

Archive ouverte UNIGE

https://archive-ouverte.unige.ch

Article scientifique

Article 2019

Published version

Open Access

This is the published version of the publication, made available in accordance with the publisher's policy.

Magnetic field effect on ion pair dynamics upon bimolecular photoinduced electron transfer in solution

Feskov, Serguei V.; Rogozina, Marina V.; Ivanov, Anatoly I.; Aster, Alexander; Koch, Marius; Vauthey, Eric

How to cite

FESKOV, Serguei V. et al. Magnetic field effect on ion pair dynamics upon bimolecular photoinduced electron transfer in solution. In: Journal of Chemical Physics, 2019, vol. 150, n° 2, p. 024501. doi: 10.1063/1.5064802

This publication URL:https://archive-ouverte.unige.ch/unige:114615Publication DOI:10.1063/1.5064802

© This document is protected by copyright. Please refer to copyright holder(s) for terms of use.

Export Citation

/iew Online

Magnetic field effect on ion pair dynamics upon bimolecular photoinduced electron transfer in solution

Cite as: J. Chem. Phys. 150, 024501 (2019); doi: 10.1063/1.5064802 Submitted: 8 October 2018 • Accepted: 17 December 2018 • Published Online: 8 January 2019

Serguei V. Feskov,¹ D Marina V. Rogozina,¹ Anatoly I. Ivanov,^{1,a)} Alexander Aster,² Marius Koch,^{2,b)} and Eric Vauthey^{2,c)}

AFFILIATIONS

¹Volgograd State University, University Avenue 100, Volgograd 400062, Russia

²Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

^{a)}Electronic mail: Anatoly.lvanov@volsu.ru ^{b)}Current address: Solvias AG, Römerpark 2, 4303 Kaiseraugst, Switzerland

^{c)}Electronic mail: Eric.Vauthey@unige.ch

ABSTRACT

The dynamics of the ion pairs produced upon fluorescence quenching of the electron donor 9,10-dimethylanthracene (DMeA) by phthalonitrile have been investigated in acetonitrile and tetrahydrofuran using transient absorption spectroscopy. Charge recombination to both the neutral ground state and the triplet excited state of DMeA is observed in both solvents. The relative efficiency of the triplet recombination pathway decreases substantially in the presence of an external magnetic field. These results were analyzed theoretically within the differential encounter theory, with the spin conversion of the geminate ion pairs described as a coherent process driven by the hyperfine interaction. The early temporal evolution of ion pair and triplet state populations with and without magnetic field could be well reproduced in acetonitrile, but not in tetrahydrofuran where fluorescence quenching involves the formation of an exciplex. A description of the spin conversion in terms of rates, i.e., incoherent spin transitions, leads to an overestimation of the magnetic field effect.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5064802

I. INTRODUCTION

Intermolecular photoinduced electron transfer (PET) between a donor D and an acceptor A is typically observed as a quenching of the excited precursor (D* or A*) and leads to the formation of a radical-ion pair (RIP), ${}^{2}D^{+}+{}^{2}A^{-}$.¹⁻⁴ PET from precursors in the singlet excited state produces singlet RIPs due to the conservation of the total spin in elementary chemical reactions. However, RIPs initially produced in the singlet state can also undergo geminate charge recombination (CR) to the triplet neutral reactants, namely, ${}^{3}D^{*}+A$ or D+ ${}^{3}A^{*}$.⁵⁻¹⁴ This phenomenon was explained in terms of a singlet-triplet spin conversion in the RIPs prior to their geminate charge recombination, ^{5,6,11} as illustrated in Fig. 1. In the case of the RIP produced upon PET between pyrene

and dimethylaniline, the spin conversion was shown to originate from the hyperfine interaction (HFI) between the electronic and nuclear spins of the radical ions.¹¹ This mechanism was subsequently invoked to describe the viscosity dependence of the quantum yield of the neutral triplet recombination product in the intermolecular PET between perylene and dimethylaniline.^{15,16} The spin conversion in RIPs is often described in terms of incoherent transitions because of the simplicity of this approach,¹⁷⁻¹⁹ although it was pointed out that the rate model is only adequate in zero magnetic field.^{17,18}

In fact, singlet-triplet spin conversion in RIPs could take place via several mechanisms. Beside the HFI mechanism, paramagnetic relaxation of the electronic spins, intersystem



FIG. 1. Overall scheme of a bimolecular photoinduced electron transfer reaction.

crossing in contact ion pairs and exciplexes, and the Δg -mechanism with an external magnetic field can also be operative.^{5,10,11,20} For organic radical ions, the HFI mechanism is usually more efficient than paramagnetic relaxation since the typical time scales of singlet-triplet transitions in RIPs due to HFI are 10^{-7} – 10^{-9} s, compared to 10^{-5} – 10^{-6} s for paramagnetic relaxation.²⁰ Moreover, the formation of exciplexes is only expected in low to medium polar solvents and in donoracceptor pairs with small driving force for charge separation (CS).

Triplet products in PET can also be formed via nongeminate recombination upon encounters of the radical ions in the bulk. In such encounters, the spins of the radicals are not correlated, and thus, the probabilities of triplet and singlet RIP formation are 0.75 and 0.25, respectively. In many experiments, however, the concentration of radical ions remains small, so bulk recombination occurs on the microsecond time scale. Therefore, this non-geminate recombination can be ignored when only considering the faster geminate processes that take place on the tens of nanosecond time scale.

We report here on our investigation of the ion pair dynamics and of the effect of an external magnetic field following the electron transfer quenching of 9,10dimethylanthracene (DMeA, Fig. 2) in the singlet excited state by the electron acceptor phthalonitrile (PN) in the highly polar acetonitrile (ACN) and medium polar tetrahydrofuran (THF). The photoinduced charge separation (CS) dynamics of the DMeA/PN pair in solvents of varying polarity were studied in detail previously using IR transient absorption (TA) spectroscopy in a 0-2 ns time window.²¹ Here, we concentrate on the dynamics of the ensuing RIPs using electronic transient absorption spectroscopy in a 0-200 ns time window with a sub-nanosecond time resolution. Investigations of the magnetic field effect (MFE) on the dynamics of ion pair recombination are still very scarce. This is due to the time window, typically 0-50 ns, within which these processes occur in solvents like ACN. Until recently, this time window was difficult to access by transient absorption spectroscopy with sufficient temporal resolution. Most of these previous studies were performed by Weller and co-workers.^{5,7,11,22} These authors studied mainly the PET between pyrene and anilines in several polar solvents using flash photolysis with 8 ns excitation pulses. In all cases, the efficiency of the triplet charge recombination was found to decrease in the presence of the magnetic field. This effect was explained by the splitting of the triplet sublevels in the presence of the magnetic field. As the field increases, the transitions between the T₊ and T₋ sublevels and the singlet state slow down and are no longer operative above a certain field, in the so-called saturation regime. In the later case, triplet to singlet conversion occurs via the T₀ sublevel only. The field above which saturation occurs depends on the HFI coupling constant of the ions and is typically of the order of 20 mT.⁵

