

## DIRECT OBSERVATION OF EFFECTS OF VISCOSITY ON THE PICO-SECOND LIFETIMES OF *trans*-STILBENE

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### Summary

Using a frequency-tunable UV picosecond laser source and a synchronously operated streak camera, the solvent viscosity dependence of the fluorescence lifetime of *trans*-stilbene was measured. Over the viscosity range from 1.2 to 230 cP the lifetime increased from 57 to 152 ps. In addition to the short component, a much longer and weaker contribution to the fluorescence time decay was recorded.

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### 1. Introduction

Application of the electro-optical streak camera, together with the mode-locked dye laser [1], has now become a well-established technique in the measurement of the lifetimes of fluorescent species [2, 3]. However, the single-shot streak camera exhibits a dynamic range of about 30 at streak velocities giving a resolution of the order of 1 ps [4]. Also relatively high power densities of the excitation radiation have to be used with very weakly fluorescing samples in order to achieve a useful intensity of the fluorescence signal. Under conditions of high power excitation, the effects of stimulated emission from the sample and other non-linearities lead to a decrease in the recorded fluorescence lifetime [2, 5, 6].

A synchroscan streak camera [7] used in conjunction with a continuous working mode-locked dye laser overcomes these difficulties. Operating at frequencies of 140 - 165 MHz, the system is capable of real-time recording with a demonstrated 3 ps time resolution and a measured dynamic range of  $4 \times 10^3$  [8, 9]. Since the fluorescence streak records are successively and precisely superimposed on one another with a stability of better than 5 ps, image intensification is not necessary; integrated records of the profiles can be obtained photographically or with an optical multichannel analyser.

In order to demonstrate the sensitivity of the instrument, we examined the viscosity dependence of the short lifetime  $\tau_1$  of *trans*-stilbene in various ethanol-glycerol solvent mixtures at constant temperature.

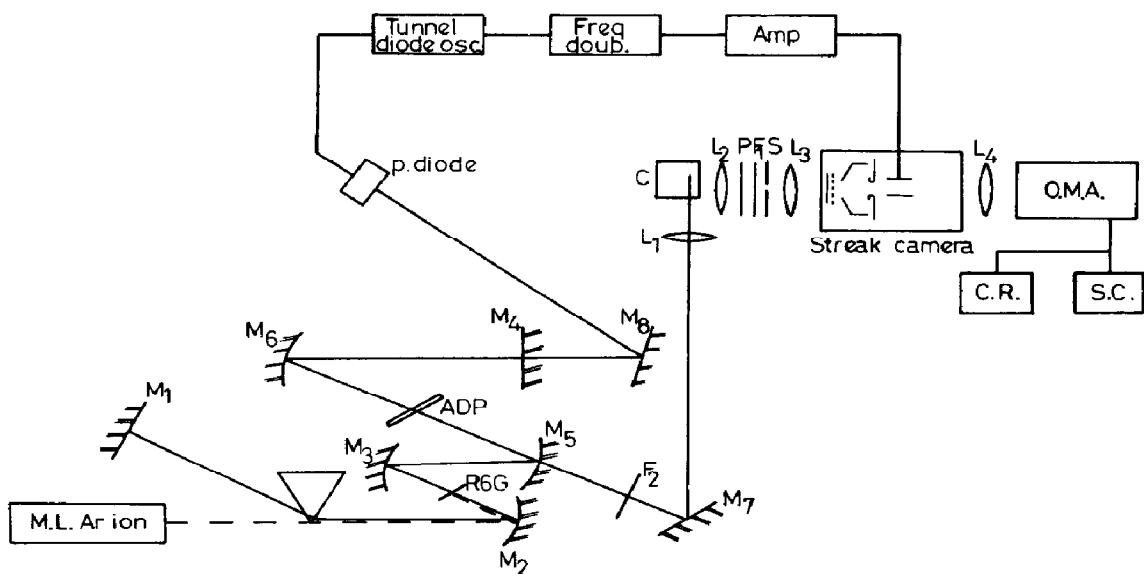


Fig. 1. A schematic diagram of the experimental arrangement.

