Supplemental file 1

Calculation of low field effect (LFE) by two-proton model

Here the Hamiltonian below is assumed ($I_1 = I_2 = 1/2$).

$$\hat{H} = \sum_{i=1,2} \frac{g_i \mu_{\mathrm{B}} B_0}{\hbar} \hat{S}_{Zi} + a_1 \hat{\mathbf{S}}_1 \bullet \hat{\mathbf{I}}_1 + a_2 \hat{\mathbf{S}}_2 \bullet \hat{\mathbf{I}}_2 \approx \omega_0 \left(\hat{S}_{Z1} + \hat{S}_{Z2} \right) + a_1 \hat{\mathbf{S}}_1 \bullet \hat{\mathbf{I}}_1 + a_2 \hat{\mathbf{S}}_2 \bullet \hat{\mathbf{I}}_2 \quad (1)$$

Difference in g values are ignored because we will discuss the spin dynamics at very low magnetic fields. Out of $2^{2+2} = 16$ eigenstates of the Hamiltonian, the 7 states below are involved in the LFE as Lewis et al.[1] reported (for the full description, see the supporting information for the original paper).

$$\left.\begin{aligned}
|2\rangle &= c_{2+} |\mathrm{T}_{+1}\alpha\beta\rangle + \frac{c_{2-}}{\sqrt{2}} \left(|\mathrm{T}_0\alpha\alpha\rangle + |\mathrm{S}\alpha\alpha\rangle \right), \\
|4\rangle &= c_{1+} |\mathrm{T}_{+1}\beta\alpha\rangle - \frac{c_{1+}}{\sqrt{2}} \left(|\mathrm{T}_0\alpha\alpha\rangle - |\mathrm{S}\alpha\alpha\rangle \right),
\end{aligned}\right\} F = +1$$

$$\left.\begin{aligned}
|6\rangle &= \frac{1}{\sqrt{2}} \left(|\mathrm{T}_0\alpha\beta\rangle + |\mathrm{S}\alpha\beta\rangle \right), \\
|7\rangle &= c_{1+}c_{2+} |\mathrm{T}_{+1}\beta\beta\rangle + \frac{c_{1+}c_{2-}}{\sqrt{2}} \left(|\mathrm{T}_0\beta\alpha\rangle + |\mathrm{S}\beta\alpha\rangle \right) \\
&\quad + \frac{c_{1-}c_{2+}}{\sqrt{2}} \left(|\mathrm{T}_0\alpha\beta\rangle - |\mathrm{S}\alpha\beta\rangle \right) + c_{1-}c_{2-} |\mathrm{T}_{-1}\alpha\alpha\rangle, \\
|11\rangle &= \frac{1}{\sqrt{2}} \left(|\mathrm{T}_0\beta\alpha\rangle - |\mathrm{S}\beta\alpha\rangle \right),
\end{aligned}\right\} F = 0$$

$$\left.\begin{aligned}
|12\rangle &= \frac{c_{2+}}{\sqrt{2}} \left(|\mathrm{T}_0\beta\beta\rangle - |\mathrm{S}\beta\beta\rangle \right) + c_{2-} |\mathrm{T}_{-1}\beta\alpha\rangle, \\
|14\rangle &= \frac{c_{1+}}{\sqrt{2}} \left(|\mathrm{T}_0\beta\beta\rangle + |\mathrm{S}\beta\beta\rangle \right) + c_{1-} |\mathrm{T}_{-1}\alpha\beta\rangle,
\end{aligned}\right\} F = -1 \quad (2)$$

and

$$\left.\begin{aligned} \omega_2 &= \frac{\omega_0+\mu_2}{2}+\frac{a_1-a_2}{4}, \\ \omega_4 &= \frac{\omega_0+\mu_1}{2}+\frac{-a_1+a_2}{4}, \end{aligned}\right\} F=+1$$

$$\left.\begin{aligned} \omega_6 &= \frac{a_1+a_2}{4}, \\ \omega_7 &= \frac{\mu_1+\mu_2}{2}-\frac{a_1+a_2}{4}, \\ \omega_{11} &= \frac{a_1+a_2}{4}, \end{aligned}\right\} F=0 \tag{3}$$

