PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

PCCP Physical Chemistry Chemical Physics Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PERSPECTIVE

Bimolecular Photoinduced Electron Transfer Reactions in Liquids under the Gaze of Ultrafast Spectroscopy

Arnulf Rosspeintner and Eric Vauthey,*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Because of their key role in many areas of science and technology, bimolecular photoinduced electron transfer reactions have been intensively studied over the past five decades. Despite this, several important questions, such as the absence of the Marcus inverted region or the structure of the primary reaction product, have only recently been solved while several still remain unanswered. Ultrafast spectroscopy has proven to be extremely powerful to monitor the entire electron transfer process and to access, with the help of state-of-the-art theoretical models of diffusion-assisted reactions, crucial information like e.g. the intrinsic charge separation dynamics beyond the diffusion limit. Additionally, extension of these experimental techniques to other spectral regions than the UV-visible, such as the infrared, has given a totally new insight into the nature, the structure and the dynamics of the key reaction intermediates, like exciplexes and ions pairs. In this Perspective, we highlight these recent progresses and discuss several aspects that still need to be addressed before a thorough understanding of these processes can be attained.

1. Introduction

Electron transfer (ET) is one of the most ubiquitous and at the same time simplest chemical reactions, and as such has and still attracts major interest.[1,2] This apparent simplicity makes ET an ideal model system for studying elementary chemical reaction dynamics. Moreover, as photoinduced ET reactions are triggered by light, their mechanism and dynamics can now be investigated with an unprecedented time resolution.[3] Moreover, photoinduced ET processes play a key role in areas as important as solar energy conversion and storage,[4-12] or light induced DNA damage.[13-15] A thorough understanding of their mechanism and of the parameters that affect their dynamics is thus a *conditio sine qua non* for further progress.

Over the past decades, experimental investigations have mostly concentrated on ET between chemically linked reactants,[16-24] allowing the vast amount of theoretical work to be put to the test and further refined.[25-33] The main advantage of studying intra- rather than intermolecular ET is that the distance between 'reactants' and their mutual orientation are in principle well defined. This allows a more direct access to the intrinsic ET dynamics. On the other hand, the linker, while allowing control of distance and orientation of the electron donor (D) and acceptor (A) moieties, is not inert and can strongly influence the electronic coupling between D and A, and hence the ET dynamics.[22,34,35] Such coupling can be very advantageous for specific applications, but complicates the comparison with the theoretical models.

Whereas intermolecular reaction dynamics in the gas phase is generally well understood, achieving a similar level of comprehension for intermolecular reaction dynamics in the liquid phase still remains a major challenge.[36] However, as most chemical reactions are not intramolecular and occur in the condensed phase, we think that bimolecular ET reactions in solution deserve more attention, especially with the availability of powerful spectroscopic tools and elaborate theoretical models of diffusion-assisted reactions that did not exist when these processes were first investigated.

Here, we will try to especially emphasize the specific features that emerge as soon as, due to its bimolecular nature, the intrinsic ET reaction becomes intimately interwoven with the mutual diffusion of the reactants. The amount of theoretical work devoted to the influence of diffusion on ET reactions by far exceeds the experimental studies. However, especially since the advent of ultrafast spectroscopic techniques, many of the beforehand disguised experimental details are now amenable to thorough comparison with the vast body of available theories. One can hope to eventually achieve a sound understanding of bimolecular photoinduced ET processes in liquid solution as well as in other environments, such as e.g. polymer matrices.

Whereas some of the “puzzles in electron transfer” discussed by Miller more than 20 years ago in his thought-provoking article have been solved,[37] others have been ignored, and new ones have emerged. The main aim of this Perspective is to discuss the progress that has been made in our understanding of bimolecular photoinduced ET reactions in liquids over the past years, mainly thanks to ultrafast spectroscopy,[38] and to address some of the 'puzzles' that, in our opinion, are still unsolved or not completely understood.

A simplified scheme of the reactions discussed in this

Perspective is depicted in **Figure 1**. Although the denomination 'bimolecular photoinduced ET' only concerns the initial fluorescence quenching step, rich information on the nature of the primary product, hence on the charge separation (CS) mechanism itself, can be obtained by investigating the other ET step, namely the charge recombination (CR), which is also bimolecular but not photoinduced.

Therefore, this Perspective is divided into three main parts, devoted to the distinct stages of the overall reaction, namely, 1) charge separation (fluorescence quenching), 2) the nature of the CS product, and 3) charge recombination. Before this, a short and ad-hoc outline of the basic theoretical aspects of ET and diffusion-influenced reactions is presented. We decided not to deviate into the vast, yet still equally partially uncharted, field of magnetic field effects, which would be worth a perspective on its own.[39-45]

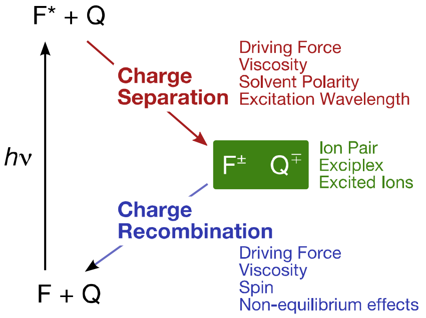


Figure 1. Overall bimolecular photoinduced electron transfer scheme. *F* and *Q* are the fluorophore and the quencher, respectively.

2. Theoretical Aspects

Almost 100 years ago, Smoluchowski recognized and theoretically described the influence of diffusion on the dynamics of processes, which are intrinsically faster than the mutual diffusional approach of the reactants.[46] His work, dealing with the coagulation dynamics of colloidal solutions, was the starting point of numerous theoretical extensions and modifications. Collins and Kimball adapted Smoluchowski's theory, that assumed an infinitely fast intrinsic reaction rate, to account for finite reaction rates.[47] Wilemski and Fixman,[48] Doktorov and Burshtein,[49] and, later, Tachiya[50] expanded this model to reactions that can also occur at remote distance. Comprehensive reviews on diffusional effects on fluorescence quenching can be found in references 51 and 52. References 53 and 54 constitute more general reviews covering theoretical developments until the mid-80s and mid-90s, respectively. More recent extensive overviews on diffusion influenced ET reactions include irreversible and reversible CS, CR as well as the effect of spin and external magnetic fields.[55,56]

Irreversible diffusion-influenced ET reactions can be described in terms of diffusion-reaction equations complemented with a theoretical model of ET as a sink term. The general strategy will be briefly outlined here.[55-61] Reversible reactions, described in refs. 55 and 56 will not be further discussed.

2.1. Diffusion-Reaction Equation

The reaction scheme in **Figure 1** can be rewritten as

$$\mathrm{F{+}Q}\overset{h\nu}{\rightarrow}\underbrace{\mathrm{F}^{*}\mathrm{+Q}}_{n(r,t)}\overset{\mathrm{CS}}{\rightarrow}\underbrace{\mathrm{F}^{\pm}+\mathrm{Q}^{\mp}}_{m(r,t)}\overset{\mathrm{CR}}{\rightarrow}\mathrm{F{+}Q}$$

Here $n(r,t)$ and $m(r,t)$ are the distance- and time-dependent pair density functions for F^*/Q and $F^{\pm}/Q^{\mp}$, respectively. For the sake of simplicity, the generation of the F^*/Q pair is assumed to proceed upon excitation with an infinitely short optical pulse, $h\nu$. The time-dependence of both pair density distributions can be evaluated with the two following coupled diffusion reaction equations:[56]

$$\frac{\partial n(r,t)}{\partial t}=\hat{L}_{\mathrm{CS}}(r)n(r,t)-w_{\mathrm{CS}}(r)n(r,t) \tag{1}$$

$$\frac{\partial m(r,t)}{\partial t}=\hat{L}_{\mathrm{CR}}(r)m(r,t)-w_{\mathrm{CR}}(r)m(r,t)+w_{\mathrm{CS}}(r)n(r,t)N(t) \tag{2}$$

where $w_x(r)$ is the distance dependent ET reaction probability for either CS or CR, $N(t)$ is the survival probability of $n(r,t)$ given below, and $\hat{L}_x$ denotes the diffusion operator for process x. The latter can account for Coulomb attraction, interparticle potentials due to e.g. solvent structure and distance-dependent diffusion coefficients, i.e. hydrodynamic effect.[62,63] The first term on the rhs of eqs. (1) and (2) accounts for the diffusive motion of the reaction partners, whereas the second term describes the disappearance of reactant pairs by either CS or CR. Finally, the third term on the rhs of eq. (2) represents the formation of ions by CS.

By solving the above equations, one can obtain experimentally observable quantities, namely the survival probability of the excited state, $N(t)$, and ion pair, $P(t)$, populations.

$$N(t)=N(0)\exp\left(-\frac{t}{\tau_0}-4\pi c\int_0^t\underbrace{\int_\sigma^\infty w_{\mathrm{CS}}(r)n(r,t')r^2\,\mathrm{d}r}_{k(t')}\mathrm{d}t'\right) \tag{3}$$

$$P(t)=4\pi c\int_\sigma^\infty m(r,t)r^2\,\mathrm{d}r \tag{4}$$

where c is the quencher concentration and τ_0 is the excited state lifetime of the fluorophore in the absence of quencher.

While for CS processes it is only necessary to solve eq.(1) with the appropriate boundary conditions, bimolecular CR is obviously more complicated as it requires the solution of the coupled CS/CR problem. As discussed in more detail below, the rate coefficient k in eq.(3) is not a constant but is time dependent.

The concentration dependence of $N(t)$ is relatively straightforward: a higher quencher concentration yields a faster fluorescence decay. However, CR exhibits a completely different concentration dependence. Inspection of eq.(4) reveals that, to first order, the quencher concentration only affects the amplitude but not the time-dependence of the observed ion signal. The effect of c on the time dependence of CR is much more subtle, stems from the third term on the rhs of eq. (2) and mostly affects the generation of ions, but not their decay. In simple terms, the ion pair, once it is generated does not care about how many other quenchers are left in the solution. While bimolecular CS constitutes a bulk process, the subsequent CR process, at least at low F* concentrations, can be considered a pair process.

