Ultrafast Measurements of Charge and Excited-State Intramolecular Proton Transfer in Solutions of 4′-(*N,N*-Dimethylamino) Derivatives of 3-Hydroxyflavone

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Transient spectra for 4′-(*N,N*-dimethylamino)-3-hydroxy- (**1a**) and 4′-(*N,N*-dimethylamino)-3-methoxyflavone (**2a**) in several solvents at room temperature are reported following excitation with pulses of approximately 100 fs fwhm. **1a** exhibits emission from both the normal excited state and from the excited tautomer produced following excited-state intramolecular proton transfer (ESIPT). Rate constants for the ESIPT process are found to vary between 3.3×10^{11} and 3×10^{10} s^{-1} depending on the solvent. Polar solvents are found to play a significant role in stabilizing the normal excited state of both **1a** and **2a**.

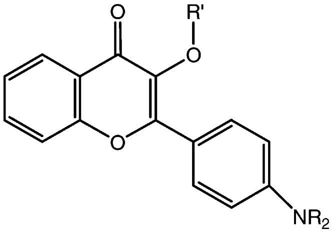
Introduction

Charge- and proton-transfer reactions are ubiquitous in the natural world, and their study continues to prove both insightful and rewarding. The initiation of such processes through the absorption of a photon of light provides the opportunity to deploy a wide panoply of spectroscopic techniques to these studies. As such, the work carried out in this field has attracted a wide range of books and reviews, a sample of which are given for charge-transfer[1,2] and proton-transfer reactions.[3−6] Of particular interest to us are chemical systems where both processes are potentially feasible so that the interplay between them is open to study.

Two examples of such systems are the substituted hydroxyflavones 4′-(*N,N*-dimethylamino)- and 4′-(*N,N*-diethylamino)-3-hydroxyflavone (**1a** and **1b** respectively, Chart 1). The parent molecule, 3-hydroxyflavone, undergoes excited-state intramolecular proton transfer (ESIPT)[5] on a subpicosecond time scale,[7−9] but this process is much slower in **1a** and **1b** where rate constants in the range $10^{10}-10^{11}$ s^{-1} have been reported.[10−13] In addition, the proton-transfer process was found to be reversible with the reverse reaction having a rate constant that varied (with solvent) between being similar to that for the forward reaction to an order of magnitude slower. These conclusions were drawn from analysis of the emission spectra and fluorescence decay kinetics of **1a** and **1b**, both of which exhibit dual emission and biexponential kinetics for both emission bands.[10−14]

All of the aforementioned properties of these molecules are very sensitive to the nature of the solvent system in which they are dissolved. As a consequence, they have considerable potential as probes or sensors in a variety of applications[15−22] and a number of elaborations of the basic structure have been proposed to enhance particular properties such as metal ion-binding ability.[17,22] We have proposed that this solvent sensitivity arises through competition between ESIPT and the formation of a twisted intramolecular charge-transfer (TICT) state.[14] This is probably too simplistic; solvent tuning of the energies of the proton-transfer and charge-transfer states must be considered.[11] Alternatively, an intermeshing of the two processes may take place[19,20] (in addition to the reversibility of the proton-transfer reaction).

CHART 1: Structures of Compounds Involved in This Work[a]



[a] **1a:** R = CH_3, R′ = H. **1b:** R = C_2H_5, R′ = H. **2a:** R = R′ = CH_3.

In this paper we present the results of a series of experiments whereby **1a** and its 3-methoxy analogue (**2a**) have been excited with femtosecond laser pulses and transient spectra measured at various time intervals following the excitation. The results provide new information about the early photophysics of **1a**, which informs the debate about the relative roles of charge and proton transfer in these systems.

Experimental Section

4′-(*N,N*-Dimethylamino)-3-hydroxyflavone (**1a**) and 4′-(*N,N*-dimethylamino)-3-methoxyflavone (**2a**) were synthesized and purified as previously described.[14] Solutions of the two compounds were prepared in spectroscopic grade solvents (Sigma-Aldrich) and steady-state absorption and emission spectra were measured on Hewlett-Packard HP8452A diode array and SPEX Fluoromax spectrometers, respectively.

