Supplementary Information

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A. RIGID LIMIT 2D-ELDOR S_{c-}

For a given spin orientation (θ, ϕ) about the dc magnetic field $\vec{B_0}$, the electron spin Hamiltonian, when including only g and A (hyperfine) tensor interactions, has the following eigenvalues:

$$\pm\frac{\hbar e}{2m_e}(\mathrm{g_{eff}B_0} + \mathrm{A_{eff}m_I}) \tag{21}$$

where $m_I \in \{-I, -I+1, ..., I-1, I\}$, e and m are the electron charge and mass,

$$\mathrm{g_{eff}} = \sqrt{(\mathrm{g_{xx}}\sin\theta\cos\phi)^2 + (\mathrm{g_{yy}}\sin\theta\sin\phi)^2 + (\mathrm{g_{zz}}\cos\theta)^2},$$

and

$$\mathrm{A_{eff}} = \sqrt{(\mathrm{A_{xx}}\sin\theta\cos\phi)^2 + (\mathrm{A_{yy}}\sin\theta\sin\phi)^2 + (\mathrm{A_{zz}}\cos\theta)^2}.$$

$\mathrm{g_{ii}}$, $\mathrm{A_{ii}}$ (in Gauss units) denote the principal values of the g and A tensors respectively. The contribution of (θ, ϕ) to the $S_{c-}(f_1, T_{mix}, f_2)$ is

$$\frac{1}{\mathrm{g_{eff}B_0} + \mathrm{A_{eff}m_I} - 2\pi \mathrm{i}\frac{\mathrm{f_0+f_2}}{\gamma}}\frac{1}{\mathrm{g_{eff}B_0} + \mathrm{A_{eff}m_I} + 2\pi \mathrm{i}\frac{\mathrm{f_0+f_1}}{\gamma}},$$

where f_0 is the ESR frequency, γ is the electron gyromagnetic ratio. Notice the lack of dependence on T_{mix}, as we didn't consider any mechanism other than the rotational diffusion that causes a longitudinal decoherence (T_1 relaxation). The overall expression for S_{c-}, after including contributions from all orientations (θ, ϕ), becomes:

$$S_{c-}(f_1, T_{mix}, f_2) = \int\int \frac{1}{-i\frac{e}{2m}(\mathrm{g_{eff}B_0+A_{eff}m_I}) + 2\pi i(f_0+f_2)}\frac{1}{i\frac{e}{2m}(\mathrm{g_{eff}B_0+A_{eff}m_I}) - 2\pi i(f_0+f_1)}P(\theta,\phi)d\theta d\phi \tag{22}$$

$$= \int\int \frac{1}{-i\frac{e}{2m}(\mathrm{g_{eff}B_0+A_{eff}m_I}) + 2\pi i(f_0+f_2)}\frac{1}{i\frac{e}{2m}(\mathrm{g_{eff}B_0+A_{eff}m_I}) - 2\pi i(f_0+f_1)}\frac{\sin\theta}{4\pi^2}d\theta d\phi \tag{23}$$

Here we assume the absence of an orienting potential[29], thus making all orientations equally likely, leading to a uniform distribution of the form $P(\theta, \phi) = \frac{\sin\theta}{4\pi^2}$.

