

**Biradical Spin Dynamics with Distance-Dependent Exchange Interaction
and Electron Transfer Efficiency**

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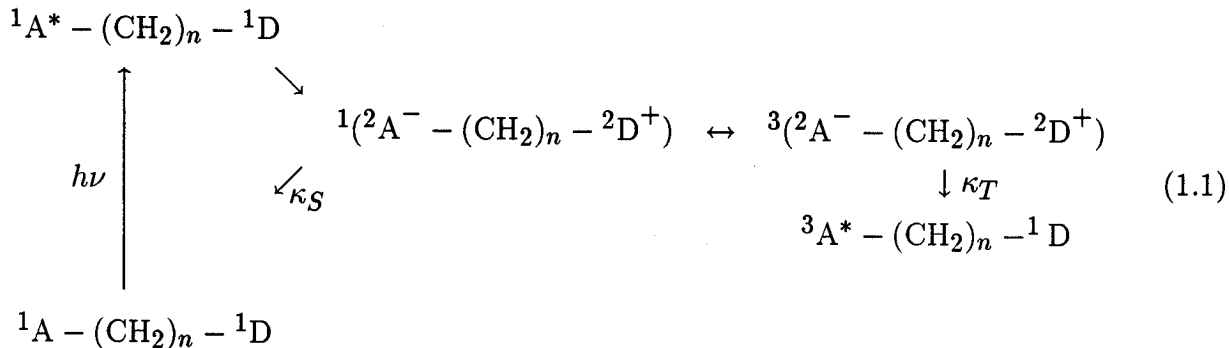
ABSTRACT

The spin dynamics and reaction kinetics of photogenerated zwitterionic biradicals of the type ${}^2\text{A}^- - (\text{CH}_2)_n - {}^2\text{D}^+$ ($n = 8, 9, 10$) are described for a model which assumes the same A-D distance dependence for a "through space" exchange interaction and for the efficiency of electron back-transfer to the singlet ground state ${}^1\text{A} - (\text{CH}_2)_n - {}^1\text{D}$ and to a triplet excited state ${}^3\text{A}^* - (\text{CH}_2)_n - {}^1\text{D}$. The model is independent of the length n of the polymethylene chain and accounts well for the three types of observations on the biradicals: the mono-exponential character of the biradical decay, the life time associated with this decay, and the magnetic field dependence of the yield of the triplet excited state.

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1. Introduction

In this letter we consider a model for electron transfer processes in organic solvents, an electron acceptor molecule ${}^1\text{A}$ (pyrene) linked by an aliphatic chain $(\text{CH}_2)_n$ to an electron donor molecule ${}^1\text{D}$ (dimethylaniline). This system has been investigated recently experimentally¹⁻⁴ as well as theoretically^{4,5-8}. The reactions follow the scheme



The molecules ${}^1\text{A} - (\text{CH}_2)_n - {}^1\text{D}$, dissolved in a polar organic solvent, form after laser excitation of the electron acceptor (${}^1\text{A}$) a zwitterionic biradical in the singlet overall spin state ${}^1({}^2\text{A}^- - (\text{CH}_2)_n - {}^2\text{D}^+)$. Here and in the following the superscripts 1, 2, and 3 refer to electron spin multiplicities, namely, singlet, doublet, and triplet, respectively. Magnetic interactions lead to the formation of the triplet spin pair state ${}^3({}^2\text{A}^- - (\text{CH}_2)_n - {}^2\text{D}^+)$. Electron tunneling between acceptor ${}^2\text{A}^-$ and donor ${}^2\text{D}^+$ moieties induces back-transfer either to the singlet ground state ${}^1\text{A} - (\text{CH}_2)_n - {}^1\text{D}$ or to the triplet excited state ${}^3\text{A}^* - (\text{CH}_2)_n - {}^1\text{D}$. The reaction route depends on the radical pair spin state at the moment of the back-transfer: a singlet biradical state leads to the ground state, a triplet biradical state leads to the triplet excited state. Experimental investigations of this system monitor spectroscopically the biradical state and the triplet excited state ${}^3\text{A}^*$.