The experiment setup for measuring transient absorption spectra at LENS has been described elsewhere[9,23,24] and is only outlined here. Femtosecond pulses (750−800 mW average

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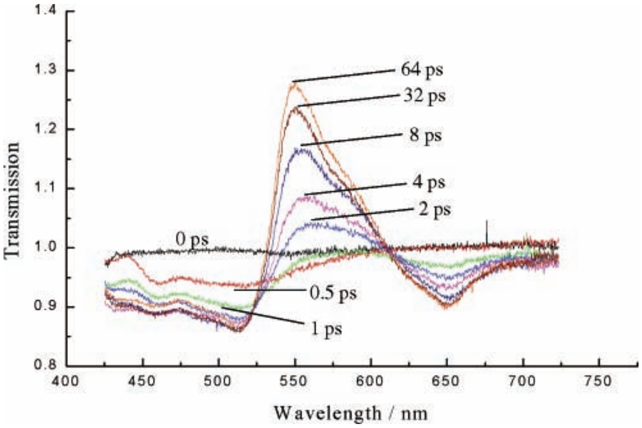

Figure 1. Transient spectra for **1a** in methylcyclohexane at pump−probe delays of 0−64 ps.

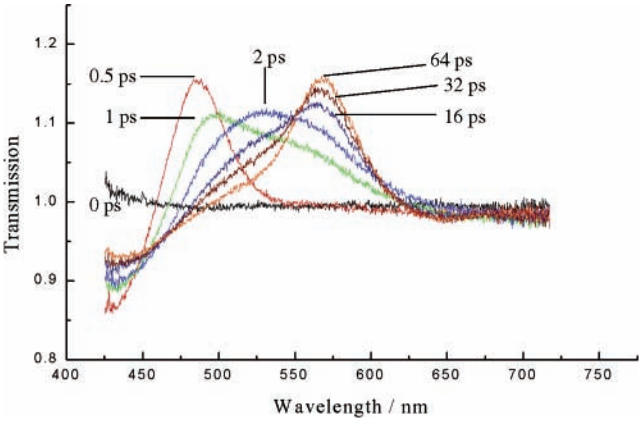

Figure 2. Transient spectra for **1a** in acetonitrile at pump−probe delays of 0−64 ps.

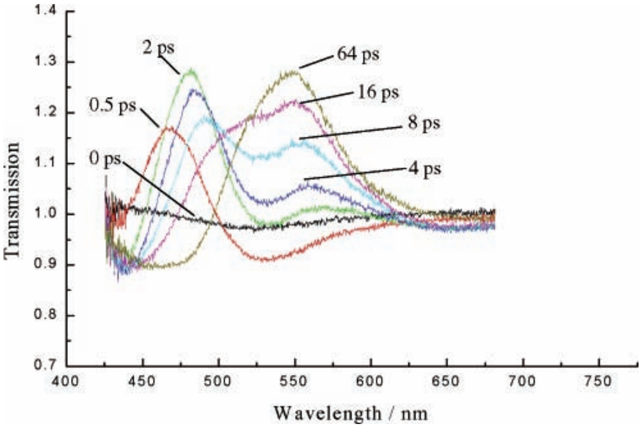

Figure 3. Transient spectra for **1a** in ethanol at pump−probe delays of 0−64 ps.

power, 90−100 fs duration) are produced by a Spectra Physics Nd:YVO$_4$ (Millennia X) pumped Ti:Sapphire (Tsunami) laser seeding a BMI Alpha 1000 regenerative amplifier. UV−visible tunability of the pump is achieved with an optical parametric generator and amplifier, whereas a broad-band UV−visible continuum is obtained by focusing part of the probe beam onto a calcium fluoride plate for the probe. The probe pulses are split (50/50) to provide signal and reference beams for detection by a spectrograph/CCD camera combination.

Results

Transient spectra were measured for the two flavones in several solvents. In the description of the results that were obtained, we must take into account that the transient spectra potentially contain contributions from transient absorption, transient bleaching and transient simulated emission. In addition, the white light continuum is slightly dispersed across the wavelength range of the spectra that are reported; i.e., a component appearing at 0 fs delay at 400 nm will occur some 800 fs later at 700 nm.[23]

Transient spectra were measured for **1a** in four solvent environments; nonpolar (methylcyclohexane), polar and aprotic (acetonitrile), polar and protic (ethanol), and nonpolar, protic, and viscous (decanol). The last solvent was chosen as a means of probing potential viscosity effects. The transient spectra for **1a** excited at 400 nm in methylcyclohexane solution are given for delays of 0−64 ps in Figure 1. The transient spectra resemble those recorded for 3-hydroxyflavone in this solvent,[9] albeit slightly red shifted (with respect to the transient emission) due to the influence of the *N*,*N*-dimethylamino substituent.

