ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 105 (1997) 197–204

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Investigation of excited-state charge transfer with structural change in compounds containing anilino subunits by subpicosecond spectroscopy [1]

Monique M. Martin, Pascal Plaza, Pascale Changenet, Yves H. Meyer

Laboratoire de Photophysique Moléculaire du CNRS (UPR 3361), Bât 213, Université Paris-Sud 91405, Orsay, France

Received 11 September 1996; accepted 12 September 1996

Abstract

Subpicosecond absorption spectroscopy and picosecond streak camera fluorometry are applied to the study of the photoinduced processes in three classes of compounds for which molecular torsion with charge localization leading to an emissive or non-emissive twisted internal charge transfer state was proposed. The compounds are classified according to their steady-state fluorescence properties: compounds having a single band without solvatochromism or a single band with solvatochromism and compounds exhibiting dual fluorescence in polar solvents. The selected compounds are di- and tri-phenylmethane and amino-rhodamine dyes for the first class, the laser dye DCM for the second class and a substituted triphenylphosphine for the third class. These compounds contain at least one electron-donating anilino-group able to rotate. In all cases, the transient spectroscopy gives evidence for an excited-state relaxation involving the formation of an intermediate state. The changes observed in the kinetics by changing the solvent viscosity and polarity and upon donor protonation bring support to a mechanism involving photoinduced charge transfer with structural change. The kinetics are tentatively discussed within the context of theories of electron transfer reactions in the condensed phase. © 1997 Elsevier Science S.A.

Keywords: Charge transfer; TICT State; Subpicosecond spectroscopy

1. Introduction

To explain the dual fluorescence of 4-dimethyl-aminobenzonitrile (DMABN) (compound I in Fig. 1) in polar solvents, Grabowski et al. proposed a mechanism based on the formation of a twisted intramolecular charge-transfer state (TICT) in the excited state [1,2]. The charge-transfer process was evidenced by time-resolved fluorescence [3–5] and picosecond absorption spectroscopy [6,7] but the structural change involved is not yet well characterized. Rotational motion of the dimethylamino group and pyramidalization of the amino nitrogen have been widely discussed as possible photoinduced distortions [2,8,9]. In connection with these studies much attention was given to charge transfer processes in flexible donor–acceptor organic compounds [10]. Three classes of compounds were considered: (i) the compounds showing a single fluorescence band with little solvent effect on the spectral position but large viscosity effect on the intensity, (ii) the compounds showing a single fluorescence band with solvent polarity dependent Stokes shift, (iii) the compounds showing dual fluorescence in polar solvents like DMABN. In all cases, internal rotation with charge localization leading to a TICT-like state was invoked by Rettig et al. [11] to explain the observed solvent effects.

In the present paper we report a comparative analysis of the results we obtained in the experimental study of the three classes of compounds described above. The studies were carried out in solution at room temperature, by transient absorption spectroscopy with a pump–probe set-up of subpicosecond resolution and/or by time-resolved fluorometry with a streak camera [12–19]. The compounds studied are sketched in Fig. 1. All these compounds contain at least one electron-donating anilino group able to rotate.

Representatives of the first class of compounds, the triphenylmethane cationic dye ethyl violet (EV, II), the diphenylmethane cationic dye auramine (Aur, III), and the amino-rhodamine cationic dye (ARh, IV) [20] have a single fluorescence band with little Stokes shift but their fluorescence yield is strongly viscosity dependent [17,21,22]. The triphenylmethane dyes have been much studied [13–15,23–30] since the pioneer works on auramine by Oster and Nishijima [21] and on crystal violet (compound II with methyl instead of ethyl substituents) by Förster and Hoffman [22]. For a complete review see references in Ref. [31]. A non-

---

[1] Presented at the International Meeting of Physical Chemistry on *Intra- and inter-molecular photoprocesses of conjugated molecules*, Riccione, Italy, July 14–18, 1996.

PII S1010-6030(96)04498-X

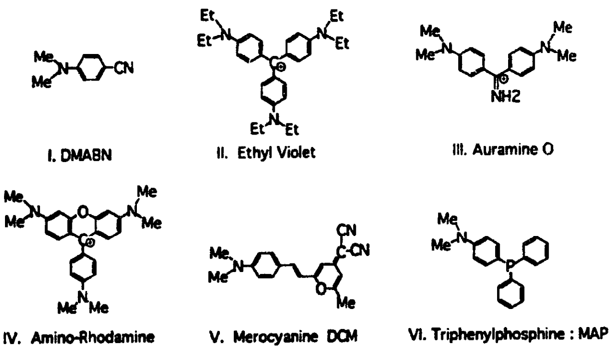

Fig. 1. Chemical structure of the compounds.

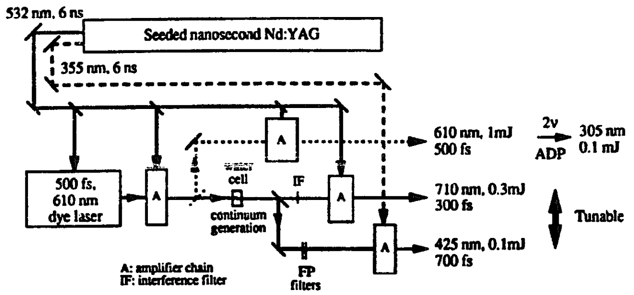

Fig. 2. Non-mode-locked subpicosecond tunable dye laser system driven by a single standard seeded 10 Hz Q-switched nanosecond Nd:YAG. Subpicosecond pulses at 610, 550, 425 and 305 nm were used as the excitation source for the fluorescence measurements or pump–probe experiments reported in the present paper.

radiative excited-state relaxation process involving rotational diffusion of the phenyl rings is generally assumed to explain the viscosity-dependent fluorescence yield of these compounds, which were used as model compounds to test theories of barrierless chemical reactions [24,28,29], but various interpretations of the relaxation mechanism were proposed [12–15,23–30].

