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Influence of Dipolar Interactions on Radical Pair Recombination Reactions Subject to Weak Magnetic Fields

Anthony R. O'Dea,[†] Ailsa F. Curtis,[†] Nicholas J. B. Green,[‡] Christiane R. Timmel,[†] and P. J. Hore*[,†]

Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory,
South Parks Road, Oxford, OX1 3QZ, U.K., and Department of Chemistry, Kings College, London,
Strand, London WC2R 2LS, U.K.

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Monte Carlo simulations of the effects of weak magnetic fields on the recombination of interacting radical pairs undergoing free diffusion in solution have been performed, with the aim of determining the influence on the low field effect of the magnetic dipolar coupling between the radicals. The suppression of singlet−triplet interconversion in the radical pair by the dipolar interaction is found to be pronounced at magnetic field strengths comparable to the hyperfine interactions in the radicals, to the extent that the low field effect is completely abolished. The averaging of the dipolar coupling by the translational diffusion of the radicals around one another is relatively efficient in the presence of strong magnetic fields but becomes ineffective in weak applied fields where the strength of the dipolar interaction is independent of the orientation of the inter-radical vector. Low field effects are only likely to be observed if the motion of the radical pair is restricted in some way so as to increase the likelihood that, having separated to the large distance required for the dipolar interaction to have a negligible effect, the radicals subsequently encounter and have the opportunity to recombine.

Introduction

It has been known for some time that magnetic fields of less than 1 mT can influence the rates and yields of radical pair reactions.[1−7] Although the origin and properties of the chemical effects of stronger magnetic fields (≥10 mT) are well characterized both experimentally and theoretically,[8−10] many details of the so-called low field effect (LFE) have yet to be elucidated. The need to understand more thoroughly how magnetic fields that are weaker than the intrinsic magnetic interactions in free radicals can nevertheless affect their reactivity has three main origins. First, magnetic field effects (MFEs) have proven to be powerful sources of information on the chemistry, kinetics, dynamics, and spin relaxation of transient radicals, and LFEs have the potential to give information not available from experiments at higher fields. Second, the LFE has been discussed in the context of putative biological effects of nonionizing electromagnetic radiation,[4] an area that seems to be in need of a physically plausible mechanism to guide experiments aimed at understanding the biochemical origins of any genuine MFE. Third, there is a proposal,[11−15] which has recently received experimental support,[16] that the mechanism by which birds detect the Earth's magnetic field (∼50 μT) as a navigational aid may rely on a magnetic field-sensitive radical pair reaction as the primary magnetoreceptor. For all these reasons, it is of interest to determine the conditions under which sizable LFEs can be expected and in particular to understand the role played by intra- and inter-radical spin interactions and their interplay with the diffusional dynamics of reacting radical pairs.

Radical pair reactions respond to applied magnetic fields because their chemistry is controlled by the magnetic interactions of the two unpaired electron spins, one on each radical. Chemical reactions in solution create radical pairs in spin-correlated states, either singlet (antiparallel electron spins) or triplet (parallel spins) according to the spin multiplicity of the precursor molecules. Rapid recombination of the geminate radical pair to form diamagnetic products usually only occurs via the singlet state (a consequence of the Pauli principle), whereas pairs in a triplet state tend to escape from the solvent cage, diffuse apart and undergo different reactions on a slower time scale. The crucial factor underlying the MFE is that singlet and triplet states are coherently interconverted by the various magnetic and spin interactions experienced by the two electrons, in particular the hyperfine couplings to magnetic nuclei and Zeeman interactions with external magnetic fields. An applied field affects the yields of reaction products by modulating the singlet−triplet interconversion process and so altering the competition between recombination of singlet pairs and escape of triplet pairs.

