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Short Communication

Relaxation of erythrosin following picosecond excitation

H. AL-OBAIDI*
Department of Applied Physics, University of Hull, Hull HU6 7RX (Gt. Britain)
G. A. OLDERSHAW
Department of Chemistry, University of Hull, Hull HU6 7RX (Gt. Britain)
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The low quantum yield of fluorescence of erythrosin B (the disodium salt of tetraiodofluorescein) in aqueous or ethanolic solution is believed to be due to efficient intersystem crossing from the excited singlet state to a triplet state, rather than to rapid internal conversion [1, 2]. Several recent investigations of the time-dependence of the fluorescence following excitation with picosecond pulses have been carried out [3 - 6]. These have all employed the ultra-rapid optical shutter of Duguay and Hansen [7] in which short powerful pulses of wavelength 1.06 μm generated by a mode-locked Nd:glass laser induce temporary birefringence in CS_2 placed between crossed polarizers. In each case erythrosin in solution in water, methanol or ethanol was excited using pulses of duration of a few picoseconds and wavelength 530 nm, produced by frequency-doubling the output of the Nd:glass laser, and the fluorescence was observed as a function of time using the optical shutter. The original report [3] that there is a significant delay between excitation and the maximum intensity of fluorescence owing to vibrational relaxation of the excited singlet state, occupying 30 - 40 ps, has not been confirmed by more recent work [4 - 6], which indicates that the time required for vibrational relaxation and solvent re-orientation is less than 1 ps.

The fluorescence lifetime of erythrosin in water has been measured as 90 [3], 57 ± 6 [4], and 110 ± 20 ps [5] and that in methanol as 140 ± 10 ps [3, 4]. We have made measurements in absorption following picosecond excitation of erythrosin which complement the studies of time-resolved light emission. Both excitation and measurement of absorption were carried out using single pulses of wavelength 532 nm generated by frequency-doubling the output of a Nd:YAG laser.

The laser system contained a Nd:YAG oscillator, a single pulse selector (consisting of two Glan-Taylor prisms and a Pockels cell activated by a laser-triggered spark gap), a laser amplifier and a KDP crystal for second-harmonic

*Present address: Atomic Energy Commission, Baghdad (Iraq).

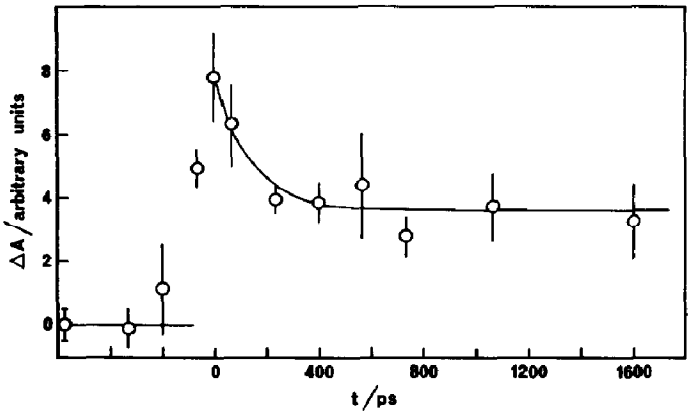

Fig. 1. Relative decrease in absorbance at 532 nm of erythrosin in methanol as a function of time after excitation.

generation. The Nd:YAG oscillator has been described previously [8] and produced a mode-locked train of pulses of wavelength 1.06 μm and duration, measured both by TPF and with a streak camera, 29 ± 8 ps. A single pulse selected from this train was amplified and passed through the KDP crystal to produce the second harmonic. After removal of radiation of the fundamental frequency with filters, a single pulse of wavelength 532 nm resulted. This pulse was then used both to excite the dye molecules and to measure subsequent changes in absorption. It was split into three parts: a main pulse (the bleaching pulse) and two subsidiary pulses (the probe pulse and the monitoring pulse). The bleaching pulse traversed a path whose length could be varied with moveable prisms and then passed through a sample cell 1 mm thick containing the erythrosin solution. The probe pulse, which was used to measure changes in absorption, was attenuated, passed through the sample cell and directed onto a fast planar photodiode connected to an oscilloscope. The time interval between the arrival of the bleaching pulse and of the probe pulse at the sample cell was varied by changing the optical path of the bleaching pulse, and the energy of the bleaching pulse was recorded by directing the monitoring pulse onto the photodiode. Changes in the absorbance of the solution at various short times (—0.4 to 1.6 ns) after the arrival of the bleaching pulse could thus be calculated.

In practice the energy of the single pulses varied by a factor of up to two from shot to shot and this caused substantial variations in the extent of bleaching. For each time delay used several shots were recorded and the absorbance change was obtained as a function of the energy of the bleaching pulse. The absorbance changes for different delay times were then normalized to a standard bleaching pulse energy. Results obtained in this way for 7×10^{-5} *M* erythrosin B in methanol are shown in Fig. 1.

Absorption of the bleaching pulse causes a decrease in the absorbance of the solution, and this decrease is shown as a function of time. Following excitation, the change of absorbance decreases rapidly, with a relaxation time of 140 ± 60 ps, to a value which is constant on the time-scale of the experi-

ment. This is most simply rationalized in terms of excitation from the ground state S_0 to the excited singlet state S_1, followed by fluorescence (rate coefficient k_{FM}) internal conversion to S_0 (k_{GM}) and inter-system crossing to a long-lived triplet state T (k_{TM}). The observed relaxation time of 140 ± 60 ps is then the lifetime of S_1 and is equal to $(k_{FM} + k_{GM} + k_{TM})^{-1}$. This result is in good agreement with the recent measurement of the fluorescence lifetime of 140 ± 10 ps [4].

The "permanent" absorbance change remaining after relaxation is due to the replacement of some of the molecules originally in S_0 by those in T. The ratio of the "final" absorbance change to the initial value is:

$$\frac{\text{final } \Delta A}{\text{initial } \Delta A} = \Phi_{TM} \frac{(\epsilon_{S_0} - \epsilon_T)}{(\epsilon_{S_0} - \epsilon_{S_1})} = 0.5 \pm 0.2$$

where Φ_{TM} is the triplet quantum yield and ϵ_i are the extinction coefficients at 532 nm. Thus if ϵ_{S_1} is zero but ϵ_T is appreciable, 0.5 ± 0.2 represents the minimum value of the triplet quantum yield.

Similar experiments were performed with erythrosin (8×10^{-5} *M*) in aqueous solution at pH 9. As in the case of the methanolic solution, the decrease in absorbance relaxed rapidly to a steady value. Experimental scatter precluded a useful measurement of the lifetime of S_1, but the ratio of the final to the initial absorbance change was 0.65 ± 0.25. This value is consistent with a high quantum yield of triplet formation. Assuming that $\Phi_{FM} = 0.02$ [1], $\Phi_{TM} = 0.98$, and $\epsilon_{S_1} = 0$, $\epsilon_T/\epsilon_{S_0}$ is calculated from the relationship given above as 0.34 ± 0.25 at 532 nm, which can be compared with a measured value of 0.26 ± 0.07 at 526 nm [1].

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