Ultrafast Photochemistry

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Abstract: Several aspects of ultrafast photochemistry in the condensed phase are discussed and illustrated by three examples from our laboratory.

Keywords: Photoinduced electron transfer · Solvation dynamics · Ultrafast processes · Upper excited states · Vibrational relaxation

1. Introduction

With the impressive development of laser technology, it is now possible to routinely generate ultrashort laser pulses from the UV to the IR. Therefore, over the past few years the number of research groups entering the field of ultrafast spectroscopy has exhibited an impressive growth [1]. This enthusiasm is due not only to the progress in technology but essentially to the fact that the femtosecond timescale is the timescale of chemistry. Indeed, nuclear motion over a few Å, which is the essence of a chemical reaction, occurs in a few tens of fs. After more than 50 years of improvement in time resolution [2], we have now the unprecedented opportunity to follow the detailed dynamics of a chemical reaction in real-time [3]. Moreover, the ability to control a chemical process by using ultrashort tailored pulses of light has been demonstrated [4].

In the liquid phase, processes such as solvent motion, vibrational cooling and vibrational dephasing occur typically in the 100 fs–10 ps range. Therefore, when considering a chemical process taking place in this ultrashort domain, the chemist can no longer think in terms of thermal equilibrium, but has to consider effects arising from coherence (electronic and especially vibrational) and from non-equilibrium. Consequently, the dynamics of an ultrafast photochemical reaction may strongly depend on the preparation of the initial excited state or, in other words, on the temporal and spectral characteristics of the excitation pulse.

It follows that several famous rules of photochemistry [5] no longer really hold when the photochemistry is ultrafast: the emission quantum yield may depend on the excitation wavelength in opposition to Vavilov's rule and upper excited states may do chemistry contrary to Kasha's rule.

The alleviation of these rules opens to the photochemist new dimensions to explore. When ultrafast, the photochemistry is no longer limited to the lowest singlet or triplet excited state in the vibrational ground state but can occur from upper electronic and/or vibrational excited states. Until now, this potential has barely been exploited. This is not due to the lack of ultrafast photochemical processes, but rather to our limited knowledge on the dynamics of upper excited states and of energy dissipation in the condensed phase.

In the following, we will try to illustrate these aspects by three examples from our laboratory.

2. Methodology

The most widely used experimental techniques for investigating ultrafast photo-induced processes in the condensed phase are certainly transient absorption and emission spectroscopies. Being background-free, fluorescence is very sensitive but is limited to emitting species. Absorption does not suffer from this limitation but is much less sensitive. Over the past years, we have been using and developing transient grating techniques [6], which combine the advantages of both absorption and emission spectroscopies. These four wave-mixing techniques (2 pump beams, 1 probe beam and 1 signal beam) are background-free and sensitive to the photoinduced changes of both absorbance and refractive index of the sample [7]. Another advantage, which is especially important in the sub-picosecond timescale is that, by controlling the wavelength, the polarisation or the timing of the different interacting laser pulses, one can easily shift from a transient absorption-type experiment to a CARS or to a photon echo experiment [8].

However, transient grating techniques do not completely replace the more conventional spectroscopies and therefore transient absorption and fluorescence up-conversion measurements are also routinely performed in our laboratory.

3. Results and Discussion

### 3.1. *The First Few Picoseconds of an Exciplex's Lifetime*

Since their first observation about 40 years ago [9], exciplexes have been very extensively studied [10]. In spite of this, there is still no direct information on their geometry [11] and on the early events following their formation. The absence of data on the latter question can be understood by considering the Scheme, which shows

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that exciplex formation requires the diffusional encounter of a molecule in an excited state, M*, and a quencher in the ground state, Q. As the exciplex is mainly stabilised by charge transfer interaction [10], its electronic structure is close to that of a radical ion pair. Consequently, the reaction from the encounter complex to exciplex can be assimilated to a charge separation (CS) process. In a typical organic solvent, the diffusional step requires several tens of ps. Moreover, when thermodynamically favourable, the CS step is in most cases much faster than diffusion, and no direct information on its dynamics can be obtained. Therefore, the time dependence of the exciplex population exhibits an initial rise with a time constant close to that for diffusional encounter. Most exciplexes are relatively long lived and decay in the ns timescale.

