Supporting Information for

Effect of Molecular Diffusion on the Spin Dynamics of a Micellized Radical Pair in Low Magnetic Fields Studied by Monte-Carlo Simulation

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Dephasing/relaxation processes induced by the initial separation dynamics of RP

Monte Carlo simulations of dephasing/relaxation processes were examined by setting a closest contact as the initial molecular coordinate (the same with eq10 in the main text)

\[ \mathbf{r}(t = 0) = R(\sin \theta_{\text{rand}} \cos \phi_{\text{rand}}, \sin \theta_{\text{rand}} \sin \phi_{\text{rand}}, \cos \theta_{\text{rand}}) \]  

(s1)
Time evolution of $T_0$ population, $T_0-T_{+1}$ and $S-T_{+1}$ coherences at 3 mT in the presence of only $H_{dd}(t)$ and $S-T_{+1}$ coherence in the presence of only $H_{f}(t)$ are shown in Figure S1. The time profiles in Figure S1a-d reflect TTR, TTD, STD by the dipolar modulation ($D$-STD), and STD by exchange modulation ($J$-STD), respectively.

Figure S1. Relaxation/dephasing processes at 3 mT calculated with closest distance $R$ as the initial RP separation at $D_{AB} = 0.25$ (red), 1 (green), 5 (blue) $\times 10^{-6}$ cm$^2$/s. a) TTR, b) TTD c) $D$-STD and d) $J$-STD. The base line in a) shows the equilibrated $T_0$ population of 1/3.

The calculated coherences/polarization in the presence of the dipolar modulation clearly show biphasic features especially when $D_{AB}$ is small (see red curves in Figure S1a-c). In the case of
the exchange modulation (Figure S1d), the coherences quickly damps to 0 within a few nanoseconds. These facts indicate the existence of very fast (< a few ns) relaxation/dephasing processes immediately after the RP formation. RP experiences very large spin-spin interactions at \( r \sim R \) as has been seen in Figure 1b in the main text. If the diffusive separation is comparable to or slower than the characteristic timescale for the strong interaction at \( r \sim R \), RP spin dynamics is strongly modulated by the fluctuating interaction, which results in the fast damping of initially given coherence/polarization. The slower decay components are likely to be attributed to damping of the residual coherence/polarization induced by the reencounter dynamics of the RP in the micelle.

The fast relaxation processes at the early times are unlikely to cause significant effect on the spin-state mixing by HFI because of following reasons. In the case of singlet-born RPs, the S–T coherence and the triplet populations (and the triplet coherences as well) do not exist at the initial stage. These coherence and population are created by the spin state mixing by HFI (~ 10 ns), which takes place after the diffusive separation enough to suppress \( J \). Thus the fast relaxation right after the RP creation cannot affect the spin state mixing, so that this effect is not considered in the present study regarding the singlet-born RP.

In triplet born systems, discussion is rather complicated and involves unclear problems about the initial spin state of the RP. If the initial spin state can be described as a statistically mixed state

\[
\rho(0) = \frac{1}{3}\left( |T_{+1}\rangle\langle T_{+1}| + |T_{0}\rangle\langle T_{0}| + |T_{-1}\rangle\langle T_{-1}| \right)
\]

as assumed in previous studies,\(^1\) the triplet coherence/polarization does not exist at the initial stage. In this case, discussion is totally the same as that for singlet-born RPs. However, if the spin coherence/polarization on the precursor triplet excited state is transferred to the triplet RP,\(^6\)
the fast TTD and TTR at early times might give considerable effect. The polarization/coherence transfer is sometimes observed by time-resolved EPR (trEPR) but its effect at low fields has not been reported. Further theoretical and experimental works would be necessary for this issue. Nevertheless, the fast relaxation/dephasing among triplet states would suppress the initially given triplet polarization/coherence resulting in the equilibrated state (eqS2) at the very initial stage of RP creation. Thus the experimentally observed relaxation/dephasing processes for triplet-born systems are considered to be not directly related to the fast processes observed here.

**Calculation of spin state mixing by modified exponential model** Simulations are carried out based on a simple exponential model with dephasing parameters obtained by the present Monte Carlo simulation. $S-T_{\pm 1}$ mixing is calculated by numerically solving a Liouville equation

$$\frac{d|\rho\rangle}{dt} = -i\hat{L}|\rho\rangle = -i(\hat{H}^r + i\hat{R})|\rho\rangle$$  \hspace{1cm} (S3)

where $|\rho\rangle$, $\hat{H}^r$ and $\hat{R}$ are vector representation of a radical pair (RP) density matrix, a commutator of spin Hamiltonian and an effective relaxation superoperator. Here chemical reactions as RP recombination are ignored as in the case of Monte Carlo simulation. The spin Hamiltonian contains Zeeman interaction and hyperfine interactions (HFIs), which are in the same form as those used for the Monte Carlo simulation, and static Hamiltonians of the exchange and the dipolar terms are ignored.

The relaxation superoperator induces TTR, STD and TTD as represented in Liouville space as
\[
R = \frac{1}{\tau_{TTR}} \left[ \frac{2}{3} |T_0 T_0 \rangle \langle T_0 T_0| + \frac{1}{3} \sum_{m=-1,1} \left( |T_m T_m \rangle \langle T_m T_m| - |T_m T_0 \rangle \langle T_0 T_m| - |T_0 T_0 \rangle \langle T_m T_m| \right) \right] \\
+ \sum_{m=-1,0,1} \left[ \frac{1}{\tau_{STD}} \left( |ST_m \rangle \langle ST_m| + |T_m S \rangle \langle T_m S| \right) \right] + \sum_{m=-1,1} \left( |T_m 0 \rangle \langle T_0 T_0| + |T_0 T_m \rangle \langle T_0 T_m| \right) 
\]

(S4)

where \( \tau_{TTR} \) and \( \tau_{TTD} \) are time constants for corresponding relaxation/dephasing processes. With regard to STD, small differences in time constants among triplet sublevels \( (T_m) \) are taken into account as \( \tau_{STD} \). The effect of second order TTR and TTD, which respectively induce relaxation and dephasing between \( T_{-1} \) and \( T_{-1} \) states, is ignored for simplicity. This treatment is rough approximation at low magnetic fields but does not cause a serious problem for the present simulation because we do not differentiate those two states to calculate the S–T mixing process.

Time evolution is started from the singlet state as

\[
|\rho(t = 0)\rangle = |SS\rangle 
\]

and the sum of \( T_{-1} \) and \( T_{1} \) populations is calculated for each time propagation as

\[
[T_{\pm 1}(t)] = \langle T_{+1} T_{+1} | e^{-i\gamma t} \rho(t = 0) \rangle + \langle T_{-1} T_{-1} | e^{-i\gamma t} \rho(t = 0) \rangle 
\]

(S6)

The solid lines in Figure 5a and b are S–T\( \pm 1 \) mixing processes at 3 mT calculated by the exponential model with relaxation/dephasing parameters obtained by the Monte Carlo simulation with the exchange and the dipolar modulations, respectively (\( D_{AB} \)-dependent time constants used here are plotted in Figure 3 in the main text). The traces accompany those directly calculated by Monte Carlo simulation with HFI (dashed lines).

References


