Subnanosecond fluorescence quenching of dye molecules in solution

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(Received 22 March 1977)

Subnanosecond fluorescence kinetics of malachite green and erythrosin were measured. The fluorescence lifetime of malachite green depends on the viscosity of the solution as $\eta^{2/3}$. The fluorescence lifetime of erythrosin decreases linearly as the concentration of water increases in a water–acetone mixture. The fluorescence quenching of malachite green and erythrosin is attributed to environmental effects on the nonradiative internal conversion and intersystem crossing rates, respectively.

INTRODUCTION

The optical properties of dye molecules in solution are known to be dependent on many environmental factors.[1–3] The fluorescence yield and lifetime as well as the absorption and emission spectra can be readily affected by various parameters of the solvent: polarity, viscosity, hydrogen bond donor or acceptor strength, *p*H, and temperature. For example, the fluorescence yield of malachite green, a triphenylmethane dye, increases by orders of magnitude when the viscosity of the solvent is correspondingly changed.[4,5] This increase of fluorescence is due to the inhibition of the rotational motion of the phenyl rings of the dye molecules in a viscous medium. Erythrosin, an iodine substituted fluorescein dye, is known to reduce its fluorescence yield from 0.5 to 0.02 when acetone is replaced by water as the solvent.[6] Dramatic changes of the fluorescence yield are intrinsically interesting for the general understanding of the radiationless transitions of dye molecules in solution. They are also of practical interest since a large fluorescence yield is one of the prime requirements for laser dyes,[7] while a low fluorescence yield and the accompanying fast decay are essential properties of the saturable dyes employed for passive mode-locking in the production of ultrashort laser pulses.[8]

We report a study of the fluorescence lifetime of malachite green as a function of solvent viscosity, and a study of the fluorescence lifetime and relative yield of erythrosin as a function of water concentration in a water–acetone mixture. The fluorescence quenching is attributed to environmental effects.

In the case of triphenylmethane dyes, Förster and Hoffmann,[5] measuring the quantum yield of fluorescence in a variety of solvents and as a function of temperature, found that the quantum yield Φ varies as $\eta^{2/3}$ for viscosity $\eta < 200$ poise (P). They proposed a phenomenological model based on the rotational motions of the phenyl rings to explain the observed $\Phi \propto \eta^{2/3}$ relation, and predicted a time dependence of $\exp(-bt^3/\eta^2)$ for the relaxation of the first excited state of the dye molecule, where b is a constant. In the past, the recovery of the ground state population after excitation has been investigated by the method of time resolved absorption.[9] Recently, Ippen *et al.*[10] employing subpicosecond dye laser pulses observed that the absorption recovery of malachite green is a single exponential for $\eta < 1$ P and a second faster exponential component appears for $\eta > 1$ P. The fast component was observed to behave close to $\eta^{2/3}$ and was attributed to the fluorescence lifetime ($S_1 \rightarrow S_0^* + h\upsilon$). The longer time component behaving close to $\eta^{1/2}$ was suggested to be the time required for thermal equilibrium in the ground state manifold ($S_0^* \rightarrow S_0$). Our present experiment is designed to *directly* measure the lifetime of the first excited state by the method of time resolved fluorescence. The measured fluorescence kinetics were single exponentials. The lifetimes, which vary as $\eta^{2/3}$ for $1 < \eta < 60$ P, are about equal to the values of the *slow* component observed in the absorption recovery experiment by Ippen *et al.*[10]

In the case of erythrosin, Umberger[11] measured the fluorescence in a variety of solvents and found that the yield and lifetime decrease as the hydrogen donor strength of the solvent increases from acetone to water. We have extended the study by measuring the lifetime and relative quantum yield in the water–acetone mixture, and have found the lifetime and yield to decrease linearly as the mole concentration of water increases in the mixture. The mechanism of the fluorescence quenching by water is an interesting subject. Enhanced internal conversion rate by protonation,[11] enhanced intersystem crossing rates, or dimerization due to linkage by water through hydrogen bonding (or bonds) are some of the possible processes. We shall discuss in this paper the experimental evidence related to these processes.

EXPERIMENTAL METHODS

The fluorescence lifetime of malachite green in glycerol at room temperature, and that of erythrosin in water are less than 100 ps. We have measured the subnanosecond fluorescence using a streak camera and an ultrafast Kerr gate.