## 2. Experimental

A schematic diagram of the experimental arrangement is shown in Fig. 1. The picosecond excitation radiation was derived as the second harmonic of a synchronously mode-locked rhodamine 6G dye laser. A Spectra Physics model 164 acousto-optically mode-locked argon ion laser modulated at 69.44 MHz pumped the dye laser (formed by mirrors  $M_1$ ,  $M_2$ ,  $M_3$  and  $M_4$ ). This dye laser, which has been described previously [10], typically produced pulses with an energy content of about 0.6 nJ and of approximately 2 ps duration, and was tunable over the wavelength range 565 - 630 nm. To obtain the second harmonic, a crystal of ammonium dihydrogen phosphate (10 mm  $\times$  10 mm  $\times$  0.75 mm thick) was included in the cavity at the common focus of mirrors  $M_5$  and  $M_6$ . These mirrors of 30 cm radius of curvature were nominally 100% reflecting at 600 nm and totally transmitting at 300 nm. With this unoptimized configuration for intracavity second harmonic generation, typical average powers of about 0.1 mW were obtained in the UV which corresponded to a peak power of approximately 0.35 W for a 2 ps pulse. The radiation which was coupled out of mirror  $M_5$  was passed through a filter  $F_2$  to remove the fundamental frequency component of the laser light, and the transmitted UV light was focused using lens  $L_1$  (focal length  $f = 7.5$  cm) into the quartz sample cell 10 mm square to give an excitation power density of about  $10 \text{ kW cm}^{-2}$ . The line of focus was just inside the output face of the cell, so that any re-absorption of the fluorescence was minimized. A lens  $L_2$  ( $f = 5$  cm) collected the fluorescence at an angle of  $90^\circ$  with respect to the incident radiation and passed it through a polarizer P and a filter  $F_1$  before it was directed on to the slit assembly of

the streak camera. The polarizer P was oriented at an angle of  $54.7^\circ$  to the direction of the incident polarization of the exciting radiation to eliminate the effects of fluorescence depolarization arising from rotational diffusion [11]. The filter  $F_1$  was selected with the maximum of its bandpass at 380 nm. Fluorescence incident on the slit S of the streak camera was focused using the lens system  $L_3$  onto the photocathode in the usual manner [1].

The sinusoidal deflection voltage of the streak camera was derived in synchronism with the laser-produced fluorescence decays by directing approximately 10% of the visible laser output coupled out of mirror  $M_4$  on to a pin photodiode which provided the electrical triggering signal for a tunnel diode oscillator. The output of this oscillator at 140 MHz was amplified to a power of about 20 W and was subsequently applied to the deflection plates of the streak camera. As a result successive images of the detected fluorescence were superimposed with an accuracy of about 2% over the central 1.5 cm region of the streak camera phosphor. An optical multichannel analyser (OMA PAR model 1205D) was optically coupled to the output phosphor of the image tube and the streaked images were recorded and were stored for display on a chart recorder CR or a storage scope SC.

The image tube used was a UV/Photochron II [12] which, when operated with a streak writing speed of  $5 \times 10^9$  cm  $s^{-1}$ , had a resolution limit of better than 5 ps at 380 nm. Time calibration was carried out in the normal manner by replacing mirror  $M_7$  with a calibrated optical delay line [7].

### 3. Results and discussion

The *trans*-stilbene (Koch Light Ltd.), which was purified by zone refining, was made up to a concentration of  $5 \times 10^{-4}$  M in various mixtures of the spectroscopic grade solvents ethanol and glycerol. To ensure adequate mixing of the solvents, the mixtures were placed in a vibration bath for some time before use. Since viscosity is temperature dependent, a temperature controlling Peltier junction was contacted to the sample cell and the temperature was monitored using a copper-constantan thermocouple which was immersed in the solution such that the junction was placed just above the focal point of the focusing lens  $L_1$ . The temperature of the solution was kept constant at  $21^\circ\text{C}$  with an overall accuracy of about  $0.5^\circ\text{C}$  for all measurements. At  $21^\circ\text{C}$  *trans*-stilbene in ethanol has a fluorescence efficiency of approximately 0.03 [13]. The fluorescence decay curves were recorded over a total integration time of about 2 s, which was equivalent to the summation of approximately  $3 \times 10^8$  decay profiles. The viscosity dependence of the *trans*-stilbene fluorescence was examined by varying the viscosity of the solution from about 1.2 cP for a 100% ethanolic solution to about 230 cP for a 10% ethanol-90% glycerol solvent mixture. Figure 2 shows typical fluorescence profiles recorded for 85% ethanol-15% glycerol and 10% ethanol-90% glycerol solvent mixtures. The recorded lifetimes are indicated in the caption to the figure. In Fig. 3 the results obtained over the viscosity region