In these previous investigations, the time evolutions of the ion and triplet state populations were significantly distorted by the \geq 8-10 ns instrument response function and could thus not be used to extract quantitative dynamic information. Here, we present a detailed analysis of the temporal evolution of the ion (²DMeA⁺) and triplet state (³DMeA^{*}) populations measured with and without magnetic field in terms of the reaction scheme shown in Fig. 1 using differential encounter theory. We will show that the data in ACN can only be well reproduced when describing the singlet-triplet spin



FIG. 2. Electron donor (chromophore), acceptor, and solvents (ε , relative permittivity; η , viscosity in cP; τ_f , fluorescence lifetime of DMeA in ns; $-\Delta G_{CS}$, driving force for charge separation in eV)²¹.

conversion of the RIP as a coherent process. The experimental results are the first to be presented. This is followed by a description of the theoretical model and finally by the analysis of the experimental data.

II. EXPERIMENTAL DETAILS

9,10-Dimethylanthracene (DMeA, Alfa Aesar, 99%) was used as received, and 1,3-dicyanobenzene (phthalonitrile, PN, Fluka, ~98%) was purified by sublimation before use. Acetonitrile (ACN, Fisher Scientific) and tetrahydrofuran (THF, Acros) were of the highest spectroscopic purity and used as received. For the transient absorption measurements, the concentration of DMeA was adjusted to have an absorbance of about 0.3 on 1 mm at the excitation wavelength (355 nm) and amounted to about $5 \cdot 10^{-4}$ M. The concentration of PN was 0.4M. The sample solutions were placed in a 1 mm quartz cuvette and bubbled with argon before and during the measurements to remove oxygen and to refresh the sample volume in the excitation spot.

The setup used to record transient absorption (TA) spectra from 0 to 200 ns with an instrument response function of 350 ps (fwhm) was described in detail in Ref. 23. Excitation was performed with 200 ps pulses at 355 nm at a repetition rate of 500 Hz generated by a passively Q-switched, frequency-doubled Nd:YAG laser (Teem Photonics, Powerchip NanoUV). Probing was achieved with white light pulses generated by focusing 100 fs pulses at 800 nm, themselves produced by a 1 kHz Ti:sapphire amplifier, in a CaF₂ plate. The pump and probe pulses were set to magic angle. All TA spectra were corrected for signals (e.g., spontaneous emission) appearing before time zero. To investigate the MFE, two permanent magnets were placed on both sides of the cuvette. This resulted in a magnetic field of approximately 150 mT at the centre of the cuvette, corresponding to the saturation regime.

III. EXPERIMENTAL RESULTS

Figure 3 shows TA spectra recorded at various time delays after 355 nm excitation of DMeA alone (a) and with 0.4M PN (b) in ACN. The early spectra measured without PN are dominated by positive bands at 585 and 370 nm that can be attributed to the $S_n \leftarrow S_1$ transition of DMeA. The decay of these features on the 10 ns time scale is accompanied by the rise of a band at 426 nm. This band can be assigned to the triplet state ³DMeA*, as its decay time shortens from >500 ns to 210 ns by going from a N₂ purged to an aerated solution. According to the amplitude of the bleach of the $S_1 \leftarrow S_0$ transition, responsible for the negative band below 400 nm, a triplet quantum yield of about 0.02 can be estimated, in agreement with the literature.²⁴

In the presence of 0.4M PN, the early TA spectra are dominated by a narrow band at 419 nm and a broader one with a vibronic structure between 530 and 710 nm, which can both be attributed to the radical cation, ²DMeA^{+, 25} The radical anion, ²PN⁻, has only significant absorption below 380 nm and cannot be seen here.²⁵ During the first 50 ns, the amplitude



FIG. 3. Transient absorption spectra recorded at various time delays after 355 nm excitation of DMeA alone (a) and with 0.4M PN (b) in ACN. (c) Difference transient absorption spectra obtained by subtracting the intensity-scaled DMeA cation spectrum [0.1 ns spectrum in (b)] from the TA spectra recorded at later time delays.

of the broad cation band decreases by about 40%, whereas the 420 nm band broadens on both sides, rises, and shifts to 426 nm. Figure 3(c) shows difference TA spectra obtained by subtracting an early TA spectrum, due only to ²DMeA⁺, from the TA spectra measured at later times. Before this, the cation spectrum was scaled so that the amplitude of the ²DMeA⁺ band between 530 and 710 nm matches that in the spectra measured at the other time delays. These difference TA spectra exhibit a single band at 426 nm due to the triplet state of DMeA. As a consequence, the changes observed during the first 50 ns correspond to a partial decay of ²DMeA⁺ and a concurrent rise of ³DMeA^{*}.

The TA measurements were also performed in ACN and 0.4M PN in the presence of an external saturating magnetic field. The resulting TA spectra are qualitatively the same. No significant magnetic field effect can be detected for the cation band [Fig. 4(a) and Fig. S1A]. However, a substantial difference can be observed in the amplitude of the ³DMeA* band, as shown in Fig. 4(b) and Fig. S1B. Figure 4 illustrates the time evolution of the amplitude of the ²DMeA⁺ and ³DMeA* bands obtained in three series of measurements. The small differences that are visible in the time profiles of the triplet state are mostly due to varying concentrations of oxygen resulting



FIG. 4. Time dependence of the DMeA.⁺ (a) and ³DMeA^{*} (b) TA signals in ACN recorded in three series of measurements with and without an external magnetic field.

from different N_2 purging efficiencies. The same series of TA measurements were carried out in THF with DMeA alone and with 0.4M PN, with and without an external magnetic field. The resulting TA spectra are very similar to those in ACN (see Fig. S2). The time dependence of the cation and triplet bands is shown in Fig. S3 and Fig. 8. Like in ACN, a significant magnetic field effect can only be observed on the triplet state. In this case as well, the amplitude of the ³DMeA* signal is substantially reduced in the presence of an external magnetic field (Fig. S4).

IV. THEORY

Differential encounter theory has been shown to be well suited for properly describing the dynamics of bimolecular photoinduced electron transfer processes in solution.^{4,12,14,15,17,26-30} According to this theory, the survival probability N(t) of the excited electron donor obeys the equation¹⁷

$$N(t) = -ck_{CS}(t)N(t) - N(t)/\tau_{D},$$

$$k_{I}(t) = \int W_{CS}(r)n(r,t) d^{3}r,$$
(1)

with the initial condition N(0) = 1. Here $k_{CS}(t)$ is the timedependent CS rate, τ_D is the fluorescence lifetime of D* in the absence of a quencher, and *c* is the quencher concentration, which is much larger than that of D* and, hence, time independent. n(r, t) is the reactant (fluorophore-quencher) pair distribution function and is the solution of the equation

$$\frac{\partial n(r,t)}{\partial t} = -W_{\rm CS}(r)n(r,t) + \hat{L}n(r,t), \qquad n(r,0) = 1, \qquad (2)$$

where \hat{L} is the diffusion operator

$$\hat{\mathbf{L}} = \frac{\mathbf{D}}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r},$$

with the diffusion coefficient D.