In the streak camera, photoelectrons produced at various times by the photons arriving at the photocathode are caused to streak across a phosphorescent screen to produce a temporal profile of the light emitting event. The streak camera used in this experiment is a prototype made by Hamamatsu. A special feature of the Hamamatsu camera is the incorporation of a channel plate in the streak tube to multiply the photoelectrons. The typical gain of the channel plate is 3

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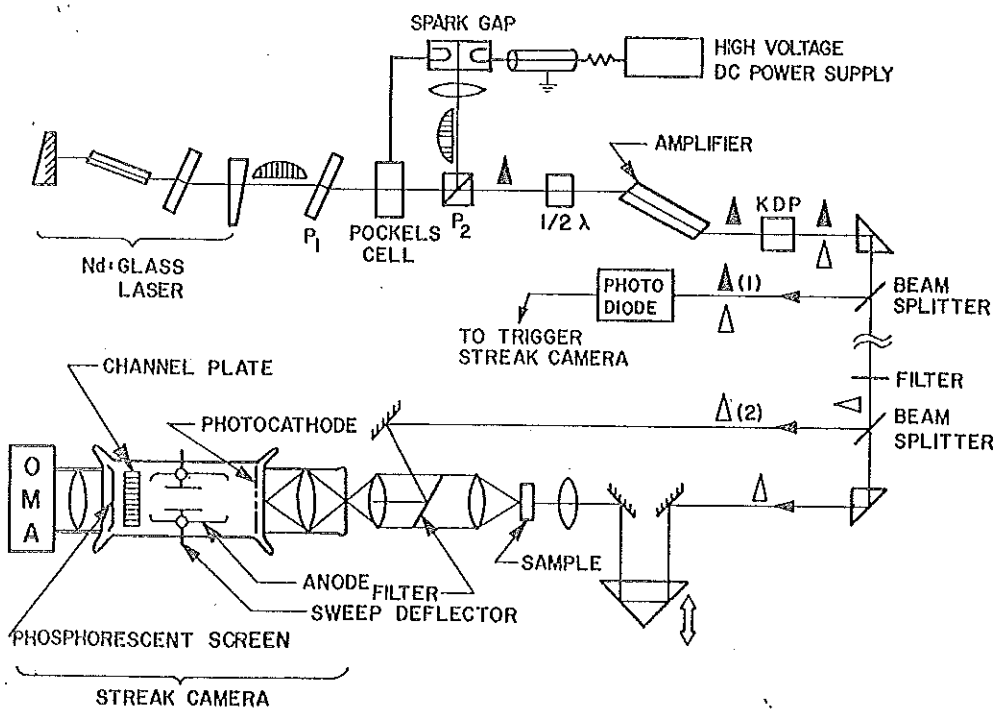
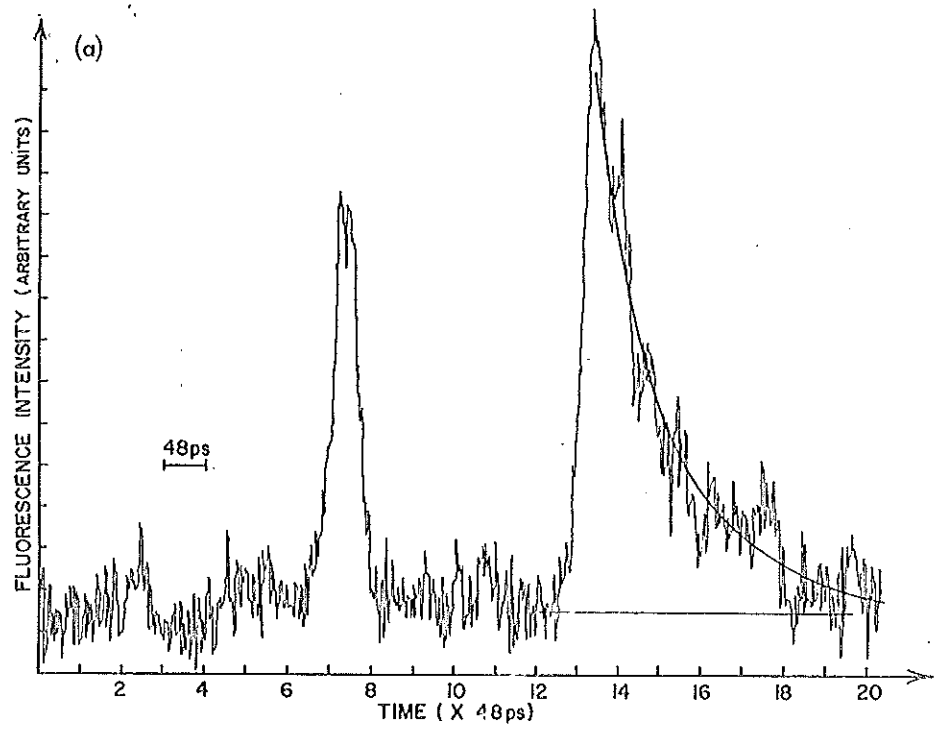


FIG. 1. Schematic of apparatus used to measure fluorescent kinetics by a streak camera. The Nd:glass laser emits a train of one hundred 1.06 μ pulses separated by ~6 ns. A single pulse in the earlier portion of the train is selected by a Pockels cell and crossed polarizers (P_1 and P_2). The high voltage pulse (~5 ns) at the Pockels cell is supplied by a laser triggered spark gap and a charged line. The single pulse (~8 ps, $\sim 10^3$ W) can be amplified. The second harmonic is generated from a phase matched potassium dihydrogen phosphate (KDP) crystal. Beam splitters provide two side beams: beam (1) triggers the streak camera; beam (2) arriving at the streak camera at an earlier time acts as a calibrating pulse. The main 0.53 μ beam excites the sample for fluorescence measurement. The fluorescence collected with $f/1.25$ optics is focused into the 30 μ slit of the streak camera. The streak produced at the phosphorescent screen is recorded by an optical multichannel analyzer (OMA).