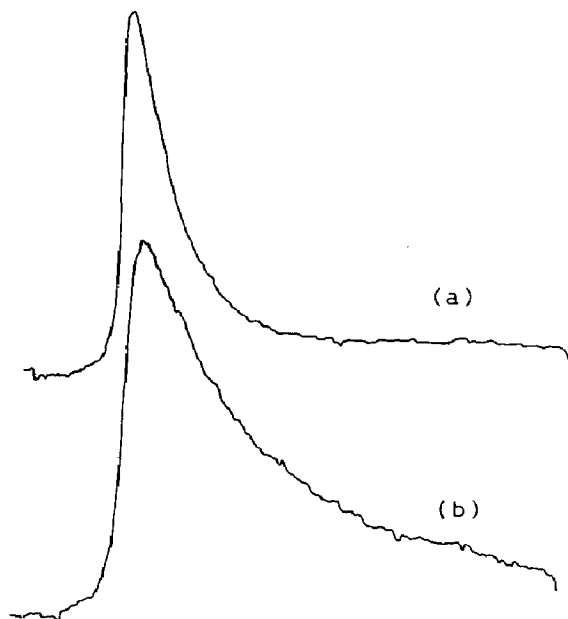


Fig. 2. Typical fluorescence decay profiles recorded for  $5 \times 10^{-4}$  M *trans*-stilbene in (a) 85% ethanol–15% glycerol ( $\tau_1 = 58$  ps) and (b) 10% ethanol–90% glycerol ( $\tau_1 = 152$  ps).

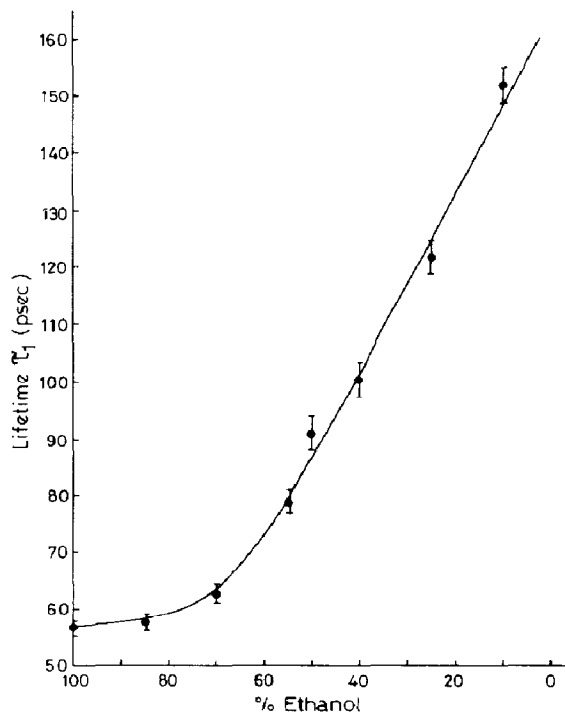


Fig. 3. Variation of the recorded lifetime of  $5 \times 10^{-4}$  M *trans*-stilbene with the percentage of ethanol in the ethanol–glycerol solvent mixture at 21 °C.

examined are summarized; they show an increase in the measured lifetime  $\tau_1$  from 57 ps for a 100% ethanolic solution (1.2 cP) to 152 ps for a 90% glycerol content (230 cP).

The theoretical model of Birch and Birks [14, 15], which describes the excitation and relaxation of *trans*-stilbene, uses the idea that the electronic energy states of stilbene are dependent on the angle of rotation of the phenyl groups about the ethylene bond [16]. The twisting in the first excited state is thought to compete with the fluorescence and with the reversibility of this twisting process; this leads to a computed temporal variation in the fluorescence intensity which is given by

$$I_F(t) = C\{\exp(-t/\tau_2) + m\exp(-t/\tau_1)\}$$

where  $C$  and  $m$  are constants which depend on the rate constants of fluorescence, of intersystem crossing and of radiationless decay to the ground states [14, 16]. The consequence of this is the prediction of two characteristic time constants  $\tau_1$  and  $\tau_2$  associated with the fluorescence decay;  $\tau_1$  is relatively short whilst the  $\tau_2$  component is much longer and weaker [15, 17].

