MEASUREMENT OF FLUORESCENCE DECAY OF RHODAMINE 6G SOLUTIONS BY TEA uv N_2 LASER EXCITATION

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Fluorescence decay of Rhodamine 6G solutions in wide dye concentration and layer thickness was investigated by a pulse fluorometer based on TEA uv N_2 laser. Deviations in τ results obtained in different experimental conditions are explained by the effect of secondary fluorescence. The molecular fluorescence decay time of Rhodamine 6G in methanol was found 4.1 ± 0.1 ns by extrapolating the experimental results to zero γ_{max}.

Introduction

There is a great deviation (3.1—6.8 ns) in decay times as measured by different investigators for Rhodamine 6G (Rh 6G) [1—4]. The measurements were performed using nitrogen and mode-locked lasers as exciting light source. When the intensity of the laser pulse is small, a bulky cuvette and considerable dye concentration is required. Fluorescence decay times (τ') as measured at various concentrations using a single cuvette (*i.e.* no variation in layer thickness) show a marked dependence on the concentration, and the $\tau'(c)$ function has a maximum [9, 10]. This effect has been explained by the present authors by self-absorption of the dye [11] and suggested a necessary correction. Although this effect was previously described for fluoresceine dye [5—7] and rigorously explained in refs, [6—8] on the basis of the theory of secondary fluorescence, the exact correction is a very difficult calculation in the general case and so it is usually neglected.

In this paper we report our experimental results concerning decay time measurements of Rh 6G (in methanol) in a wide range of dye concentration (c) and layer thickness (l). A simple experimental method is suggested to determine the molecular or true decay time (τ) of Rh 6G from the measured values (τ'); the obtained data are explained qualitatively on the basis of the theory of secondary fluorescence.

Material and experimental method

For measuring fluorescence decay time we applied the single pulse method using a transverselly excited atmospheric pressure nitrogen (TEA N_2 laser $\lambda_{ex} = 337$ nm) laser as exciting light source. The experimental arrangement and the evaluation method were described in our previous paper [10]. Rh 6G was purchased from Merck (Switzerland) and purified by chromatographic method. As solvent methanol, (MeOH) free of water, was used.

Results

The experimental results of the fluorescence decay time for Rh 6G solutions are summarized in Table I as a function of dye concentration and layer thickness. For every solution the maximum of the extinction coefficient ($\gamma_{max}=2.3\cdot\varepsilon_{max}\cdot c\cdot l$) is also given in Table I to include the γ_{max} dependence of τ'.

The measured τ' values of Rh 6G in MeOH versus the logarithm of concentration are shown in Fig. 1. As seen a great variety of τ' values (full trace) can be

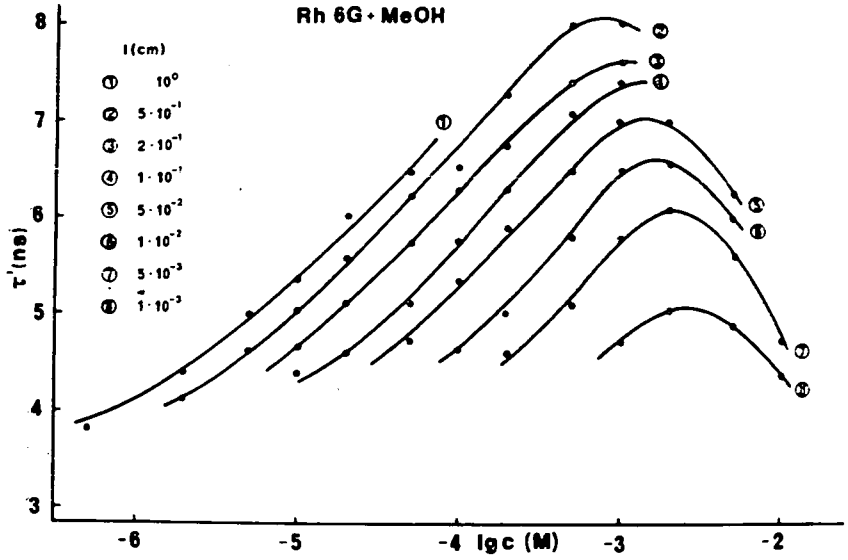


Fig. 1. Fluorescence decay time values (τ') of Rhodamine 6G in methanol (Rh 6G+MeOH) measured at several layer thickness (l) ($l=10^{\circ}-10^{-3}$ cm, ①–⑧, solid lines) versus the logarithm of dye concentration (lg c).