At a delay of 500 fs, transient absorption occurs across most of the spectral range and there is evidence (in the light of the spectra at longer delays) that there is stimulated emission between 525 and 600 nm. However, at this delay value, the dispersion of the white light continuum is still effective, thus giving rise to the appearance of a band between 450 and 550 nm and no signal change in the 600−750 nm region. Similar comments may be made about the spectrum at a delay of 1 ps, but here transient absorption is also observed between 600 and 700 nm. At even longer delay times, the three spectral regions become even more distinct—transient absorption from 425 to approximately 525 nm and from 610 to 750 nm and stimulated emission in between. The shape of the stimulated emission band appears to change with time. The band exhibits a peak at approximately 550 nm and a shoulder around 580 nm. The ratio of the intensities at these two wavelengths clearly increases with increased delay time (Figure 1). However, it is possible that this is simply caused by changes in the transient absorption that can reasonably be assumed to also be occurring over this wavelength range. It is also noticeable that the intensity of the stimulated emission changes in a manner similar to that of the red transient absorption. However, the blue transient absorption band reaches a stable intensity after ∼8 ps.

The transient spectra observed in acetonitrile solution (Figure 2) are markedly different to those recorded in methylcyclohexane. There is no transient absorption to speak of except at the blue edge of the spectral range and the spectra are dominated by stimulated emission. In contrast to the stimulated emission in methylcyclohexane, the emission in acetonitrile initially occurs at a much lower wavelength (with a peak at ∼450 nm at 500 fs delay) but shifts spectrally over the time range employed until it peaks at approximately 570 nm after 64 ps. Inspection of the intermediate spectra reveals that there are two distinct events in the evolution of the stimulated emission—a red shift of the initially observed emission band followed by its decay and the concomitant growth of the emission at 570 nm, whose emission maximum appears to be invariant with delay time. The short wavelength range of the transient absorption at the blue end of the spectrum may be the result of competition with the stimulated emission, which covers a greater wavelength range in acetonitrile compared to methylcyclohexane. However, the absence of any obvious transient absorption in the red is in marked contrast to the situation in methylcyclohexane.

Similar results are observed for **1a** in ethanol (Figure 3). Compared to acetonitrile, there is more distinction between the two emission bands but the evolution of the spectra appears to

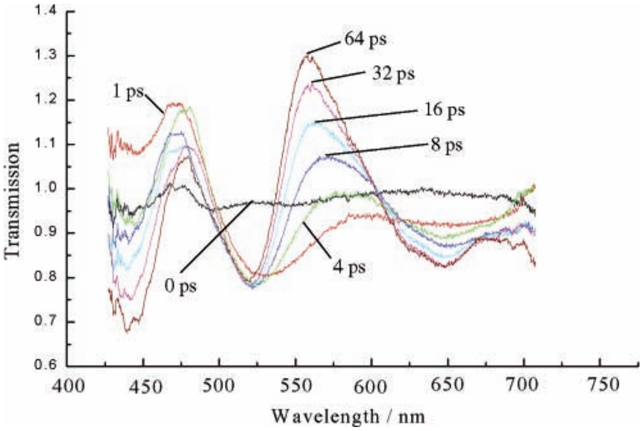

Figure 4. Transient spectra for **1a** in 1-decanol at pump−probe delays of 0−64 ps.

be comparable. There is also more evidence of transient absorption than in acetonitrile, albeit weak at the red end of the spectral range. It is noticeable that the maximum of the stimulated emission in Figure 3 at the longest delay time is somewhat to the red of the steady-state fluorescence maximum.[14] We ascribe this partly to the fact that the latter spectrum is time-averaged over the whole of the **1a** emission and will therefore inevitably exhibit its emission maximum at a shorter wavelength due to the early time blue emission shown in Figure 3. We also consider that the stimulated emission in Figure 3 at the longer delay times is biased toward the red as a consequence of the contribution from transient absorption referred to earlier.