As mentioned earlier, the RIPs are initially produced in the singlet state due to spin conservation. It is convenient to describe the subsequent spin evolution of the RIPs as a coherent process with the *r*-dependent spin density matrix $\hat{m}(r, t)$. The spin Hamiltonian has the form

$$H = H_{el} + H_{hfi},$$
(3)

where the first term

$$H_{el} = \omega_{\rm D} S_{\rm Dz} + \omega_{\rm A} S_{\rm Az} + J(r) \left(\frac{1}{2} + 2\mathbf{S}_{\rm D} \mathbf{S}_{\rm A}\right)$$
(4)

accounts for the interaction of the RIP with the magnetic field and the singlet-triplet splitting. The second term introduces HFI between the electronic spin of the donor $S_D = 1/2$ and the effective spin of the nucleus I = 1/2,

$$H_{\rm hfi} = AIS_{\rm D},\tag{5}$$

where A is the HFI coupling constant, $S_A = 1/2$ is the spin of the acceptor, $\omega_D = g_D \mu_e B$ and $\omega_A = g_A \mu_e B$ are the Larmor frequencies of ²DMeA⁺ and ²PN⁻ in the magnetic field B, g_A and g_D are the electronic *g* factors, μ_e is the Bohr's magneton, and 2J(*r*) is the singlet-triplet splitting of the RIP.

The possibility to model the interactions between the electronic spin and a number of nuclear spins by the interaction with a single nuclear spin with an effective HFI constant was discussed earlier in Ref. 31. In the case of the DMeA/PN pair, all the HFI constants of the radical ions have been measured.^{32,33} Here, we only consider the interaction with the donor electronic spin since the effective HFI constant of ²DMeA⁺ is more than three times larger than those of ²PN⁻⁻.

The effective HFI constant is estimated as follows. For the short-lived radical pairs, the HFI-induced singlet-triplet transitions are shown to be controlled by a single parameter–the effective constant a_{eff} , irrespective of the number of magnetic nuclei.³¹ This parameter is calculated as

$$a_{\rm eff} = \sqrt{\frac{1}{3}} \sum a_k^2 I_k (I_k + 1),$$
 (6)

where a_k are the HFI constants of the radical ions and I_k are their nuclear spins. This allows modeling the singlet-triplet evolution with a single effective nuclear spin I = 1/2 and with the effective HFI constant A = $2a_{eff}$.³¹ For the ²DMeA⁺/²PN⁻ pair, the value of this constant is estimated to be A = 0.4 ns⁻¹. It should be noted that the effective hyperfine coupling constant, a_{eff} , defined by Eq. (6), includes the HFIs of both DMeA and PN radical ions, as prescribed in Ref. 31.

J. Chem. Phys. **150**, 024501 (2019); doi: 10.1063/1.5064802 Published under license by AIP Publishing

In general, a system of three S = 1/2 spins has 8 basis states so that the evolution of the RIP density matrix is described by 64 coupled equations. This number however can be strongly reduced if we take into account symmetry properties of the spin Hamiltonian \hat{H} .³⁴ Indeed, the spin interactions in Eq. (3) guarantee the conservation of the z-projection of the total spin

$$\hat{\Sigma}_z = \hat{S}_{Dz} + \hat{S}_{Az} + \hat{I}_z.$$

As a result, the spin ensemble splits into four subensembles with a given projection of the total spin on the *z* axis, $\Sigma_z = \pm 3/2$ and $\Sigma_z = \pm 1/2$. The $\Sigma_z = +3/2$ and -3/2 subensembles are never populated and thus can be neglected. On the other hand, the $\Sigma_z = +1/2$ and -1/2 subensembles are fully equivalent since both involve one singlet and two triplet states and have the same \hat{H} matrix. The population dynamics of these subensembles are the same, and one can therefore consider only one of them, say, $\Sigma_z = +1/2$. This implies the following spin states to be taken into account:

$$|S,\alpha\rangle = \frac{1}{\sqrt{2}} (\alpha_e \beta_e - \beta_e \alpha_e) \alpha_{\rm N},$$

$$|T_0,\alpha\rangle = \frac{1}{\sqrt{2}} (\alpha_e \beta_e + \beta_e \alpha_e) \alpha_{\rm N}, \quad |T_+,\beta\rangle = \alpha_e \alpha_e \beta_{\rm N}.$$
(7)

In this truncated basis, the RIP spin density operator $\hat{m}(r,t)$ is a 3 \times 3 matrix, and its evolution obeys the equation $^{17,35-37}$

$$\frac{\partial \hat{m}(r,t)}{\partial t} = \hat{\tilde{L}}\hat{m}(r,t) - i[\hat{H},\hat{m}(r,t)] - \frac{1}{2}\{\hat{W}_{R}(r),\hat{m}(r,t)\} + \hat{f}(r,t), \quad (8)$$

where \hat{H} is the spin Hamiltonian of the RIP, \hat{W}_R is the reaction operator accounting for charge recombination both to the ground singlet state and to the locally excited triplet state, and the square brackets $[\ldots]$ and the braces $\{\ldots\}$ stand for the commutator and anticommutator, respectively. The Smoluchowski operator

$$\hat{\tilde{L}} = \frac{\tilde{D}}{r^2} \frac{\partial}{\partial r} r^2 e^{-V/k_{\rm B}T} \frac{\partial}{\partial r} e^{V/k_{\rm B}T}$$
(9)

takes into account the Coulomb interaction between the ions

$$V(r) = -\frac{e^2}{\varepsilon(r)r}$$

with spatial dispersion of the dielectric constant³⁸

$$\varepsilon(r) = \frac{\varepsilon_0}{1 + \left(\frac{\varepsilon_0}{\varepsilon_{\infty} - 1}\right)\gamma \exp(-r/\Lambda)}.$$
(10)

Here $\gamma = 2(\Lambda^2/\sigma^2)(ch(\sigma/\Lambda) - 1)$, Λ is the correlation length of solvent polarization fluctuations,³⁸ ε_{∞} and ε_0 are the solvent optical and static dielectric constants, and σ is the contact radius and is supposed to be the same for neutral molecules and radical ions. Here we use the value $\Lambda = 1.6$ Å, which corresponds to the effective radius of an acetonitrile molecule. It should be noted, however, that spatial dispersion effects, which are only operative at short distances between radical-ions, are expected to be weak in systems with relatively slow chemical kinetics. In the DMeA/PN system considered here, the majority of geminate RIPs spend most of their lifetime far from contact distances, where $\varepsilon(r)$ effects are not significant. This is the reason why other short-range effects on the diffusion coefficient and solvent reorganization energy are neglected.

