

Field dependency of Parahydrogen Induced Hyperpolarization (PHIP) of ^1H and ^{19}F in Earth's Magnetic Field

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Introduction

Although NMR at low and ultra-low fields suffers from strongly reduced signal-to-noise ratio (SNR) it provides several advantages among them the simultaneous detection of proton and heteronuclei resonances.[1] Additionally, NMR spectrometers based on induction coils using the B_0 provided by the magnetic field of the earth are mobile and inexpensive compared to high-field devices. Usually, the low SNR is increased by pre-polarizing the sample but other strategies such as hyperpolarization methods may offer a much higher degree of polarization. Recently, PHIP-induced transfer of hyperpolarization to ^{19}F was demonstrated in the earth's magnetic field. To generate and transfer hyperpolarization, field cycling had to be applied.[2] [3] Here, we demonstrate that field cycling through fields in the mT range allows transferring PHIP-generated hyperpolarization to ^{19}F . Additionally, we show that this transfer is field-dependent.

Methods

The measurement of small substrate concentrations under earth's field conditions was proven by a coil-based earth's field NMR spectrometer which was optimized for standard 10 mm-NMR sample tubes. The detection coil was designed as a gradiometer to reduce environmental noise.

The sample contained 0.3 ml 1-ethynyl-3-fluorobenzene (Sigma Aldrich, Germany), 1.7 ml acetone-d₆ (eurisotop, France) and the dissolved catalyst [Rh (cyclo-octadiene) diphenyl-phosphanyl butane)][BF₄] (Santa Cruz Biotec, USA). The hydrogenation of 1-ethynyl-3-fluorobenzene to 3-fluorostyrene was induced by shaking the sample for 10 s under a parahydrogen atmosphere of about 6 bar. The reaction scheme is depicted in fig. 1.

Subsequently the sample was inserted into the detection coil of the earth's magnetic field spectrometer and a variable preparation field of several mT (fig. 2) was switched on with a time constant of 11 ms. After 3 s the preparation field was diabatically turned off within 4 ms and a 90° excitation pulse with a frequency of 1820 Hz was applied. Afterwards the signal was acquired for 0.7 s with a bandwidth of 180 Hz and a FFT was performed.

Results and Discussion

Without PHIP, the substance did not show any NMR signal in a single scan spectrum even when applying a prepolarization field of 62.4 mT and a 90° excitation pulse. After applying the PHIP procedure the substance exhibited clear resonances at the proton frequencies of about 1880 Hz and the fluorine frequencies around 1770 Hz (fig. 3). Figure 2 shows the field dependency of the signal magnitude.

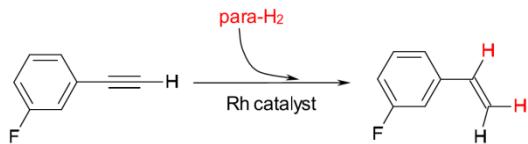


Fig. 1 Reaction scheme: hydrogenation of 1-ethynyl-3-fluorobenzene to 3-fluorostyrene.

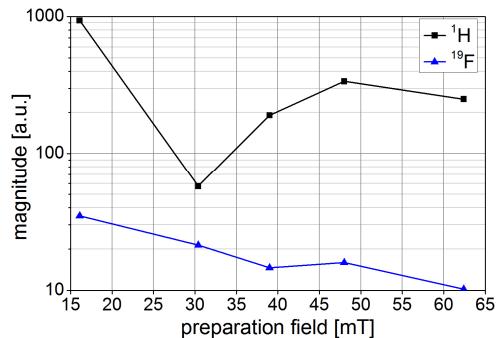


Fig. 2 Dependency of the signal magnitude on the preparation field.

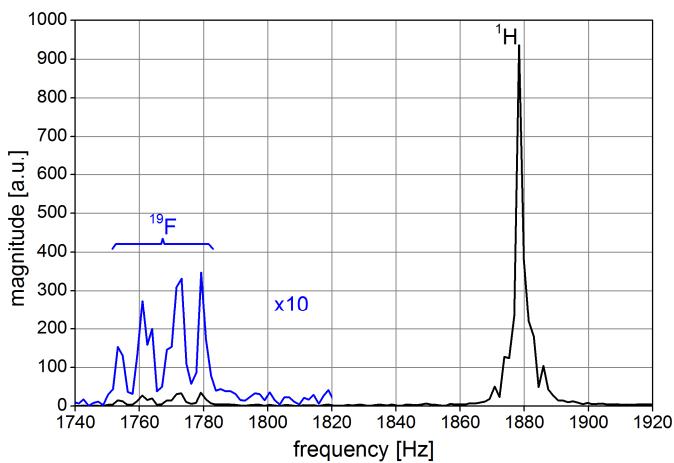


Fig. 3 Single scan magnitude spectrum of hyperpolarized 3-fluorostyrene.

Conclusion

These results show, that both the diabatic-adiabatic field cycling procedure with zero crossing of Hamans et al.[3] as well as our field cycling procedure (first increasing and then lowering the field strength) converts the induced p-H₂ spin order into hyperpolarization of the added protons and the coupled fluorines within 3-fluorostyrene. The efficiency of the conversion depends on the field strength (fig. 2). The simultaneous detection of hyperpolarized ^1H and ^{19}F at low field allows the direct comparison of the signal intensities between ^1H and ^{19}F resonances which is important for a quantitative analysis of the spectra and the hyperpolarization transfer efficiency. The sensitivity gain due to PHIP is strong enough to detect single shot NMR spectra at very low fields even if no NMR signals are observed originating from Boltzmann population.

References

[1] S. Appelt et al., *Chem. Phys. Letters* 440, 308-312, **2007**. [2] U. Bommerich et al., *Phys. Chem. Chem. Phys.* 12, 10309-10312, **2010**. [3] B.C. Hamans et al., *J. Magn. Reson.* 212, 224-228, **2011**.