The merocyanine dye DCM (**V**) belongs to the second class of compounds, it is highly fluorescent in polar solvents and its spectrum exhibits a strong solvatochromism [32–34]. The fluorescence was attributed to a highly polar excited state but the detailed mechanism of the photoinduced charge transfer in this compound is the object of much controversy [16,35–39]. Studies on similar compounds such as dimethylamino-cyanostilbene derivatives, where bridged derivatives could be prepared, brought experimental facts in favor of the formation of a TICT-like state [11,40,41].

The third class of compounds is illustrated by the triphenylphosphine derivative (MAP, **VI**) which has a chemical structure similar to that of the propeller-shaped triphenylmethane cationic dye (**II**) but has a pyramidal geometry instead of a planar one. This compound exhibits a dual fluorescence in polar solvents [18,19,42,43] and might be a good model for a generalization of the theories of photoinduced activated charge transfer with structural change which were developed to describe solvent effects in the TICT state formation route and kinetics in DMABN [44].

The results reported here give evidence for a relaxation mechanism involving the rapid formation of an emissive or non-emissive transient state in all cases [12–19]. A common mechanism involving charge transfer and structural changes in the three classes of compounds is considered. Although we should make a distinction between charge shift which can occur in organic cations and the charge separation which occurs in neutral molecule such as DMABN we shall call the transient state a charge-transfer (CT) state in all cases. The relaxation rate of non-emissive CT states is discussed in terms of energy gap law [45] and the role of solute structural change and solvent dynamics on the charge-transfer kinetics is tentatively discussed.

2. Experimental

2.1. Subpicosecond laser source

The subpicosecond laser source is a non-mode-locked home-made dye laser system described elsewhere [46] and sketched in Fig. 2. The basic system produces 500 fs, 400 μJ pulses around 610 nm starting from a single seeded Q-switched Nd:YAG laser (10 Hz, 6 ns). Tunable high power pulses in the 400–800 nm region are obtained by focusing the 500 fs red pulses into a water cell in order to generate a white light continuum which is then filtered and amplified in dye amplifiers pumped by the second or third harmonic of the same Nd:YAG pump. Subpicosecond UV excitation pulses can be obtained after amplification and frequency doubling of the continuum or of the basic 500 fs red pulses.

2.2. Pump–probe set-up

Time-resolved transient absorption spectra were measured by the pump–probe technique. The 610 nm laser pulses provided the pump pulses for ethyl violet (**II**) [12–14]. Filtering and amplification of the continuum provided the pump pulses for amino-rhodamine (**IV**) at 550 nm [17] and for auramine (**III**) and DCM (**V**) at 425 nm [16]. The triphenylphosphine derivative (**VI**) was pumped at 305 nm by frequency doubling the amplified basic red pulses up to 1 mJ [18,19]. In the latter case, the residual fundamental beam was separated from its harmonic and used to generate a white light continuum in a 1 cm water cell, which was used as the probe in the pump–probe set-up. When pump pulses were tuned at 610 nm or at 550 nm, part of the incident beam was used to generate the continuum probe [13,14,17], but when pump pulses were tuned at 425 nm a second beam was produced at 700 nm, according to the scheme shown in Fig. 2, to generate the continuum probe [16]. In all cases, the probe was split into two beams sent, respectively, through the sample and a reference cell. Both transmitted beams were simultaneously analysed with a polychromator (Jarrell–Ash, resolution 3 nm) and a computer-controlled double diode array detector (Princeton Instruments Inc.). The polarization of the pump light was set at the magic angle (54.7°) relative to the polarization of the probe light. Data were accumulated over up to 2000 laser shots without pulse discrimination. The samples were recirculated. The change in optical density of the samples are obtained with an error of ±0.005.

2.3. Time-resolved fluorescence set-up

Fluorescence decays were recorded with a 4 ps resolution streak camera (ARP Strasbourg) and collected at the magic angle. A properly advanced reference pulse and the fluorescence decay were both measured on the same camera trace. An accumulated decay trace was obtained by superposition of the reference pulse of each trace to eliminate the jitter in triggering the camera sweep. For amino-rhodamine and ethyl violet, fits with monoexponential or multiexponential decays were searched with a commercial software [12,17], but for the substituted triphenylphosphine the fluorescence decays were fitted with exponentials reconvoluted by the response function of the camera [18,19].

2.4. Samples

Auramine O was purchased from Aldrich and used without further purification. Details about other solutes and solvents suppliers were given in previous publications [12–14,16–19]. In time-resolved experiments, the sample concentrations were chosen so that the excitation light was well absorbed in a 1 mm cell (OD ~ 0.3 to 1.2). Solutions were deaerated with a nitrogen flow when needed. The experiments were performed at room temperature.

3. Results and discussion

3.1. Transient spectroscopy of ethyl violet, amino-rhodamine and auramine

3.1.1. Ethyl violet (II) and amino-rhodamine (IV)

The main features of the time-resolved transient absorption spectra that we measured for ethyl violet (EV) and amino-rhodamine (ARh) samples in ethanol are recalled in Figs. 3 and 4 respectively [13,14,17]. The transient spectra $\Delta D(t)$ represent the excited sample optical density, at a given pump–probe delay, minus that of the unexcited sample D_0. It is seen that immediately after excitation, transient absorption ($\Delta D > 0$) is observed for both dyes below 520 and 480 nm, respectively, net gain ($\Delta D < 0$, no ground state bleaching) above 640 and 600 nm and bleaching in the range of the ground state absorption.

