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# Femtosecond observation of intramolecular charge- and proton-transfer reactions in a hydroxyflavone derivative

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Received 10 May 2004

Available online 17 July 2004

## Abstract

In this Letter, we report on direct observation of ultrafast intramolecular charge-transfer (ICT) reaction versus proton motion in 4'-dimethylaminoflavanol (DMAF) in solution. In an apolar medium, upon femtosecond excitation of a non planar structure of DMAF the ICT does not occur, and an abnormally slow (2 ps) proton motion takes place. In polar solvents, the ICT is very fast (100–200 fs) and the formed structure is stabilised in an extent that proton motion takes place in few or tens of ps. To our best knowledge, this is the first observation of competitive and related charge and proton transfers dynamics.

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## 1. Introduction

The essence of chemical and physical events reflected in the change of matter is due to electron and energy exchange, the breaking, making and rotating of chemical bonds [1,2]. The driving force behind these processes originates from induced orbitals interaction leading to charge- or energy-redistribution/transfer and thus to swings in electronic affinity or chemical ability/reactivity of the involved atoms, groups or molecules. A particular case in which the energetic properties span a wide range of energy upon the above changes is the H-bond. Because of its special unique character (energy, directionality and quantum tunneling) and the related phenomena in influencing the behavior of many systems ranging from material to life sciences, the related proton (or H-atom) transfer is one of the most important studied reactions [3–7]. In addition to that, proton (or hydrogen atom) motion might be coupled to charge transfer giving

rise to different mechanisms of chemical reactivity in real time of reactions.

A prototype system showing intramolecular charge- and proton-transfer reaction following an electronic excitation is 4'-dimethylaminoflavanol (DMAF) (Fig. 1A) [8–16]. Recently, we have reported on the tuning of proton motion mechanisms in DMAF by changing the nature (mainly governed by the polarity) of the medium [14]. In weakly polar media, the charge transfer (CT) structure emits at around 500 nm, while that of the formed proton-transferred tautomer is around 600 nm. In the first family of solvents, the CT and T structure are not equilibrated in contrast to the second family where slow picosecond (ps) equilibrium takes place between both structures of DMAF.

Here, we continue our efforts in elucidating the mechanism of both processes in real time of reaction. So far, armed with a femtosecond (fs)-time resolution, we were able to observe for the first time (at the best of our knowledge) the relationship between both ultrafast dynamics in the same systems in different media. We believe that the result shown here may constitute an

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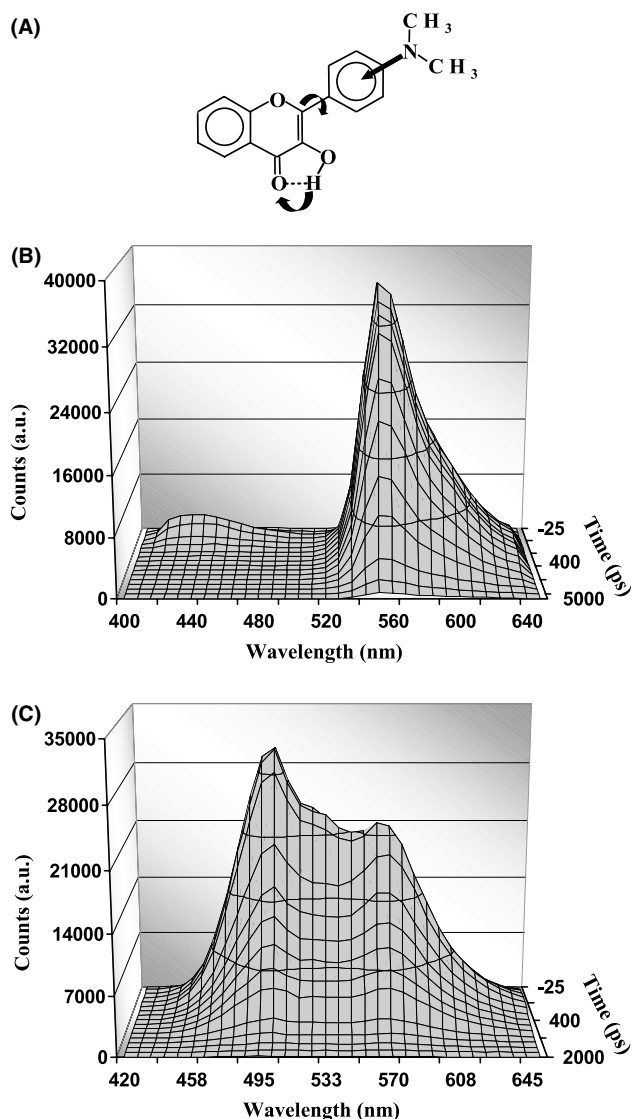


