Time resolved fluorescence of trans-Stilbene in the picosecond regime

J. R. Taylor, M. C. Adams, and W. Sibbett
Optics Section, Blackett Laboratory, Imperial College, Prince Consort Road, London SW7 2BZ U.K.

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The Synchroscan streak camera system has been used to examine the temperature dependence of the fluorescence decay of trans-Stilbene between -10 and 30°C. Two components of the fluorescence have been detected; a short one varying between 125 and 64 psec over the range and a much weaker longer one varying from 690 to 1450 psec. The presence of the longer component may indicate a return to the trans geometry following initial photoisomerization.

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Several experimental investigations into the time resolved fluorescence profile of trans-Stilbene (trans- 1,2 Diphenylethylene) have been carried out to give an insight into the fundamental reaction kinetics leading to an explanation of the trans-cis photoisomerization process. In order to account for deviations from a single exponential decay of the temporal fluorescence intensity, following optical excitation of trans-Stilbene, Birch and Birks introduced a model to explain the overall relaxation process based on the idea that the energy of the electronic states of Stilbene depended on the angle of rotation of the phenyl group about the ethylene bond. This twisting in the first excited state of trans-Stilbene was postulated to compete with the fluorescence. The equations governing the reactions are

\[ \begin{align*}
I_{t} + h\nu &\rightarrow I_{t}^{*}, \\
I_{t}^{*} &\rightarrow I_{t} + h\nu, \\
I_{t}^{*} &\rightarrow I_{c}^{*}, \\
I_{c}^{*} &\rightarrow \alpha I_{t} + (1 - \alpha)I_{c}, \\
I_{p}^{*} &\rightarrow \alpha I_{t} + (1 - \alpha)I_{c},
\end{align*} \]

where \( t, c, \) and \( p \) represent the trans-, cis-, and twisted configurations, respectively, of Stilbene, \( K_{f} \) and \( K_{c} \), the rate constants for deexcitation of the excited (*) trans-Stilbene-singlet (1) state by fluorescence and intersystem crossing, and \( K_{d} \), the radiationless decay constant of the twisted excited state to the ground state in the cis or trans form. The reversibility of the twisting process, governed by the \( K_{p} \) and \( K_{p}' \) rate constants for the thermally activated \( t^{*} \rightarrow p^{*} \) and \( p^{*} \rightarrow t^{*} \) internal conversion, led to a computed temporal variation in the fluorescence intensity \( I_{f}(t) \) given by

\[ I_{f}(t) = C K_{f} [\exp(-t/\tau_{1}) + m \exp(-t/\tau_{2})], \]

where \( C \) and \( m \) are constants depending on the rate constants already defined and the characteristic decay time constants \( \tau_{1} \) and \( \tau_{2} \). This form postulates the existence of a very short lifetime governed by time constant \( \tau_{1} \) together with a much longer lifetime component associated with \( \tau_{2} \).

Conventional pulsed streak cameras have a rather limited dynamic range at the highest sweep rates needed for picosecond resolution. This hinders their ability to resolve two decay components, particularly if the ratio of their intensities approaches the limit of the dynamic range of the instrument, which is typically \( \sim 30 \) for 2-psec resolution.

The Synchroscan streak camera system is capable of real time recording of luminous events at a rate of \( \sim 140 \text{ MHz} \) with a resolution limit of \( < 5 \text{ psec} \) and a stability better than 5 psec. The precise nature of the superposition of the fluorescence records and the low values of the instantaneous photoelectron currents give rise to a recorded dynamic range of \( 4 \times 10^{3} \). Consequently this camera is ideally suited to the measurement of low-intensity picosecond fluorescence profiles and any associated small variations in these. In this letter we report on the time resolved variation with temperature of trans-Stilbene fluorescence in the temperature range \(-10-30^\circ\text{C}\).
TABLE I. Variation of recorded dual fluorescence decay times with temperature.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$\tau_1$ psec</th>
<th>$\tau_2$ psec</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.5</td>
<td>64</td>
<td>1450</td>
</tr>
<tr>
<td>24</td>
<td>70</td>
<td>1300</td>
</tr>
<tr>
<td>22.5</td>
<td>75</td>
<td>1285</td>
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<td>19.5</td>
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<td>1265</td>
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<td>14</td>
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<td>1140</td>
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<td>88</td>
<td>1035</td>
</tr>
<tr>
<td>7.5</td>
<td>90</td>
<td>850</td>
</tr>
<tr>
<td>4</td>
<td>99</td>
<td>795</td>
</tr>
<tr>
<td>0</td>
<td>103</td>
<td>725</td>
</tr>
<tr>
<td>-2.5</td>
<td>107</td>
<td>700</td>
</tr>
<tr>
<td>-5.5</td>
<td>117</td>
<td>690</td>
</tr>
<tr>
<td>-8.5</td>
<td>125</td>
<td></td>
</tr>
</tbody>
</table>

corresponding to a peak power of $\sim0.35$ W for a 2-psec pulse. The $uv$ radiation was coupled out through mirror $M_5$, and a filter $F_2$ was used to eliminate any transmitted visible radiation. After a reflection off mirror $M_7$ (100% at 300 nm), the $uv$ was focused using lens $L_1$ ($f = 7.5$ cm) into the 10-mm square quartz sample cell $C$. Typically the peak focused power density was $\sim 10$ KW cm$^{-2}$ and the line of focus was directed just inside the output face of the sample cell to minimize any reabsorption of the resulting fluorescence. The fluorescence was detected at 90° with respect to the incident beam. A lens $L_2$ ($f = 5$ cm) collected the radiation and passed it through a polarizer $P$, set at 54.7° to the incident polarization to eliminate the effects of fluorescence depolarization, and a filter $F_1$, with its bandpass maximum at the peak of the trans-Stilbene fluorescence. The radiation incident on the slit $S$ of the streak camera was focused onto the streak camera photocathode using lens $L_3$.