The dependence of the LFE on the number, magnitude, and distribution of electron−nuclear hyperfine couplings in the two radicals that constitute the spin-correlated radical pair has been studied in some detail.[6,17] In the context of the LFE, much less work has been done on the effects of the electron−electron spin−spin interactions and their modulation by the relative translational motion of the radicals in solution. The general features of the MFE on a static radical pair with a fixed radical−radical separation, in the absence of radical−radical interactions, can be stated as follows. For a radical pair formed initially in a singlet state and able to recombine only from the singlet state, the LFE, if present, is seen as a fall in the recombination yield when the field is increased from zero, followed by a more gradual rise that levels out when the field is much stronger than

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* Author for correspondence. Fax: +44 1865 275410. E-mail: peter.hore@chem.ox.ac.uk.
[†] University of Oxford.
[‡] Kings College.

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the root-mean-square hyperfine interaction.[6] The minimum recombination probability occurs at a magnetic field strength somewhat smaller than the average hyperfine coupling. The whole magnetic field effect, including the LFE, has the opposite phase if the radical pair is formed in a triplet state. The LFE owes it existence to *degenerate* zero-field states of the radical pair spin system, which are no longer degenerate in the presence of a weak magnetic field. Because the exchange interaction J between the two electron spins removes some or all of the degeneracies that exist in zero field, one might expect the LFE to be destroyed or significantly attenuated for electron Zeeman interactions ($g\mu_B B/\hbar$) weaker than J (g is the g-value of the radical and B is the strength of the applied magnetic field).[6]

For freely diffusing radicals in solution, however, the steep decay of the exchange interaction with increasing radical−radical separation R becomes important. Geminate radical pairs are normally formed in solution, e.g., by photoinduced bimolecular electron or hydrogen atom transfer, at a separation (≤ 1 nm) where $J(R) \gg g\mu_B B/\hbar$ such that the Zeeman interaction is ineffectual for singlet−triplet interconversion. However, in nonviscous solvents, the radicals are able to diffuse apart rapidly to a separation at which $J(R) \leq g\mu_B B/\hbar$ allowing the Zeeman interaction to influence the interconversion of the singlet and triplet states of the pair. If the radicals subsequently diffuse back into contact after a period of spin evolution in this exchange-free region beyond ~1 nm they once again experience a strong exchange interaction, but by then the weak field has had its effect on the wave function of the radical pair, and all the exchange does is prevent further spin evolution. It can therefore be anticipated that $J(R)$ should not affect the LFE too much provided the radicals have a reasonable probability of first separating to a point at which $J(R)$ is small and then returning to allow recombination of singlet pairs to occur.[6]

Qualitatively similar, but quantitatively different effects can be anticipated for the magnetic dipole−dipole interaction between the two electron spins, arising out of the different strength and range of the dipolar coupling and its dependence on the orientation of the radical pair with respect to the magnetic field direction. The influence of inter-radical dipolar interactions on the spin evolution of radical pairs is customarily assumed to be negligible. To the best of our knowledge, only two detailed theoretical studies have been published and both were focused on the electron spin polarization observed at high fields in time-resolved electron paramagnetic resonance spectra.[18,19] Here, we present the results of a Monte Carlo simulation study of the effects of weak magnetic fields on the recombination of interacting radical pairs undergoing free diffusion in solution, with the aim of determining how dipolar couplings between the radicals affect the magnitude of the LFE.

Methods

Finite difference techniques have been used extensively to calculate the spin dynamics of diffusing radical pairs using the stochastic Liouville equation to describe the spin and motional dynamics.[20,21] Although probably the method of choice when all interactions are isotropic, this approach becomes less attractive in the presence of anisotropy[19,22] because it becomes necessary to include a full three-dimensional description of the diffusive motion. Consequently, we have adopted the Monte Carlo simulation approach described by Green and colleagues.[23−25] The diffusion of each radical is modeled as a free diffusion in a continuous three-dimensional space, sampled with discrete time steps, in which the three-dimensional particle displacement in a jump is taken from a spherical Gaussian distribution with mean zero and standard deviation $\sqrt{2D_S\delta t}$, where δt is the time-step. Both radicals have been taken to have the same diffusion coefficient D_S, although this is not necessary, because only the relative diffusion of the pair is relevant. The spin evolution of the radical pair wave function $\Psi(t)$ at the end of each time-step is calculated as