Fig. 1. (A) Molecular structure of 4'-dimethylamino-2-naphthol (DMAF) in its enol form. The arrows indicate possible events upon electronic excitation. Picosecond time-resolved emission spectra of DMAF in (B) methylcyclohexane, and in (C) acetonitrile.

important finding for a better understanding the proton-transfer dynamics in solution.

## 2. Experimental

DMAF was synthesised using Algar–Flynn–Oyamada reaction [17], and purified by means of a repeated recrystallisation from methanol solutions. All the used solvents (spectroscopy grade, Sigma–Aldrich) were purified by standard procedures, before use. Picosecond time-resolved emission spectra (TRES) were done using a time-correlated single-photon counting picosecond spectrophotometer (FluoTime 200, Picoquant) described earlier [18]. Magic-angle fluorescence decays

were recorded at different wavelengths (of 7 nm step) and exciting at 371 nm ( $\sim 60$  ps, 20 MHz) and the TRES were constructed using the Fluofit package (Picoquant).

Femtosecond time-resolved emission transients were measured using fluorescence up-conversion technique. Briefly, the system consists of a femtosecond Ti:sapphire oscillator (Tissa 100, CDP) pumped with a 5-W diode laser (Verdi 5, Coherent). The pulses (60 fs, 450 mW) were centred on 786 nm at 82 MHz repetition rate. The light beam was doubled in 1-mm BBO crystal and a dichroic mirror was used to separate the fundamental from the doubled beam (393 nm) sent for sample excitation. Typically, the energy of the excitation pulse at the sample was  $\sim 0.5$  nJ. The polarization of the excitation light was set at the magic angle with respect to that of gating pulse. The remaining fundamental light was used to gate the emission of the sample that flows in a 1-mm (or 0.4-mm) quartz rotating cell. The emission was collected and focused into a 0.3-mm BBO crystal (type I) using reflective optics. The gating pulse was time delayed and also focused into the nonlinear crystal to overlap with the sample fluorescence. The resulting up-converted signal in the UV region was filtered and entered to a double monochromator and detected with a photomultiplier tube. The cross correlation of the apparatus measured by gating the Raman signal from solvent is  $\sim 170$  fs for 1-mm sample cell. The data were convoluted with the cross-correlation signal and fitted to a multi-exponential function using the Fluofit package. The quality of the fits was characterised in terms of residual distribution and reduced  $\chi^2$  value. All experiments were done at  $293 \pm 1$  K.

## 3. Results and discussion

With steady-state excitation DMAF exhibits two emission bands, and their intensities and spectral positions depend on the nature of the solvent. Therefore reversible and irreversible proton motion was observed [14]. For example in apolar or weakly polar solvents like methylcyclohexane (MCH) or tetrahydrofuran (THF), the ps measurements have suggested an irreversible proton-transfer reaction in the enol (E) or the charge-transfer (CT) structure leading to the final tautomer (T). While in highly polar solvents like acetonitrile (AC), an excited-state equilibrium between CT and T structures is established. For clarity, Fig. 1 shows ps time-resolved spectra (TRES) of DMAF in MCH and in AC when excited at 371 nm. While in MCH the blue (440 nm) emission band (due to the initially excited enol, E, structure) vanishes after few ps, and the green–yellow one is standing up in the ns regime, in AC the situation is different. At earlier times (ps domain) the emission is centred around the 490-nm band (due to CT structure). 200 ps after the excitation, the relative emission intensity

of the formed tautomer (570 nm) does not change with that of CT, indicating the establishment of equilibrium between both structures and therefore a reverse proton motion in T to give CT. In THF, behaviour similar to that recorded in MCH was observed, except that the blue band centred at 475 nm and due to CT structure is not in equilibrium with T form. Therefore, the solvent nature has large influence on the potential energy sur-

face (PES) of charge and proton-transfer reaction of DMAF.

