Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Photochemistry and Photobiology A: Chemistry 179 (2006) 1–12

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Invited Paper

Investigations of bimolecular photoinduced electron transfer reactions in polar solvents using ultrafast spectroscopy[☆]

Eric Vauthey [*]

Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva, Switzerland

Received 2 November 2005; received in revised form 16 December 2005; accepted 16 December 2005
Available online 19 January 2006

Abstract

Several controversial questions in the field of bimolecular photoinduced electron transfer reactions in polar solvents are first briefly reviewed. Results obtained in our group using ultrafast spectroscopy and giving a new insight into these problems will then be described. They concern the driving force dependence of the charge separation distance, the formation of the reaction product in an electronic excited state, the absence of normal region for weakly exergonic charge recombination processes and the excitation wavelength dependence of the CR dynamics of donor–acceptor complexes.

Keywords: Photoinduced electron transfer; Ultrafast spectroscopy; Charge recombination; Donor–acceptor complexes; Non-equilibrium dynamics

1. Introduction

Over the past decades, photoinduced electron transfer (ET) processes have been among the most investigated chemical reactions. A deep understanding of the parameters that control ET is crucial not only for applications, such as for example solar energy conversion, but also for the development of theoretical models allowing the dynamics of chemical processes to be predicted.

Intensive experimental investigation of photoinduced ET, and in particular charge separation (CS),[1] really started in the 1960s under the impulse of Weller and co-workers [1–4]. A seminal experiment performed by this group was the determination of the driving force dependence of the bimolecular quenching rate constant in solution [5,6]. The quenching rate constant was found to increase with increasing exergonicity up to a value corresponding to the diffusion rate constant and to remain unchanged even at very negative values of the driving force, ΔG_{CS}. This result was in strong contradiction with the theory developed a few years earlier by Marcus [7–9].

Since then, the Marcus inverted region, i.e. the decrease of the rate constant of highly exergonic ET with increasing driving force, has been reported for many types of ET processes [10–19]. However, up to now, there is still no univocal observation of the inverted region for photoinduced bimolecular CS reactions in solution. Among the various hypotheses that have been proposed to account for this different free energy dependence, one can cite the following:

- Radical ions, which are the primary product of CS between closed shell reactants, are characterised by low-lying electronic excited states that could in principle be populated upon a highly exergonic CS. In this case, the effective driving force is no longer strongly negative and the process does not take place in the inverted regime [6].
- The distance between the reactants at which CS occurs increases with the driving force [20–23]. Indeed, according to the expression proposed by Marcus and based on the dielectric continuum approximation [24], the solvent reorganisation energy, λ_s, increases with increasing interionic distance. Therefore, the activation energy of a highly exergonic ET is predicted to be larger at contact than at remote distances.

Although, none of these hypotheses could be either validated or refuted, the second one seems to be presently the most widely

---

[☆] Part of this work was presented at the International Conference on Photochemistry 2005, held 25–29 July in Cairns, Australia.

[*] Tel.: +41 22 379 6537; fax: +41 22 379 6518.
E-mail address: eric.vauthey@chiphy.unige.ch.

[1] CS is defined as an electron transfer between two neutral reactants.

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.12.019

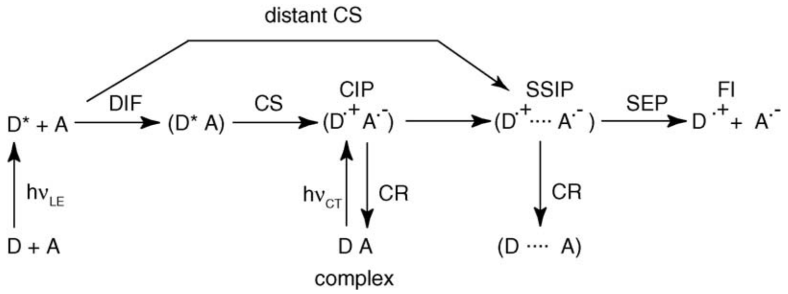

Fig. 1. Most widely used reaction scheme of a bimolecular photoinduced electron transfer reaction in polar solvents.

accepted. It is indeed often assumed that the primary product of weakly exergonic bimolecular CS is a contact ion pair (CIP), also called tight or intimate ion pair, while the product of more exergonic reactions is a solvent-separated ion pair (SSIP), also called loose ion pair (LIP) [25–27]. In polar solvents, these pairs can either dissociate to free solvated ions or recombine to the neutral ground state. This is summarised by the reaction scheme shown in Fig. 1. Albeit the exact structure of these transient species is still essentially unknown, CIPs constituted of aromatics ions are supposed to have a sandwich type structure with a typical centre-to-centre interionic distance of the order of 3.5 Å [25,28], as found for donor–acceptor complexes (DACs) in crystals [29,30]. CIPs can exhibit fluorescence and can thus be considered as exciplexes with a very large charge transfer character [31–33].[2] The fluorescence quantum yield of CIPs is generally very small, because the radiative rate constant associated to such a charge transfer transition is in most cases smaller than the rate constants of dissociation and charge recombination. CIPs can also be generated upon excitation in the charge transfer band of DACs [34].

Even less information exist on the structure of SSIPs. For some authors [25,27,35], a SSIP is a species with well-defined geometry and rate constants of dissociation and charge recombination. For others [23,36,37], a SSIP can rather be considered as two diffusing ions at distances where CR is still effective. Interionic distances going from 7 Å up to more than 12 Å have been reported [21–23,25,28,38].

The existence of two different types of ion pairs is further supported by the pioneering work of Mataga and co-workers [39,40], which have found that the driving force dependence of the dynamics of charge recombination (CR) is different for ion pairs generated by bimolecular quenching and for ion pairs produced by direct charge transfer (CT) excitation of DACs. In the first case, a bell-shaped free energy gap law, which can be discussed in term of the semi-classical Marcus theory, was found. In the second case, an almost perfectly exponential free energy gap law was measured. While in the first case, both the inverted and the normal regions were observed [41], only the inverted behaviour was detected with excited DACs [39]. From this work, the authors concluded that bimolecular quenching results to LIPs, whose CR follows the prediction of Marcus theory, and that direct CT excitation generate CIPs, whose CR is better described in terms of radiationless transition [39,40]. Other hypotheses have also been proposed to account the 'unusual' free energy gap law observed with CIPs [42–44]. According to Gould et al. [43], this behaviour is due to the fact that the variation of driving force achieved by changing the constituents of the DACs is accompanied by a parallel variation of both the solvent reorganisation energy and the electronic coupling constant, V. Non-equilibrium dynamics has also been proposed to account for the lack of the normal region for CR of CIPs [44,45].

This short overview shows that there is still no consensus on the exact mechanism of CS in polar solvents and on the CR dynamics of the resulting ion pairs and that there are still many questions to be answered.

In the following, some of our approaches to try to answer these questions using ultrafast laser spectroscopy will be described.

2. Contact or long distance ET?

A major question concerning bimolecular CS processes in solutions is the distance at which the reaction occurs. As stated above, Marcus theory predicts that weakly exergonic processes require contact, while more exergonic quenching should in principle be faster at larger distances [20]. The first prediction has been confirmed experimentally by the observation of exciplex fluorescence from the quenching product even in acetonitrile (ACN) [32,33,46]. As no exciplex fluorescence could be observed in processes more exergonic that about −0.4 eV, it has been concluded by several authors [26,31] that the primary quenching product was in this case a SSIP, in agreement with theoretical prediction. Up to now, most experimental information concerning the quenching distance in solution has been obtained from analysis of the so-called transient effect observed in the fluorescence decay of the excited reactant in the presence of quencher [47–52]. The transient effect leads to a non-exponential decay of the fluorescence [53]. Indeed, at a given quencher concentration, there is always a subpopulation of excited molecules with a reaction partner at a distance where CS can occur without significant diffusion. Because of this phenomenon, quenching is a non-Markovian processes, i.e. the actual quenching rate is time dependent. The extraction of the quenching distance from the transient effect is not a straightforward process but requires the fit of a theoretical model of diffusion-assisted ET to the experimental data. Moreover, the

---

[2] In this paper, the term 'exciplex' is used to designate a bimolecular excited complex stabilised by substantial charge transfer.

results also depend on the model used to describe the distance dependence of ET. The most used one is most certainly the Collins–Kimball model in its long time limit [54], which provides an effective quenching radius at which quenching occurs with an intrinsic, diffusion-free, CS rate constant, k_0. Mataga and co-workers [48] have used this approach to determine the driving force dependence of k_0 in ACN. However, no systematic driving force dependence of the quenching radius could be observed and values ranging between 5.4 and 13.8 Å were obtained. Other models, where a distance dependence of the ET rate constant is explicitly included, have also been developed [37]. Because of the relatively low time resolution of the fluorescence setups used, most experiments have been performed in rather viscous polar solvents such as ethylene glycol. An analysis of the transient effect performed in solvents of different viscosity indicates that the quenching distance decreases with decreasing viscosity [51]. Finally, it should be noted that apart from the investigation of Mataga and co-workers [48], no systematic investigation of the driving force dependence of the transient effect in ACN has been performed yet. Therefore, a univocal experimental support of the driving force dependence of the quenching distance is still lacking.

