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Solid State Dynamic Nuclear Polarization of ^{1}H Nuclear Spins at 0.3 T and 4.2 K

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Abstract Here, I report solid state Dynamic Nuclear Polarization (DNP) of ^{1}H nuclear spins at 0.3 T and 4.2 K. The DNP polarizer was developed based on a commercial X-band Electron Spin Resonance (ESR) modified for DNP, in combination with a NMR console and a liquid-Helium cryostat. By detuning magnetic field, DNP spectrum was measured to find the optimal condition. At +3 mT detuned from on-resonance field, ^{1}H NMR signal of 60:40 glycerol/water frozen solution doped with 20 mM perdeuterated-Tempone was amplified 43 times. The ^{1}H spin polarization obtained at 4.2 K is over 3100 times higher than that at 300 K. The width of the DNP spectrum, which is five times broader than ESR spectrum, is inconsistent with solid effect or thermal mixing, and presumably suggests a different DNP mechanism.

Keywords Solid state dynamic nuclear polarization, Hyperpolarization

Introduction

High magnetic field, produced by superconducting magnet, plays a crucial role for improving signal-to-noise ratio in Nuclear Magnetic Resonance (NMR). There have been, however, alternatives such as Dynamic Nuclear Polarization (DNP), which enhances NMR signal via transferring electron spin polarization to nuclear spins.[1-8] The polarization transfer is driven by microwave (MW) irradiation at near Electron Spin Resonance (ESR) frequency. The max enhancement is the ratio of the electron and nuclear spin gyromagnetic ratio (γ_e/γ_n), which leads to enhancement of two or three orders of magnitude, in principle.[1,2]

Except for Overhauser-DNP[2] and chemically-induced DNP[9], which enhance liquid samples, solid state phases are encountered in DNP since low temperature and high field creates a high electron spin polarization. Once hyperpolarized state is induced on the nuclear spins, various techniques can be applied. MAS (Magic Angle Spinning) enables to measure high-resolution *in-situ* NMR spectrum.[3] Dissolution-DNP, instead, dissolves the frozen sample into superheated water, and carries out *ex-situ* NMR after transferring the dissolved sample.[4,6,-8]

Although high field (> 3T) is widely used in solid state DNP researches, the theories of DNP mechanisms reveal that DNP efficiency is higher as magnetic field becomes lower.[5,10] Thus, one may expect to build a cost-efficient DNP polarizer working at low magnetic fields, built solely with solid-state devices. To this end, the effect of low magnetic field should be investigated carefully. Here, I report solid state DNP of ^{1}H nuclear spins in a frozen phase at 0.3 T and 4.2 K. The optimal

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magnetic field condition was searched via field sweeping with a fixed MW frequency. In comparison with polarization at room-temperature, 3100-fold enhancement of ^{1}H polarization was achieved. The DNP mechanism for explaining the DNP spectrum will be discussed.

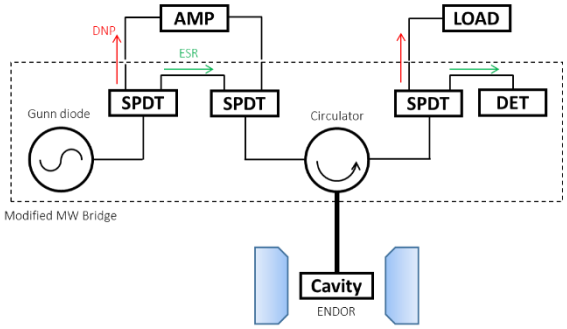

Figure 1. Illustration of microwave-bridge modified for DNP. In DNP mode, MW power generated by gunn-diode enters the amplifier externally mounted. MW reflected from cavity is dissipated at 50 ohm load, isolated from detector.

Experimental Methods

The DNP system is based on a commercial X-Band ESR spectrometer (JEOL-X310), which is modified for DNP experiments by request. It can operate in two modes, ESR or DNP. ESR mode is for recording ESR spectrum. In DNP mode, however, the MW switches installed in MW bridge guides MW power from Gunn-diode source to an external GaAs amplifier (15 W). The amplified MW, then, enters into cavity, in which sample locates. If there is MW power reflection from the cavity, it will be dissipated at external 50 Ohm load, causing no damage to detector in the bridge. AFC (Automatic Frequency Control) unit becomes deactivated in the DNP mode effectively because MW can't reach to the detector. Thus, the resonance frequency of the cavity should remain unchanged while running DNP experiments. Water refrigerant circulates through the outer shell of the cavity and a chiller controls its temperature. In addition, electromagnet is a part of the ESR system, which can produce 0.65 T at a maximum.