In contrast, the spectra recorded in the second, more viscous alcohol 1-decanol exhibit more similarities to the behavior observed in methylcyclohexane than to those in ethanol. In 1-decanol we see the formation of two distinct stimulated emission bands, with peaks at 475 and 560 nm, which do not converge throughout the measurement period (Figure 4). In fact, part of the 475 nm band appears to decay within this time to yield a transient absorption band at shorter wavelength. There is also transient absorption lying between the two emission bands and at the red end of the spectra (as in methylcyclohexane).

Kinetic data for selected wavelengths across the transient spectra was extracted by averaging the transient absorption/emission signal over a 10 nm bandwidth around the wavelength of interest and plotting this as a function of time. A significant number of wavelengths were chosen for analysis, but the results obtained are more than adequately represented by the fitting parameters, which are given in Table 1. The wavelengths selected for presentation in Table 1 usually represent the absorption or emission maximum of a spectral feature in each of the transient spectra. All of the kinetic traces require two or three exponential components to achieve an acceptable fit, with the first of the components being indeterminable due to the time resolution of the LENS system. We allocate a value of ≤100 fs to this component. In methylcyclohexane the blue transient absorption feature exhibits a rise time of approximately 1.7 ps in addition to the instrument-limited rise time. These two components are also observed at 550 and 650 nm but in the former case, the preexponential factor for the 1.7 ps component has a negative sign as this component relates to an increase in emission at 550 nm. At these two longer wavelengths, a third component of 8.5 ps is also required to give an adequate fit to the data. This also comprises a rise time for either emission (at 550 nm) or absorption (at 650 nm). We do not observe an obvious decay component at any wavelength across the transient spectra.

For acetonitrile solution at 470 nm the usual instrument-limited rise is observed to yield emission that then decays to form a weak absorption feature with (rapid) decay times of 360 fs and 1.3 ps. At longer wavelengths such as 520 and 570 nm, a small amount of transient absorption is observed initially, which is then transformed into a stimulated emission with a rise time of approximately 300 fs. At 520 nm, the stimulated emission then decays with a lifetime of some 33 ps whereas at 570 nm the emission intensity continues to increase, with the same 33 ps lifetime.

The three lifetimes of ∼300 fs, 1.3 ps, and 33 ps are also appropriate for fitting the time-dependent Stokes shift (TDSS)[25] of the stimulated emission $C(t)$:

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \tag{1}$$

where ν is the wavelength of the emission maximum at times zero, t, and infinity. $C(t)$ versus t for **1a** in acetonitrile is shown in Figure 5a. The optimal fit for these data is a triexponential with time constants of 300 fs, 1.6 ps (compared to 1.3 ps from the earlier kinetic analyses), and 33 ps.

The kinetic behavior of **1a** in ethanol is similar to that observed in acetonitrile. We observe similar fast dynamics with instrument-limited and 300 fs time constants, but in this case we observe only one picosecond component of 8.0−9.0 ps. The kinetics clearly show the initial 470 nm emission decreasing in intensity as the emission maximum shifts to the red (Figure 3) with concomitant rise times being observed at 520 and 550 nm

TABLE 1: Fitting Parameters for the Transient Spectral Kinetics and Time-Dependent Stokes Shifts of 1a in Various Solvents

solvent	wavelength	τ_1/fs	τ_2/ps	τ_3/ps	A_1	A_2	A_3
methylcyclohexane	470	≤100	1.60		0.23	0.34	
	520	≤100	1.80		0.43	0.29	
	550	≤100	1.60	8.50	0.40	−1.50	−0.60
	550	≤100	5.60		0.14	−0.88	
	650	≤100	1.60	8.50	0.27	0.27	0.44
acetonitrile	470	≤100	0.36	1.30	−1.00	0.95	0.24
	520	≤100	0.27	33.00	0.69	−1.32	0.60
	570	≤100	0.33	33.00	0.44	−0.93	−0.50
	TDSS	300	1.60	33.00			
ethanol	470	≤100	0.28	8.60	−1.70	2.50	−0.31
	520	≤100	0.30	8.10	1.00	−0.70	−1.60
	550	≤100	0.30	8.10	0.75	−2.10	−0.39
	650	≤100	8.10	27.00	0.90	0.60	−1.50
	TDSS	300	8.20				
1-decanol	520	≤100	2.20	120	1.75	0.44	−1.80
	550	≤100	3.70	33.00	1.68	−2.78	−3.70
	650	≤100	3.00	120	0.55	0.45	−0.55