B. FAILURE OF THE ORIGINAL METHOD

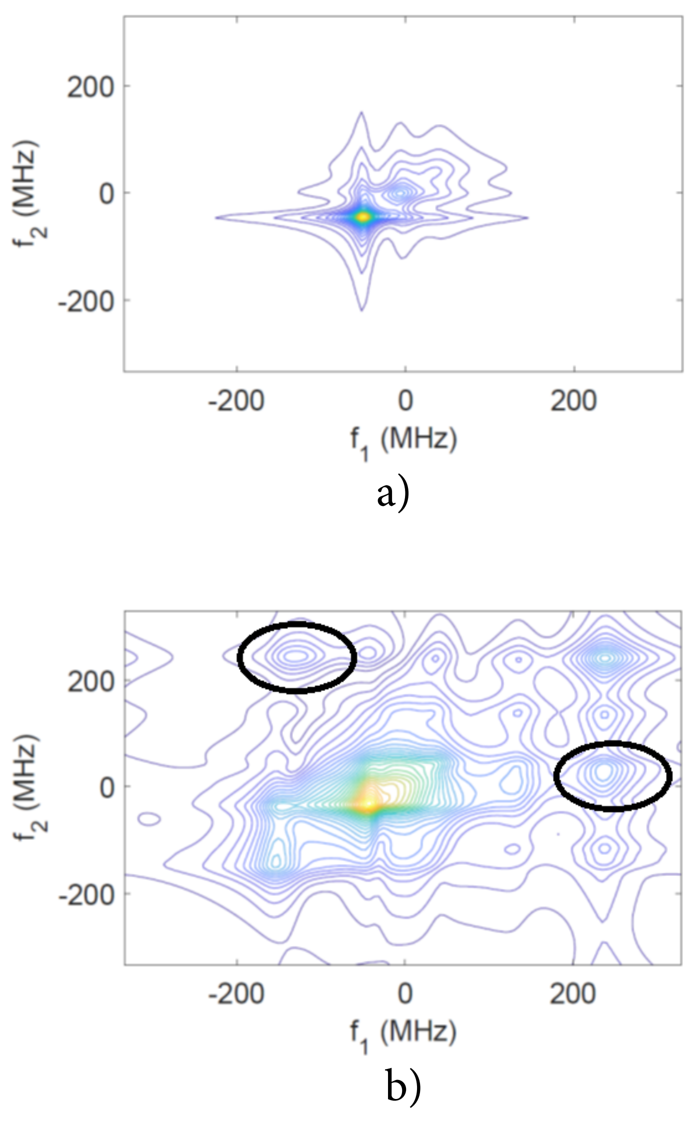


FIG. B.1: 2D-ELDOR spectra at 95 GHz simulated with the original algorithm. In a), $R_\parallel = 10^9$, $R_\perp$=5×10^8 rad$^2/s$. In b), $R_\parallel = 10^7$, $R_\perp$=5×10^6 rad$^2/s$. Here $T_{mix} = 0\ ns$. Encircled regions highlight unexpected cross-peaks. See also Fig. 4.

C. APPLICATION TO DYNAMIC EXCHANGE BETWEEN PROTEIN CONFORMATIONS: SAME PLOTS, BUT WITH AUTO-PEAKS SUBTRACTED, TO BETTER SHOW EXCHANGE CROSS-PEAKS