One way of investigating the intrinsic CS dynamics is to eliminate the diffusion step by using the quencher as the solvent. This approach has been used by several groups to study the ultrafast dynamics of bimolecular electron transfer (ET) in electron donating solvents [12]. In those cases however, the product was a genuine ion pair and thus no exciplex emission was observed.

We are investigating the dynamics of CS in electron donating solvents like anilines using weaker electron acceptor molecules, such as perylene (Pe) and cyanoperylene (CPe). Referring to the Scheme, M is the acceptor, Q is the electron donating solvent and the diffusion step is eliminated, M and Q being in contact. The fluorescence spectrum obtained after excitation of CPe in N,N-dimethylaniline (DMA) is shown in
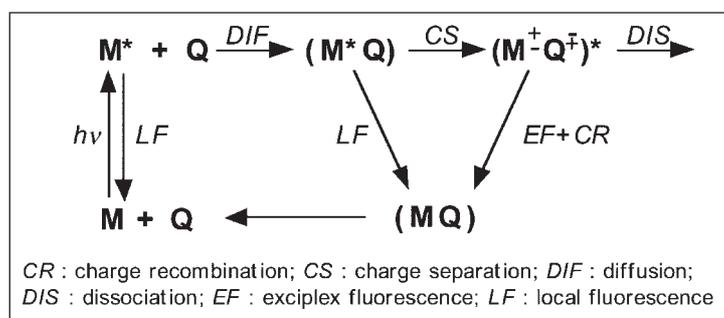
Fig. 1A. As a comparison, the fluorescence spectrum of CPe* in a non-reacting solvent, toluene, is also shown. The band below 550 nm is the local fluorescence of CPe*, while the broad band above 550 nm originates from the $(CPe^{·-}DMA^{·+})^*$ exciplex. Fig. 1B shows the early fluorescence dynamics measured by up-conversion at four different wavelengths in this exciplex band upon excitation of CPe. For comparison, the fluorescence dynamics at 500 nm, due to the local fluorescence of CPe* in DMA, is also shown. From this decay, the time constant of CS is about 300 fs. The time profile of the exciplex emission is strongly wavelength dependent. At short wavelength, an intense and fast decay component with a time constant around 4 ps is observed. It becomes weaker and slower as the wavelength increases and at 675 nm, a weak rising component appears. This wavelength dependence corresponds to a temporal variation of the exciplex fluorescence spectrum during the first few ps: a decrease of the band intensity and a shift to longer wavelengths. After this, the spectrum remains unchanged and is essentially the same as that measured by steady state fluorescence. This initial spectral dynamics can be ascribed to the transition from an exciplex in the geometry of the neutral reactant having a relatively small charge transfer character to an equilibrated ex-ciplex with a larger charge transfer. This process involves reorientational motion of the reaction partners and of the surrounding solvent molecules as well. As solvation occurs, the exciplex is stabilised and its emission spectrum shifts toward longer wavelengths, a process known as dynamic Stokes shift. Moreover, the degree of charge transfer of an exciplex is known to increase with the solvent polarity. This increase is accompanied by a decrease of the oscillator strength for the emission, *f*. The initial decrease of the band intensity observed here corresponds precisely to a solvation induced transition from a weakly polar, excimer-like, exciplex (relatively large *f*) to a highly polar, ion pair-like, exciplex (smaller *f*). This interpretation is supported by multiplex transient grating experiments, where the absorption spectrum of the primary product was monitored [13]. In this case, the anion part of the exciplex (CPe$^{·-}$) was found to become narrower and more intense with time, confirming that the exciplex is getting more ion-pair like.

These ultrafast spectroscopy experiments have allowed us to observe the fine details of a CS process and the formation of a very important intermediate in photochemistry.