$\times 10^3$. In Fig. 1 the experimental setup is shown. A sample of the dye solution was excited by a 6 ps, 0.53 μ pulse. The fluorescence at the rear end of the sample cell was collected by an $f/1.25$ lens into the 30 μ slit of the streak camera. The intensity of the streak was recorded by an intensity calibrated optical multichannel analyzer (OMA by Princeton Applied Research) and an x–y recorder. The average streak rate $\Delta x/\Delta t$ at a particular channel of the OMA(x) was calibrated by pulses separated by a known temporal separation. A calibration curve for $(\Delta x/\Delta t)$ was used to deconvolute the signal obtained from the OMA: since $I(t)\Delta t = I(\Delta t/\Delta x)\Delta x \equiv i(x)\Delta x$, hence $I(t) = i[x(t)](\Delta x/\Delta t)$, where $I(t)$ is the fluorescence intensity as a function of time, $i(x)$ is the measured fluorescence as a function of the channel number, and $(\Delta x/\Delta t)(x)$ is the streak rate as a function of the channel number x. The streak camera used in this experiment contains four nominal streak rates: 15 mm (full range) for 10, 5, 2, and 1 ns. The streak rates were found to vary by less than ± 5% over the nominal 2 and 1 ns range, ± 10% over the 5 ns range, and ± 40% over the 10 ns range. The calibrated ranges of the streaks are 5.2, 2.1, 0.96, and 0.40 ns over the 500 channels (12.5 mm length) of the OMA for the nominal 10, 5, 2, and 1 ns rates, respectively. The resolution of the streak is about 1/40 of the total streak on the OMA. Therefore, the limiting time resolution is about 10 ps.

The optical Kerr gate operates under the optical field of the laser pulse. The principle and operation were previously described.[12–14] Using CS_2 as the Kerr liquid, and the 8 ps, 1.06 μ laser pulse as the gate activating pulse, the time resolution of the gate is about 10 ps. The chief difference between the operations of the Kerr gate and the streak camera is that the Kerr gate only yields one data point on the $I(t)$ curve at a given time for each laser shot whereas the streak camera produces the full curve $I(t)$ for a single laser shot. The time in a gate experiment is varied by varying the optical path length of the gate activating pulse. The time range studied is generally limited to about one ns which is determined by the length of the translation stage used for varying the path length. In addition, since the light transmission of the gate depends nonlinearly on the intensity of the activating pulse, normalization[14] must be performed. (The normalization is performed by dividing the Kerr signal by the total fluorescence signal and the square of the 1.06 μ gate activating signal.) Despite the disadvantages of the Kerr gate, we have found that results obtained from the Kerr gate and streak camera are in good agreement.

The fluorescent kinetics with lifetimes greater than one nanosecond were also measured by using a combination of a fast photodiode (Hadron 105C, S-20 surface) and fast oscilloscope (Tektronix 519). The biplanar photodiode has a risetime of 0.3 ns, and the 519 oscilloscope has a bandwidth of 1000 MHz. The results obtained from this combination are in good agreement with those obtained from the streak camera.