The biradical electron transfer system described constitutes an interesting microcavity reaction, since the aliphatic chain confines the diffusion-reaction process of ${}^2\text{A}^-$ and ${}^2\text{D}^+$ to a small volume. This confinement implies also that the distance-dependent electron exchange interaction acting between ${}^2\text{A}^-$ and ${}^2\text{D}^+$ can influence strongly the spin dynamics and, thereby, the reaction process. In fact, previous calculations⁵⁻⁸ showed that the observed magnetic field dependence of the yield of triplet products ${}^3\text{A}^* - (\text{CH}_2)_n - {}^1\text{D}$ can be reproduced under the assumption of a “through space” exchange interaction. These calculations modelled the exchange interaction as exponentially decreasing with increasing distance between ${}^2\text{A}^-$ and ${}^2\text{D}^+$.

In the calculations reported in Refs. 5–8 it had been assumed, however, that the rate constant for back-electron transfer is independent of the separation of the radical moieties ${}^2\text{A}^-$ and ${}^2\text{D}^+$. This assumption is inconsistent with the spatial dependence assumed for the exchange interaction which should exhibit the same spatial dependence as the electron transfer rate. The question arises if the good agreement between theory and observation reported in Refs. 5–8 may have been fortuitous. The purpose of this letter is to present calculations that include the proper distance dependence of the electron transfer rate. We will show, that these calculations describe the observed biradical reaction behaviour actually very well: they reproduce the observed mono-exponential decay of the biradical state, the dependence of the observed biradical life time on the length of the $(\text{CH}_2)_n$ chain as well as the magnetic field dependence of the triplet yield.

The calculations do not have to be calibrated for each length of the polymethylene chain, i.e. separately for $n = 8, 9$, and 10 , but rather a single rate parameter κ_o (preexponential constant, see eq. (2.7)) suffices to obtain a good representation for all three biradicals.

2. Theory

2.1. The Stochastic Liouville Equation

We seek to evaluate the density matrix $\rho(r, t)$ of the electron and nuclear spin states of the biradical system at distance r . Assuming distance-dependent rates $\kappa_S(r)$ and $\kappa_T(r)$ for electron back-transfer the spin density matrix $\rho(r, t)$ of the biradical obeys a generalized stochastic Liouville equation

$$\partial_t \rho(r, t) = (-i\mathbf{H}^{\mathbf{x}}(r) - \mathbf{K}^+(r) + \mathbf{L}^{\mathbf{x}}(r))\rho(r, t). \quad (2.1)$$

The operator $\mathbf{H}^{\mathbf{x}}(r)$ denotes the Liouville operator associated with the Hamiltonian $H(r)$ of a doublet pair, i.e. $\mathbf{H}^{\mathbf{x}}(r)\rho = [H(r), \rho]_-$. The Hamiltonian $H(r)$ has the form

$$\begin{aligned} H(r) &= H_A + H_D + J(r)(Q_T - Q_S) \\ H_i &= \sum_k a_{ik} \vec{I}_{ik} \cdot \vec{S}_i + \vec{B} \cdot \vec{S}_i, \quad i = A, D \\ Q_T &= \frac{3}{4} + \vec{S}_A \cdot \vec{S}_D, \quad Q_S = \frac{1}{4} - \vec{S}_A \cdot \vec{S}_D. \end{aligned} \quad (2.2)$$

We employ the same model of a “through space” exchange interaction as in Ref. 5–8. For details of the notation employed here the reader is referred to these references. The distance

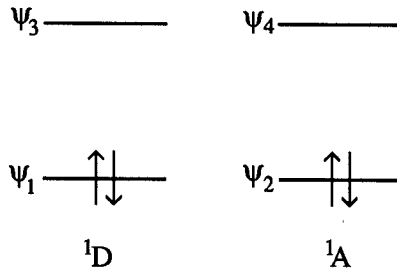


Fig. 1: Schematic diagram of the electronic orbitals ('HOMO' and 'LUMO') of the donor acceptor system employed to obtain eq. (2.4) for the exchange interaction.