CR : charge recombination; CS : charge separation; DIF : diffusion;
DIS : dissociation; EF : exciplex fluorescence; LF : local fluorescence
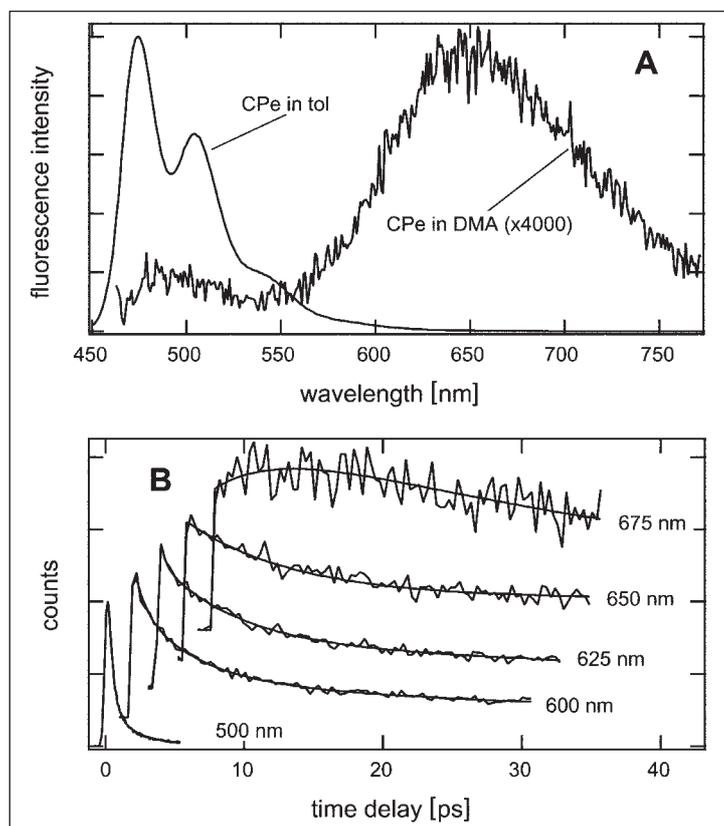
Scheme

Fig. 1. A) Emission spectra of CPe in toluene and in DMA. B) Time profiles of the normalised fluorescence intensity measured at several wavelengths with CPe in DMA.

3.2. *Nonequilibrium Effects on the Free Energy Dependence of Charge Recombination Dynamics*

In the above example, the emission measured during the first few ps is due to the non-equilibrated exciplex. Apart from the initial spectral changes, the formation of the exciplex out of equilibrium has no influence on its population dynamics, because the latter is very slow. We will now discuss an example where the population dynamics is so fast that it occurs almost completely out of equilibrium [14].

Fig. 2 shows the multiplex TG spectrum measured after excitation with a 30 fs pulse at 530 nm in the charge transfer band of a donor–acceptor complex (DAC) composed of 1,2,4-trimethoxybenzene (TMB) and pyromellitic dianhydride (PMDA) in valeronitrile (VaCN). The nature of a TG spectrum has been discussed in detail in [6b,c]. Practically, a TG spectrum is similar to the corresponding transient absorption spectrum, the major difference being that the former is always positive and background-free. The excited state of a DAC is essentially a geminate ion pair (GIP) and therefore the intense band in Fig. 2 originates from PMDA$^{\cdot-}$. The decay of the band is due to charge recombination (CR) to the ground state and occurs with a time constant of 770 fs. Fig. 3 shows cuts through the free energy surfaces of the ground and excited states of a DAC along the solvation coordinate. For TMB-PMDA in VaCN, the free energy gap, ΔG_{CR}, amounts to 1.7 eV and therefore optical excitation with a 530 nm photon (E = 2.3 eV) populates the excited state far from equilibrium. Relaxation to the equilibrium, which involves not only solvent modes but also intramolecular and intracomplex degrees of freedom, occurs on several timescales. After intramolecular vibrational relaxation in a few tens of fs, the vibrationally hot excited molecules cool down in a few ps by interaction with the surrounding medium. Solvent relaxation proceeds *via* both inertial motion occurring in about 100 fs and diffusive motion, which is viscosity dependent and takes place with a time constant of about 5 ps in the case of VaCN [15]. This implies that, for TMB-PMDA in VaCN, CR occurs while the excited complex is still hot and before the solvent has fully relaxed.