2.1. Electron Transfer

We will briefly review the main equations and predictions of the semi-classical description of Marcus non-adiabatic ET theory.[25,26,64]

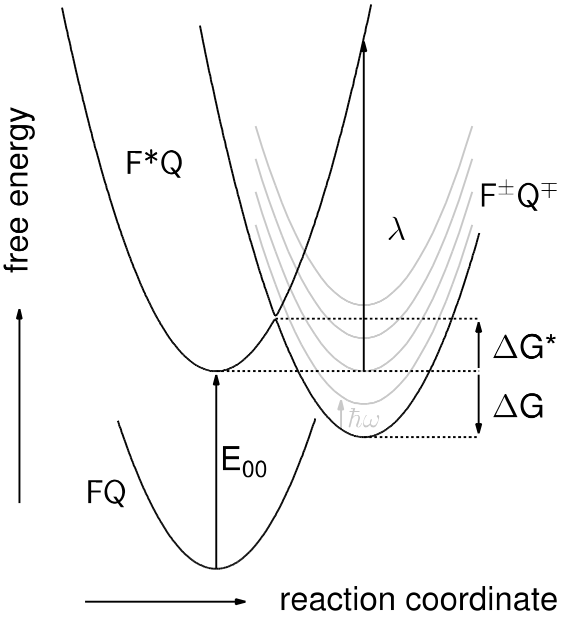


Figure 2. Diabatic free-energy curves for a photoinduced electron transfer reaction.

The ET reaction probability as a function of distance, $w(r)$, is given by

$$w(r)=\frac{2\pi}{\hbar}V(r)^2\left(\frac{1}{k_\mathrm{B}T\,\lambda(r)}\right)^{1/2}\times\mathrm{FC} \qquad (5a)$$

$$\mathrm{FC}=\sum_{n=0}^{\infty}e^{-S}\left(S^n/n!\right)\exp\left(-\frac{\left(\Delta G(r)+\lambda(r)+n\hbar\omega\right)}{4\lambda(r)k_BT}\right) \qquad (5b)$$

$$S=\lambda_\mathrm{qm}/\hbar\omega \qquad (5c)$$

where V denotes the electronic coupling matrix element between reactants and products, $\lambda(r)$=$\lambda_\mathrm{s}(r)$+ λ_i is the reorganisation energy of classically-described solvent and intramolecular modes, λ_qm is the reorganisation energy of the quantum mechanically-described intramolecular modes with an average frequency ω, and ΔG is the ET driving force (Figure 2).

The driving force for photoinduced CS in polar solvents is given by the Weller equation:[65]

$$\Delta G_\mathrm{CS}(r)=e\left[E(\mathrm{D}^+/\mathrm{D})-E(\mathrm{A}/\mathrm{A}^-)\right]-E_{00}-\frac{e^2}{4\pi\varepsilon_0\varepsilon_s r} \qquad (6)$$

where e is the elementary charge, $E(X)$ the reduction potential of species X, E_{00} the 0-0 electronic transition energy, and ε the dielectric constant of the solvent. The driving force for the ensuing CR process can be equivalently obtained from

$$\Delta G_\mathrm{CR}(r)=-E_{00}-\Delta G_\mathrm{CS}(r)$$
$$=-e\left[E(\mathrm{D}^+/\mathrm{D})-E(\mathrm{A}/\mathrm{A}^-)\right]+\frac{e^2}{4\pi\varepsilon_0\varepsilon_s r} \qquad (7)$$

Using the dielectric continuum description of the solvent and assuming point charges, the solvent contribution to $\lambda(r)$ is given by[66]

$$\lambda_\mathrm{s}(r)=\frac{e^2}{4\pi\varepsilon_0\sigma}\left(\frac{1}{n^2}-\frac{1}{\varepsilon}\right)\left(2-\frac{\sigma}{r}\right) \qquad (8)$$

where σ denotes the contact radius of the reactants, and n the refractive index of the solvent. The intramolecular classical contribution can be estimated as

$$\lambda_\mathrm{i}=\sum_j\frac{f_j^r f_j^p}{f_j^r+f_j^p}\Delta q_j^2 \qquad (9)$$

where f_j^r and f_j^p are the jth force constant of the reactant and product vibration and Δq denotes the displacement from the reactant to the product equilibrium position.

Some of the remarkable predictions of this model comprise:

- A non-monotonous dependence of the reaction rate constant on driving force, namely an increase of $w(r)$ with the driving force as long as $-\Delta G < \lambda$, the so-called *Marcus normal region*, until a maximum at $-\Delta G = \lambda$, and a subsequent decrease as $-\Delta G > \lambda$, the *Marcus inverted region*;
- A strong influence of solvent polarity on the ET dynamics, as it affects both the reorganisation energy and the driving force;
- A shift of the reaction zone from contact to off-contact with increasing driving force.[67]

As solvent modes are strongly involved in the reaction coordinate, the ET timescale can in principle not be shorter than that of the solvent fluctuations. Therefore, for describing ultrafast ET, a modified eq.(5a) that takes the finite dielectric response of the solvent into account, should be used. More details about solvent-controlled ET dynamics can be found in refs.[31,68,69]

3. Charge Separation

The simplest experimental approach to access the dynamics of photoinduced CS reactions is to perform time-resolved and steady-state fluorescence quenching experiments, i.e. to monitor the survival probability of the excited reactant population, $N(t)$. However, the determination of the relevant rate constants from such measurements is not really straightforward, because, as shown in eq.(3), the rate coefficient of the bimolecular reaction is time-dependent.

This can be understood by considering the three different regimes of a bimolecular quenching process (Figure 3):

1) *The static regime*: directly after optical excitation of the fluorophore, the reaction first takes place between reactant

pairs at optimal distance for CS. In this case, no diffusion is required and the quenching rate is identical to the intrinsic CS rate constant, $k_0=k_{CS}$, which remains constant during this process.

2) *The transient or non-stationary regime*: once all optimally arranged pairs have reacted, quenching occurs between reactant pairs that are more and more separated and which have time to undergo some diffusion. Thus, the distance distribution between the F*/Q pairs gradually shifts towards larger separation distances and the reaction rate decreases continuously with time.

3) *The stationary regime*: eventually, all the pairs initially present upon excitation have reacted, and new pairs can only be produced upon mutual diffusion of F* and Q. As a consequence, an equilibrium between the formation and the decay of pairs is attained, giving rise to a constant reaction rate, k_∞.

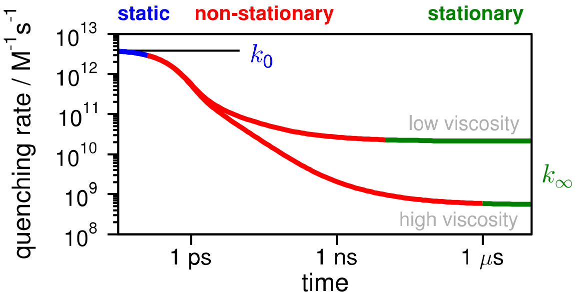


Figure 3. Characteristic time-dependence of the reaction rate for an irreversible diffusion-limited reaction.

This time-dependence of k gives rise to non-exponential fluorescence decays and nonlinear Stern-Volmer plots (Figure 4), the slope of which is generally used to extract reaction rates. Care should be taken that the Stern-Volmer plots only reflect effects from excited state reactions. Appropriate corrections for ground-state complex formation are thus mandatory.[70,71]

As shown in Figure 3, the temporal change of the quenching rate is particularly large when the intrinsic CS process is much faster than diffusion. This is often the case in viscous solvents, where the duration of the transient regime can be particularly large and extend beyond the lifetime of F^*. In such case, the stationary regime is never reached.

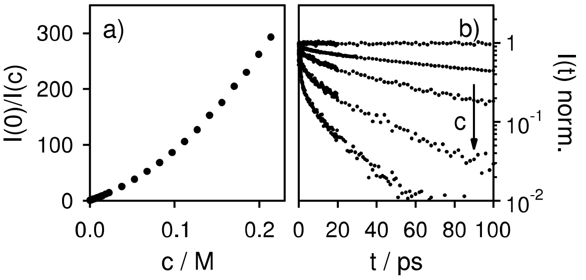


Figure 4. Effect of the time dependence of the quenching rate on A) the Stern-Volmer plot and B) the fluorescence decay obtained with 2,9,10-tricyanoanthracene and N,N-dimethylaniline in acetonitrile.

These effects can significantly complicate the analysis of fluorescence quenching experiments and may lead to substantial errors in the data interpretation if not being accounted for. For example, CS quenching rate constants much faster than diffusion have been reported in room-temperature ionic liquids and ascribed to specific properties of these solvents. Similarly, previously undetected Marcus inversions at comparatively low driving forces, i.e. $-\Delta G < 0.5$ eV, have been observed for CS quenching reactions in room-temperature ionic liquids and in confined media, such as micelles. Both observations could be shown to be spurious and due to too simple a data analysis, neglecting transient effects, which are particularly pronounced in these viscous media.[72-74]

However, it is important to realise that, although this non-Markovian nature of diffusion-limited processes complicates the data analysis and the determination of the stationary quenching rate constant, k_∞, it offers an inestimable opportunity to access to information on the faster intrinsic reaction rate, $k_0=k_{CS}$.[75-82] Most of the experimental studies, which are much more scarce than the theoretical works in this area, indeed aimed at gaining insight into the intrinsic reaction and its nature. Whereas Eads et al. could show that the Smoluchowski and Collins-Kimball models should be extended by introducing a distance dependent ET reaction probability,[76,83] Tachiya,[84] Fayer,[79] and Grampp[82] and co-workers confirmed the theoretical predictions that the effective quenching distance increases with increasing viscosity. In addition, the Fayer and Grampp groups showed the limits of the continuum description of the solvent and obtained better agreement with the experimental results by accounting for the solvent structure and by including the hydrodynamic effect, i.e. the distance dependence of the diffusion coefficient, $D(r)$.[63,82]

At the present stage, the combination of high quality ultrafast and steady-state emission measurements with an appropriate theoretical model is clearly the best way to access the CS dynamics beyond the diffusion limit and to minimise possible ambiguities or misinterpretations of the extracted parameters. Clearly more systematic experimental studies of photoinduced bimolecular CS are required to further refine these theoretical models.

