

LENGTH DEPENDENCE OF THE MAGNETIC FIELD MODULATED TRIPLET YIELD OF PHOTOGENERATED BIRADICALS

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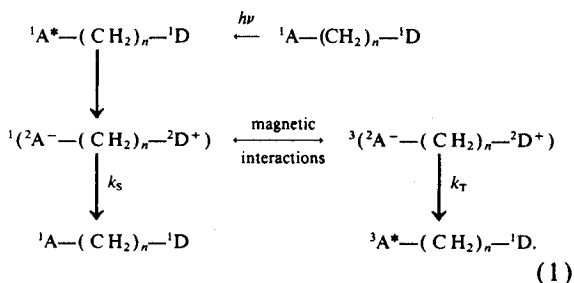
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The magnetic field dependence of the triplet yield of biradicals of the type ${}^2A^+-(CH_2)_n-{}^2D^-$ has been calculated for three different lengths $n=8, 9,$ and 10 of the linking aliphatic chain. The calculations are based on the solution of the stochastic Liouville equation under the assumption of a "through space" exchange interaction and compare well with experimental observations. We show that the field dependence of the triplet yield is governed by the "spectrum of the exchange interaction".

1. Introduction

In a previous paper [1] we have shown, following work by de Kanter et al. [2], that the magnetic field dependence of the triplet yield in biradical photoinduced electron transfer [3,4] can be explained through a stochastic folding motion of the polymethylene chain linking the intermediate radicals. The reaction observed in refs. [3,4] follows the reaction scheme



1A and 1D denote the electron acceptor (pyrene) and donor (dimethylaniline) in their electronic ground state. After excitation by a nanosecond laser flash these molecules transfer an electron and, thereby, become radical ions ${}^2A^+$ and ${}^2D^-$ each carrying an unpaired electron spin. The two electron spins are initially in an overall singlet state ${}^1({}^2A^--(CH_2)_n-{}^2D^+)$. Magnetic perturbations reorient the spins and induce the formation of an overall triplet

state ${}^3({}^2A^--(CH_2)_n-{}^2D^+)$. The electron can return by jumping from ${}^2A^-$ back to ${}^2D^+$. Energetically there are two routes open: the electron jump can either lead to the singlet ground state ${}^1A-(CH_2)_n-{}^1D$ or to the triplet excited state ${}^3A^*-(CH_2)_n-{}^1D$. Which route is taken depends on the instantaneous overall spin state of the radical pair, i.e. electron back-transfer from the ${}^1({}^2A^--(CH_2)_n-{}^2D^+)$ state populates the singlet ground state, back transfer from the ${}^3({}^2A^--(CH_2)_n-{}^2D^+)$ state populates the triplet excited state. The triplet excited state ${}^3A^*$ can be monitored spectroscopically.

An important contribution to the observed magnetic field effect on the triplet yield is due to an exchange interaction between the unpaired electron spins on ${}^2A^+$ and ${}^2D^-$. The origin of this interaction is a matter of dispute: it is either transmitted through the space (solvent) between the radicals or through the polymethylene chain [5]. In any case the interaction should be stochastically modified through the folding motion of the polymethylene chain. The aim of our work [1,6] has been to show that, *no matter what the origin of the exchange interaction, its main effect can be cast into a single spectral line shape function which includes both the range of interaction strengths adopted in the various folding patterns as well as the stochastic folding dynamics*. We have argued, however, that the spectral line shape function which explains the observed magnetic field effects

can be reconciled with "through space" exchange interaction.

The line shape function description is based on the "static ensemble approximation [1,6] for the stochastic quantum system. This approximation strictly holds only for biradical lifetimes shorter than observed. In this Letter we present calculations based on the solution of the stochastic Liouville equation (SLE) which can account for biradical lifetimes consistent with the observations. We want to show that the new description improves the agreement with the experimental data [3,4]; however, the "static ensemble approximation" provides a satisfactory description as well. We conclude, therefore, that an explanation of the exchange mechanism of polymethylene-linked biradicals should focus on the line shape function presented in this Letter.

Similar calculations and further experimental investigations have been completed recently by the Göttingen group [7].