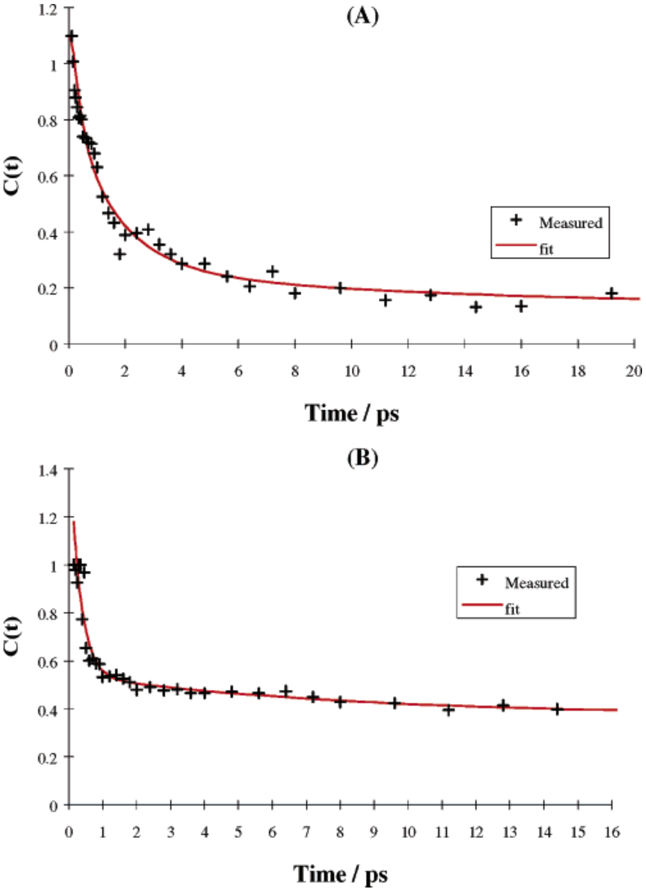

Figure 5. Time-dependent Stokes shift, *C*(*t*) measurements for **1a**: (A) in acetonitrile (fit to third-order exponential decay ($\tau_1 = 0.3$ ps, $\tau_2 = 1.6$ ps, $\tau_3 = 33$ ps)); (B) in ethanol (fit to second-order exponential decay ($\tau_1 = 0.3$ ps, $\tau_2 = 8.2$ ps)).

(Table 1). In ethanol, the red transient absorption band is sufficiently intense to enable its kinetics to be fitted, with a two-component rise (instrument-limited and 8 ps time constants) and a 27 ps decay. Finally, the TDSS data for **1a** in ethanol is shown in Figure 5b where the kinetic components of 300 fs and 8.0 ps are once again reproduced.

Solutions of **1a** in 1-decanol exhibit kinetics significantly different from those observed in other solvents. In this case we observe stimulated emission bands at 470 and 550 nm, but the time-dependent Stokes shift present in acetonitrile and ethanol does not occur in 1-decanol. The data below 500 nm show large amplitude variations (even with integration over a wavelength range), such that the dynamics could not be resolved. The reason for this is unclear, given that the data at wavelengths >500 nm and in the other solvent systems does not show this behavior.

To inform our understanding of the excited-state mechanism(s) for **1a**, we have also undertaken measurements of the transient spectra of **2a** in organic solvents at room temperature.

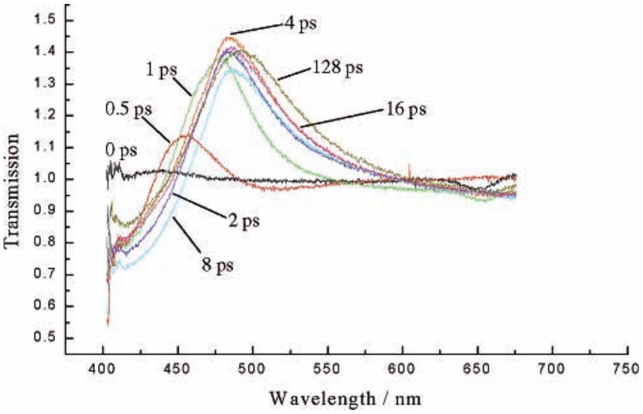

Figure 6. Transient spectra for **2a** in acetonitrile at pump−probe delays of 0−128 ps.