$$\Psi(t + \delta t) = \exp[-\mathrm{i}\hat{H}(t)\delta t]\Psi(t) \tag{1}$$

assuming δt is small enough that the spin Hamiltonian $\hat{H}(t)$ can be regarded as time-independent during the interval $t \rightarrow t + \delta t$. The propagator in this expression is calculated by numerical diagonalization of $\hat{H}(t)$ at the beginning of each time step. At each step the probability of an encounter is calculated, conditional on the simulated pair separation distance at the start and the end of the time-step. This method, the Bessel bridge,[23] has the virtue of removing all discretisation errors from the encounter probability [N. J. B. Green and S. M. Pimblott, unpublished work].

When the radicals encounter one another (at $R = R^*$) during their random walk, they are allowed to recombine with a probability equal to the square modulus of the singlet character of $\Psi(t)$ at the time of the encounter. Following an unreactive (triplet) encounter the wave function of the pair is set equal to the projection of $\Psi(t)$ on the triplet subspace. Thus the recombination of singlet pairs is treated as diffusion controlled, whereas triplet pairs are totally unreactive. Acceptable statistics for the ultimate singlet recombination yield Φ_S were obtained by calculating 40,000 diffusive trajectories, for $0 \leq t \leq 400$ ns.

Distance-dependent time steps were used to accelerate the simulation. Because of the use of the Bessel bridge encounter probability, which is exact for all step sizes, the time step only needs to be sufficiently small that (i) the spin Hamiltonian can be assumed constant throughout the step (angular diffusion) and (ii) there should be no significant possibility of an unreactive encounter followed by spin evolution and a subsequent reaction all within the same time-step. The minimum time step used (at short separations) was 10 ps, and the maximum time step permitted was 100 ps. In between, the time step was calculated such that there was a probability of 0.95 that the relative change in the interparticle distance was less than 10%.

To test the simulation code (in the absence of inter-radical interactions), and to assess how closely the recombination yield has approached its asymptotic limit in 400 ns, exact solutions of the stochastic Liouville equation were obtained for comparison. The method used [N. J. B. Green, unpublished work] is similar to the approximate method described by Hansen and Pedersen,[26] except that it is not a steady-state method but gives the full Laplace transform of the time-dependent density matrix, it permits the pairs to be formed at an arbitrary initial separation, rather than at the encounter distance, and it does not make the approximation that some of the off-diagonal density matrix elements are zero at the encounter distance, thus retaining the coherence of the triplet states in an unreactive encounter.

Monte Carlo calculations were performed for a one-nucleus radical pair in which one of the radicals carries a single spin-$^1/_2$ nucleus. The spin Hamiltonian comprised terms for the isotropic Zeeman interactions of the two electrons spins, an isotropic electron−nuclear hyperfine interaction, and electron−

TABLE 1: Default Values of Parameters Used in the Monte Carlo Simulations

a	g	R_0	R^*	θ_0	J_0	β	D_S
1 mT	2.0020	1 nm	0.5 nm	0	16 T	21.4 nm^{-1}	10^{-10} m^2 s^{-1}

electron exchange and dipolar interactions (in angular frequency units):

$$\hat{H} = g\mu_B B_0(\hat{S}_{Az} + \hat{S}_{Bz}) + a\hat{I}\cdot\hat{S} - J(R)\left(\frac{1}{2} + 2\hat{S}_A\cdot\hat{S}_B\right) + \hat{H}_D(R,\Omega) \quad (2)$$

where R is the radical−radical distance, Ω specifies the orientation of the radical pair, and the magnetic field is along the z-axis. The other quantities have their customary meanings. As usual,[20,27] the exchange interaction is assumed to depend exponentially on R:

$$J(R) = J_0 \exp(-\beta[R - R^*]) \quad (3)$$

where R^* is the encounter distance and β is a range parameter. The final term in eq 2 is the usual dipolar coupling Hamiltonian:[28]

$$\hat{H}_D(R,\Omega) = \frac{\mu_0}{4\pi}\gamma_e^2\hbar\left[\frac{\hat{S}_A.\hat{S}_B}{R^3} - 3\frac{(\hat{S}_A\cdot\mathbf{R})(\hat{S}_B\cdot\mathbf{R})}{R^5}\right] \quad (4)$$

A modest improvement in the speed of the calculation was obtained by assuming the exchange and dipolar interactions to be negligible for $R > 5$ nm.