2.1. *Determination of the CR rate constant of ion pairs*

One approach for obtaining a new insight in the nature of the primary quenching product is the investigation of its CR dynamics. Although CR dynamics of photogenerated ion pairs has been investigated rather intensively, the CR rate constant, k_{CR}, has been in most cases determined indirectly from the free ion yield [13,25,26,55–59], Φ_{ion}:

$$\Phi_{\text{ion}} = \Phi_{\text{q}} \frac{k_{\text{sep}}}{k_{\text{sep}} + k_{\text{CR}}} \tag{1}$$

where Φ_{q} is the quenching efficiency and k_{sep} is the rate constant of dissociation of the ion pair into free solvated ions. The latter rate is generally assumed to amount to $5 \times 10^{8}\ \text{s}^{-1}$ in ACN.

The CR rate constant can be determined directly by monitoring the decay of the ion population by transient absorption or equivalent time-resolved techniques [11,60]. In most cases, this decay can be well reproduced by an exponential function with a decay constant, k_{obs}. Additionally, a very slow decay component due to the free ion population is also observed if $\Phi_{\text{ion}} \neq 0$. Under these conditions, one can reasonably assume that $k_{\text{obs}} = k_{\text{sep}} + k_{\text{CR}}$ and therefore, if Φ_{ion} is known, both k_{CR} and k_{sep} can be determined. A first result of such direct measurements is that the assumption of $k_{\text{sep}} = 5 \times 10^{8}\ \text{s}^{-1}$ in ACN is not valid. Indeed, k_{sep} values ranging from $\sim 10^{8}$ to $1.5 \times 10^{9}\ \text{s}^{-1}$ have been found [11,60–63]. Because of this, the indirectly determined k_{CR} values have to be considered with caution. Moreover, the absolute error on Φ_{ion} being of the order of 0.01, the uncertainty on k_{CR} becomes very large when the ion yield is small. For example, the directly determined k_{CR} value for the ion pair generated upon quenching of 9,10-dicyanoanthracene by *N*,*N*-dimethylaniline in ACN amounts to $3.3 \times 10^{11}\ \text{s}^{-1}$ [63], while indirect measurements give a 10 times smaller value [13]! Finally, it should be noted that the magnetic field effect on Φ_{ion} has been shown to result to more reliable indirectly measured k_{CR} values than Eq. (1) [64,65].

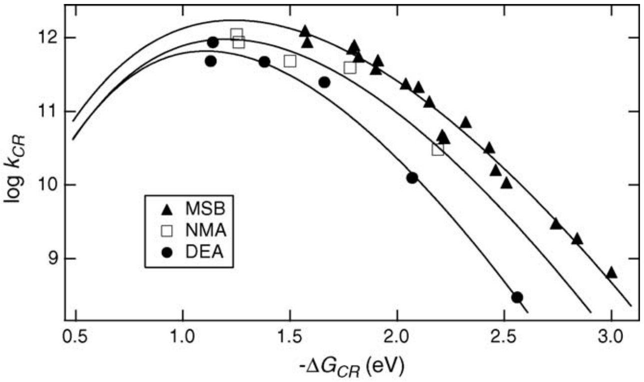

Fig. 2. Free energy dependence of the CR of ion pairs generated upon CS quenching of cyanoanthracene derivatives by methoxy-substituted benzenes (MSB), *N*-methylaniline (NMA) and *N*,*N*-diethylaniline (DEA). The solid line are the best fits of the non-adiabatic ET transfer theory (see Ref. [63] for more detail).

Fig. 2 shows the driving force dependence of the CR rate constant measured with a series of cyanoanthracenes as electron acceptors and various quenchers (methoxybenzenes and anilines) in ACN [63]. As shown by the continuous lines, these rate constants can be reasonably well reproduced using the semi-classical expression of the non-adiabatic ET [9,66] if the electronic coupling constant, *V*, and especially the reorganisation energy associated to high frequency modes, λ_i, are allowed to vary with the different types of donors. Possible reasons for such a variation have been discussed in detail in Ref. [63]. This figure also represents the first direct measurement of the CR rate constant of ion pairs generated upon CS quenching in the barrierless regime, allowing a precise determination of *V*. The best-fit curves shown in Fig. 2 have been obtained with *V* values of the order of $100\ \text{cm}^{-1}$. This is 5–10 times larger than the values obtained from indirect measurements of k_{CR} [13,25,57,59]. Such small coupling constants have been used as an argument in favour of the formation of SSIPs upon quenching [25]. Our larger values indicate that the ions in the pair are probably more strongly coupled than two ions separated by solvent molecules.

2.2. *Heavy atom effect on CR*

Another insight in the nature of the CS product has been obtained by investigating the heavy atom effect on the CR dynamics of ion pairs [67]. As shown by the energy level scheme in Fig. 3, the reactants were chosen so that the resulting ion pair has two CR pathways, one to the neutral ground state (singlet CR) and the other to the neutral triplet state (triplet CR). Two mechanisms can favour the latter channel [68,69]:

(1) Hyperfine interaction in the ion pair originally in the singlet state can induce a spin flip allowing triplet CR to the detriment of singlet CR. For this mechanism to be operative, the singlet and triplet states of the ion pair have to be nearly degenerate, i.e. the exchange interaction in the pair has to

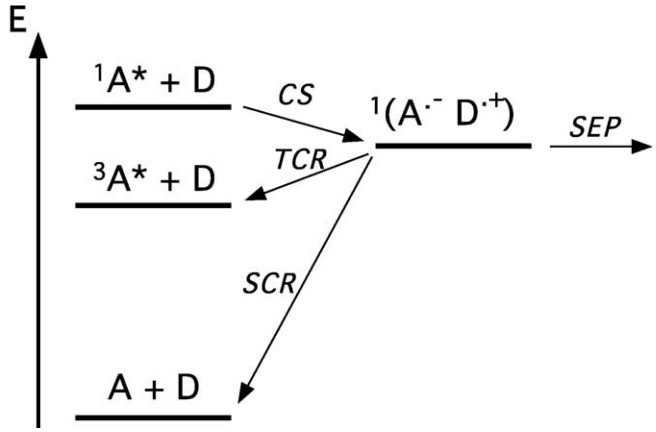

Fig. 3. Energy level diagram of the states involved in the CR of an ion pair with a heavy atom.

be very weak [70], implying a negligibly small orbital overlap of the ions. Triplet CR via hyperfine interaction can be substantially slowed in the presence of an external magnetic field, which lifts the degeneracy of the triplet sublevels [71].

(2) Spin-orbit coupling is a mechanism that is well known for lifting the forbiddance of transitions between electronic states of different spin multiplicity. Triplet CR induced by spin-orbit coupling is only possible for strongly coupled, exciplex-like, ion pairs [71]. In this case, triplet CR can be viewed as an intersystem crossing. Triplet CR by spin-orbit coupling can thus be strongly enhanced by the presence of a heavy atom on one of the ions [72–74].

Fig. 4 shows the transient grating spectra measured at various time delays after excitation of 9,10-dicyanoanthracene (DCA) by bromoanisole in ACN [67]. As explained in detail elsewhere [75], a transient grating spectrum is very similar to a transient absorption spectrum, the major difference being that, in the first case, the intensity is always positive. The main advantage of the transient grating technique is its superior sensitivity. These spectra show the presence of both the radical anion and the triplet state of DCA. The same measurement performed with anisole, i.e. without the heavy atom, results to a spectrum that does not exhibit any triplet state band. From the time evolution of the spectrum, a triplet CR rate constant of 2.45 ns^{-1} is obtained. Using iodoanisole instead of bromoanisole results to a 20-fold increase of the triplet CR rate constant. Replacement of DCA by stronger electron acceptors gave similar ultrafast, heavy atom induced triplet CR. This indicates that with these systems, where ΔG_{CS} could be varied between −0.15 and −0.61 eV, the quenching product is a strongly coupled, exciplex-like, ion pair. Therefore, the −0.4 eV upper limit, often invoked for exciplex or CIP formation in polar solvents [26,31] is, in this case at least, underestimated.

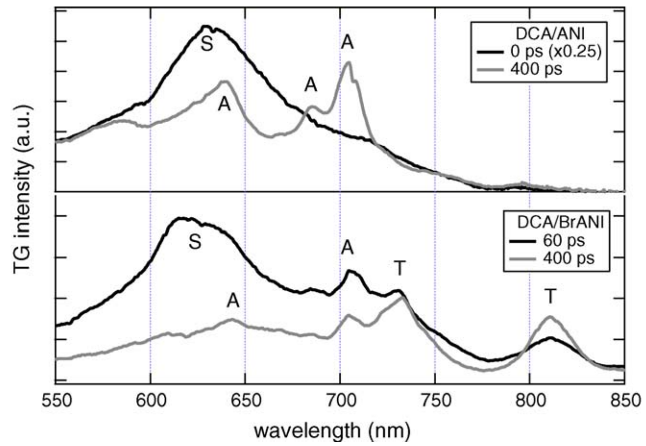

Fig. 4. Transient grating spectra measured at various time delays after excitation of solutions of 9,10-dicyanoanthracene (DCA) with anisole (ANI, top) and bromoanisole (BrANI, bottom) in ACN (S, A and T design ^{1}DCA*, $\mathrm{DCA}^{\bullet -}$ and ^{3}DCA* bands, respectively).