Another indication for the occurrence of nonequilibrium dynamics is that the measured CR time constant depends on the excitation wavelength. Indeed, it decreases from 1 ps to 680 fs upon varying the excitation wavelength from 400 to 550 nm. This indicates that the further the excited state is populated from equilibrium, the slower is the CR. This can be understood by considering the semi-classical theory of non-adiabatic ET [16] (see Fig. 3). A high-energy photon prepares the excited state very far from equilibrium and the initial value of the Franck-Condon (FC) factor is small, hence the probability for CR is weak. As the system relaxes, the FC factor increases and, if it reaches values allowing CR to compete with relaxation, CR can occur before equilibrium is reached. Excitation with a less energetic photon prepares the excited state in a region where the FC factor is larger and therefore CR is faster.

Fig. 4A shows the free energy dependence of the CR rate constant measured with DACs composed of PMDA and methoxybenzene derivatives in VaCN after excitation at 400 nm [14]. The broken line is the prediction of a theoretical model, which takes non-equilibrium dynamics into account [17]. The solid line is the prediction of non-adiabatic ET theory, where CR is only possible from equilibrium. In this model, CR cannot be faster than solvation and therefore the plateau observed in the free energy dependence corresponds to the inverse solvation time of VaCN. The observed rate constants lie all above this plateau, indicating the occurrence of nonequilibrium CR. Another major difference between these two models can be observed in the weak driving force regime ($-\Delta G_{CR} < 1$ eV): the 'equilibrium model' predicts a decrease of the CR rate constant with decreasing driving force, while the 'nonequilibrium model' predicts the opposite. The origin of this difference can be easily understood by considering the potential curves illustrated in Fig. 4B. In the equilibrium model, the weakly exergonic CR is a thermally activated process with an activa-
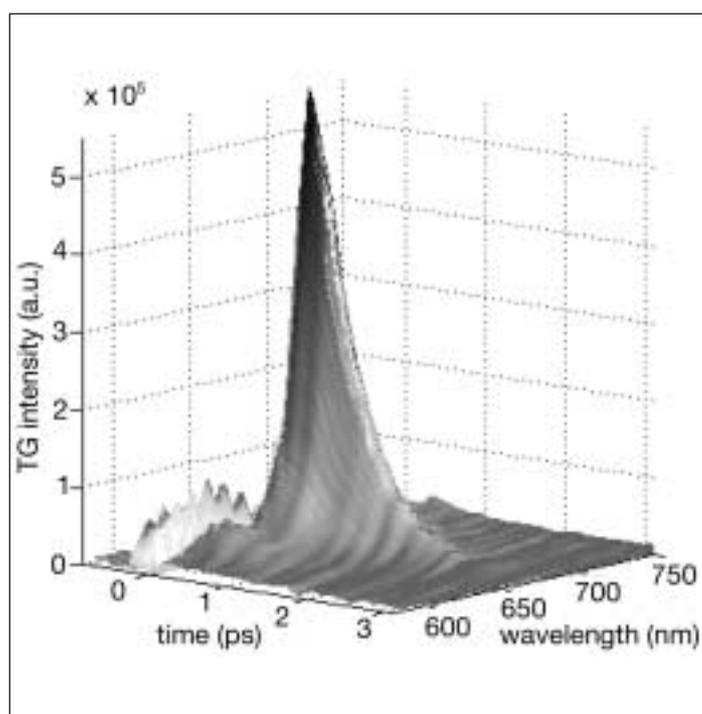