dependence assumed for $J(r)$ is^{9,*}

$$J(r) = J_o \exp(-\alpha r); \quad J_o = 9.46 \cdot 10^9 \text{G}; \quad \alpha = 2.136 \text{\AA}^{-1}. \quad (2.3)$$

The damping constant α for the exchange interaction assumed here for flexible biradicals is larger than values of about $\alpha = 1 \text{\AA}^{-1}$ resulting from experimental investigations of exchange interactions in other types of bridged diradicals in Ref. 10–13. The larger α value of 2.136\AA^{-1} used by us is justified by the fact that “through-space” singlet–triplet splitting in an organic solvent is due to superexchange involving disordered solvent molecules. The disorder, due to rotational diffusion, manifests itself on a shorter time scale than the spin pair dynamics, i.e. the solvent–mediated exchange interaction is affected by motional narrowing effects and might reflect the superexchange interaction in the extreme motional narrowing limit. In this limit the interaction is intermediate between a value corresponding to optimal overlap of orbitals between solvent molecules and values corresponding to unfavourable overlaps, i.e. the interaction should exhibit a faster decay than in case of donor acceptor systems with a rigid bridge, or donor acceptor pairs in glasses and proteins.

The exchange interaction between the radical moieties in the molecular system of system Ref. 1–4 should have two major contributions which involve electron transfer between half-filled orbitals ψ_1 and ψ_4 of donor ($^2\text{D}^+$) and acceptor ($^2\text{A}^-$), respectively, and between ψ_1 and the filled orbital ψ_2 of $^2\text{A}^-$. The orbitals are presented in fig. 1 for the ground state $^1\text{D} + ^1\text{A}$. The contributions which arise when the exchange interaction is determined in 2nd and

*We have employed an α value with four digit accuracy to be compatible with Ref. 9.

3rd order perturbation theory¹⁴ are together

$$J(r) = -\frac{V_{14}(r)^2}{\Delta_1(r)} + \frac{V_{12}(r)^2 J_{\text{int}}}{\Delta_2(r)^2} \quad (2.4)$$

In this expression $V_{ij}(r)$ denotes the transfer matrix element between orbitals i and j , J_{int} denotes the exchange matrix element which describes the splitting between singlet and triplet excited states in the acceptor ($J_{\text{int}} = E(^1A^*) - E(^3A^*)$), $\Delta_1(r)$ denotes the energy difference $E(^2D^+ + ^2A^-) - E(^1D + ^1A)$ and $\Delta_2(r)$ denotes the energy difference $E(^2D^+ + ^2A^-) - E(^1D + ^1A^*)$. The distance dependence of $J(r)$ is dominated by the exponential decay (with increasing r) of $V_{ij}^2(r)$, the energy denominators $\Delta_i(r)$ in comparison exhibit only a weak algebraic dependence on r . The simple spatial dependence in eq. (2.3) neglects the r -dependence of Δ_i and assumes identical spatial decays for $V_{14}(r)$ and $V_{12}(r)$. The latter assumption appears to be justified since the spatial dependence of $V_{14}(r)$ and $V_{12}(r)$ is governed by overlap between valence orbitals near the edges of donor and acceptor moieties and, hence, should be approximately the same.

The operator $\mathbf{K}^+(r)$ in eq. (2.1), given by

$$\mathbf{K}^+(r) = \kappa_S(r)Q_S^+ + \kappa_T(r)Q_T^+, \quad (2.5)$$

accounts for the decay of the biradical state. Here the operators Q_i^+ , $i = S, T$ are defined through $Q_i^+ \rho = [Q_i, \rho]_+$. The functions $\kappa_S(r)$ and $\kappa_T(r)$ describe the distance-dependent rate of the electron back-transfer in the singlet and triplet channel, respectively, and will be discussed below.