3.1. Driving-Force Dependence

One of the most captivating questions concerning bimolecular photoinduced ET can be traced back to a series of seminal experiments by Rehm and Weller aiming at putting to the test the driving-force dependence of the ET rate constant predicted by Marcus theory.[65,85] The fluorescence quenching rate constant, $k_q \sim k_\infty$, of almost 60 F/Q pairs in acetonitrile, covering a driving-force range of more than 2.5 eV, was studied. As a matter of fact, almost the entire outcome of their experiment, which has since been reproduced many times,[86-90] was puzzling and still remains a matter of debate (Figure 5).

The first puzzle is that no inverted region is observed, contrary to almost all the other types of ET reactions, namely intramolecular CS,[91] charge shift,[17,92] or CR.[93,94]

Various authors, including Weller and Mataga, have suggested that this could be due to the opening of additional CS pathways leading to the formation of excited radical ions at high driving forces (see also section 4.3).[85,95] We could recently show, using ultrafast Vis-pump IR-probe spectroscopy in collaboration with the Nibbering group, that excited radical ions can indeed be generated upon photoinduced bimolecular CS reactions.[96] The distance dependence of the ET reaction probability has also been invoked to explain the apparent absence of the Marcus inverted region.[67,97,98] Mataga and co-workers, and more recently, our group have measured the dynamics of bimolecular fluorescence quenching with ps- to fs-time resolution and, in collaboration with G. Angulo, have used a diffusion-reaction equation approach combined with Marcus theory to extract the intrinsic electron transfer rate, $k_0 = k_{CS}$.[70,77] While the relatively low time-resolution and the omission of steady-state data led to relatively strongly scattered data in ref. [77], the combined analysis of femtosecond up-conversion data with steady-state fluorescence quenching experiments in ref. [70] yielded the experimental bimolecular CS rates, k_0, shown in Figure 5. These data reveal that CS in acetonitrile is more than two orders of magnitude faster than diffusion. Moreover, only a very attenuated inverted region can be observed. Extrapolation of this ΔG dependence until CS becomes smaller than diffusion indicates that the observation of the inverted region in a Rehm-Weller-type quenching experiment would require F/Q pairs with unrealistically large CS driving force.

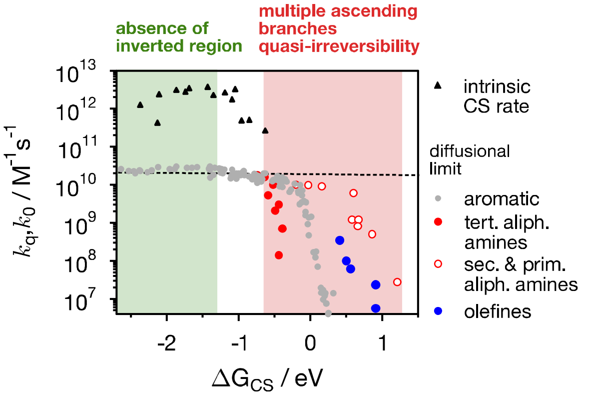


Figure 5. Driving-force dependence of the quenching rate constant, k_q, measured in typical Rehm-Weller experiments (circles) and of the intrinsic CS rate constant, k_0 (triangles), with some of the remaining puzzles. (Black triangles data taken from ref.[70], gray dots data from refs.[85,89,90], tertiary aliphatic amines data from ref.[99], other data from ref.[100].

Less known, though not less intriguing, is the fact that the usually good agreement between theory and experiment in the quasi-resonance region, i.e. $\Delta G \sim 0$, is misleading. At such low driving forces, reverse back ET to the F*/Q reactant state should become equally fast or even faster than the forward CS. Unless the CS product decays very quickly, this reverse transfer should significantly reduce the quenching efficiency and worsen the good agreement between the experiments and theories for irreversible transfer. To circumvent this difficulty, Rehm and Weller assumed rather arbitrarily a CR of the reaction product to the ground state fast enough to make CS quasi irreversible.[85] More recently, Burshtein showed that CR to the excited triplet state of the neutral products, i.e. ^{3}F*/Q, could also suppress reversibility.[101] A more thorough discussion on this question can be found in reference 56.

A third puzzle is the observation by Jacques and co-workers,[100,102] as well as Inada et al. of multiple Rehm-Weller plots, i.e. distinct and shifted free-energy dependences of the quenching rate constants, for different classes of electron donors, e.g. aromatic and aliphatic amines, in the quasi-resonance region (Figure 5). These authors proposed that the magnitude of the Coulombic stabilization of the radical ion pairs is not the same for the various types of quenchers and, thus, gives rise to different driving forces. An alternative explanation, based on the reversibility of the CS discussed above, has been proposed by Burshtein and Ivanov.[103] When the triplet recombination of the radical ion pair is a dominant process, variations in its rate constant can lead to multiple Rehm-Weller plots.

Whereas the absence of the inverted region in the Rehm-Weller experiment is now understood and has been shown to have various origins, several questions concerning CS in the low driving force regime still remain to be answered.

3.2. CS in Nonpolar Solvents

In the outer-sphere ET theory discussed in Section 2, the reaction coordinate is in large part associated with solvent modes. Indeed, ET occurs once the reactant and product free energies are equal. This condition is largely achieved through the thermal fluctuations of the solvent polarisation. This contribution from the solvent modes is reflected in λ_s (eq.(8)). In addition, solvent polarity has a major effect on the energetics, via the solvation energy of the ions and the Coulombic interactions between them (eqn. (6)). As a consequence a pronounced dependence of the ET rate on solvent polarity is expected. For example, as the total reorganisation energy is substantially reduced by going from a polar to an apolar solvent, the inverted region is predicted to occur at considerably smaller driving force. In order to make λ_s twice as small as in acetonitrile, solvents with a dielectric constant below 3-4 should be used. However, the experimental studies in such conditions are very scarce, and the few systematic experimental investigations on the driving-force dependence in totally apolar solvents have yielded rather unexpected results.[87,104] Using nanosecond time-resolved fluorescence, Chen et al. found that CS quenching in cyclohexane remains essentially diffusion controlled up to a driving force of approximately 2 eV and does not show any inversion.[87] From the analysis of the transient effect in the fluorescence quenching of five F/Q pairs in liquid paraffin covering a large ΔG range, Burel et al.[104] obtained unexpectedly large intrinsic CS rate constants, that they attributed to full and remote CS, contrary to the common view that quenching in nonpolar solvents occurs exclusively via exciplex formation (see also 4.2.).[105,106] In a subsequent article, Tachiya and Seki proposed that, because the inter-reactant distance strongly affects the energy of the ensuing ion pair via the unscreened Coulomb potential, it could be a major constituent of the reaction coordinate in apolar solvents.[107]

Despite the relatively modest amount of experimental data in apolar solvents, they point to very efficient CS and an absence of inverted region like in polar solvents. Therefore, the question arises whether solvent polarisation is indeed such a crucial parameter for ET, at least at large exergonicities, as is usually assumed, or whether this process should not be viewed as a "conventional" radiationless transition where high-frequency intramolecular modes play the dominant role.[108]

An absence of the inverted region was recently reported for photoinduced CS between quantum dots and organic acceptors in heptane.[109] The authors accounted for this deviation from Marcus ET theory in terms of an Auger-assisted process, i.e. by the excitation of the hole simultaneously to CS. This explanation is somehow equivalent to the Weller hypothesis of the formation of excited ions mentioned above.

Considering the scarce experimental data and the fact, that most ET reactions of technological relevance, as e.g. in organic solar cells, occur in low polarity media,[110] further investigations in weakly and non polar environment seem to be mandatory.

3.3. CS in reacting solvents

A convenient way to eliminate the effects of translational diffusion while maintaining the bimolecular nature of the reaction consists in employing one of the reaction partners, so far mostly aromatic amines, as solvent.[111-118] In this way, every excited fluorophore is already completely surrounded by potential reaction partners, thus allowing diffusionless ET. However, the observed quenching dynamics are still multiphasic and appear to be faster, at least partially, than solvent relaxation. Various approaches have been proposed to interpret these findings:

- Yoshihara and co-workers[113,119] have applied the Sumi-Marcus ET model,[29] which expands the reaction coordinate into two dimensions, one associated with slow modes, mostly due to the solvent, and the other comprising faster modes. In this model, ET can be faster than solvent relaxation as the path toward the product state can diverge from the minimum free-energy pathway, by making a 'detour' along the dimension associated with the fast modes.
- Based on molecular dynamics simulations, Castner and co-workers discussed the multiphasic reaction dynamics in terms of a temporal variation of the electronic coupling between the excited fluorophore and the fluctuating environment.[116]
- On our side, we could reproduce the observed fluorescence quenching dynamics measured with perylene derivatives in N,N-dimethylaniline (DMA) by using a model where the donors surrounding the excited fluorophore are sorted into three groups: those with optimal orientation for CS, and those requiring rotational or translational diffusion.[117,118] The probability for a donor to belong to the first group was proposed to be strongly influenced by dipole-dipole interactions between the reactants. In a more recent investigation,[120] these electrostatic interactions between the reactants were shown to modulate the angular dependence of the reaction probability and thus to induce orientational effects on the quenching rate. These effects were found to be also effective when the donor is diluted down to 0.2 M in a non-reactive solvent of the same polarity.

3.4 Excitation Wavelength Dependence

Dipolar interactions between the reactants have several important effects on the quenching dynamics in apolar or weakly polar solvents, which have been largely overlooked until very recently. One of them is the so-called dielectric enrichment that leads to a much larger local concentration of quencher around the polar fluorophore than in the bulk.[121] As a consequence, static quenching and transient effects may become prominent at much lower bulk quencher concentrations than in polar solvents, and at a given quencher concentration, quenching may be faster in apolar than in polar solvents.[122] The magnitude of this enrichment depends on the polarity of the reactants and solvent and can lead to a doubling or more of the local quencher concentration.[121] Moreover, if the fluorophore exhibits solvatochromism in absorption, the presence of polar quenchers in its surrounding affects its $S_1 \leftarrow S_0$ transition energy. Therefore, because of the distribution of the local quencher concentration, the absorption band is inhomogeneously broadened and various subpopulations of fluorophores, differing by the composition of their surrounding, can be selectively photoexcited. If quenching is faster than the fluctuations of the composition of the fluorophore environment, its dynamics will depend on the excitation wavelength. Such an effect has recently been reported by our group with several polar fluorophores, including coumarins, and polar aromatic amines in nonpolar solvents.[122] Acceleration of the fluorescence quenching by a factor as large as 4-5 was observed by varying the excitation wavelength from the maximum to the red edge of the absorption band. Such red-edge effect should be quite general for ET processes in low polarity and viscous or rigid media, and deserves further scrutiny.