2.3. *Looking for the normal region for CR*

The above approach can unfortunately not be used to investigate very exergonic CS processes, because the ion pair state has to lie above the triplet state of one of the reactants. According to the investigation performed about 20 years ago by Mataga and co-workers [11,76,77], the CR dynamics of ion pairs formed upon highly exergonic quenching is very slow. For example, a CR time constant of 1.6 ns was reported for the perylene (Pe)/tetracyanoethylene (TCNE) pair in ACN [11,76,77]. As in this case the driving force for CR is small, i.e. $\Delta G_{\mathrm{CR}} > -1$ eV, such a slow CR is in agreement with the Marcus theory for the normal region. A slow CR is also compatible with a pair having a rather large interionic distance, as expected from the above-mentioned model of ΔG-dependent quenching distance. This investigation represents, to our knowledge, the only direct observation of the normal region for CR.

Several attempts from our group to observe the normal region for such CR processes proved to be unsuccessful [63,67]. For example, the weakly exergonic CR ($\Delta G_{\mathrm{CR}} = -0.65$ eV) of the ion pair formed upon the highly exergonic quenching ($\Delta G_{\mathrm{CS}} = -2.17$ eV) of tetracyanoanthracene (TCA) by *N*,*N*,*N*′*N*′-tetramethyl-*p*-phenylenediamine (TMPD) is complete after a few picoseconds [63]! Fig. 5 shows intensity-normalised transient spectra obtained with this donor–acceptor pair. The narrowing of the band, which is due to both $\mathrm{TCA}^{\bullet -}$ and $\mathrm{TMPD}^{\bullet +}$, can be reasonably ascribed to the vibrational cool-

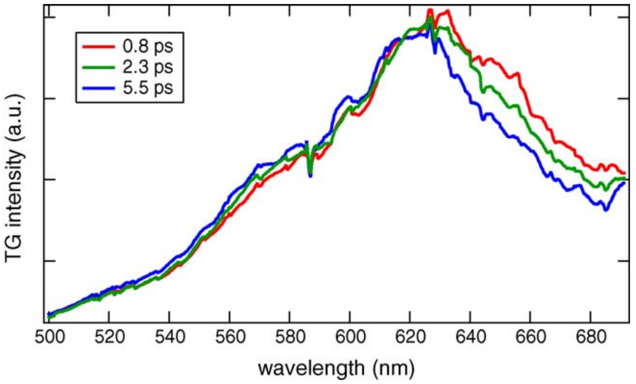

Fig. 5. Intensity normalised transient grating spectra measured at various time delays after excitation of TCA in the presence of 1 M TMPD in ACN.

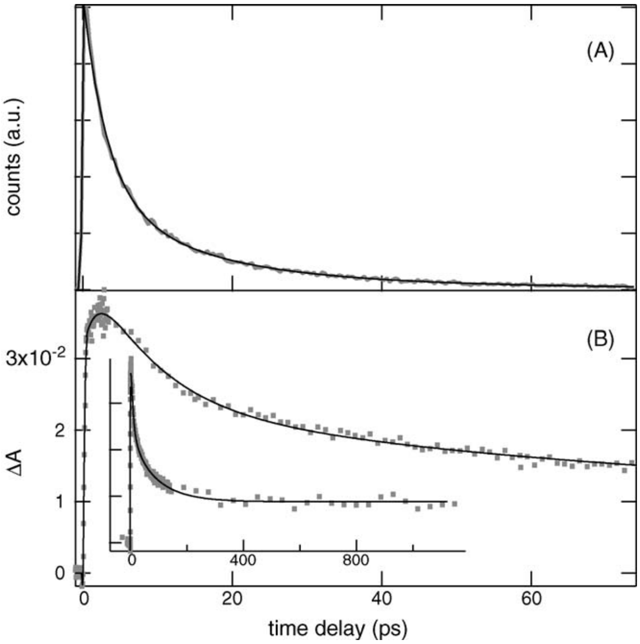

Fig. 6. (A) Time profile of the fluorescence intensity of a solution of Pe in the presence of 0.9 M TCNE in ACN (grey) and best triexponential fit (black). (B) Time profile of the transient absorption at 535 nm of the same solution (grey) and best fit of Eq. (2) (black).

ing of the quenching product. This indicates that CR occurs most probably before the ion pair has reached thermal equilibrium. Various aspects of non-equilibrium CR dynamics will be discussed in more detail in the next section. In order to understand the origin of the discrepancy between our findings, i.e. ultrafast CR, and the above-mentioned observation of slow CR [11,76,77], we have undertaken a reinvestigation of the CR dynamics of the Pe/TCNE system [78] using a superior time resolution than that available at the time of the original experiment, which was of the order of 30–50 ps. Fig. 6B shows the time profile of the transient absorbance due to Pe$^{\bullet+}$ measured after excitation of Pe in the presence of 0.9 M TCNE [78]. This kinetics is strongly non-exponential and depends markedly on the quencher concentration. After about 500 ps, the signal intensity remains constant up to several nanoseconds. This plateau is due to the absorption of the free ion population, which decays by homogeneous recombination in the microsecond timescale. The free ion yield determined at the same concentration by transient photoconductivity amounts to only 0.02. This indicates that the initial signal intensity accounts for only 10% of the total ion population, although the whole excited Pe population is quenched as shown by time-resolved fluorescence measurements (Fig. 6A). These measurements also show that the timescales of CS and of CR are not largely different and therefore the simple procedure described above cannot be used to determine the CR rate constant. Instead, the time profile of the observed ion population, $P_{\text{ion}}^{\text{obs}}(t)$, was described by the following convolution integral:

$$P_{\text{ion}}^{\text{obs}}(t) = \int_0^t P_{\text{ion}}^{\text{int}}(t-t') \cdot \dot{P}_{\text{S}_1}(t')\text{d}t' \qquad (2)$$

where $P_{\text{ion}}^{\text{obs}}(t)$ is the time dependence of the ion population assuming instantaneous formation at $t=0$ and $P_{S1}(t)$ is the time evolution of the excited Pe population, which has been measured precisely by fluorescence up-conversion. The continuous line in Fig. 6B is the best fit of Eq. (2) to the observed data using a tri exponential function for $P_{\text{ion}}^{\text{obs}}(t)$. The best-fit parameters indicate that more than 90% of the ion pair population decay in less than 5 ps and that only a minor fraction undergoes the slow CR reported in the initial investigation [11,76,77]. The time resolution of this experiment was too low to observe the ultrafast CR components and therefore the slow component was improperly attributed to the entire ion pair population. The fit of Eq. (2) to the data measured at lower quencher concentrations, down to 0.16 M, resulted to similar small time constants [78].

Such an ultrafast CR dynamics found with Pe/TCNE and the other systems discussed above indicates that the major product of highly exergonic CS quenching is a strongly coupled ion pair. Indeed, to account for such small CR time constants, a V value of the order of 120 cm^{-1} has to be invoked, implying that the ions are formed at contact distance. In other words, the ultrafast CR dynamics found here is totally incompatible with long distance ET quenching.

One way to reconcile the ΔG-dependent ET distance model and the ultrafast CR dynamics is to invoke the formation of the ion pair in an electronic excited state. In this case, the quenching is not longer highly exergonic and CS at contact distance is expected. In the case of Pe/TCNE, the four lowest electronic excited state of Pe$^{\bullet+}$ are energetically accessible [79]. There is, however, no spectroscopic evidence for the formation of such an excited Pe$^{\bullet+*}$/TCNE$^{\bullet-}$ product. Transient spectra measured after the excitation of Pe$^{\bullet+}$ at 532 nm in sulfuric acid show that Pe$^{\bullet+*}$ does not absorb significantly between 470 and 750 nm [80]. Moreover, ground state recovery measurements of Pe$^{\bullet+}$ after excitation at 532 nm indicate an excited state lifetime of 3 ps [81]. Therefore, the observation of an electronic excited product in such reactions is a challenging task.

The transient effect observed in the fluorescence decay of Pe* quenched by TCNE has been analysed using the differential encounter theory including the distance dependence predicted by Marcus theory [82]. The experimental data could only be reproduced by assuming two quenching pathways: a weakly exergonic one leading to the excited product and thus occurring at contact distance, and a highly exergonic one resulting to the ionic product in the electronic ground state and occurring at larger distance. This result was used to reproduce the time profile of the ion population shown in Fig. 6 using the so-called unified theory [37], which also takes the distance dependence of CR into account. The experimental data could only be reproduced in the intermediate time-range, i.e. between 100 and 700 ps, the stronger disagreement being observed at earlier time [83]. The origin of this discrepancy is still not clear. It should nevertheless be noted that the theoretical models used to analyse the transient effect consider the solvent as a continuum and the reactants as spheres. Therefore, orientation effects, which have been shown to play a very important role in ultrafast ET processes [84,85], are totally overlooked. This should be kept in mind when interpreting the parameters obtained from such an analysis. Indeed, a

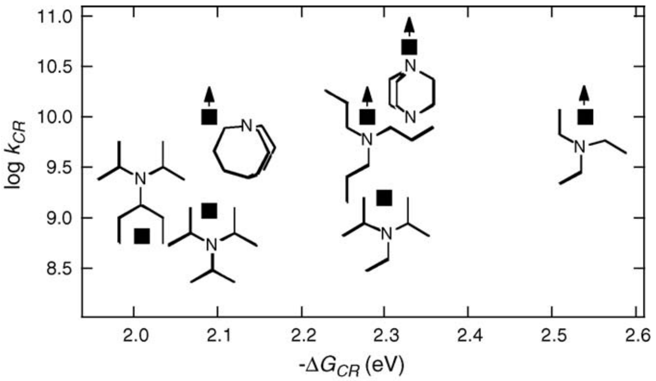

Fig. 7. Free energy dependence of the rate constant of CR of ion pairs formed upon quenching of Pe by aliphatic amines (squares with an arrow represent lower limit values).

quenching distance obtained from the theoretical fit larger than contact may in fact correspond to reactants in contact but poorly oriented for ET.

