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Supporting Information

SAMBADENA Hyperpolarization of ^{13}C-Succinate in an MRI: Singlet-Triplet Mixing Causes Polarization Loss

Stephan Berner,* Andreas B. Schmidt, Mirko Zimmermann, Andrey N. Pravdivtsev, Stefan Glöggler, Jürgen Hennig, Dominik von Elverfeldt, and Jan-Bernd Hövener*

Supplementary Information

1. Quantification of polarization yield

The ^{13}C hyperpolarization yield was quantified by comparing the MR signals of the hyperpolarized sample and a thermally equilibrated reference (≈ 7 mL acetone with a natural abundance of ^{13}C of $F_{REF} \approx 1.1$ % and $F_{REF} \times c_{REF} \times V_{REF} \approx 0.1$ mol ^{13}C). The absolute polarization level is given by

$$P = P_{REF} \times N_{REF} \frac{F_{REF} \times c_{REF} \times V_{REF} \times S_{HP}}{F_{HP} \times c_{HP} \times V_{HP} \times S_{REF}}$$

Here, the index "HP" or "REF" denotes parameters of the hyperpolarized or reference sample, respectively. N is the number of scans ($N_{HP} = 1$), c is a concentration, V is a sample volume, S is a numerically integrated signal in the real spectrum (TopSpin 3.5, Bruker, Germany) and F is a fraction of ^{13}C nuclei (here, $F_{HP} = 0.99$ and $F_{REF} = 0.01$). V_{HP} was 800 µL because during bubbling 200 – 300 µL were flushed out of the reactor (and the active volume of the receiver coil). P_{REF} is the thermal polarization at room temperature ($T = 293$ K) and field strength of $B_0 = 7$ T. According to the Boltzmann statistic, P_{REF} equals to:

$$P_{REF}\,(^{13}C, 7T) = \tanh\left(\frac{\hbar \gamma_C B_0}{2 k_B T}\right) = 6.137 \times 10^{-6}$$

Here, ħ is the reduced Planck constant and γ_C is the gyromagnetic ratio of ^{13}C nuclei. Note that a pH_2 fraction of 100 % and complete hydrogenation were assumed for quantification, which was not the case in the experiments. As a result, the reported polarization levels are likely underestimated. The spectra were processed with a line broadening (corresponding to 10 Hz or 1 Hz for data acquired with the MRI system or the NMR spectrometer, respectively) and automatic phase- and baseline correction (TopSpin 3.5, Bruker, Germany).

2. ^1H NMR spectra during bubbling with pH_2

The field homogeneity was probed during bubbling and hydrogenation. To this end, 1 mL of H_2O was filled into the reactor, which was sealed subsequently. 20 bar pH_2 were filled from the bottom of the reactor abruptly by opening a magnetic valve V1 for two seconds using setup 1 and setup 2. A series of global ^1H scans (10° flip angle, TR = 300 ms) were performed during t_{pH2} and t_{delay} or t_{bypass}. For quantification, a Lorentzian was fitted to the spectra and the Full Width Half Maximum (FWHM) was determined (Figure S1). Field homogeneity is significantly improved by using setup 2 (smaller line width and less fluctuation). In both cases, however, the NMR signal was extremely broadened during bubbling and quantification of the line width was not possible. An exemplary spectrum is provided (Figure S2).

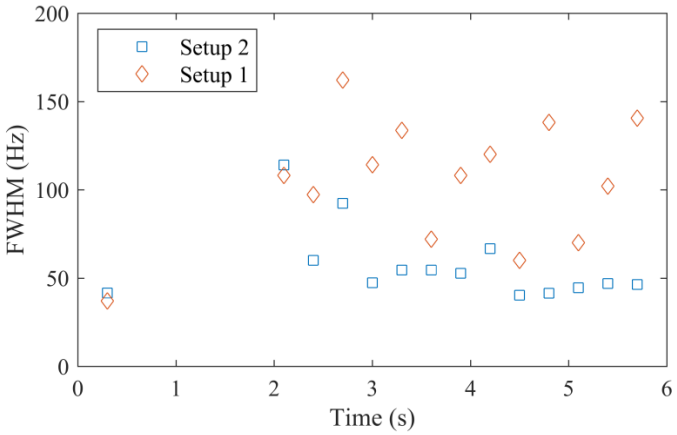

Figure S1: Line width of the ^1H water resonance during bubbling using setup 1 and setup 2. *During bubbling ([0.3, 2] seconds), distortions of the field lead to signal cancellation and fitting was not possible. After roughly two seconds, the water was tranquilized and Lorentzian-like line shapes were obtained. Note that at t = 0.3s, bubbles were not formed yet.*

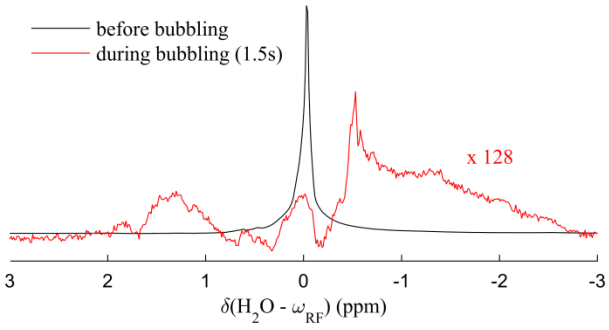

Figure S2: Poor field homogeneity during bubbling leads to signal cancellation. *Global ^{1}H spectra were acquired before (**black** line) and during bubbling pH_2 (**red** line; 1.5s after opening the pH_2 valve V1). The red spectrum is magnified by a factor of 128.*

3. MLEV16 sequence signal in oscilloscope

A loop coil was placed in the isocenter of the $^{1}H/^{13}C$ receive-transmit coil and connected to an oscilloscope (TDS 1002, Tektronix, USA). An MLEV16 sequence ($t_{MLEV,90°}$ = 1ms) was played out for 5 seconds and the induced signal in the loop coil was recorded (Figure S3). The length of one 90° excitation was set to $t_{MLEV,90°}$ = 1ms. Note that the power limitations of the resonator were met and the complete decoupling sequence was played out. Hence, low polarization does not originate from interrupted MLEV16 sequences but rather from bad field homogeneity and (off-resonant) decoupling during t_{pH2} and t_{delay}.

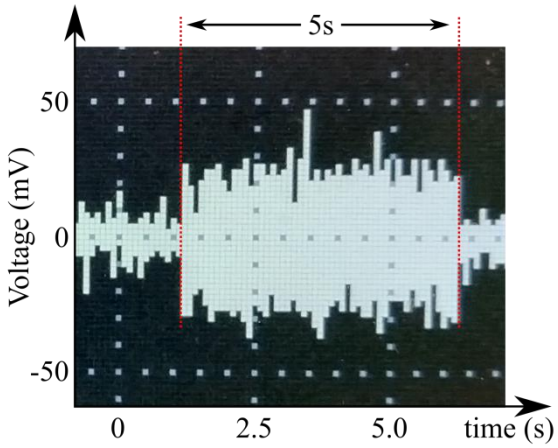

Figure S3: Monitoring of an MLEV decoupling sequence. *To verify that the decoupling sequence is not stopped due to power limitations of the volume resonator, an MLEV16 decoupling sequence was monitored. Decoupling was played out for 5 seconds by the volume resonator, while a loop coil was placed in its isocenter and the induced voltage in the loop was recorded with an oscilloscope. The decoupling sequence was not interrupted as the vendor's power limitations were met.*