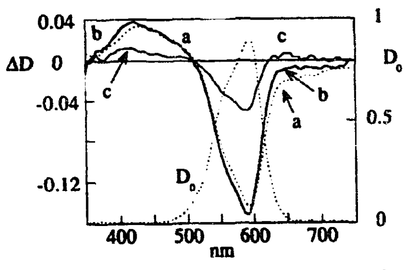

Fig. 3. Time-resolved photoinduced change in optical density (ΔD, left scale) of a solution of ethyl violet in ethanol after subpicosecond excitation around 610 nm. Pump–probe delays: curve a, 1 ps; curve b, 3 ps; curve c, 13 ps. D_0, spectrum of the unexcited sample (right scale).

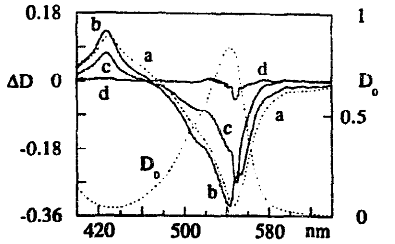

Fig. 4. Time-resolved photoinduced change in optical density (ΔD, left scale) of a solution of amino-rhodamine in ethanol after subpicosecond excitation at 550 nm. Pump–probe delays: curve a, 1 ps; curve b, 5 ps; curve c, 15 ps; curve d, 50 ps. D_0, spectrum of the unexcited sample (right scale).

The main common feature of the time-resolved absorption spectra of EV and ARh is a fast change in shape within 5 ps after excitation. For ARh, the transient absorption rapidly decreases around 460 nm, whereas a new absorption peak keeps growing near 430 nm. For EV, ΔD remains constant between 450 and 500 nm whereas a broad peak rises in the 390–430 nm range. Simultaneously, a fast decrease in the gain signal is observed for both compounds in the red wavelength range whereas the bleaching observed between 480 and 540 nm for ARh and between 510 and 600 nm for EV remains constant or increases slightly. Once the red gain signal has vanished, a slight but reproducible, red absorption band remains together with the blue absorption. Complete deactivation is achieved in about 50 ps for ARh and 25 ps for EV. In a viscous solvent such as decanol, EV and ARh exhibit slower but similar spectral changes as those found in ethanol and their LE fluorescence decays were found to be non-exponential [13,14,17].

We proposed a similar scenario in these molecules [15], attributing the initial red gain and initial blue transient absorption to the locally excited (LE) state directly populated by the laser excitation and the delayed, blue-shifted, absorption band to a photoinduced non-emissive transient state reached from the LE state. We also attributed the absorption which appears at long pump–probe delays in the red wavelength range to this transient state. Since we did not observe such a transient state for ARh solutions containing hydrochloric acid [17], that is when the electron donor site of the aniline subunit is blocked by protonation [8,20], we concluded that the photoinduced process involves intramolecular charge transfer.

3.1.2. Auramine (III)

Although Auramine (Aur) is used as a fluorescent sensor [47], due to its large sensitivity to solvent viscosity originally evidenced by Oster and Nishijima [21], the photoinduced processes in this molecule are not well known. We report here a picosecond study of this compound. The time-resolved

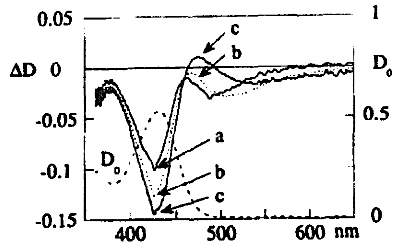

Fig. 5. Time-resolved photoinduced change in optical density (ΔD, left scale) of a solution of auramine in ethanol after subpicosecond excitation at 425 nm. Pump–probe delays: curve a, 1 ps; curve b, 2 ps; curve c, 4 ps. D_0, spectrum of the unexcited sample (right scale).

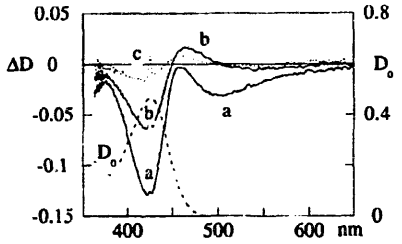

Fig. 7. Time-resolved photoinduced change in optical density (ΔD, left scale) of a solution of auramine in decanol after subpicosecond excitation at 425 nm. Pump–probe delays: curve a, 10 ps; curve b, 100 ps; curve c, 300 ps. D_0, spectrum of the unexcited sample (right scale).

spectra measured for Aur solutions in ethanol are given in Figs. 5 and 6.

Immediately after excitation (Fig. 5(a), $\Delta t = 1$ ps), bleaching and net gain are respectively observed below and above 470 nm but the spectra do not show any positive ΔD. Then, the gain signal decreases leaving place to a transient absorption around 480 nm (Fig. 5(c), $\Delta t = 4$ ps) while the negative ΔD in the ground state absorption range keeps increasing and a temporary isosbestic point is evidenced at 460 nm. Since an increase of the bleaching signal is no longer possible once the excitation process is finished, we explain the spectral changes by the assumption that both the LE state absorption and the ground state depletion contribute to the transient ΔD spectra below 460 nm. Thus the decay of the LE state population, which can be followed by the gain decay, leads to the apparent increase of the bleaching. The isosbestic point at 460 nm and the transient absorption increase at 480 nm can be explained by the formation of a non-emissive transient state from the LE state in a similar way as for EV and ARh. For such a model the differential optical density reads:

$$\Delta D(\lambda,t) = -0.43L\{\{\sigma_g^{LE}(\lambda)+\sigma_a(\lambda)\}N_{LE}(t) + \{\sigma_g^{x}(\lambda)+\sigma_a(\lambda)\}N_x(t)\} \qquad (1)$$

where L is the cell length, σ_a the ground-state absorption cross-section, σ_g^{LE} the difference of the stimulated emission σ_e^{LE} and the absorption cross section σ_u^{LE} of the LE state, σ_g^x that of the transient X state, and N_{LE} and N_x the LE and X states populations, respectively. If we consider a fast and unique deactivation process from LE towards X, leaving the total excited population $N_{LE}(t)+N_x(t)$ constant on a picosecond time scale, isosbestic points with $\Delta D = \text{constant} \neq 0$ are expected at wavelengths where $\sigma_g^{LE}(\lambda) = \sigma_g^x(\lambda)$.