The source term $\hat{f}(r,t)$ in Eq. (8), which represents the production of RIPs from neutral reactants, is given by¹⁷

$$\hat{f}(r,t) = W_{\rm CS}(r)n(r,t)N(t)\hat{P}_{\rm S}.$$
(11)

One can see that the positions in space where the RIPs are created coincide with those where the neutral reactant pairs are consumed. The projection operator $\hat{P}_S = |S\rangle\langle S|$ ensures that the RIPs appear only in the singlet state. As far as CS and CR proceed essentially as non-contact reactions between distant reactants, both n(r, t) and m(r, t) obey reflective boundary conditions at $r = \sigma$,

$$\hat{J}_{n}n\Big|_{r=\sigma} = 4\pi r^{2} D \left.\frac{\partial n}{\partial r}\right|_{r=\sigma} = 0,$$

$$\hat{J}_{m}\hat{m}(r,t)\Big|_{r=\sigma} = 4\pi r^{2} D e^{-V/k_{\rm B}T} \frac{\partial}{\partial r} e^{V/k_{\rm B}T} \hat{m}\Big|_{r=\sigma} = 0.$$
(12)

Here \hat{J}_n and \hat{J}_m are the diffusive flux operators for neutral reactants and RIPs. Additionally, Eq. (8) is solved with the zero initial conditions, $\hat{m}(r, 0) = 0$.

The operator $\hat{W}_{R}(r)$ quantifies the recombination of the RIPs to both the ground singlet and the triplet excited states of DMeA with the rates $W_{RS}(r)$ and $W_{RT}(r)$, respectively, and is expressed as

$$\hat{W}_{R}(r) = W_{RS}(r)\hat{P}_{S} + W_{RT}(r)\hat{P}_{T},$$
 (13)

where \hat{P}_S and \hat{P}_T are the projection operators onto the singlet and triplet states. The build-up kinetics of the singlet and triplet CR products are calculated as^17

$$P_{\rm S}(t) = \frac{c}{2} \int W_{\rm RS}(r) \operatorname{Tr} \{ \hat{P}_{\rm S}, \hat{m}(r, t) \} d^3r = \psi_{\rm RIP} \varphi_{\rm S}(t),$$

$$P_{\rm T}(t) = \frac{c}{2} \int W_{\rm RT}(r) \operatorname{Tr} \{ \hat{P}_{\rm T}, \hat{m}(r, t) \} d^3r = \psi_{\rm RIP} \varphi_{\rm T}(t),$$
(14)

where

$$\psi_{\rm RIP} = c \int d^3r \int_0^\infty {\rm Tr}\hat{f}(r,t) \, dt \tag{15}$$

is the quantum yield of the primary RIP formation, which is related to the fluorescence quantum yield $\psi_{\rm fl}$ as $1 - \psi_{\rm RIP} = \psi_{\rm fl}$; $\varphi_{\rm S}(t)$ and $\varphi_{\rm T}(t)$ are the probabilities of the singlet and triplet charge recombination of the RIP. The probability of diffusive separation of the RIP into free ions is $\varphi_{\rm sep}(t) = 1 - \varphi_{\rm S}(t) - \varphi_{\rm T}(t)$, and the yield of free ions to the bulk is $\phi = \psi_{\rm RIP}\varphi_{\rm sep}$.

The rate constants of charge separation, $W_{CS}(r)$, as well as of the singlet and triplet recombination, $W_{RS}(r)$ and $W_{RT}(r)$, can be calculated with the Marcus expression [Eq. (17)] with the distance-dependent reorganization energy

J. Chem. Phys. **150**, 024501 (2019); doi: 10.1063/1.5064802 Published under license by AIP Publishing



FIG. 5. Energy level scheme (not to scale) pertaining to photoinduced ET with a D^*/A pair.

$$\lambda(r) = \lambda_i + \lambda_m \left(2 - \frac{\sigma}{r}\right),\tag{16}$$

which includes the contributions from low-frequency intramolecular modes λ_i and from the medium, the latter having a value of λ_m at contact.

In the DMeA/PN pair, charge recombination to the singlet ground state proceeds in the Marcus inverted region so that intramolecular quantum vibrational modes have to be included. Assuming a single effective high-frequency mode, the rate constant is given by³⁹

$$W_{j}(r) = V_{j}^{2}(r)\sqrt{\frac{\pi}{\lambda(r)k_{\rm B}T}} \sum_{n=0}^{\infty} \frac{\mathrm{S}^{n}e^{-\mathrm{S}}}{n!} \exp\left\{-\frac{\left[\Delta\mathrm{G}_{j}+\lambda(r)+\Omega n\right]^{2}}{4\lambda(r)k_{\rm B}T}\right\}.$$
(17)

Here j = CS, RS, and RT correspond to CS, singlet, and triplet CR, respectively, $V_j(r) = V_j(\sigma) \exp(-(r - \sigma)/l)$ are the distancedependent electronic coupling energies, ΔG_j are the free energies of the corresponding electron transfer reactions (Fig. 5), $S = \lambda_q / \Omega$ is the electron-vibronic coupling parameter (the Huang-Rhys factor),⁴⁰ and λ_q is the reorganization energy of the effective high-frequency intramolecular mode with the frequency Ω (the Planck constant $\hbar = 1$, and the frequency is measured in energy units).

V. ANALYSIS OF THE TEMPORAL EVOLUTION OF THE RADICAL CATION AND TRIPLET STATE POPULATIONS

The above model was used to analyze the experimental results obtained with the DMeA/PN pair. The set of model equations was solved numerically using the FLUT code.⁴¹ This code is implemented as a hierarchy of C++ classes representing the key entities of the model–the concepts of the diffusion space,⁴² the distance-dependent electronic transitions, the spin subsystem with the coherent/incoherent spin evolution, etc. The numerical method employs the Chebyshev time propagation scheme with the spatial finite-differencing

operator obeying the detailed balance condition.⁴³ Validation of the code was performed using several benchmark tests, and agreement with exact analytic solutions in important limiting cases was obtained. Conservation of the total population of all electronic states was checked before the simulations and was controlled during the numerical experiments as well. The total population differed from unity by less than 10^{-7} .

Simulation results were fitted to the experimental data obtained with and without external magnetic field. The analysis was carried out with the following quantities: (1) the time-dependent population $P_{RIP}(t)$ of radical-ion pairs, taking into account both spin states ${}^{1}[^{2}D^{+}...^{2}A^{-}]$ and ${}^{3}[^{2}D^{+}...^{2}A^{-}]$ and (2) the time-dependent population $P_{T}(t)$ of the product of triplet geminate charge recombination $[{}^{3}D...{}^{1}A]$. The temporal evolution of the RIP population was calculated as

$$P_{\rm RIP}(t) = c \int \mathrm{Tr}\,\hat{m}(r,t)\,d^3r,\tag{18}$$

whereas $P_T(t)$ was obtained from Eq. (14).

