

FLUORESCENCE QUENCHING OF RHODAMINE 6G IN METHANOL AT HIGH CONCENTRATION

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The fluorescence lifetime of rhodamine 6G dissolved in methanol is measured over a wide concentration region from 10^{-5} to 0.6 mol/l. The rapid reduction of fluorescence lifetime above 10^{-2} mol/l is found to be mainly due to energy transfer to quenching centers. The decrease of the fluorescence lifetime is limited by the finite fluorescence lifetime of the quenching centers of ≈ 1 ps.

1. Introduction

Molecules promoted to excited electronic states relax to the ground state by radiative and radiationless transitions. The relaxation of highly excited singlet (triplet) states to the first excited singlet (triplet) state generally occurs by radiationless transitions [1–7]. In the lowest excited singlet state spontaneous emission competes with internal conversion (equi-energetic S_1-S_0 transition and vibrational relaxation within the S_0 potential well) and intersystem crossing (S_1-T transition) [2–7]. Relaxation of the lowest triplet state to the S_0 ground state is spin forbidden and occurs mainly by the radiationless process of $T-S_0$ intersystem crossing.

For rigid dye molecules in liquid solution at low concentration the spontaneous emission generally dominates and a high fluorescence quantum yield is observed. For flexible molecules the radiationless internal conversion reduces the fluorescence lifetime and makes it strongly viscosity dependent [7–12]. S_1 -state depopulation by S_1-T intersystem crossing is generally slow [13]. The process is caused by spin-orbit coupling. The presence of heavy atoms or paramagnetic molecules (e.g. O_2) enhances the transfer [5–8].

The fluorescence quantum yield of dye solutions may be reduced by addition of quenching substances (impurity quenching [2–7]). Electrolyte admixtures may cause aggregation of dye molecules (salting-out). Addition of molecules absorbing in the fluorescence region of the substance results in energy transfer mechanisms (donor-acceptor complexes [2–6,14], sensitized fluorescence [2–6]).

At high concentrations self-quenching of the fluorescence is experienced. This concentration quenching is due to the formation of dimers or other quenching complexes which have very fast radiationless deexcitation channels [2–6]. The quenching complexes behave like flexible molecules in low viscous solvents and relax by fast internal conversion. They are often treated as non-fluorescent species [15]. In some cases excited dimers fluoresce in a shifted wavelength region (excimer emission) [3–6].

In this paper we measure the fluorescence lifetime and the fluorescence quantum efficiency of rhodamine 6G in methanol within a wide concentration region. The strong decay of fluorescence lifetime and fluorescence quantum efficiency at concentrations above 10^{-2} mol/l [15,16] is found to be mainly due to energy transfer to bimolecular rhodamine 6G quenching centers. From the data a fluorescence lifetime of the quenching centers of $\approx 1 \pm 0.5$ ps is extracted.

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2. Experimental

Rhodamine 6G from Kodak was used without further purification. The solvent was analytic grade methanol from Merck. For concentrations $C > 10^{-3}$ mol/l a thin cell of adjustable thickness was applied (inset of fig. 1). The path length was adjusted to a transmission of $T \approx 0.1$ at $\lambda = 526.5$ nm (approximately S_0 - S_1 absorption maximum). This thin-cell arrangement hinders fluorescence re-absorption and secondary fluorescence (high transmission in fluorescent region) [2,4] and amplified spontaneous emission (weak gain since high transmission) [17,18].

The experimental arrangement for the fluorescence lifetime and fluorescence quantum efficiency measurements is depicted in fig. 1. Single picosecond second-harmonic light pulses ($\Delta t \approx 4$ ps, fwhm) from a passively mode-locked Nd-phosphate glass laser are used as excitation source. The fluorescence lifetimes are measured with a fast single-sweep streak camera (Hamamatsu model C1587 with M1952 plug-in, time resolution ≤ 2 ps). The backward fluorescence light is directed to the streak camera. The fluorescence traces are analysed with the Hamamatsu C2280 temporal disperser which is interfaced to the read-out vidicon.