Transient spectra for **2a** in methylcyclohexane exhibit initial weak absorption with two peaks at approximately 410 and 460 nm with a long tail to the red. Within 1 ps the formation of a further broad absorption band centered around 550 nm is observed, together with an emission feature between 400 and 500 nm at longer delay times. The observed spectra are not well resolved in terms of signal amplitude in this solvent and restrict us to qualitative comments as extraction of kinetics data is impractical.

Transient spectra were also recorded for **2a** in ethanol and acetonitrile. The spectra in the two solvents exhibit quite similar behavior as typified by the data given in Figure 6 for acetonitrile. Transient absorption is observed at the lowest wavelengths probed, with emission being observed at higher wavelengths. An emission with a peak at 460 nm (450 nm in ethanol) is present within 500 fs, and this is observed to red shift to 490 nm (520 nm in ethanol) and increase in intensity over a period of a few picoseconds. In ethanol, this wavelength shift continues over the whole of the time scale probed.

The wavelength integrated kinetics for **2a** are given in Table 2. As for compound **1a**, an instrument-limited component is observed in both solvents at all wavelengths. In the case of acetonitrile solvent at wavelengths above approximately 480 nm, this is convoluted with ultrafast and picosecond components of the order of 300−400 fs and 1.3−1.4 ps, respectively. Below 480 nm, the data at the shortest delays contains oscillations over the peak that we are unable to interpret and that mask the fast response of the compound. We can only tentatively assign a longer lived component of some 16 ps time constant to the observed behavior. In ethanol, the picosecond component is an order of magnitude longer-lived than in acetonitrile (Table 2). Once again, these various time constants are reproduced by the TDSS data.

Discussion

The behavior of **1a** (and **2a**) in the 100 ps following excitation and the roles played by charge and proton transfer in the

TABLE 2: Fitting Parameters for the Transient Spectral Kinetics and Time-Dependent Stokes Shifts of 2a in Acetonitrile and Ethanol

solvent	wavelength	τ_1/fs	τ_2/ps	τ_3/ps	A_1	A_2	A_3
acetonitrile	470	≤100	16.00		−2.70	−0.61	
	520	≤100	0.30	1.30	−0.60	−0.77	−1.18
	570	≤100	0.40	1.40	0.67	−0.75	−0.31
	TDSS	400	1.30				
ethanol	470	≤100	2.60	18.00	−4.40	−3.60	6.51
	520	≤100	0.30	15.00	1.40	−1.70	−3.20
	550	≤100	0.30	18.00	0.70	−0.64	−1.90
	TDSS	300	2.60	18.00			

photophysics of these compounds may be elucidated through a comparison of the properties of the two compounds in the various solvents used in this study. The key experiments appear to us to be the transient spectral measurements performed on **1a** in ethanol and acetonitrile. Our understanding of these spectra are facilitated by the parallel measurements on **2a** in these solvents, and the picture is further added to by the experiments on **1a** in methylcyclohexane and 1-decanol.

First of all we note that the excited state of the methoxyflavone (**2a**), which, of course, cannot undergo ESIPT, is stabilized by reorganization of the solvent over a few picoseconds (in acetonitrile) or a few tens of picoseconds (in ethanol). The time constants found here are in good agreement with those reported by Horng et al.[26] in their comprehensive study of the solvation dynamics of coumarin 153 and other workers such as van der Meer et al.[27] and Biswas and Bagchi.[28] In acetonitrile, Horng et al. report a biexponential decay with time constants of 89 and 630 fs and a characteristic average time constant ($\langle\tau\rangle$) of 260 fs. Biswas and Bagchi's prediction is for time constants of 177 fs and 3.5 ps. The values presented in Table 2 lie intermediate between these two sets of expectations. Unsurprisingly, the picture in ethanol is much more complex with four exponential components being required to fit the dynamics of coumarin 153 in this solvent.[26] Their time constants vary from 30 fs to 30 ps with a $\langle\tau\rangle$ of 16 ps. Van der Meer et al.[27] observe a range of time constants in their study of a series of styryl dyes but their time constants (obtained from biexponential fits) all fall within the 30 fs to 30 ps range reported earlier with $\langle\tau\rangle$ varying from 2.6 to 10.7 ps. Once again, we consider that the time constants that we extract from the dynamics of **2a** in ethanol are in complete accord with these observations. We conclude from the observation of the time-dependent Stokes shift that this excited state has a higher dipole moment than the ground state, thereby involving charge transfer − probably from the *N*,*N*-dimethylamino—or possibly the (*N*,*N*-dimethylamino)-phenyl—moiety to the flavone ring.