$$\left.\begin{aligned} \omega_{12} &= -\frac{\omega_0-\mu_2}{2}+\frac{a_1-a_2}{4}, \\ \omega_{14} &= -\frac{\omega_0+\mu_1}{2}-\frac{a_1-a_2}{4}, \end{aligned}\right\} F=-1$$

where

$$\mu_i = \sqrt{\omega_0^2 + a_i^2} \tag{4}$$

and

$$c_{i\pm}^2 = \frac{\mu_i \pm \omega_0}{2\mu_i} \tag{5}$$

The time dependent singlet population for the singlet-born radical pair is described as

$$P_{\mathrm{S}}(t) = \frac{1}{Z}\sum_{m,n}\left|\langle n|\hat{P}_{\mathrm{S}}|m\rangle\right|^2 e^{i\omega_{mn}t} \tag{6}$$

By applying a magnetic field, breakdown of zero-field degeneracy occurs for the 4 pairs of eigenstates (note that $\omega_6 = \omega_{11}$ at any magnetic field), so that the oscillation becomes active as

$$\begin{aligned} P_{\mathrm{S}}^{2-4}(t) &= \left|\langle 2|\hat{P}_{\mathrm{S}}|4\rangle\right|^2 e^{i\omega_{2-4}t} = \frac{1}{4}c_{1-}^2c_{2-}^2 \exp\left\{i\left(-\frac{\mu_1-\mu_2}{2}+\frac{a_1-a_2}{2}\right)t\right\} \\ P_{\mathrm{S}}^{6-7}(t) &= \left|\langle 6|\hat{P}_{\mathrm{S}}|7\rangle\right|^2 e^{i\omega_{6-7}t} = \frac{1}{4}c_{1-}^2c_{2+}^2 \exp\left\{-i\left(\frac{\mu_1+\mu_2}{2}-\frac{a_1+a_2}{2}\right)t\right\} \\ P_{\mathrm{S}}^{7-11}(t) &= \left|\langle 7|\hat{P}_{\mathrm{S}}|11\rangle\right|^2 e^{i\omega_{7-11}t} = \frac{1}{4}c_{1+}^2c_{2-}^2 \exp\left\{i\left(\frac{\mu_1+\mu_2}{2}-\frac{a_1+a_2}{2}\right)t\right\} \\ P_{\mathrm{S}}^{12-14}(t) &= \left|\langle 12|\hat{P}_{\mathrm{S}}|14\rangle\right|^2 e^{i\omega_{12-14}t} = \frac{1}{4}c_{1+}^2c_{2+}^2 \exp\left\{i\left(-\frac{\mu_1-\mu_2}{2}+\frac{a_1-a_2}{2}\right)t\right\} \end{aligned} \tag{7}$$

Let us assume that the total HF coupling is constant ($a_1 > a_2 > 0$) as

$$
\begin{aligned}
&a \equiv a_1 + a_2 \\
&r \equiv a_2 / a_1 \quad (0 \le r \le 1) \\
&R \equiv \omega_0 / a \quad (0 \le R)
\end{aligned} \tag{8}
$$

Thus

$$
\begin{aligned}
a_1 &= \frac{a}{1+r} \\
a_2 &= \frac{ar}{1+r}
\end{aligned} \tag{9}
$$

$$
\begin{aligned}
\mu_1 &= \sqrt{\omega_0^2 + a_1^2} = \sqrt{a^2R^2 + \frac{a^2}{(1+r)^2}} = a\sqrt{R^2 + \frac{1}{(1+r)^2}} \\
\mu_2 &= \sqrt{\omega_0^2 + a_2^2} = \sqrt{a^2R^2 + \frac{a^2r^2}{(1+r)^2}} = a\sqrt{R^2 + \frac{r^2}{(1+r)^2}}
\end{aligned} \tag{10}
$$

The angular frequency parts of eq. 7 is thus rewritten as

$$
\begin{aligned}
\omega_{2-4} = \omega_{12-14} &= \left(-\frac{\mu_1 - \mu_2}{2} + \frac{a_1 - a_2}{2}\right) = \frac{a}{2}\left(-\sqrt{R^2 + \frac{1}{(1+r)^2}} + \sqrt{R^2 + \frac{r^2}{(1+r)^2}} + \frac{1-r}{1+r}\right) \ge 0 \\
-\omega_{6-7} = \omega_{7-11} &= \left(\frac{\mu_1 + \mu_2}{2} - \frac{a_1 + a_2}{2}\right) = \frac{a}{2}\left(\sqrt{R^2 + \frac{1}{(1+r)^2}} + \sqrt{R^2 + \frac{r^2}{(1+r)^2}} - 1\right) \ge 0
\end{aligned} \tag{11}
$$

