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Field-Cycled Proton-Electron Double-Resonance Imaging (FC-PEDRI) of ^{15}N Nitoxice Free Radicals at 1.1 mT EPR Field

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ABSTRACT

Field-Cycled Proton-Electron Double-Resonance Imaging (FC-PEDRI) was used to image ^{15}N nitroxide free radicals by saturation of π Electron Paramagnetic Resonance (EPR) transitions. To locate EPR π transitions, field-cycled dynamic nuclear polarization (FC-DNP) experiments were performed with a 1 mM ^{15}N D_{17} TEMPOL solution sample (a ^{15}N nitroxide system) at an EPR frequency of 52.52 MHz. FC-PEDRI experiments were performed at a low magnetic field of 1.1 mT for EPR with a proton NMR detection field of 59 mT. The SNR of the difference image was larger than that using ^{14}N nitroxide.

Keywords: -

INTRODUCTION

Proton-Electron Double-Resonance Imaging (PEDRI) is a powerful technique for imaging free radicals in biological samples or animals. This technique has been developed by irradiation both electrons (EPR) and protons (NMR) in a sample. Also called Dynamic Nuclear Polarization Imaging (DNPI) or Overhauser Imaging (OI), it utilizes the Overhauser effect (Overhauser, 1953), involving the observation of the NMR signal of a solvent while irradiating the EPR resonance of a free radical solute. The free radical's unpaired electrons are irradiated by applying irradiation (radiowave or microwave) at the EPR frequency, and the NMR signal is obtained in the usual way by applying pulses of a radiowave at NMR frequency. If there is good magnetic coupling between the unpaired electrons and the water hydrogen nuclei, the EPR irradiation can cause a transfer of polarization from the electrons to the nuclear spins or the solvent nuclei under study, resulting in a large increase in amplitude of the observed NMR signal.

Field-Cycled PEDRI or FC-PEDRI has been developed to reduce the problem of high RF power deposition in a sample from the EPR irradiation, without reducing the image signal-to-noise ratio (SNR) (Lurie. *et al.*, 1989). Field-Cycled Dynamic Nuclear Polarization (FC-DNP) has been also developed to allow the positions and amplitudes of EPR spectral lines to be determined via the Overhauser effect (Lurie, McLay *et al.*, 1991). In addition, with the use of FC-DNP, FC-PEDRI of ^{14}N (electronic spin S = 1) nitroxide free radicals by saturation of π transitions was reported at a magnetic field between 0.3-6.2 mT with an EPR frequency in the 45-133 MHz range (Polyon *et al.*, 2006). In these frequencies, SNR of the difference images from saturation of π transitions were between 2.1 and 6.

The purpose of this work was to image ^{15}N (electronic spin S = 1/2) nitroxide free radicals at low EPR frequency and low evolution magnetic field.

EXPERIMENTAL DETAILS

FC-PEDRI experiments were performed with a 5.5 ml sample of 1 mM ^{15}N D_{17}-TEMPOL solution for the ^{15}N system (T_1 of 924 ms) at EPR frequencies ranging from 45 MHz to 133 MHz. In the experiments a 5.5 ml $CuSO_4$ solution (which is not a free radical) was used as a reference sample. In our work, FC-DNP experiments were first performed to obtain EPR spectra of π transitions, and then FC-PEDRI experiments were carried out. All studies were carried out at room temperature using the whole-body sized field-cycling MRI system (Lurie *et al.*, 1998). An EPR pulse was produced by our eight-leg circularly-polarized low-pass birdcage resonator (Polyon *et al.*, 2006). In addition, a solenoid coil tuned to 2.495 MHz was used to detect the NMR signal at a magnetic field of 59 mT.

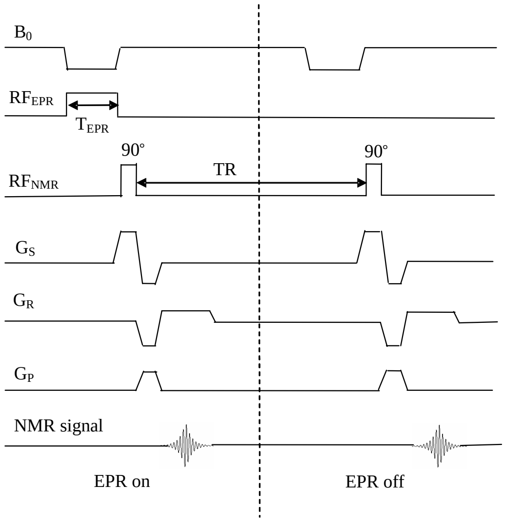


Figure 1 An interleaved FC-PEDRI pulse sequence. A period of EPR irradiation precedes every alternate NMR excitation, allowing 'with EPR' and 'without EPR' images to be collected effectively simultaneously.