To examine the dynamics in real time of reaction, Fig. 2 shows the fs-resolved fluorescence transients of the emission of DMAF in MCH, THF and in AC at different wavelengths of observation. To begin with, at the fs regime the transients are remarkably different, reflecting different behaviours of charge and proton motions

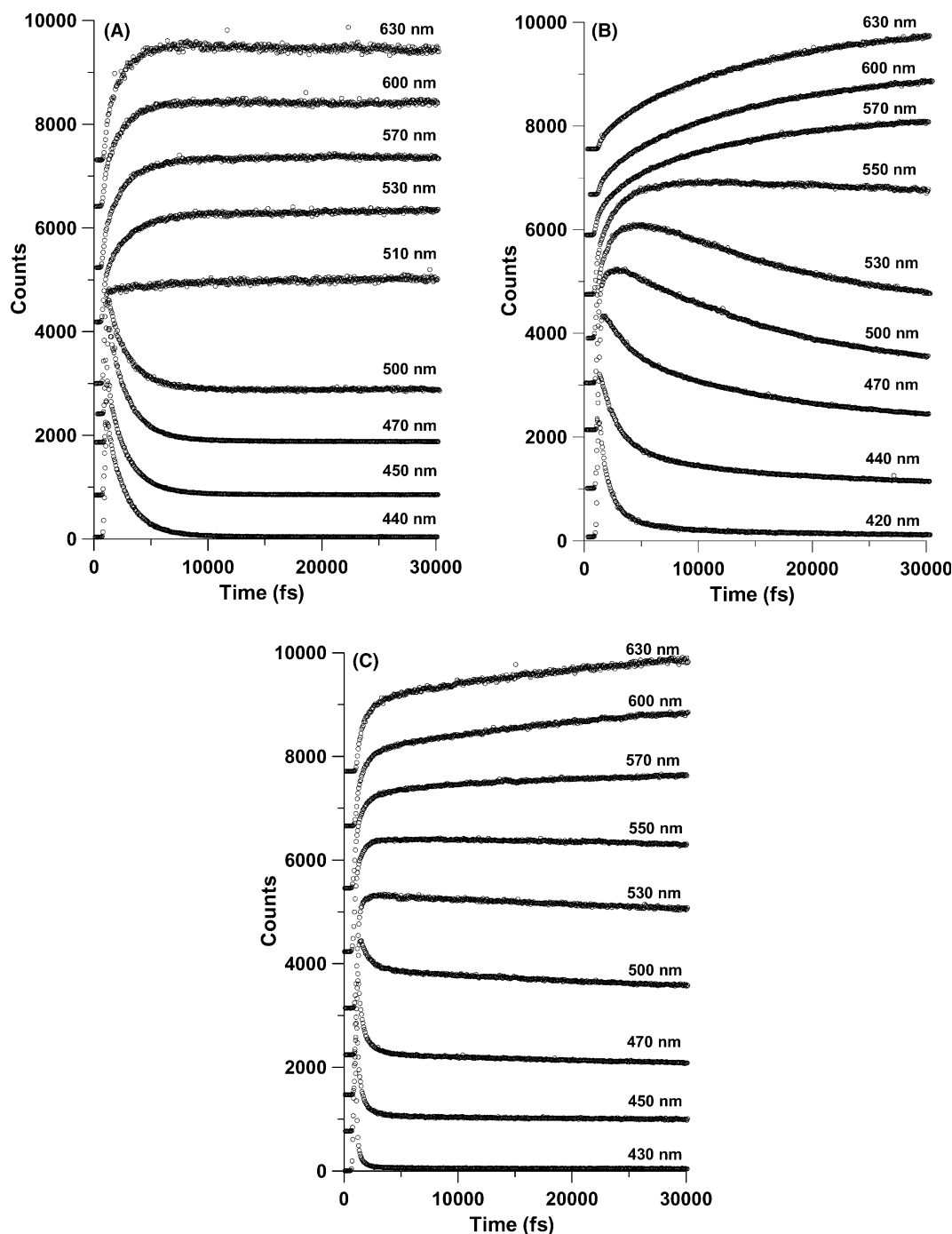


Fig. 2. Femtosecond (fs)-emission transients of DMAF in (A) methylcyclohexane (MCH), (B) tetrahydrofuran (THF), and in (C) acetonitrile (AC) at different wavelengths of observation as indicated.