4. Nature of the Primary Product

In principle, bimolecular photoinduced CS should eventually result in the formation of radical ions. However, the exact nature of the primary product may differ, depending on various factors such as e.g. the driving force, the solvent and quencher concentration. As a consequence, a large variety of primary CS products have been invoked. Thanks to the recent progress in ultrafast spectroscopy, our understanding of the exact nature of these species is continuously increasing.

4.1 Ion pairs

The observation by Leonhardt and Weller of the perylene radical anion in a flash photolysis study of the fluorescence quenching of perylene by an aromatic amine in acetonitrile was an unambiguous evidence of the occurrence of excited-state ET.[123] Later on, it was realised that free ions could also be generated upon direct excitation into the charge-transfer band of donor/acceptor complexes in polar solvents, however, with a substantially smaller yield.[124-128] This difference was explained by the existence of different types of ion pairs, depending on the excitation scheme, bimolecular CS quenching yielding so-called loose ion pairs (LIPs), and charge-transfer excitation resulting in tight ion pairs (TIPs).[129,130] Many other denominations can be found in the literature for LIPs, such as solvent-shared or solvent-separated ion pairs, as well as for TIPs, like intimate or contact ion pairs. The common point of all these names is the existence of ion pairs with different extent of coupling between them. In the following, we will keep the LIP and TIP notation, as it does not imply anything about the presence or absence of solvent molecules between the ions; an observation which could not be established so far. LIPs and TIPs have very similar electronic absorption spectra and, therefore, the experimental distinction between them is mostly based on the fact that TIPs, being strongly coupled, can exhibit charge transfer fluorescence.[131,132] However, this coupling also favours CR to the neutral reactants and thus, this emission is generally very weak. Nevertheless, this feature has allowed evidencing that TIPs can also be generated upon bimolecular CS quenching.[133,134]

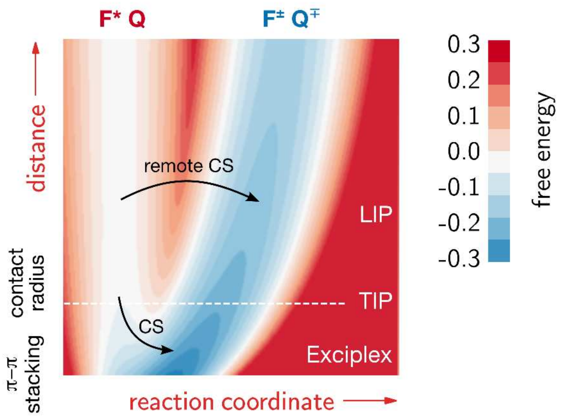


Figure 6. Schematic representation of the free energy surface for the various primary reaction products of a bimolecular photoinduced CS (adapted from references [135] and 44).

Direct spectroscopic distinction of LIPs and TIPs has recently been demonstrated using femtosecond transient IR absorption spectroscopy.[136] The C≡N stretching band associated with the radical anion in the LIP was found to be narrower and blue-shifted relative to the same band in the TIP. These experiments, performed on a donor/acceptor pair with a large driving force for CS, have revealed that the primary quenching product depends on the reactant pair distribution, which itself depends on the quencher concentration. High concentrations favour static quenching and the formation of TIPs, whereas, at low concentrations, quenching is mostly dynamic and yields preferentially LIPs. In other words, when the reactants are not already at optimal distance/orientation, they have to diffuse until the electronic coupling is large enough to make CS faster than further diffusion. As a consequence, LIPs are not the primary products of weakly exergonic CS quenching processes, because, in this case, a large electronic coupling is required to compensate for the large activation barrier.

Although polarized transient IR absorption measurements have evidenced an anisotropic mutual orientation of the ions in a TIP,[136] TIPs and especially LIPs should not be viewed as species with a well-defined structure. They should rather be considered as two limits in the manifold of possible types of ion pairs (Figure 6).

Further experiments based on time-resolved vibrational spectroscopy, such as transient IR absorption and femtosecond stimulated Raman spectroscopies,[137,138] can be expected to yield deeper structural insight into these species.

4.2 Exciplexes

Exciplexes are predominantly generated upon intermolecular CS quenching in nonpolar and weakly polar environments, but not exclusively.[139,140] The name exciplex encompasses a wide variety of excited bimolecular complexes with various degrees of charge transfer, hence different oscillator strengths for emission. Therefore, the above-mentioned TIP should also be considered as a form of exciplex. The common characteristic of exciplexes is that their charge-transfer character is formally not unity. Indeed, complete charge separation is not possible as long as the molecular orbitals of the constituents overlap. Large research activity has been devoted to the role of exciplexes in bimolecular CS processes,[124,130,135,141-144] one of the questions being whether this reaction yields entirely exciplexes or whether LIPs could also be generated in parallel. Like for TIPs, the most typical spectroscopic feature of exciplexes is their fluorescence, which is broad and structureless, as expected for a charge-transfer transition.

Transient electronic absorption spectroscopic data on these species are very scarce and point to absorption spectra very similar to those of the ions.[132,145] Fluorescence-based studies, including magnetic field effect investigations,[43-45,90] reveal a strong dependence of the exciplex yield and charge-transfer character on the polarity of the environment and on the CS driving force. As the solvent polarity and driving force rise, the charge-transfer character increases and the probability to directly form LIPs augments. However, it should be noted that relying only on emission to infer that exciplexes are generated could be misleading. Indeed, their radiative rate constant decreases with the extent of charge transfer and additionally their lifetime decreases with increasing driving force (see Section 5). Therefore, short-lived exciplexes with high charge-transfer character are essentially non-fluorescent, and the quasi-impossibility to detect them by their emission does not allow their presence to be ruled out.

Time-resolved vibrational spectroscopy appears to be a promising technique to investigate both the structure and the dynamics of exciplexes. In a recent transient IR absorption study on the CS quenching of various excited donors by phthalic anhydride in THF and acetonitrile, several IR absorption bands of the exciplex could be unambiguously evidenced when using the weakest electron donor (Figure 7).[146] It was thus possible to spectrally distinguish vibrational bands of the locally-excited donor, of both radical ions as well as of the exciplex and to monitor the temporal evolution of all these species. Global target analysis of the transient IR spectra allowed the determination of the IR spectrum of each of the transient species. Polarization controlled measurements point to a face-to-face mutual orientation of the constituents in the exciplex, confirming the close similarity of exciplexes and TIPs. Further transient IR investigations with other donor/acceptor pairs in a wider variety of solvents are in progress.

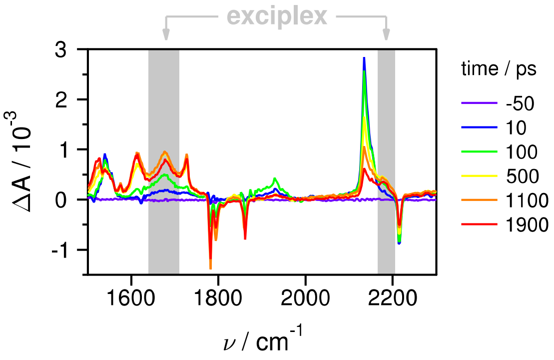


Figure 7. Transient IR absorption spectra recorded after 400 nm excitation of 9-cyanoanthracene in the presence of phthalic anhydride in tetrahydrofuran.[146] The bands, which can be attributed to the exciplex, are marked in gray.

Transient 2D-IR spectroscopy should soon arrive at a level of sensitivity where it can be applied to investigate these systems.[147] When using donor/acceptor pairs with adequate vibrational markers, totally new information on the mutual orientation of the constituents will be at hand.

4.3. Excited Ions

As mentioned in Section 3.1), the formation of excited ions has been proposed as the primary product of highly exergonic CS.[81,85,95,148-152] Most organic radical ions have low lying electronic excited states, generally below 2 eV, that can in principle be directly populated upon photoinduced CS.[153] Although the above hypothesis was proposed more than 40 years ago,[85] direct spectroscopic evidence of the involvement of excited ions in such a reaction is still missing. The reason for this lies mostly in their elusive nature, having excited-state lifetimes of a few picoseconds or less.[152,154-160] This property, in combination with the finite rate of their production upon CS, prevents the build-up of significant and detectable transient concentrations. However, strong evidence of the formation of excited ions has recently been obtained by measuring, using transient IR absorption spectroscopy, how the energy dissipated upon ultrafast CS and CR is redistributed into the vibrational modes of the reaction partners.[96] For moderately exergonic reactions, both donor and acceptor were found to be vibrationally hot, pointing to an even energy redistribution. For highly exergonic reactions, on the other hand, asymmetric energy redistribution with a very hot donor and a relatively much colder acceptor was observed. This difference was attributed to the formation of the donor cation in an electronic excited state upon CS, followed by its ultrafast internal conversion to the ground state.[96]

One can be confident that, with the recent advances in femtosecond-resolved broadband fluorescence up-conversion spectroscopy,[161] one should be soon able to directly observe the fluorescence from excited radical ions generated in such a highly exergonic process.