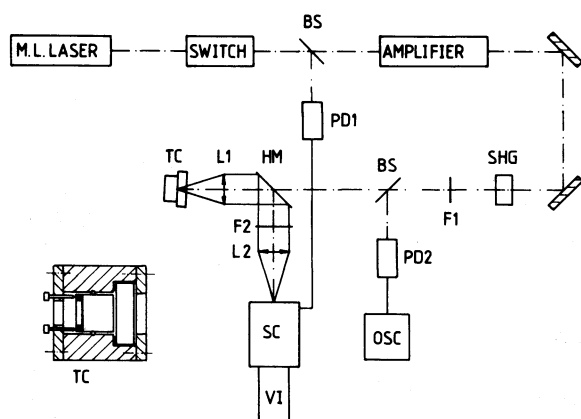


Fig. 1. Experimental arrangement. SHG: KDP crystal for second harmonic generation; BS: beam splitters; F1, F2: filters; HM: 50% cube beamsplitter; L1: lens ($f = 5$ cm); L2: lens ($f = 15$ cm); PD1, PD2: photodetectors; OSC: transient digitizer; SC: streak camera; VI: vidicon; TC: thin cell. Inset shows schematic cross section of thin cell.

The fluorescence quantum yield is measured with the same experimental arrangement. Only the streak-camera is operated in focal mode (no temporal deflection). The fluorescence signal S_F is proportional to the absorbed second-harmonic light energy [$S_F \propto q_F(1-T)E$, q_F is the fluorescence quantum efficiency, T the dye transmission at second-harmonic frequency and E the incident second-harmonic pulse energy]. The proportionality constant is eliminated by normalizing the fluorescence signal to the fluorescence at low concentration (reference $S_0 \propto q_0(1-T_0)E_0$, concentration 10^{-3} mol/l, $q_0 \approx 0.9$ [15]). From the ratio $S_F/S_0 = [q_F(1-T)E]/[q_0(1-T_0)E_0]$ the fluorescence quantum efficiency at concentration C is obtained:

$$q_F = \frac{\tau_F}{\tau_{\text{rad}}} = \frac{S_F(1-T_0)E_0}{S_0(1-T)E} q_0, \quad (1)$$

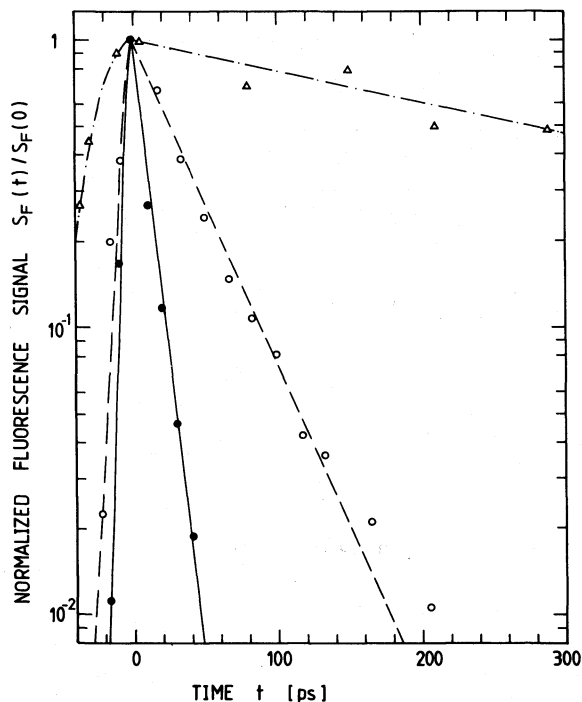
τ_F is the fluorescence lifetime and τ_{rad} is the radiative lifetime. The input pulse energy E was kept below 10^{-8} J to avoid amplified spontaneous emission in the plane parallel to the cell window [18]. An increase in energy by a factor of 50 had no influence on the fluorescence quantum efficiency. The fluorescence quantum yield may be used to determine the fluorescence lifetime. Use of eq. (1) with $q_0 = \tau_0/\tau_{\text{rad},0}$ gives

$$\tau_F = \frac{S_F(1-T_0)E_0}{S_0(1-T)E} \frac{\tau_{\text{rad}}}{\tau_{\text{rad},0}} \tau_0, \quad (2)$$

