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Study of Polymer Dynamics by Magnetic Field Dependent Biradical Reactions

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1. Introduction

The discovery a decade ago [1–3] that reactions involving pairs of radicals often show a pronounced dependence on external magnetic fields in the range of 10 to 1000 Gauss has been exploited in recent years to study the mechanisms of chemical and biochemical reactions and also develop novel chemistry. Examples include the paramagnetic - diamagnetic exchange between dimethylaniline molecules [4,5], electron transfer at the interface of organic crystals [6], the primary electron transfer in the photosynthetic reaction center [3,7,8], radical recombination and polymer growth and other radical reactions in micelles [9], isotope enrichment [10,11] and others [12].

An important aspect of magnetic field dependent reactions between two radicals is the length of time needed between formation and recombination of the reaction intermediates [3,11,13]. Reaction times in the range of 1ns to 1μs or longer are a prerequisite for any influence of magnetic interactions. One possibility to control this time is to place the reaction into micelles which act as a cage that prevents a fast escape of the radicals and, thereby, extend the reaction time [9,11]. Another possibility is to connect two radicals by a polymer chain of suitable length [14–16]. The polymer chain also prevents the escape of the radicals. However, in the latter case the problem arises in how far the folding motion of the polymer chain interferes with the recombination kinetics and the magnetic interactions which contribute to the outcome of this recation. In this contribution we want to study this problem. It will be shown that the dependence of reaction products on an external magnetic field is strongly influenced by the folding motion of the polymer chain. Our study is based on observations in Ref. 17 of magnetic field dependence of the photoinduced electron transfer between electron donor and acceptor groups connected by aliphatic chains $-(CH_2)_n-$ of various length n. Similar observations were made more recently on a recombination reaction involving two radicals connected with the same aliphatic chains [18]. Parts of the following study will be published in more detail in Ref. 19.

2. Theory

The photoinduced electron transfer reaction observed in Ref. 17 (see also Refs. 1-3) follows the reaction scheme:

$$
\begin{array}{ccccc}
{}^1A^* - (CH_2)_n - {}^1D & \xleftarrow{h\nu} & {}^1A - (CH_2)_n - {}^1D & & \\
\downarrow & & & & \\
{}^1({}^2A^- - (CH_2)_n - {}^2D^+) & \longleftarrow & \begin{array}{c}\textit{magnetic}\\ \textit{inter-}\\ \textit{actions}\end{array} & \longrightarrow & {}^3({}^2A^- - (CH_2)_n - {}^2D^+) \\
\downarrow \tau_o & & & & \downarrow \tau_o \\
{}^1A - (CH_2)_n - {}^1D & & & & {}^3A^* - (CH_2)_n - {}^1D
\end{array}
\qquad (1)
$$

${}^1A$ and ${}^1D$ denote the electron acceptor and donor in their electronic ground state. After excitation by a nanosecond laser flash these molecules transfer an electron and, thereby, become radical ions ${}^2A^+$ and ${}^2D^-$, the index 2 indicates that the ions each posses a magnetic moment due to an unpaired electron spin. The two electron spins are initially in an overall singlet state ${}^1({}^2A^- - (CH_2)_n - {}^2D^+)$, i.e. loosely spoken 'antiparallel'. Magnetic perturbations reorient the electron spins and induce the formation of an overall triplet state ${}^3({}^2A^- - (CH_2)_n - {}^2D^+)$, i.e. of a 'parallel' state. 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 momentaneous 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. This observation yields then information about the reorientation of the unpaired electron spins of the ${}^2A^- - (CH_2)_n - {}^2D^+$ radical ion pair.

