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Reference

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ET in non-polar solvents

Bimolecular photoinduced electron transfer in non-polar solvents beyond the diffusion limit

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Electron transfer (ET) quenching dynamics in non-polar solvents are investigated using ultrafast spectroscopy with a series of six fluorophore/quencher pairs, covering a driving-force range of more than 1.3 eV. The intrinsic ET rate constants, \( k_0 \), deduced from the quenching dynamics in the static regime, are of the order of \( 10^{12} \text{ to } 10^{13} \text{ M}^{-1}\text{s}^{-1} \), i.e. at least as large as in acetonitrile, and do not exhibit any marked dependence on the driving force. A combination of transient electronic and vibrational absorption spectroscopy measurements reveal that the primary product of static quenching is a strongly coupled exciplex that decays within a few picoseconds. More weakly coupled exciplexes with a longer lifetime are generated subsequently, during the dynamic, diffusion-controlled, stage of the quenching. The results suggest that static ET quenching in non-polar solvents should be viewed as an internal conversion from a locally-excited state to a charge-transfer state of a supermolecule rather than as a non-adiabatic ET process.

I. INTRODUCTION

Since the pioneering work of Weller and co-workers,1–5 bimolecular photoinduced electron transfer (ET) processes have been thoroughly investigated.6–24 This interest stems not only from the fact these are the simplest intermolecular chemical reactions and are thus benchmarks for testing chemical kinetics theories, but also from their involvement in many applications, including photopolymerisation,25–30 solar energy conversion,31–34 and organic synthesis.35–39 In all these cases, ET is used to produce free ions and, therefore, most investigations were carried out in polar environments, where solvation energy can sufficiently attenuate the Coulombic barrier for the dissociation of the ion pair. Much less is known about bimolecular photoinduced ET in non-polar environments. Such media do not favour the formation of free ions and are thus not suitable for many applications. However, understanding these processes in non-polar solvents is important for at least two reasons. 1) For applications such as organic photovoltaics,40–44 ET has often to take place in solid environments, like polymers, which are characterised by a low dielectric constant. Moreover, only little reorganisation of the medium surrounding the reactants is possible under these conditions. 2) In most theoretical descriptions of ET, the reaction coordinate is strongly associated with solvent polarisation.35–48 For example, in Marcus theory,45,50 thermal fluctuations are required to reach solvent configurations where the reactant and product states are degenerate. This is only possible in polar media where the energy of these states can be significantly modulated by solvent polarisation. Other coordinates than those related to the solvent must be operative to make ET feasible in non-polar media.

Most previous studies in non-polar solvents were carried out using stationary and nanosecond time-resolved fluorescence. They concentrated on relatively weakly exergonic ET where the quenching product could be identified as an exciplex, thanks to its characteristic emission.5,51,52 Interestingly, unexpectedly large quenching rate constants were observed even at negative ET driving forces (\( \Delta G_{ET} > 0 \)).53,54 This was explained by the stabilisation energy associated with exciplex formation that is not included when calculating \( \Delta G_{ET} \) according to the conventional Weller equation. Additionally, the authors suggested that, in this case, the coupling between the reactants is so large that ET is an adiabatic process, and is thus distinct from the non-adiabatic ET discussed in Marcus theory.

Fewer investigation can be found on more exergonic processes, where exciplex emission is not detected. Abdullah and Kemp found that the driving-force dependence of the quenching rate constant, \( k_q \), is qualitatively the same as in polar solvents:55 \( k_q \) first increases with \( -\Delta G_{ET} \) up to a value corresponding to the diffusion limit, and then remains constant with further increase of the driving force. By contrast, Chen et al. reported on an approx. 10-fold decrease of \( k_q \) upon going from \( \Delta G_{ET} = -0.65 \text{ to } -1.7 \text{ eV} \) using phenanthrene derivatives as fluorophores and strong electron acceptors as quenchers in cyclohexane (CHX).56 A similar effect was observed with these reactant pairs in dimethylformamide (DMF) but not in acetonitrile (ACN), where the quenching remained diffusion controlled. The authors invoked the Marcus inverted region to account for this behaviour in CHX and DMF, and explained its absence in ACN by the participation of the solvent as a relay for ET. No further observation of inverted region for bimolecular photoinduced ET in non-polar solvents was reported since. Interestingly, Holroyd and Miller recently observed the inverted region for electron attachment to organic molecules in non-polar liquids.57 Thanks to the high mobility of the solvated electron, this process was not diffusion controlled and rate constants of electron attachment as large as \( 10^{13} \text{ M}^{-1}\text{s}^{-1} \) were measured.

The determination of the intrinsic ET rate constant, \( k_0 \), in a diffusion-controlled process requires measuring the quenching dynamics with a sufficiently high time resolution to detect the early stage of this process.25,58 Directly after excitation, quenching occurs in reactants pairs at distances and orientations allowing ET to take place without diffusion. After this initial static stage, quenching enters the transient regime...
where its rate decreases with time down its diffusion-limited value, \( k_\infty \). This time dependence of the quenching coefficient can be analysed using theoretical models of diffusion-assisted reaction, \(^{59-63}\) such as the Differential Encounter Theory (DET), \(^{14}\) which takes into account both the time dependence of the reactant-pair distribution and the distance dependence of ET.