following the nature of the medium. In MCH, the transients can be divided into two families: (i) a family for which the interrogated dynamics is for wavelengths lower than 510 nm, and this corresponds mainly to excited E dynamics, and (ii) a family corresponding to wavelengths longer than 510 nm, and this reflects the emission dynamics of T. For (i), the transients show fast decays almost done at 10 ps, while for (ii) the transients exhibit fast rises and very slow (ns) decays. In THF, a relatively polar solvent ( $f(\epsilon,n)=0.44$ ), where ICT in DMAF takes place [14], the transients can be grouped into three families. (i) transients for the 420–470 nm region (mainly E emission), (ii) transients for the 480–530 nm region and this correspond mostly to the emission of CT state; and family (iii) for wavelengths longer than 530 nm, and this is the region of T emission. In AC, a highly polar solvent ( $f(\epsilon,n)=0.71$ ), three categories of transients can be observed, behaviour not very different from that THF solution. (i) region of 430–500 nm (E emission), (ii) region for 490–550 nm (CT state emission)

and (iii) region for wavelengths longer than 570 nm (T emission). Fig. 3 shows a comparison of fs-transients in the used solvents for three typical wavelengths of observation, and Table 1 gives the data of the multi-exponential fits of the corresponding transients. As illustrated in Fig. 4, for THF and AC transients in region (iii), two components were needed to accurately fit the rising part. The ns components have been measured using a larger window of observation (up to 1.6 ns) or a ps-single photon counting system, and their values were fixed for accurate fitting of the fs-transients.

The trend showing the shortening of both fast and ultrafast times with the polarity of the medium is clear (Table 1), and is indicative of the involvement of an ICT process in excited DMAF in polar solvents (THF and AC), while it is absent in MCH. The ICT process is statically and dynamically sensitive to the polarity and viscosity of the medium as it is directly connected to the degree of planarity of the dimethyl aminophenyl moiety to that of the flavone part, and to the inductive