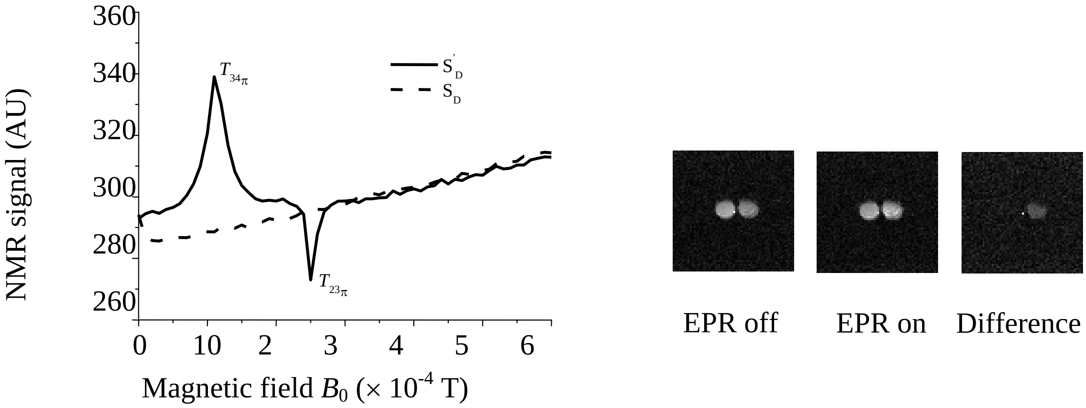
FC-PEDRI experiments were performed by using an evolution magnetic field fixed for saturation of a π transition obtained from the previous FC-DNP experiments. An interleaved FC-PEDRI pulse sequence, used with a spin warp for free radical imaging (Figure 1) with EPR irradiation time (T_{EPR}) of 400 ms, detection time (T_D) of 60 ms, echo time (*TE*) of 26 ms, and repetition time (*TR)* of 1200 ms, was used to allow images with and without EPR irradiation to be collected.

Subtraction yielded a difference image which shows non-zero intensity only in regions of the sample containing the free radical of interest.

The images were 64x64 with a field of view (FOV) of 80 mm, a slice thickness of 25 mm, and an EPR power (*P*) of 15 W.

RESULTS AND DISCUSSION

Figure 2 shows FC-DNP spectra and three 64x64 images (EPR-off, EPR-on and difference) from FC-PEDRI experiments at an EPR frequency of 52.52 MHz with two 5.5 ml tube samples of 1 mM D_{17}-TEMPOL (a ^{15}N nitroxide system) and $CuSO_4$ solutions. From the FC-DNP technique, the spectra show two EPR peaks of $T_{34\pi}$ and $T_{23\pi}$ transitions. S'_D and S_D are NMR signals with and without EPR irradiation, respectively.



(a) (b)

Figure 2 Results of FC-DNP (a) FC-PEDRI (b) experiments

In order to obtain low EPR power deposition in the sample, FC-PEDRI experiments with saturation of $T_{34\pi}$ were used with T_{EPR} of 400 ms, *TE* of 26 ms, *TR* of 1200 ms, FOV of 80 mm, a slice thickness of 25 mm and *P* of 15 W with the evolution magnetic field of 1.1 mT. This transition is obtained with a positive enhancement factor of 1.17. The measured SNR of the difference image was 5.6.

CONCLUSIONS

In order to obtain low EPR power deposition in the sample and still a good SNR, this work focused on experiments with ^{15}N nitroxide free radicals in a low magnetic field (1.1 mT) at a low EPR frequency (52.52 MHz) by saturation of the $T_{34\pi}$ transition, because it can be saturated at low magnetic field and low frequency. With a large positive enhancement factor, a good NMR signal can be obtained compared with our previous work (Polyon *et al.*, 2006). In our work the size of the sample was limited by the small double-resonance RF coil assembly.

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