2. Theory

The spin dynamics of the biradical ${}^2A-(CH_2)_n-{}^2D^+$ is described by the stochastic Liouville equation for the spin density matrix $\rho(t)$

$$\partial_t \rho(t) = (-iH^x - k + L)\rho(t) \quad (2)$$

The terms occurring in this equation will be explained below. The density matrix $\rho(t)$ is a function of the electron and nuclear spin states, and of the configuration of the polymethylene chain. H^x is the Liouville operator associated with the Hamiltonian H . Electron back-transfer is described by the reaction constant k , and L accounts for the stochastic motion of the polymethylene chain. The spin Hamiltonian H of the biradical system has the form [8]

$$H = H_1 + H_2 + J(\frac{1}{2} + 2S_1 \cdot S_2),$$

$$H_i = B \cdot S_i + \sum_k a_{ik} I_{ik} \cdot S_i, \quad i = 1, 2.$$

H_i describes the Zeeman interaction of the electron spin S_i with the external magnetic field B , and the hyperfine coupling of the electron spin S_i with the nuclear spins I_{ik} . The constants a_{ik} account for the strength of the hyperfine coupling. For pyrene and DMA the constants are given for example in ref. [1].

The exchange interaction J causes a dependence of the Hamiltonian H on the configuration of the polymethylene chain. In the following we adopt a model of an exchange interaction dependent only on the distance r between the radical ions. This model has been used by de Kanter et al. [2] to explain the magnetic field dependence of biradical CIDNP in the form

$$J(r) = J_0 \exp(-\alpha r),$$

$$J_0 = 9.46 \times 10^9 \text{ G}, \quad \alpha = 2.136 \text{ \AA}^{-1}. \quad (3)$$

Since the polymethylene chain undergoes a folding motion, the distance r is a stochastic variable. The distribution of end-end distances $p(r, t)$ in a "mean field" description satisfies the Fokker-Planck equation [9]

$$\partial_t p(r, t) = L(r) p(r, t),$$

$$L(r) = D \partial_r p_0(r) \partial_r [p_0(r)]^{-1}. \quad (4)$$

D denotes the effective diffusion coefficient. We have used $D = 4 \times 10^{-5} \text{ cm}^2/\text{s}$ in our calculations. This value is smaller than the relative diffusion coefficient $4.53 \times 10^{-5} \text{ cm}^2/\text{s}$ for pyrene and DMA in acetonitrile [10] and is comparable to the diffusion coefficient $5 \times 10^{-5} \text{ cm}^2/\text{s}$ for the restricted diffusion (RD) model of ref. [2]^{#1}. The function $p_0(r)$ is the equilibrium distribution of end-end distances. This distribution is not available from experiments. We have chosen an analytical function

$$p_0(r) = r^2 (r - r_{\max})^2 \exp\{-[(r - r_1)/r_2]^2\} \quad (5)$$

that provides a smooth fit to end-end distributions generated by computer simulation [1]. To model aliphatic chains with 8, 9, and 10 $-CH_2-$ groups we used the parameters r_{\max} , r_1 and r_2 as given in table 1.

3. Solution of the stochastic Liouville equation

The observable reported in refs. [3,4] is the yield $\Phi_T(B)$ of triplet products ${}^3A^*$. This can be obtained from the spin density matrix $\rho(t)$ by the relation

^{#1} The restricted diffusion (RD) model of ref. [2] is a discretization of the Fokker-Planck equation (4).

Table 1

Parameters used in eq. (5) to model the end-end distance distribution $p_0(r)$ for biradicals linked by polymethylene chains of 8, 9, 10 $-CH_2-$ groups

	$n=8$	$n=9$	$n=10$
r_{\max}	10.5	11.5	12.5
r_1	20	25	30
r_2	4	5	6

$$\Phi_T(B) = k \int_0^{\infty} dt \operatorname{tr} [Q_T \rho(t)] . \quad (6)$$

Under the assumption of a distribution of the end-end distance r according to the equilibrium distribution $p_0(r)$ and identical quantum mechanical initial conditions $\rho(t=0)$ at all end-end distances, eqs. (6) and (2) lead to

$$\Phi_T(B) = k \operatorname{tr} \left(Q_T \int dr [k + iH^x(r) - L(r)]^{-1} \times p_0(r) \rho(0) \right) . \quad (7)$$

Since H^x is real symmetric eq. (7) can be reduced to a real form. With the definition

$$\begin{aligned} R_{ijkl} &= H_{ikjl}^x - H_{iklj}^x, & i \leq k \wedge j > l, \\ &= -(H_{ikjl}^x + H_{iklj}^x), & i > k \wedge j < l, \\ &= -H_{ikjl}^x, & i > k \wedge j = l, \end{aligned} \quad (8)$$

eq. (7) assumes the form

$$\Phi_T(B) = k \operatorname{tr} \left(Q_T \int dr [k + R(r) - L(r)]^{-1} \times p_0(r) \rho(0) \right) . \quad (9)$$