The motion of the unpaired electron spins is governed by the magnetic interactions collected in the Hamiltonian [1,3,19]

$$
\begin{aligned}
H[J(r)] &= H_1 + H_2 + J(r)[\tfrac{1}{2} + 2\vec{S}_1 \cdot \vec{S}_2] \quad , \\
H_i &= \vec{B} \cdot \vec{S}_i + \textstyle\sum_k a_{ik} \vec{I}_{ik} \vec{S}_i \qquad i = 1,2 \quad .
\end{aligned}
\qquad (2)
$$

H_i describes the interaction of the electron spin S_i of the radical ion ${}^2A^-$ (i=1) or ${}^2D^+$ (i=2) with the external magnetic field B (Zeeman interaction) and with the nuclear spins I_{ik} (hyperfine coupling) where k numbers the different nuclei of either of the radical ions. The constants a_{ik} account for the strengths of the hyperfine coupling, the values for the molecules pyrene (A) and dimethylaniline (D) are provided, for example in Refs. 13, 19.

J(r) in (2) describes the exchange interaction between the two unpaired electron spins. The strength of the exchange interaction depends on the distance r between the radical ions. The

following distance dependence has been suggested [16]

$$
J(r) = J_o exp(-\alpha r), \qquad J_o = 9.46 \cdot 10^9 \text{Gauss}, \qquad \alpha = 2.136 \text{Å}^{-1}. \qquad (3)
$$

The distance dependence of the exchange interaction couples the electron spin motion to the folding motion of the aliphatic chain which connects donor and acceptor groups. The folding of the chain leads to a continuous change of the distance r between the chain ends. The resulting stochastic variations dr of r are

$$
dr = D\, \partial_r ln[p_o(r)]\, dt + \sqrt{D}\, dW_t. \qquad (4)
$$

In this stochastic differential equation dW_t describes Gausian white noise. The function $p_o(r)$ is the equilibrium distribution for the end-end distances r. This function is not available from observation. We have generated $p_o(r)$ by means of a molecular dynamics calculation [20]. End-end distances for chains with 9 and 10 aliphatic groups are presented in Fig. 1. The distributions show that r varies between 6Å and 12Å. As a result of the distance dependence (3) the exchange interaction varies stochastically between 10^4 Gauss and 10^{-2} Gauss, i.e. varies over several orders of magnitude.

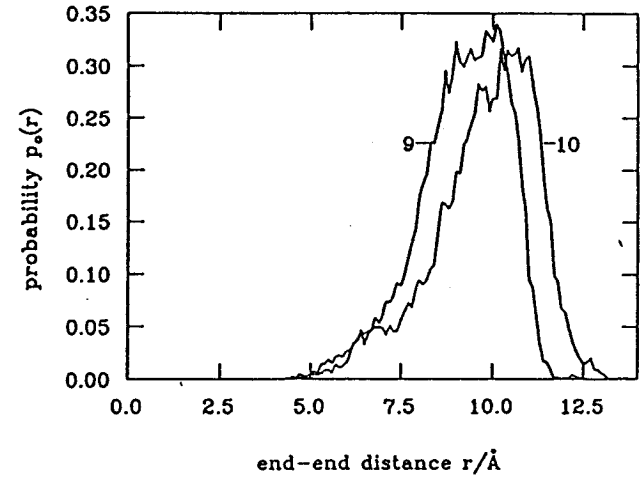


Figure 1. Distribution of end-end distances for the polymers $CH_3-(CH_2)_n-CH_3$ resulting from a molecular dynamics simulation. The hydrogen atoms in this compound were not explicitly described but only included through an increase of the van der Waals radii of the carbon atoms. These atoms were subject to random forces and friction. For actual calculations we have replaced these distributions by smoothed functions.

Since the exchange interaction J in the spin Hamiltonian (2) is a strongly varying stochastic quantity the unpaired electron spins of ${}^2A^- - (CH_2)_n - {}^2D^+$ constitute a stochastic quantum system. A proper description involves the simulation of the time dependence of r(t) at discrete time steps $t = \Delta t, 2\Delta t, \ldots$ by means of (4), the determination of $J(n\Delta t)$ for each time

step according to (3), the evaluation of the propagation operator $exp\{-iH[(n\Delta t)\Delta t]\}$ for the time interval $[n\Delta t, (n+1)\Delta t]$, and finally the average $< \ldots >$ of the resulting time ordered propagation operator [21, 22] over many histories of r(t): [19]

$$U(N\Delta t) = < exp\{-iH[J(N\Delta t)]\Delta t\} exp\{-iH[J((N-1)\Delta t)]\Delta t\} \ldots \quad \text{N factors} > . \tag{5}$$

Obviously the calculation of U(t) is extremely cumbersome and an alternativ theory is desirable.