For delay times longer than 4 ps (Fig. 6) both transient absorption and bleaching signal decay and at 50 ps delay the ground state absorption has almost completely recovered. The time-resolved spectra observed in decanol are shown in Fig. 7. As observed for EV and ARh, the spectral changes are similar to those observed in ethanol but they occur at a slower rate.

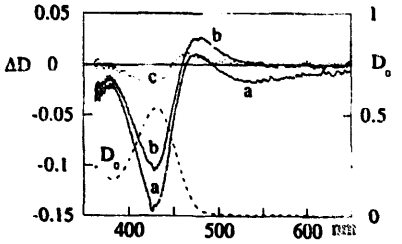

Fig. 6. Time-resolved photoinduced change in optical density (ΔD, left scale) of a solution of auramine in ethanol after subpicosecond excitation at 425 nm. Pump–probe delays: curve a, 4 ps; curve b, 10 ps; curve c, 50 ps. D_0, spectrum of the unexcited sample (right scale).

3.1.3. Relaxation mechanism and kinetics

The time-resolved spectra give evidence for the fast formation of a non-emissive transient species in the excited state in all compounds. One can thus conclude to a common relaxation mechanism in the three compounds and claim that comparison with ARh brings support to Rettig's proposal that the photoinduced process in di- and triphenylmethane dyes involves an excited state charge transfer [8,10,25,27]. Since Oster and Nishijima's work, the photoinduced process in di- and triphenylmethane dyes has been described as a barrierless process involving internal rotation of the phenyl rings. Bridged triphenylmethane dyes where the rotation of two phenyls is blocked were indeed found to have a fluorescence yield 10 to 60 times larger than the unbridged corresponding compounds [25]. We thus propose to illustrate the probed process in EV, ARh and Aur by Fig. 8.

The photoinduced charge-transfer reaction is described by an adiabatic process in the S_1 state involving the rotational motion of the substituted aniline moiety. The charge transfer is barrierless and a crossing of the excited and ground state potential curves is drawn in the region of the twisted CT state to explain its non-emissive character. When going from EV to ARh and Aur, the energy gap between S_0 and the locally excited state increases since the ground state absorption is blue shifted. The same shape of the excited state potential is assumed since the CT state formation time is about the same for the three compounds in ethanol (~4 ps for EV and Arh, ~3 ps for Aur). The formation time is smaller than the solvation time (16 ps in ethanol [48]) indicating the role of intramolecular modes in the CT process [49]. In Fig. 9, it is seen that the decay rate of the twisted CT state decreases exponentially when the S_1–S_0 energy gap increases from EV (~7 ps) to ARh (~13 ps) and Aur (~30 ps).

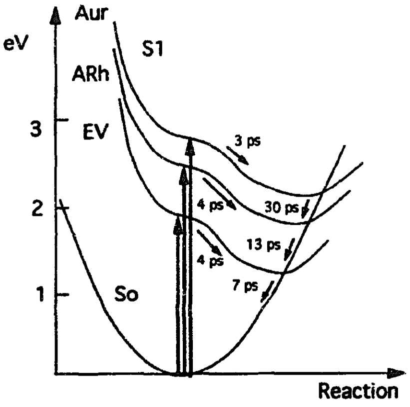

Fig. 8. Scheme of free energy curves illustrating the photoinduced adiabatic charge transfer in ethyl violet (EV) amino-rhodamine (ARh) and auramine (Aur) solutions in ethanol with similar kinetics. The free energy curve of the excited state is tuned to higher energies when going from EV to Aur. The charge transfer state is non emissive and its decay rate decreases when the energy gap between the free energy curves increases. The back charge transfer leading to the ground state is in the inverted regime.

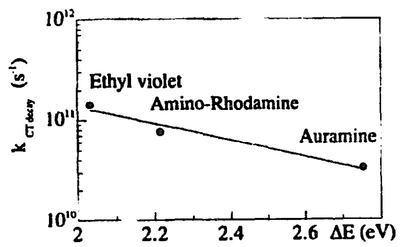

Fig. 9. Charge-transfer state decay rate of ethyl violet, amino-rhodamine and auramine plotted against the energy gap ΔE between the locally excited (LE) state and the ground state S_0. Assuming similar free energy curves in the excited state for the three molecules Fig. 8 the change in the LE–S_0 reflects the change in the free energy gap between the charge-transfer state and the ground state. The decay rate is found to decrease exponentially when ΔE increases.

It is worth comparing this result to the energy gap dependence found by Asahi et al. for the charge recombination (CR) rate of compact ion pairs [45]. The authors interpret their observation by analogy with the theory of radiationless transitions in the weak coupling limit [50,51], stressing the role of intramolecular high frequency modes in the charge recombination. From systematic investigations they could give evidence to a variation of k_{CR} proportional to $\exp(-\beta\Delta G^0)$, where ΔG^0 is the absolute value of the free energy gap between the contact ion pair and the ground state. The CT decay rate of EV, ARh and Aur are plotted in Fig. 9 against the LE–S_0 gap. As long as the S_1 adiabatic potential is roughly the same for the three compounds, the values of ΔG^0 are just shifted by a constant value from the LE–S_0 gap. The slope leads to a value of $\beta = 1.9$ eV^{-1} which is smaller than most of the values reported by Asahi et al. for several series of charge-transfer complexes [45]. Within this theory no solvent polarity effect is expected on the charge recombination rate. This was indeed previously observed for EV [12]. In decanol, both the rates for the CT state formation and the decay rates were found to decrease in the three compounds. From stationary experiments, solvent viscosity is expected to slow down the formation rate [17,21,22]. The observation of a slower decay of the CT state in a viscous solvent suggests that rotational diffusion of the phenyl rings is also involved in the deactivation pathway. These results may bring support to previous demonstrations that electron transfer in the inverted region requires not only solvent dynamics but also high- and low-frequency intramolecular modes [52].