2.4. Steric effect on CR

Another indication against long distance ET, at least in non-viscous solvents like ACN, has been obtained by measuring the effect of steric hindrance on the CR dynamics of ion pairs [62]. Fig. 7 shows a logarithmic plot of the CR rate constants of ion pairs formed upon CS quenching of perylene by a series of tertiary aliphatic amines as a function of the driving force. This increase of k_{CR} with increasing driving force is totally opposite to the inverted behaviour that is usually found with highly exergonic CR. This unusual dependence is actually due to the steric hindrance of the electron donors. One can clearly see that the CR correlates very well with the degree of steric encumbrance around the nitrogen atom of the amine. This means that the CR rate constant decreases continuously when the shortest possible distance between the N atom of the amine and the aromatic plane of the acceptor increases from about 3 to 5 Å. As discussed in more details in Ref. [62], the effect of other parameters, such as the reorganisation energy associated to high frequency modes, on the variation of k_{CR} can be safely ruled out. This result is in contradiction with the ΔG-dependent ET distance model. Indeed, as CR is highly exergonic and occurs in the inverted region, the most favourable distance should be far from contact. Therefore, steric hindrance should have no impact on the CR dynamics, contrary to the observation.

To summarise this section, we can say that none of our direct measurements of CR dynamics of ion pairs indicate the occurrence of long distance CS and CR in ACN. Long distance ET has been measured in rigid media or in covalently linked donor–acceptor pairs [86–88]. However it is always relatively slow, i.e. slower than diffusion in a non-viscous solvent. Moreover, intramolecular ET has always been found to decrease with increasing spacer length [87–89], even with non-rigid linkers [90]. One should note that the ΔG-dependent ET distance model is essentially based on the distance dependence of the solvent reorganisation energy. In this expression, like in the Born equation, the solvent is described as a dielectric continuum and the ions are considered as charged spheres [24]. This model certainly works well for ions at large distances and/or ions much larger than the solvent molecules. However, its adequacy to model precisely small aromatic molecules at relatively short distances in organic solvents should be questioned.

From our measurements, it seems that there are indeed two types of ion pairs. However, in ACN at least, the appellation *tight* and *loose* as used by some authors [40], seems to be more adequate to design these two types of ion pairs than *contact* and *solvent-separated*:

(1) In a *tight ion pairs*, the ions in contact have a rather precise mutual orientation where the electronic coupling is optimal. Such ion pairs can be generated by CT excitation of DACs or upon very weakly exergonic quenching. In the first case, CT excitation warrants an optimal orientation as the oscillator strength is directly proportional to V^2 [91]. In the second case, only those encounter complexes where the coupling is large can undergo CS during their lifetime.
(2) In a *loose ion pair*, the ions are also in contact but with a less precise mutual orientation. In this case, the electronic coupling is substantial but in general smaller than in the first type. These pairs are formed upon CS quenching. It is reasonable to assume that the larger the driving force, the less strict the orientation requirement for efficient CS quenching.

In other words, we suggest that, in non-viscous solvents at least, a ΔG-dependence of the mutual orientation of the reactants might be more realistic than a ΔG-dependence of the distance.

3. Electronically excited CS product?

As mentioned in Section 1, the hypothesis of the formation of the CS product in an electronic state to account for the absence of inverted region has never been confirmed or refuted so far. A major reason for this is probably the difficulty to observe excited radical ions in the condensed phase. Indeed, only a very small number of radical ions are known to fluoresce [80,92–97]. Moreover, the very few investigations on their excited state dynamics have shown that the ground state recovery of radical ions is ultrafast and takes place in picosecond timescale [80,81,98,99]. This result, together with a relatively small oscillator strength for the D_0–D_1 transition of many radical ions, can explain this lack of fluorescence, which moreover should often occur in the near IR region. Finally, the excited state absorption spectrum of most ions is unknown. Therefore, the observation of excited ions upon highly exergonic CS quenching first requires a deeper knowledge on the photophysics of these species.

In order to avoid these difficulties, we have considered the opposite process, i.e. highly exergonic CR of ion pairs [100,101]. As discussed above, these processes are well known to occur in the inverted region. However, contrary to highly exergonic CS quenching, there is in general no electronic state between the ion pair and the neutral ground states that can be populated upon CR.

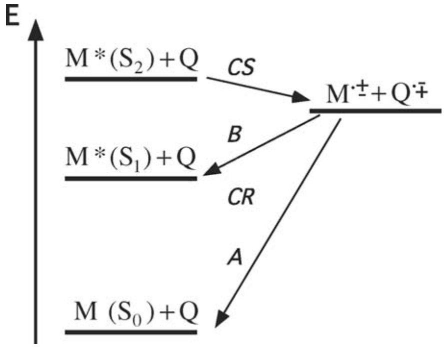

Fig. 8. Energy levels involved in the photoinduced CS between a molecule *M* in the S_2 state and a weak quencher *Q*.

We have therefore considered donor–acceptor systems with an energy level scheme similar to that shown in Fig. 8 [100,101]. In this case, CS occurs between one of the reactants in the S_2 state and a weak quencher. The resulting ion pair can undergo spin-allowed CR via two different pathways: (A) a highly exergonic to the neutral ground state and (B) a weakly exergonic to the neutral product with one partner in the S_1 state. This situation is equivalent to that of CS with a highly exergonic pathway to the ion pair product in the ground state and a weakly to moderately exergonic pathway to the excited product. In a first stage, molecules with a relatively long S_2 lifetime, such as azulene, benzazulene and xanthione have been used as electron acceptors [100]. With all these molecules, the free ion yield upon S_2 quenching by various donors is smaller than 0.03. Moreover, CR was found to be faster than the CS step itself and thus only a lower limit value of k_{CR} of the order of $2 \times 10^{10}\ \mathrm{s}^{-1}$ could be estimated. Replacing azulene by perylene, which has the same reduction potential but which undergoes CS from the S_1 state, results to a much larger free ion yield (>0.2) and a 100-times smaller k_{CR} value. In other words, the inverted region is totally suppressed for CR if an electronic excited state of the product is energetically accessible. Because azulene, benzazulene and xanthione have all a very short S_1 lifetime, the population of this state upon CR could not be unambiguously established.

To circumvent this problem, Zn-tetraphenylporphine (ZnTPP), which is known to exhibit both S_2 and S_1 fluorescence, was used as reactant [101]. The drawback of ZnTPP is it very short S_2 lifetime ($\tau_{S_2} = 1.5$–2.5 ps [102]), which requires high quencher concentrations. Fig. 9A shows the stationary fluorescence spectrum of ZnTPP with various quencher concentrations. The intensity of the S_2 fluorescence band clearly decreases upon addition of quencher, while that of the S_1 band remains unchanged. This is a clear indication that the ion pair resulting from S_2 quenching recombines to the excited neutral product only. If this were not the case, the intensity of the S_1 fluorescence would also decrease upon S_2 quenching. From the analysis of S_2 fluorescence decays and S_1 fluorescence rises such as those shown in Fig. 9B and C, CR time constants between 300 and 500 fs were found, depending on quencher and solvent.

In conclusion, these experiments have shown that, when energetically allowed, CR to an electronic excited product is very efficient and suppresses the occurrence of the inverted regime. There is in principle no reason why this should not also be the case for CS quenching. Nevertheless, this still needs to be clearly demonstrated.

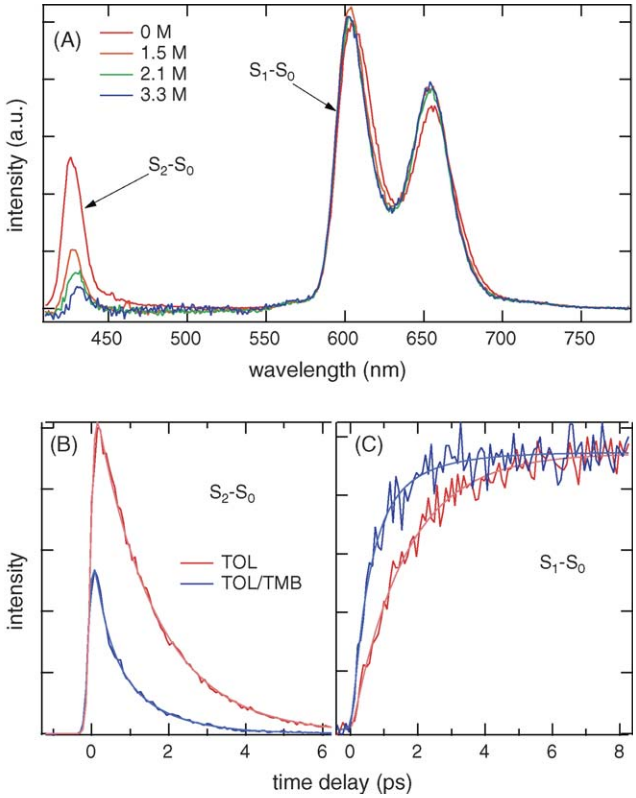

Fig. 9. (A) Stationary fluorescence spectra of ZnTPP with various concentrations of 1,2,4-trimethoxybenzene (TMB) in ACN and time profiles of (B) the S_2 and (C) S_1 fluorescence intensity measured with ZnTPP in toluene (TOL) and in a 1:1 TMB/TOL mixture. The smaller initial S_2 fluorescence intensity in TMB/TOL indicates a quenching component that is too fast to be resolved.

