

Dynamic Nuclear Polarization of Oxygen-17

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Materials and Methods

a. Sample Preparation: Samples were prepared by mixing appropriate amounts of *d*₈-glycerol, D₂O and 35% to 74% ¹⁷O labeled H₂O in 60:40 v/v% *d*₈-glycerol - H₂¹⁷O; 60:30:10 v/v% *d*₈-glycerol - D₂O - H₂¹⁷O; 60:30:10 v/v% *d*₈-glycerol - D₂O - H₂O with 20 mM TOTAPOL. All isotopes were purchased from Cambridge isotope laboratories and used without further purification. DNP samples were center-packed into 4 mm (40-50 μl volume) sapphire rotors (Insaco Inc.). Vespel drive tips were cryo-epoxied, and Kel-F spacers were used to center the samples in the rotors.

b. DNP-enhanced solid-state NMR spectroscopy: DNP experiments were performed using a custom-built instrument, consisting of a 140 GHz gyrotron and a 212 MHz (¹H frequency) MAS NMR spectrometer (courtesy of D. Ruben). Spectra were recorded using a custom-built 4 mm double resonant (¹H and ¹⁷O) circuit and a 4 mm Revolution NMR Kel-F stator. Experiments were performed under static conditions at temperatures < 88 K.

All one-dimensional experiments were acquired using cross-polarization echo experiment. High-power decoupling of 80 to 90 kHz was applied during acquisition for all experiments. Contact times were varied between 0.3 and 3 ms, while ¹⁷O Hartmann-Hahn match condition was optimized to a $\gamma B_1 = 35$ kHz. Recycle delays were set to 8 seconds. CP-QCPMG¹ was used to determine the spin-spin relaxation (*T*₂). ¹⁷O{¹H} SEDOR experiments were recorded using similar parameters as the ones described above with 16 co-added transients and a recycle delay of 6 s. Fixed time SEDOR was implemented using a 5 μs increment on the ¹H channel. Two-dimensional ¹⁷O{¹H} HETCOR and HETCOR-QCPMG experiments were recorded using 64 and 8 co-added transients, a dwell time of 1

to 10 μ s and 40 to 64 t_1 points. Spectra were referenced relative to liquid water (at 298 K) set to 0 ppm. Spectra were processed within NMRPIPE² software².

c. *Calculations:* SIMPSON 3.1³ simulations were performed using two- to five-spin systems including one ¹⁷O spin and up to four ¹H spins in order to determine the average ¹H-¹⁷O bond length. Each simulation employed powder averaging over ZCW986 crystallite orientations and a full set of dipolar coupling tensors prepared using the SIMMOL software.⁴ On average, a three-spin simulation took five minutes per 100 iterations while running in parallel on 8 - 2.66 GHz cores. All simulations either converged or reached a local optimum after 100-300 iterations. Experimental spectra were simulated using WSolids⁵ and SPINEVOLUTION⁶ in order to determine the quadrupolar coupling parameters for ¹⁷O.

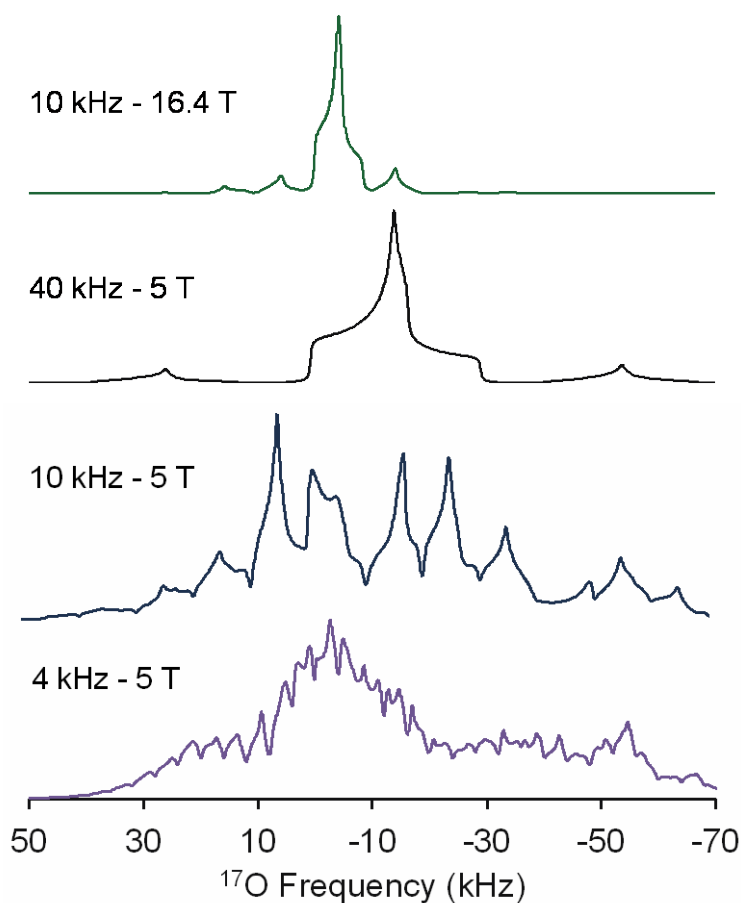


Figure S1: ¹⁷O MAS NMR SPINEVOLUTION simulation of a water site ($C_Q = 6.8$ MHz, $\eta = 1$, $\delta_{iso} = 0$ ppm) at 5 T (DNP field in this paper) and 16.4 T (high field). Due to the quadrupolar interaction, MAS (>35 kHz) would be required to isolate the CT from the spinning sidebands. An alternative option is increasing the main magnetic field

whereby the CT is narrowed allowing a lower spinning frequency (i.e., 10 kHz at 16.4 T) to narrow the 2nd order powder pattern.