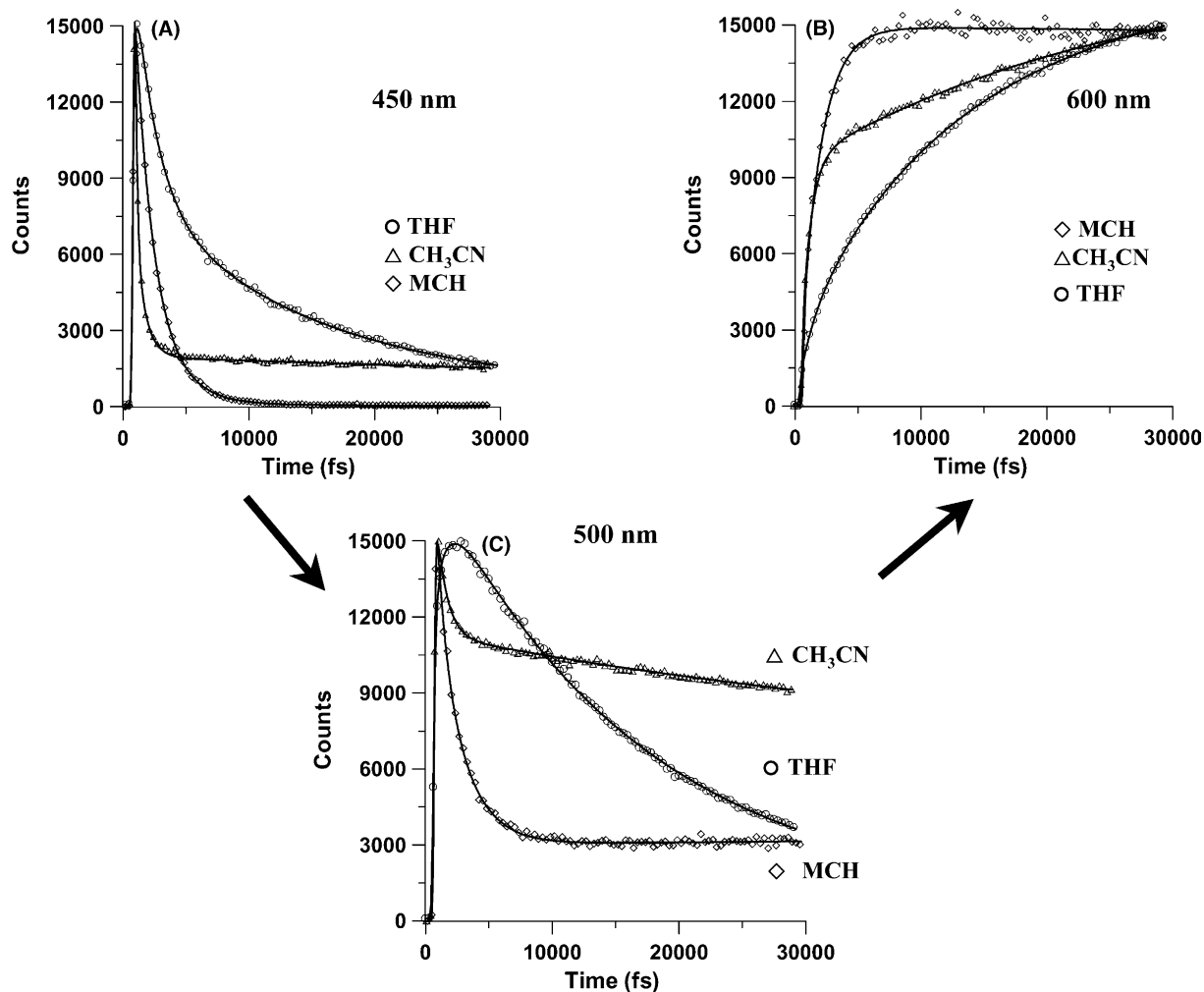


Fig. 3. Fs-emission transients in MCH, THF and in AC observed at (A) 450 nm, (B) 500 nm, and (C) 600 nm. The solid lines are the fits of the experimental data.

Table 1

Values of the time constants of the multi-exponential fitting of the fs-emission transients of DMAF at three representative wavelengths of its dynamics in the used media

| Solvent            | $\lambda/\text{nm}$ | $\tau_1/\text{fs}$ |         | $\tau_2/\text{ps}$ |         | $\tau_3/\text{ps}$ |         | $\tau_4/\text{ns}$ |          | $\chi^2$ | $F(\epsilon, n)$ |
|--------------------|---------------------|--------------------|---------|--------------------|---------|--------------------|---------|--------------------|----------|----------|------------------|
| MCH                | 450                 | 400                | (0.14)  | 1.8                | (0.86)  | —                  |         | —                  |          | 1.344    | 0.00             |
|                    | 500                 | 368                | (0.20)  | 1.9                | (0.63)  | —                  |         | 1.4*               | (0.03)   | 1.436    |                  |
|                    | 600                 | —                  |         | 1.6                | (−0.43) | —                  |         | 1.4*               | (0.57)   | 1.559    |                  |
| THF                | 430                 | 180                | (0.29)  | 1.1                | (0.60)  | 12                 | (0.10)  | 1.2*               | (<0.01)  | 1.466    | 0.44             |
|                    | 500                 | 148                | (−0.28) | 1.0                | (−0.17) | 16                 | (0.55)  | 1.2*               | (<0.001) | 2.536    |                  |
|                    | 600                 | —                  |         | 1.0                | (−0.06) | 11                 | (−0.42) | 0.3*               | (0.52)   | 1.295    |                  |
| CH <sub>3</sub> CN | 450                 | 105                | (0.71)  | 0.6                | (0.23)  | 55*                | (0.06)  | —                  |          | 1.588    | 0.71             |
|                    | 500                 | 93                 | (−0.46) | 0.7                | (0.21)  | 58*                | (0.33)  | —                  |          | 1.680    |                  |
|                    | 600                 | —                  |         | 0.6                | (−0.10) | 56*                | (−0.37) | 0.4*               | (0.52)   | 1.577    |                  |

The sign (−) before the values of the normalized amplitude (to 1) indicates a rising component in the transient. For THF solution at 450 nm, we observed a 200-fs rising (−0.21) component.  $F(\epsilon, n)$  is the reaction dielectric field parameter of the solvent, where  $\epsilon$  is the dielectric constant and  $n$  is the refractive index, respectively. The star is for fixed value of these time constants.