3.2. Transient spectroscopy of the merocyanine dye DCM

The merocyanine dye DCM (V) exhibits a single, broad, intense and strongly red-shifted fluorescence band in polar solvents [32–34], which was attributed to a highly polar excited state ($\mu \sim 26$ D) [32,33]. On the other hand, this molecule undergoes trans–cis photoisomerization, but the photoisomerization yield decreases when the solvent polarity increases [33]. The formation of a polar TICT-like state in competition with the photoisomerization was proposed to explain the effect of solvent polarity [11,34]. Recently, several groups carried out ultrafast/fast spectroscopy experiments on DCM solutions [16,35–39,53]. The question whether the primary events probed in this molecule are the solvation of the excited state [35,37,38] or the rapid formation of a charge-transfer state [16,36,39] is much debated. Our results are in favor of the latter mechanism [16].

3.2.1. Evidence for a CT state formation

Fig. 10 shows the time-resolved spectra observed for a solution of DCM in the weakly polar solvent tetrahydrofuran (THF) within 5 ps after excitation. In this solvent the fluorescence Stokes shift is about 4400 cm^{-1}. For pump–probe delays from 1.5 to 4.5 ps, although no change in the population of the excited state is expected (nanosecond lifetime), the transient spectra exhibit the following changes: a red-shifted net gain band rises around 615 nm together with new differential absorption maxima around 540 nm and 420 nm. A temporary isosbestic point (constant ΔD for a given lapse of time at a given wavelength) in the time-resolved spectra is observed at 580 nm. For delays ranging between 5 and 40 ps, a further small evolution of the transient spectra is observed and was discussed in a previous publication by comparison with other solvents [16]. For delays longer than

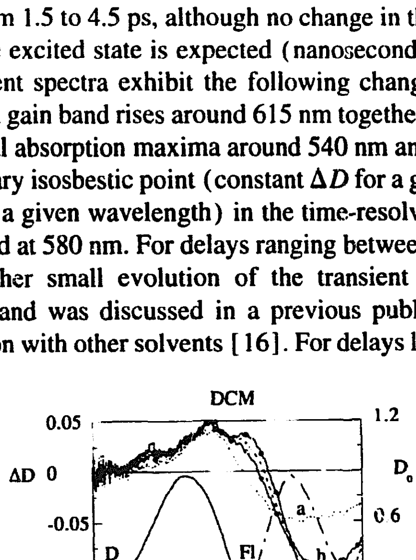

Fig. 10. Change in optical density (ΔD, left scale) of DCM solutions in tetrahydrofuran within 4.5 ps after excitation at 425 nm giving evidence to a temporary isosbestic point in the gain spectra at 580 nm: curve a, 0.5 ps; curve b, 1.5 ps; curve c, 2.5 ps; curve d, 4.5 ps. Unexcited solution optical density D_0 (right scale) and steady-state fluorescence spectra (Fl, arbitrary unit).

50 ps no major change in shape could be detected in the time-resolved spectra. At all wavelengths, the $\Delta D(t)$ curves have a nanosecond decay.

The observation of a temporary isosbestic point in the net gain spectra can be interpreted by Eq. (1), with the consecutive formation of two emissive states: LE and X. As long as the total excited-state population remains constant, a temporary isosbestic point can be observed at a wavelength where the difference $\sigma_g = \sigma_e - \sigma_u$ of the stimulated emission σ_e and the absorption cross-section σ_u of the LE state is the same as that of the transient state. The isosbestic point is observed for a negative Δ at wavelengths where the ground state does not absorb ($\sigma_a = 0$) indicating that at these wavelengths both LE and X states have positive σ_g and thus a dominant stimulated emission cross-section. The red-shifted gain maximum as well as the differential absorption rising at 540 nm (Fig. 10) can be attributed to the transient X state. When the solvent polarity is increased from THF to methanol and acetonitrile [16], the gain maximum is shifted from 615 to 650 nm, indicating that the intermediate X state is polar. These experimental facts support the hypothesis of the formation of an emissive CT state from the emissive LE state of DCM [34].

3.2.2. Charge-transfer kinetics and solvent dynamics

We made similar observations in various solvents and the lapse of time during which the temporary isosbestic point was observed was found to be solvent dependent [16]. This lapse of time does not depend only on the charge-transfer rate since spectral changes such as red-shift of the charge-transfer gain band due to solvation dynamics and narrowing due to vibrational cooling destroy the isosbestic point. However, the maximum amplitude of the transient absorption band at 540 nm that we attributed mainly to the CT state is reached in 2–3 ps in acetonitrile, ~4 ps in THF, ~8 ps in methanol or benzonitrile, and 12–15 ps in ethylene glycol, suggesting that solvation time [48,54] is an important parameter in the charge-transfer kinetics. In acetonitrile, the 540 nm band is already observed during the excitation pulse indicating that the charge-transfer rate has a subpicosecond component. It is worth noting that a temporary isosbestic point was recently reported by Ernsting's group for DCM in methanol, at a femtosecond time scale but at a shorter wavelength [39]. One may perhaps reconciliate their observation and ours by considering that the LE state decay is non-exponential and that femtosecond experiments provide an observation time window for the initiation of the LE → CT reaction, the isosbestic point between the LE and CT state gain spectra being rapidly destroyed by the solvation induced red-shift of the CT state gain spectrum, whereas picosecond experiments provide an observation window for the tail of the reaction monitoring the slowest part of the solvation dynamics.