C.1. Development of dynamic exchange cross-peaks as a function of mixing time

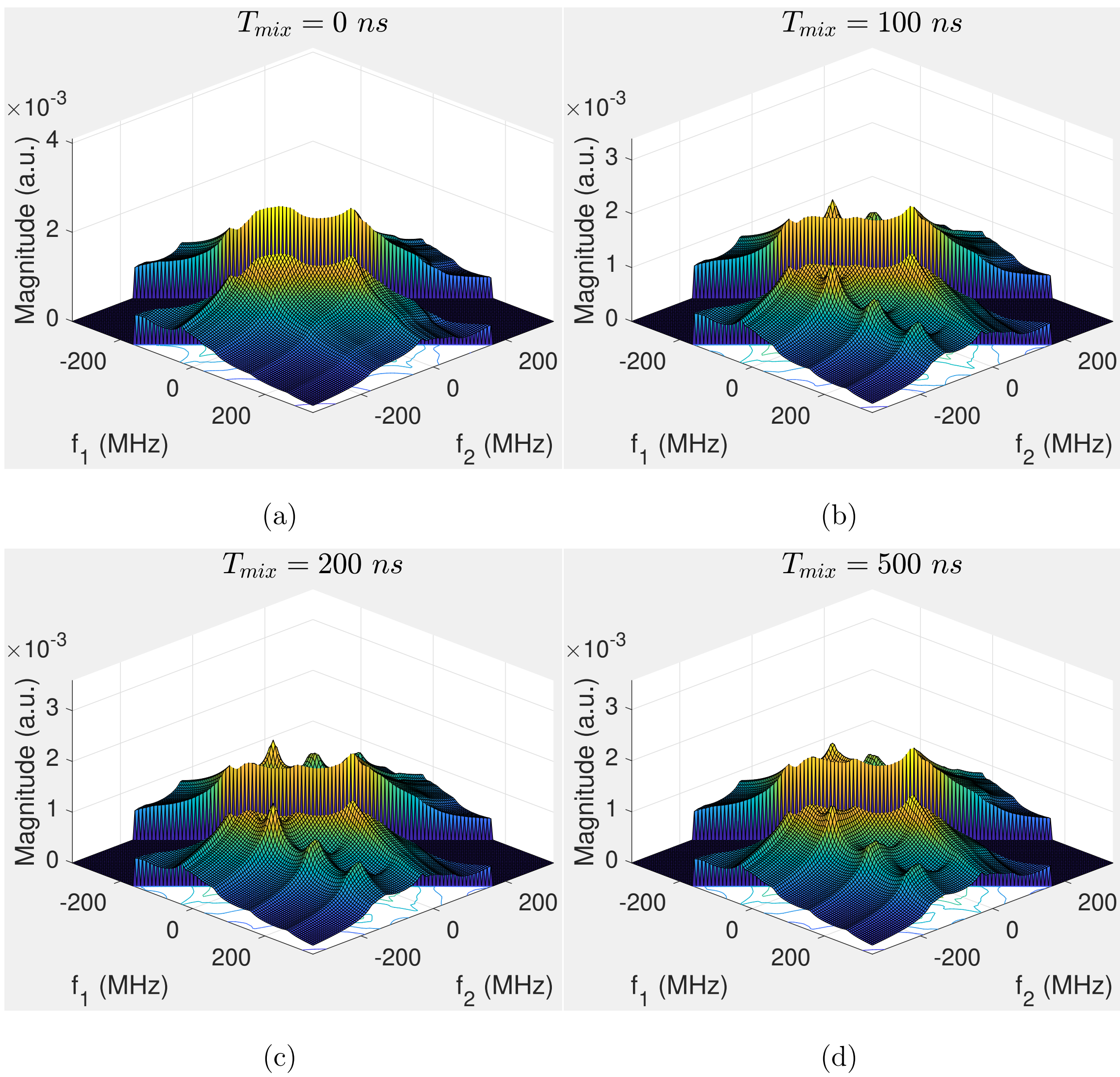
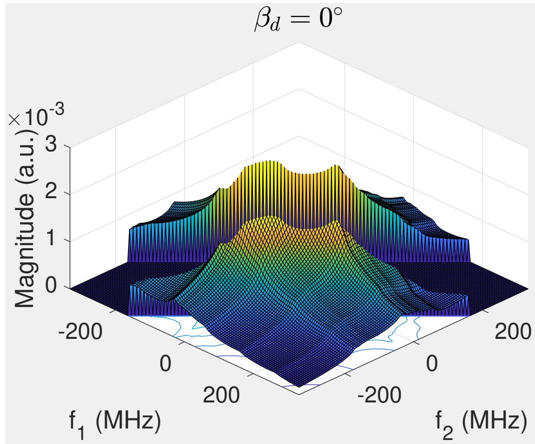
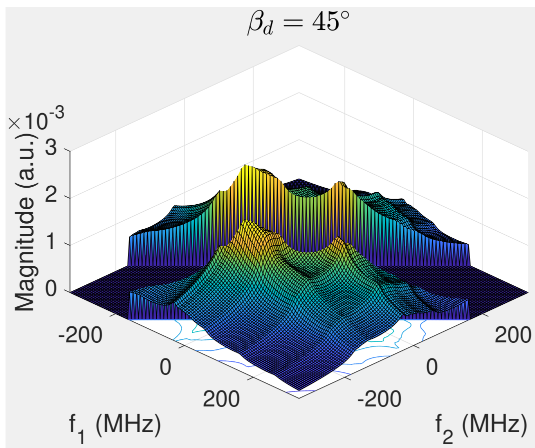


FIG. C.1: Effect of dynamic exchange on slow-motional 2D-ELDOR spectra, as a function of mixing time. Here $k_{sym} = 10^6\ s^{-1}$, $R_{\|} = 10^5\ s^{-1}$, $R_{\perp} = 5 \times 10^4\ s^{-1}$. Both conformations have the same mole fraction, i.e., $c_A = c_B = 0.5$. a) $T_{mix} = 0\ ns$, b) $T_{mix} = 100\ ns$, c) $T_{mix} = 200\ ns$, d) $T_{mix} = 500\ ns$. The jump angle, β_d is $90°$. Other parameters same as Fig. 4.

