Introduction

The addition of malachite green to the saturable absorber DQOCI has been reported (1) to increase the stability of operation of a mode-locked CW dye laser.  It has been suggested (2) that this result could be due to the renonuance transfer of excited electronic state energy (3) between DQOCI and malachite green.  DQOCI, which gives subpicosecond pulses when used by itself to mode-lock the CW rhodamine 6G dye laser (4), also produces an improvement in performance when added to the DODCI solution.  The extension (5) of the "Synchroscan" streak-camera (6) for use with pulses from CW mode-locked lasers, greatly facilitates the carrying out of electronic excitation energy transfer measurements.  Using low peak power (<300W) picosecond laser pulses for excitation, nonlinear effects in the experimental solutions are avoided while precisely superimposed successive fluorescence streak-records on the image-tube phosphor permit integration of <1000 pulses (<0.5x) with a vidicon optical multi-channel analyser (OMA) (7).  This direct linear detection in real time of complex fluorescence decay curves, obtainable with single-shot streak cameras (4) and, effectively, photon-counting with digitization and storage can be combined in my convenient system.  With the low values of instantaneous photo-electron currents involved no further image intensification is needed to avoid photomultiode saturation or image-tube space charge effects (8).  We report detailed measurements, of the effects on the lifetime of DQOCI dissolved in 0.01 mol viscosity solvent ethanol, when DQOCI or malachite green is added to the solution.

Experimental Arrangement

The arrangement used is shown in Figure 1.  The synchronously pumped (5) CW rhodamine 6G laser was tunable from 565 to 538 nm, and produced ~2ps pulses (<0.6x) at a repetition rate of 140MHz.  The train of excitation pulses was focused into the sample cell to give peak power densities of ~1W cm\(^{-2}\).  A polarizer, P, compensated for any fluorescence depolarization (10).  Successive identical streak records were superimposed on the image tube phosphor at the 140 MHz repetition rate while maintaining an integrated time-resolution of 4ns to 3ps.  The variation from linearity of the streak was measured to be better than 3%.  A dynamic range of 4 x 125 was demonstrated for the OMA system used to record and store the streaked images, before display on a VDU or printing on a chart recorder.  At its normal streaking speed in repetitive mode the S2U Photochron II image tube has a resolution of ~5aps for 12th at 200x.  To record the complete fluorescence decay curves of the samples the tube was operated at a writing speed of 5 x 10^6 cm sec\(^{-1}\) giving a resolution limit of ~2aps.

639
Various concentrations of the additive were used (see Table 1) for a constant DDOCT concentration of 10^{-6} M. The excitation laser wavelength was tuned to 570 nm, and the centre of the observed fluorescence bandwidth (1.5 nm) was set to 615 nm. The average fluorescence lifetime of a 10^{-6} M ethanolic solution of DDOCT at room temperature, taken from several traces similar to Figure 2(A), gave a value of 1150 ± 40 ps, in good agreement with values previously reported (11). Increasing the malachite green concentration led to significant decreases in the measured lifetime. The departure from exponential decay became more dominant as the malachite green concentration approached and became greater than that of the DDOCT. A similar behaviour was also observed when DDOCT was added. For concentrations of 10^{-6} M DDOCT and above, a contribution due to DDOCT fluorescence became evident with a lifetime of 15 ps. DDOCT lifetimes were determined after allowing for the effects of the short lifetime DDOCT fluorescence on the recorded traces.

**Table 1**

<table>
<thead>
<tr>
<th>Acceptor Concentration</th>
<th>Malachite Green</th>
<th>DDOCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x 10^{-5} M</td>
<td>1140</td>
<td>515</td>
</tr>
<tr>
<td>5 x 10^{-5} M</td>
<td>1950</td>
<td>450</td>
</tr>
<tr>
<td>1 x 10^{-4} M</td>
<td>223</td>
<td>240</td>
</tr>
<tr>
<td>2.5 x 10^{-4} M</td>
<td>52</td>
<td>51</td>
</tr>
<tr>
<td>5 x 10^{-4} M</td>
<td>71</td>
<td>69</td>
</tr>
<tr>
<td>7.5 x 10^{-4} M</td>
<td>81</td>
<td>72</td>
</tr>
<tr>
<td>1 x 10^{-3} M</td>
<td>75</td>
<td>82</td>
</tr>
<tr>
<td>2.5 x 10^{-3} M</td>
<td>510</td>
<td>-</td>
</tr>
<tr>
<td>5 x 10^{-3} M</td>
<td>530</td>
<td>-</td>
</tr>
<tr>
<td>7.5 x 10^{-3} M</td>
<td>260</td>
<td>-</td>
</tr>
</tbody>
</table>

**Discussion**

For resonance energy transfer under conditions for which Forster kinetics apply, the rate of energy transfer from excited donor to acceptor molecule is given by

\[ R_{60} \text{ (exc)} / R_{60} \text{ (free)} \] (1)

where \( R_{60} \) is the fluorescence lifetime of donor in the absence of excitation energy transfer, \( R_{60} \text{ (exc)} \) is the intermolecular distance and \( R_{60} \text{ (free)} \) is the critical transfer distance (3). The time evolution of the fluorescence intensity, \( I_F(t) \), is modified to a non-exponential decay of the form

\[ I_F(t) = I_0 (1 - e^{-k t}) \] (2)

A graph of \( I_F(t) / I_0 \) against \( t \) should give a straight line dependence of \( 1 / I_0 \) on \( t \) (2, 3, 9). This linear dependence can be seen from Figure 3 which relates to a 5 x 10^{-5} M malachite green in 10^{-6} M DDOCT. Similar graphs were plotted for the other concentrations. Assuming that Forster kinetics were valid over the complete range of acceptor concentrations used, the critical transfer distance \( R_{60} \) was calculated from the linear plots above. Table 1 shows that the change in \( R_{60} \), with concentration in much solute at the higher concentrations and tends to level out. Computer plots of the
Fig. 1 Schematic of experimental arrangement.

Fig. 2 Fluorescence decay curves of $10^{-4}$M DODCI in ethanol with (a) 0, (b) $10^{-5}$M, (c) $10^{-4}$M, (d) $1.25 \times 10^{-3}$M malachite green added. The time scan for each trace was kept constant.

Fig. 3 Log($I_t(t)/I_0(t)$) as a function of $1/t$, $5 \times 10^{-4}$M malachite green.
function (2) for 1.0, (a) were drawn and fitted against the experimental data. For a 2.5 x 10−4 M solution of malachite green the computed form of 1.0, (a) fits the experimentally recorded fluorescence trace very well. However, at low concentrations of the acceptor, deviations from the theoretical Forster equation become apparent, showing that the correction term introduced by the Forster theory is not valid in this region. A similar effect was also found for DODCI as the acceptor. Taking the values of R0, obtainable for the five highest concentrations used for both acceptors gives average R0 values of 45.4 Å for malachite green and 61.8 Å for DODCI, respectively.

The ability of the synchronous pico-second streak-camera to resolve small changes in fluorescence lifetimes of dye under low power excitation greatly facilitates accurate direct measurements of resonance energy transfer from donors with nanosecond and sub-nanosecond fluorescence lifetimes, since the excited-state decay kinetics can be studied with a time resolution of 40 ps. Further studies with the synchronous system, of excitation transfer on a pico-second time scale are planned, in particular between DODCI and its photosensitizer (3).

References
3. Th. Fortster, Dissusions Faraday Soc. 27 (1959) 7
9. J.P. Ryan, L.S. Goldberg and D.J. Bradley: Optics Commun. 27 (1978) 127