Whereas a relatively large number of investigations of the time-dependent quenching rate coefficient have been reported in polar media, only a very limited number of studies were performed in non-polar solvents. Burel et al. investigated the fluorescence quenching of 9-cyanoanthracene and 9,10-dicyananthracene (DCA) by three electron donors in paraffin. \(^{64}\) The decays were analysed with a DET-like model assuming an exponential ET-distance dependence. The authors concluded that quenching occurs mostly at contact with the two weakest donors and is remote with the strongest donor. Similar conclusions were proposed by Scully et al. from the analysis of the >3 ns fluorescence dynamics of a porphyrin quenched by quinones in alkanes of increasing viscosity. \(^{65}\) Interestingly, the intrinsic ET rate constants, \( k_0 \), measured by Burel et al. were found to be larger in paraffin than in the highly-polar ethylene glycol. \(^{64}\) Similar intrinsic ET rate constants in CHX and ACN were reported by Liang et al. from the analysis of the fluorescence quenching of DCA by dimethylaniline (DMA). \(^{23}\)

To account for these results, Murata and Tachiya proposed a general model of ET quenching in solvents of varying polarity that involves both a non-adiabatic and an adiabatic ET mechanism. \(^{66}\) The first one operates at moderate to large driving force. It can be described by Marcus theory in polar environments and by a variant proposed by Tachiya and Seki in non-polar media, \(^{67}\) where the reaction coordinate is the inter-reactant distance. The second mechanism is favoured at contact distances where coupling is large, and results in the formation of an exciplex. It dominates in the weak driving-force regime, where large coupling is required for quenching to be operative. However, the authors did not discuss whether the adiabatic exciplex mechanism also operates at moderate to large driving forces in the static quenching regime.

To the best of our knowledge, fluorescence quenching dynamics studies in non-viscous and non-polar solvents with a sufficient time resolution to observe the early static stage and, thus, to extract the intrinsic ET rate constant, \( k_0 \), are still lacking. Here, we report on our investigation of the fluorescence quenching of DCA and tricyanoanthracene (TrCA) by three electron donors in hexane (HX) with a time resolution better than 250 fs (Figure 1). The intrinsic ET rate constant, \( k_0 \), is determined over a driving-force range equivalent to 0.85 to 2.1 eV in ACN. We show that the \( k_0 \) values in HX are as large as those measured a few years ago in ACN with the same reactant pairs. \(^{68}\) Insight into the nature of the quenching product is obtained using visible and IR transient absorption spectroscopy. The results suggest that the primary product of the static quenching is a strongly coupled exciplex, whereas the later stages of quenching result in a looser ion-pair like exciplex. The effect of solvent polarity on the nature of the quenching product is also discussed.

II. EXPERIMENTAL

A. Samples

9,10-Dicyano-anthracene (DCA, Kodak) was recrystallized. Perdeuterated DCA (DCA-\( d_8 \)) was synthesized as described in ref. 69. 2,9,10-Tricyano-anthracene (TrCA) was synthesized as described in ref. 70. 1,2,4-Trimethoxybenzene (Aldrich, 97%) and N,N-dimethylaniline (DMA, Aldrich, 99%) were distilled under reduced pressure and the latter stored in the dark under argon. N,N,N’,N’-Tetramethyl-p-phenylene-diamine (TMP, Aldrich 99%) was sublimed under reduced pressure and stored dry in the dark. The solvents, acetonitrile (ACN), carbon tetrachloride (CCI\(_4\)), cyclohexane (CHX), n-hexane (HX), and tetrahydrofuran (THF), were all of spectroscopic grade and used as received.

B. Steady-State Spectroscopy

Electronic absorption spectra were recorded on a Cary 50 spectrometer, whereas fluorescence spectra were measured on a Fluoromax-4 (Jobin Yvon) and corrected using a set of secondary emissive standards. \(^{71}\) Correction for the inner-filter effect (due to either dilution of the sample and/or residual absorption of the quencher) were performed as described in ref. 72. The Stern-Volmer plots were constructed from the integrated fluorescence intensities at different quencher concen-

![Fluorophores](image)

FIG. 1. Structure and properties of the fluorophores (electron acceptors) and quenchers (electron donors). \( \tau_0 \): fluorescence lifetime; \( E(S_1) \): \( S_1 \) state energy; \( E(A/A^-) \): reduction potential vs SCE; \( E(D^+/D) \): oxidation potential vs SCE.
trations using only wavelengths at which reabsorption effects, as well as Rayleigh and Raman scattering were negligible. All measurements were done with aerated solutions.

C. Time-Resolved Fluorescence

Nanosecond time-resolved fluorescence dynamics were measured using the time-correlated single photon counting (TCSPC) technique with the setup described in ref. 69. Excitation was carried out with a laser diode at 395 nm (LDH-P-C-405, PicoQuant). The pulse duration was 60 ps and the full width at half maximum (FWHM) of the instrument response function (IRF) was about 200 ps. A Glan-Taylor polariser placed in front of the sample ensured linearly polarised excitation light. The fluorescence was collected at magic angle relative to the polarisation of the excitation pulse and passed through an interference filter with 8 nm bandwidth centred at 450 nm.

Femtosecond time-resolved emission decays were recorded using a fluorescence up-conversion set-up described in ref. 73, 74. Excitation was performed at 400 nm using the frequency-doubled output of a Kerr lens mode-locked Ti:Sapphire laser (Mai Tai, Spectra-Physics). The angle between the polarisation of pump pulses and that the gate pulses was at magic angle. The up-converted signal was focused into a monochromator equipped with a photomultiplier tube (Hamamatsu R1527P) working in photon counting mode. The full width at half maximum (FWHM) of the Gaussian IRF amounted to approximately 250 fs. The emission wavelength was chosen such that the fluorescence time profiles without quencher were essentially flat over the first 100 ps after excitation. All time-resolved fluorescence measurements were done with aerated solutions.