obtained with varying c and l values. For comparison solid lines connect the τ' values obtained for the same cuvette thickness. The curves increase gradually from 4—4.5 ns to a maximum of 5—8 nsec (at the concentration of 1—$2\cdot10^{-3}$ M), and then decrease due to concentration quenching. We could not measure τ' values at very low concentration part of these curves.

As the Fig. 1. shows the dependence on c is not a true one, because of curves are different varying the layer thickness. A re-plot is shown in Fig. 2 where τ' values (full trace) versus cuvette thickness are shown. For comparison again solid lines connect the experimental points obtained at the same concentration. As seen the measured data decrease if the thickness tends to zero, and this effect is more pronounced at higher concentrations. The curves tend to the same limit value of decay time, about 4.0—4.2 ns, when decreasing the cuvette thickness. The dependence on l is also not a true connection between τ' and l.

We plotted the decay time data as a function of γ_{-max} (a parameter which contains the product of c and l). The measured τ' values belonging to the same extinction coefficient are a little different, namely the diameter (d) of the laser beam in

Table I

	τ' (*ns*) $\gamma_{max} = 2.3 \cdot \varepsilon_{max} \cdot c \cdot l$									
l (cm)	10^{0}	$5 \cdot 10^{-1}$	$2 \cdot 10^{-1}$	10^{-1}	$5 \cdot 10^{-2}$		10^{-2}	$5 \cdot 10^{-3}$		10^{-3}
lg l	0	−0.3	−0.7	−1.0	−1.3		−2.0	−2.3		−3.0
$m = R/l$	0.5	1.0	2.5	5.0	10		50	100		500
c (M)										
$5 \cdot 10^{-7}$	3.8 *0.11*									
$2 \cdot 10^{-6}$	4.3 *0.45*	4.1 *0.23*								
$5 \cdot 10^{-6}$	5.0 *1.15*	4.6 *0.6*								
$1 \cdot 10^{-5}$ ①	5.35 *2.3*	5.0 *1.15*	4.65 *0.45*	4.4 *0.23*						
$2 \cdot 10^{-5}$ ②	6.0 *4.5*	5.55 *2.3*	5.1 *0.9*	4.55 *0.45*						
$5 \cdot 10^{-5}$ ③	6.45 *11.5*	6.2 *5.75*	5.7 *2.3*	5.1 *1.15*	4.7 *0.6*					
$1 \cdot 10^{-4}$ ④		6.5 *11.5*	6.3 *4.5*	5.7 *2.3*	5.35 *1.15*		4.6 *0.23*			
$2 \cdot 10^{-4}$ ⑤		7.3 *23.0*	6.7 *9.0*	6.3 *4.5*	5.9 *2.3*		5.0 *0.45*	4.6 *0.23*		
$5 \cdot 10^{-4}$ ⑥		*8.0*	7.4 *23.0*	7.1 *11.5*	6.45 *5.75*		5.8 *1.15*	5.1 *0.6*		
$1 \cdot 10^{-3}$ ⑦			7.65	7.4 *23.0*	7.0 *11.5*		6.5 *2.3*	5.8 *1.15*		4.7 *0.23*
$2 \cdot 10^{-3}$ ⑧					7.0 *23.0*		6.55 *4.5*	6.1 *2.3*		5.05 *0.45*
$5 \cdot 10^{-3}$					6.25		6.0 *11.5*	5.6 *5.75*		4.9 *1.15*
$1 \cdot 10^{-2}$								4.7 *11.5*		4.4 *2.3*