In the following, it will be convenient to use the customary dipolar coupling parameter $D(R)$:

$$D(R) = -\frac{3}{2}\frac{\mu_0}{4\pi}\frac{\gamma_e^2\hbar}{R^3} \quad (5)$$

The spin evolution arising from the nuclear Zeeman interaction, the difference between the two Zeeman interactions (the "Δg mechanism"), and the anisotropic parts of g tensors and hyperfine interactions is considered negligible for the rapidly tumbling radicals and low field strengths ($B < 1$ mT) considered. These terms were not included in the spin Hamiltonian.

The initial condition for the radical pair was taken to be a singlet state at $R = R_0 > R^*$, with equal probabilities of the $m_I = \pm{}^1/_2$ nuclear spin configurations. The initial orientation of the pair, which is in principle important when the dipolar coupling is included in the calculation, is given by θ_0, the angle between the radical−radical vector and the z-axis. (In reality, all values of cos θ_0 are equally likely for an isotropic initial distribution.) Unless otherwise stated, the default values given in Table 1 were used for the various parameters. The values for J_0 and β were taken from a study of acyl-ketyl biradicals[29] and are typical for radical pairs in solution. The distance dependence of $J(R)$ and $D(R)$ used in the simulations is shown in Figure 1.

Results

The calculated magnetic field effect on the singlet recombination yield Φ_S at $t = 400$ ns for $0 \leq B \leq 10$ mT is shown in Figure 2 in the presence and absence of the exchange and dipolar interactions. No significant dependence on θ_0 was found when the dipolar interaction is present, and none was expected or found in its absence (not shown). Evidently the translational motion of the radicals around one another is rapid enough that the direction of the interparticle vector is randomized on the time scale of the spin evolution. Each of the four traces in Figure 2 shows the MFE averaged over three initial orientations of the radical pair with respect to the field direction. That the values of Φ_S are somewhat below 0.5, can easily be understood. If there were no singlet−triplet interconversion, the radical pair would remain as a singlet, every encounter would be reactive and Φ_S would equal the probability that the radicals encounter, i.e., R^*/R_0 (= 0.5 in this case). However, singlet−triplet interconversion, driven by hyperfine interactions and modified by Zeeman, exchange, and dipolar interactions, causes some encounters to occur in an unreactive triplet state leading to a lower recombination yield.

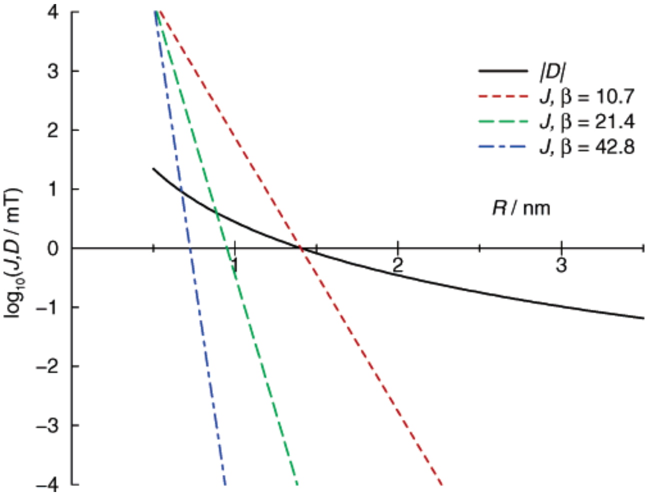

Figure 1. Exchange $J(R)$ (broken lines) and dipolar $D(R)$ (solid line) interactions used in the simulations (in mT on a logarithmic scale) as a function of radical−radical separation R for $R^* = 0.5$ nm, $J_0 = 16$ T, and $\beta = 10.7$ nm^{-1} (short dashed), 21.4 nm^{-1} (long dashed), and 42.8 nm^{-1} (dot−dashed). The magnitude of the hyperfine interaction (1 mT) is indicated by the horizontal line at log (J, D/mT) = 0.