Once the propagator U(t) is available the probability $p_T(t, B)$ to find the chained radical ion pair ${}^2A^- - (CH_2)_n - {}^2D^+$ in a triplet state for an external magnetic field B can be calculated

$$p_T(t, B) = (1/Z) Tr[Q_T U(t) Q_S] \quad . \tag{6}$$

Here Z is the number of nuclear spin states and Q_T (Q_S) is the projection operator onto the triplet (singlet) electron spin states. The yield of triplet products ${}^3A^* - (CH_2)_n - {}^1D$ is then

$$\phi_T(B) = \int_0^\infty dt\, p_T(t, B)\, exp(-t/\tau_o) \tag{7}$$

where τ_o^{-1} is the reaction rate constant for reactions as given in the scheme (1). For details see the Ref. 19. We have carried out the corresponding calculations for different realizations of stochastic exchange interactions. However, we have also succeeded to develop a simpler description of the electron spin motion with a stochastic exchange interaction. This description is both more practical as well as yields more insight into the magnetic field dependence observed for chained radical ion pairs.

3. Approximate Description

The stochastic exchange interaction enters the dynamics of the unpaired electron spins in a simple manner: in a proper basis it adds only terms to the diagonal of the spin Hamiltonian (2) with values $+J[r(t)]$, 0 and $-J[r(t)]$. The effect of the exchange interaction is to seperate the triplet (electron - nuclear spin) states from the singlet (electron - nuclear spin) states by $2J[r(t)]$. One expects that the main effect of the stochastic exchange interaction is that of a two state system representing the manifold of singlet and triplet states, the energy seperation $\Delta E = 2J[r(t)]$ between which is fluctuating.

A stochastic two level system can be probed by a time-dependent perturbation which contributes to the off diagonal elements of the respective Hamiltonian. The resulting system is described by the socalled spectral line shape function which predicts the frequency dependence of transitions between level 1 and level 2. The spectral line shape function can also be interpreted as the distribution of energy differences between the two levels. In the electron - nuclear spin system singlet → triplet transitions are induced by the hyperfine coupling which contributes the off-diagonal elements of (2) in the proper representation. One might assume that the spectral

line shape function q(j) corresponding to the stochastic exchange interaction, which according to Kubo [23] is calculated

$$q(j) = (1/\pi) Re < \{i[2j - 2J(r)] - L(r)\}^{-1} > \quad , \tag{8}$$

can describe the effective separation of electron spin singlet and triplet levels. This assumption implies that the stochastic quantum system with time-dependent Hamiltonian H[J(t)] behaves similarly to an ensemble of quantum systems with time-independent Hamiltonians H(j), the effective exchange interactions being distributed according to q(j). The respective spin system is described by the operator

$$U(t) \simeq \int_{-\infty}^{+\infty} dj\, q(j)\, exp[-iH(j)t] \quad . \tag{9}$$