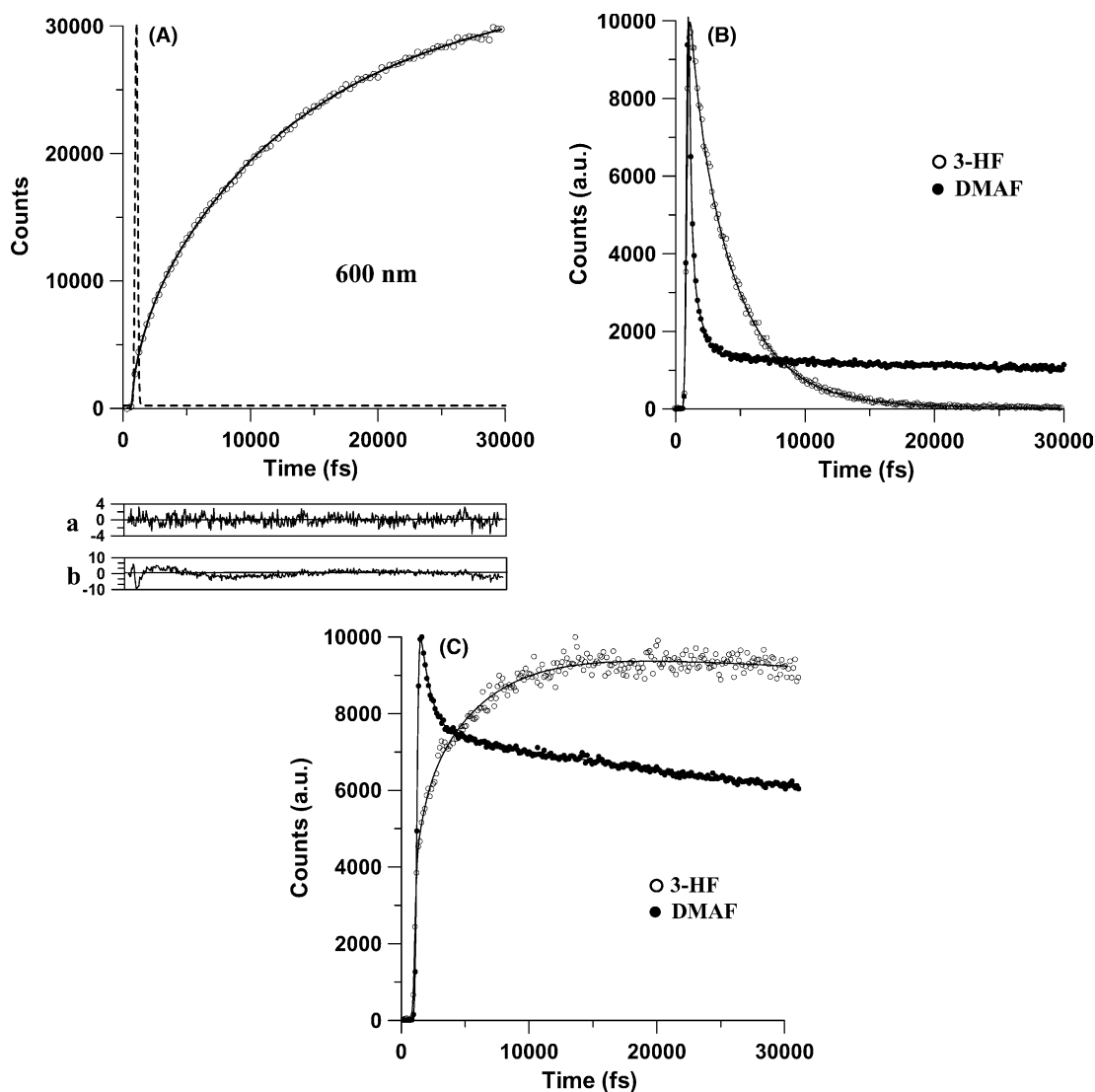


Fig. 4. (A) Fitted (solid lines) fs-emission transient of DMAF in THF at 600 nm showing the need of a three-exponential function with two rising components (residual distribution (a)) for an accurate fit of the rise. The dashed peak is the cross correlation from the Raman signal. Comparison of fs-emission transients of 3-hydroxyflavone (3HF) and DAMF in acetonitrile observed at (B) 450 nm and (C) 500 nm upon fs-excitation at 365 nm (the solid lines correspond to the multi-exponential fit).

effect of the amino group on such event. Therefore, in an apolar solvent like MCH, the ICT process should not favourable and relaxation/torsion to a planar configuration where this process should take place is not helped by its nature. Further more, electronic coupling/crossing between ( $n,\pi^*$ ) and ( $\pi,\pi^*$ ) states in E makes abnormally slower ( $\sim 2$  ps) the proton motion in DMAF when compared to its parent molecule, 3-hydroxyflavone (3HF, without the electron donating amino group). In fact, using 3HF in AC, we observed an ultrafast (30–50 fs) and fast (3.2 ps) components in the decay of E and rise of T (Fig. 4). These times are different from those observed in DMAF ( $\sim 100$  fs, 700 fs and 55 ps), and are in agreement with the results from fs-transient absorption measurements [19].