4. Non-equilibrium CR dynamics

4.1. *Ultrafast CR of excited donor–acceptor complex*

As shown above, CR of ion pairs formed upon CS quenching can be ultrafast, especially when the energy gap to the neutral product is small. In the Pe/TCNE case, the CR dynamics can be substantially faster than the CS step and becomes therefore very difficult to monitor. One way to circumvent this problem is to generate the ion pair upon direct excitation of the CT band of a DAC. An advantage of this approach is that the resulting ion pair is now undeniably a CIP, or rather a tight ion pair as discussed above. As mentioned in Section 1, the experimentally observed energy gap law for the CR of ion pairs generated upon CT excitation departs substantially from the predictions of Marcus theory, especially in the weak exergonic region, where the normal regime is not observed [39,40,42]. One hypothesis to explain this deviation [43] is that the DACs used for such investigation are chemically so different, that other parameters than the driving force are changing. Another hypothesis [40] suggests that in this case, CR essentially involves intramolecular

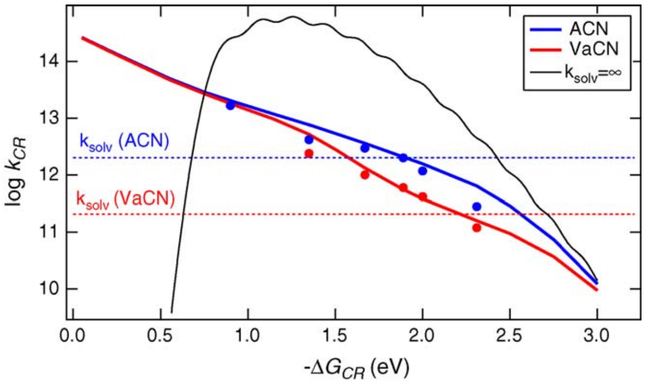

Fig. 10. Free energy dependence of the CR rate constant of excited DACs calculated using the hybrid model in ACN, in VaCN and assuming an instantaneous solvent relaxation (continuous lines) and comparison with the experimental data (filled circles) and with the rate constants of diffusive solvation, k_{solv} (dotted lines).

high frequency modes and is thus independent of the solvent. To test these ideas, we have investigated the CR dynamics of a series of chemically very similar DACs composed of pyromellitic dianhydride (PMDA) as electron acceptor and methoxy-substituted benzenes as electron donors in solvents of varying polarity and with different dielectric relaxation time [103,104]. Fig. 10 shows the driving force dependence of the CR dynamics of these DACs measured after CT excitation at 400 nm in valeronitrile (VaCN) and in ACN. Contrarily to other systems investigated [105], the CR dynamics measured here exhibits a clear solvent dependence. The dotted horizontal lines are the inverse solvation times of VaCN and ACN and correspond to the largest possible ET rate constants in these solvents according to equilibrium ET theory [106,107]. Most of the measured rate constants lie above these values indicating that CR is faster than diffusive solvation. In other words, CR occurs before the solvent has equilibrated around the newly formed ion pair. The thick solid lines in Fig. 10 are the free energy gap laws predicted by a non-equilibrium model of ET [108,109], which consists of the classical two-dimensional Sumi–Marcus model [110] with a quantum–mechanical description of the high frequency intramolecular modes of the final state. For these simulations, both inertial and diffusive solvent motions were included [103]. For comparison, the black line depicts the case where equilibrium is reached instantaneously. In this hybrid model, the CR dynamics is influenced by the dynamic properties of the solvent but is not limited by solvent relaxation. Indeed, depending on the energy gap, some solvent relaxation is needed for the ion pair population to reach a region where the Franck–Condon factor is large enough to enable CR. Apart from accounting for the observed dependence, this model also predicts a continuous increase of the CR rate constant upon decreasing exergonicity, i.e. an absence of the normal region, as experimentally observed by Mataga and co-workers with excited DACs [39], and by ourselves with ion pairs generated upon CS quenching [63,78]. As shown in Fig. 11, CR in the normal regime is a thermally activated process, where the reactants are originally in equilibrium. However, the ion pair population generated by both CS quenching and CT excitation is prepared far from equilibrium and therefore, if the electronic coupling constant is large enough, CR can occur before equilibrium has been reached. Non-equilibrium effects seem therefore to account very well for the ultrafast CR of photogenerated ion pairs.

4.2. Excitation wavelength effects

An important aspect of non-equilibrium CR is that its dynamics depends on how far from equilibrium the ion pair population is initially prepared. For CR processes occurring in the inverted and barrierless regimes, the dynamics should be faster if the initial ion pair population is located close to equilibrium. The opposite effect is expected for processes occurring in the normal region, where only ion pairs formed far from equilibrium can recombine before being trapped in the equilibrium configuration. Consequently, the non-equilibrium CR dynamics of ion pairs produced by CT excitation should depend on the excitation wavelength. Of course, because of the Franck–Condon principle, an equilibrated ion pair population for which CR is in the normal regime cannot be optically prepared upon CT excitation. Theoretical calculations performed by Ivanov and co-workers, using

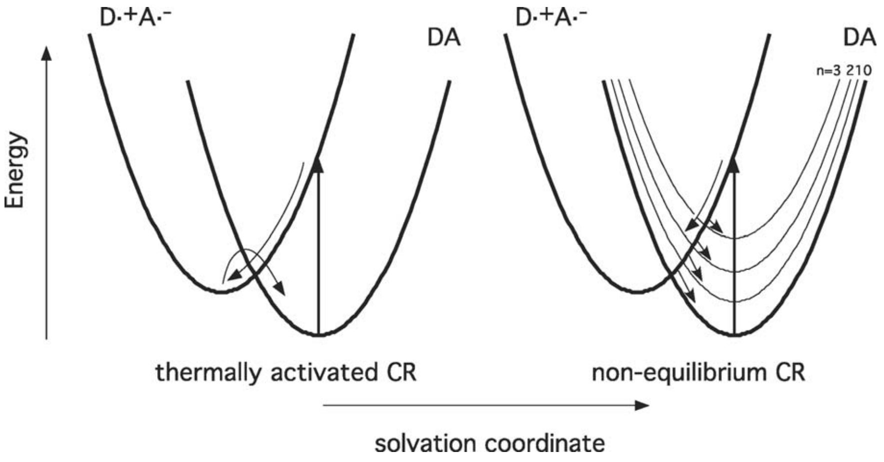

Fig. 11. Comparison of thermally activated and non-equilibrium CR using cuts in the free energy surface of the ground and excited states of a DAC along the solvation coordinate. The thin parabolas represent vibrational excited states.

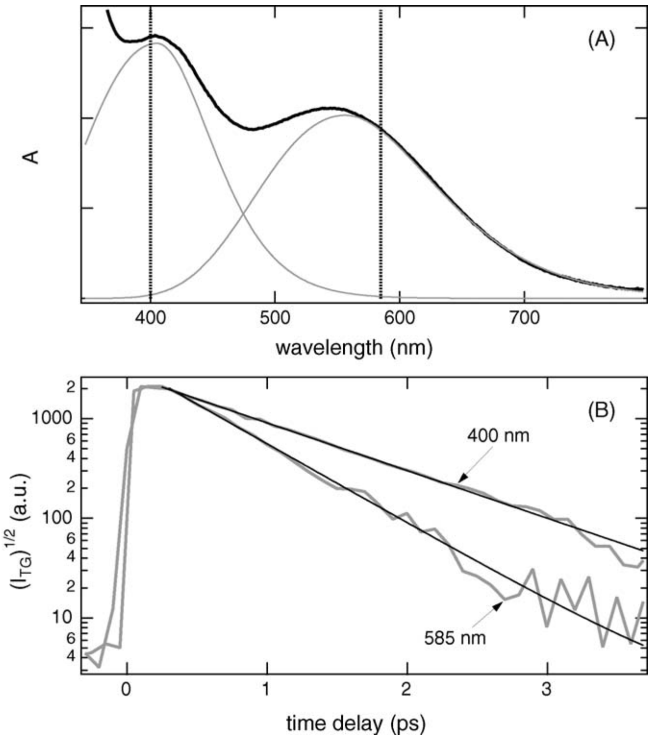

Fig. 12. (A) Absorption spectrum of DEA/PMDA in ACN (thick line). Asymmetric Gauss functions used to reproduce the absorption spectrum (thin lines). The vertical lines represent the excitation wavelengths. (B) Logarithmic plot of the time evolutions of the excited state population measured by transient grating with DEA/PMDA upon 400 and 585 nm excitation and best single-exponential fits.