A significant part of the model parameters introduced above is known from independent experiments, some of them being listed in Fig. 2. The energies of the first excited singlet and the triplet states of DMeA are E_S = 3.08 eV and E_T = 1.67 eV.^{21,44}

The typical value of the solvent reorganization energy in ACN is $\lambda_m = 0.75$ eV.² This value is related to the dielectric properties of the solvent according to the Marcus equation

$$\lambda_m = \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0}\right) \lambda_{m0},\tag{19}$$

where λ_{m0} is independent of dielectric permittivities. In THF, λ_m amounts to 0.53 eV. The Larmor frequencies of ²DMeA⁺ and ²PN⁻⁻ are $\omega_D = \omega_A = 0$ and 26.5 ns⁻¹ in zero and in a saturated magnetic field, B = 150 mT. The frequency of the quantum intramolecular mode was set as $\Omega = 0.15$ eV. The decay length of all electronic couplings was taken as l = 1Å and $\sigma = 6$ Å. The diffusion coefficients in ACN and THF, D = 370 and 270 Å²/ns, were estimated using the well-known equation

$$D = \frac{k_{\rm B}T}{6\pi\eta} \left(\frac{1}{R_1} + \frac{1}{R_2}\right),\tag{20}$$

where η is the solvent viscosity and $R_1 \approx R_2$ are the effective donor and acceptor radii. The electronic couplings, V_{CS} , V_{RS} , V_{RT} , and the Huang-Rhys factor, S, were variable parameters.

Figure 6 shows comparisons of the simulated ion and triplet state populations with the experimental time profiles of the ²DMeA⁺ and ³DMeA^{*} TA band intensity up to 50 ns. In this time window, the effect of bulk processes is still insignificant so that only geminate processes were included in the theoretical analysis. The electronic coupling energies and the Huang-Rhys factors were kept the same for both CS and CR to the singlet and triplet products. The best-fit values are



FIG. 6. Comparison between the simulated (solid lines) and measured (symbols) time profiles of DMeA⁺ (a) and ³DMeA^{*} (b) in ACN. The simulations were performed within the Hamiltonian (coherent) model of spin conversion.

 $V_{CS} = V_{RS} = V_{RT} = 0.021 \text{ eV}$ and S = 2.28. The equality of all the electronic coupling energies, $V_{CS} = V_{RS} = V_{RT}$, was postulated as a first step in the fitting procedure in order to reduce a number of variable parameters. It turned out, however, that these energies do not need to be varied independently.

The initial growth of the RIP population at short times (up to 0.5 ns) is due to the fast charge separation process upon photoexcitation of DMeA convolved with the instrument response function of the TA setup. The subsequent sharp decrease of $P_{RIP}(t)$ with the following evolution to a quasiplateau arises from the competition between the recombination of the singlet born RIPs to the singlet ground state and their diffusive separation. Since the diffusion coefficient is assumed to be known and both CS and CR rates, W_{CS} and W_{RS} , are determined by two independent parameters S and $V_{CS} = V_{RS}$, their values can be found from a fit of $P_{RIP}(t)$ to the experimental data in zero magnetic field. The kinetics of $P_{RIP}(t)$ in saturated magnetic field as well as those of $P_T(t)$ in zero and saturated fields were then simulated without any adjustable parameters.

Figure 6(a) points to good agreement between the simulated and measured ion kinetics both at short times [see the inset in Fig. 6(a)] and on a longer time scale. The effect of the external magnetic field on $P_{\text{RIP}}(t)$ is small, within the limit of error of the experimental data. On the other hand, the time profile of the triplet DMeA population [Fig. 6(b)] is only well reproduced at short time, up to 10–15 ns. This discrepancy most probably results from the "effective spin" approximation

used here for modeling the spin transitions. This approximation is known to be only applicable at short times, $a_{\rm eff} t \ll 1.^{31}$ In general, the interaction between the electronic spin and a single nuclear spin leads to coherent quantum transitions at the frequency A in zero field and A/2 in saturated magnetic field.⁴⁵ The resulting oscillations of the populations are visible in the simulated time profiles in Fig. 6(b). Their difference in frequency in the zero-field and high-field limits is also visible. These oscillations, however, are blurred by the dispersion of the time at which the RIPs are generated so that they are barely seen, especially at longer times. Moreover, the electronic spin of ²DMeA⁺ actually interacts with many nuclear spins with different HFI constants, resulting in a more complex spin dynamics and a smearing of the oscillations. This is probably the reason why they do not appear in the experimental data.

Another important difference between the predictions of the "single effective spin" model and the general multi-spin model is the influence of the number of nuclear spins on the average singlet and triplet populations.⁴⁵ Obviously, on a time scale larger than an oscillation period, the dynamics of triplet recombination is determined by the average triplet RIP population. Since the average triplet RIP population increases with the number of interacting nuclear spins,45 an underestimation of the MFE on the triplet DMeA yield is expected with the single effective spin approximation. This effect is clearly visible in Fig. 6. On longer time scales, beyond the time window considered here, paramagnetic relaxation becomes operative and equalizes the populations of all four RIP spin states.⁴⁶ In the case of the DMeA/PN pair, paramagnetic relaxation does not play any noticeable role up to 50 ns. This conclusion is based on the analysis of the predictions of the incoherent spin transition model illustrated in Fig. 7. Indeed, this model is applicable when the spin evolution is controlled by spin relaxation. If spin relaxation had a significant effect on spin transitions at 50 ns, then the magnitude of the MFE would be much larger than that measured experimentally, as shown by the incoherent model.

Figure 7 shows the results of numerical simulations with the same parameters as used in Fig. 6 but within a rate model of the spin transitions. Details on the description of incoherent spin conversion in RIPs can be found in the supplementary material. There, the quantum yields of the neutral singlet and triplet products are calculated with the additional assumption of contact charge separation and recombination. The calculated MFE for the triplet DMeA population is considerably larger than that observed experimentally. A variation of the rate constant $k_{\rm ST}$ of singlet-triplet transitions in the RIPs results in a significant variation of the triplet yield but has a minor effect on the magnitude of the MFE. As shown in the supplementary material, the contact rate model generally predicts a stronger MFE than that found experimentally.

Another important difference between the two models is expected for the time dependence of ³DMeA^{*}. At early time, the Hamiltonian (coherent) model predicts the buildup



FIG. 7. The same as in Fig. 6 but with the simulations performed using a rate (incoherent) model of spin conversion.

of triplet DMeA to be proportional to t^2 , whereas the rate (incoherent) model predicts a linear dependence on time. This results in a significant difference in the initial rise of $P_T(t)$, which is visible in Figs. 6 and 7. The coherent model predicts a considerably slower initial buildup of the triplet population than the rate model. The fact that the coherent model describes much better the initial triplet state dynamics is a strong evidence of the occurrence of coherent spin transitions in the ²DMeA⁺/²PN⁻ pairs.