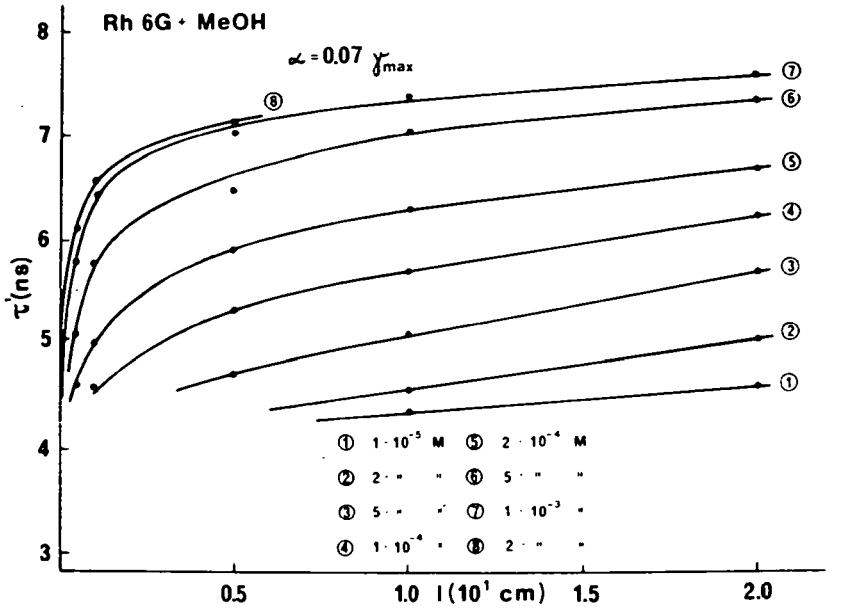
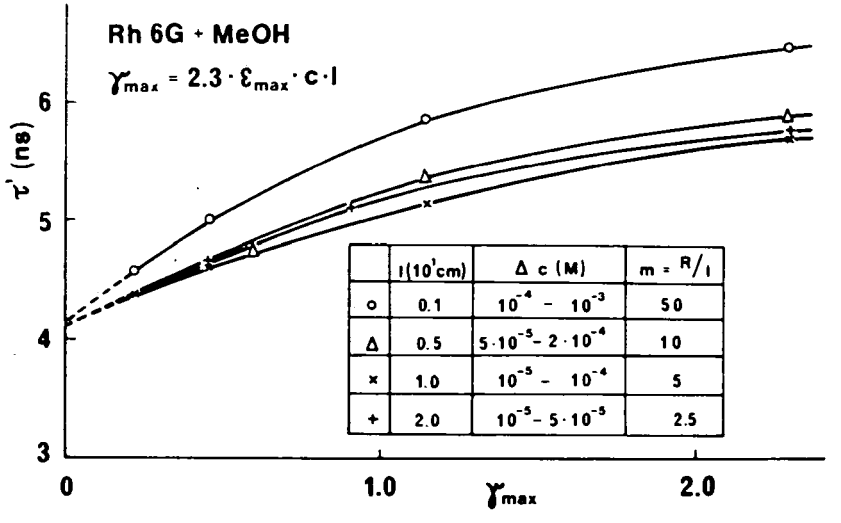


Fig. 2. Fluorescence decay time values (τ') of Rhodamine 6G in methanol (Rh 6G+MeOH) measured at several dye concentrations *(c)* ($c = 10^{-5} - 2 \cdot 10^{-3}$ M, ①–⑧, solid lines) versus the layer thickness *(l)*.



	l(10¹cm)	Δ c (M)	m = R/l
o	0.1	$10^{-4} - 10^{-3}$	50
Δ	0.5	$5 \cdot 10^{-5} - 2 \cdot 10^{-4}$	10
×	1.0	$10^{-5} - 10^{-4}$	5
+	2.0	$10^{-5} - 5 \cdot 10^{-5}$	2.5

Fig. 3. Fluorescence decay time values (τ') of Rhodamine 6G in methanol (Rh 6G+MeOH) ($0, \Delta, x, +$) as a function of the maximum extinction coefficient (γ_{max}). The solid lines connect the τ' values obtained at the same layer thickness *(l)*, so at the same *m* parameters ($m = R/l$). Δc is the concentration range used for measurements when $0.2 < \gamma_{max} \leqq 2.3$.

every case was constant ($d=1$ cm, so $R=0.5$ cm), and at the same time the layer thickness decreased with increasing concentration, *i.e.* the geometrical circumstances continuously changed, and so the $m=R/l$ ratio rapidly increased. Thus we connected those τ' data, which belong to the same layer thickness. By means of this representation we can determine the molecular fluorescence decay time when extrapolating these curves to zero γ_{max}; and a value of 4.1 ± 0.1 ns is obtained.