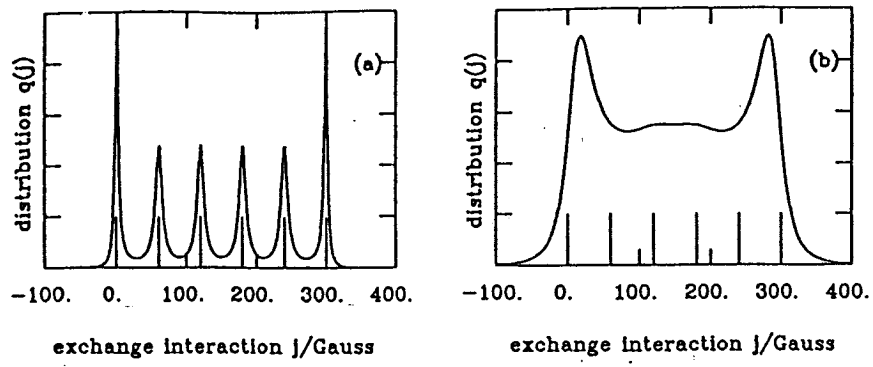
4. An Example

Before we apply this approxiation to the polymer system ${}^2A^- - (CH_2)_n - {}^2D^+$ we like to demonstrate its validity for a simple example. This example serves also as an illustration of the frequency dependent distribution function q(j) which plays a central role in the analysis of the observed magnetic field dependence of the reaction (1). We envision a system in which the exchange interaction can assume only six discrete values J_i: 0, 60, 120, 180, 240 and 300 Gauss; the system is supposed to undergo first order transitions between the realizations J_i governed by a simple rate constant τ^{-1}.

Figure 2 presents the resulting spectral line shape function q(j) for three different rate constants τ^{-1}: 10^{-2}, 1, 10^2 ns^{-1}. For slow jumps betwen the J_i values q(j) exhibits six peaks centered around the values J_i, $i = 1, \ldots, 6$. For fast jumps q(j) peaks around the average J-value $< J >= (1/6) \sum_i J_i$. For intermediate jump rates the distribution q(j) is smeared out over the whole range of J_i values. We have described the triplet yield resulting from such system in two ways: (I) we simulated the random jumps between the six states with different J_i-values by an algorithm which replaced (4); we have then determined the propagator (5) and evaluated (6), (7). (II) we have applied the approximation (8), (9) with q(j) as in Fig. 2c.

Figure 3 compares the result of the two calculations. The close comparision between the triplet yields $\phi_T(B)$ evaluated by means of a simulation and the approximation (8), (9) demonstrates the validity of the latter. However, we like to point out that the approximation (8), (9) is accurate only for fast reactions. For slow reactions, e.g. reaction times $\tau_o \geq 10$ ns, the approximation predicts too small values of $\phi_T(B)$, but describes the relative magnetic field dependence rather well. This is demonstrated in Fig. 4. In Ref. 19 we have shown that the approximation (8), (9) holds also for the case of polymer folding as described by the stochastic diffential equation (4).

5a



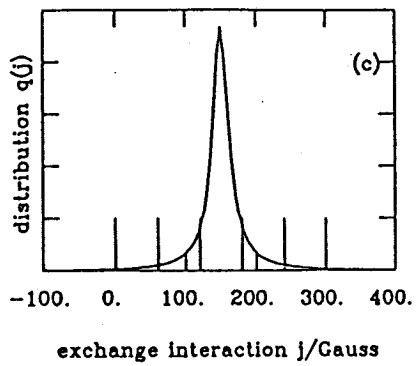


Figure 2. Disribution of singlet - triplet energy differences 2j as given by the function q(j) of (8). The sample system can exist in six different states i to which correspond six different exchange interactions: 0, 60, 120, 180, 240 and 300 Gauss. Three different first order transfer rate constants τ^{-1} had been assumed: (a) 10^{-2} ns^{-1}; (b) 1 ns^{-1}; (c) 10^{-2} ns^{-1}.