3.2.3. Charge transfer and structural change

Concerning the hypothesis of a TICT nature of the emissive CT state, one cannot tell from our experiments whether the CT process is accompanied by single-bond twisting. A reaction involving internal rotation is not excluded. Information on the geometrical change in the course of a reaction is difficult to obtain by time-resolved electronic spectroscopy unless the spectra of the species involved are already well known.

Table 1
Fast component of the decay of the LE state of MAP in solvents of various dielectric constants ϵ and viscosity η

Solvents	t_{LE} (ps) ± 10%	ϵ	η (cP)
Dioxane	16	2.21 (25°) [a]	1.44 (15°) [a]
Diethylether	13	4.33 (20°) [a]	0.24 (20°) [a]
Ethyl acetate	11	6.02 (25°) [a]	0.43 (25°) [a]
THF	7	7.58 (25°) [a]	0.55 (20°) [a]
Triacetin	40	7.11 (20°) [b]	22 (20°) [b]
Ethanol	10	24.55 (25°) [a]	1.08 (25°) [a]
Acetonitrile	<3	37.50 (20°) [a]	0.37 (30°) [a]

[a] Ref. [56].
[b] Ref. [57].

3.3. Time-resolved fluorescence of MAP

The dimethylamino-phenyl diphenylphosphine (MAP, VI) can be viewed as a neutral triphenylmethane dye (II) with a phosphorous atom as the central atom [42]. This compound shows a single fluorescence band in non-polar solvents and one additional red-shifted band in polar solvents [18,19,42]. In a solvent of medium polarity, the steady state spectrum could be decomposed into two sub-bands and from the observed polarity-dependent Stokes shift, the long-wavelength band could be attributed to a highly polar excited state ($\mu \sim 20$ D) [18,19]. A precursor–successor relationship LE → CT could be established from fluorescence decay measurements in both the short-wavelength and the long-wavelength region of the steady state spectrum [18,19]. Furthermore, both selected spectral regions show the same long (ns) decay component indicating that a rapid equilibrium establishes between the LE state and CT state populations during the excited lifetime.

3.3.1. Solvent polarity and CT kinetics

The short-lived component of the LE state decay is given in Table 1 for solvents of increasing dielectric constant. It is seen that the charge-transfer rate increases with polarity in non-protic solvents [18,19], which is expected for a barrier crossing CT process in the Marcus normal region. Assuming a pre-exponential factor of 10^{12} to 10^{13} s^{-1} for the rate constant, the barrier in THF is estimated at about 2 kcal mole^{-1}. In the polar protic ethanol, the LE state decay is found to be slower than in the less polar THF. In DMABN, the C state formation process is known to possess a higher activation barrier in protic solvent. This was attributed to the decrease of the electron-donor character of the dimethylamino group as the result of hydrogen bonding with the solvent [55]. This may also explain our result.

3.3.2. Solvent viscosity and CT kinetics

In triacetin which has the same polarity as THF but has a viscosity 40 times larger, the fast decay of the LE band is slowed down by a factor of 6 whereas we found a factor of 1.5 for DMABN [18,19]. Solvent viscosity effects on MAP were also reported in alcohols at high pressures [43]. As discussed above the solvent–viscosity effect on the excited state decay of triphenylmethane dyes is explained by the friction that the solvent opposes to the phenyl ring rotation [21,22]. A similar process may be involved for the charge-transfer process in MAP [42]. Furthermore, since MAP has a pyramidal shape, the phenyl ring rotation may be hindered by internal constraint. This constraint could be the source of an intramolecular barrier to the CT process, although more complex structural change involving the pyramid opening cannot be ruled out [19].

4. General discussion

The experiments described above are in favor of a photoinduced mechanism involving intramolecular charge shift or charge transfer in the three classes of compounds examined here. Di- and tri-phenylmethane dyes as well as amino-rhodamine provide examples for barrierless adiabatic reactions leading to a non emissive charge-transfer state. The laser dye DCM and the substituted triphenylphosphine MAP provide examples for quasi-barrierless and small barrier activated reactions leading to an emissive charge-transfer state. In all cases intramolecular dynamics and solvent dynamics are likely to be involved, although the direct characterization of solute structural changes which are supposed to accompany the reaction remains to be made. Many experimental and theoretical studies were devoted to the role of solvent dynamics in electron transfer reaction kinetics during the last fifteen years. Describing the solvent as a dielectric continuum, theoretical treatments [58–60] evidenced that the upper limit for the electron transfer rate should be the reverse of the longitudinal relaxation time τ_L. By considering both intramolecular and solvent dynamics Sumi and Marcus [49] found that for reactions which require more solvent reorganization energy than nuclear reorganization energy the reactant decay may be non exponential with an initial component shorter than τ_L. Grote and Hynes [61] showed that for activated reactions the friction that a solvent opposes to the barrier crossing is determined by events on the time scale of the reciprocal of the barrier frequency and the role of short time-range solvent dynamics in barrier crossing electron transfer reactions in non-Debye solvents was stressed [62]. From experimental studies of dipole solvation dynamics by time-resolved fluorescence Stokes shift and molecular dynamic simulation it is now well-known that solvent dynamics occur on various time scales and average solvation times (τ_s) are given for a variety of solvents (see references in Refs. [48,54]). Ultrafast spectroscopy experiments on bianthryl gave evidence for solvent controlled charge-transfer processes with the rates being that of solvation [63]. On the other hand, recent investigations showed that the electron transfer reactions in the inverted regime require three degrees of freedom involving solvent motion and both low- and high-frequency intramolecular modes [52]. Theoretical description of photoinduced TICT reactions taking into account both intramolecular twisting and solvent frequencies were applied to DMABN. The results could give evidence to solvent-dependent paths on a two-dimensional excited state free energy surface [44].