The observed contrast and trends for the rises and decays are very clear and suggest the following. To begin with, part of the 100–400 fs decay components in the three solvents is due to intramolecular-vibrational energy redistribution (IVR), and solvent/polarisation response which occurs in this time scale [20]. Therefore,

in addition to these dynamics, upon fs-excitation of DMAF in MCH, an intramolecular proton-transfer reaction in E occurs and takes place in  $\sim 1.6$  ps to give T. In THF, the fs decay (region of E) and rise (region of CT) are coupled and give the time constant ( $\sim 160$  fs) for the ICT reaction in E to produce CT. Within this structure a proton motion takes place in  $\sim 14$  ps as suggested by the decay (region ii) and the rise (region iii). It is worth noting that vibrational relaxation (VR)/cooling process in hot CT and T should occur in a similar time scale (ps-regime). In THF, the 1-ps component decaying in region i and rising in regions (ii) and (iii) with a larger contribution in (ii) (Table 1) might be due to a H-bonding interaction between the OH group of DMAF and the oxygen atom of THF (a weakly H-bond accepting solvent). Note that this kind of interactions may lead to the formation of anionic structure of DMAF at the excited state. Ionic DMAF generated in strongly basic media emits at around 510 nm. Further more, a comparable time ( $\sim 2$  ps) has been observed using 1,4-dioxane, a relatively weaker H-bond accepting solvent. Other