Identical behavior is observed for **1a** in ethanol and acetonitrile, but in addition, at the same time as we observe the initial emission band shifting to the red, a second emission band (even further to the red of the initial one) also starts to manifest itself. The second band must result from the tautomer formed by excited-state intramolecular proton transfer (given the similarity of the behavior in the aprotic acetonitrile and the protic ethanol). As the spectra evolve (Figures 2 and 3), the shorter wavelength band continues to shift to the red and diminish in intensity whereas the tautomer band increases in intensity (and may also shift spectrally, although this may be due to the overlap with a transient absorption component around 550 nm). The "normal" fluorescence from **1a** and **2a** therefore originates from an excited state that involves a significant degree of charge transfer, and the tautomer excited state resulting from the ESIPT process may also be convolved with an element of charge transfer.

The kinetic data for the two compounds in acetonitrile (Tables 1 and 2) suggest that the kinetic components of ≈300 fs and 1−2 ps refer to the solvent reorganization around the "normal" excited state and the 33 ps time constant is related to the ESIPT process. The latter value correlates well with the 70 ps lifetime for this process quoted by Roshal et al.[12] Obviously, one has to exercise care when considering the dynamics of **1a** given the possibility of ESIPT alongside any solvation effects. However, it is reassuring to note that, as for **2a**, the time constants recovered from the experimental dynamics of **1a** in acetonitrile and ethanol agree well with the literature.[26,27] The behavior of the two compounds in ethanol is qualitatively identical to that in acetonitrile, but the time constant for the proton-transfer process is less accessible. On the basis of the time constants required to fit the transient emission from the methoxy compound, it appears that the 8−9 ps time constant exiting from the fitting of the kinetics of the hydroxy derivative is a convolution of the ESIPT value and the longer solvent reorganization time constant observed for **2a** of 15−18 ps. Our data are of insufficient quality to allow us to fit two time constants instead of the 8−9 ps one for **1a**, but if our assumption is correct about this being a superposition of ESIPT and solvent reorganization, we can put an upper limit of 8 ps on the ESIPT time constant. Neither of the two recent reports[12,13] on the reversible proton transfer in **1a** used an alcohol solvent, so we do not have literature data to compare as in the case of acetonitrile as solvent.

The acetonitrile and ethanol polar solvents clearly play a major role in stabilizing the "normal" excited state. The relative weakness of the transient spectral data for **2a** in methylcyclohexane compared to the two polar solvents correlates with our previous report of an order of magnitude decrease in the fluorescence quantum yield and lifetime for this compound in methylcyclohexane.[14] These changes are related to an order of magnitude increase in the nonradiative decay rate.[29] It is therefore unsurprising that we observe no "normal" fluorescence for **1a** in MCH—only emission from the proton-transferred tautomer.

The transient spectra of the hydroxy compound in 1-decanol are similar to those in methylcyclohexane, except for the observation of some transient emission that can be ascribed to the "normal" excited state in the 400−500 nm range. The consistent red shift in the emission maximum that is observed in acetronitrile and ethanol is absent for 1-decanol. These findings are not surprising given that 1-decanol, although an alcohol, is relatively nonpolar ($\epsilon = 8.1^{30}$). However, the enhanced level of "normal" fluorescence compared to **1a** in MCH is probably attributable to specific hydrogen-bonding effects that interrupt the ESIPT process. Two time constants are extracted from the kinetics; one approximately 3 ps and the second at least an order of magnitude greater. Horng et al. report spectral response functions for 1-decanol that have (two) time constants in the subpicosecond region, a third time constant of 43.4 ps, and a fourth one of 373 ps.[26] The longer of our two values for 1-decanol could be correlated with these latter two time constants. However, we note that the data of Figure 4 suggest that the emission maximum is changing only slightly at longer time scales even though the intensity continues to increase significantly. This suggests that the longer of the two time constants that we observe, as well as the shorter, is linked to a proton-transfer process. We conclude that the ≈3 ps time constant is due to the ESIPT process and that the longer value derives from excited states that either undergo intermolecular excited-state proton transfer or that break any intermolecular hydrogen band and then undergo ESIPT.

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