The operator $\mathbf{L}^{\mathbf{x}}$ in eq. (2.1) accounts for the stochastic motion of the polymethylene chain. In a “mean field” description of the polymer the distribution $q(r)$ of distances r between the unpaired electron spins in the biradical satisfies the Fokker-Planck equation

$$\partial_t q(r, t) = l(r)q(r, t); \quad l(r) = D \partial_r p(r) \partial_r [p(r)]^{-1}. \quad (2.6)$$

$p(r)$ is the equilibrium distribution of r . In this description $\mathbf{L}^{\mathbf{x}}$ is the direct product $\mathbf{L}^{\mathbf{x}} = \mathcal{I} \otimes l(r)$ of the identity Liouville operator \mathcal{I} with the Fokker-Planck operator $l(r)$. The distributions $p(r)$ for the three investigated polymethylene chains, i.e. for $n = 8, 9$, and 10 , as well as the diffusion coefficient D have been given in Ref. 8.

2.2. Distance Dependence of the Electron Transfer Rate

In our previous descriptions of magnetic field-dependent reactions of biradicals we assumed a distance-independent electron transfer efficiency. Recently Busmann et al.⁴ used a distance-dependent electron transfer rate described by a step function, while using an exponentially distance-dependent exchange interaction. We want to argue now that the transfer rate constants for electron back-transfer in the singlet and in the triplet radical pair states $\kappa_S(r)$ and $\kappa_T(r)$ should assume the same distance dependence as the “through-space” exchange interaction discussed above. In fact, the spatial dependencies of the two rates are $\kappa_S(r) \sim V_{14}^2(r)$ and $\kappa_T(r) \sim V_{12}^2(r)$. However, for the same reasons as for the exchange interaction one can assume identical spatial dependencies for $\kappa_S(r)$ and $\kappa_T(r)$. We will express then both transfer rates through

$$\kappa(r) = \kappa_o \exp(-\alpha r) \quad (2.7)$$

where the constant α is identical to the one occurring in eq. (2.3) for the distance dependence of J , i.e. $\alpha = 2.136 \text{ \AA}^{-1}$. The constant κ_o cannot be obtained directly from theoretical considerations. The criterion for the choice of κ_o is the experimentally observed life time of the biradical state, i.e. we have to choose κ_o such, that the observed decay of the biradical state is reproduced. Since the experimental observation shows a mono-exponential decay we have no information about a difference of the electron transfer rates in the singlet and the triplet state, respectively. Therefore, we assume $\kappa_S(r) = \kappa_T(r) = \kappa(r)$.

To determine κ_o we take the trace over the generalized stochastic Liouville equation, i.e. eq. (2.1), for the biradical. This eliminates the spin dynamics described by \mathbf{H}^x and we obtain the equation which governs the time dependence of the concentration $c(r, t)$ of biradicals in a conformation with a distance r between the unpaired electron spins

$$\partial_t c(r, t) = [l(r) - \kappa(r)]c(r, t). \quad (2.8)$$

The total concentration $N(t)$ of biradicals is $N(t) = \int c(r, t) dr$. Since the experimental observation shows a mono-exponential decay of the biradical concentration one expects a mono-exponential decay for $N(t)$. The decay time is then $\kappa_{\text{eff}}^{-1} = \int_0^\infty dt N(t) / N(t=0)$. This time is identical to the first passage time for the reaction-diffusion system governed by (2.8) and is given by¹⁵

$$\kappa_{\text{eff}}^{-1} = \int [l(r) - \kappa(r)]^{-1} c(r, t=0) dr. \quad (2.9)$$

