Supplementary Information

Table of contents:

A. NUMBER OF FREQUENCY GRID POINTS NEEDED FOR AN ACCURATE 2D-ELDOR SPECTRUM

To estimate the number of grid points necessary to obtain an accurate 2D-ELDOR spectrum, we first calculate a reference 2D-ELDOR spectrum with $n = 1000$ frequency grid points through the regular Arnoldi method. We can be confident that $n = 1000$ corresponds to an extremely high resolution 2D-ELDOR spectrum. Then for $n = 100, 200, 300, 500$, we calculate the 2D-ELDOR spectrum through the regular Arnoldi method again. For each value of n, we use spline interpolation to interpolate to the reference case ($n = 1000$). For each point in the 2D-frequency grid of 1000×1000 points, we then evaluate the relative error between the true value of $S_{c-}(f_1, f_2)$ and the interpolated value of $S_{c-}(f_1, f_2)$ based on the smaller value of n. The maximum of the relative errors (MRE) over the 1000×1000 grid, for each value of n, is shown in Fig. A.1. As expected, this error decays to 0 as the grid becomes finer, i.e., n increases. We take our threshold to be 1% MRE, to guarantee a sufficiently accurate calculation for purposes of non-linear least squares fitting to experimental data.

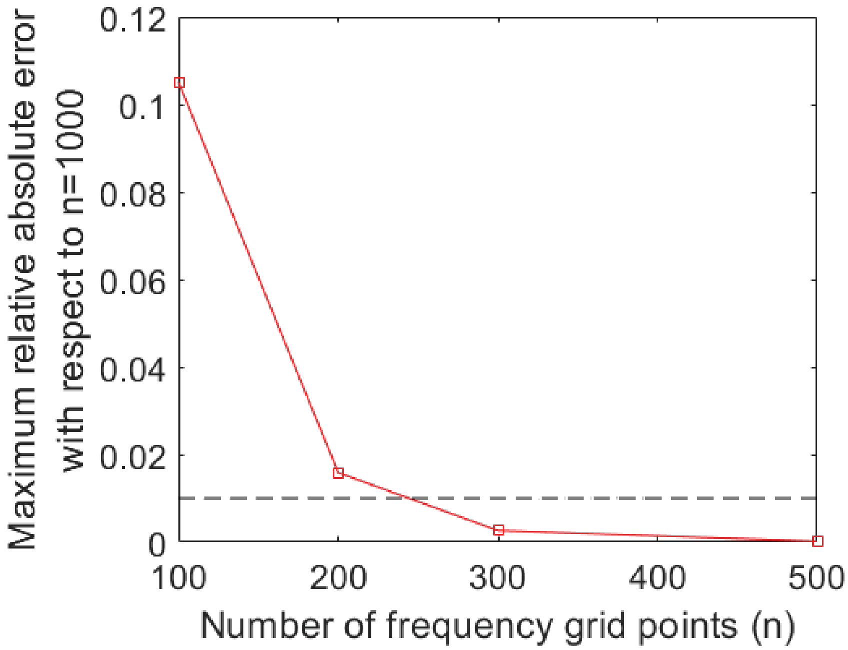

FIG. A.1: $R_{\parallel} = 10^5 s^{-1}, k_{sym} = 10^6 s^{-1}$, mixing time $T_{mix} = 500\ ns$. The black dotted line indicates the 1 % error level, corresponding to $n \sim 250$. Other parameters are as in Fig. 6.

B. NUMBER OF FREQUENCY GRID POINTS NEEDED FOR AN ACCURATE CW SPECTRUM

To estimate the number of grid points necessary to obtain an accurate CW spectrum, we first calculate a reference integrated CW spectrum with $n = 1000$ frequency grid points. We can be confident that $n = 1000$ corresponds to an extremely high resolution CW spectrum. Then for $n = 100, 200, 300, 500$, we calculate the integrated CW spectrum again. For each value of n, we use spline interpolation to interpolate to the reference case ($n = 1000$). For each point in the 1D-frequency grid of 1000 points, we then evaluate the relative error between the true value of $S_{c-}(f_1, f_2)$ and the interpolated value of $S_{c-}(f_1, f_2)$ based on the smaller value of n. The maximum of the relative errors (MRE) over the 1000 frequency grid points, for each value of n, is shown in Fig. B.1. As expected, this error decays to 0 as the grid becomes finer, i.e., n increases. We take our threshold to be 1% MRE, to guarantee a sufficiently accurate calculation for purposes of non-linear least squares fitting to experimental data.

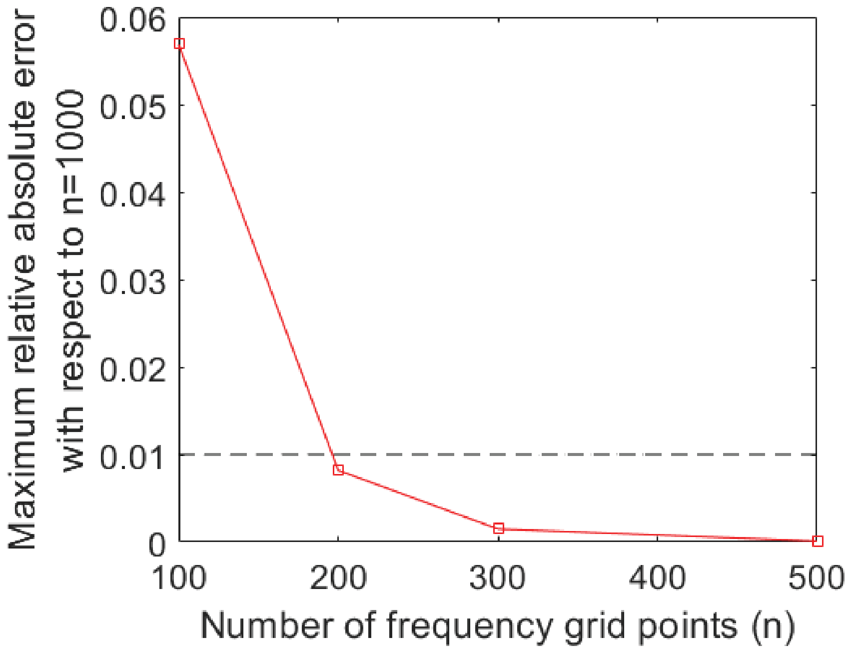

FIG. B.1: $R_{\|} = 10^5 s^{-1}$, diffusion tilt angle $\beta_d = 90°$. The black dotted line indicates the 1% error level, corresponding to $n \sim 200$.