5. Charge Recombination

One of the main practical applications of bimolecular photoinduced CS reactions is the production of free radical ions. Achieving a large free ion yield requires CS to be rapid, and, inversely, CR to be as slow as possible, thus increasing the lifetime of the ion pair. As the ion pairs are produced upon a diffusion-assisted process, the initial reactant pair distribution for CR is entirely governed by the details of the CS. Thus, this process should in principle be described within the theoretical framework outlined in section 2.1. However, whereas there is comparatively little experimental work on the diffusional effects on CS, the number of studies dealing with combined CS/CR reactions on the same level of theory is much smaller.[57,58,61,162-166] Despite their very limited number, these works have allowed for gaining significant insight into the nature and peculiarities of diffusion influenced follow-up reactions and have helped explaining effects such as e.g. the nontrivial viscosity dependence of free ion yields.[164] On the other hand, in most studies on CR, the ion pairs have been considered as species for which a well-defined lifetime can be defined.[132,167-171] Although this so-called 'exponential' treatment of CR has been sometimes criticised and may indeed give an oversimplified picture of the real process, it has the advantage of yielding numbers, such as CR rate constants, that are very useful when investigating the effect of various parameters, such as e.g. the driving force, on the CR dynamics. Moreover, in non-viscous solvents like acetonitrile, where most studies have been carried out, the ion pair dynamics is generally well accounted for by the exponential model.

5.1 Driving-Force Dependence

Contrary to the initial photoinduced bimolecular CS step, CR of the ion pairs is generally highly exergonic, with a driving force typically larger than 1 to 1.5 eV. A few years after its first experimental observation for intramolecular charge-transfer processes,[93,172,173] the inverted region was reported for the CR of ion pairs formed upon bimolecular photoinduced CS.[94,167,174] In polar solvents, CR occurs typically on the ps timescale at $-\Delta G_{CR} \sim 1.2$-1.5 eV and slows down by 3 to 4 orders of magnitude at $-\Delta G_{CR} \sim 3$ eV.[171] This is in stark contrast to the driving force dependence observed for bimolecular CS (Figure 8), where the Marcus inverted region is basically absent.[70] The origin of this discrepancy between CS and CR is still a matter of debate but can most probably be traced back to the presence of low lying electronic excited states of the CS product (Section 4.3) and to the different nature of CS and CR, the first being a bulk process, and the second a geminate one. This latter property is strikingly revealed by the comparison of CR in an inert and in a reactive solvent.[175] Once the ion pair has formed, identical CR dynamics are observed in both types of solvent over the entire driving force range studied.

The distinct driving-force dependence of CR, compared to CS, has strong consequences for the free ion yield and, in a non-viscous solvent like acetonitrile, a free ion yield larger than 0.2 requires $-\Delta G_{CR} \geq \sim 2.5$ eV. As a consequence, the non-observation of free ions in a fluorescence quenching experiment cannot be invoked to discard ET as the quenching mechanism.

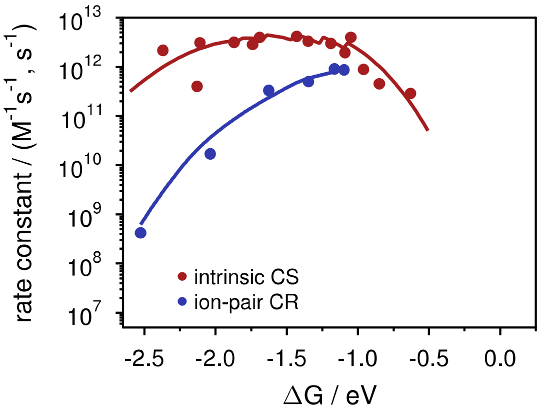


Figure 8. Comparison of the driving force dependence of the intrinsic bimolecular CS rate constant and the inverse ion-pair lifetime, taken from refs. [70] and [175]. The stationary bimolecular CS rate constant is also is shown for comparison.

As mentioned in Section 4, several types of ion pairs, LIPs and TIPs being limiting cases, can be distinguished, depending on the mode of formation, i.e. direct charge-transfer excitation of complexes or bimolecular CS, and on other parameters such as the polarity or viscosity of the environment and the CS driving force. Comparative studies of CR dynamics of ion pairs generated by the two modes have revealed that CR in both LIPs and TIPs exhibits the inverted region.[126,127,176-179] However, as the electronic coupling in TIPs is substantially larger than in LIPs, CR is generally much faster in the former than in the latter at the same driving force. Another major difference appears at small driving forces: whereas the CR dynamics of LIPs levels off and even slows down as the driving force decreases below ~1.5 eV,[94,171] in agreement with Marcus theory for the normal region, CR of TIPs increases continuously with decreasing driving force and does not exhibit the normal behaviour.[151,180,181] This difference arises from non-equilibrium effects as will be discussed below.

Whereas the inverted region is now well established for the CR of ions pairs, the dynamics in the small driving force region deserves further scrutiny as it is often dominated by non-equilibrium effects, opening interesting perspectives for e.g. an excitation wavelength dependence. Additionally, a detailed study on how the driving-force dependence of the CR dynamics varies with the solvent is still missing. Finally, a more systematic use of theoretical models of diffusion-assisted reactions should be applied to the ion pair dynamics to evaluate the limit of the exponential model used so far and to obtain a more realistic picture of this process.

5.2 The Effect of Spin

All the CR processes discussed above are spin-allowed, the reactant and product states having the same spin multiplicity, in general a singlet one. However, bimolecular photoinduced CS can occur between a molecule in a triplet excited state and a quencher, resulting in a triplet ion pair.[182-185] Just as for the singlet ion pairs discussed above, there is a wide distribution of triplet ion pairs differing by their coupling. Although these species are much less documented than their singlet counterparts, their common feature is the spin forbidden nature of their CR to the neutral ground state. However, if the reactants have low lying triplet-excited states, CR of the triplet ion pair to these states is spin allowed.[186-189] Otherwise, in polar environments, triplet ion pairs dissociate essentially entirely into free ions.[182] In conditions where dissociation is not possible, i.e. in viscous and or non-polar environments, CR eventually takes place.[190] This can involve various mechanisms depending on the coupling between the ions. The singlet-triplet energy gap is directly related to the exchange integral, which itself depends on the orbital overlap of the ions, hence on their coupling. As a consequence, singlet and triplet LIPs are quasi degenerate and conversion between both states can take place via the hyperfine interaction. For pairs composed of ions of aromatic hydrocarbons, this process occurs on the 10-100 ns timescale.[42,191] For TIPs, on the other hand, the singlet-triplet splitting is too large for this mechanism to be operative and, in this case, CR to the neutral ground state can be viewed as an intersystem-crossing. The presence of heavy atoms in the ion pair can favour this process as well as the intersystem crossing from the singlet to the triplet TIP.[192,193]

5.3 Non-equilibrium effects

When ultrafast, CR of ion pairs often takes place before the pair has fully equilibrated. Relaxation to the equilibrium involves solvent modes as well as intramolecular and probably intra-ion pair modes. Not much is known about the latter, but they can be expected to play a more important role in non-polar or weakly polar solvents, where the Coulomb interaction is the strongest. On the other hand, solvent relaxation dominates in polar environment and the diffusive part of its dynamics scales with the viscosity, ranging from about 0.6 ps in acetonitrile to several hundreds of ps in long alcohols or in room temperature ionic liquids.[194-196] In such cases, the CR dynamics is non-exponential and depends on how far from equilibrium the ion pairs have been initially produced.[197,198] These non-equilibrium effects have been shown to lead to the suppression of the normal region for the CR of TIPs.[59,151,179-181,199] CR in the normal region is a thermally activated process and its observation requires the initial state to be in thermal equilibrium (Figure 9). However, if the TIPs are initially formed far from equilibrium, CR can occur before their relaxation is complete and is then activationless. This is possible if the energy gap is not too large and if the electronic coupling is substantial as in TIPs. On the other hand, electronic coupling in LIPs is small and, thus, these pairs relax entirely and their CR exhibits the normal behaviour. In such cases, CR in TIPs can be faster by more than three orders of magnitude than in LIPs.[151,180] Such non-equilibrium or hot CR can be theoretically described using the semi-classical variant of the two-dimensional Sumi-Marcus model, that accounts for example for ET processes faster than solvation.[29,200,201] Just the opposite effect, i.e. solvation induced retardation, was observed for CR close to the activationless regime of ET.[175,202] The ions are generated out of equilibrium thus placing the driving force for recombination deeply in the inverted region. Upon solvent relaxation the driving force decreases and CR becomes feasible. Indeed, the recombination rate in the activationless region was found to be faster in acetonitrile than in slower solvents like benzyl-acetate.[175]

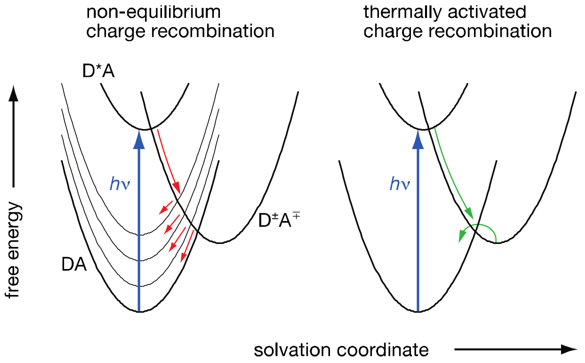


Figure 9. Comparison of the energy schemes for non-equilibrium and thermally activated charge recombination.

Tuning the excitation wavelength allows the initial structure of the TIP, including the surrounding solvent, to be varied within the Franck-Condon window offered by the absorption band of the donor/acceptor complex: the shorter the excitation wavelength, the further from equilibrium the TIP is formed. An excitation wavelength dependence of the CR of TIPs has been reported with several donor/acceptor complexes in polar solvents.[180,203,204] For example, with the isodurene / tetracyanoethylene complex in valeronitrile, the CR dynamics was found to be faster and closer to exponential upon 620 nm than upon 480 nm excitation. This effect was explained by arguing that if the TIPs are formed far from equilibrium, some relaxation is required before the Franck-Condon factor is sufficiently large for CR to take place. An excitation wavelength dependence has also been theoretically predicted for bimolecular photoinduced CS processes in cases where the equilibrium solvent coordinates of the ground and excited states of the reactants and of the ion pair differ substantially.[205] However, this effect still requires experimental confirmation.

Significantly more systematic experimental work is still necessary to gain insight on the non-equilibrium effects accompanying CR reactions, e.g. at extremely large CS driving forces, and to put the few existing theoretical models to a test.[206,207]

6. Conclusions

A comprehensive understanding of bimolecular charge separation and recombination reactions requires efforts on various fronts. On the one hand, the theoretical description of irreversible (lately also for reversible) reactions by the diffusion-reaction equation formalism has been put on solid grounds. In addition, more recent theoretical works have included non-equilibrium effects into the description for the intrinsic electron transfer dynamics.