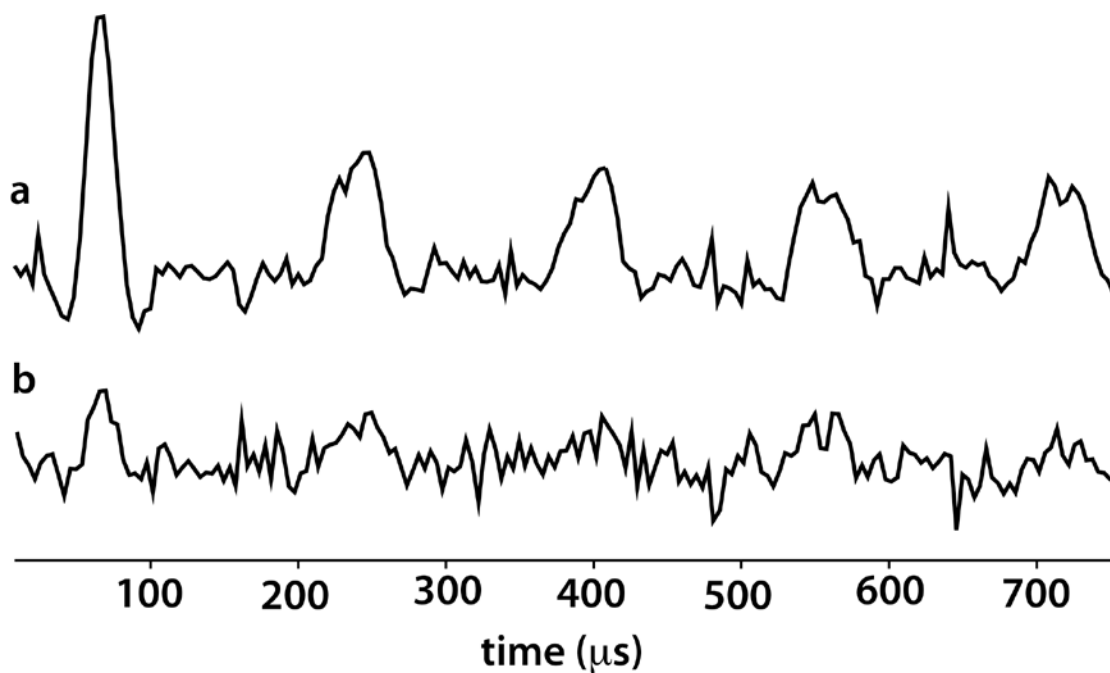


Figure S2: ^{17}O FID from a CP-CPMG DNP NMR experiment displaying the first five echoes for a 60 d⁸-glycerol/ 30 D₂O / 10 H₂¹⁷O using 35% labeled H₂O and an identical sample with natural abundance (N.A. ^{17}O - 0.038 %).

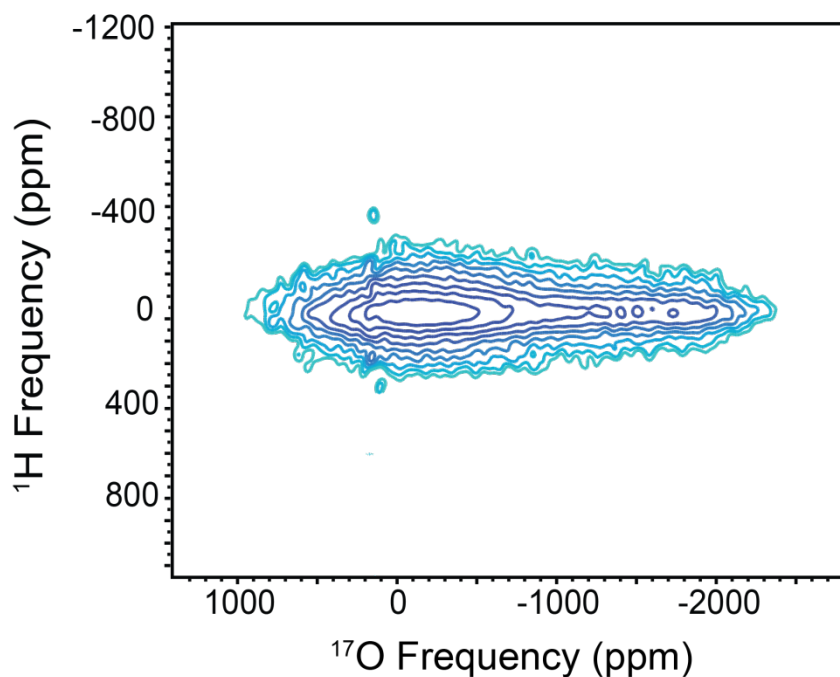


Figure S3: $^{17}\text{O}\{^1\text{H}\}$ HETCOR spectra of a water/glycerol glass using solid-state DNP NMR.

References:

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