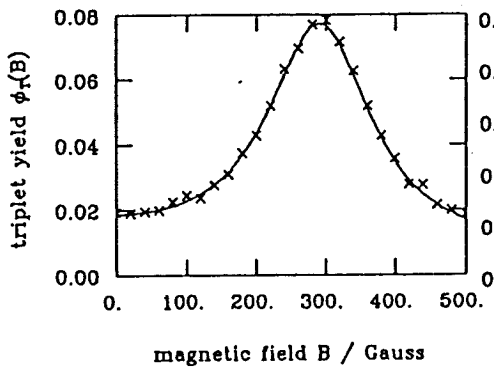


Figure 3. Magnetic field dependence of the triplet yield $\phi_T(B)$ for the stochastic quantum system of Fig. 2 evaluated by simulation (x x x) and evaluated by the approximation involving (8) and (9) (—)

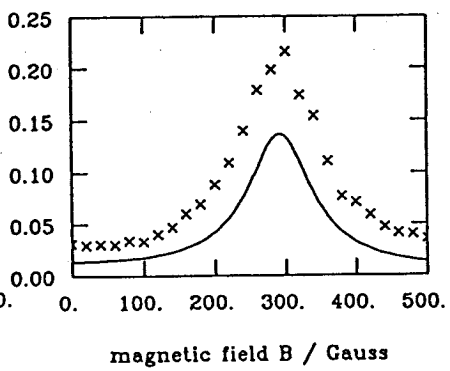


Figure 4. Demonstration of the error connected with the approximation (8), (9): the diagram shows the magnetic field dependence of the triplet yield $\phi_T(B)$ as evaluated by a simulation (x x x) and by the approximation (—) for a long reaction time, i.e. τ_o = 10ns

5. Comparison between Theory and Experiment

In Fig. 5 we present the distribution q(j) for the biradical system for the case of slow, intermediate and fast folding described by the diffusion coefficients D = $4 \cdot 10^{-6}$, $4 \cdot 10^{-5}$, and $4 \cdot 10^{-4}$ $cm^2 s^{-1}$, respectively. The different distributions show that the folding dynamics with increasing D shifts the spectrum of exchange interactions from small values centered around J = 50 Gauss to intermediate values centered around 200 Gauss and further to large values centered around 400 Gauss. One expects that concomitantly the magnetic field dependence of the triplet yield $\phi_T(B)$ shows a resonance maximum corresponding to the crossing of the S and T_{-1} levels which shifts to larger magnetic field values with increasing D.