On the other hand, state-of-the-art time-resolved spectroscopy gives now access to a wide range of wavelengths, from the deep UV to the far IR, and timescales, from the subfemto- to the millisecond regimes. Clearly, both theoretical and experimental tools have not been fully exploited yet for bimolecular photoinduced ET processes. Although our present understanding of these reactions is relatively good, many important questions, that we have tried to emphasize in this perspective, still wait for an answer. Additionally, further work where the various key parameters are systematically varied is still necessary.

Doing this will not only increase our understanding but will allow further progress in various areas, such as solar energy conversion, where these processes are deeply involved.

Acknowledgements

This work was supported by University of Geneva and the Swiss NSF (200020-147098). We warmly thank all past and present co-workers and collaborators for their contributions.

Notes and references

[a] *Department of Physical Chemistry, University of Geneva, 30 Quai Ernest Ansermet, Geneva, Switzerland. Fax: +41 22 379 65 18; Tel: +41 22 379 65 37; E-mail: eric.vauthey@unige.ch*

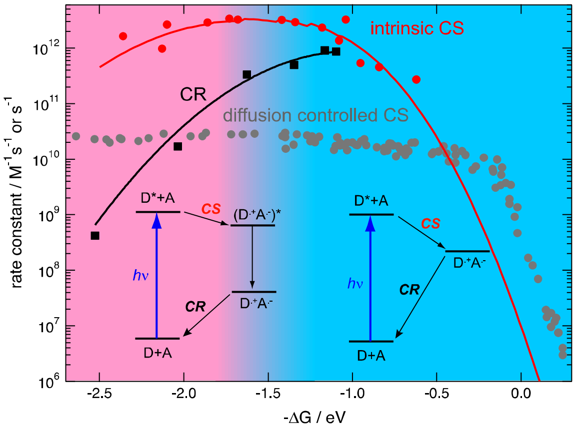
1. M. Bixon and J. Jortner, *Adv. Chem. Phys.*, 1999, **106**, 35-202.
2. V. Balzani, ed., *Electron Transfer in Chemistry*, J. Wiley, New York, 2001.
3. A. Rosspeintner, B. Lang and E. Vauthey, *Annu. Rev. Phys. Chem.*, 2013, **64**, 247-271.
4. F. Würthner, Z. Chen, F. J. M. Hoeben, P. Osswald, C. C. You, P. Jonkheijm, J. v. Herrikhuyzen, A. P. H. J. Schenning, P. P. A. M. vanderSchoot, E. W. Meijer, E. H. A. Beckers, S. C. J. Meskers and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2004, **126**, 10611-10618.
5. P. V. P. Kamat, *J. Phys. Chem. C*, 2007, **111**, 2834-2860.
6. D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2009, **42**, 1890-1898.

7. T. M. Clarke and J. R. Durrant, *Chem. Rev.*, 2010, **110**, 6736-6767.
8. A. J. A. Heeger, *Chem. Soc. Rev.*, 2010, **39**, 2354-2371.
9. B. P. Fingerhut, W. Zinth and R. d. Vivie-Riedle, *Phys. Chem. Chem. Phys.*, 2009, **12**, 422-432.
10. R. D. Pensack and J. B. Asbury, *The Journal of Physical Chemistry Letters*, 2010, **1**, 2255-2263.
11. S. D. Dimitrov, A. A. Bakulin, C. B. Nielsen, B. C. Schroeder, J. Du, H. Bronstein, I. McCulloch, R. H. Friend and J. R. Durrant, *J. Am. Chem. Soc.*, 2012, **134**, 18189-18192.
12. H. Zhu, Y. Yang and T. Lian, *Acc. Chem. Res.*, 2013, **46**, 1270-1279.
13. F. D. Lewis, R. S. Kalgutkar, Y. Wu, X. Liu, J. Liu, R. T. Hayes, S. E. Miller and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2000, **122**, 12346-12351.
14. B. Giese, *Ann. Rev. Phys. Chem.*, 2002, **71**, 51-70.
15. Y. Zhang, J. Dood, A. A. Beckstead, X.-B. Li, K. V. Nguyen, C. J. Burrows, R. Improta and B. Kohler, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 11612-11617.
16. H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven and N. S. Hush., *J. Am. Chem. Soc.*, 1987, **109**, 3258-3269.
17. G. L. Closs and J. R. Miller, *Science*, 1988, **240**, 440.
18. M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435-461.
19. D. Gust, T. A. Moore, A. L. Moore, A. N. Macpherson, A. Lopez, J. M. DeGraziano, I. Gouni, E. Bittersmann, G. R. Seely and et al., *J. Am. Chem. Soc.*, 1993, **115**, 11141-11152.
20. M. Bixon, J. Jortner and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1994, **116**, 7349.
21. C. Lambert, G. Nöll and J. Schelter, *Nat. Mater.*, 2002, **1**, 69-73.
22. B. Albinsson and J. Mårtensson, *J. Photochem. Photobiol. C*, 2008, **9**, 138-155.
23. S. Wallin, C. Monnereau, E. Blart, J.-R. Gankou, F. Odobel and L. Hammarström, *J. Phys. Chem. A*, 2010, **114**, 1709-1721.
24. V. Markovic, D. Villamaina, I. Barabanov, L. M. L. Daku and E. Vauthey, *Angew. Chem. Int. Ed.*, 2011, **50**, 7596-7598.
25. R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.
26. J. Ulstrup and J. Jortner, *J. Chem. Phys.*, 1975, **63**, 4358-4368.
27. L. D. Zusman, *Chem. Phys.*, 1980, **49**, 295-304.
28. P. Siders and R. A. Marcus, *J. Am. Chem. Soc.*, 1981, **103**, 748-752.
29. H. Sumi and R. A. Marcus, *J. Chem. Phys.*, 1986, **84**, 4894-4914.
30. J. T. Hynes, *J. Phys. Chem.*, 1986, **90**, 3701-3706.
31. J. Jortner and M. Bixon, *J. Chem. Phys.*, 1988, **88**, 167.
32. T. Fonseca, *J. Chem. Phys.*, 1989, **91**, 2869-2880.
33. M. Tachiya, *J. Phys. Chem.*, 1993, **97**, 5911-5916.
34. F. D. Lewis, J. Q. Liu, W. Weigel, W. Rettig, I. V. Kurnikov and D. N. Beratan, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 12536–12541.
35. O. S. Wenger, *Acc. Chem. Res.*, 2011, **44**, 25-35.
36. A. J. Orr-Ewing, *J. Chem. Phys.*, 2014, **140**, 090901-090901.
37. J. R. Miller, 'Puzzles of Electron Transfer', in *Electron Transfer in Inorganic, Organic, and Biological Systems*, American Chemical Society, 1991, pp. 265-276.
38. E. Vauthey, *J. Photochem. Photobiol. A*, 2006, **179**, 1-12.
39. K. Schulten and A. Weller, *Biophys. J.*, 1978, **24**, 295.
40. Y. Tanimoto, M. Takayama, M. Itho, R. Nakagaki and S. Nagakura., *Chem. Phys. Lett.*, 1986, **129**, 414.
41. N. L. Lavrik, Y. N. Molin, U. Werner and H. Staerk, *J. Chem. Phys.*, 1993, **99**, 9304.
42. P. Gilch, F. Pöllinger-Dammer, C. Musewald, M. E. Michel-Beyerle and U. E. Steiner, *Science*, 1998, **281**, 982-984.
43. D. R. Kattnig, A. Rosspeintner and G. Grampp, *Angew. Chem. Int. Ed.*, 2008, **47**, 960-962.
44. D. R. Kattnig, A. Rosspeintner and G. Grampp, *Phys. Chem. Chem. Phys.*, 2011, **13**, 3446-3460.
45. S. Richert, A. Rosspeintner, S. Landgraf, G. Grampp, E. Vauthey and D. R. Kattnig, *J. Am. Chem. Soc.*, 2013, **135**, 15144-15152.
46. M. von Smoluchowski, *Z. Phys. Chem.*, 1918, **92**, 129-168.
47. F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, 1949, **4**, 425-437.
48. G. Wilemski and M. Fixman, *J. Chem. Phys.*, 1973, **58**, 4009-4019.
49. A. B. Doktorov and A. I. Burshtein, *Sov. Phys. JETP*, 1976, **41**, 671-677.
50. M. Tachiya, *Radiat. Phys. Chem.*, 1983, **21**, 167-175.
51. J. Keizer, *Chem. Rev.*, 1987, **87**, 167-180.
52. A. Szabo, *J. Phys. Chem.*, 1989, **93**, 6929-6939.
53. S. A. Rice, '*Diffusion Limited Reactions*', Elsevier, New York, 1985.
54. E. Kotomin and V. Kuzovkov, '*Modern Aspects of Diffusion-Controlled Reactions: Cooperative Phenomena in Bimolecular Processes*', Elsevier New York, 1996.
55. A. I. Burshtein, *Adv. Chem. Phys.*, 2000, **114**, 419-587.
56. A. I. Burshtein, *Adv. Chem. Phys.*, 2004, **129**, 105-418.
57. R. C. Dorfman and M. D. Fayer, *J. Chem. Phys.*, 1992, **96**, 7410-7410.
58. L. Song, S. F. Swallen, R. C. Dorfman, K. Weidemaier and M. D. Fayer, *J. Phys. Chem.*, 1993, **97**, 1374.
59. P. A. Frantsuzov and M. Tachiya, *J. Chem. Phys.*, 2000, **112**, 4216-4220.
60. V. O. Saik, A. A. Goun, J. Nanda, K. Shirota, H. L. Tavernier and M. D. Fayer, *J. Phys. Chem. A*, 2004, **108**, 6696.
61. A. Goun, K. Glusac and M. D. Fayer, *J. Chem. Phys.*, 2006, **124**, 084504.
62. S. F. Swallen, K. Weidemaier and M. D. Fayer, *J. Chem. Phys.*, 1996, **104**, 2976-2986.
63. K. Weidemaier, H. L. Tavernier, S. F. Swallen and M. D. Fayer, *J. Phys. Chem. A*, 1997, **101**, 1887-1902.
64. R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265-322.
65. D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 834.
66. R. A. Marcus, *J. Electroanal. Chem.*, 2000, **483**, 2-6.
67. B. S. Brunschwig, S. Ehrenson and N. Sutin, *J. Am. Chem. Soc.*, 1984, **106**, 6858.
68. I. Rips, J. Klafter and J. Jortner, *J. Phys. Chem.*, 1990, **94**, 8557.
69. H. Heitele, *Angew. Chem. Int. Ed. Eng.*, 1993, **32**, 359-377.
70. A. Rosspeintner, G. Angulo and E. Vauthey, *J. Am. Chem. Soc.*, 2014, **136**, 2026-2032.
71. J. R. Lakowicz, '*Principles of Fluorescence Spectroscopy, 3rd edition*', Springer, New York, 2011.
72. M. Liang, A. Kaintz, G. A. Baker and M. Maroncelli, *J. Phys. Chem. B*, 2011, **116**, 1370-1384.
73. M. Koch, A. Rosspeintner, G. Angulo and E. Vauthey, *J. Am. Chem. Soc.*, 2012, **134**, 3729-3736.
74. A. Rosspeintner, M. Koch, G. Angulo and E. Vauthey, *J. Am. Chem. Soc.*, 2012, **134**, 11396-11399.
75. T. L. Nemzek, *J. Chem. Phys.*, 1975, **62**.
76. D. D. Eads, B. G. Dismer and G. R. Fleming, *J. Chem. Phys.*, 1990, **93**, 1136-1148.
77. S. Nishikawa, T. Asahi, T. Okada, N. Mataga and T. Kakitani, *Chem. Phys. Lett.*, 1991, **185**, 237.
78. S. Murata, S. Y. Matsuzaki and M. Tachiya, *J. Phys. Chem.*, 1995, **99**, 5354-5358.
79. V. S. Gladkikh, A. I. Burshtein, H. L. Tavernier and M. D. Fayer, *J. Phys. Chem. A*, 2002, **106**, 6982-6990.
80. E. Krystkowiak and A. Maciejewski, *J. Chem. Phys.*, 2002, **117**, 5802.
81. V. Gladkikh, A. I. Burshtein, G. Angulo, S. Pagès, B. Lang and E. Vauthey, *J. Phys. Chem. A*, 2004, **108**, 6667.