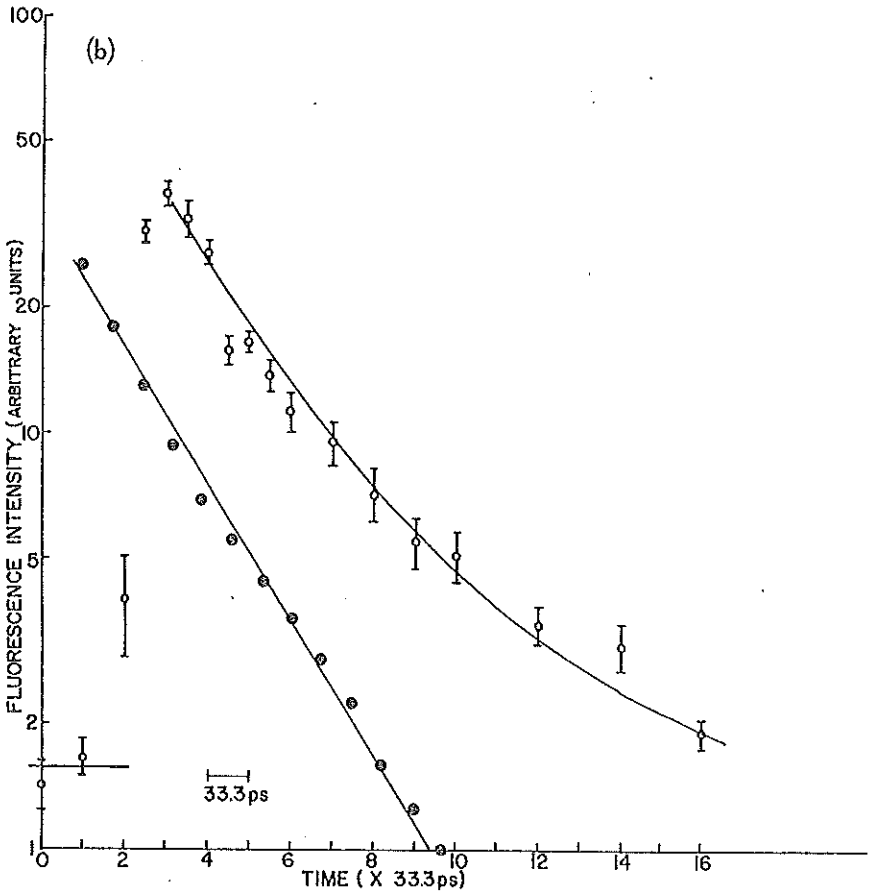


FIG. 2. (a) Fluorescence kinetics of malachite green in glycerol at 28 °C measured by the streak camera. The pulse at left is a calibrating pulse arriving at the camera at an earlier time. (b) Single exponential nature of the fluorescence decay of malachite green in solution, ●, full trace of the decay curve in Fig. 2 (a); solid line has a decay time of ~90 ps. ○, kinetics measured by optical Kerr gate at 26 °C, the solid line is $I = 16 + 320 \exp(-t/100\ \text{ps})$. Both curves are arbitrarily shifted from the zero of the abscissa.

In the experiment the emission from a mode-locked Nd:glass laser was used. A single pulse is selected in the earlier portion of the laser train by a spark gap and Pockels cell. The second harmonic pulse at 0.53 μ was used to excite the fluorescence. The pulsewidth is about 6 ps. The range of the photon flux density at the sample is about 10^{14}–10^{15} photons/cm^2. No difference in the flourescent kinetics was observed when the sample was

excited with a single pulse or a train of 100 pulses separated by 6 ns. In the latter case, the total Kerr signal was electronically integrated.

The fluorescence spectra of the dye solution were measured by a steady state fluorometer which consisted of a light source coupled to a monochromator, a light chopper, a spectrometer with a photomultiplier, and a lockin amplifier. The fluorescence from a thin sample cell was collected at 45° from the front surface.

The chemicals malachite green (99% certified, Eastman Kodak), erythrosin disodium salt (practical, Eastman Kodak), acetone (spectral quality, Fisher), and anhydrous glycerol (J. T. Baker) were used without further purification. The concentration of malachite green was 5×10^{-4} M in a sample length of 5 mm, and the concentration of erythrosin was 2×10^{-4} M in a sample length of 1 mm. The viscosities of glycerol and glycerol–water mixtures at various temperatures were obtained from standard tables.[15] A viscosity range of 1–60 P was covered. The malachite green samples were placed in an optical Dewar. The temperature of the sample was changed by flowing cooled nitrogen gas into the Dewar.

EXPERIMENTAL RESULTS

The fluorescent kinetics of malachite green in gylcerol at room temperature measured by the streak camera and the Kerr gate are shown in Fig. 2. The decay of malachite green fluorescence is characterized by a single exponential. The lifetimes measured at different viscosities are plotted in Fig. 3. The range of viscosity covered in the experiment is from 1 to 60 P. The slope of the log–log plot in Fig. 3 is about 2/3, indicating $\tau\propto\eta^{2/3}$. We also have plotted the absorption recovery times measured by Ippen *et al.*[10] in Fig. 3. It is interesting to note that the absorption recovery times of the *slow* component[10] fall close to the measured fluorescence lifetime and the $\eta^{2/3}$ line, except for the faster recovery times ($\tau<5$ ps) measured by Ippen *et al.*[10] at $\eta<0.1$ P.

The fluorescent kinetics of erythrosin in water measured by the streak camera are shown in Fig. 4. The decay in Fig. 4 is a single exponential with a lifetime of 78 ps. In Fig. 5, the fluorescence lifetimes at room temperature are plotted against the mole fraction of the water in a water–acetone mixture. The fluorescence lifetime of erythrosin in acetone determined to be 2.4 ns, reduces linearly to 75 ± 5 ps as water is added. The measured values of erythrosin fluorescence lifetime are in reasonable agreement with the previously reported values. In water, the reported values are 57 ± 6 ps,[16] 80 ps,[6] 90 ps,[17] and 110 ± 20 ps.[18] In acetone, values at 2.6 ns[17] and 3.5 ns[11] have been reported. We have also measured the relative quantum yield of fluorescence by a steady state fluorometer at 45° from the front surface of the sample cell. The relative fluorescence yield, plotted in Fig. 5, varies linearly as the mole fraction of water.

