Singlet excitation in intermediate magnetic equivalence regime and the field cycling study of singlet-triplet leakage

Boris Kharkov, [a] Xueyou Duan, [b] Emily S. Tovar, [b] James W. Canary [b] and Alexej Jerschow [*b]

[a.] *Laboratory of Biomolecular NMR, Saint Petersburg State University, Saint Petersburg, Russia.*
[b.] *Department of Chemistry, New York University, 100 Washington Sq. East, New York, NY 10003 USA*
E-mail: alexej.jerschow@nyu.edu

1. Measuring chemical shift difference and the in-singlet J-coupling constant

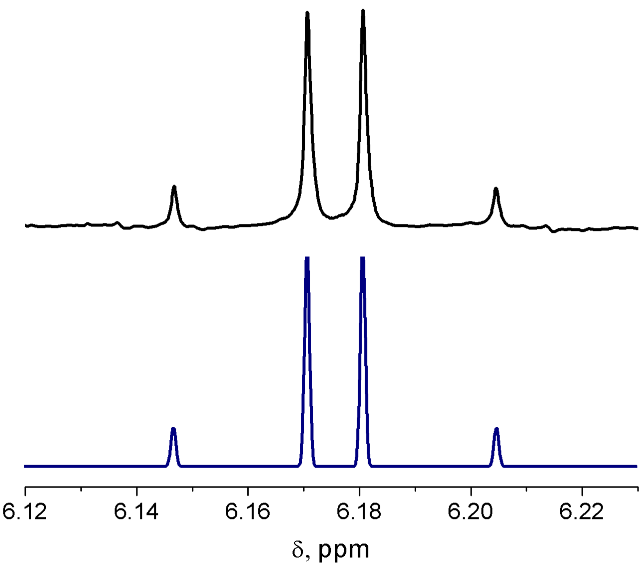

Fig. S1. Experimental (top) and simulated (bottom) ^{1}H spectra of vinyl protons in the *tert*-butyl propyl maleate diester (structure **2**).

Since the vinyl hydrogens in maleate are in the intermediate coupling regime, the chemical shift difference and the in-singlet J-coupling constant were determined by fitting the experimental ^{1}H vinyl multiplet. The simulated and the experimental spectra are compared in Figure S1, and the procedure gave $\Delta\delta = 0.024$ ppm for the shift difference, and $J = 12$ Hz for the coupling constant.

2. M2S/CSS spin state trajectory simulation

Figure S2 shows the simulated trajectory of four density matrix components in the course of the M2S/CSS singlet excitation sequence (Figure 1 in main text). The simulation parameters corresponded to those used in the experiment, except that the finite duration of the pulses was neglected, and the number of cycles was different, for the reason described in the main text ($n_1 = 12$). At the end of the sequence, a complete transfer of the x-magnetization to singlet-triplet coherence is achieved, as represented by the buildup of the $I_{y1} - I_{y2}$ component, at time point $t = 514\ ms$ (time from the beginning of pulse program to the end of the "n_1" pulse train), as seen in Fig. S2.