D. Visible Transient Absorption (Vis-TA)

The Vis-TA setup with an IRF of ~200 fs was described in ref. 75, 76. Excitation was performed at 400 nm with the frequency-doubled output of a 1 kHz Ti:Sapphire amplifier system (Spitfire, Spectra-Physics). The irradiance on the sample was about 0.5 mJ/cm². A supercontinuum generated in a CaF₂ plate was used for probing. The polarisation of the probe pulses was at magic angle relative to that of the pump pulses. The samples were located in a quartz cuvette of 1 mm path length and were continuously stirred by N₂ bubbling. Their absorbance was between 0.1 and 0.2 at the excitation wavelength. No significant degradation of the samples was observed throughout the measurements.

E. IR Transient Absorption (IR-TA)

IR-TA measurements were carried out with the same setup as described in ref. 77, 78. Excitation was achieved with 400 nm pulses generated by frequency doubling part of the output of a 1 kHz amplified Ti:Sapphire system (Solstice, Spectra-Physics). Probing was achieved with the output of an optical parametric amplifier (TOPAS-C, Light Conversion) connected to a difference-frequency mixing module (NDFG, Light Conversion) and polarised at magic angle relative to the pump pulse. Detection was performed with a 2x64 element MCT array (Infrared Systems Development) connected with a spectrogaph (Triax190, 150 lines per mm, Horiba) resulting in a spectral resolution of 1.5 cm⁻¹. All measurements were done with aerated solutions. Sample handling and data acquisitions were the same as described in ref. 77, 78.

III. RESULTS

A. Stationary Spectroscopy

Figure 2 shows the electronic absorption spectra of DCA and TrCA in HX with different concentrations of TMB and TMP, respectively. Addition of quencher leads to an increased absorbance below 400 nm due to its own absorption as well as to an attenuation of the vibrational structure and to a small red shift of the band (see also Figure S1). These spectral changes point to a significant coupling between the fluorophores and the quenchers already in the ground state. This coupling most probably arises from the modest solubility of the fluorophores in HX. The latter should favour their preferential solvation by the aromatic quencher molecules, allowing for larger solvation energy through dispersion interactions. Further evidence of coupling is given by a weak but distinct additional band centred around 750 nm observed with the TrCA/TMP pair, that can be assigned to a charge-transfer transition. Significantly weaker absorption features that could also arise from such a transition can be detected with the other TMP- and DMA-containing pairs (Figure S2). An equilibrium constant for ground-state complex formation of ~ 9 and ~ 2 could be estimated for the TrCA/TMP and DCA/TMP pairs, respectively. For the other pairs, the equilibrium constant is below 0.5. These spectra point to the coexistence of two fluorophore subpopulations: i) one with a quencher molecule in close contact giving rise to a 'distorted' absorption spectrum and, in some cases to a charge-transfer band, and ii) one without such a quencher molecule and associated to an absorption spectrum similar that in pure HX. With the 400 nm pump wavelength used in the time-resolved experiments, both subpopulations are excited. However, even for the strongly coupled reactants, excitation is mostly localised on the chromophore, the charge-transfer band being at longer wavelengths.

Addition of quencher to DCA and TrCA solutions leads to a significant decrease of fluorescence intensity. After correction for the Raman scattering and weak emission from the quencher (esp. TMP, see Figure S3), the shape of the emission spectrum is essentially independent of quencher concentration. Moreover, no new emission band that could be attributed to an exciplex could be detected up to 650 nm. Given the significant distortion of the absorption spectrum upon addition of quencher, this insensitivity of the emission spectral shape to the quencher may seem surprising. It can however be explained by considering that the subpopulation of strongly
coupled fluorophores has a very short fluorescence quantum yield due to ultrafast quenching and thus does not contribute significantly to the time-integrated fluorescence intensity. In other words, the stationary fluorescence spectra reflect mostly the subpopulation of fluorophores without a nearby quencher molecule.

Figure 3A,B depicts steady-state Stern-Volmer plots obtained from the decrease of the integrated stationary fluorescence intensity of DCA and TrCA upon addition of the electron donors (eq.1). These plots are qualitatively very similar for all six fluorophore/quencher (F/Q) pairs, and depart from linearity. This indicates that the quenching coefficient, $\kappa$, in the Stern-Volmer equation, depends on the quencher concentration, $c$:

$$\frac{\phi(0)}{\phi(c)} = \frac{\int_{\text{band}} I(\lambda, 0) \, d\lambda}{\int_{\text{band}} I(\lambda, c) \, d\lambda} = \frac{\int_0^\infty I(t, 0) \, dt}{\int_0^\infty I(t, c) \, dt} = 1 + \kappa(c) \tau_0 c, \quad (1)$$

where $\phi$ is the fluorescence quantum yield and is proportional to the integral of stationary fluorescence intensity, $I(\lambda)$, as well as to the time-integrated fluorescence decay, $I(t)$, and $\tau_0$, the excited-state lifetime of the fluorophore without quencher.