Dye molecules are known to form nonfluorescing aggregates in water solution or at high concentration. In general, an absorption peak associated with the dye aggregates will appear in the absorption spectra.[19] We have measured the absorption spectra of erythrosin in water solution for dye concentrations of 2×10^{-3} M, 2×10^{-4} M, 2×10^{-5} M, and 2×10^{-6} M. The absorption spectra shows a main peak at 527 nm with a shoulder at about 492 nm. At 2×10^{-6} M the optical density ratio between 492 and 527 nm is about 0.3. As the concentration increases to 2×10^{-3} M, the ratio increases gradually to about 0.4. More importantly, the fluorescence lifetime of the solutions were found to be constant within experimental error for concentrations 2×10^{-5} M to 2×10^{-3} M. Therefore it can be safely assumed that no appreciable aggregation exists in the solution, at a concentration of 2×10^{-4} M. This conclusion is consistent with other reports on dimerization of fluorescein and eosin dyes in solution.[20]

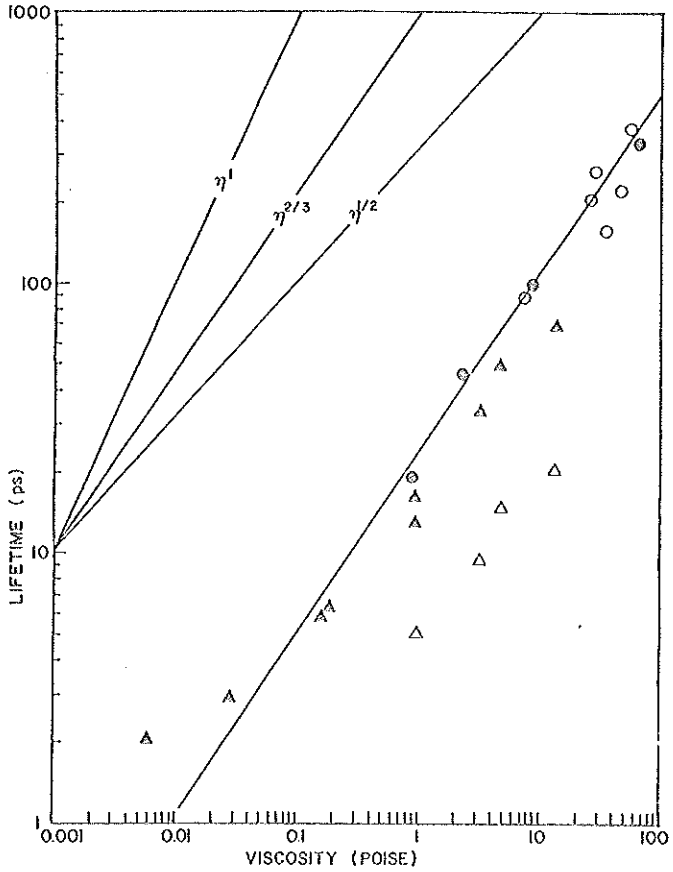
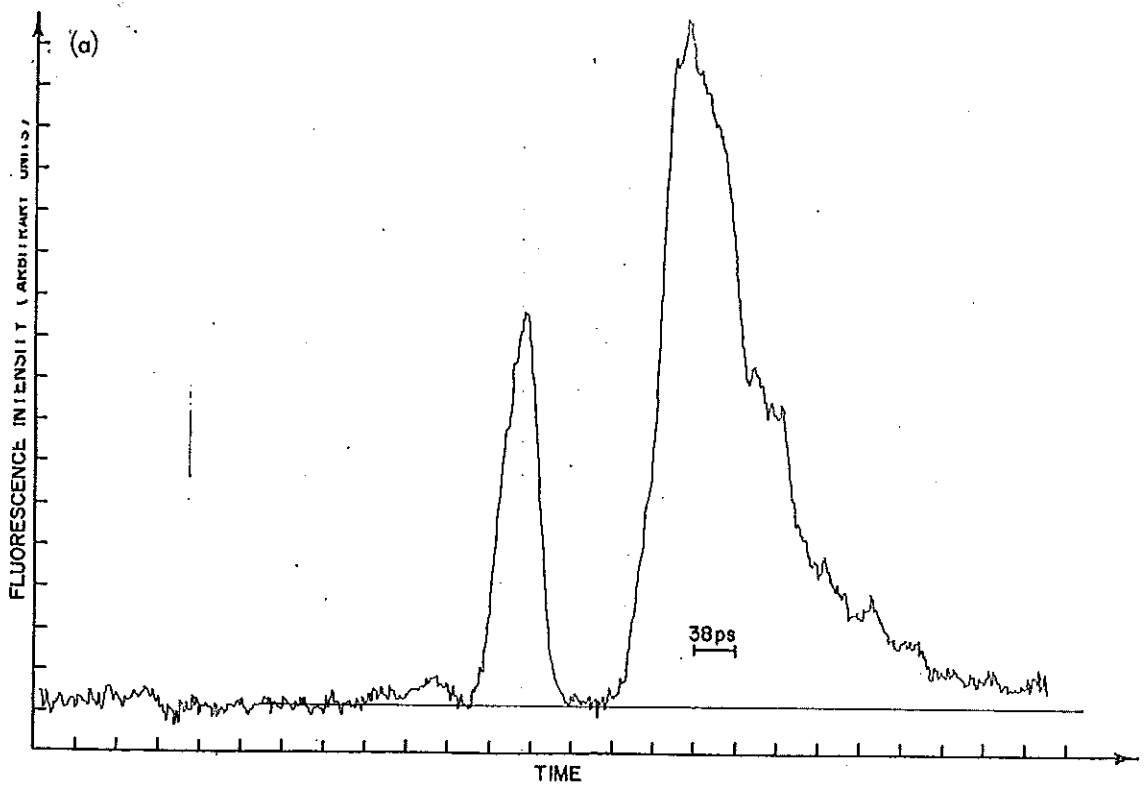