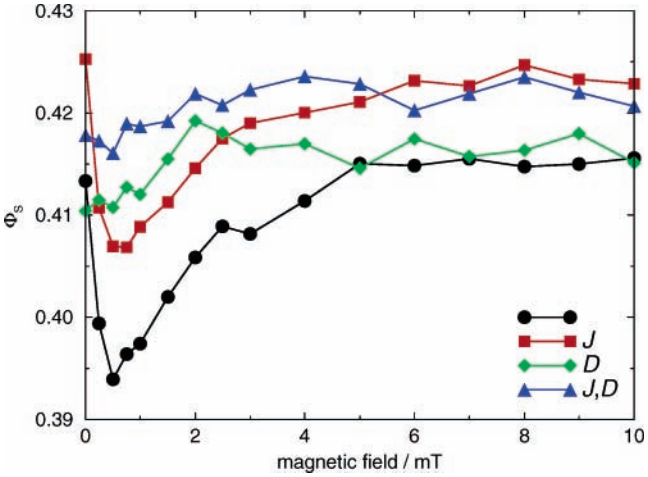

Figure 2. Monte Carlo simulations of the radical pair recombination yield Φ_S as a function of applied magnetic field B averaged over the three values of θ_0, 0, 45°, and 90°: (circles) $J(R) = 0$, $D(R) = 0$; (squares) $J(R) \neq 0$, $D(R) = 0$; (diamonds) $J(R) = 0$, $D(R) \neq 0$; (triangles) $J(R) \neq 0$, $D(R) \neq 0$. The default values of the parameters used here and for all subsequent figures are given in Table 1. The standard deviations of the calculated Φ_S values are ~0.0014.

The following features of the MFE can be noted in Figure 2. (1) In the absence of the dipolar interaction, there is a pronounced LFE with a minimum at $B \approx 0.5$ mT. (2) The exchange interaction causes a general increase in the product yield, an effect that is a little more pronounced at low fields

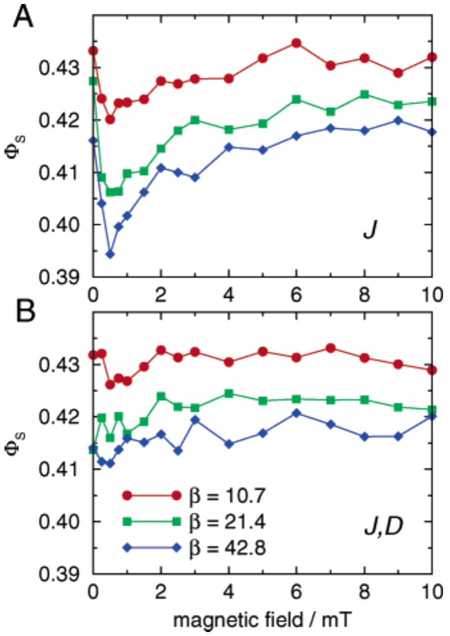

Figure 3. Monte Carlo simulations of the radical pair recombination yield Φ_S as a function of applied magnetic field B for three values of the exchange range parameter β = 10.7 nm^{-1} (circles), 21.4 nm^{-1} (squares), and 42.8 nm^{-1} (diamonds): (A) $D(R) = 0$; (B) $D(R) \neq 0$. The standard deviations of the calculated Φ_S values are ~0.0024.

such that the depth of the LFE minimum is slightly reduced by the presence of $J(R)$. (3) The dipolar interaction, however, has a profound effect at low field. Whether or not an exchange interaction is present, the LFE is abolished by $D(R)$ leaving almost no field-dependence between 0 and 10 mT. (4) By contrast, the dipolar interaction has only a minor effect at high field.