τ_0 is the fluorescence lifetime of the reference rhodamine 6G-methanol solution of $C_0 = 10^{-3}$ mol/l. $\tau_{\text{rad},0}$ is the radiative lifetime at the reference concentration C_0 while τ_{rad} is the radiative lifetime at concentration C . Since the integrated S_0 - S_1 absorption spectrum is nearly independent of concentration [19], τ_{rad} is nearly independent of concentration and we use $\tau_{\text{rad}} = \tau_{\text{rad},0}$.

3. Results

In fig. 2 three fluorescence traces for different dye concentrations are presented ($C = 0.04, 0.1$ and 0.2 mol/l). They were obtained by streak camera measurements. Within the experimental



accuracy the trailing parts of the fluorescence curves decrease exponentially.

In fig. 3 the measured fluorescence lifetimes and fluorescence quantum efficiencies are presented. The open circles give the fluorescence lifetimes. The open triangles indicate the fluorescence quantum efficiencies. The solid triangle represents the measured fluorescence quantum efficiency for a solid rhodamine 6G film on a glass plate. Because of eq. (2), the triangles obtained by fluorescence yield measurements (right-hand ordinate) also give the fluorescence lifetimes (left-hand ordinate).

Up to 10^{-2} mol/l the fluorescence lifetime is

◀ Fig. 2. Streak camera. Fluorescence traces for rhodamine 6G in methanol. Points taken from data of temporal analyser. Straight lines indicate exponential decay. Solid curve (closed circles): concentration $C = 0.2$ mol/l; $\tau = 10$ ps. Dashed curve (open circles): $C = 0.1$ mol/l, $\tau = 39$ ps. Dash-dotted curve (triangles): $C = 0.04$ mol/l, $\tau = 357$ ps.