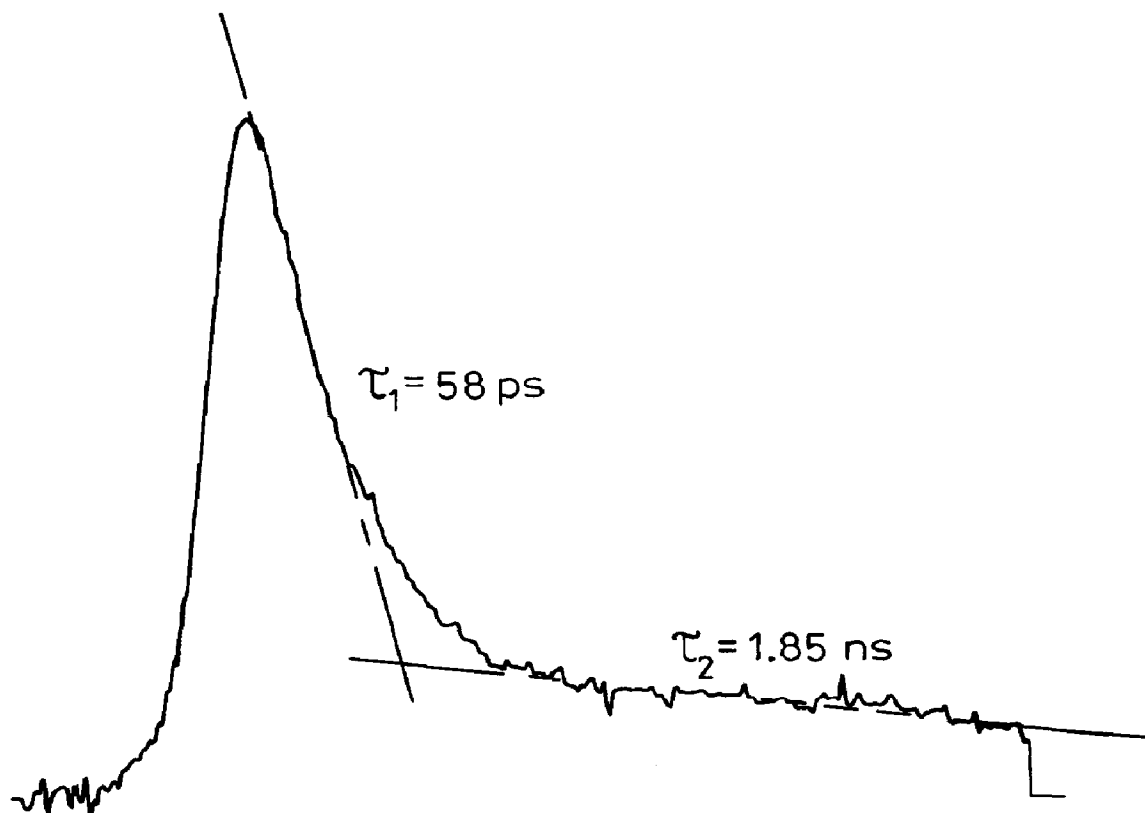


Fig. 4. A semilogarithmic plot of the recorded fluorescence profile shown in Fig. 2(a).

A longer lifetime contribution is not obvious from the linear plots of the fluorescence decay shown in Fig. 2. However, two components of the decay are evident when the results are displayed on a semilogarithmic plot, as shown in Fig. 4. The measured decay times of 58 ps and 1.85 ns are, within experimental error, consistent with the theoretically predicted values [15, 17]. The initial intensity of the longer lifetime component was less than 2% of the intensity of the shorter lifetime component. It would not have been distinguishable from the background noise in a single-shot streak camera record, where the typical dynamic range is approximately 30 for a temporal resolution of about 2 ps [4].

At the high sweep rates used in the synchronously driven streak camera to provide adequate resolution of the shorter  $\tau_1$  component, the actual recording time window was relatively small (approximately 470 ps). As a consequence the accuracy in the determination of the lifetime of the longer-lived component was limited. When the sweep rate is slowed down by decreasing the r.f. power to the streak deflection plates, a greater time window can be obtained. This degrades the time resolution to about 20 ps for a 2 ns sweep duration.

The application of the synchroscan streak camera to the detection and measurement of low intensity and short duration fluorescence profiles has

been clearly demonstrated in these measurements. The greater dynamic range of this instrument is particularly well suited to the measurement of luminous events where two or more components of the decay may be present with widely varying intensities. In *trans*-stilbene the appearance of a longer lifetime component in the fluorescence may indicate a return to the *trans* geometry from the twisted configuration. More detailed results on the variation of  $\tau_1$  and  $\tau_2$  with temperature in an isohexane–methylcyclohexane solution will be submitted for publication at a later date.

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