Low RF-field strength cross polarization combined with photo-induced non-persistent radicals for clinically applicable dDNP

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Low RF-field strength cross polarization combined with photo-induced non-persistent radicals for clinically applicable dDNP

Work in progress

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Cross Polarisation for SPINlab-like polarisers using non-persistent radicals is demonstrated.

The efficiency of the transfer from protons to carbon is modest at the currently achievable low B₀ fields of 4-5 kHz still yielding 13C polarisation levels up to 15 %. Based on the presented results, we foresee polarisation levels superior to direct 13C DNP in our next generation of double-tuned probes incorporating local tune and match.

Abstract

We demonstrate the possibility of ¹H Dynamic Nuclear Polarization followed by cross polarization to carbon (DNP-CP) using a modified low cost benchtop console (Kea2) equipped with an external amplifier (Tomco) and a SPINlab-like dissolution DNP polarizer i.e. using the same fluid path and allowing for hyperpolarization of a full human dose. Cross polarization (CP) using Laboratory Frame De- and Remagnetisation (LAFDR) was found superior to alternative sequences at the limited B₀ fields employed. Faster build-up rates compared to ¹C DNP are demonstrated using TEMPOL (4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl) and DNP-CP. ¹C polarisations up to 15 % are achieved using non-persistent UV-induced radicals.

Introduction

Dissolution Dynamic Nuclear Polarization (dDNP) is used to enhance the MR signals in imaging by factors of 10,000 and in general to eliminate the relaxation effect, the radical essential for DNP needs to be removed during dissolution. Use of pyruvic acid (PA) non-persistent photo-induced radicals for dDNP has been demonstrated to solve this issue and recently polarization build-up on protons with t_{1/2} = 690 s and 70 % polarization has been presented⁴.

Methods

Overview

CP by Laboratory Frame De- and Remagnetisation (LAFDR)

Experimental Results

DNP-CP using TEMPOL as radical

DNP-CP using UV-induced radicals

DNP-CP using UV-induced radicals with broadened linewidth due to hyperfine coupling

Results

The efficiency of DNP-CP depends on the build-up rate and final polarization achieved on protons as well as the transfer efficiency of the CP sequence.

1. For B₀=5 kHz LAFDR (fig. B) was found to outperform other CP sequences (data not shown).

2. On the TEMPOL containing sample, DNP-CP using optimised LAFDR outperforms ¹C DNP for build-up times < 1 hour, and 20% ¹C polarization was achieved in only 20 min (fig. C).

3. Using ¹¹CJCPA as the substrate for non-persistent radicals gives a too narrow EPR-line for efficient ¹H DNP resulting in poor DNP-CP performance (fig. D).

4. Introduction of hyperfine coupling to the unpaired electron by ¹C labelling in position 2 increases the EPR linewidth yielding fast ¹H DNP build-up, but a polarization of only 18 %, and therefore still inefficient DNP-CP (fig. E).

5. Deuterating the methyl group of PA increases the ¹H DNP polarization to 62 % and maintains the efficiency of CP. This yields a final ¹C polarization of 15 % after CP (fig. F).

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Conclusion and Outlook

We have demonstrated DNP-CP on a clinical-compatible SPINlab-like polarising using a low-cost benchtop console equipped with an external amplifier. Moreover, the technique has been combined with non-persistent UV-induced radicals. At the current state, with B₀=5 kHz, direct ¹C DNP still outperforms the DNP-CP. However, the goal is to implement local tuning of the probe to achieve sufficient B₀ fields to increase the transfer efficiency. We expect that sufficiently strong B₀ fields are achievable for this setup to outperform direct ¹C DNP both with respect to build up rates and polarization levels.

References