As illustrated in Figure 3C,D, the dependence of $\kappa$ on quencher concentration appears at $c \gtrsim 5 \text{ mM}$. Below this value, it remains of the order of $3 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$. This value is close to the diffusion rate constant in HX, $k_d = 2.3 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$, calculated for reactants of the same size. At concentrations above 5 mM, $\kappa$ increases to values that are well above the diffusion limit. This concentration dependence of $\kappa$ is a direct effect of the static and transient stages of the quenching and reflects the time dependence of the reactant pair distribution.

B. Time-resolved Spectroscopy

1. Time-resolved fluorescence

In principle, the value of $\kappa$ extrapolated to $c = 0$ should correspond to the quenching rate constant in the stationary regime, $k_\infty$. This value can also be determined from the slow quenching dynamics:

$$\frac{\tau_0}{\tau_\text{long}} = 1 + k_\infty \tau_0 c, \quad (2)$$

where $\tau_\text{long}$ is the time constant associated with the slowest decay component of the excited-state population. The latter was determined from time-resolved measurements on the nanosecond timescale using TCSPC.

Figure 4A depicts fluorescence decays measured by TCSPC with TrCA and different concentrations of DMA, whereas Figure 4B shows the corresponding Stern-Volmer plots according to eq.2 together with those for other F/Q pairs. These plots are linear, indicating that the slow quenching dynamics is not affected by the static and transient stages of the quenching. The $k_\infty$ values obtained from the slope of these plots are listed in Table I. These rate constants reflect ET quenching in its stationary stage, where the mutual approach of the reactants by diffusion and their decay by ET have equilibrated. They are close to the $\kappa$ values obtained from the steady-state Stern-Volmer plots extrapolated to $c = 0$.

Access to the static stage of ET quenching was obtained from the early fluorescence dynamics measurements with an IRF of about 250 fs. Time profiles of the fluorescence intensity measured with DCA and TrCA and different quenchers are depicted in Figure S4. These decays are strongly non ex-
FIG. 4. A) Nanosecond fluorescence dynamics measured with TrCA and different concentrations of DMA in HX and B) Stern-Volmer plots obtained from the decrease of the slowest decay component, \( \tau_{\text{long}} \).

FIG. 5. Concentration normalised fluorescence dynamics, \( R(t) \), of the F/Q pairs in HX obtained from measurements at \( c = 0.1, 0.2 \) and 0.3 M.

The quenching parameter and can be described as:

\[
I_t(t,c) = I_t(t,0) \exp \left( -c \int_0^t k(t') \, dt' \right),
\]

where \( k(t) \) is the time-dependent ET quenching rate coefficient. The 'pure' quenching dynamics can be extracted by taking the logarithm of the experimental time-profiles divided by \( I_t(t,0) \) and further division by \( c \) to give:

\[
R(t) = \frac{1}{c} \ln \left( \frac{I_t(t,c)}{I_t(t,0)} \right) = -\int_0^t k(t') \, dt'.
\]

Figure 5 indicates that the \( R(t) \) resulting from measurements at three concentrations are essentially identical, revealing that \( k(t) \) itself does not depend on the quencher concentration. In principle, analysis of the experimental \( k(t) \) can be performed using a theoretical model of diffusion-assisted reactions, which relies on a model for the distance-dependence of ET. However, as the main objective of the present study is the determination of the intrinsic ET rate constant, \( k_0 \), such analysis requires knowledge of a large number of parameters related to the diffusion of the reactants and to the ET reaction itself. Instead, \( k_0 \) was determined from the initial slope of \( R(t) \). To do this, the experimental \( R(t) \) were fitted with the following equation:

\[
R(t) = \sum_{i=1}^n A_i \exp(-t/\tau_i) - k_\infty t - \sum_{i=1}^n \frac{A_i}{\tau_i},
\]

where the last term on the right-hand side is a vertical shift that ensures that \( R(0) = 0 \). The first 500 fs of \( R(t) \) were not included in the analysis to avoid the uncertainties on \( k(t) \) on the timescale of the IRF. The sum of three exponential functions with the best-fit parameters listed in Table S1 was sufficient to properly reproduce the data. To check the consistency of these parameters, they were used to calculate the fluorescence time-profiles at different quencher concentrations using eq.(3). These decays were then time-integrated to simulate the steady-state Stern-Volmer plots according to eq.(1).

As illustrated in Figure S5, the experimental steady-state Stern-Volmer plots are qualitatively well reproduced, although the calculated quenching efficiencies are systematically slightly smaller than those measured. These deviations can be explained by existence of ultrafast quenching components that are missed when neglecting the first 500 fs of \( R(t) \). Finally, the parameters obtained from the fit of eq.(5) were used to estimate the intrinsic ET rate constant:

\[
k_0 = -\left( \frac{dR(t)}{dt} \right)_0 = \sum_{i=1}^n \frac{A_i}{\tau_i} + k_\infty.
\]

The resulting \( k_0 \) values are listed in Table I and plotted in Figure 6 as a function of the ET driving force together with those of \( k_\infty \). Given the neglect of the first 500 fs of the quenching
ET in non-polar solvents

![Graph]

FIG. 6. Dependence of $k_{\infty}$ and $k_0$ in HX on the ET driving force calculated in ACN, together with literature values in ACN.

dynamics, these intrinsic rate constants should be considered as lower-limit values. Figure 6 also shows the $k_0$ and $k_{\infty}$ values reported a few years ago in ACN with 14 F/Q pairs, including those investigated here, as well as quenching rate constants in ACN reported in literature, and corresponding to $k_{\infty}$.