The degree of nuclear spin hyperpolarization induced by DNP can be monitored by performing *in-situ* NMR. NMR probe consists of RF coil inside ENDOR (Electron Nuclear Double Resonance) cavity and the two variable capacitors externally positioned. The tuning range is from 13 to 15 MHz, covering ^{1}H NMR frequency at around 0.35 T. A commercial NMR console (Tecmag SCOUT) handles Tx and Rx RF units. RF amplifier (100 W) is used to generated high power pulses for solid echo sequence. A liquid-Helium cryostat (Oxford ESR900) is mounted through the cavity so that it cools down sample space with continuous flow of liquid helium. The difference in temperature between the sensors in the cryostat and in sample tube was confirmed to be negligible at 4.2 K.

The sample used for solid-state DNP was 60:40 glycerol/water mixture, in which glycerol prevents crystalizing and, thereby, produces a glassy phase at low temperature. The T_1 time of the un-doped sample at 0.35 T and 4.2 K was measured to be 8.9 s. Afterwards, Per-Deuterated-TEMPONE (PDT) was doped with the concentration of 20 mM.

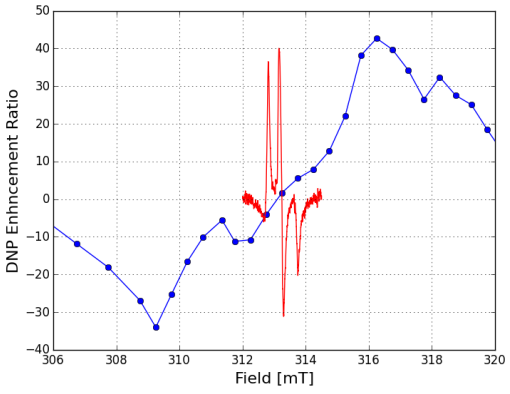

Figure 2. (Blue) ^{1}H NMR signal enhancement ratio at 4.2 K as a function of external magnetic field detuning. (Red) ESR spectrum of 60:40 glycerol/water frozen solution doped with 20 mM PDT.

Results

Solid-state DNP requires MW frequency detuning in order to obtain the maximal enhancement. The optimal MW frequency depends on DNP mechanism, which is governed by ESR linewidth, NMR frequency. At high fields, magnetic field is fixed because of superconducting magnet. MW frequency, then, is varied to measure DNP spectrum. MW antennae used in high-field DNP have low-Q values resulting enough bandwidths covering the width of DNP spectra. For X-band DNP system used in the present study, however, frequency sweep is not adequate because of high-Q cavity. The bandwidth of ENDOR cavity is only around 10 MHz. Thus, magnetic field was swept instead.

Figure 2 presents the DNP enhancement ratio as a function of external magnetic field. The sample temperature was 4.2 K. NMR signals from ^{1}H nuclear spins were recorded using solid-echo sequence. The pulse width and the time interval between the pulses were 5 us and 10 us, respectively. In prior to solid-echo sequence, MW was applied for 20 s. The frequency of MW was fixed as 9031 MHz. Magnetic field was varied from -7 to + 7 mT with respect to the center of ESR spectrum, 313 mT. ESR spectrum of PDT radicals doped in the sample is shown in red curve. The vertical axis of Fig.2 indicates the radio between enhanced and unenhanced echo intensities. The DNP spectrum exhibits positive and negative maximums at +3 and -4 mT detuned magnetic fields. Overall, the DNP spectrum is asymmetric having the positive maximum higher than the negative one.

The T_1 relaxation time of undoped sample (60:40 glycerol/water frozen solution) was 8.7 s at 4.2 K, while the polarization time constant was 3.8 s as shown in Fig. 3. The equation of nuclear spin polarization (P) can be described as

$$P = \exp\left(\frac{\eta \gamma_N B_0}{2 k_B T}\right),$$

in which γ_N is gyromagnetic ratio of nuclear spin and η is the enhancement ratio. According to this, the maximum ^{1}H polarization shown in Fig.1 corresponds to 0.37 %. This value is over 3100 times higher than the ^{1}H spin polarization in thermal equilibrium at 0.35 T and 300 K, as illustrated in Fig. 4.