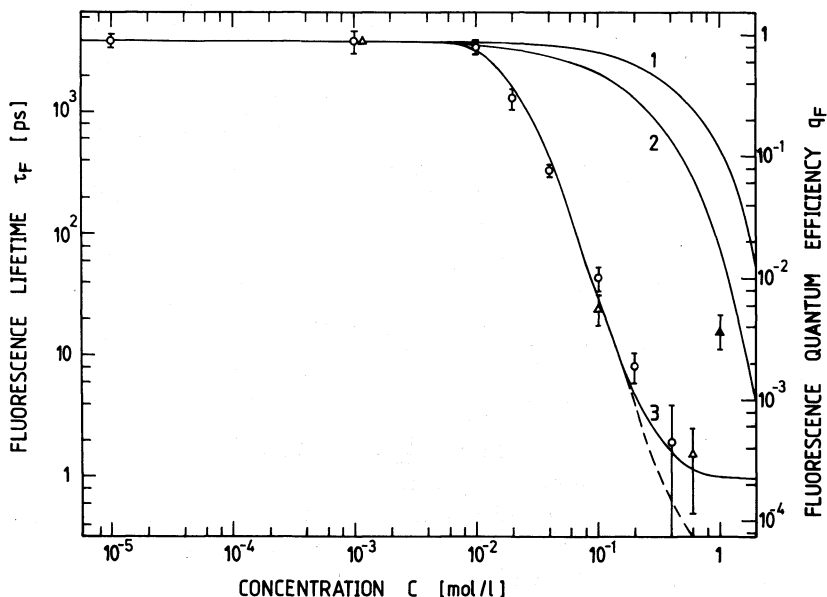


Fig. 3. Fluorescence lifetime and fluorescence quantum efficiency versus concentration for rhodamine 6G dissolved in methanol. Open circles: measured τ_F values; open triangles: measured fluorescence quantum efficiencies; solid triangle: fluorescence quantum efficiency of a rhodamine 6G film. Curve 1: influence of quenching centers on fluorescence quantum efficiency [eq. (10) with $V = 3.5$ nm³]. Curve 2: influence of quenching centers and diffusion on fluorescence quantum efficiency [eq. (12) with $\tau_0 = 3.9$ ns, $\eta = 5.6 \times 10^{-3}$ J s/m³ and $T = 295$ K]. Curve 3: fluorescence quantum efficiency due to initial quenching centers, diffusion and energy transfer [eq. (14) with $C_0 = 4 \times 10^{-3}$ mol/l and $q_Q = 2.25 \times 10^{-4}$]. Dashed curve: monomer fluorescence quantum efficiency alone [first term of eq. (14)].

independent of concentration ($\tau_F = 3.9 \pm 0.5$ ns). Then the fluorescence lifetime decreases rapidly with increasing concentration. At 0.4 mol/l the fluorescence lifetime is shorter than the pump pulse duration and the time-resolved streak traces give only an upper limit of the decay time. The fluorescence quantum yield measurement is applicable over the whole concentration region. At a concentration of 0.6 mol/l a lifetime of $\tau_F = 1.5 \pm 1$ ps is found. For the solid film the fluorescence yield measurements give a fluorescence lifetime of 15 ± 5 ps.

4. Discussion

The observed dependence of fluorescence lifetime on concentration is analysed with the model sketched in fig. 4. After excitation there are ground-state monomers (open circles), ground-state quenching centers (two open circles within dashed circles), excited monomers (crosses), and

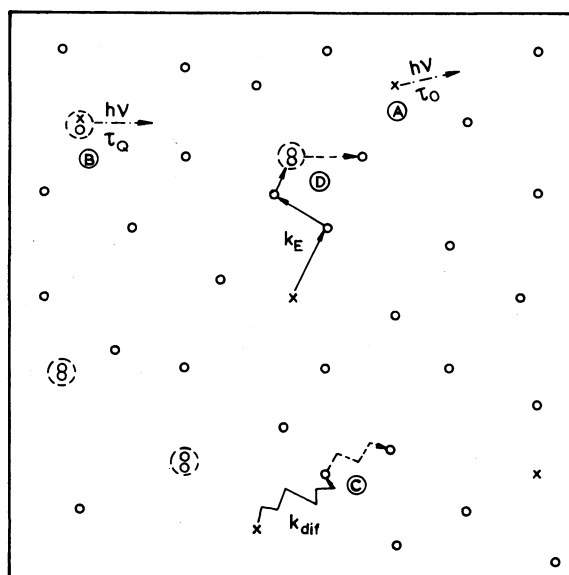


Fig. 4. Illustration of deactivation processes of excited molecules. Open circles: unexcited molecules; crosses: excited molecules; dashed circles: reaction centers. Process A: excited monomer fluorescence. Process B: excited quenching center fluorescence. Process C: formation of excited quenching centers by diffusion. Process D: formation of excited quenching centers by energy transfer.

excited quenching centers (open circle and cross within dashed circle). The excited monomers are assumed to relax with a fluorescence lifetime τ_0 and a fluorescence quantum efficiency q_0 ($\tau_0 = q_0 \tau_{\text{rad}}$, process A in fig. 4). The excited quenching centers are assumed to relax with a fluorescence lifetime τ_0 and a fluorescence quantum efficiency q_Q (process B in fig. 4).

