponentials.

$$\bar{\tau} = \frac{\sum_{i=1}^{3} A_i \tau_i^2}{\sum_{i=1}^{3} A_i \tau_i}, \tag{17}$$

where τ_i are the decay times and A_i the preexponential factors. Obviously these decay times have no physical meaning although very good fits are obtained.

The data was also fitted with the decay law expressed by Eq. (11) which can be rewritten as

$$I(t) = C \exp\left(-\frac{t}{\tau_0}\right)\left\{1 + \sum_{i=1}^{n} C_i (k_r t)^i\right\} \tag{18}$$

where C_i are polynomial coefficients and C is a preexponential factor.

In order to evaluate the reliability of the coefficients to be extracted from real data, simulated decay curves were generated with a variable number of coefficients C_i between zero and ten, according to Eq. (18) and fixing τ_0 at 7.14 ns.

TABLE I. Mean fluorescence lifetimes of 9, 10-diphenylanthracene (DPA) in benzene at 25 °C for different emission wavelengths (λ_{em}) and concentrations of DPA.

λ_{em}/nm	[DPA] = 1.0 E–3 M	[DPA] = 1.0 E–2 M	[DPA] = 5.0 E–2 M
400	8.0	8.2	8.2
410	8.3	8.6	8.5
420	8.6	9.4	10.0
430	8.6	9.5	10.3
440	8.6	9.5	10.8
450	8.6	9.6	10.6

The decays obtained were convoluted with an experimental lamp profile and poissonian synthetic noise was added. When different coefficients are used deviations from exponentiality were observed in agreement with the experimental results presented above. Analysis of these decays with the decay function (18) using a smaller number of terms shows that for the simulated conditions only the first and second coefficients can be accurately recovered. The remaining coefficients have poor precision and in some cases even negative values are obtained. These limitations are rather severe because the coefficients are strongly correlated as can be concluded from the nondiagonal elements of the correlation matrix (usually close to ± 11). Only when the same number of coefficients is used in the generated and in the fitting curve more than two coefficients are recovered with precision. In the experimental case, however, one is extracting a limited number of terms from an infinite series.

The experimental decays were analyzed with τ_0 fixed at 7.14 ns and using a number n of terms in the series varying between two and three depending on the DPA concentration. Some typical decays analyzed assuming the decay function (18) are shown in Fig. 3. Good fits were obtained as indicated by the weighted residuals. For $[\mathrm{DPA}] = 1.0 \times 10^{-3}$ M, two terms ($n = 2$) in Eq. (18) are sufficient to fit the data. The coefficient C is approximately independent of the emission wavelength for decays obtained with the same number of counts at the maximum, which is reasonable since C is a normalization constant. The remaining coefficients C_i ($i = 1,2$) are presented in Fig. 4. It is apparent that both C_1 and C_2 increase with the emission wavelength becoming approximately constant for $\lambda_{em} > 430$ nm. With the 1.0×10^{-2} M solution the decays measured at $\lambda_{em} < 430$ nm can be fitted with two terms in the series but for $\lambda_{em} > 430$ nm a third term is necessary. The trends of C_1 and C_2 are similar to those observed with the solution of concentration equal to 1.0×10^{-3} M. These coefficients are also presented in Fig. 4. The value of the third coefficient (C_3) fluctuates between 5% and 10% of C_2 showing that the number of parameters

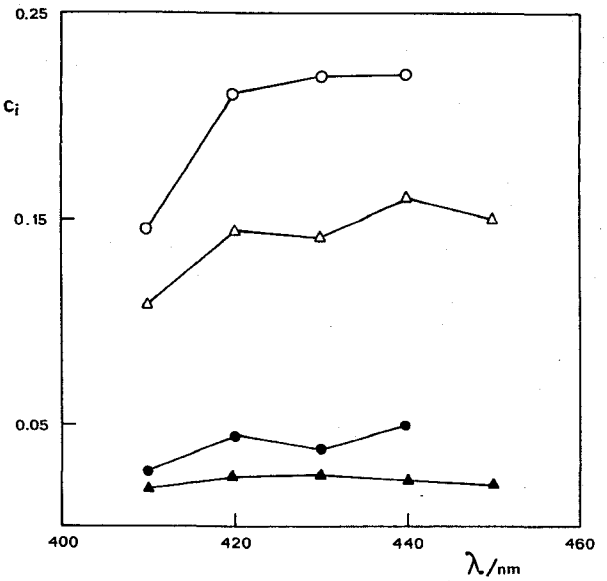

FIG. 4. Decay parameters vs emission wavelength. (Δ) C_1, $[\mathrm{DPA}] = 1.0 \times 10^{-3}$ M; ($\blacktriangle$) C_2, $[\mathrm{DPA}] = 1.0 \times 10^{-3}$ M; (O) C_1, $[\mathrm{DPA}] = 1.0 \times 10^{-2}$ M; ($\bullet$) C_2, $[\mathrm{DPA}] = 1.0 \times 10^{-2}$ M.