FIG. 3. Fluorescence lifetime as a function of the viscosity of the solution. ○, streak camera result; ⊙, optical Kerr gate result; ▲, slow component of the absorption recovery time of Ippen *et al.*[10]; △, fast component of the absorption recovery times of Ippen *et al.*[10].

CONCLUSION AND DISCUSSION

The temporal profile of fluorescence measures the relative population of the first excited state molecules at a given time. The measured rate of fluorescence decay is the sum of the radiative ($S_1\rightarrow S_0^*+h\upsilon$), nonradiative internal conversion ($S_1\rightarrow S_0^*$), and intersystem crossing ($S_1\rightarrow T_1$) rates. The radiative lifetimes of the dye molecules, which can be estimated from the absorption spectra and the 0–0 transition,[21] do not change much in the



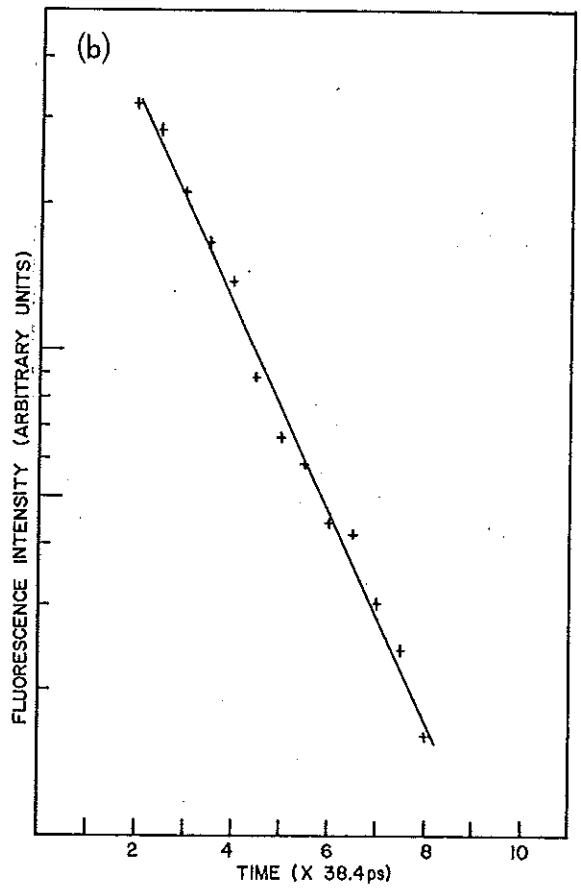


FIG. 4. (a) Fluorescence kinetics of erythrosin in water measured by the streak camera. (b) Single exponential nature of the fluorescence decay of erythrosin in solution. +, full trace of the decay curve in Fig. 4 (a); solid line has a decay time of 78 ps. The curve is arbitrarily shifted from the zero of the abscissa.

various solutions studied. The intersystem crossing efficiency in malachite green is small. This conclusion is borne out from the observation of the *fast* and *complete* absorption recovery in the ground state recovery experiment by Ippen *et al.*[10] A similar conclusion has also been reached in the crystal violet experiment.[9] Therefore the observed variation of fluorescence lifetime in malachite green can be interpreted as the change