Simulations of $P_{RIP}(t)$ and $P_T(t)$ were also performed in THF using the same parameters as in ACN, except for the solvent dielectric constants and reorganization energy and the CS/CR free energy gaps. The comparison between these simulations and the experimental data is presented in Fig. 8. The simulated ion population at long times is strongly overestimated compared to the experimental data both in zero and saturated magnetic fields. The main reason for this discrepancy is the singlet recombination W_{RS} that is predicted to be much slower in THF than in ACN. This difference is due to the much larger free energy gap ΔG_{RS} and smaller solvent reorganization energy λ_m in THF, which shift CR further into the Marcus inverted region compared to ACN and almost suppress singlet charge recombination. As a result, the buildup of the triplet DMeA population in THF is predicted to be considerably slower than that in ACN.

It should be noted that the yield of the triplet recombination product in THF cannot be increased further by increasing the coupling parameter V_{RT} . To confirm this, the effect of V_{RT} on $P_T(t)$ was simulated as illustrated in Fig. 9. The results



FIG. 8. Comparison between the simulated (coherent model, solid lines) and measured (symbols) time profiles of ions (a) and triplet excited states (b) in THF.

point to an opposite dependence on $V_{\rm RT}$ in the two solvents. In ACN, the triplet DMeA yield increases with the electronic coupling, whereas it decreased in THF. This rather unexpected



FIG. 9. Simulated kinetics of ${}^{3}\text{DMeA}^{*}$ in ACN (a) and THF (b), calculated in the zero-field limit for a few values of V_{T} .

result can be explained as follows. Obviously, the CR rate is determined by both the rate constant and frequency of ion encounters. Given the lower dielectric constant of THF, the frequency of ion encounters is higher than that in ACN due to a larger Coulomb attraction. At first sight, the triplet yield should be expected to be larger in THF. However, we observe here the well-known suppression of the evolution of a quantum system (here the singlet-triplet transitions) as a result of the interaction with other systems.¹⁶ The spin state of the RIP evolves coherently from singlet to triplet and back, whereas the triplet RIP state decays via triplet CR. Mathematically, this recombination results in the decay of both the diagonal and off diagonal elements of the spin density matrix $\hat{m}(r, t)$. The decay of the diagonal elements reflects CR itself, whereas that of the non-diagonal elements decreases the probability of singlettriplet conversion. Therefore, if the triplet recombination rate and the Onsager radius are large enough, as in a solvent with a small dielectric constant like THF, the singlet-triplet transitions are strongly suppressed. As a result, an increase of W_{RT} leads to a decrease of the spin transition probability and, thus, in the decrease of the triplet quantum yield that is shown in Fig. 9. In the more polar ACN, this effect is not operative due to a weaker Coulomb interaction that results in less frequent ion encounters.

The influence of the singlet-triplet splitting 2J(r) on the ion and triplet state dynamics has also been simulated. A large splitting is known to prevent singlet-triplet transitions in the RIPs. Since the magnitude of J(r) decays rapidly with interionic distance r, the spin conversion is assumed to be operative only when r exceeds a certain R_{cutoff} value that has to be larger than the contact radius σ . In the simulations, this distance was set to R_{cutoff} = 8 Å. Variation of R_{cutoff} however was found to have no significant effect on $P_{RIP}(t)$ and $P_{T}(t)$. It should also be noted that the exchange interaction does not only halt the singlet-triplet conversion but also dephases singlet-triplet coherence.⁴⁷ For the relatively slow RIP kinetics investigated here, the minor effect of halting the singlet-triplet conversion was directly confirmed by simulations, which showed that a variation of R_{cutoff} has a negligible effect on RIP kinetics. The effect of the S/T dephasing on the RIPs kinetics was not investigated directly here, but the agreement between the experimental and simulated build-up kinetics of the triplet neutral products without adjustable parameters points to a minor role of this interaction in the molecular system studied here.

Apparently, the main reason for the discrepancy between the simulations and the experimental data in THF is that the model does not include the formation of an exciplex. Previous investigations of the ET quenching of DMeA by PN in solvents of varying polarity evidenced the formation of an exciplex in low- and medium polarity solvents like THF but not in highly polar solvents like ACN.²¹ Spectroscopically, this exciplex is characterised by a spectrum very similar to that of the RIP in the visible but not in the IR. In THF, the exciplex can be formed upon quenching of the excited precursor as well as from the RIPs.⁴⁸⁻⁵⁰ These latter pathways compete efficiently with the singlet and triplet recombination of the RIPs. As a consequence, recombination to the neutral ground state and to the triplet DMeA occurs almost entirely from the exciplex. Therefore, the data shown in Fig. 8 should mostly reflect the decay of the exciplex and not of the RIP. A quantitative description of the exciplex dynamics and the associated MFE requires more elaborate models than that used here.⁴⁹ It should include the reversible stage of the exciplex formation that cannot be described within the unified encounter theory used here.¹⁸

Coming back to ACN, Figs. 4 and 6 show that the decay of the ion population in the 0-50 ns time window is bimodal. The fast component is due to geminate singlet charge recombination and has been observed with many other ion pairs using fs-ps pump probe spectroscopy.51-54 The slower component, which accounts here for about 10% of the total decay, is also due to geminate recombination to both singlet and triplet products, as testified by the presence of the MFE. This decay reveals that the ions are still correlated with a few tens of ns after their generation and have a significant probability to reencounter and to recombine. This is substantially longer than the few ns that have often been assumed for the formation of free ions in ACN.55,56 This slow decay component is missed in conventional fs-ps pump-probe experiments that are generally performed within a time window going up to a few ns. In these experiments, the time profile of the TA signal intensity after the initial decay appears as a plateau, which is often ascribed to free ions. Such interpretation leads to an overestimation of the free ion yield and to an oversimplification of the ion pair dynamics. Comprehensive understanding of these dynamics requires access to a sufficiently broad time window with an adequate temporal resolution combined with an analysis, like the differential encounter theory used here, which accounts properly for diffusion and its interplay with electron transfer.

VI. CONCLUSIONS

The effect of an external magnetic field on the recombination dynamics of geminate ion pairs produced upon bimolecular photoinduced electron transfer between DMeA and PN has been investigated both experimentally and theoretically. A significant MFE was observed on the triplet yield of DMeA populated upon geminate recombination of the ion pairs. The measured time profiles of the triplet state population in a highly polar solvent without and with an external magnetic field could be quantitatively reproduced at short time within the differential encounter theory provided that the spin-conversion in the geminate ion pairs induced by the hyperfine-coupling interaction is described as a coherent process. A description of this spin conversion as an incoherent process in terms of rate constants predicts a significantly larger MFE than observed.