Fig. 2. Multiplex transient grating spectrum measured after excitation with a 30 fs pulse at 530 nm in the charge transfer band of the TMB/PMDA complex in VaCN. The weak spectral feature at time zero is due to the optical Kerr effect of the solvent.
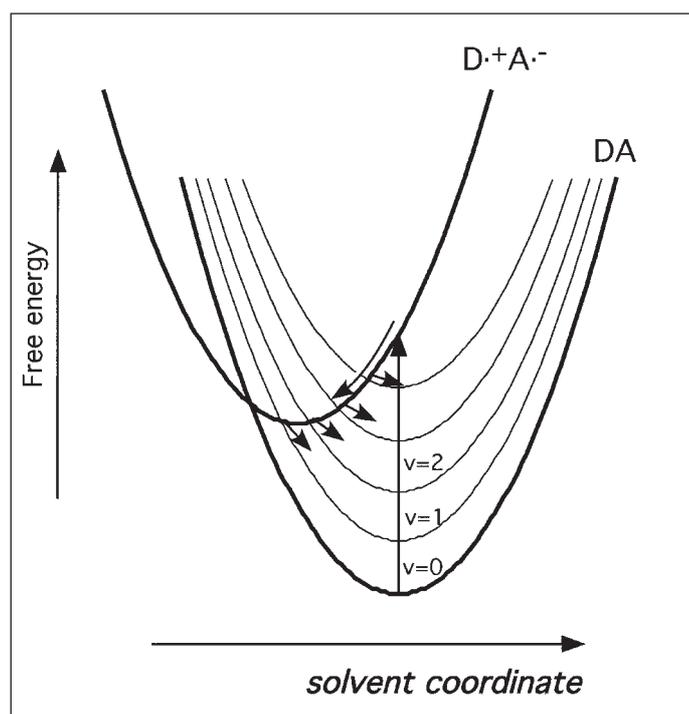

Fig. 3. Cuts in the free energy surfaces of the ground and excited states of a DAC along the solvation coordinate. The thin parabolas correspond to vibrational excited states of the electronic ground state.

tion barrier increasing with decreasing driving force (path 1). In the nonequilibrium model, CR can occur before the excited state population is trapped in the equilibrium configuration (path 2). Several years ago, Mataga and co-workers have indeed reported rate constants for weak exergonic CR much faster than predicted by equilibrium models [18]. Several very different hypothesis have been proposed to account for this discrepancy [19]. Our investigation clearly indicates that this behaviour originates to a large extent from nonequilibrium effects.

This investigation has shown that the preparation of the reactant strongly influences the CR dynamics. At the moment, we are only investigating the effect of the excitation energy. The next step is to study the influence of the pulse shape, in order to test the feasibility of coherent control on such a system.

3.3. *CS from an Upper Excited State Followed by CR to an Excited State*

As discussed above, ET theory predicts that, in the high exergonicity regime ($-\Delta G_{ET} > 1.5$ eV), the ET rate constant de-creases with increasing driving force (inverted region). However, this effect has never been observed for diffusional CS between two neutral molecules. To account for this discrepancy, it has been suggested that the product – the radical ions – is formed in an electronic excited state and therefore the ET is no longer highly exergonic. The detection of excited radical ions in liquids is very difficult due to their lack of emission and to their very short lifetime [20]. Consequently, to test the above hypothesis, we have investigated the opposite reaction, *i.e.* the formation of an excited neutral product upon CR of two radical ions, initially formed by ET quenching of a molecule in the second singlet excited state [21]. As shown in Fig. 5, the ensuing geminate ion pair has two possible CR pathways: a) a highly exergonic one to the neutral ground state and b) a moderately exergonic one resulting in the formation of one of the neutral product molecules in an electronic excited state. Fig. 6A shows the decay of the S_2 fluorescence of Zn-tetraphenylporphine (ZnTPP) in toluene with and without the electron donor 1,2,4-trimethoxybenzene (TMB) [22]. In toluene,