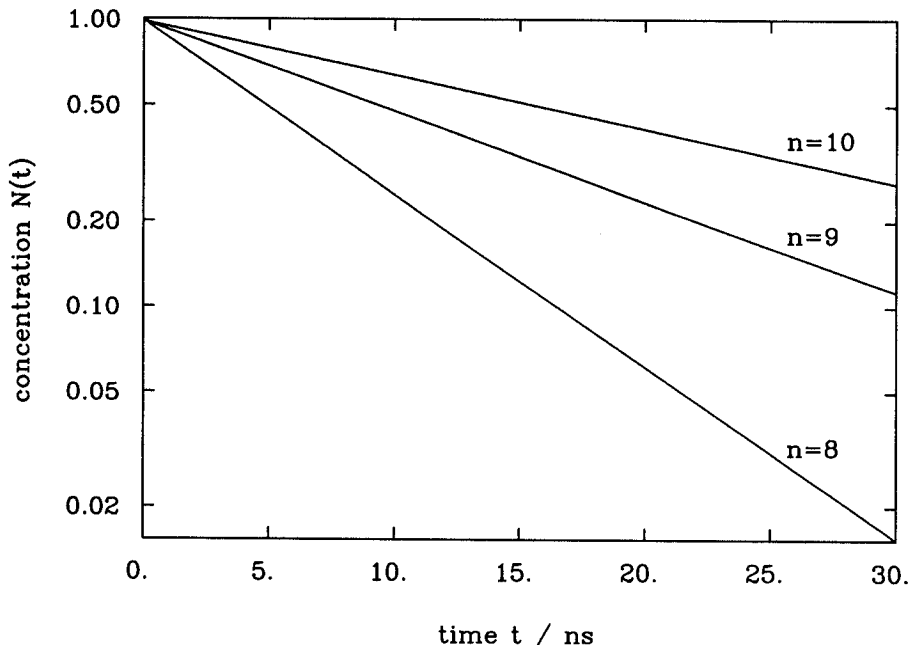


Fig. 2: Time dependence of the biradical concentration $N(t)$ for three lengths $n = 8, 9$, and 10 of the aliphatic chain $(\text{CH}_2)_n$ linking donor and acceptor groups. The solution was obtained by numerical integrating eq. (2.8). The linear decrease of the biradical concentration in this logarithmic plot shows that our calculations reproduce the observed mono-exponential decay.

This expression has to be evaluated numerically. For this purpose one discretizes the distance r between the unpaired electron spins. The Fokker-Planck operator $l(r)$ is then replaced by a master operator \mathbf{l} and $\kappa(r)$ is replaced by a diagonal matrix \mathbf{k} .

3. Results and Discussion

3.1. Time Dependence of the Biradical Decay

Given κ_o and applying eq. (2.9) allows one to determine the effective life times $\tau_{eff,n} = \kappa_{eff,n}^{-1}$ for the three lengths of the polymethylene chain $(\text{CH}_2)_n$ investigated. We have adopted the κ_o value $1.3 \cdot 10^6 \text{ns}^{-1}$ which yields the following satisfactory agreement between calculated and observed life times: (calc.) $\tau_{eff,8} = 7.25 \text{ ns}$, $\tau_{eff,9} = 13.75 \text{ ns}$, $\tau_{eff,10} = 22.75 \text{ ns}$; (obs.) $\tau_{obs,8} = 9 \pm 2 \text{ ns}$, $\tau_{obs,9} = 14.5 \pm 1 \text{ ns}$, $\tau_{obs,10} = 20.5 \pm 0.5 \text{ ns}$.

It is important to note that **only a single** value of κ_o is needed to describe the three biradicals. We want to demonstrate now that our model also reproduces the observed mono-exponential decay of the biradical concentration. For this purpose we solved eq. (2.8) numerically. In fig. 2 the concentration $N(t)$ of biradicals is plotted logarithmically against the