The exact asymptotic solution of the stochastic Liouville equation for $J(R) = D(R) = 0$ (not shown) has essentially the same field dependence and LFE as the corresponding Monte Carlo simulation except for a field-independent offset in Φ_S of ~+0.015. This small discrepancy, which does not affect the qualitative conclusions of the present study, arises from the radical encounters that occur after the 400 ns time-limit of the Monte Carlo simulations. If the Laplace variable in this calculation is set equal to $(400\pi \text{ ns})^{-1}$, instead of zero, the exact solution becomes indistinguishable from the Monte Carlo simulation.

Figure 3 shows the effect of the range of the exchange interaction, with and without dipolar coupling. As anticipated, the larger the region of space in which singlet–triplet interconversion is inhibited by the exchange interaction, the larger the value of Φ_S. This is true whether the dipolar interaction is present or not. Doubling or halving J_0, keeping β fixed at the default value has a negligible effect on the MFE (not shown).

Finally, Figure 4 explores the influence of the diffusion rate. As the motion becomes faster, the radicals encounter on a shorter time scale, leaving less time for conversion out of the singlet state, resulting in an increased recombination yield and a smaller LFE (for $D(R) = 0$). The dipolar interaction abolishes the LFE, as before, and has a greater effect on Φ_S at high field when the diffusion is slower. The exact solutions of the stochastic Liouville equation for the $J(R) = D(R) = 0$ case (not shown) have the same field dependence as the Monte Carlo calculations but are offset to higher singlet yields. The offsets, ~0.06, ~0.015, and ~0.0 for $D_S = 10^{-9}$, 10^{-10}, and 10^{-11} m^2 s^{-1}, respectively, reflect the larger number of radical pairs at the slower diffusion rates that have yet to encounter by the end of the Monte Carlo calculation (400 ns).

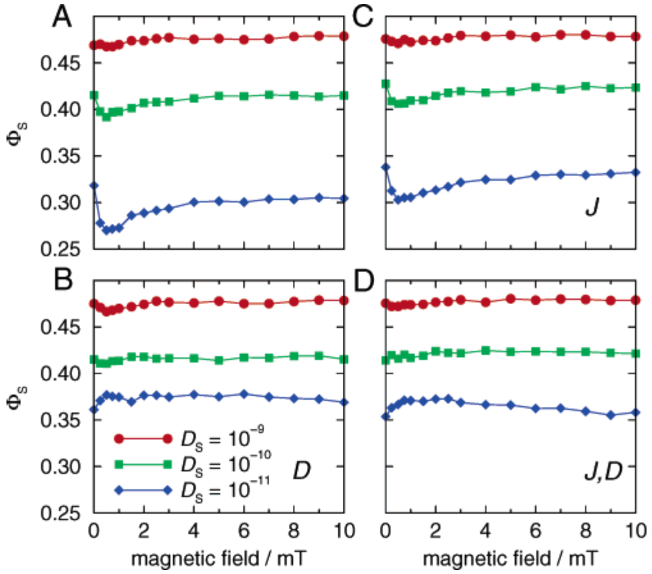

Figure 4. Monte Carlo simulations of the radical pair recombination yield Φ_S as a function of applied magnetic field B for three values of the diffusion coefficient $D_S = 10^{-9}$ m^2 s^{-1} (circles), 10^{-10} m^2 s^{-1} (squares), and 10^{-11} m^2 s^{-1} (diamonds): (A) $J(R) = 0$, $D(R) = 0$; (B) $J(R) \neq 0$, $D(R) = 0$; (C) $J(R) = 0$, $D(R) \neq 0$; (D) $J(R) \neq 0$, $D(R) \neq 0$. The standard deviations of the calculated Φ_S values are ~0.0024.