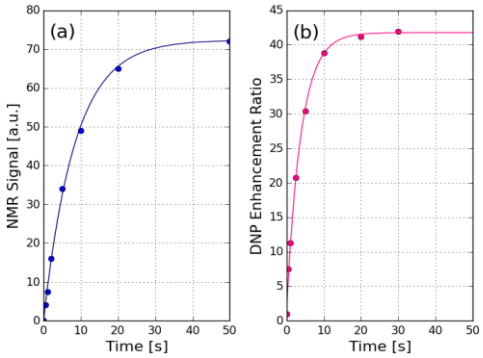

Figure 3. (a) T_1 relaxation curve of undoped 60:40 glycerol/water frozen solution at 4.2 K and 0.3 T. T_1 is 8.9 s. (b) DNP polarization curve of doped sample at 0.3 T and 4.2 K, in which the polarization time is 3.8 s.

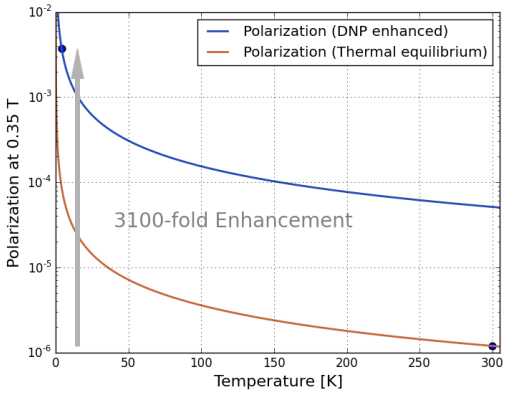

Figure 4. ^{1}H nuclear spin polarization curve unenhanced (Orange) and enhance by solid-state DNP (Blue), under 0.35 T as a function of temperature.

Discussion

The DNP spectrum in Fig. 2 is significantly broader than the ESR line width (=$\Delta\omega_e$). $\Delta\omega_e$ was measured to be around 1 mT as shown in Fig.1. The linewidth

is determined by hyperfine splitting due to ^{14}N nuclear spin in PDT. At the ESR spectrum center, ^{1}H NMR frequency ($=\omega_N$) is 13.7 MHz. Since 1 mT corresponds to 28 MHz for electron spins, the +3 mT field detuning for the maximal enhancement in Fig. 2 corresponds to 84 MHz detuning, which is over 6 times that of ω_N.

There seems to be no clear explanation for this extraordinarily large broadening of the DNP spectrum. Because PDT is not a bi-radical, cross-effect is not considerable here. Also, differential solid effect can't be applied because $\Delta\omega_e$ is twice as high as ω_N.[5] Thus, one may expect that unsolved solid effect and thermal mixing take place at low fields. However, unresolved solid effect and thermal mixing lead to polarization maximum at nearly $\pm\Delta\omega_e$, and this is certainly inconsistent with the result in Fig. 2.

In this work, the max polarization obtained by solid-state DNP at 0.35 T and 4.2 K is 0.37 %. A low magnetic field such as 0.35 T is obviously the main factor limiting nuclear spin polarization. According to the Eq. (1), however, if one can increase the enhancement ratio η, the disadvantage of using low field in DNP could be compensated. In addition, theories suggest that a higher enhancement can be expected because solid effect and thermal mixing efficiencies scale as B_0^{-2} and B_0^{-1}, respectively.[5] The present work, however, indicates that the present understanding of the solid state DNP mechanism at low field seems to be insufficient to explain the broad DNP spectrum.

Conclusion

Solid state DNP of ^{1}H spins at 0.35 T and 4.2 K was performed with 60:40 glycerol/water frozen solution doped with 20 mM PDT. The DNP system was developed based on X-Band ESR spectrometer modified for DNP. The max polarization obtained was 3100 higher than that in thermal equilibrium at room temperature. The extraordinarily large field detuning required for the max polarization is not explainable with solid effect or thermal mixing mechanisms. This presumably indicates a new DNP mechanism at low fields, which needs to be investigated thoroughly in order to achieve a higher nuclear spin polarization at low fields.

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