the S_2 lifetime of ZnTPP amounts to 1.5 ps while in the presence of a high TMB concentration, the decay is biexponential with 1.5 ps (40%) and 370 fs (60%) components. Moreover, the initial intensity is reduced, indicating that an important fraction of the quenching occurs in less than 100 fs and cannot be resolved in this experiment. Fig. 6B shows the early dynamics of the S_1 fluorescence in toluene with and without TMB. In toluene, the S_1 risetime is equal to the S_2 lifetime and corresponds to the S_2–S_1 internal conversion. In the presence of quencher, it is much faster and amounts to 460 fs. Moreover, the amplitude of the signal after the initial rise is independent of the presence of quencher. This indicates that after the ultrafast S_2 fluorescence quenching, the resulting ion pair undergoes CR in a few hundreds of fs to the neutral product in the excited state, ZnTPP*(S_1)+D. If CR to the neutral ground state (path a) was also operative, the amplitude of the S_1 fluorescence would be strongly reduced, contrary to the observation. If an excited product can be formed in a CR reaction, there is no evident reason why this should not also be the case for a highly exergonic CS process. However, the experimental proof that this also happens in a CS remains a challenging task. We are presently designing new experiments that should hopefully answer this question. For example, we can now measure the ground state recovery dynamics of a radical ion excited at different time delays after its formation by photoinduced ET. Fig. 7 shows the dynamics of ground state recovery upon excitation with a 30 fs pulse of the perylene radical cation, 1 ns after its formation by photoinduced ET with an electron acceptor. Our preliminary measurements indicate that these dynamics exhibit a marked dependence on the 'age' of the cation.

4. Concluding Remarks

We have tried here to give a flavour of what ultrafast spectroscopy can bring to the photochemist. The first example showed that it is possible to follow in real time all the details of a photochemical reaction, from the decay of the excited reactant to the formation of the 'hot' product followed by
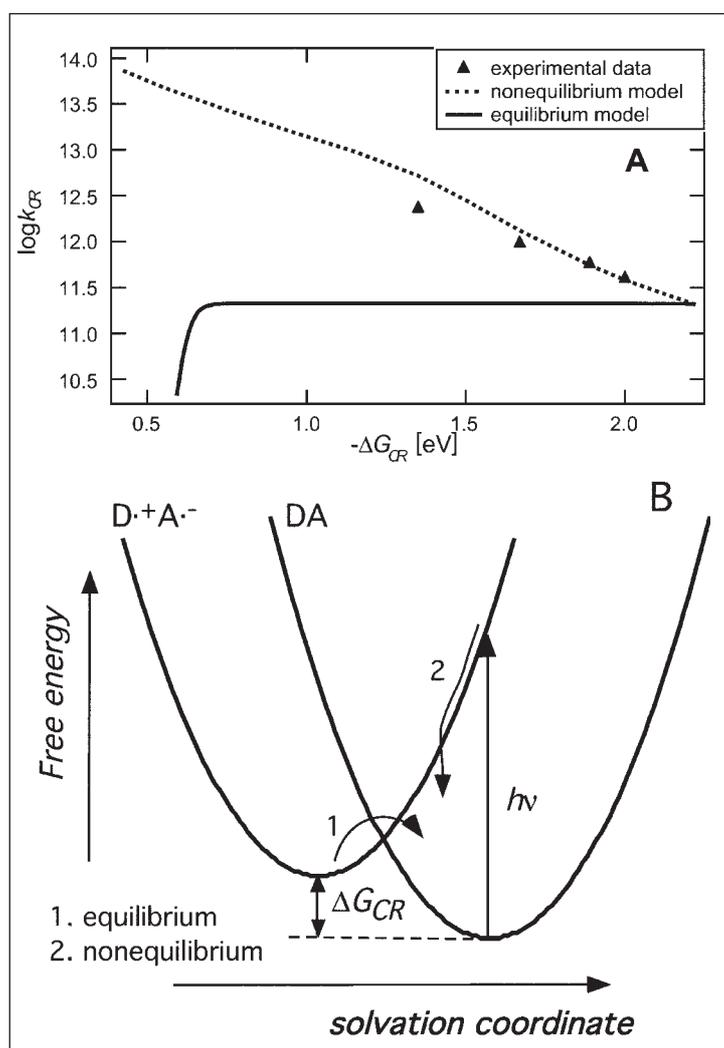

