DIRECT MEASUREMENT OF THE VIBRATIONAL DECAY
OF DYE MOLECULES IN THE EXCITED STATE

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Measurements of the risetime of the fluorescence in spontaneous emission yield direct measurements of the vibrational deactivation time of the excited states of dye molecules. This decay time is 40 ± 5 psec for erythrosin in water and 33 ± 5 psec for erythrosin in methanol.

In this paper we report measurements of rapid transient fluorescence from erythrosin molecules in different solvents. Measurements of the rise time of the fluorescence (mean induction time) are exceedingly important because this time is *directly* related to the *vibrational decay* time of the excited electronic state if the measurement of this time is accomplished in *spontaneous* emission. Optical gates [1] have been previously used [2] to determine the onset of stimulated emission where valuable information on the dynamics of laser action is obtained. This onset time is indirectly related to the vibrational lifetime because of the gain factors in stimulated emission.

In our experiment a modelocked Nd: glass laser emits $1.06\,\mu$ pulses of pulsewidth 6 psec as measured by two-photon fluorescence [3]. These pulses generate second harmonic pulses at $0.53\,\mu$ and of 4 psec duration upon passage through a KDP crystal. The experimental arrangement is shown in fig. 1. A dielectric mirror M_1 which reflects at $0.53\,\mu$ and transmits at $1.06\,\mu$ directs the different wavelength pulses along separate delay paths. Samples of erythrosin in different solvents are placed in the $0.53\,\mu$ beam which has been circularly polarized with a quarter waveplate. The $0.53\,\mu$ beam is reduced in size from 1 cm to 0.5 cm on the erythrosin samples. The fluorescence from the erythrosin samples is collected and collimated through the optical gate [1], a system of two crossed polaroids with a cell of carbon disulphide placed in between. The $1.06\,\mu$ beam follows a path which can be adjusted by a variable optical delay and is reduced in size to 1 mm upon passage through the 1 cm long carbon disulphide cell. The fluorescence after passing through the gate is focused into a monochromator so that the time dependence of the fluorescence can be recorded as a function of wavelength.
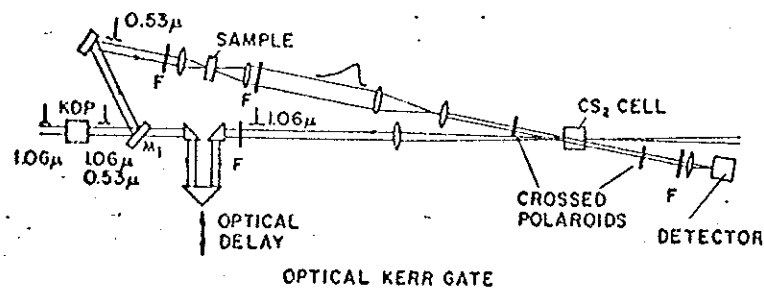

Fig. 1. Experimental arrangement of optical gate detection system.

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The zero point of the optical gate, the point when the two beams coincide in time and space in the carbon disulphide cell, was determined by timing the 0.53μ pulses relative to the 1.06μ pulses with a pure solvent instead of a sample. This prompt curve was 8 psec wide with a peak to noise background of 10^3 with no background above the noise level over the experimental range. The intensity of the 1.06μ and the 0.53μ beams, total fluorescent intensity, and fluorescent intensity signal through the gate at a particular wavelength were detected and displayed on a dual beam oscilloscope simultaneously using appropriate delay cables.

The time response of the fluorescence was also studied with a Hadron 105C S-20 photodetector connected to a Tektronix 519 oscilloscope with a total resolution time of 0.5 nsec. Both the optical gate and 519 scope systems were shown to be operating properly by calibrating the systems with a sample of rhodamine 6G in ethanol where the fluorescence intensity profile was an exponential curve decaying in 5 nsec, a result similar to that of Mack [4] and others.

The high purity erythrosin was the disodium salt $C_{20}H_6I_4O_5Na_2$ which dissolves in water, acetone and the alcohols. Similar results were obtained with erythrosin without sodium, which also dissolved in alcohols. Concentrations of $2 \times 10^{-4}M$ were used in the experiments here described.

The experimental results showing the fluorescence intensity as a function of time for erythrosin in water and methanol are plotted in fig. 2. Experimentally the fluorescence of erythrosin in water detected at 5800 Å reaches a sharp peak 60 psec after excitation, and rapidly decays to the $1/e$ point in 90 psec. From the peak shift of 60 psec and the decay time of 90 psec, the total vibrational decay time is measured to be 40 ± 5 psec. For erythrosin in methanol the fluorescence profile reached a peak 55 psec after excitation and then decays to its $1/e$ point 140 psec later. The vibrational decay time for erythrosin in methanol was estimated from measurements to be 33 ± 5 psec. Results at 5600 Å are similar to those obtained at 5800 Å. The oscilloscope traces with the emission detected with a fast photodiode verify the ultrashort fluorescence decay of erythrosin in water and methanol and confirm a long decay, 2.6 nsec, for erythrosin in acetone.

The reason for the short decay time of erythrosin in water, methanol, and isopropanol is the low quantum efficiency in those solvents. In water the quantum efficiency is 0.02 [5]. The measured decay time is approximately given by $Q\tau_0$ where τ_0 is the radiative fluorescence lifetime (a few nanoseconds) and Q is the quantum efficiency; this time can be quite short, and in the case of erythrosin in water is ≈ 100 psec.

Perhaps the lifetime results are consistent with the mechanism for energy transfer to the vibrational modes of the solvent in the sense that methanol has many more vibrational, librational, and rotational degrees of freedom than water.
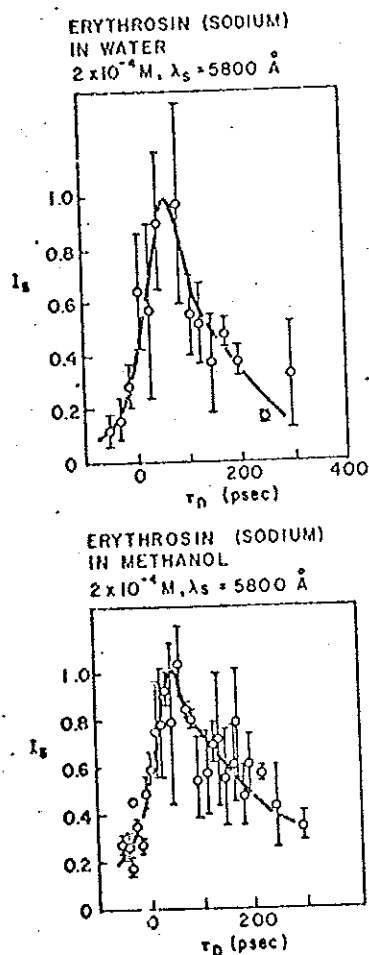

Fig. 2. Fluorescence emission from erythrosin as a function of time delay in water and methanol.

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