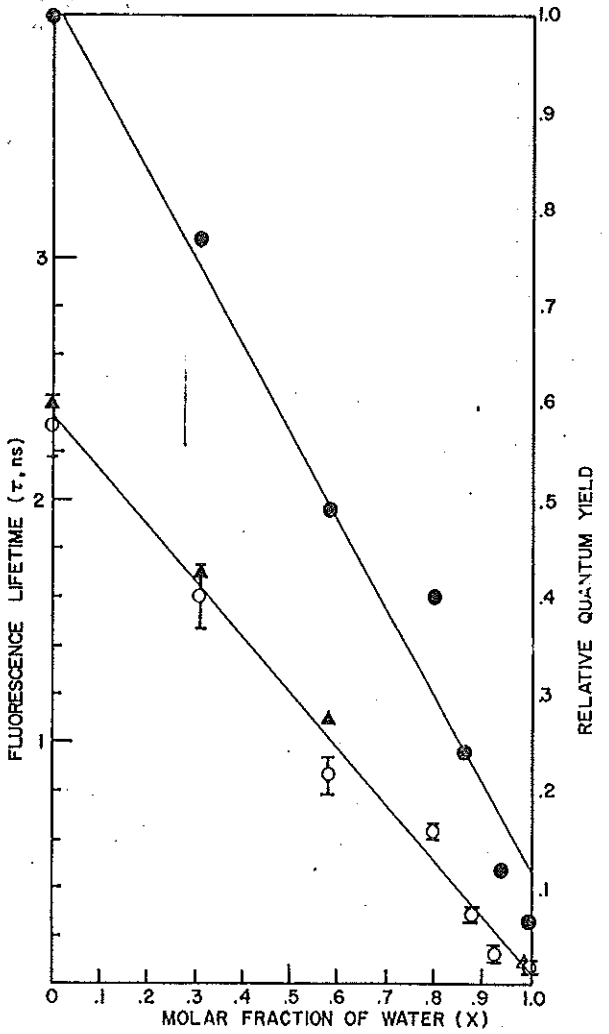


FIG. 5. Fluorescence lifetime (τ) of erythrosin in $2\times10^{-4}M$ solution of water–acetone mixture as a function of molar fraction of water (x) (left ordinate); ○, streak camera result, fast photodiode and oscilloscope result; △ optical Kerr gate result. Relative quantum yield ●(Φ) and a function of x (right ordinate).

of the internal conversion rate in the dye solution.

The measured viscosity dependence of the fluorescence lifetime of malachite green is about $\eta^{2/3}$, which agrees with the measurements of the fluorescence yield by Förster and Hoffmann.[5] They have also theoretically predicted the $\eta^{2/3}$ dependence; but the theoretical time dependence $\exp(-bt^3/\eta^2)$ was not confirmed in this experiment.

In Fig. 3 the values of the *slow* component of the absorption recovery time observed by Ippen *et al.*[10] are close to the measured fluorescence lifetime. At lower viscosity, their data points at (~0.18 P, ~6 ps) are close to the $\eta^{2/3}$ line, though the very low viscosity data points (0.03 P, 3 ps) and 0.006 P, 2.1 ps) are somewhat above the $\eta^{2/3}$ line. In view of the reasonably good agreement between the measured fluorescence lifetime and the slow component of the absorption recovery time,[10] we are tempted to conclude that the observed slow component of the absorption recovery is the kinetics of $S_1 - S_0^*$, contrary to the interpretation[10] that this slow component is the time required for the equilibration of the S_0^* manifold. As for the fast component it is possible that this is the time required for $S_1^* \rightarrow S_0^*$ nonradiative, or S_1^* equilibration. In principle the S_1 equilibration time can be observed from the fluorescence risetime. In our present experiment, however, the risetime is instrument resolution limited to 10 ps. Recently, Shank *et al.*[22] have reported the S_1 equilibration time for large dye molecules, e.g., rhodamine 6G, is less than 0.2 ps, and is *independent* of solvent properties. Presumably the S_0 equilibration time would be on the same order of magnitude. Therefore, the interpretation of the short component remains in doubt.

Returning to the fluorescence lifetime of malachite green, it should be noted that a discrepancy exists between the measured fluorescence lifetime and the lifetime calculated from the quantum yield measurement by Förster and Hoffmann.[5] Using the estimated radiative lifetime of malachite green in glycerol at about $\tau_0 = 3.5$ ns, the fluorescence lifetime calculated by $\tau = \tau_0\Phi$ from the Φ values of Förster and Hoffmann[5] would be about a factor of 4 smaller than the measured values. A similar discrepancy in crystal violet was also noted by Magde and Windsor.[9]

In erythrosin, past research[23,24] studying the effect of halogenation of fluorescein dyes have suggested that the decrease of fluorescence yield from fluorescein to eosin and erythrosin is due not only to an increased intersystem crossing rate but also to an increased internal conversion rate. These results together with some unpublished data which suggested an even weaker triplet yield for erythrosin in water were the basis for Umberger[11] to suggest that the fluorescence quenching of erythrosin in water is mainly the result of an enhanced internal conversion by protonation. Since then Bowers and Porter[25] have directly measured the triplet yield of various xanthane dyes in water: For erythrosin, at pH 9 the triplet yield was determined to be 1.07 ± 0.13, and the fluorescence yield at 0.02. Varying the solvent, the triplet yield varies. In methanol, the triplet yield is reported to be 0.6.[26] Since the fluorescence yield in acetone is about 0.55, the maximum possible triplet yield in acetone is only 0.45. Therefore, we believe the fluorescence quenching in acetone–water mixture of this experiment and in the series of solvents studied by Umberger is the consequence of the variation of the intersystem crossing rate. Consequently, if the observed correlation between fluorescence quenching and solvent proticity is to be meaningful, it strongly suggests that the erythrosin molecules in solvents with higher hydrogen-bond-donor strengths have larger intersystem crossing rates. A heavy atom, such as the iodine atom in erythrosin, provides larger spin–orbital coupling so as to increase the probability of intersystem crossing. Hydrogen bonding with the electronegative atoms in erythrosin, oxygen or even iodine, apparently either perturbs the orbital motion of the π electrons or affects the density of states, thereby producing an even larger singlet to triplet crossing rate.