The $k_{\infty}$ values found here in HX are slightly above those in ACN, in agreement with the smaller viscosity of HX. This confirms that, with these F/Q pairs, quenching in the stationary regime is a diffusion-controlled process. Figure 6 reveals that, in the static limit, quenching is as fast or even faster in HX than in ACN, independently of the driving force.

Nuclear tunnelling has been shown to strongly accelerate highly exergonic ET processes and to attenuate the driving force dependence of the ET rate constant in the inverted region. The role of intramolecular vibrational modes on ET has been evidenced for the charge recombination of radical ion pairs through the observation of an isotope effect. A decrease of the CR rate constant by a factor of 1.12 to 1.8 was observed in ACN upon perdeuteration of the fluorophore and/or of the quencher. To test this, we measured the quenching dynamics of the fluorescence of perdeuterated DCA, DCA-$d_8$, by TMP in HX. As shown in Figure S6, the fluorescence dynamics of DCA and DCA-$d_8$ in the presence of 0.25 M TMP are the same within the experimental error.

2. Visible Transient Absorption (Vis-TA)

To have an insight into the nature of the fluorescence quenching product, Vis-TA measurements were performed with two F/Q pairs, namely DCA/TMB and DCA/DMA in HX. As illustrated in Figure 7, the transient spectra at early time exhibit a broad positive band with distinct maxima at 430 and 640 nm. These two features can be observed with DCA alone (Figure S7) and can be assigned to $S_0\leftrightarrow S_1$ transitions of DCA*($S_1$). They decay in a few ps and the ensuing spectra consist of a quasi-structureless band starting from about 430 nm and extending beyond 700 nm. For DCA/TMB, this band decays completely with a ~240 ps time constant. In the case of DCA/DMA, the decay occurs on a ns timescale, beyond the time window of the experiment.

Figure S8 presents a comparison between these Vis-TA spectra after subtraction of the absorption bands of DCA*($S_1$) and literature spectra of DCA radical anion and quencher radical cations. Although these ion spectra show absorption in the same region as the measured Vis-TA band, the distinct maxima of the ions are not visible. These ion features can be clearly observed in the Vis-TA spectra reported for the DCA/DMA pair in medium-polar solvents. Therefore, one can conclude that the primary product of the fluorescence quenching in non-polar solvents is not an ion pair, but rather an exciplex, i.e. an excited bimolecular complex with a significant charge-transfer character. The absence of exciplex emission can be explained by a negligible fluorescence quantum yield, due to a small transition dipole moment for emission, as expected for a charge-transfer transition, and/or to the short lifetime of the exciplex itself.

![Graph]

FIG. 7. Vis-TA spectra recorded at different time delays after excitation of DCA and 0.4 M TMB (top) and DMA (bottom) in HX. The absorption spectra of DCA$^{-}$ (from Ref. 87) and DMA$^{+}$ (from Ref. 86) are also shown for comparison. TMB$^{+}$ absorbs in the same region as DMA$^{+}$.88

3. IR Transient Absorption (IR-TA)

Further insight into the nature of the quenching product in non-polar solvents was obtained from IR-TA measurements. Because of the poor solubility of DCA and TrCA in HX, these experiments were carried out in CHX with the DCA/Q pairs only.
The early stages of quenching should produce mostly strongly coupled pairs, tight ion pairs (TIPs), that recombine rapidly to the neutral F/Q ground state, hence the fast decay of the 2145 cm\(^{-1}\) shoulder. The later diffusion stage of quenching produces predominantly less coupled pairs, loose ion pairs (LIPs), that are longer lived, and are responsible for the residual 2145 cm\(^{-1}\) band. In the present case, the TIPs and LIPs have too similar spectra in the \(-\mathrm{C}=\mathrm{N}\) stretching region to be distinguished. However, their recombination dynamics are distinct.

In the medium polar THF, the shoulder at 2145 cm\(^{-1}\) grows within the first ps (Figures S12-13). During the next 20-25 ps, the whole band looses about 30% of its intensity, while the shoulder shifts to 2150 cm\(^{-1}\). Finally, the band decays entirely on a 85 to 160 ps timescale, depending on the quencher. These data also suggest two types of ion-pair like quenching products: i) a short-lived one responsible for the 2145 cm\(^{-1}\) shoulder generated at early time, and ii) a longer-lived one, associated with the 2150 cm\(^{-1}\) shoulder produced upon diffusional quenching. Based on these results, the 2150 cm\(^{-1}\) band measured in CHX can be assigned to an ion-pair like product as well.

Finally, to check whether the spectral continuum found in CHX, but not in THF and ACN, is a characteristic of a non-polar environment, IR-TA measurements were also carried out in the non-polar CCl\(_4\). Figures S15-16 confirm the presence of such continuum at early time with both TMB and DMA (TMP was not investigated). With DMA, this continuum is dominant and the 2150 cm\(^{-1}\) band of the ion-pair like product becomes only apparent after about 30-40 ps, once the continuum has almost completely decayed. With TMB, the decay of the DCA\(^*\)(S\(_1\)) band and the concomitant rise of the 2145 cm\(^{-1}\) are clearly visible. These results confirm that this spectral continuum is a distinct feature of the quenching product in non-polar environments.