Discussion

A. Exchange Interaction. The influence of the exchange interaction on the calculated singlet yield is not unexpected. The increase in Φ_S caused by $J(R)$ arises from inhibition of singlet–triplet interconversion, an effect that is more pronounced the longer the range of the interaction. The effect of $J(R)$ on the LFE is greater than at higher fields because the crucial singlet–triplet mixing process is slower at low field. In general, when $B \ll a$, an exchange interaction stronger than B will inhibit spin evolution in the radical pair, whereas for $B \gg a$, the exchange must be stronger than a to have a significant effect. The range of separations for which $J(R)$ is important is therefore larger at low field than at high field (and larger for smaller β).

Additionally, we note that there is no evidence here for "2J resonances" arising from the level crossings of the singlet state with the T_{+1} or T_{-1} triplet state.[30–33] Although similar in appearance to the LFE, these features should become more pronounced as the range of the exchange interaction is increased, in contrast to the behavior shown in Figure 3.

B. Dipolar Interaction. Essentially similar effects are found for the dipolar interaction, except that the suppression of singlet–triplet interconversion, as judged by the value of Φ_S, is much more pronounced at low field, to the extent that the LFE is completely abolished. This arises because $D(R)$ has a much longer range than the exchange interactions considered here: $D(R)$ does not fall below 0.5 mT until the radicals have separated by 1.8 nm, compared to 0.99 nm for the default exchange interaction. The volumes of the space in which $D(R)$ and $J(R)$ are greater than 0.5 mT (and $R > R^*$) are 22.8 and 3.5 nm^3, respectively.

On this basis, one would also expect the dipolar interaction to increase Φ_S significantly at high field: in fact, $D(R)$ is rather less effective in this respect than $J(R)$. This—at first sight surprising—result arises from the orientation dependence of the dipolar interaction. In a strong magnetic field, $B \gg D(R)$, the electron spins are quantized along the field direction, and the dipolar interaction is purely anisotropic, with a $(3 \cos^2 \theta - 1)$ dependence on the angle θ between the field direction and the inter-radical vector. This interaction averages to zero for sufficiently rapid and extensive modulation of θ by the relative translational diffusion of the radicals around one another. Hence, $D(R)$ is less important at high field than might otherwise be expected, especially for fast diffusion, as found in the simulations.

We can estimate the diffusion rate necessary to average the dipolar coupling at high field, as follows. Suppose the radicals move around one another at a separation R with a relative translational diffusion coefficient $2D_S$. To get efficient averaging, the product of $D(R)$ and τ, the average time required to achieve a significant change in θ, must be small. Taking $\Delta\theta = 1$ rad, the radicals thus move an average distance $d = R\Delta\theta = R$ during the interval τ. Combining the relation $\tau \approx d^2/8D_S$ with $|D(R)|\tau \ll 1$, one finds $D_S R \gg 6 \times 10^{-20}$ m^3 s^{-1}. Thus, the default value of D_S used here (10^{-10} m^2 s^{-1}) is likely to cause relatively efficient averaging of $D(R)$ provided R is larger than 1 nm, as is observed.

In weak fields, however, where $B \ll D(R)$, the two coupled electron spins are quantized along the vector connecting the two radicals, and the strength of their interaction is independent of θ. Averaging does not therefore occur, allowing $D(R)$ to have the strong influence on the LFE noted above. The customary assumption, when dealing with radical pairs in nonviscous solution, is that the dipolar coupling is negligible because of the rapid motion of the radicals. Although this may be acceptable at high field and at separations where $B \gg D(R)$, it is certainly questionable at low field, as the present results demonstrate.

The principal conclusion from this study is that the dipolar interaction is very efficient at quenching the LFE for radical pairs in solution. We speculate that LFEs are *only* likely to be observed if the motion of the radical pair is restricted in some way so as to increase the likelihood that, having separated to the large distance required for the dipolar interaction to have a negligible effect, the radicals subsequently encounter and have the opportunity to recombine. Obvious possibilities that have been discussed before in this context are attractive Coulomb forces between charged radicals[1,2,34,35] and encapsulation of the radical pair in a micelle or vesicle.[7,36−39]

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