The fluorescence lifetime and relative yield of erythro-

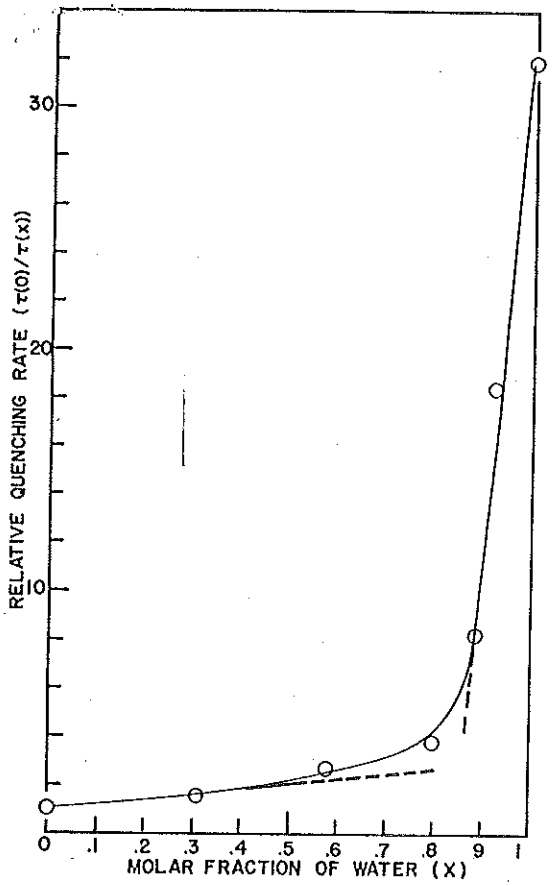


FIG. 6. Relative quenching rate $[\tau(0)/\tau(X)]$ as a function of molar fraction of water (X). The dashed lines represent $\tau(0)/\tau(X) = 1 + kX$, $k = 2$, and $\tau(0)/\tau(X) = \tau(0)/\tau(1)[1 - k'(1 - X)]$, $k' = 210$.

sin were observed to have the same functional dependence on the concentration of water (X) in the solution. This is a natural consequence of the relationship $\tau(X) = \Phi(X)\tau_0$, provided that τ_0, the radiative lifetime, is independent of (X). The dependence on the concentration of water is best understood by expressing the quenching in the form of a relative rate $\tau(0)/\tau(X)$ as a function of X. As shown in Fig. 6, the relative rate $\tau(0)/\tau(X)$ increases as X does; it increases slowly, almost linear in X, for $X < 0.8$, and then rapidly, for $X > 0.8$. In the range of $0 < X < 0.8$, $\tau(0)/\tau(X)$ increases from 1 to 4; and in $0.8 < X < 1$, it increases from 4 to 32. This behavior can be interpreted in terms of the kinetics of solvent quenching. It should first be recognized that water molecules play a duel role here as quencher and solvent. In solvent quenching, molecules located in the nearest neighborhood of the dye molecule quench the fluorescence. In a mixed solvent, the composition of the solvent molecules in the immediate surrounding of the dye molecule depends primarily on the relative affinity of the dye molecule to the components of the mixed solvent, and the composition of the solvent. The relative affinity is likely a function of X, because mutual interactions among the solvent components can influence the interaction between dye and solvent. The quenching, directly related to the composition of the immediate surrounding of the dye molecule, would follow the Stern–Volmer equation.[27] At low concentration of water (small X), the quenching rate is $\tau(0)/\tau(X) = 1 + kX$, where k is a measure of the efficiency of quenching which depends on the relative affinity. The deviation of $\tau(0)/\tau(X)$ from linearity in X for $X < 0.8$ is due to a weak X dependence of k. Similarly, at low concentration of acetone (large X), the quenching rate reduces as the concentration of acetone $(1 - X)$ increases, and $\tau(0)/\tau(X) = \tau(0)/\tau(1)[1 - k'(1 - X)]$; here k' is analogous to k. For the water–acetone mixture, $k' \gg k$, producing a sharp bending feature in the $\tau(0)/\tau(X)$ curve. It implies that acetone is much more efficient in promoting the fluorescence than the water in quenching. Should the affinity to the solvent component be comparable, the quenching rate would increase gradually.

In summary, picosecond fluorescent kinetics were measured with a streak camera and an optical Kerr gate with a 10 ps time resolution. The malachite green fluorescence lifetime is dependent on the solution viscosity as $\eta^{2/3}$. The erythrosin fluorescence lifetime is linearly dependent on the concentration of water in the water–acetone mixture. The quenching of fluorescence in malachite green is attributed to the nonradiative internal conversion process. The quenching of fluorescence in erythrosin in water–acetone mixtures is interpreted in terms of the kinetics of solvent quenching, and is attributed to the change in the intersystem crossing rate. A theory is needed to account for the effect of solvent molecules on the radiationless transitions in dye molecules.

ACKNOWLEDGMENTS

We acknowledge the generosity of the Hamamatsu Company for the use of the Hamamatsu streak camera. This research is in part supported by NSF grants PCM 175-133155-A01 and DMR 73-02392-A01, and CUNY FRAP 11451. RRA is an Alfred P. Sloan Fellow.

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