both the time-dependent perturbation theory and the stochastic point transition approach predict that, with the exception of very weakly exergonic processes ($\Delta G_{CR} > -0.4$ eV), the CR dynamics should slow down with decreasing excitation wavelength [111–113]. To confirm this prediction, we have undertaken an experimental investigation of the effect of excitation wavelength on various DACs in polar solvents [114,115]. As the constituants of all the DACs investigated absorb very far from the CT absorption bands, wavelength effects associated to local excitation could be safely eliminated. In a first stage, DACs exhibiting two distinct CT absorption bands have been investigated (see Fig. 12A). Such complexes consist of a strong electron acceptor such as PMDA or TCNE and methoxy-substituted benzenes or anilines. The two CT bands originate from the removal of the degeneracy of the HOMOs of benzene upon substitution [116]. Moreover, because of the different symmetries of the HOMO and HOMO-1 of substituted benzenes, each CT band corresponds to a DAC with a distinct mutual orientation of its constituents [117]. As shown in Fig. 12B with a DAC composed of *N*,*N*-diethylaniline (DEA) and PMDA, the decay of the ion pair population measured upon excitation in the high energy CT band (CT2) is markedly slower than that measured after excitation in the low energy CT band (CT1). The same effect has been observed in the slower relaxing solvent VaCN and with the 1,2,4-trimethoxybenzene (TMB)/PMDA pair, which also exhibits two CT absorption bands. As the CT2 state is located about 0.9 eV above the CT1 state, recombination from the CT2 state is expected, according to the energy gap law found for such complexes [103], to be about 16 times slower than that from the CT1 state. Therefore, the relatively small excitation wavelength effect that has been observed here indicates that the main deactivation pathway of the CT2 state is not CR to the neutral ground state but rather internal conversion to the CT1 state, wherefrom CR occurs. The observed excitation wavelength effect can be rationalised in terms of different DAC geometries. CT1 band irradiation results to the excitation of complexes with a geometry favouring a large overlap of the donor's HOMO with the acceptor's LUMO. This geometry is also favouring a large electronic coupling constant for CR. On the other hand, CT2 excitation interacts mainly with complexes having a geometry favouring a large overlap of the donor's HOMO-1 with the LUMO of the acceptor. However, because in this case the HOMO-LUMO overlap is not optimal, this geometry can be expected to be less favourable for CR.

This excitation wavelength effect has most probably nothing to do with non-equilibrium dynamics for at least two reasons:

(1) The decay of the CIP population is exponential, while non-equilibrium dynamics should lead to a non-exponential decay.
(2) The excitation wavelength effect is qualitatively the same in fast and slow relaxing solvents. Non-equilibrium effects are only expected when CR is substantially faster than solvation. This is clearly not the case for DEA/PMDA in ACN where the CR time constant amounts to 900 and 550 fs upon CT2 and CT1 excitation, respectively, while the diffusive solvation time of ACN amounts to 500 fs.

On the other hand, the time constants measured in VaCN with both TMB/PMDA and DEA/PMDA complexes are substantially faster than diffusive solvation. Despite this, only a very weak wavelength effect, close to the error limit, could be measured with TMB/PMDA upon excitation in the CT1 band.

In order to investigate whether this apparent absence of a wavelength effect, at least between 620 and 480 nm, is due to a too slow CR dynamics, DACs with the stronger acceptor TCNE were investigated. Substantially faster CR dynamics were indeed observed, but an excitation wavelength effect was only observed with the TMB/TCNE DAC in ACN, whose absorption spectrum is shown in Fig. 13A. Upon long wavelength excitation, the time profile of the $\text{TCNE}^{\bullet-}$ population exhibits an ultrafast decay with a time constant that can be estimated to be of the order of 50–80 fs, as illustrated in Fig. 13B. Upon shorter excitation wavelength, the decay profile is biphasic with the same ultrafast component and with additionally a slow component that does not show any decay up to a time delay of 100 ps. The relative amplitude of this component increases with decreasing excitation wavelength as shown in Fig. 13B. Interestingly, this slow component is absent when using weaker electron donors and in slower relaxing solvents like VaCN and octanenitrile (OcCN). This biphasic decay is similar to that found with ion pairs formed upon quenching of Pe by TCNE and is explained by the occurrence of both ultrafast non-equilibrium CR and slow thermally activated CR (see Fig. 11) upon short excitation wavelength.

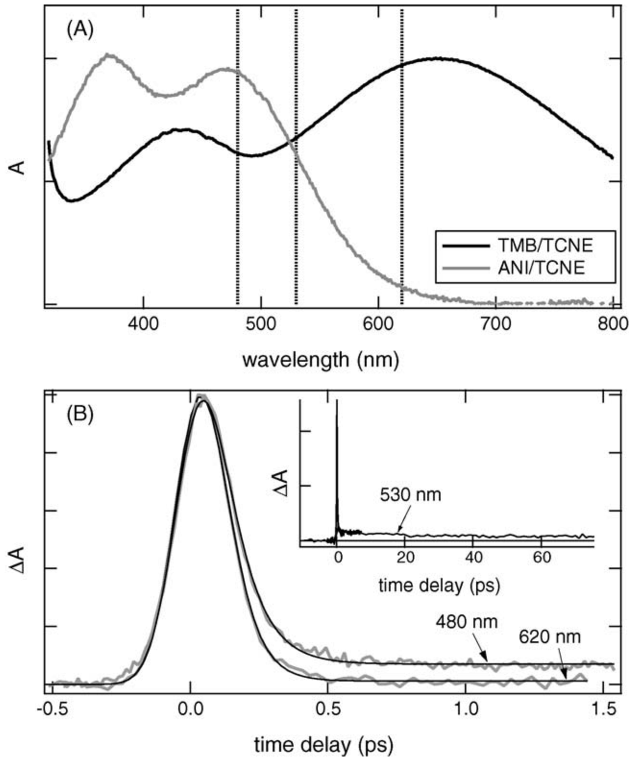

Fig. 13. (A) Absorption spectra of anisole/TCNE and TMB/TCNE in ACN. The vertical lines represent the excitation wavelengths. (B) Time profiles of the transient absorption of $TCNE^{\bullet -}$ recorded with TMB/TCNE in ACN upon different excitation wavelengths and best exponential fits.

Long wavelength irradiation predominantly leads to the formation of ion pairs with large *V* value for CR. Therefore, these ion pairs can undergo non-equilibrium CR and thus never reach equilibrium. On the other hand, bluer irradiation results to ion pairs with relatively smaller *V* and therefore the entire population cannot recombine before reaching equilibrium. Thus a fraction of the ion pair population is trapped in the equilibrium configuration and undergoes slow thermally activated CR, which is at the origin of the slow decay component. In slower solvents, non-equilibrium CR is favoured and thus the slow component is absent. Moreover, with weaker donors, CR is in the barrierless or the inverted region and is thus never thermally activated. Consequently, a slow CR component is not expected. With such weaker donors, like veratrol and anisole, the CR dynamics is not only monophasic but also slower as expected for a larger driving force. In ACN, the CR dynamics with both veratrol/TCNE and anisole/TCNE is independent of the excitation wavelength at least between 620 and 480 nm. On the other hand, a small but reproducible wavelength effect was measured with anisole/TCNE in both VaCN and OcCN. As shown in Fig. 14, the decay of the ion pair population in OcCN is slower upon 480 nm than upon 620 nm excitation. Moreover, these decays cannot be reproduced with an exponential function. A very good agreement was obtained by convolving the instrument response function with the following expression:

$$f(t) = A \exp\left[-\left(\frac{t}{\tau}\right)^{s}\right] \tag{3}$$

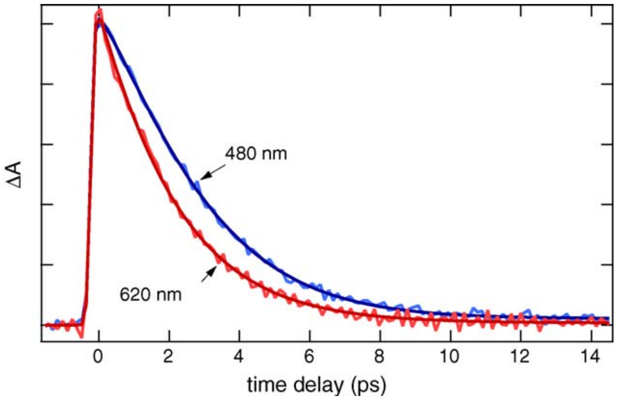

Fig. 14. Time profiles of the transient absorption of $TCNE^{\bullet -}$ measured with anisole/TCNE in OcCN upon excitation at 620 and 480 nm and best fits of Eq. (3).

This function with $s < 1$ is known as the stretched exponential and is used to describe relaxation occurring in a large range of timescales [118]. However, *s* values larger than 1, had to be used to reproduce the $TCNE^{\bullet -}$ population dynamics. This corresponds to a situation where the decay is initially relatively slow and accelerates with time. Interestingly, the value of *s* was found to increase with decreasing wavelength, from 1.1 at 620 nm to 1.3 at 480 nm. Similar measurements have been performed with isodurene, pentamethylbenzene and hexamethylbenzene as electron donor. A qualitatively similar wavelength effect was measured with isodurene in VaCN and OcCN. With the other two donors, the CR dynamics was essentially the same at 620 and 480 nm.

The slowing down of the excited state decay and the increase of non-exponential character with decreasing excitation wavelength is precisely what is expected for non-equilibrium CR dynamics. Moreover, the effect is only observed when the CR is faster than the diffusive solvation time, i.e. in VaCN and OcCN.