Fig. 4. A) Comparison of the observed free energy dependence of the CR rate constant of excited DACs with those predicted using nonequilibrium and equilibrium models. B) Cuts in the free energy surfaces of the ground and excited states of a DAC along the solvent coordinate in the case of a weakly exergonic CR.
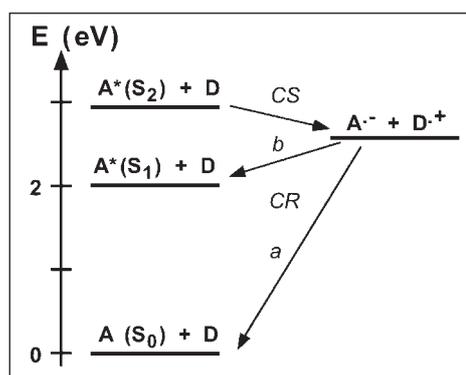
Fig. 5. Energy diagram of the states involved in the photoinduced electron transfer of ZnTPP (A) with an electron donor (D). (CS: charge separation; CR: charge recombination).
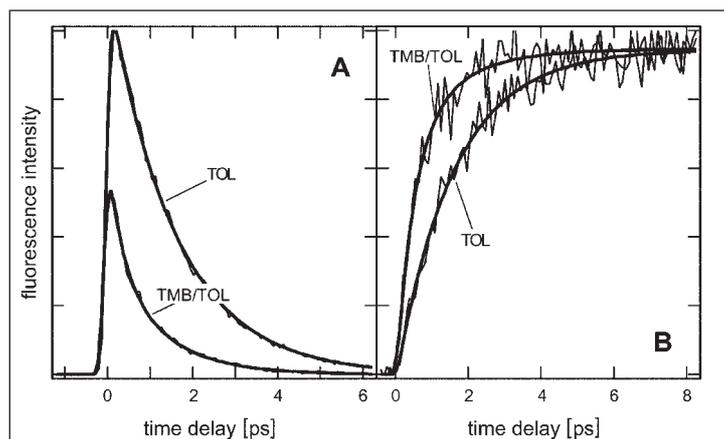

Fig. 6. Time profiles of the S_2 (A) and S_1 (B) fluorescence of ZnTPP in toluene and in a 1:1 TMB/toluene mixture.
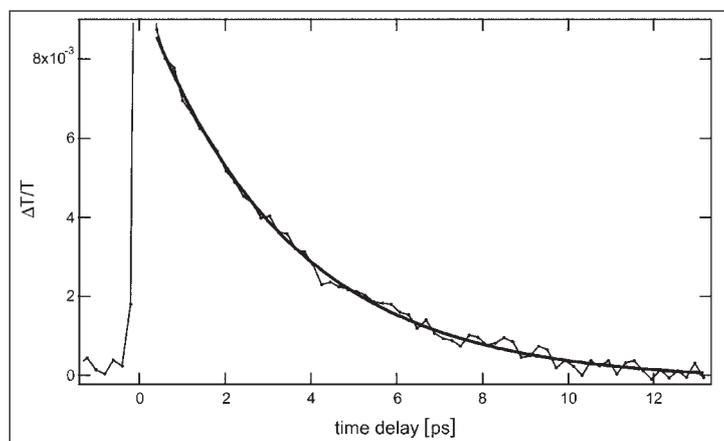

Fig. 7. Ground state recovery dynamics of perylene radical cation excited at 540 nm 1 ns after its formation by photoinduced ET with an electron acceptor in acetonitrile.

its relaxation to the equilibrium. As illustrated by the second example, the finite relaxation time of a photoexcited reactant can strongly influence its reaction dynamics. This feature offers the possibility to control the reaction pathway by playing with the energy and the shape of the excitation pulse. Finally, upper excited states are not infinitely short-lived. Therefore, chemistry can also occur from there. In the third example, such upper excited state photochemistry was used to generate a geminate ion pair located above the singlet excited state of one of the reactants. The excited state of a transient like a geminate ion pair can also be considered as an upper excited state. The investigation of their dynamics as a function of the 'age' of the transient may prove to be a valuable tool for obtaining important structural information.

The perspective for new experiments is essentially limited by our imagination.

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