Introduction

The purpose of this project is to develop pulsed dynamic nuclear polarization (DNP) techniques at high magnetic fields. Currently, pulsed DNP is desirable but not available at high fields [1]. Previous studies only presented data at X-band (0.35 T or 9.5 GHz) [2]. This project takes advantage of the state-of-the-art high power pulse EPR spectrometer (HiPER) operating at 3.35 T (94 GHz) and 1 kW power. The HiPER spectrometer was upgraded to excite and detect NMR signals efficiently, necessary for DNP experiments. DNP experiments were successfully performed on HiPER using continuous wave (CW) microwaves and using arbitrarily formed pulses at large peak pulse powers.

Experimental

The EPR and DNP enhanced NMR spectra were recorded using the high power pulse spectrometer HiPER at the EMR facility of the NHMFL, Tallahassee, with microwave source frequency $\nu = 94 \pm 0.5$ GHz. The spectrometer was upgraded with a SpinCore NMR spectrometer and custom non-resonant EPR probe with an integrated saddle coil for NMR. The HiPER spectrometer was used with a 2-channel arbitrary waveform generator to modulate the 94 GHz signals for pulsed and frequency chirp DNP sequences.

Results and Discussion

A $^{13}$C DNP field profile is shown in Fig. 1a. A sample of $^{13}$C-glycerol/H$_2$O (60/40 volume ratio) doped with 40 mM trityl-OX063 was used. The positive and negative peaks are separated by the $^{13}$C Larmor frequency, which is indicative of the cross effect. The fact that enhancement is saturated at low microwave power (~200 mW) further supports the cross effect mechanism. We obtained maximum enhancement of ~1,500 (~60% efficiency).

A $^1$H DNP field profile is shown in Fig. 1b, obtained on a sample of glycerol-d8/D$_2$O/H$_2$O (60/30/10 volume ratio) doped with 10 mM trityl-OX063. As opposed to the result in Fig. 1a), the EPR linewidth of trityl-OX063 is narrow compared to the $^1$H Larmor frequency, resulting in a solid effect field profile. The positive and negative peaks are separated by twice the $^1$H Larmor frequency. Furthermore, the enhancement (~30) is far from saturation at 200 mW of power, another characteristic of the solid effect. When pulsing with high power microwave, we obtained an NMR signal enhancement of 185 with ~5 W average microwave power (5 μs pulse / 1 kW peak power / 1 kHz repetition rate).

Preliminary chirp microwave pulses, shown in Fig. 1c, were recorded of the type used in integrated solid effect (ISE) pulsed DNP. The pulse length was 1 μs during which the frequency was swept in a range of 200 MHz by modulating with a 2-channel arbitrary waveform generator. The waveform was detected at 94 GHz.

Conclusions

In summary, we were able to perform NMR/DNP experiments on HiPER and generate chirp microwave pulses at 94 GHz. Preliminary results using low power CW as well as high power pulses are highly promising. Our next step will be performing pulsed DNP sequences including NOVEL and ISE as proposed previously.

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References