If one compares the absorption spectra of all the DACs investigated, one realises that this wavelength effect is only present with DACs for which the 620–480 nm range corresponds to the red edge of the CT absorption band (i.e. TMB/PMDA, anisole/TCNE and isodurene/TCNE). This can be understood by considering that the CT absorption band is dominated by several vibronic transitions. Consequently, upon excitation at the centre or the blue edge of the CT band, the excess energy is not only deposited in the solvent modes but also in the vibrational modes. Because of this, the correlation between excitation wavelength and the location of the ion pair population along the solvation coordinate is lost.

In summary, this observation of a wavelength dependence is a clear indication of the occurrence of non-equilibrium CR dynamics of ion pairs formed upon CT excitation. As ion pairs generated upon CS quenching are also formed far from equilibrium, such a non-equilibrium dynamics should also play an important role especially if the ions are strongly coupled, as it is the case for example with the Pe/TCNE system. Strong deviation from the predictions of Marcus theory is thus expected.

5. Conclusion and outlook

The results presented here indicate that the exact mechanism of photoinduced bimolecular ET reactions is more complex than generally assumed. Indeed, in the early days of the investigations of these processes, the time resolution was limited to the nanosecond timescale. Consequently, the reaction scheme that is still often used has essentially been elaborated from indirect measurements of the ion pair dynamics. Moreover, some hypotheses, like the long transfer distance of exergonic reactions, rely essentially on theoretical expressions that describe the solvent as a continuum and the reactants as spheres. One should therefore be very careful when trying to extract very precise information from such expressions.

There is still some work to be done before a reliable picture of bimolecular photoinduced ET reactions is obtained. The structure of the intermediates involved in these processes, i.e. ion pairs and exciplexes is still unknown. Time-resolved vibrational spectroscopy, which has been very scarcely used in this field [119–122], should give a new insight. Time-resolved multidimensional IR spectroscopy, which is just emerging [123,124], might prove to be a powerful tool to investigate the geometry of these bimolecular complexes. A recent investigation of the excited state lifetime of photogenerated radical ions using pump–pump–probe spectroscopy indicates that the decay dynamics is not the same when the ions are free or when they are paired [81]. Such experiments might also deliver interesting information on the conversion dynamics of these intermediates.

The formation of radical ions in an electronic excited state upon highly exergonic ET quenching still need to be directly established. However, this probably requires first a deeper knowledge of the photophysics of radical ions. This would also be useful for other fields, like for example astrochemistry [125,126]. A good understanding of the parameters that favour the formation of excited states upon ET should also be important for the development of new devices like organic light emitting diodes. Finally, we have evidenced the importance of non-equilibrium dynamics in ultrafast CR processes. The fact that the CR dynamics depends on the preparation of the ion pair offers interesting perspective to influence or even control charge transfer processes by tuning the temporal shape of the excitation pulse [127]. Even if this does not find practical applications, this will certainly deepen our understanding on these very important reactions.

Acknowledgements

I wish to thank all my co-workers and colleagues who have been associated to the investigations described here. Continuous support from the Swiss National Science Foundation is also acknowledged.

References

[1] H. Leonhart, A. Weller, Z. Phys. Chem. N. F. (1961) 277.
[2] H. Knibbe, D. Rehm, A. Weller, Z. Phys. Chem. 56 (1967) 95–98.
[3] H. Knibbe, D. Rehm, A. Weller, Ber. Bunsenges. 72 (1968) 257.
[4] A. Weller, Pure Appl. Chem. 54 (1982) 1885.
[5] A. Weller, D. Rehm, Ber. Bunsenges. Phys. Chem. 73 (1969) 834.
[6] D. Rehm, A. Weller, Isr. J. Chem. 8 (1970) 259.
[7] R.A. Marcus, J. Chem. Phys. 24 (1956) 966.
[8] R.A. Marcus, J. Chem. Phys. 43 (1965) 679.
[9] R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.
[10] J.R. Miller, L.T. Calcaterra, G.L. Closs, J. Am. Chem. Soc. 106 (1984) 3047.
[11] N. Mataga, T. Asahi, Y. Kanda, T. Okada, T. Kakitani, Chem. Phys. 127 (1988) 249.
[12] I.R. Gould, D. Ege, S.L. Mattes, S. Farid, J. Am. Chem. Soc. 109 (1987) 3794.
[13] E. Vauthey, P. Suppan, E. Haselbach, Helv. Chim. Acta 71 (1988) 93.
[14] M.R. Wasielewski, N.P. Niemczyk, W.A. Svec, E.B. Pewitt, J. Am. Chem. Soc. 107 (1985) 1080.
[15] G.S. Beddard, M.P. Irvine, R.J. Harrison, J.K.M. Sanders, Chem. Phys. 104 (1986) 315.
[16] P. Chen, R. Duesing, G. Tapolsky, T.J. Meyer, J. Am. Chem. Soc. 111 (1989) 8305.
[17] A. Kapturkiewicz, Chem. Phys. 166 (1992) 259.
[18] D.M. Guldi, K.D. Asmus, J. Am. Chem. Soc. 119 (1997) 5744.
[19] N. Mataga, H. Chosrowjan, Y. Shibata, N. Yoshida, A. Osuka, T. Kikuzawa, T. Okada, J. Am. Chem. Soc. 123 (2001) 12422.
[20] B.S. Brunschwig, S. Ehrenson, N. Sutin, J. Am. Chem. Soc. 106 (1984) 6858.
[21] M. Tachiya, S. Murata, J. Phys. Chem. 96 (1992) 8441.
[22] A.I. Burshtein, Chem. Phys. 247 (1999) 275–291.
[23] T. Kakitani, A. Yoshimori, N. Mataga, J. Phys. Chem. 96 (1992) 5385.
[24] R.A. Marcus, J. Electroanal. Chem. 483 (2000) 2–6.
[25] I.R. Gould, S. Farid, Ace. Chem. Res. 29 (1996) 522.
[26] K. Kikuchi, Y. Takahashi, M. Hoshi, T. Niwa, T. Katagiri, T. Miyashi, J. Phys. Chem. 95 (1991) 2378.
[27] G.J. Kavarnos, N.J. Turro, Chem. Rev. 86 (1986) 401.
[28] A. Weller, Pure Appl. Chem. 16 (1968) 115–123.
[29] T.T. Harding, S.C. Wallwork, Acta Crystallogr. 8 (1955) 787.
[30] N.D. Jones, R.E. Marsh, Acta Crystallogr. 15 (1962) 809.
[31] I.R. Gould, R.H. Young, L.J. Mueller, S. Farid, J. Am. Chem. Soc. 116 (1994) 8176.
[32] K. Kikuchi, T. Niwa, Y. Takahashi, H. Ikeda, T. Miyashi, M. Hoshi, Chem. Phys. Lett. 173 (1990) 421.
[33] M.G. Kuzmin, J. Photochem. Photobiol. A 102 (1996) 51.
[34] M. Itoh, T. Mimura, Chem. Phys. Lett. 24 (1974) 551.
[35] K.S. Peters, J. Lee, J. Phys. Chem. 96 (1992) 8941.
[36] M. Tachiya, Chem. Phys. Lett. 159 (1989) 505.
[37] A.I. Burshtein, Adv. Chem. Phys. 114 (2000) 419–587.
[38] C. Zhong, J. Zhou, C.L. Braun, J. Phys. Chem. A 108 (2004) 6842.
[39] T. Asahi, N. Mataga, J. Phys. Chem. 93 (1989) 6575.
[40] N. Mataga, H. Miyasaka, Adv. Chem. Phys. 107 (1999) 431.
[41] N. Mataga, Radiat. Phys. Chem. 21 (1983) 83.
[42] S.M. Hubig, T.M. Bockman, J.K. Kochi, J. Am. Chem. 118 (1996) 3842.
[43] I.R. Gould, D. Noukakis, L. Gomez-Jahn, J.L. Goodman, S. Farid, J. Am. Chem. Soc. 115 (1993) 4405.
[44] M. Tachiya, S. Murata, J. Am. Chem. Soc. 116 (1994) 2434.
[45] P.A. Frantsuzov, M. Tachiya, J. Chem. Phys. 112 (2000) 4216.
[46] I.R. Gould, S. Farid, J. Phys. Chem. 96 (1992) 7635.
[47] C.F. Shannon, D.D. Eads, J. Chem. Phys. 103 (1995) 5208.
[48] S. Nishikawa, T. Asahi, T. Okada, N. Mataga, T. Kakitani, Chem. Phys. Lett. 185 (1991) 237.
[49] A.D. Scully, T. Takeda, M. Okamoto, S. Hirayama, Chem. Phys. Lett. 228 (1994) 32.
[50] S. Murata, M. Tachiya, J. Phys. Chem. 100 (1996) 4064.
[51] V.S. Gladkikh, A.I. Burshtein, H.L. Tavernier, M.D. Fayer, J. Phys. Chem. A 106 (2002) 6982–6990.
[52] X. Allonas, P. Jacques, A. Accary, M. Kessler, F. Heisel, J. Fluoresc. 10 (2000) 237.