In this work, the rate found for the barrierless charge-transfer process in EV, ARh and Aur in ethanol is larger than $1/\tau_s$, which indicates the role of intramolecular modes in the charge-transfer reaction. The tentative explanation of the CT state relaxation rate in terms of energy gap law indicates the role of intramolecular high-frequency modes in the charge recombination process and the decrease of the rate in decanol indicates the role of long time-range solvent dynamics likely as a friction opposed to the phenyl ring rotation. From our experiments, it is difficult to extract the charge-transfer rate in DCM but the solvation time appears to be an important parameter in the observed spectral changes. It is worth noting that DCM was used as a molecular component of a fluoroionophore for cation sensing applications [64], and the possibility of using the photoinduced charge transfer as a trigger for cation ejection was studied [65,66]. The absence of well-known viscosity effect on the fluorescence yield of this molecule might indicate that the charge-transfer process does not involve large amplitude structural change such as the rotation of the whole anilino group. The charge-transfer rate observed for MAP in weakly polar solvents is smaller than $1/\tau_s$ and the rate is likely to be controlled by a small intramolecular activation barrier. The viscosity effect observed in medium polarity solvents can thus be explained by the role of the long time-range of the solvent dynamics in the crossing of the small barrier [61]. In acetonitrile, where the process is expected to be quasi-barrierless, the rate is too rapid to be accurately measured with our streak camera, it might be controlled by the subpicosecond solvent dynamics.

5. Conclusion

Time-resolved transient absorption and gain spectroscopy with subpicosecond excitation and time-resolved fluorescence decay measurements with a streak camera were applied to the study of the photoinduced processes in three classes of flexible donor–acceptor compounds all containing one anilino group as the electron donor. The experiments give evidence for the fast formation of a transient state through a barrierless or small barrier activated process in all cases. The transient state could be attributed to an emissive charge-transfer state in the cases of the laser dye DCM and the dimethylamino-substituted triphenylphosphine MAP, and to a non emissive charge-transfer state in the case of the amino-rhodamine ARh. By comparison with the latter compound formation of a non-emissive charge-transfer state was also concluded for the di-phenylmethane auramine and the triphenylmethane ethyl violet. No direct information could be obtained on the structural changes which were deduced from the observed viscosity effect. In several cases the observed charge-transfer kinetics was found to be faster than the solvation time indicating the role of intramolecular modes in the reaction. These studies support the assumption of a common mechanism proposed for these compounds [10].

Acknowledgements

This work was supported in part by the Chemistry Department of CNRS-France (GDR 1017). The authors acknowledge helpfull discussions with Prof. J. T. Hynes.

References

[1] Z.R. Grabowski, K. Rotkiewicz, W. Rubaszewka and E. Kirkor-Kaminska, Acta Phys. Pol. A, 54 (1978) 767.

[2] Z.R. Grabowski and J. Dobkowski, Pure Appl. Chem., 55 (1983) 245.

[3] Y. Wang, M.Mc Auliffe, F. Novak and K.B. Eisenthal, J. Phys. Chem., 85 (1981) 3736

[4] F. Heisel and J.A. Miehé, Chem. Phys. Lett., 100 (1983) 183.

[5] F. Heisel, J.A. Miehé and J.M.G. Martinho, Chem. Phys., 98 (1985) 243. F. Heisel and J.A. Miehé, Chem. Phys. Lett., 128 (1986) 323.

[6] C. Rullière, Z.R. Grabowski and J. Dobkowski, Chem. Phys. Lett., 137 (1987) 408.

[7] T. Okada, N. Mataga and W. Baumann, J. Phys. Chem., 91 (1987) 760.

[8] V. Bonacic-Koutecky, F. Heisel, E. Lippert, J.A. Miehé and W. Rettig, Adv. Chem. Phys., 68 (1987) 1.

[9] T. von der Haar, A. Hebecker, Y. Il'Ichev, W. Kühnle and K.A. Zachariasse, in A. Tramer (ed.), Fast Elementary Processes in Chemical and Biological Systems, AIP, 1996, p. 295.

[10] W. Rettig, Angew. Chem. Int. Ed. Engl., 25 (1986) 971.

[11] W. Rettig, W. Majenz, R. Lapouyade and G. Haucke, J. Photochem. Photobiol. A: Chem., 62 (1992) 415.

[12] M.M. Martin, E. Bréhéret, F. Nesa and Y.H. Meyer, Chem. Phys., 130 (1989) 279.

[13] M.M. Martin, P. Plaza and Y.H. Meyer, Chem. Phys., 153 (1991) 297

[14] M.M. Martin, P. Plaza and Y.H. Meyer, J. Phys. Chem., 95 (1991) 9310.

[15] M.M. Martin and P. Plaza, in Y. Gauduel and P.J. Rossky (ed.), Ultrafast Reaction Dynamics and Solvent Effects, Vol.298, American Institute of Physics, New York, 1994, p. 410.

[16] M.M. Martin, P. Plaza and Y.H. Meyer, Chem. Phys., 192 (1995) 367.

[17] P. Plaza, N. Dai Hung, M.M. Martin, Y.H. Meyer, M. Vogel and W. Rettig, Chem. Phys., 168 (1992) 365.

[18] P. Changenet, P. Plaza, M.M. Martin, Y.H. Meyer and W. Rettig, in A. Tramer (ed.), Fast Elementary Processes in Chemical and Biological Systems, AIP, 1996, p. 363.

[19] P. Changenet, P. Plaza, M.M. Martin, Y.H. Meyer and W. Rettig, J. Chim. Phys., (1996) in press.

[20] M. Vogel, W. Rettig, R. Sens and K.H. Drexhage, Chem. Phys. Lett., 147 (1988) 452.

[21] G. Oster and Y. Nishijima, J. Am. Chem. Soc., 78 (1956) 1581.