To evaluate (9) we discretized the distribution $p_0(r)$ following ref. [2]. Our calculation differed from that in ref. [2] in which $p_0(r)$ was divided in segments of equal probability in that we divided $p_0(r)$ in segments of equal width dr . The discretization transforms the differential operator $L(r)$ into a tridiagonal matrix L' . Eq. (9) then reads

$$\Phi_T(B) = k \operatorname{tr} \{ Q_T \langle 0 | [k + R - L']^{-1} | 0 \rangle \rho(0) \} ,$$

(10) with $|0\rangle$ and $\langle 0|$ being the right and left eigenvectors of L' to the eigenvalue zero. The algorithm employed for the numerical evaluation of (10) was Gaussian elimination for a *block-tridiagonal* matrix [11]. We reduced the dimension of the numerical problem by taking only one nuclear spin at each radical site. The hyperfine coupling constants a_i have been adjusted according to

$$a_i = \left(\frac{4}{3} \sum_k a_{ik} I_{ik} (I_{ik} + 1) \right)^{1/2} , \quad (11)$$

which gives the correct effective coupling [8].

4. Results and discussion

In a previous paper [12] we presented calculated triplet yields for biradical systems ${}^2A^--(CH_2)_n-{}^2D^+$ with $n=8, 9$, and 10, based on the "static ensemble approximation" [6] for the solution of the SLE. This approximation is strictly valid only for short reaction times τ ; consequently we adopted $\tau_{th}=1$ ns in our calculation, which is shorter than the observed lifetimes $10 \leq \tau_{exp} \leq 20$ ns. We found reasonable agreement between the calculated triplet yields and the experimental values. The calculations predicted maxima of the triplet yield at magnetic fields B_{max} which compared well with the corresponding experimental values. However, the relative increase $R_{max} = \Phi_T(B_{max})/\Phi_T(B=0)$ of the field dependence of $\Phi_T(B)$ was not reproduced very accurately for $n=9$ and 10. We attributed this deviation to the difference in the reaction times τ_{exp} and τ_{th} .

With the method described in section 3 we calculated triplet yields using reaction rates k consistent with the experimentally observed rates for electron back-transfer, i.e. $k = \tau_{exp}^{-1}$. In fig. 1 we present the triplet yields $\Phi_T(B)$ for biradical systems ${}^2A^--(CH_2)_n-{}^2D^+$ with $n=8, 9$, and 10. In table 2 we give the experimental and theoretical values of B_{max} , the half-width of the maximum B_{hw} , R_{max} , and R_{∞} defined below.

The results given in table 2 confirm our previous findings that the magnetic field dependence of the triplet yield in biradical electron transfer experiments can be explained by a "through space" ex-

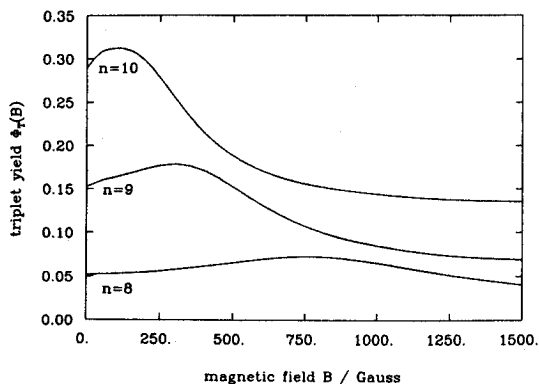


Fig. 1. Calculated magnetic field dependence of the triplet yield $\Phi_T(B)$ for the biradical ${}^2A^--(CH_2)_n-{}^2D^+$: $n=8, 9$, and 10 .

change interaction in conjunction with the stochastic folding motion of the linking polymethylene chain. The calculated values of B_{\max} agree better than our former calculations with the observations. The agreement between observation and calculation is also improved in the quantity R_{\max} for $n=10$ and 9 . The calculations, like the experiments, show an increase in ratio R_{\max} for decreasing chain length. The ratio R_{\max} for biradicals is of the order of 10%, while for a system with a constant exchange interaction corresponding to the position of the maxima, R_{\max} would be several hundred percent. We find also reasonably good agreement in the half-width of the maxima. The half-widths increase in a similar way to the ratio R_{\max} for decreasing chain length. A deviation of the calculated values from observation arises in the ratio R_{∞} defined by $R_{\infty} = \Phi(B=5000 \text{ G})/\Phi(B=0 \text{ G})$. This shortcoming may be due to our simplifying assumption that the reaction rate for electron back-transfer is the same for

the singlet and triplet channel. The experimentally monitored decay of the biradical state could be fitted with a single exponential [4], which seems to argue for our assumption. However, the decay constant shows a magnetic field dependence. This arises if the rates for singlet and triplet recombination differ.