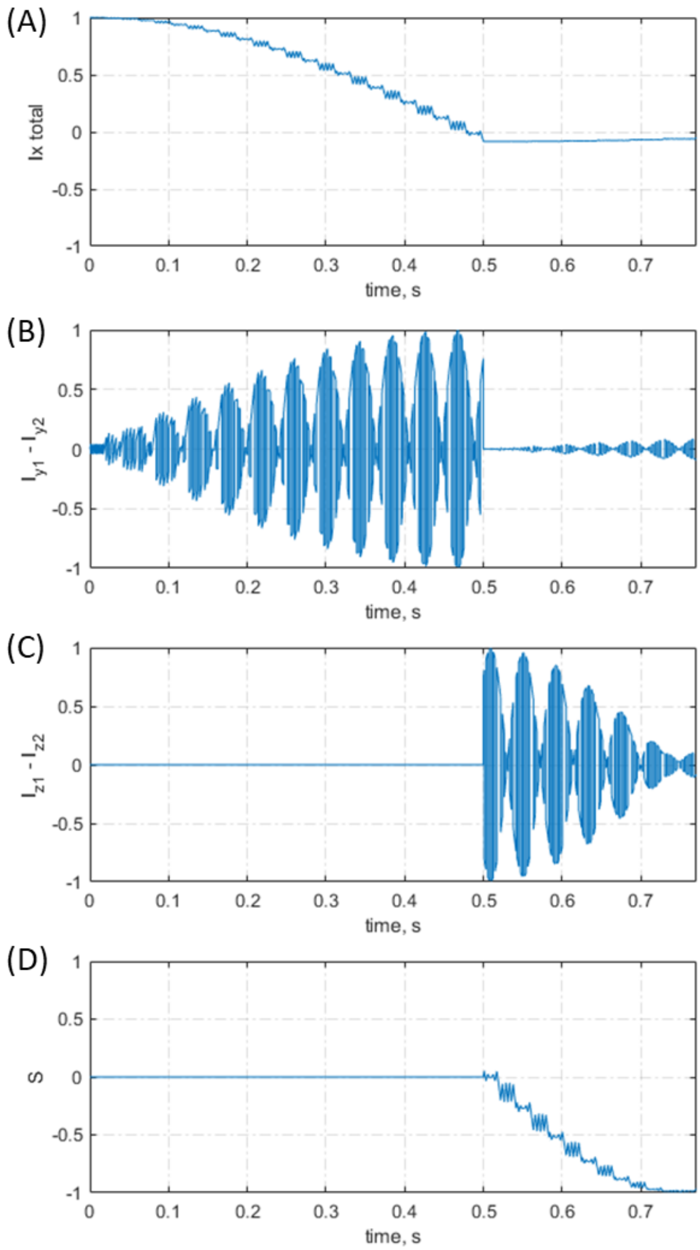

Fig. S2. Trajectories of different density matrix components during the M2S/CSS pulse sequence.

After that, a 90º pulse followed by a CSS element of $1/4J$ duration turns this component into $I_{z1} - I_{z2}$ singlet-triplet coherence, at time point $t = 535$ ms. This coherence is transferred to singlet order by $n_2 = 6$ cycles with CSS sequences inserted in the delays between them, at time point $t = 792$ ms.

3. Sample lift for field cycling

A sample lift was designed for transporting the sample to desired positions within the magnet bore during the pulse sequence upon the receipt of a trigger signal. The apparatus was based on an Arduino Uno microcontroller and the programming code and the Arduino circuit scheme can be obtained from the authors upon request

The correspondence between position and magnetic field was established using a field calibration chart provided by Bruker for this magnet (Figure S3).

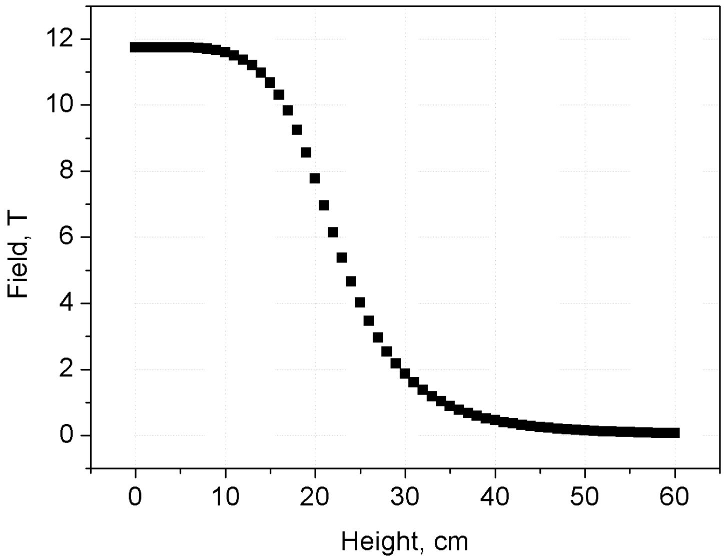

Fig. S3. Magnet field calibration profile. Provided by Bruker for this magnet.