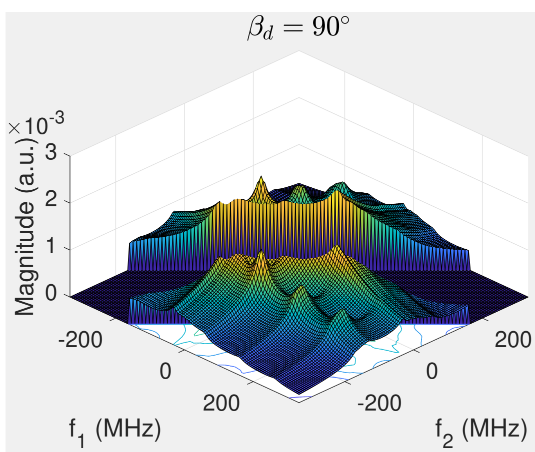
C.2. Dependence of dynamic exchange cross-peaks on β_d



(a)



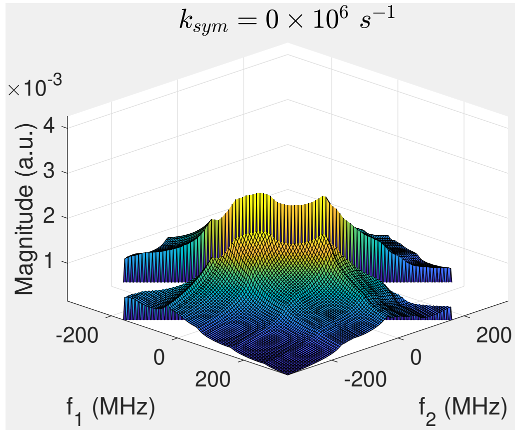
(b)



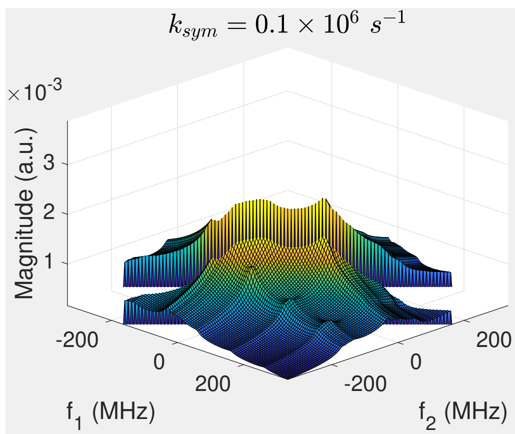
(c)

FIG. C.2: Effect of dynamic exchange on slow-motional 2D-ELDOR spectra, as a function of β_d: a) $\beta_d = 0°$, b) $\beta_d = 45°$, c) $\beta_d = 90°$. Here $T_{mix} = 200\ ns$, $k_{sym} = 10^6 s^{-1}$, $c_A = c_B = 0.5$. Other parameters same as Fig. 6.

C.3. Dependence of dynamic exchange on k_{sym}



(a)



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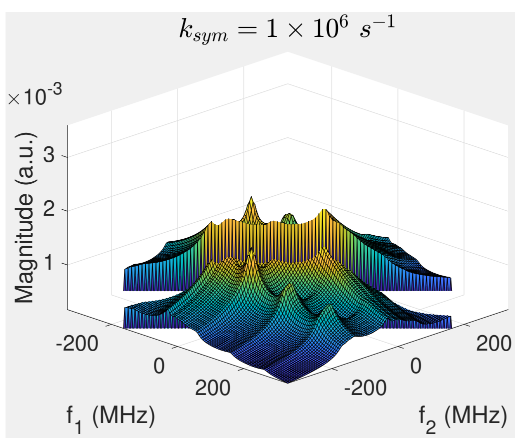

(c)

FIG. C.3: Effect of k_{sym} on slow-motional 2D-ELDOR spectra: a) $k_{sym} = 0s^{-1}$ (no exchange), b) $k_{sym} = 10^5 s^{-1}$, c) $k_{sym} = 10^6 s^{-1}$. Here $T_{mix} = 200\ ns$, jump angle $\beta_d = 90°$, and $c_A = c_B = 0.5$. Other parameters same as Fig. 6.