Figure 8 shows IR-TA spectra recorded in the \(-\mathrm{C}=\mathrm{N}\) stretching region with DCA alone and after addition of 0.3 M quencher. The evolution-associated spectra obtained from their global analysis assuming a series of consecutive exponential steps are depicted in Figure S9. The IR-TA spectra with DCA alone show a single positive band at 2170 cm\(^{-1}\) due to the anti-symmetric \(-\mathrm{C}=\mathrm{N}\) stretching band of DCA\(^*\)(S\(_1\)). In the presence of the two weakest donors, TMB and DMA, the initial IR-TA spectra consist of a positive continuum over the whole spectral window and a broad band extending from 2130 to 2170 cm\(^{-1}\) with a distinct maximum coinciding with the \(-\mathrm{C}=\mathrm{N}\) band of DCA\(^*\)(S\(_1\)). The continuum decreases in a few ps, whereas the broad band narrows and transforms into a band with a maximum at 2150 cm\(^{-1}\). Finally, this band decays in 400 ps with TMB and on a few nanoseconds timescale with DMA. By contrast, only the continuum decaying within ~20 ps is visible with the strongest quencher TMP. Very similar spectra and dynamics are observed with the DCA-\(\delta\)/Q pairs in CHX (Figures S10-S11).

To better understand these results in CHX, the same measurements were repeated in the highly polar ACN and the medium polar THF (Figures 9 and S12-14). The initial continuum measured in CHX is absent in both ACN and THF. The early spectra are dominated by the DCA\(^*\)(S\(_1\)) band at 2160 cm\(^{-1}\). With TMB and DMA, this band exhibits a shoulder around 2145 cm\(^{-1}\), which appears at later time with TMP. With TMB, the shoulder vanishes in <10 ps, but with DMA and TMP, it transforms into a band that decays on the ns timescale after the complete decay of the DCA\(^*\)(S\(_1\)) band. This 2145 cm\(^{-1}\) band can be assigned to the anti-symmetric \(-\mathrm{C}=\mathrm{N}\) stretching vibration of the fluorophore radical anion, DCA\(^-\).

These results in ACN reflect the complex non-exponential decay of DCA\(^*\)(S\(_1\)) and the formation of ion pairs with different extents of coupling.\(^{90-92}\) The early stages of quenching...
IV. DISCUSSION

A. Driving-force dependence of the quenching rate constant

The above results reveal that fluorescence quenching is diffusion controlled for the six F/Q pairs investigated here in HX. Table I and Figure 6 indicate that the intrinsic quenching rate constant, $k_0$, is at least two orders of magnitude larger than diffusion, independently of the driving force, and is at least as large as in ACN. Given the predominant role of solvent in ET theories, $105-109$ this result is quite unexpected. It is however consistent with previous studies carried out with a smaller number of F/Q pairs and a lower temporal resolution. $12,13$ By stabilising the charged product, solvation contributes significantly to the ET driving force. The latter can be estimated in HX with the Weller equation for ET in ACN after removal of the dipolar solvation energy. $90$ For the F/Q pair investigated here, the ET driving force in HX should be smaller than in ACN by about 0.8 eV, and should thus vary from 0.05 to 1.3 eV. In principle, ET in HX cannot be discussed in terms of Marcus theory as solvent polarisation, which is absent here, is the main reaction coordinate. $110$ Nevertheless, this theory predicts the inverted region to appear at lower driving force as solvent polarity decreases, because of the smaller reorganisation energy. In a theoretical model of ET in non-polar media, Tachiya and Seki predict the onset of the inverted region at about 0.5-0.6 eV. $67$ Although this value is within the driving-force range spanned by the F/Q pairs studied here, Figure 6 does not exhibit any evidence of an inversion.

Several hypotheses were proposed to account for the absence of an inverted region in polar solvents. They include the population of the ion-pair product in an electronic excited state, $3,14$ ET at non-contact distances where solvent reorganisation energy is larger, $95,96$ and the break down of the linear dielectric response. $97$ The last two hypotheses can obviously not be invoked in non-polar solvents. Although there is strong indirect evidence that electronically excited ions can be produced upon ET in polar solvents, $71,94,98,99$ direct detection of excited ions is still missing, mostly due to their very short lifetime. $100$ An additional explanation for the lack of inverted region could be that the ET quenching associated with $k_0$ is not a non-adiabatic process and, thus, cannot be discussed in terms of Marcus theory or any equivalent golden-rule formalism. This idea was proposed by several authors to account the unexpectedly large quenching rate constants measured around $\Delta G_{ET} = 0.6,54,66$ These authors suggested that, in this case, quenching occurs adiabatically and results in the formation of an exciplex. However, such mechanism was not invoked for more exergonic ET. In this case, ET was suggested to rather occur at remote distance and, as a result of a smaller electronic coupling, to proceed non-adiabatically. However, moderate to highly exergonic ET quenching in the static regime was not considered.

The experimentally observed inverted regions are generally less steep than the normal region because of the occurrence of nuclear tunnelling, $101-104$ that is accounted for in the semiclassical Marcus theory and in the equivalent golden-rule descriptions of ET. $52,83$ According to these models, the ET dynamics in the inverted region is very sensitive to changes in the high-frequency intramolecular modes. Consequently, the absence of an isotopic effect on the intrinsic ET rate constant is at odds with these non-adiabatic treatments of ET and rather suggests an adiabatic ET quenching mechanism.

B. Nature of the quenching product

The Vis-TA data point to a quenching product that is distinct from that in ACN and that could correspond to an exciplex. The IR-TA spectra confirm this difference between polar and non-polar solvents, with the presence of the spectral continuum in the latter. Such an IR absorption feature could have a vibrational or an electronic origin. Observation of vibrational exciplex bands have been recently reported in low to medium polar solvents. $77,105$ Their frequency is intermediate between those measured with the neutral and the reduced species, as expected for a partial charge transfer. Furthermore, these bands are characterised by a relatively large width, of the order of 30 cm$^{-1}$. This is still too narrow to account for the continuum, which could itself arise from a band with a width of more than 300-400 cm$^{-1}$. The broad IR band observed on top of the continuum could be interpreted as such an exciplex vibrational band. This band narrows on a similar timescale as the disappearance of the continuum.