which can be extracted from the fluorescence decay curves is limited, as was already observed from the simulated results. When $[\mathrm{DPA}] = 5.0 \times 10^{-2}$ M the fluorescence decay at $\lambda_{em} = 410$ nm is reasonably fitted with two terms but at least three terms are necessary for longer wavelengths.

V. DISCUSSION AND CONCLUSIONS

The results presented in Fig. 1 show the inadequacy of the simple correcting formula (15) that neglects the modification of the initial distribution of excited molecules within the cell by successive processes of absorption emission.

Time-resolved fluorescence measurements allow a deeper analysis of the problem. The mean lifetimes of DPA

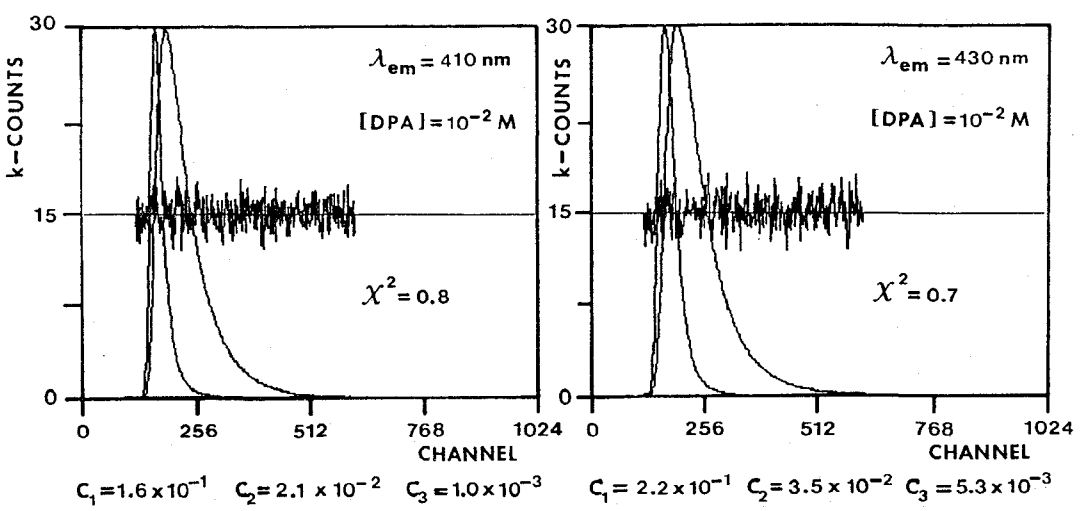

FIG. 3. Fluorescence decay curves of DPA solutions analyzed with the decay function (18).

TABLE II. Escape probability ratios of 9, 10-diphenylanthracene (DPA) solutions in benzene at 25 °C for different emission wavelengths (λ_{em}) and concentrations of DPA.

	[DPA] = 1.0 E-3 M		[DPA] = 1.0 E-2 M	
λ_{em}/nm	S_2/S_1	S_3/S_1	S_2/S_1	S_3/S_1
410	0.71	0.88	0.66	0.58
420	0.94	1.16	0.95	0.91
430	0.92	1.23	1.00	0.78
440	1.05	1.09	1.00	1.00
450	1.00	1.00	...	...

in the blue region increase with the wavelength but remain constant for wavelengths greater than the cutoff of the absorption (see Table I). The same result was obtained for different systems by several authors.[5,6] The contribution of the successive processes of emission for the overall decay (11) is dependent on the escape probability S_n which is also wavelength dependent. The escape probability $S_n(\lambda)$ is expected to be 1.0 in the red part of the spectrum irrespective of n. In the blue region, $S_n(\lambda)$ must be lower than 1.0, and dependent on n and λ. The trends of variation with λ of the mean lifetime implies that $S_n(\lambda)$ should decrease with n for a certain λ, and the more the lower the λ. In order to quantify these results the parameters shown in Fig. 4 were analyzed.