82. A. Rosspeintner, D. R. Kattnig, G. Angulo, S. Landgraf, G. Grampp and A. Cuetos, *Chem. Eur. J.*, 2007, **13**, 6474-6483.
83. C. F. Shannon and D. D. Eads, *J. Chem. Phys.*, 1995, **103**, 5208.
84. S. Murata and M. Tachiya, *J. Phys. Chem.*, 1996, **100**, 4064-4070.
85. D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259-271.
86. R. Ballardini, G. Varani, M. T. Indelli, F. Scandola and V. Balzani, *J. Am. Chem. Soc.*, 1978, **100**, 7219-7223.
87. J. M. Chen, T. I. Ho and C. Y. Mou, *J. Phys. Chem.*, 1990, **94**, 2889-2896.
88. T. M. McCleskey, J. R. Winkler and H. B. Gray, *J. Am. Chem. Soc.*, 1992, **114**, 6935-6937.
89. T. Niwa, K. Kikuchi, N. Matsusita, M. Hayashi, T. Katagiri, Y. Takahashi and T. Miyashi, *J. Phys. Chem.*, 1993, **97**, 11960-11964.
90. A. Rosspeintner, D. R. Kattnig, G. Angulo, S. Landgraf and G. Grampp, *Chem. Eur. J.*, 2008, **14**, 6213-6221.
91. N. Mataga, H. Chosrowjan, Y. Shibata, N. Yoshida, A. Osuka, T. Kikuzawa and T. Okada, *J. Am. Chem. Soc.*, 2001, **123**, 12422-12423.
92. D. M. Guldi and K. D. Asmus, *J. Am. Chem. Soc.*, 1997, **119**, 5744-5745.
93. M. R. Wasielewski, M. P. Niemczyk, W. A. Svec and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 1080-1082.
94. N. Mataga, T. Asahi, Y. Kanda, T. Okada and T. Kakitani, *Chem. Phys.*, 1988, **127**, 249-261.
95. N. Mataga, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 3623-3624.
96. M. Koch, A. Rosspeintner, K. Adamczyk, B. Lang, J. Dreyer, E. T. J. Nibbering and E. Vauthey, *J. Am. Chem. Soc.*, 2013, **135**, 9843-9848.
97. M. Tachiya and S. Murata, *J. Phys. Chem.*, 1992, **96**, 8441.
98. A. I. Burshtein and A. I. Ivanov, *Phys. Chem. Chem. Phys.*, 2007, **9**, 396-400.
99. T. N. Inada, K. Kikuchi, Y. Takahashi, H. Ikeda and T. Miyashi, *J. Photochem. Photobiol.*, 2000, **137**, 93-97.
100. P. Jacques and X. Allonas, *J. Photochem. Photobiol. A*, 1994, **78**, 1-5.
101. A. I. Burshtein and K. L. Ivanov, *J.Phys.Chem. A*, 2001, **105**, 3158-3166.
102. P. Jacques, E. Haselbach, A. Henseler, D. Pilloud and P. Suppan, *J. Chem. Soc. Faraday Trans.*, 1991, **87**, 3811.
103. A. I. Burshtein and K. L. Ivanov, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4115.
104. L. Burel, M. Mostafavi, S. Murata and M. Tachiya, *J. Phys. Chem. A*, 1999, **103**, 5882-5888.
105. J. B. Birks, '*Photophysics of Aromatic Molecules'*, Wiley, New York, 1970.
106. N. Mataga, *Pure Appl. Chem.*, 1984, **56**, 1255-1268.
107. M. Tachiya and K. Seki, *J. Phys. Chem. A*, 2007, **111**, 9553-9559.
108. N. Mataga, T. Okada and H. Masuhara, eds., *Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena*, North-Holland, Amsterdam; New York, 1992.
109. H. Zhu, Y. Yang, K. Hyeon-Deuk, M. Califano, N. Song, Y. Wang, W. Zhang, O. V. Prezhdo and T. Lian, *Nano Lett.*, 2013, **14**, 1263-1269.
110. M. Hilczer and M. Tachiya, *J. Phys. Chem. C*, 2010, **114**, 6808-6813.
111. K. Kemnitz and K. Yoshihara, *Chem. Lett.*, 1991, 645-648.
112. Y. Nagasawa, A. P. Yartsev, K. Tominaga, A. E. Johnson and K. Yoshihara, *J. Am. Chem. Soc.*, 1993, **115**, 7922-7923.
113. H. Shirota, H. Pal, K. Tominaga and K. Yoshihara, *J. Phys. Chem. A*, 1998, **102**, 3089.
114. S. Engleitner, M. Seel and W. Zinth, *J. Phys. Chem. A*, 1999, **103**, 3013-3019.
115. Q.-H. Xu, G. D. Scholes, M. Yang and G. R. Fleming, *J. Phys. Chem. A*, 1999, **103**, 10348-10358.
116. E. W. Castner Jr., D. Kennedy and R. J. Cave, *J. Phys. Chem. A*, 2000, **104**, 2869-2885.
117. A. Morandeira, A. Fürstenberg, J.-C. Gumy and E. Vauthey, *J. Phys. Chem. A*, 2003, **107**, 5375-5383.
118. A. Morandeira, A. Fürstenberg and E. Vauthey, *J. Phys. Chem. A*, 2004, **108**, 8190-8200.
119. K. Yoshihara, K. Tominaga and Y. Nagasawa, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 696.
120. G. Angulo, A. Cuetos, A. Rosspeintner and E. Vauthey, *J. Phys. Chem. A*, 2013, **117**, 8814-8825.
121. P. Suppan, *J. Chem. Soc. Faraday Trans. 1*, 1987, **83**, 495-509.
122. R. Letrun and E. Vauthey, *J. Phys. Chem. Lett.*, 2014, **5**, 1685-1690.
123. H. Leonhardt and A. Weller, *Z. Phys. Chem. N. F.*, 1961, **29**, 277-280.
124. Y. Hirata, Y. Kanda and N. Mataga, *J. Phys. Chem.*, 1983, **87**, 1659-1662.
125. J. M. Masnovi and J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 7880-7893.
126. I. R. Gould, R. Moody and S. Farid, *J. Am. Chem. Soc.*, 1988, **110**, 7242-7244.
127. T. Asahi and N. Mataga, *J. Phys. Chem.*, 1989, **93**, 6575-6578.
128. O. F. Mohammed and E. Vauthey, *J. Phys. Chem. A*, 2008, **112**, 5804-5809.
129. I. R. Gould and S. Farid, *Acc. Chem. Res.*, 1996, **29**, 522-528.
130. N. Mataga and H. Miyasaka, *Adv. Chem. Phys.*, 1999, **107**, 431-496.
131. I. R. Gould, D. Noukakis, L. Gomez-Jahn, R. H. Young, J. L. Goodman and S. Farid, *Chem. Phys.*, 1993, **176**, 439-456.
132. E. Vauthey, C. Högemann and X. Allonas, *J. Phys. Chem. A*, 1998, **102**, 7362-7369.
133. K. Kikuchi, T. Niwa, Y. Takahashi, H. Ikeda, T. Miyashi and M. Hoshi, *Chem. Phys. Lett.*, 1990, **173**, 421-424.
134. P.-A. Muller, C. Högemann, X. Allonas, P. Jacques and E. Vauthey, *Chem. Phys. Lett.*, 2000, **326**, 321-327.
135. S. Murata and M. Tachiya, *J. Phys. Chem. A*, 2007, **111**, 9240-9248.
136. O. F. Mohammed, K. Adamczyk, N. Banerji, J. Dreyer, B. Lang, E. T. J. Nibbering and E. Vauthey, *Angew. Chem. Int. Ed.*, 2008, **47**, 9044-9048.
137. D. W. McCamant, P. Kukura and R. A. Mathies, *J. Phys. Chem. A*, 2003, **107**, 8208-8214.
138. A. Weigel and N. P. Ernsting, *J. Phys. Chem. B*, 2010, **114**, 7879-7893.
139. H. Knibbe, D. Rehm and A. Weller, *Z. Phys. Chem.*, 1967, **56**, 95-98.
140. M. Gordon and W. R. Ware, eds., *The Exciplex*, Academic Press, New York, 1975.
141. A. Weller, *Pure & Appl. Chem.*, 1982, **54**, 1885-1888.
142. I. R. Gould, R. H. Young, L. J. Mueller and S. Farid, *J. Am. Chem. Soc.*, 1994, **116**, 8176-8187.
143. N. Mataga, H. Chosrowjan and S. Taniguchi, *J. Photochem. Photobiol. C*, 2005, **6**, 37-79.
144. M. G. Kuzmin, I. V. Soboleva and E. V. Dolotova, *J. Phys. Chem. A*, 2007, **111**, 206-215.
145. S. Ojima, H. Miyasaka and N. Mataga, *J. Phys. Chem. A*, 1990, **94**, 4147-4152.
146. M. Koch, R. Letrun and E. Vauthey, *J. Am. Chem. Soc.*, 2014, **136**, 4066-4074.
147. P. Hamm and M. T. Zanni, '*Concepts and Methods of 2D Infrared Spectroscopy'*, Cambridge University Press, Cambridge, 2011.
148. J. V. Beitz and J. R. Miller, *J. Chem. Phys.*, 1979, **71**.
149. K. Kikuchi, T. Katagiri, T. Niwa, Y. Takahashi, T. Suzuki, H. Ikeda and T. Miyashi, *Chem. Phys. Lett.*, 1992, **193**, 155.
150. P.-A. Muller and E. Vauthey, *J. Phys. Chem. A*, 2001, **105**, 5994.

