

MRI of ^1H Long-Lived States Originated from ParaHydrogen Induced Polarization in Cs-Symmetric Molecules using a Clinical MRI System

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Purpose

Parahydrogen Induced Polarization (PHIP) creates a hyperpolarized spin state by hydrogenation of a double or triple bond with parahydrogen (1). A drawback of all the hyperpolarization techniques, in particular those based on ^1H , is the limited lifetime T_1 . A longer lifetime can be achieved by storing the hyperpolarization as a singlet spin state. A requirement for the singlet state preservation is the reduction of the chemical shift difference usually achieved by moving the sample to a low field, or applying dedicated pulse sequences (2). Recently, it was shown for the Cs-symmetric molecule dimethyl maleate that the hyperpolarized proton singlet state can be stored at 7 T for 4 min (3,4) with no need of RF pulses. To yield measurable magnetization the sample was transported to the resonance magnetic field at 0.1 T allowing for singlet-triplet conversion via level anti-crossing. Here, the singlet-triplet conversion is performed inside the observation field by an RF pulse sequence and combined with imaging.

Methods

Experiments were performed on a 1.5 T clinical NMR scanner (Magnetom Sonata, Siemens) using a homemade double resonant $^1\text{H}/^{13}\text{C}$ coil optimized for 10 mm NMR tubes. 500 mg of the precursor molecule dimethyl acetylenedicarbonate were filled with 10 mg catalyst and 2.6 g acetone into an NMR pressure tube. The samples were heated up to 70°C, pressurized with 4 bar of 93% enriched parahydrogen and vigorously shaken inside the bore of the NMR scanner for 5 s. After a delay of 3 min, the singlet-triplet conversion was realized with the chemical shift scaling (CSS) sequence (5), which generates an effective Hamiltonian, scaling the chemical shift by a factor $\lambda = \tau_2/(\tau_1 + \tau_2)$. To allow the singlet triplet conversion, the chemical shift difference of the vinyl and the methyl groups in the dimethyl maleate molecule needs to be scaled from the magnetic field B_0 of 1.5 T to the resonance field of 0.1 T. Therefore, τ_1 and τ_2 were set to 12.56 ms and 1 ms, respectively. 80 cycles of the CSS sequence were used, whereas the phases of the successive 180° pulses follow an XY-16 supercycle. The CSS sequence was used prior to every phase encoding step of a gradient echo sequence (FA: 90° , TR/TE: 1700/3.5 ms, FOV: 20x20 mm, 16x16 pixel) using a centric reordering scheme. The decay of the signal with the number of conversions was obtained by acquiring an FID after each conversion with the same TR time. This measurement was used to correct the kSpace data of the imaging experiments.

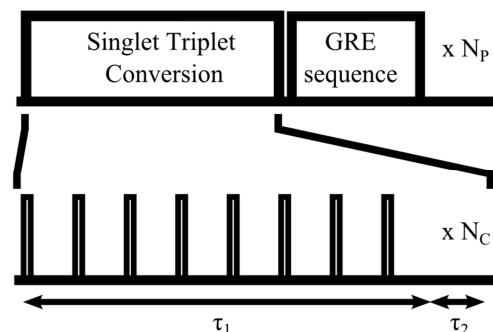


Fig. 1. Sequence scheme. Before every k-space line of the GRE sequence a singlet triplet conversion was performed by the CSS sequence using $N_c=80$ cycles.

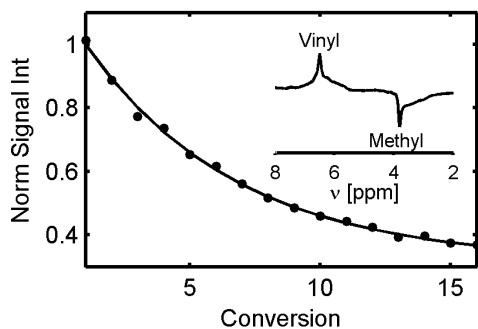


Fig. 2. Exponential decay of the signal using multiple singlet-triplet conversions. An example spectrum is shown top right.

Results

An example spectrum of dimethyl maleate after a singlet-triplet conversion realized by the CSS sequence is shown in Figure 2. The reference measurements show that the 16th conversion yields a signal of around 40% in comparison to the first. However, the signals show only small deviations from the fitted exponential decay. The image shows an SNR up to 40 (c.f. Fig. 3). In phase direction small artifacts are visible outside the sample. Notice that the proton image was acquired after a waiting time of 3 min inside the observation field.

Discussion

The CSS sequence shows a good feasibility to realize the singlet-triplet conversion avoiding the movement of the sample. The sequence can be combined with an imaging sequence, whereas the exponential decay should be corrected reducing the width of the point spread function (PSF) in phase direction. However, further investigations should be performed to find a compromise between PSF optimization and SNR, which is reduced by the decay correction. Alternatively, one singlet-triplet conversion can be combined with an EPI or RARE echo train. Nevertheless, the SNR amplitude being acquired 3 min after the reaction is so far mainly limited by the small amount of conversion realized by the catalyst. The inhomogeneity inside the NMR tube is caused by susceptibility artifacts.

Conclusion

A new method was developed to realize the singlet-triplet conversion in a Cs-symmetric molecule by an RF sequence. The potential to combine this method with imaging sequences has been shown. The use of the singlet state originated from pH_2 gave the possibility to acquire an image of hyperpolarized protons after a waiting time of minutes. This is an important requirement to fulfill in many applications as for example imaging with medical purposes.

References

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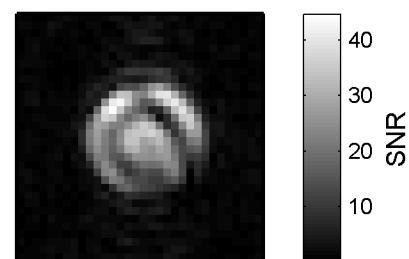


Fig. 3. Image of hyperpolarized dimethyl maleate in a 10 mm NMR tube using the singlet-triplet conversion in combination with a gradient echo sequence.