Based on this, we propose that the continuum has an electronic origin. The width of electronic absorption bands in liquids is typically of the order of 500 cm$^{-1}$. Such band would appear as an almost flat continuum in the 120 cm$^{-1}$ spectral window used here. Mid-IR electronic transitions were reported for delocalised polarons in open-shell cations of conjugated oligomers and doped conjugated polymers, $106,107$ as well as for delocalised excitons in multibranched donor-acceptor chromophores. $108,109$ If the exciplex is described as the mixing of the $A^+D$ and $A^-D^+$ non-adiabatic states, $110$ this mid-IR band could be associated with a transition from the lower exciplex state with a strong $A^-D^+$ character to the upper exciplex state with a large $A^+D$ contribution (Figure S17). In this case, the transition energy should reflect the energy gap between the $A^-D^+$ and $A^+D$ at the exciplex equilibrium geometry, and should thus be related to $\Delta G_{ET}$. If we assume that the ET driving force in HX is about 0.8 eV smaller than in ACN, this transition should be at about 0.4 eV for DCA/DMA and 1 eV for DCA/TMP. This is at higher energy than the mid-IR spectral window monitored here. However, these values do not take into account the fact that, directly after its formation, the exciplex should be vibrationally hot. Consequently, its absorption spectrum should be significantly red shifted with respect to that of the equilibrated exciplex. Therefore, the continuum is tentatively assigned an electronic charge-transfer transition of the non-equilibrated exciplex. The absence of this band in polar solvents excludes any electronic transition localised on either $A^-$ or $D^+$. The decay of this continuum can be described as a sum of exponential functions with time constants of the order of 1, 5 and 20 ps (Figure S9). These timescales are consistent with those of vibrational relaxation in liquids. $111,112$
The Vis-TA data indicate that the decay of the DCA*(S1) bands, which occurs in a few picoseconds is not accompanied by a significant rise of the broad exciplex band. This suggests that a fraction of the quenching product is decaying on a similar timescale. Therefore, the decay of the IR continuum is not only due to the thermalisation of the associated exciplex but also to its recombination to the ground state. This fast charge recombination can be accounted for by the large electronic coupling of these exciplexes generated upon static quenching. A recent IR-TA investigation in medium polar solvents pointed to the formation of short-lived tight exciplexes upon static quenching and longer-lived loose exciplexes upon dynamic quenching. The transient data measured here in CHX can be interpreted likewise. For the DCA/TMB and DCA/TMP pairs, the decay of the continuum due to a tight exciplex is followed by the rise of the 2150 cm⁻¹ band. The latter can be attributed to less coupled exciplexes, i.e. loose exciplexes, generated upon dynamic quenching. The 2150 cm⁻¹ band is not observed with the DCA/TMP pair. This suggests that the loose exciplex population recombines on a shorter timescale than its formation. This is consistent with the significantly smaller energy gap between the exciplex and the ground state for this pair. Additionally, Figure S1 indicates that 400 nm irradiation should preferentially excite the fluorophore subpopulation with a nearby quencher molecule. This can further account for the absence of the 2150 cm⁻¹ band, that should rather result from the excitation of less coupled reactant pairs.

![FIG. 10. General scheme for ET quenching in non-polar solvents.](image)

A general scheme of ET quenching in non-polar solvents is proposed in Figure 10. It should be noted that these tight and loose exciplexes should not be considered as species with well-defined structures. They rather designate representative forms in a broad distribution according to intra-pair distance/orientation and coupling strength.

C. Comparison with polar solvents

Our results reveal that k0 is at least as large in HX as in ACN, suggesting a minor role of the environment in the static stage of ET quenching. This is consistent with static quenching being an adiabatic process as a consequence of the large coupling between the reactants. The fact that k0 in HX is larger than in ACN points to an even larger coupling in HX. This could be explained by the very limited solubility of DCA and TrCA in HX compared to ACN or to aromatic solvents. This should favour their preferential solvation by the aromatic quencher molecules through dispersion interactions. This should also lead to a larger coupling between the reactants, as suggested by the electronic absorption spectra (Figure 2), and influence the reactant pair distribution in favour of a larger extent of static quenching. This effect is indeed observed when comparing the R(t) profiles measured here in HX with those reported earlier in ACN. As illustrated in Figure 11, the amplitude of the early decay component of R(t), which mostly reflects static quenching, is systematically larger in HX than in ACN.

![FIG. 11. Comparison of the concentration-normalised quenching dynamics, R(t), in HX and ACN (from ref. 68.)](image)

Although solvent polarity has little direct effect on the intrinsic ET quenching rate constant, apart for that associated with the reactant-pair distribution, it influences considerably the nature of the quenching product. In both solvents, the product of static quenching should be a pair of strongly coupled ions with substantial molecular orbital overlap, and, thus, incomplete charge-transfer character. However, no exciplex band can be observed in polar solvents. This difference is most probably due to the inertial component of dipolar solvation, that occurs in less than 100 fs, and rapidly stabilises a product with a large charge-transfer character. For this reason, the early ET quenching product in polar solvents has a higher ion-pair character than in HX. Consequently, this species is

![FIG. 11. Comparison of the concentration-normalised quenching dynamics, R(t), in HX and ACN (from ref. 68.)](image)
usually referred to as a tight ion pair rather than as a tight exciplex. However, depending on the ET driving force, the difference between these species can be rather subtle.