Synchronizing the luminous event to the continuous sinusoidal deflection voltage of the streak camera was achieved by directing $\sim 10\%$ of the visible laser output from mirror $M_4$ (R $\sim 95\%$) off mirror $M_6$ onto a pin photodiode. The resulting electrical signal was then used to trigger a tunnel diode oscillator, the output of which was frequency doubled to $\sim 140$ MHz amplified to a power of $\sim 20$ W, and then applied to the deflection plates of the streak camera. This allowed successively streaked images to be accurately superimposed on the image tube phosphor. A measured linearity of the streak of better than 2% was recorded over the 1.5-cm central region of the phosphor. An optical multichannel analyzer (OMA PAR model 1205D) was optically coupled to the phosphor using an $F/1.5$, 8 cm focal length lens, and the images were recorded and stored for subsequent display on a chart recorder CR, or storage scope SC.

The image tube used was a Photochron II type with a $uv$ transmitting input window. When operated at its maximum writing speed, the tube has a resolution limit of better than 5 psec at 380 nm. Time calibration was carried out in the usual manner by replacing mirror $M_7$ by a calibrated optical delay line.

To correlate with previously published results, a $5 \times 10^{-3}$ M solution of trans-Stilbene (Koch Light Ltd. and purified by zone refining) was used in a 3:2 mixture of methycyclohexane: isohexane. A Peltier junction was contacted to the sample cell $C$. The temperature of the solution was monitored using a copper constant thermocouple, the junction of which was immersed in the solution just above the focal point of lens $L_1$. An accuracy in setting and measuring the temperature of 0.5°C was achieved over the range $-10$–$30$°C.

The fluorescence decay curves were recorded over a total integration time of $\sim 2$ sec which represents a summation of $\sim 3 \times 10^8$ fluorescence decay profiles. Figures 2(a) and 2(b) shows typical decay curves recorded for the $5 \times 10^{-3}$ M solution of trans-Stilbene at 14 and 0°C each with a characteristic decay time $\tau_1$ of 84 and 103 psec, respectively. From Table I it can be seen that the measured time decay $\tau_1$ varied continuously from 64 psec at 29.5°C to 125 psec at $-8.5$°C, which is in good agreement with the values calculated from quantum efficiency measurements. Assuming the activated decay process of the fluorescent state takes a form given by the Arrhenius equation $1/\tau(T) - 1/\tau(77 K) = A \exp (-E_p/RT)$, where $\tau(77 K)$ is the fluorescence lifetime at

![FIG. 2. Typical picosecond time resolved fluorescence decays of a $5 \times 10^{-3}$ M solution of trans-Stilbene at (a) 14°C and (b) 0°C, with the corresponding semi-logarithmic plots (c) and (d), respectively.](image-url)

![FIG. 3. Graph of $\ln[1/\tau(T) - 1/\tau(77 K)]$ against $1/T$ (K), see text for notation.](image-url)
77 K, which is 1650 psec, and \( E_{\nu} \) is the activation energy for the process, then a graph of \( \ln \left( \frac{1}{\tau(T)} \right) - \ln \left( \frac{1}{\tau(77 \text{ K})} \right) \) versus \( 1/T \) should give a straight line dependence of gradient \( -E_{\nu}/R \) (see Fig. 3). From Fig. 3, this gives values of 2.9 \( \pm \) 0.3 Kcal mol\(^{-1}\) for the activation energy and 1.9 \( \times \) 10\(^{12}\) sec\(^{-1}\) for the frequency factor \( A \), which are in good agreement with those of Heisel \textit{et al.}^4

From Eq. 1, the theoretical model predicts that a second much longer time decay constant \( \tau_2 \) should be present. From the fluorescence decay profiles on a linear scale, the presence of this second decay is not obvious. However, when plotted on a semi-logarithmic scale [see Figs. 2(c) and 2(d) for recordings at 14 and 0 C, respectively], a second much longer decay was clearly present. In Table I, where the temperature variation is listed, it can be seen that as the temperature decreased from 29.5 to \(-5.5\) C, the associated measured values of \( \tau_2 \) decreased. At \(-8.5\) C, some system noise together with the temporal window of the scan used prevented an accurate measurement of the decay time. This trend with temperature for the longer decay constant is as predicted,\(^5^,9\) although the measured lifetimes are smaller than expected.\(^6\) The accuracy in the measurement of these longer decays was restricted by the limited extent of the useful region of the scan, associated with the OMA detector head size. This was governed by the fact that the camera was operated near its maximum writing speed in order to adequately resolve the time decay of the shorter component. Also, the intensity of the longer component has an initial intensity which was 2\% that of the fast decay. Consequently, the lifetime of the longer component could only be measured to an accuracy of \( \pm 10\% \) at best. For more detail of this longer fluorescence decay, the duration of the scan could have been increased at the expense of some temporal resolution, and the number of integrations could also have been increased.

The suitability of the repetitively operating streak camera has been clearly demonstrated in these dual fluorescence measurements. The high sensitivity and large dynamic range allow information to be obtained on a picosecond time scale that would otherwise be lost in the noise of streaks of similar fluorescence profiles recorded by standard single-shot streak cameras. These initial measurements and the detection of a long lifetime component in the trans-Stilbene fluorescence give some further confirmation of the model used to describe the photoisomerization mechanism of trans-Stilbene and the reversibility of the \( 1_{\nu} \) to \( 1_{\nu}^* \) process. It is planned that a more detailed study of this and similar reactions will be carried out using the Synchroscan streak camera system.

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