Sub-picosecond Pump-probe Spectroscopy of ESIPT in 3-Hydroxyflavone

Stuart M. Ormson,[a] Denis LeGourrierec,[a] Robert G. Brown*[a] and Paolo Foggi[b]

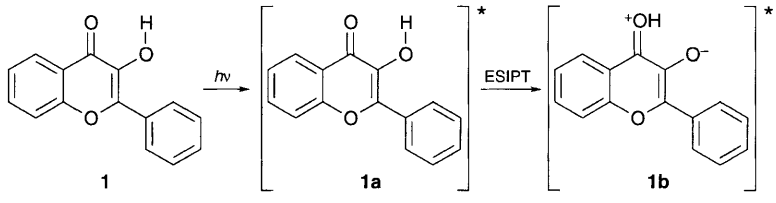
[a] *Chemistry Department, University of Central Lancashire, Preston, Lancashire, UK PR1 2HE*
[b] *LENS, Largo E. Fermi 2, 50125, Florence, Italy*

Sub-picosecond pump-probe spectroscopy of 3-hydroxyflavone in a range of solvents reveals the presence of two transient species which are assigned to the initial Franck–Condon excited state and the proton-transferred tautomer.

The considerable interest in excited-state intramolecular proton transfer (ESIPT) in the last 10–15 years[1,2] has to some extent been stymied by the speed of the ESIPT process itself. Attempts to measure the ESIPT rate constant in a wide range of compounds by time-resolved fluorescence spectroscopy have in the vast majority of cases only succeeded in placing a lower limit (of the order of 10^{11} s^{-1}) on this rate constant. Of course, such measurements are only possible when the system is fluorescent.

The apparent rate of the ESIPT process clearly requires the use of femtosecond excitation coupled to transient absorption and/or emission measurements and a series of such experiments have been carried out by Elsaesser and coworkers on systems such as 2-(2′-hydroxyphenyl)benzothiazole[3] and by Schwartz *et al.* on the well-studied 3-hydroxyflavone (**1**) system.[4] The latter recorded transient absorption kinetics for **1** in methylcyclohexane and methanol at 540 and 620 nm following excitation at 295 and 310 nm. The profiles all exhibited biexponential rise kinetics with risetimes of 80–210 fs and approximately 10 ps. The former was attributed to the ESIPT process (Scheme 1) and the latter to solvated molecules of **1** which have to break an intramolecular hydrogen bond before they can undergo ESIPT.

We have performed the first sub-picosecond pump-probe measurements of this system where transient absorption spectra are measured as a function of the delay time between the pump (200 fs FWHM at 295 nm) and the probe (white light 350–650 nm) pulses. The experimental set-up used for these measurements is described in ref. 5. The transient absorption spectrum of **1** in cyclohexane 500 fs after the excitation pulse exhibits two absorption bands between 410 and 500 nm and between 550 and 600 nm (Fig. 1). The latter is contaminated by the laser fundamental (590 nm) but there is a clear absorption feature present in this wavelength range. At longer delay times up to 10 ps the absorbance of this transient band increases—as does the absorbance of the band at lower wavelength. However, the spectral distribution of this latter band evolves with time with the absorption maximum moving from approximately 430 nm at the earliest delay times to approximately 460 nm at 10 ps or later. The spectrum of this band then remains approximately constant and simply decays with time (Fig. 2) with a lifetime of the order of 5.0 ns. This closely matches the fluorescence lifetime of the proton-transferred tautomer of 3-hydroxyflavone (species **1b**) in cyclohexane.[6] The shape of the band in the 550–600 nm region also changes with time but these changes are less noticeable. At longer delay times, the spectra are also