Besides the better agreement with experiment this calculation shows that our approximate description in refs. [1,12] gives essentially correct results. This description is based on the "spectrum of the exchange interaction"

$$I(2j) = (1/\pi) \int_{-\infty}^{\infty} dt \exp(i2jt) \times \left\langle \exp\left(-i \int_0^{\infty} dt' 2J(t')\right) \right\rangle \quad (12a)$$

(which holds for any mechanism for the exchange interaction that results in a stochastic time dependence of J), and describes the system by an evolution operator for the density matrix

$$U^x = \int_{-\infty}^{\infty} dj I(2j) U_0^x(j),$$

where $U_0^x(j)$ is the evolution operator for a system with static exchange interaction j (static ensemble approximation). For the particular exchange mechanism introduced in section 2 the spectrum reads

$$I(2j) = (2/\pi) \text{Re}\langle 0 | [i2(j-\mathbf{J}) - \mathbf{L}]^{-1} | 0 \rangle. \quad (12b)$$

As shown in fig. 2, $I(2j)$ closely correlates with the field dependence of $\Phi_T(B)$. The maxima in $I(2j)$

Table 2
Experimental and theoretical quantities describing the magnetic field dependence of the triplet yield $\Phi_T(B)$. The experimental data are taken from ref. [4]. The values in parentheses for B_{\max}^{th} and R_{\max}^{th} are values from a previous calculation [12] based on the "static ensemble approximation". All values of B are given in G

n	B_{\max}^{exp}	B_{\max}^{th}	$B_{\text{hw}}^{\text{exp}}$	$B_{\text{hw}}^{\text{th}}$	R_{\max}^{exp}	R_{\max}^{th}	R_{∞}^{exp}	R_{∞}^{th}
8	750	760 (730)	510	635	1.33	1.41 (1.30)	0.75	0.47
9	285	300 (300)	230	305	1.29	1.17 (1.10)	0.64	0.39
10	111	110 (70)	90	145	1.06	1.08 (1.01)	0.61	0.45

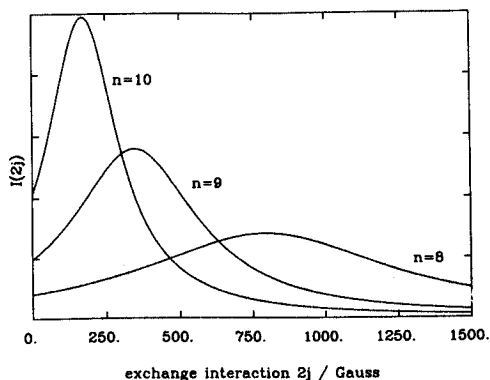


Fig. 2. "Spectrum of the interaction" $I(2j)$ as defined in eqs. (12) for the biradical ${}^2A^--(CH_2)_n-{}^2D^+$: $n=8, 9,$ and 10 .

correspond to the maxima in $\Phi_T(B)$ for the three chain lengths with $2j_{\max} \approx B_{\max}$. The width of the maxima of $I(2j)$ increases in the same way as the width of $\Phi_T(B)$ with decreasing chain length, and the ratio $I(2j_{\max})/I(0)$ increases as R_{\max} with decreasing number of linking $-CH_2-$ groups. These similarities between $I(2j)$ and $\Phi_T(B)$ demonstrate that the "spectrum of the exchange interaction" which is very easy to determine properly relates exchange interaction, the stochastic motion of the polymethylene chain and the observed magnetic field dependence of the triplet yield.

5. Conclusion

By solving the stochastic Liouville equation for the spin motion in a biradical we have confirmed our previous result that the magnetic field dependence of the triplet yield in electron transfer experiments can be reproduced in calculations involving a "through space" exchange interaction modulated by the stochastic folding motion of the linking $-CH_2-$ chain. We obtained better agreement between our calculations and experiment by using realistic biradical lifetimes. For a further investigation of whether the exchange interaction is mediated "through space" or through the aliphatic chain (superexchange) we consider it sufficient to examine the "spectrum of the exchange interaction" as defined in eq. (12). Any mechanism for the exchange interaction which yields the same "spectrum of the exchange interaction" as

those in fig. 2 is consistent with the observed $\Phi_T(B)$. In this respect it would be of particular interest to examine whether different diffusion coefficients and decay parameters (cf. eq. (3)) for through space exchange result in identical spectra for the exchange interaction.

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