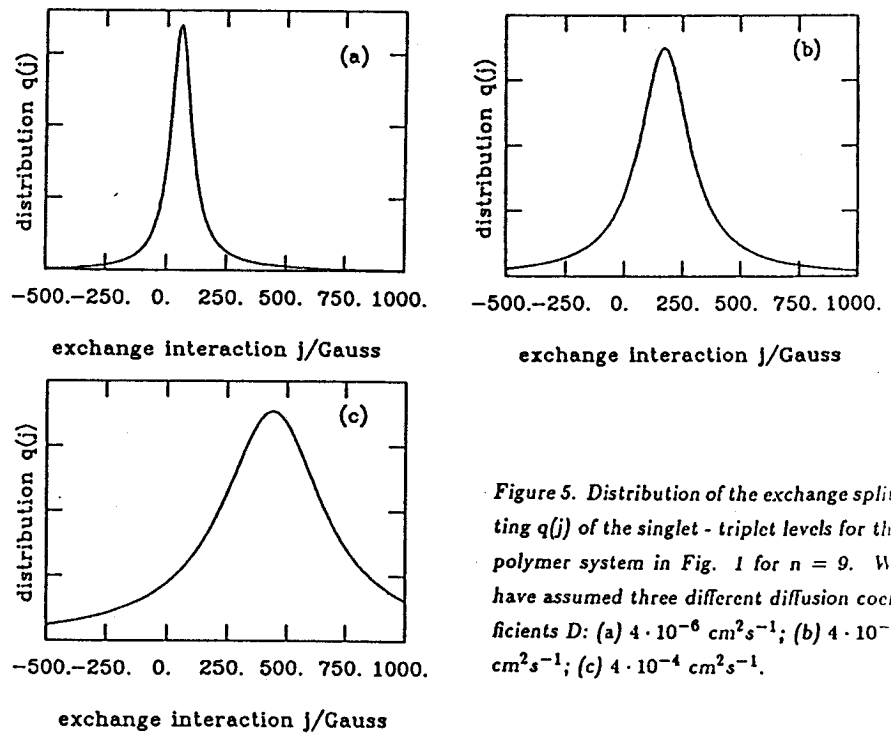


Figure 5. Distribution of the exchange splitting q(j) of the singlet - triplet levels for the polymer system in Fig. 1 for n = 9. We have assumed three different diffusion coefficients D: (a) $4 \cdot 10^{-6}$ $cm^2 s^{-1}$; (b) $4 \cdot 10^{-5}$ $cm^2 s^{-1}$; (c) $4 \cdot 10^{-4}$ $cm^2 s^{-1}$.

A value of the diffusion coefficient of $4 \cdot 10^{-5}$ $cm^2 s^{-1}$ is most reasonable for an aliphatic chain with a pyrene (A) and a dimethylaniline (D) end group. This value is somewhat smaller than the sum of the diffusion coefficients for free end groups [13], the difference accounting for the viscous drag due to the aliphatic chain. In Fig. 6 we present the corresponding magnetic field dependence predicted for the triplet yield $\phi_T(B)$ for biradical systems $^2A^- - (CH_2)_n - {}^2D^+$

for n = 8, 9, 10. Our predictions are in reasonable agreement with the observations of Ref. 17. For n = 10 the calculations predict a maximum at B = 730 Gauss, the increase measuring 30 percent of the zero field value. The observed characteristics are 750 Gauss and 35 percent. The corresponding values for n = 9 are (theoretical) 300 Gauss, 10 percent and (observed) 285 Gauss and 25 percent. For n = 8 we predict a maximum at 70 Gauss and 1 percent increase whereas the observations are 111 Gauss and 5 percent. The deviations between theory and experiment most likely stem from the difference of the reaction times in the calculations (τ_o = 1 ns) and the observations (τ_o > 10 ns) [24], and from errors due to the simplification that equal reaction rates for singlet and triplet recombination had been assumed.

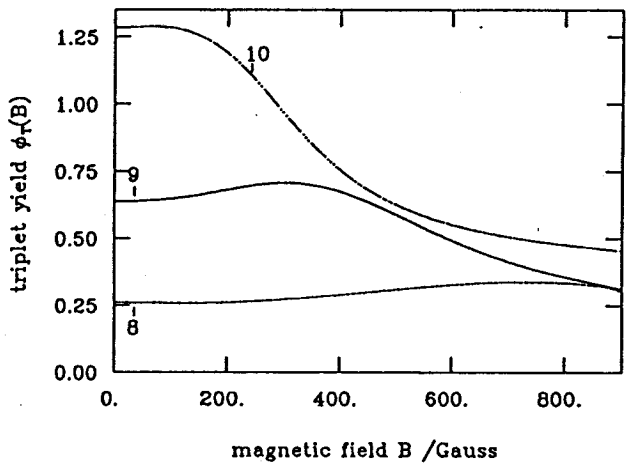


Figure 6. Magnetic field dependence of the triplet yield $\phi_T(B)$ predicted for the biradical system $^2A^- - (CH_2)_n - {}^2D^+$: (a) n = 8; n = 9; n = 10.

The analysis of the experiments in Ref. 17 shows that the spin pair dynamics of polymeric biradicals is influenced by a stochastic folding motion. This folding motion explores the exchange interaction J(r) between the radical ends of the polymer. The observable, the magnetic field dependent triplet yield $\phi_T(B)$ is very sensitive to the strength and the distance dependence of the exchange interaction. The analysis of observations as in Refs. 17, 18 should provide information on the exchange interaction mediated by organic solvents. This information is of great importance for an understanding of organic electron conduction, e.g. in photosynthesis. We hope that the investigations of Refs. 17, 18 will be extended to cover a wider range of organic solvents in order to learn in how far the distance dependence of the exchange interaction as described by (3) depends on the electronic properties of solvents., e.g. their reduction and oxydation energies.

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