[22] T. Förster and G. Hoffman, Z. Phys. Chem. N.F., 75 (1971) 63.

[23] V. Sundström and T. Gillbro, J. Chem. Phys., 81 (1984) 3463.

[24] B. Bagchi, G.R. Fleming and D.W. Oxtoby, J. Chem. Phys., 78 (1983) 7375.

[25] M. Vogel and W. Rettig, Ber. Bunsenges. Phys. Chem., 89 (1985) 962.

[26] D. Ben-Amotz and C.B. Harris, Chem. Phys. Lett., 119 (1985) 305.

[27] M. Vogel and W. Rettig, Ber. Bunsenges. Phys. Chem., 91 (1987) 1241.

[28] D. Ben-Amotz and C.B. Harris, J. Chem. Phys., 86 (1987) 4856.

[29] D. Ben-Amotz and C.B. Harris, J. Chem. Phys., 86 (1987) 5433.

[30] T. Robl and A. Seilmeier, Chem. Phys. Lett., 147 (1988) 544.

[31] D.F. Duxbury, Chem. Rev., 93 (1993) 381.

[32] M. Meyer and J.C. Mialocq, Opt. Commun., 64 (1987) 264.

[33] M. Meyer, J.-C. Mialocq and B. Perly, J. Phys. Chem., 94 (1990) 98.

[34] W. Rettig and W. Majenz, Chem. Phys. Lett., 154 (1989) 335.

[35] D.C. Easter and A.P. Baronavski, Chem. Phys. Lett., 201 (1993) 153.

[36] H. Zhang, A.M. Jongman, P. van der Meulen and M. Glasbeek, Chem. Phys. Lett., 224 (1994) 551.

[37] S. Pommeret, T. Gustavsson, R. Naskrecki, G. Baldacchino and J.C. Mialocq, J. Mol. Liq., 64 (1995) 101.

[38] T. Gustavsson, G. Baldacchino, J.C. Mialocq and S. Pommeret, Chem. Phys. Lett., 236 (1995) 587.

[39] N.P. Ernsting, private communication; S.A. Kovalenco, N.P. Ernsting and J. Ruthmann, in press.

[40] J.F. Létard, R. Lapouyade and W. Rettig, J. Amer. Chem. Soc., 115 (1993) 2441.

[41] R. Lapouyade, A. Kuhn, J.F. Letard and W. Rettig, Chem. Phys. Lett., 208 (1993) 48.

[42] M. Vogel, W. Rettig and P. Heimbach, J. Photochem. Photobiol. A: Chem., 61 (1991) 65.

[43] K. Hara, N. Kometani and O. kajimoto, J. Phys. Chem., 100 (1996) 1488.

[44] T. Fonseca, H.J. Kim and J.T. Hynes, J. Photochem. Photobiol. A: Chem., 82 (1994) 67.

[45] T. Asahi, M. Ohkohchi and N. Mataga, J. Phys. Chem., 97 (1993) 13132.

[46] N. Dai Hung, P. Plaza, M.M. Martin and Y.H. Meyer, Appl. Opt., 31 (1992) 7046.

[47] B. Valeur, in S.G. Schulman (ed.), Molecular Luminescence Spectroscopy, Vol.77, Wiley, New York, 1993, p. 25.

[48] M.L. Horng, J.A. Gardecki, A. Papazyan and M. Maroncelli, J. Phys. Chem., 99 (1995) 17311.

[49] H. Sumi and R.A. Marcus, J. Chem. Phys., 84 (1986) 4894.

[50] R. Englman and J. Jortner, J. Mol. Phys., 18 (1970) 145.

[51] K. Freed and J. Jortner, J. Chem. Phys., 52 (1970) 6272.

[52] G.C. Walker, E. Akesson, A.E. Johnson, N.E. Levinger and P.F. Barbara, J. Phys. Chem., 96 (1992) 3728.

[53] P. van der Meulen, H. Zhang, A.M. Jongman and M. Glasbeek, J. Phys. Chem., 100 (1996) 5367.

[54] M. Maroncelli, P.V. Kumar, A. Papazyan, M.L. Horng, S.J. Rosenthal and G.R. Fleming, in G. Y and R.P. J (eds.), Ultrafast Reaction Dynamics and Solvent Effects, Vol.298, American Institute of Physics, New York, 1994, p. 310.

[55] F.H. Long and K.B. Eisenthal, in M.A. El-Sayed and I. Tanaka and Y. Molin (eds.), Ultrafast Processes in Chemistry and Photobiology, Blackwell Science, London, 1995, p. 129.

[56] J.A. Riddick and W.B. Bunger, Organic Solvents, Wiley-Interscience, New York, 1970, p. 1041.

[57] Y.J. Chang and E.W.J. Castner, J. Chem. Phys., 99 (1993) 7289.

[58] L.D. Zusman, Chem Phys, 49 (1980) 295.

[59] H. Frauenfelder and P.G. Wolynes, Science, 229 (1985) 337.

[60] I. Rips and J. Jortner, J. Chem. Phys., 87 (1987) 2090.

[61] R.F. Grote and J.T. Hynes, J. Chem. Phys., 76 (1980) 2715.

[62] J.T. Hynes, J. Phys. Chem., 90 (1986) 3701.

[63] T.J. Kang, W. Jarzeba, P.F. Barbara and T. Fonseca, Chem. Phys., 149 (1990) 81.

[64] J. Bourson and B. Valeur, J. Phys. Chem., 93 (1989) 3871.

[65] M.M. Martin, P. Plaza, N. Dai Hung, Y.H. Meyer, J. Bourson and B. Valeur, Chem. Phys. Lett., 202 (1993) 425.

[66] M.M. Martin, P. Plaza, Y.H. Meyer, F. Badaoui, J. Bourson, J.P. Lefevre and B. Valeur, J. Phys. Chem., 100 (1996) 6879.