Better agreement between theory and the population dynamics measured at longer times would require going beyond the single effective nuclear spin approximation used here to describe the hyperfine interaction. This would add a very significant level of complexity and increase the number of adjustable parameters to the model without bringing much more insight into the ion-pair dynamics than that obtained here.

This study also reveals that the ion pairs remain correlated for several tens of nanoseconds even in a highly polar and non-viscous solvent like acetonitrile. This is significantly longer than the few nanoseconds that are often assumed.

The relatively simple model used here cannot be applied in medium-polarity solvents where exciplexes play an important role. Our results point to a substantial MFE in such solvents as well. However, in order to understand its origin, additional experimental work and theoretical developments are needed.

SUPPLEMENTARY MATERIAL

In the supplementary material, some details of the contact model of incoherent spin conversion in RIPs are presented. It is shown that the contact rate model generally predicts a stronger MFE than that observed in the experiments. Transient absorption spectra recorded at various time delays after 355 nm excitation of DMeA alone and with 0.4M PN in THF also are pictured.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (Project No. 16-13-10122), the Swiss National Science Foundation (Project No. 200020-165890), and the University of Geneva.

REFERENCES

¹A. Weller, "Exciplex and radical pairs in photochemical electron transfer," Pure Appl. Chem. **54**, 1885-1888 (1982).

²I. R. Gould and S. Farid, "Dynamics of bimolecular photoinduced electrontransfer," Acc. Chem. Res. **29**, 522-528 (1996).

³N. Mataga and H. Miyasaka, "Electron transfer and exciplex chemistry," Adv. Chem. Phys. **107**, 431-496 (2007).

⁴A. Rosspeintner and E. Vauthey, "Bimolecular photoinduced electron transfer reactions in liquids under the gaze of ultrafast spectroscopy," Phys. Chem. Chem. Phys. **16**, 25741-25754 (2014).

⁵K. Schulten, H. Staekand, A. Weller, H.-J. Werner, and B. Z. Nickel, "Magnetic field dependence of the geminate recombination of radical ion pairs in polar solvents," Z. Phys. Chem. **101**, 371-390 (1976).

⁶Z. Schulten and K. Schulten, "The generation, diffusion, spin motion, and recombination of radical pairs in solution in the nanosecond time domain," J. Chem. Phys. **66**, 4616 (1977).

⁷A. Weller, H. Staerk, and R. Treichel, "Magnetic-field effects on geminate radical-pair recombination," Faraday Discuss. Chem. Soc. **78**, 271-278 (1984).

⁸M. Ottolenghi, "Charge-transfer complexes in the excited state. Laser photolysis studies," Acc. Chem. Res. **6**, 153-160 (1973).

⁹M. E. Michel-Beyerle, R. Haberkorn, W. Bube, E. Steffens, H. Schroeder, H. J. Neusser, E. W. Schlag, and H. Seidlitz, "Magnetic field modulation of geminate recombination of radical ions in a polar solvent," Chem. Phys. **17**, 139-145 (1976).

¹⁰B. Brocklehurst, "Spin correlation in the geminate recombination of radical ions in hydrocarbons. I. Theory of the magnetic field effect," J. Chem. Soc., Faraday Trans. 2 72, 1869–1884 (1976). ¹¹H. J. Werner, H. Staerk, and A. Weller, "Solvent, isotope, and magnetic field effects in the geminate recombination of radical ion pairs," J. Chem. Phys. **68**, 2419-2426 (1978).

¹²A. A. Neufeld, A. I. Burshtein, G. Angulo, and G. Grampp, "Viscosity dependence of geminate recombination efficiency after bimolecular charge separation," J. Chem. Phys. **116**, 2472 (2002).

¹³G. Angulo, G. Grampp, A. A. Neufeld, and A. I. Burshtein, "Delayed fluorescence due to annihilation of triplets produced in recombination of photo-generated ions," J. Phys. Chem. A **107**, 6913-6919 (2003).

¹⁴V. S. Gladkikh, A. I. Burshtein, G. Angulo, and G. Grampp, "Quantum yields of singlet and triplet recombination products of singlet radical ion pairs," Phys. Chem. Chem.Phys. 5, 2581-2588 (2003).

¹⁵D. V. Dodin, A. I. Ivanov, and A. I. Burshtein, "Noncontact bimolecular photoionization followed by radical-ions separation and their geminate recombination assisted by coherent HFI induced spin-conversion," J. Phys. Chem. A **112**, 889-897 (2008).

¹⁶A. I. Ivanov and A. I. Burshtein, "The double-channel contact recombination and separation of geminate radical ion pairs in a Coulomb well," J. Phys. Chem. A **112**, 6392-6397 (2008).

¹⁷A. I. Burshtein, "Unified theory of photochemical charge separation," Adv. Chem.Phys. **114**, 419-587 (2000).

¹⁸A. I. Burshtein, "Non-Markovian theories of transfer reactions in luminescence and chemiluminescence and photo- and electrochemistry," Adv. Chem. Phys. **129**, 105-418 (2004).

¹⁹V. S. Gladkikh, G. Angulo, and A. I. Burshtein, "Production of free radicals and triplets from contact radical pairs and from photochemically generated radical ions," J. Phys. Chem. A **111**, 3458-3464 (2007).

²⁰U. E. Steiner and T. Ulrich, "Magnetic field effects in chemical kinetics and related phenomena," Chem. Rev. **89**, 51-147 (1989).

²¹M. Koch, G. Licari, and E. Vauthey, "Bimodal exciplex formation in bimolecular photoinduced electron transfer revealed by ultrafast time-resolved infrared absorption," J. Phys. Chem. B **119**, 11846-11857 (2015).

²²A. Weller, F. Nolting, and H. Staerk, "A quantitative interpretation of the magnetic field effect on hyperfine-coupling-induced triplet formation from radical ion pairs," Chem. Phys. Lett. **96**, 24-27 (1983).

²³ B. Lang, S. Mosquera-Vazquez, D. Lovy, P. Sherin, V. Markovic, and E. Vauthey, "Broadband ultraviolet-visible transient absorption spectroscopy in the nanosecond to microsecond time domain with sub-nanosecond time resolution," Rev. Sci. Instrum. **84**, 073107 (2013).

²⁴B. Stevens and B. E. Algar, "Photoperoxidation of unsaturated organic molecules. II. Autoperoxidation of aromatic hydrocarbons," J. Phys. Chem. 72, 3468-3474 (1968).

²⁵T. Shida, Electronic Absorption Spectra of Radical Ions (Elsevier, Amsterdam, 1988), Vol. 34.

²⁶A. I. Burshtein, "Geminate recombination after binary photoionization," Chem. Phys. Lett. **194**, 247-251 (1992).