Scheme 1

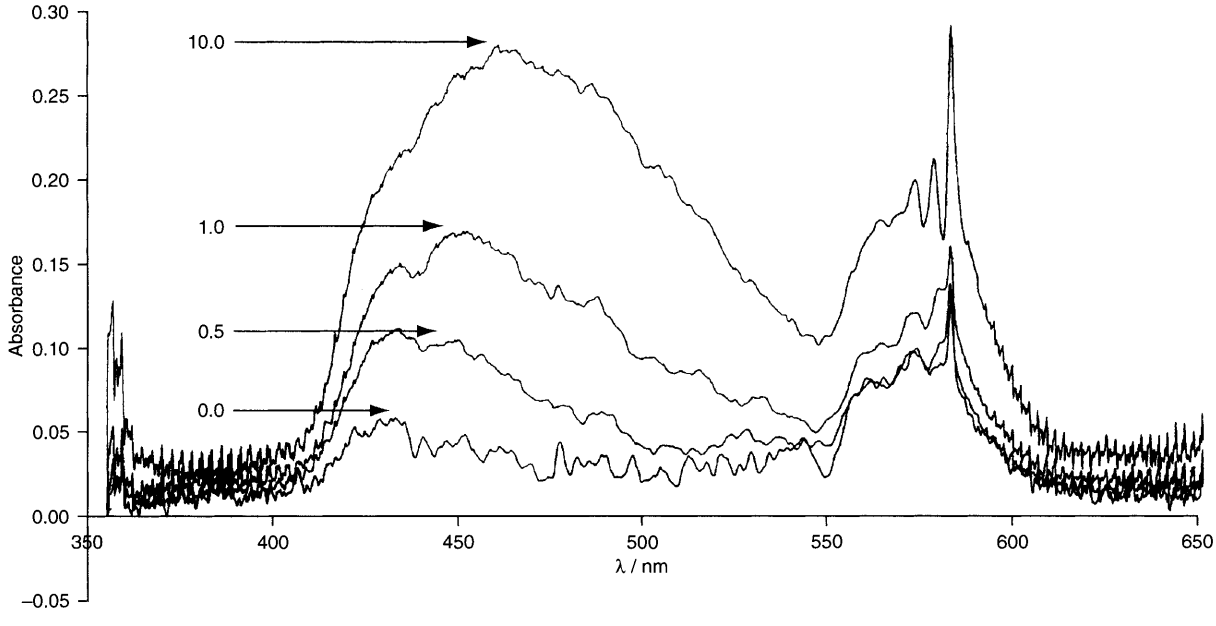


Fig. 1 Transient absorption spectra of 3-hydroxyflavone (5.9×10^{-4} mol dm^{-3} in cyclohexane) at delays of 0, 0.5, 1.0 and 10.0 ps between the pump and probe pulses

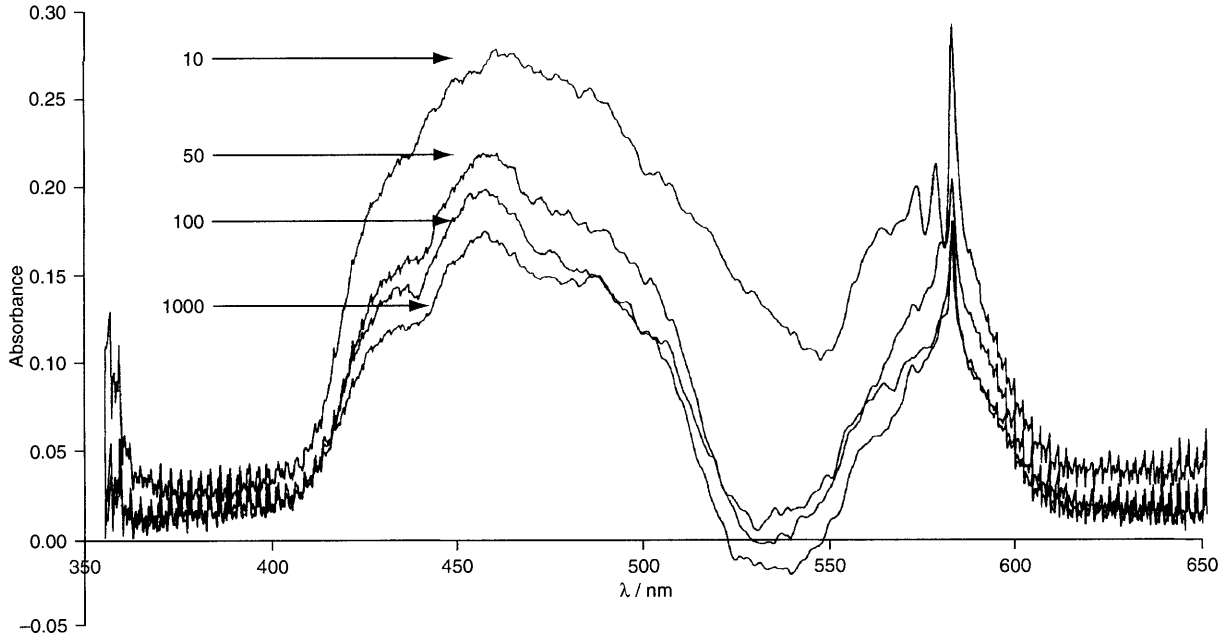
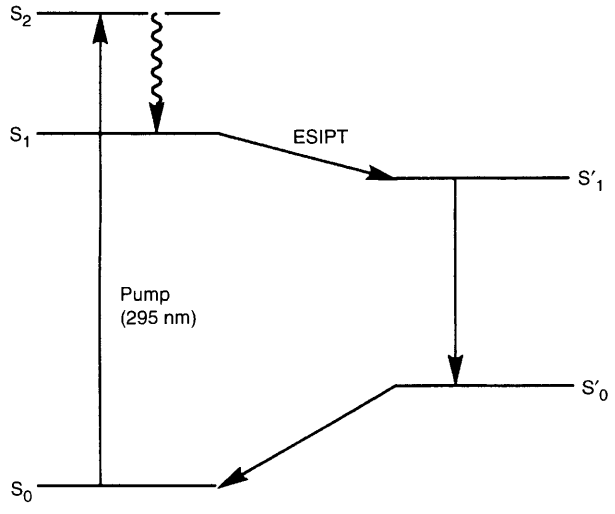