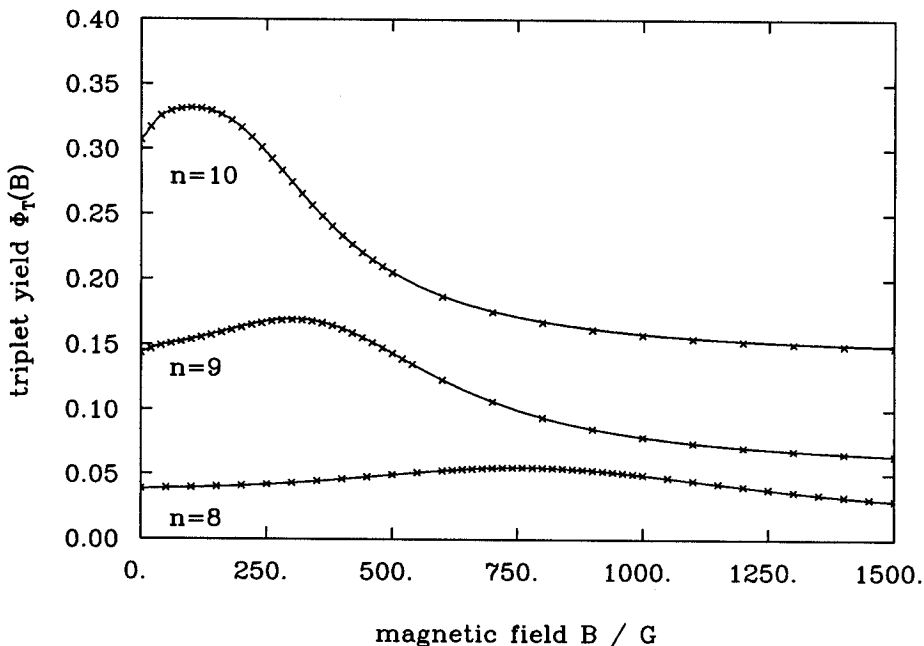


Fig. 3: Comparison of triplet yields $\Phi_T(B)$ calculated with an exponentially decaying electron transfer rate $\kappa(r)$ (—) with triplet yields calculated for distance-independent transfer rates $\kappa_{eff,n}$, $n = 8, 9$, and 10 (\times).

time t . The linear decay in this representation shows that the biradical concentration, in fact, decays mono-exponentially for all three chain lengths.

In the next section we will compare the results for the magnetic field dependence of the triplet yield of the present investigation with the results of our previous investigations which assumed a distance-independent rate constant for back-transfer.

3.2. Field Dependence of the Triplet Yield

The observable which allows to compare theory and experiment is the magnetic field dependence of the triplet yield $\Phi_T(B)$ ^{4,8}. The triplet yield $\Phi_T(B)$ is given by

$$\Phi_T(B) = \int_0^\infty \kappa(r) \text{tr} \left\{ \left[-i\mathbf{H}^x - \mathbf{K}^+ + \mathbf{L}^x \right]^{-1} \rho(r, t = 0) \right\} dr. \quad (3.1)$$

Our solution of this equation followed Ref. 8.

In fig. 3 the results of two calculations of triplet yields are compared. The solid lines (—) represent calculations with the distance-dependent transfer rate $\kappa(r) = \kappa_0 \exp(-\alpha r)$ for the three lengths n of the polymethylene chain, $n = 8, 9$, and 10 , and the crosses (\times) represent calculations with distance-independent transfer rates $\kappa_{eff,n}$, $\kappa_{eff,8} = 7.25$, $\kappa_{eff,9} = 13.75$, and $\kappa_{eff,10} = 22.75$. The triplet yields calculated with the two different models show no differences. This implies that the distance dependence of the electron transfer for the three

biradicals investigated does not affect the triplet yield. Since the results for $\kappa(r) \equiv \kappa_{obs,n}$ agreed well with the observed magnetic field dependence we can conclude that the chosen spatial dependence of the rate constant for the back-transfer of electrons is satisfactory. Further investigations of the field dependence of the triplet yield should not need to invoke a distance-dependent electron transfer rate since this distance dependence appears to affect the kinetics of the system only to a negligible extent.

3.3. Conclusions

For a consistent description of the hyperfine coupling induced reaction kinetics of zwitterionic biradical systems we introduced the same spatial dependence for the rate constant of electron back-transfer and for the exchange interaction. Due to rapid stochastic variations of the distance between donor and acceptor induced by the Brownian motion of the polymethylene chain, the biradical exhibits a mono-exponential decay to products. The effective life time of the biradical state can be reproduced well using a single rate constant parameter for the rate constant of electron back-transfer. The stochastic motion of the polymethylene chain is found to average the decay rates in the various conformations of the biradical to one effective decay rate; the exchange interaction, however, does not appear to be averaged to an effective mean value, but rather a broad distribution of exchange interaction strengths affect the spin dynamics.

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