Within the lifetime of the excited monomers diffusion may bring an excited monomer and a ground-state monomer near together. Both molecules form an excited quenching center with lifetime τ_Q (process C in fig. 4). The diffusion rate constant is given by the Debye equation [2-6]:

$$k_{\text{dif}} = 4\pi(2a)(2D)N = (8N_A k_B T / 3\eta)C, \quad (3)$$

where a is the interaction radius of a monomer, $D = k_B T / 6\pi\eta a$ is the diffusion coefficient of a monomer in the solvent, $N = N_A C$ is the number density of dye molecules (dimension m^{-3}), $N_A = 6.022045 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant, C is the dye concentration (dimension mol/m^3), $k_B = 1.380662 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant, T is the temperature and η is the dynamic viscosity of the solvent (dimension $\text{J s}/\text{m}^3$). The diffusion length of two monomers within the fluorescence lifetime τ_F is $l_{\text{dif}} = 2(2D\tau_F)^{1/2}$ [20].

Within the lifetime τ_Q of the excited quenching center the diffusion continues and disintegrates the fraction of $f_k = k_{\text{dif}} / (k_{\text{dif}} + 1/\tau_Q)$ quenching centers to monomers ($Q^* \rightarrow M + M^*$). The effective rate constant for diffusion-controlled quenching center formation becomes $k'_{\text{dif}} = k_{\text{dif}}(1 - f_k)$, i.e.

$$k'_{\text{dif}} = k_{\text{dif}} / (1 + k_{\text{dif}} \tau_Q). \quad (4)$$

Since the following analysis gives $k_{\text{dif}} \ll \tau_Q$, k'_{dif} may be approximated by k_{dif} .

Besides diffusion an excited molecule may transfer its excitation energy to a nearby unexcited molecule getting itself unexcited [2-6]. This hopping mechanism may bring - after some steps - the excitation energy to a reaction center where fast radiationless decay occurs (process D in fig. 4). The energy transfer is generally due to dipole-dipole interaction. The rate of dipole-dipole energy transfer k_{ET} is proportional to R^{-6} , where R is the distance between the dipoles. The

rate k_{EQ} of energy transfer to quenching centers is proportional to the rate of energy transfer k_{ET} and to the mole fraction x_Q of quenching centers [2]:

$$k_{EQ} = k_{ET}x_Q = \frac{1}{\tau_0} \left(\frac{R_0}{R} \right)^6 x_Q = \frac{1}{\tau_0} \left(\frac{C}{C_0} \right)^2 x_Q. \quad (5)$$

R_0 is the critical transfer distance of energy transfer (energy transfer rate $k_{ET} = \tau_0^{-1}$) and C_0 is the critical transfer concentration.

Within the lifetime τ_Q of the excited quenching centers, an energy back transfer to monomers occurs ($Q^* + M \rightarrow Q + M^*$). The fraction of excited molecules that escape the quenching centers is $f_B = k_{ET}(1 - x_Q) / [k_{ET}(1 - x_Q) + 1/\tau_Q]$. The effective rate of excited quenching center formation by energy transfer reduces to $k_E = k_{ET}x_Q(1 - f_B)$, i.e.

$$k_E = \frac{1}{\tau_0} \left(\frac{C}{C_0} \right)^2 x_Q \left[1 + \frac{q_Q}{q_0} \left(\frac{C}{C_0} \right)^2 (1 - x_Q) \right]^{-1}, \quad (6)$$

where $\tau_Q/\tau_0 = q_Q/q_0$ is used.

The quenching centers consist mainly of two molecules which are so near together that they interact mutually. They may be formed by the chemical reaction of dimer formation (bound ground-state dimers) or they are formed by molecules which are occasionally (by statistics) near together without chemical binding (unbound ground-state dimers). The mole fraction x_Q of molecules in quenching centers (equal twice the fraction of quenching centers is composed of the mole fraction x_D of molecules in dimers and of the mole fraction x_S in statistical quenching centers:

$$x_Q = x_D + x_S. \quad (7)$$

The mole fraction of molecules in bound dimers, x_D , is obtained from the law of mass action for the chemical reaction $M + M \rightleftharpoons D$. The dimerization constant is $K_D = [D]/[M]^2 = (x_D/2)/Cx_M^2 = x_D/[2C(1 - x_D)^2]$ and the mole fraction comes out to be

$$x_D = 1 + \frac{1}{4CK_D} - \left[\left(1 + \frac{1}{4CK_D} \right)^2 - 1 \right]^{1/2}. \quad (8)$$

The mole fraction of molecules in statistically

formed quenching centers (unbound dimers), x_S , is given by [2,21,22]:

$$x_S = 1 - \exp(-VN_A C), \quad (9)$$

where V is the volume of a quenching center.