Fig. 2 Transient absorption spectra of 3-hydroxyflavone (5.9×10^{-4} mol dm^{-3} in cyclohexane) at delays of 10, 50, 100 and 1000 ps between the pump and probe pulses



Scheme 2

distorted by stimulated emission from **1b** (which peaks at 525 nm.)[6] Such emission was also observed by Schwartz *et al.* in their measurements.[4] The behaviour of **1** in the solvents methanol and acetonitrile (data not shown) is very similar to that observed in cyclohexane.

Our interpretation of these spectral changes starts with the assumption that the spectra observed at delay times of 10 ps or later correspond to $S'_1 \rightarrow S'_n$ transitions of **1b** (Scheme 2). The consistent spectral distribution (neglecting the effects of emission) and the decay time of the transient absorption all support this and the spectral maximum agrees with previous (longer timescale) measurements.[7] The evolution of the transient spectra in the first 10 ps suggest a precursor to **1b** absorbing maximally at 430 nm and *ca.* 570 nm which converts to **1b** over the 10 ps timescale. The obvious assignment for this species is the S_1 state of **1a** which undergoes ESIPT to yield S'_1 (Scheme 2). We have no evidence for a species intermediate between **1a** and **1b** as proposed by Rullière and Declémy.[7]

This interpretation is at odds with the conclusions drawn by Schwartz *et al.* who postulate ultrafast (100–200 fs) and somewhat slower (10 ps) ESIPT steps. We certainly observe strong initial absorption in the region of 550–600 nm but this is not matched by the expected absorption at lower wavelengths (Fig. 2) which both we and Rullière and Declémy[7] suggest as being characteristic of **1b**. The transient kinetics measured by Schwartz *et al.* at 540 and 620 nm would only observe the higher wavelength band(s) shown in Figs. 1 and 2. On the basis of our data, these two wavelengths will detect both **1a** and **1b** and the 100–200 fs risetime in their work may therefore reflect the formation of **1a**. This is not unreasonable given that excitation wavelengths in the region of 300 nm (used both here and by Schwartz *et al.*)[4] excite the S_2 (or higher) state of **1** which will need to decay to the S_1 state (**1a**) prior to ESIPT.

We thank the University of Central Lancashire for support and for research studentships (S. M. O., D. L. G.) and the Commission of the European Communities for financial support under the contracts No. CHGE-CT20007 and No. ERBCHRXCT940466.

Received, 25th July 1995; Com. 5/04935K

References

1 S. M. Ormson and R. G. Brown, *Prog. React. Kinet.*, 1994, **19**, 45; D. LeGourrierec, S. M. Ormson and R. G. Brown, *Prog. React. Kinet.*, 1994, **19**, 211.
2 L. G. Arnaut and S. J. Formosinho, *J. Photochem. Photobiol. A*, 1993, **75**, 1; S. J. Formosinho and L. G. Arnaut, *J. Photochem. Photobiol. A*, 1993, **75**, 21.
3 W. Frey, F. Laermer and T. Elsaesser, *J. Phys. Chem.*, 1991, **95**, 10391.
4 B. J. Schwartz, L. A. Peteanu, C. B. Harris, *J. Phys. Chem.*, 1992, **96**, 3591.
5 P. Foggi, L. Pettini, I. Sànta, R. Righini and S. Califano, *J. Phys. Chem.*, 1995, **99**, 7439.
6 S. M. Ormson, R. G. Brown, F. Vollmer and W. Rettig, *J. Photochem. Photobiol. A.*, 1994, **81**, 65.
7 C. Rullière and A. Declémy, *Chem. Phys. Lett.*, 1987, **134**, 64.