The decay coefficients C_i are related to the a_n parameters and to the $S_n(\lambda)/S_1(\lambda)$ ratios by

$$C_i = \frac{S_{i+1}(\lambda)}{S_1(\lambda)} \cdot \frac{a_i}{i!} \tag{19}$$

For wavelengths where there is no absorption the S_n/S_1 ratios are all equal to 1.0 as stated above and the a_n coefficients can be obtained. From these and using relation (6) the absorption coefficients α_n were calculated. The α_1 values are, respectively, 0.15 and 0.22 for the 1.0×10^{-3} M and 1.0×10^{-2} M solutions, the α_2 being, respectively, 0.28 and 0.45. The ratios S_2/S_1 and S_3/S_1 for different wavelengths were calculated in the blue region using relation (19) once known the a_n values. These ratios are presented in Table II.

It was observed for each concentration an increase of α_n with n, the same being true for the ratio S_n/S_1. This result can be understood on the basis of a gradually deeper penetration of excitation with each reabsorption process. For front-face measurements the reabsorption leads to a distribution that moves with time into the interior of the sample cell. The absorption coefficients α_n must therefore increase with n owing to the increase of the average path for absorption. The value of $\alpha_2 = 0.45$ recovered from the 1.0×10^{-2} M solution reasonably agrees with the theoretical limit [see Eq. (2)] of 0.41 calculated as the fractional area of the molecular fluorescence emission that lies at shorter wavelengths than the absorption cutoff of a very concentrated solution (425 nm). The other values are lower indicating that the reabsorption probability is lower than unity. The same reasoning explains the ratio of S_n/S_1 being lower than 1.0 and its decrease with n, which is due to the increase of the mean path for the emitted light that the monochromator sees.

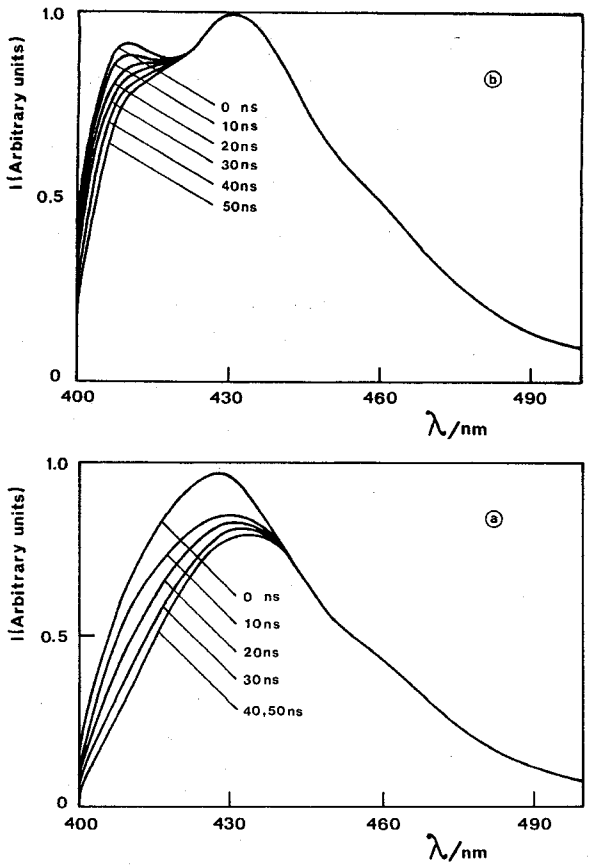

FIG. 5. Time resolved fluorescence spectra of DPA solutions. (a) [DPA] = 5.0×10^{-2} M; (b) [DPA] = 1.0×10^{-3} M.

Further insight is provided by the time resolved fluorescence spectra of DPA solutions presented in Figs. 5(a) and 5(b). In the blue region of the spectrum (400–430 nm) the fluorescence intensity is lower for longer times which reflects the evolution of the spatial distribution function. As time progresses, the average excited molecule is gradually deeper located, hence the average path of the outcoming photons is also gradually growing with time, increasing their probability of absorption within the absorption region, i.e., the blue portion of the emission.

In conclusion the model presented is able to account for the observed decay variation with wavelength and concentration. Extracted parameters were in reasonable agreement with theoretical expectations when available.

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