V. CONCLUSIONS

Our study of the ultrafast ET quenching dynamics reveals that solvent polarity plays a minor role in the static regime, where quenching occurs with reactant pairs already in contact. However, the solvent can significantly influence the reactant-pair distribution, especially with aromatic reactants. This minor solvent dependence arises from the large electronic coupling in the reactant pairs that, in the static regime, should somehow be considered as supermolecules. In this case, quenching could be viewed as an internal conversion from a locally-excited state to a charge-transfer state.

Because of this strong electronic coupling, the quenching product is a tight exciplex with incomplete charge transfer rather than an ion pair. Consequently, this quenching process cannot be discussed in terms of Marcus theory for non-adiabatic ET. The absence of an inverted region is, thus, not surprising. In principle, internal conversion slows down with increasing energy gap. The absence of such an energy gap law for \( k_0 \) could be explained by the high density of vibrational states and the relatively modest energy gaps. This can also account for the rather large scattering of the intrinsic rate constant \( k_0 \).

Our findings are in excellent agreement with the bimolecular ET model proposed by Murata and Tachiya that distinguishes adiabatic contact ET, resulting in an exciplex, and diffusional non-adiabatic ET, producing an ion-pair like species. In this model, exciplexes are only invoked at small to moderate driving force, where contact is required to make ET efficient. Here, we show that exciplexes are also formed in more exergonic ET in the static regime, where the reactant pairs are in contact. In the dynamic regime, quenching occurs as soon as the reactants are at a distance where coupling is sufficiently large to enable ET without further diffusion. Our data do not allow determining the quenching distance. However, even if quenching is remote, the strong Coulombic attraction and the absence of dipolar solvation should favour the collapse of the ensuing ion pair into an exciplex.

SUPPLEMENTARY MATERIAL

Additional spectroscopic data. Evolution-associated difference spectra obtained from the global analysis of the transient-absorption data.

DATA AVAILABILITY

The data that support the findings of this study are openly available at https://zenodo.org/ at http://doi.org/10.5281/zenodo.3744563.

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ET in non-polar solvents

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ET in non-polar solvents


Fluorophores

DCA
\[
\begin{align*}
\tau_0 & : 11.6 \text{ ns} \\
E(S_1) & : 2.95 \text{ eV} \\
E(A/A^-) & : -0.98 \text{ V}
\end{align*}
\]

TrCA
\[
\begin{align*}
\tau_0 & : 13.3 \text{ ns} \\
E(S_1) & : 2.93 \text{ eV} \\
E(A/A^-) & : -0.70 \text{ V}
\end{align*}
\]

Quenchers

TMB
\[
\begin{align*}
E(D^+/D) & : 1.12 \text{ V}
\end{align*}
\]

DMA
\[
\begin{align*}
E(D^+/D) & : 0.78 \text{ V}
\end{align*}
\]

TMP
\[
\begin{align*}
E(D^+/D) & : 0.10 \text{ V}
\end{align*}
\]
The top graph shows the normalized intensity over time for different quenchers. The x-axis represents time in nanoseconds (ns), and the y-axis represents normalized intensity. The different lines and markers correspond to various quenchers:

- Blue line: TrCA
- Green line: TrCA + 10 mM DMA
- Pink marker: IRF

The bottom graph shows the normalized lifetime ($\tau_0/\tau_{long}$) plotted against quencher concentration in millimoles (mM). The x-axis represents quencher concentration, and the y-axis represents the normalized lifetime. The markers correspond to different quenchers:

- Blue circles: DCA/TMB
- Green circles: DCA/DMA
- Red circles: DCATMP
- Blue squares: TrCA/TMB
- Green squares: TrCA/DMA
- Red squares: TrCA/TMP
\[ \Delta G_{ET}(HX) / eV \]

\[ \Delta G_{ET}(ACN) / eV \]

| \( k_0 \): | non polar | polar (from ref. 81) |
| \( k_\infty \): | non polar | polar (from ref. 81) |

from ref. 3, 80
The image shows a graph with spectral data for DCA/TMB and DCA/DMA. The x-axis represents the wavenumber in units of $10^3$ cm$^{-1}$, ranging from 16 to 24, and the y-axis represents the change in absorbance ($\Delta A$) on a logarithmic scale from $-1$ to $2 \times 10^3$. The graph includes data points at various time intervals: 0.5 ps, 1.5 ps, 10 ps, 50 ps, 100 ps, 200 ps, 500 ps, and 1000 ps. The legend indicates the color coding for each time point: red for 0.5 ps, orange for 1.5 ps, yellow for 10 ps, green for 50 ps, blue for 100 ps, cyan for 200 ps, purple for 500 ps, and black for 1000 ps. Additional lines represent $DCA^-$ (dashed black) and $DMA^+$ (dotted black) for comparison.
static  
locally excited state  
A*D  ⇄ A*D  ⇄ A* + D  

dynamic  
ET quenching  
charge-transfer state, exciplex  
A:D\textsuperscript{+}  ⇄ A:D\textsuperscript{+}  

Recombination  
neutral ground state  
A:D  ⇄ A:D  ⇄ A + D  

local excitation  
electronic coupling