C.4. Dependence of dynamic exchange on the ESR frequency

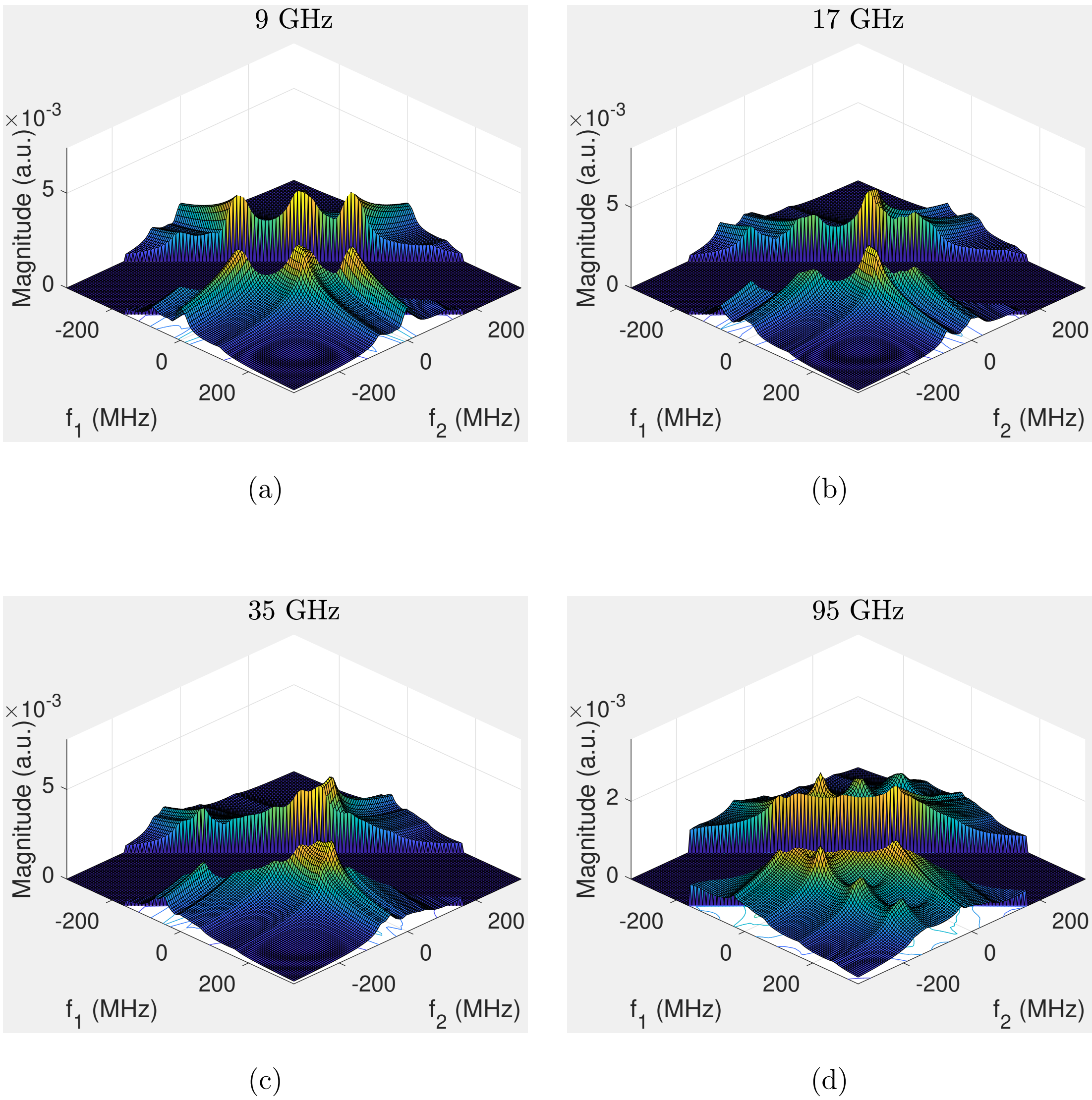

FIG. C.4: Effect of ESR frequency on slow-motional 2D-ELDOR spectra: a) 9 GHz, b) 17 GHz, c) 35 GHz, d) 95 GHz. Here $T_{mix} = 200\ ns$, $c_A = c_B = 0.5$, $k_{sym} = 10^6 s^{-1}$, jump angle $\beta_d = 90°$. Other parameters same as Fig. 6.