In the excitation process monomers and molecules in quenching centers are excited. The strong radiationless deactivation of excitation in quenching centers reduces the fluorescence light. The fluorescence quantum efficiency reduces due to the presence of quenching centers to

$$\begin{aligned} q_F &= (1 - x_Q)q_0 + x_Qq_Q \\ &= (1 - x_Q)(q_0 - q_Q) + q_Q. \end{aligned} \quad (10)$$

The fluorescence intensity decays accordingly to

$$\begin{aligned} I_F(t) &= I_F(0) \left[(1 - x_Q) \exp(-t/\tau) \right. \\ &\quad \left. + x_Q \exp(-t/\tau_Q) \right], \end{aligned} \quad (11)$$

with $\tau = \tau_0$. The fluorescence is composed of two single-exponential decay components (monomers and quenching centers).

The inclusion of the formation of excited quenching centers by diffusion approximately leads to [6]

$$q_F \approx (1 - x_Q) \frac{q_0 - q_Q}{1 + \kappa_{dif} C} + q_Q \quad (12)$$

and τ of eq. (11) becomes:

$$\tau \approx \frac{\tau_0 - \tau_Q}{1 + \kappa_{dif} C} + \tau_Q. \quad (13)$$

The abbreviation $\kappa_{dif} = \tau_0 k'_{dif}/C \approx \tau_0 k_{dif}/C$ is used in eq. (13).

The additional inclusion of energy transfer to fluorescence quenching centers leads to

$$\begin{aligned} q_F &\approx (1 - x_Q)(q_0 - q_Q) \\ &\quad \times \left\{ 1 + \kappa_{dif} C + x_Q \left(\frac{C}{C_0} \right)^2 \right. \\ &\quad \left. \times \left[1 + \frac{\tau_Q}{\tau_0} \left(\frac{C}{C_0} \right)^2 (1 - x_Q) \right]^{-1} \right\}^{-1} + q_Q \end{aligned} \quad (14)$$

and τ of eq. (11) becomes

$$\tau \approx (\tau_0 - \tau_Q) \times \left\{ 1 + \kappa_{\text{dif}} C + x_Q \left(\frac{C}{C_0} \right)^2 \times \left[1 + \frac{\tau_Q}{\tau_0} \left(\frac{C}{C_0} \right)^2 (1 - x_Q) \right]^{-1} \right\}^{-1} + \tau_Q. \quad (15)$$

The calculated curves in fig. 3 clarify the importance of the various fluorescence quenching processes. Curve 1 depicts the fluorescence quenching due to the excitation of quenching centers [eq. (10)]. An analysis of the absorption spectra of rhodamine 6G dissolved in methanol suggests that bound dimer formation is very weak ($x_D \approx 0$) and the quenching centers are due to neighbouring molecules ($x_Q \approx x_S$) [19]. A volume of $V = 3.5 \text{ nm}^3$ [eq. (9)] is assumed for the quenching centers [19]. (Curve 1 does not strongly depend on whether x_Q is due to x_D or x_S .) Curve 2 is obtained by considering the processes of excitation of quenching centers and of diffusion [eq. (12)]. Curve 3 includes deactivation by reaction centers, diffusion, and energy transfer [eq. (14)]. The curve is fitted to the experimental quantum efficiency at $C = 0.1 \text{ mol}/\ell$ ($C_0 = 4.0 \times 10^{-3} \text{ mol}/\ell$, $R_0 = (3/4\pi N_A C_0)^{1/3} = 4.63 \text{ nm}$) and $C = 0.6 \text{ M}/\ell$ ($q_Q = 2.25 \times 10^{-4}$). The dashed curve represents the first term of eq. (14) (monomer fluorescence).