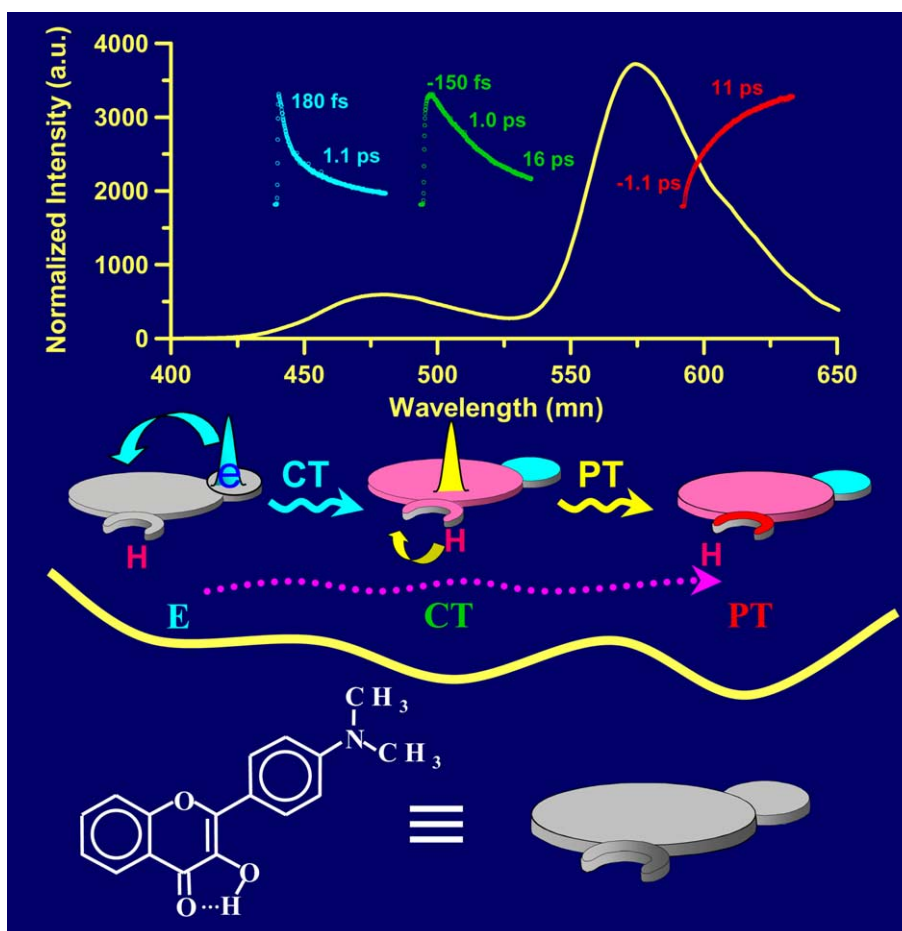


Fig. 5. A dissection of the fluorescence emission of DMAF in THF and corresponding to the different dynamical regions described in the text. The corresponding transients are shown on the top with the time constants as inset. Bottom: Representation (not in scale) of the potential-energy curve of DMAF at  $S_1$  involving E, CT, T, related ultrafast reactions and wavepackets indicated by the arrows. A possible (see text) direct reaction of E to give T is illustrated by the broken arrow.



possible mechanisms for the 1-ps decaying and rising component in THF are: (i) a direct proton-transfer reaction in E to give T as it happens in MCH solution, and/or (ii) a twisting of the aminophenyl moiety around the C–C bond linking both aromatic parts in E and giving a planar and relaxed configuration. The dynamics of all the examined processes might contribute by some extent to the 1-ps component observed in THF. In AC, in addition to IVR and ultrafast solvent response and because the 100-fs decay of E (region (i)) corresponds to the formation time of CT (region (ii)), we assigned this component to the CT event taking place in E upon electronic excitation. The 700-fs time, mainly decay at regions (i) and (ii) and a rise at (iii) might be due to proton motion in the formed and non equilibrated CT state to give T. However, H-bonded DMAF to AC or direct reaction of solvent-relaxed and favourably twisted E to give T may also happen in this time scale, as discussed for THF solution. Later, and upon solvation of CT and T, forward and back proton motions take place in 70 and 140 ps, respectively, equilibrating both forms [14]. This slow equilibrium should occur through tunnelling.

Fig. 5 is a simplified dissection of the different dynamical regions described above in THF with the potential-energy curve illustrating the wavepacket associated to charge (or electron) and proton motions in E and CT structures to give the final tautomer. For simplicity of the figure, the scenario for the dynamics of DMAF H-bonded to the solvent and equilibrated CT and T were not included.

#### 4. Conclusion

In this Letter, we have shown results giving a direct relationship between an intramolecular proton-transfer reaction and its driving force reflected on an ultrafast ICT process. In an apolar medium, the ICT is not favourable and the proton motion takes place in 1.6 ps, abnormally slowed down probably due to the mixing between ( $\pi, \pi^*$ ) and ( $n, \pi^*$ ) states, and nonplanarity of the excited E form. However in polar media (THF and acetonitrile) the dynamics of ICT is ultrafast (100–200 fs) giving rise to a CT state which gives in the ps regime the final tautomer. The dynamics of charge versus pro-

ton motions observed here is reminiscent to those of many chemical and physical events in artificial and natural/biological systems.

#### Acknowledgements

This work was supported by the MCYT (Spain) and the JCCM through projects BQU-2001-4972E, MAT-2002-00301 and PAI-02-004. We thank Dr. A.D. Roshal for the help in the synthesis of DMAF.

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