[53] S.A. Rice, Comprehensive chemical kinetics, in: C.H. Bamford, C.F.H. Tripper, R.G. Compton (Eds.), Diffusion-Limited Reactions, vol. 25, Elsevier, Amsterdam, 1985.
[54] F.C. Collins, G.E. Kimball, J. Colloid Sci. 4 (1949) 425.
[55] T. Ohno, A. Yoshimura, H. Shioyama, N. Mataga, J. Phys. Chem. 91 (1987) 4365.
[56] G. Grampp, G. Hetz, Ber. Bunsenges. Phys. Chem. 96 (1992) 198.
[57] T. Kircher, H.-G. Löhmannsröben, Phys. Chem. Chem. Phys. 1 (1999) 3987.
[58] D. Burget, P. Jacques, E. Vauthey, P. Suppan, E. Haselbach, J. Chem. Soc. Faraday Trans. 90 (1994) 2481.
[59] S.S. Jayanthi, P. Ramamurthy, J. Phys. Chem. 101 (1997) 2016.
[60] E. Vauthey, C. Högemann, X. Allonas, J. Phys. Chem. A 102 (1998) 7362.
[61] E. Vauthey, J. Phys. Chem. A 101 (1997) 1635.
[62] E. Vauthey, J. Phys. Chem. A 104 (2000) 1804.
[63] E. Vauthey, J. Phys. Chem. A 105 (2001) 340.
[64] P. Gilch, M. Linsenmann, W. Haas, U.E. Steiner, Chem. Phys. Lett. 254 (1996) 384.
[65] P. Gilch, F. Pöllinger-Dammer, C. Musewald, M.E. Michel-Beyerle, U.E. Steiner, Science 281 (1998) 982.
[66] N.R. Kestner, J. Logan, J. Jortner, J. Phys. Chem. 78 (1974) 2148.
[67] O. Nicolet, E. Vauthey, J. Phys. Chem. A 107 (2003) 5894.
[68] A. Weller, Z. Phys. Chem. N.F. 130 (1982) 129.
[69] U.E. Steiner, W. Haas, J. Phys. Chem. 95 (1991) 1880.
[70] K. Schulten, A. Weller, Biophys. J. 24 (1978) 295.
[71] H.J. Werner, H. Staerk, A. Weller, J. Chem. Phys. 68 (1978) 2419.
[72] U. Steiner, G. Winter, Chem. Phys. Lett. 55 (1978) 364.
[73] R.E. Föll, H.E.A. Kramer, U.E. Steiner, J. Phys. Chem. 94 (1990) 2476.
[74] K. Kikuchi, M. Hoshi, T. Niwa, Y. Takahashi, T. Miyashi, J. Phys. Chem. 95 (1991) 38.
[75] C. Högemann, M. Pauchard, E. Vauthey, Rev. Sci. Instrum. 67 (1996) 3449.
[76] N. Mataga, Y. Kanda, T. Okada, J. Phys. Chem. 90 (1986) 3880.
[77] N. Mataga, Y. Kanda, T. Asahi, H. Miyasaka, T. Okada, T. Kakitani, Chem. Phys. 127 (1988) 239.
[78] S. Pagès, B. Lang, E. Vauthey, J. Phys. Chem. A 108 (2004) 549.
[79] S. Hirata, T.J. Lee, M. Head-Gordon, J. Chem. Phys. 111 (1999) 8904–8912.
[80] P. Brodard, A. Sarbach, J.-C. Gumy, T. Bally, E. Vauthey, J. Phys. Chem. A 105 (2001) 6594.
[81] S. Pagès, B. Lang, E. Vauthey, in: J.T. Hynes, M. Martin (Eds.), Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science, Elsevier Science Publishers, Amsterdam, 2004, p. 319.
[82] V. Gladkikh, A.I. Burshtein, G. Angulo, S. Pagès, B. Lang, E. Vauthey, J. Phys. Chem. A 108 (2004) 6667.
[83] V.S. Gladkikh, A.I. Burshtein, S.V. Feskov, A.I. Ivanov, E. Vauthey, J. Chem. Phys. 133 (2005) 244510.
[84] E.W. Castner Jr., D. Kennedy, R.J. Cave, J. Phys. Chem. A 104 (2000) 2869.
[85] A. Morandeira, A. Fürstenberg, J.-C. Gumy, E. Vauthey, J. Phys. Chem. A 107 (2003) 5375.
[86] J.R. Miller, Science 189 (1975) 221.
[87] G.L. Closs, J.R. Miller, Science 240 (1988) 440.
[88] M.R. Roest, A.M. Oliver, M.N. Paddon-Row, J.W. Verhoeven, J. Phys. Chem. A 101 (1997) 4867.
[89] M.A. Ratner, J. Jortner, in: M.A. Ratner, J. Jortner (Eds.), Molecular Electronics, Blackwell Science, Inc., Oxford, 1997, p. 5.
[90] N. Mataga, S. Nishikawa, T. Asahi, T. Okada, J. Phys. Chem. 93 (1990) 1443.
[91] N.S. Hush, Prog. Inorg. Chem. 8 (1967) 391.
[92] S. Pankasem, K.K. Iu, J.K. Thomas, J. Photochem. Photobiol. A 62 (1991) 53.
[93] D.T. Breslin, M.A. Fox, J. Phys. Chem. 98 (1994) 408.
[94] C. Joblin, F. Salama, L. Allamandola, J. Chem. Phys. 102 (1995) 9743.
[95] A.R. Cook, L.A. Curtiss, J.R. Miller, J. Am. Chem. Soc. 119 (1997) 5729.
[96] K. Zimmer, M. Hoppmeier, A. Schweig, Chem. Phys. Lett. 293 (1998) 366.
[97] K. Zimmer, B. Gödicke, M. Hoppmeier, H. Meyer, A. Schweig, Chem. Phys. 248 (1999) 263.
[98] J.-C. Gumy, E. Vauthey, J. Phys. Chem. A 101 (1997) 8575.
[99] L. Zhao, R. Lian, L.A. Shkrob, R.A. Crowell, S. Pommeret, E.L. Chronister, A.D. Liu, A.D. Trifunac, J. Phys. Chem. 108 (2004) 25.
[100] P.-A. Muller, E. Vauthey, J. Phys. Chem. A 105 (2001) 5994.
[101] A. Morandeira, L. Engeli, E. Vauthey, J. Phys. Chem. A 106 (2002) 4833.
[102] G.G. Gurzadyan, T.-H. Tran-Thi, T. Gustavsson, J. Chem. Phys. 108 (1998) 385–388.
[103] O. Nicolet, E. Vauthey, J. Phys. Chem. A 106 (2002) 5553.
[104] O. Nicolet, E. Vauthey, in: R.D. Miller, M.M. Murnane, N.F. Scherer, A.M. Weiner (Eds.), Ultrafast Phenomena XIII, Springer, Berlin, 2003, p. 432.
[105] T. Asahi, M. Ohkohchi, N. Mataga, J. Phys. Chem. 97 (1993) 13132.
[106] I. Rips, J. Jortner, J. Chem. Phys. 88 (1988) 818.
[107] H. Heitele, Angew. Chem. Int. Ed. Engl. 32 (1993) 359.
[108] H. Sumi, R.A. Marcus, J. Chem. Phys. 84 (1986) 4272.
[109] G.C. Walker, E. Akesson, A.E. Johnson, N.E. Levinger, P.F. Barbara, J. Phys Chem. 96 (1992) 3728.
[110] H. Sumi, R.A. Marcus, J. Chem. Phys. 84 (1986) 4894.
[111] A.I. Ivanov, F.N. Belikeev, R.G. Fedunov, E. Vauthey, Chem. Phys. Lett. 372 (2003) 73.
[112] R.G. Fedunov, S.V. Feskov, A.I. Ivanov, O. Nicolet, S. Pagès, E. Vauthey, J. Chem. Phys. 121 (2004) 3643.
[113] V.A. Mikhailova, A.I. Ivanov, E. Vauthey, J. Chem. Phys. 121 (2004) 6463.
[114] O. Nicolet, A.I. Ivanov, E. Vauthey, in: J.T. Hynes, M. Martin (Eds.), Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science, Elsevier Science Publishers, Amsterdam, 2004, p. 331.
[115] O. Nicolet, N. Banerji, S. Pagès, E. Vauthey, J. Phys. Chem. A 109 (2005) 8236.
[116] L.E. Orgel, J. Chem. Phys. 23 (1955) 1352.
[117] E.-M. Voigt, J. Am. Chem. Soc. 86 (1964) 3611.
[118] O. Edholm, C. Blomberg, Chem. Phys. 252 (1999) 221–225.
[119] E. Vauthey, D. Phillips, A.W. Parker, J. Phys. Chem. 96 (1992) 7356.
[120] E. Vauthey, A.W. Parker, D. Phillips, B. Nohova, J. Am. Chem. Soc. 116 (1994) 9182.
[121] T. Tahara, H.-o. Hamaguchi, J. Phys. Chem. 96 (1992) 8252.
[122] T. Fournier, S.M. Tavender, A.W. Parker, G.D. Scholes, D. Phillips, J. Phys. Chem. A 101 (1997) 5320.
[123] N.-H. Ge, R.M. Hochstrasser, Phys. Chem. Commun. 3 (2002) b109935c.
[124] S. Woutersen, P. Hamm, J. Phys. Condens. Mater. 14 (2002) R1035.
[125] D.K. Bohme, Chem. Rev. 92 (1992) 1487.
[126] T.P. Snow, V.L. Page, Y. Keheyan, V.M. Bierbaum, Nature 391 (1998) 259–260.
[127] T. Brixner, G. Gerber, Chem. Phys. Chem. 4 (2003) 418.