²⁷R. C. Dorfman and M. D. Fayer, "The influence of diffusion on photoinduced electron transfer and geminate recombination," J. Chem. Phys. 96, 7410-7422 (1992).

²⁸A. Rosspeintner, D. R. Kattnig, G. Angulo, S. Landgraf, G. Grampp, and A. Cuetos, "On the coherent description of diffusion-influenced fluorescence quenching experiments," Chem. Eur. J. **13**, 6474-6483 (2007).

²⁹S. V. Feskov and A. I. Burshtein, "Double-channel photoionization followed by geminate charge recombination/separation," J. Phys. Chem. A **113**, 13528-13540 (2009).

³⁰G. Angulo, A. Rosspeintner, B. Lang, and E. Vauthey, "Optical transient absorption experiments reveal the failure of formal kinetics in diffusion assisted electron transfer reactions," Phys. Chem. Chem. Phys. **20**, 25531-25546 (2018).

³¹K. M. Salikhov, "Theory of magnetic effects in radical reactions at zero field," Chem. Phys. 82, 145-162 (1983).

³²A. Reymond and G. K. Fraenkel, "New method for the synthesis of radical cations of aromatic hydrocarbons," J. Phys. Chem. **71**, 4570-4572 (1967). ³³I. C. Lewis and L. S. Singer, "Electron spin resonance of radical cations produced by the oxidation of aromatic hydrocarbons with SbCl₅," J. Chem. Phys. **43**, 2712 (1965).

 34 N. N. Lukzen, J. B. Pedersen, and A. I. Burshtein, "Singlet and triplet products of the geminate recombination of a radical pair with a single magnetic nucleus (I = 1/2)," J. Phys. Chem. A **109**, 11914–11926 (2005).

³⁵N. Korst and A. Lazarev, "Relaxation in the spin system induced by stochastic disturbance," Physica 42, 31-40 (1969).

³⁶J. B. Pedersen and J. H. Freed, "Theory of chemically induced dynamic electron polarization. I," J. Chem. Phys. **58**, 2746-2762 (1973).

³⁷J. B. Pedersen and J. H. Freed, "Theory of chemically induced dynamic electron polarization. II," J. Chem. Phys. **59**, 2869–2885 (1973).

³⁸A. A. Kornyshev and J. Ulstrup, "Polar solvent structural parameters from protonation equilibria of aliphatic and alicyclic diamines and from absorption bands of mixed-valence transition-metal complexes," Chem. Phys. Lett. **126**, 74-80 (1986).

³⁹R. A. Marcus and N. Sutin, "Electron transfer in chemistry and biology," Biochim. Biophys. Acta **811**, 265–322 (1985).

⁴⁰K. Huang and A. Rhys, "Theory of light absorption and non-radiative transitions in F-centres," Proc. R. Soc. A **204**, 406-423 (1950).

⁴¹S. V. Feskov and A. E. Nazarov, "FLUT: A numerical code for simulations of multistage photoinduced electron transfer reactions in viscous solutions," AIP Conf. Proc. **2040**, 020010 (2018).

⁴²E. B. Krissinel and N. Agmon, "Spherical symmetric diffusion problem," J. Comput. Chem. **17**, 1085-1098 (1996).

⁴³E. Pines, D. Huppert, and N. Agmon, "Geminate recombination in excited state proton transfer reactions: Numerical solution of the Debye-Smoluchowski equation with backreaction and comparison with experimental results," J. Chem. Phys. **88**, 5620-5630 (1988).

⁴⁴V. Gray, D. Dzebo, A. Lundin, J. Alborzpour, M. Abrahamsson, B. Albinsson, and K. Moth-Poulsen, "Photophysical characterization of the 9,10disubstituted anthracene chromophore and its applications in triplet-triplet annihilation photon upconversion," J. Mater. Chem. C **3**, 11111-11121 (2015).

⁴⁵D. V. Dodin, A. I. Ivanov, and A. I. Burshtein, "Hyperfine interaction mechanism of magnetic field effects in sequential fluorophore and exciplex fluorescence," J. Chem. Phys. **138**, 124102 (2013).

⁴⁶A. I. Burshtein, "Recombination and separation of photochemically created radical-ion pairs subjected to incoherent spin-conversion," Chem. Phys. **323**, 341-350 (2006).

⁴⁷E. W. Evans, D. R. Kattnig, K. B. Henbest, P. J. Hore, S. R. Mackenzie, and C. R. Timmel, "Sub-millitesla magnetic field effects on the recombination reaction of flavin and ascorbic acid radicals," J. Chem. Phys. **145**, 085101 (2016).

⁴⁸M. Koch, R. Letrun, and E. Vauthey, "Exciplex formation in bimolecular photoinduced electron-transfer investigated by ultrafast time-resolved infrared spectroscopy," J. Am. Chem. Soc. **136**, 4066-4074 (2014).

⁴⁹S. Richert, A. Rosspeintner, S. Landgraf, G. Grampp, E. Vauthey, and D. R. Kattnig, "Time-resolved magnetic field effects distinguish loose ion pairs from exciplexes," J. Am. Chem. Soc. **135**, 15144–15152 (2013).

⁵⁰H. M. Hoang, T. B. V. Pham, G. Grampp, and D. R. Kattnig, "Exciplexes versus loose ion pairs: How does the driving force impact the initial product ratio of photoinduced charge separation reactions?" J. Phys. Chem. Lett. 5, 3188-3194 (2014).

⁵¹N. Mataga, T. Asahi, Y. Kanda, T. Okada, and T. Kakitani, "The bell-shaped energy gap dependence of the charge recombination reaction of geminate radical ion pairs produced by fluorescence quenching reaction in acetonitrile solution," Chem. Phys. **127**, 249-261 (1988).

⁵²K. S. Peters and J. Lee, "Picosecond dynamics of stilbene-olefin contact and solvent separated radical ion pairs: Role of electron transfer and radical ion pair diffusion," J. Am. Chem. Soc. **115**, 3643-3646 (1993).

⁵³S. M. Hubig, T. M. Bockman, and J. K. Kochi, "Optimized electron transfer in charge-transfer ion pairs. Pronounced inner-sphere behavior of olefin donors," J. Am. Chem. Soc. **118**, 3842-3851 (1996).

⁵⁴E. Vauthey, "Direct measurements of the charge recombination dynamics of geminate ion pairs formed upon electron transfer quenching at high donor concentration," J. Phys. Chem. A **105**, 340–348 (2001).

⁵⁵I. R. Gould, D. Ege, S. Mattes, and S. Farid, "Return electron transfer within geminate radical ion pair. Observation of the Marcus inverted region," J. Am. Chem. Soc. **109**, 3794-3796 (1987).

⁵⁶E. Vauthey, P. Suppan, and E. Haselbach, "Free energy dependence of the ion yield of photoinduced electron transfer reactions in solution," Helv. Chim. Acta **71**, 93–99 (1988).