151. S. Pagès, B. Lang and E. Vauthey, *J. Phys. Chem. A*, 2004, **108**, 549-555.
152. D. A. Horke, Q. Li, L. s. Blancafort and J. R. R. Verlet, *Nature Chem.*, 2013, **5**, 711-717.
153. T. Shida, E. Haselbach and T. Bally, *Acc. Chem. Res.*, 1984, **17**, 180.
154. J.-C. Gumy and E. Vauthey, *J. Phys. Chem. A*, 1997, **101**, 8575-8580.
155. P. Brodard, A. Sarbach, J.-C. Gumy, T. Bally and E. Vauthey, *J. Phys. Chem. A*, 2001, **105**, 6594-6601.
156. L. Zhao, R. Lian, I. A. Shkrob, R. A. Crowell, S. Pommeret, E. L. Chronister, A. D. Liu and A. D. Trifunac, *J. Phys. Chem.*, 2004, **108**, 25-31.
157. A. N. Okhrimenko, A. V. Gusev and M. A. J. Rodgers, *J. Phys. Chem. A*, 2005, **109**, 7653-7656.
158. S. Pagès, B. Lang and E. Vauthey, *J. Phys. Chem. A*, 2006, **110**, 7547-7553.
159. M. J. Hope, M. P. Higlett, D. L. Andrews, S. R. Meech, I. D. Hands, J. L. Dunn and C. A. Bates, *Chem. Phys. Lett.*, 2009, **474**, 112-114.
160. J. Grilj, E. N. Laricheva, M. Olivucci and E. Vauthey, *Angew. Chem. Int. Ed.*, 2011, **50**, 4496-4498.
161. X.-X. Zhang, C. Würth, L. Zhao, U. Resch-Genger, N. P. Ernsting and M. Sajadi, *Rev. Sci. Instrum.*, 2011, **82**, 063108.
162. S. F. Swallen and M. D. Fayer, *J. Chem. Phys.*, 1995, **103**, 8864.
163. H. L. Tavernier, M. M. Kalashnikov and M. D. Fayer, *J. Chem. Phys.*, 2000, **113**, 10191-10191.
164. A. A. Neufeld, A. I. Burshtein, G. Angulo and G. Grampp, *J. Chem. Phys.*, 2002, **116**, 2472-2479.
165. G. Angulo, G. Grampp, A. A. Neufeld and A. I. Burshtein, *J. Phys. Chem.*, 2003, **107**, 6913-6919.
166. V. S. Gladkikh, A. I. Burshtein, G. Angulo and G. Grampp, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2581.
167. I. R. Gould, D. Ege, S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1987, **109**, 3794-3796.
168. I. R. Gould, D. Ege, J. E. Moser and S. Farid, *J. Am. Chem. Soc.*, 1990, **112**, 4290.
169. S. L. Mattes and S. Farid, *Acc. Chem. Res.*, 1982, **15**, 80-86.
170. E. Vauthey, *J. Phys. Chem. A*, 2000, **104**, 1804.
171. E. Vauthey, *J. Phys. Chem. A*, 2001, **105**, 340-348.
172. J. R. Miller, L. T. Calcaterra and G. L. Closs, *J. Am. Chem. Soc.*, 1984, **106**, 3047-3049.
173. G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield and J. R. Miller, *J. Phys. Chem.*, 1986, **90**, 3674-3683.
174. E. Vauthey, P. Suppan and E. Haselbach, *Helv. Chim. Acta*, 1988, **71**, 93-99.
175. A. Rosspeintner, G. Angulo and E. Vauthey, *J. Phys. Chem. A*, 2012, **116**, 9473-9483.
176. I. R. Gould and S. Farid, *J. Phys. Chem.*, 1992, **96**, 7635-7640.
177. T. Asahi, M. Ohkohchi and N. Mataga, *J. Phys. Chem.*, 1993, **97**, 13132-13137.
178. S. M. Hubig, T. M. Bockman and J. K. Kochi, *J. Am. Chem. Soc.*, 1996, **118**, 3842-3851.
179. O. Nicolet and E. Vauthey, *J. Phys. Chem. A*, 2002, **106**, 5553-5562.
180. R. G. Fedunov, S. V. Feskov, A. I. Ivanov, O. Nicolet, S. Pagès and E. Vauthey, *J. Chem. Phys.*, 2004, **121**, 3643-3656.
181. V. V. Yudanov, V. A. Mikhailova and A. I. Ivanov, *J. Phys. Chem. A*, 2010, **114**, 12998-13004.
182. E. Haselbach, E. Vauthey and P. Suppan, *Tetrahedron*, 1988, **44**, 7335-7344.
183. H. Miyasaka, K. Morita, K. Kamada and N. Mataga, *Chem. Phys. Lett.*, 1991, **178**, 504-510.
184. E. Haselbach, P. Jacques, D. Pilloud, P. Suppan and E. Vauthey, *J. Phys. Chem.*, 1991, **95**, 7115.
185. F. D. Lewis, A. K. Thazhathveetil, T. A. Zeidan, J. Vura-Weis and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2009, **132**, 444-445.
186. C. Högemann and E. Vauthey, *J. Phys. Chem. A*, 1998, **102**, 10051-10059.
187. P. P. Levin, I. V. Khudyakov and V. A. Kuzmin, *J. Phys. Chem.*, 1989, **93**, 208.
188. U. E. Steiner and W. Haas, *J. Phys. Chem.*, 1991, **95**, 1880.
189. M. R. Roest, A. M. Oliver, M. N. Paddon-Row and J. W. Verhoeven, *J. Phys. Chem. A*, 1997, **101**, 4867.
190. P. P. Levin, P. F. Pluzhnikov and V. A. Kuzmin, *Chem. Phys. Lett.*, 1988, **147**, 283.
191. M. E. Michel-Beyerle, R. Haberkorn, W. Bube, E. Steffens, H. Schröder, H. J. Neusser, E. W. Schlag and H. Seidlitz, *Chem. Phys.*, 1976, **17**, 139-145.
192. O. Nicolet and E. Vauthey, *J. Phys. Chem. A*, 2003, **107**, 5894-5902.
193. I. R. Gould, J. A. Boiani, E. B. Gaillard, J. L. Goodman and S. Farid, *J. Phys. Chem. A*, 2003, **107**, 3515-3524.
194. M. L. Horng, J. A. Gardecki, A. Papazyan and M. Maroncelli, *J. Phys. Chem.*, 1995, **99**, 17311-17337.
195. B. Lang, G. Angulo and E. Vauthey, *J. Phys. Chem. A*, 2006, **110**, 7028-7034.
196. E. W. Castner, C. J. Margulis, M. Maroncelli and J. F. Wishart, *Annu. Rev. Phys. Chem.*, 2011, **62**, 85-105.
197. A. I. Ivanov, F. N. Belikeev, R. G. Fedunov and E. Vauthey, *Chem. Phys. Lett.*, 2003, **372**, 73-81.
198. V. S. Gladkikh, A. I. Burshtein, S. V. Feskov, A. I. Ivanov and E. Vauthey, *J. Chem. Phys.*, 2005, **123**, 244510-244511.
199. M. Tachiya and S. Murata, *J. Am. Chem. Soc.*, 1994, **116**, 2434-2436.
200. H. Sumi, *J. Mol. Liquids*, 1985, **65/66**, 65.
201. G. C. Walker, E. Akesson, A. E. Johnson, N. E. Levinger and P. F. Barbara, *J. Phys. Chem.*, 1992, **96**, 3728-3736.
202. E. Vauthey and P. Suppan, *Chem. Phys.*, 1989, **139**, 381.
203. O. Nicolet, N. Banerji, S. Pagès and E. Vauthey, *J. Phys. Chem. A*, 2005, **109**, 8236-8245.
204. S. V. Feskov, V. N. Ionkin, A. I. Ivanov, H. Hagemann and E. Vauthey, *J. Phys. Chem. A*, 2008, **112**, 594-601.
205. S. S. Khohlova, V. A. Mikhailova and A. I. Ivanov, *J. Chem. Phys.*, 2006, **124**, 114507.
206. S. V. Feskov, A. O. Kichigina and A. I. Ivanov, *J. Phys. Chem. A*, 2011, **115**, 1462-1471.
207. A. I. Ivanov and V. A. Mikhailova, *Russ. Chem. Rev.*, 2011, **79**, 1047-1070.

Table of content graphic



This perspective highlights the recent progress in our understanding of bimolecular photoinduced electron transfer processes that could be achieved thanks to ultrafast spectroscopy