A comparison of the calculated curves with the experimental points indicates that the excitation energy hopping to quenching centers is the dominant relaxation mechanism in rhodamine 6G–methanol solution at high concentration. The fluorescence lifetime of the quenching centers is found to be about a factor of 4000 shorter than that of the monomers. The solid rhodamine 6G film has a factor of 10 higher fluorescence quantum efficiency than the high concentrated solution. In the solid film all molecules have near neighbours so that $x_Q = 1$ and the fluorescence light results from emission of the quenching centers. The fluorescence lifetime of the quenching centers in the solid film is about a factor of 15 longer than in the methanolic solution. The reduced flexibility of the molecule clusters in the solid reduces the radiationless relaxation rate.

Eq. (11) represents the fluorescence decay of two components with different decay times τ and τ_Q . The fast decay component could not be resolved from the streak camera traces (see fig. 2), since $\tau_Q \approx 1 \text{ ps}$ is faster than the pulse duration $\Delta t \approx 4 \text{ ps}$ of the excitation source and faster than the response time of the streak camera. The time constant for energy transfer is time dependent at low concentrations in viscous media [23–27]. If the diffusion length l_{dif} is short and the mean molecular distance $\bar{x} = (N_A C)^{-1/3}$ is large compared to the critical transfer distance R_0 , a fluorescence decay proportional to $\exp(-\xi t^{1/2})$ is expected (ξ is a constant) [23–27]. In our case the diffusion length within the radiative lifetime is $l_{\text{dif}} = 2(2k_B T \tau_{\text{rad}} / 6\pi\eta a)^{1/2} \approx 1.2 \text{ nm}$ ($\eta = 5.6 \times 10^{-3} \text{ J s}/\text{m}^3$, $a \approx 1 \text{ nm}$), the critical transfer distance is $R_0 = 4.63 \text{ nm}$, and the mean molecular distance at the critical concentration of $C_0 = 4 \times 10^{-3} \text{ mol}/\ell$ is $\bar{x} = 7.46 \text{ nm}$. These data would lead to a $\exp(-\xi t^{1/2})$ decay at C_0 . But at the critical concentration the deactivation by energy transfer is still negligibly small, since the mole fraction of quenching centers is small [$x_S(C_0) = 0.0084$, see eq. (9)] and many energy transfer steps are necessary to reach a quenching center. For concentrations of appreciable fluorescence quenching $C > 2 \times 10^{-2} \text{ mol}/\ell$ the mean molecular distance becomes $\bar{x} < 4.4 \text{ nm}$, i.e. $\bar{x} < R_0$. All molecules are within the critical region of energy transfer and the fluorescence decay time τ behaves time independent. The fluorescence decreases exponential in time as observed experimentally [see eq. (11) and fig. 2].

The radiationless depopulation of the excited quenching centers is thought to occur via internal conversion. Ground state absorption recovery time measurements (bleaching experiments) support this assumption (absorption recovery time is found to be approximately equal to fluorescence decay time) [18].

5. Conclusions

The fluorescence of rhodamine 6G dissolved in methanol could be measured up to the saturation concentration ($\approx 0.66 \text{ mol}/\ell$) without disturbances by reabsorption, secondary fluorescence

and amplified spontaneous emission due to the application of a backward fluorescence measurement technique with a variable thin cell. The rapid decrease of fluorescence lifetime above 10^{-2} mol/l was found to be due to excited state energy hopping to quenching centers. A finite lifetime of the quenching center fluorescence (two rhodamine 6G molecules in near contact) of ≈ 1 ps was observed which limits the decay of the fluorescence lifetime at very high concentrations.

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