These indicate that the mixing frequencies linearly increases with the total coupling a at very low magnetic fields where $\omega_0 << a$ ($R \sim 0$). The first derivative of ω_{2-4} is

$$
\frac{\partial \omega_{2-4}}{\partial r} = \frac{a}{2}\left(\frac{1}{\sqrt{(1+r)^4 + R^2(1+r)^6}} + \frac{r}{\sqrt{r^2(1+r)^4 + R^2(1+r)^6}} - \frac{2}{(1+r)^2}\right) \tag{12}
$$

This value is maximised when $R = 0$ irrespective of r values, so that

$$
\begin{aligned}
\frac{\partial \omega_{2-4}}{\partial r}(\max) &= \frac{a}{2}\left(\frac{1}{\sqrt{(1+r)^4}} + \frac{r}{\sqrt{r^2(1+r)^4}} - \frac{2}{(1+r)^2}\right) \\
&= \frac{a}{2}\left(\frac{1}{(1+r)^2} + \frac{1}{(1+r)^2} - \frac{2}{(1+r)^2}\right) = 0
\end{aligned} \tag{13}
$$

Thus

$$
\frac{\partial \omega_{2-4}}{\partial r} \le 0 \tag{14}
$$

at any r and R values in the defined range.

On the other hand, the first derivative of $-\omega_{6-7}$ is

$$\begin{aligned}\frac{-\partial\omega_{6-7}}{\partial r} &= \frac{a}{2}\left(\frac{r}{\sqrt{r^2(1+r)^4+R^2(1+r)^6}}-\frac{1}{\sqrt{(1+r)^4+R^2(1+r)^6}}\right)\\ &= \frac{a}{2}\left(\frac{r}{\sqrt{r^2(1+r)^4+R^2(1+r)^6}}-\frac{r}{\sqrt{r^2(1+r)^4+r^2R^2(1+r)^6}}\right)\end{aligned} \tag{15}$$

Since $0 < r < 1$, $R^2 > r^2R^2$, so that

$$\frac{-\partial\omega_{6-7}}{\partial r} \leq 0 \tag{16}$$

From these calculations, it turns out that all the four angular frequencies monotonically decrease with increasing r, which means that the mixing frequency is lower for similar HF coupling constants for the two radicals.

Dependence of ω_{2-4} and $-\omega_{6-7}$ on r at $R = 0.168$, which is the same condition for the $B_0 = 0.6$ mT and $a/2\pi = 100$ MHz as shown in Figure 3 in the main text, is shown in Figure S1-1.

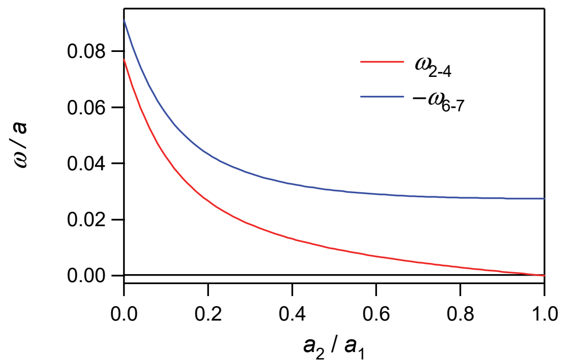

Figure S1-1. Dependence of the relative mixing frequency $\omega/(a_1+a_2)$ on the relative HF coupling a_2/a_1 at a low magnetic field of $\omega_0/a = 0.168$.

The mixing frequencies are almost ten times lower than the total HF coupling at $r = 0$ (HF coupling on only one radical) and reduces significantly with increasing r (more balanced HF couplings for the two radicals).

[1] A. M. Lewis, T. P. Fay, D. E. Manolopoulos, C. Kerpal, S. Richert and C. R. Timmel, J. Chem. Phys. **149**, 034103 (2018).