Discussion

The overlap of the absorption and fluorescence spectra, as well as the fluorescence absolute quantum yield, of Rh 6G is basically similar to the corresponding parameters of fluorescein dye. Our results regarding Rh 6G, also described by others [9, 10] (*i.e.* significant dependence of the measured time τ' on concentration, layer thickness, and geometrical circumstances), can be explained by taking secondary fluorescence into account; the relevant theory was worked out a long time ago. In this study we give a qualitative interpretation of our experimental results referring to [6—8, 13—15].

According to the theory of secondary fluorescence the primary fluorescence is followed by the self-absorption and then the secondary fluorescence of the dye molecules, *etc.* This effect lengthens the molecular or true decay time τ, and the relation between τ and τ' can be written as follows [6, 8]:

$$\tau = \tau'(1-\varkappa),$$

where $\varkappa$ is the ratio of the intensity of secondary and primary fluorescence. This $\varkappa$ correction is a very complicated function of α, β, γ and m parameters. We can say about these parameters in the case of our experiments the followings:

(1) $\alpha=2.30\cdot\varepsilon(\lambda_{ex})\cdot c\cdot l$ (where $\lambda_{ex}=337$ nm) is the optical density of the solution at the exciting wavelength; in every case approximately 7% of the maximum optical density (*i.e.* $\alpha=0.07\gamma_{max}=0.07\beta_{max}$, Table I).

(2) $\beta(\lambda')=2.30\cdot\varepsilon(\lambda')\cdot c\cdot l$ is a function of the optical density in the investigated part of the fluorescence spectrum. During the measurement the photodiode observed the total fluorescence spectrum, so β_{max} is equal to the value obtained at the maximum of the absorption spectrum. This fact makes $\varkappa$ correction more difficult.

(3) $\gamma(\lambda'')=2.30\cdot\varepsilon(\lambda'')\cdot c\cdot l$ is a function of the optical density between the short wavelength part of the fluorescence and the long wavelength part of the absorbance. Since the maximum of the absorption spectrum is in the range of the overlap, γ_{max} is also equal to the value obtained at the absorption maximum, so $\gamma_{max}=\beta_{max}$.

(4) $m=R/l$, where R denotes the radius of the exciting light beam after the diaphragm (and the cuvette). Since R was constant, m is inversely proportional to the layer thickness l (Table I, Fig. 3.).

According to [6, 8, 13, 15] the $\varkappa$ correction is a monotonously varying function of γ_{max} and $m\cdot\beta(\lambda)$ was the same as compared to α and γ in every case and thus we conclude that if the $\tau'(\gamma_{max}, m)$ function is known from experiments (Fig. 3.) and $\gamma_{max}<0.5$ as well as $m<5$ holds, then the τ' values do not deviate from τ more than 4—5%; this is the experimental error of our measurements.

Summing up we reported (*a*) a graphic method for the estimation of τ from experimentally obtained τ'; (*b*) an experimental verification of the theory of secondary fluorescence by measuring τ' of Rh 6G dye in different solutions.

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ИЗМЕРЕНИЕ ВРЕМЕНИ ЗАТУХАНИЯ ФЛУОРЕСЦЕНЦИИ РАСТВОРОВ РОДАМИНА 6Ж ВОЗБУЖДЕННОЙ «uv» TEA N_2 ЛАЗЕРОМ

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Зависимость времени затухания флуоресценции растворов родамина 6Ж от концентрации растворов и толщины образца, изменяющихся в широкой области, была исследована с использованием атмосферического азотного лазера. Различия между получаемыми результатами при разных экспериментальных условиях объяснены по теории вторичной флуоресценции. Молекулярное время затухания флуоресценции родамина 6Ж в метаноле получалось $4{,}1 \pm 0{,}1$ нс экстраполяцией экспериментальных данных когда $\gamma_{\text{макс}}$ стремится к нулю.