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Overhauser dynamic nuclear polarization for benchtop NMR system using a permanent magnet of 1.56 T

Yeon-seong Lee[1], Duk-Young Lim[1], and Jeong Hyun Shim[2,*]

[1]HMR Co., Ltd, Bucheon 14703, Republic of Korea
[2]Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea

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Abstract Overhauser dynamic nuclear polarization (O-DNP) has been an efficient method to boost the thermal nuclear polarization in liquids at room temperature. However, O-DNP for a benchtop NMR using a permanent magnet has remained unexplored yet. In this work, we report the development of an O-DNP system adopting a permanent magnet of 1.6 T. Q-band (~43 GHz) high-power amplifier produced 6 W microwave for saturation. Instead of resonator, we used an open-type antenna for the microwave irradiation. For several representative small molecules, we measured the concentration and frequency dependences of the enhancement factor. This work paves the way for the development of a benchtop DNP-NMR system overcoming its disadvantage of low quality signal when using a permanent magnet.

Keywords Overhauser dynamic nuclear polarization, Benchtop NMR, Hyperpolarization, permanent magnet

Introduction

Overhauser dynamic nuclear polarization (O-DNP) has the longest history among the various techniques of hyperpolarization.[1,2] Although its first experimental demonstration was performed with a metallic solid[1], liquid phases, such as free radical solutions, have become the main subject of O-DNP studies later[3]. The thermal polarization of electron spins in the radical can be transferred to that of the nuclear spins when the electron spin polarization is saturated via cw microwave irradiation.[1] The overall enhancement ϵ is defined as:[2,3]

$$\epsilon = 1 - \xi \cdot f \cdot s\frac{|\gamma_S|}{\gamma_I}.$$

This includes three key parameters, the coupling factor ξ, the leakage factor f, and the saturation factor s. γ_S and γ_I are the gyromagnetic ratios of electron and nuclear spin, respectively. When the cross-relaxation between the electron and the nuclear spin is dominant over the self-relaxation among the nuclear spins, the leakage factor f becomes close to unity. With a sufficiently high microwave power, thus, the maximum enhancement is expected to be $\xi\frac{|\gamma_S|}{\gamma_I}$: The sign and amplitude are determined by the coupling factor.

O-DNP can be usefully applied in benchtop NMR, since it incorporates a permanent magnet for small-size and mobility. Commercial benchtop NMR products have magnetic fields ranging from 1.4 T to 1.9 T. Such field strengths are certainly lower than what superconducting magnets can generate and is considered to be the limitation of benchtop NMR systems. As pointed out by Halse[4], hyperpolarization can significantly increase the sensitivity of benchtop

* Address correspondence to: **Jeong Hyun Shim,** Korea Research Institute of Standards and Sciences, Daejeon 34113, Republic of Korea; E-mail: jhshim@kriss.re.kr

(or compact) NMR. This may lead to new applications. Unfortunately, the studies on O-DNP with a benchtop NMR system has remained unexplored yet.[4] In this work, we report the development of a benchtop DNP-NMR system based on a permanent magnet of 1.6 T, with high-power microwave in Q-band (~ 43 GHz). The enhancement factors of several chemicals were measured, supporting that O-DNP effectively enhances the sensitivity of benchtop NMR.

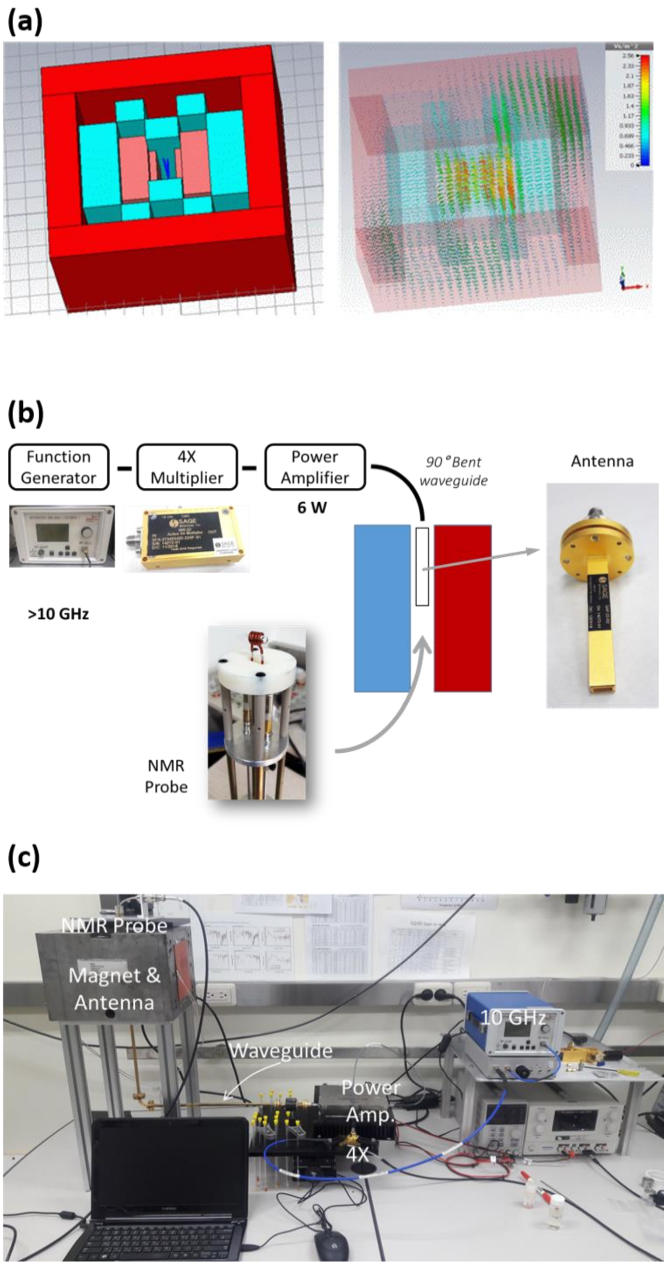

Figure 1. (a) Simulation for the design of a permanent magnet. (b) Schematic of the microwave setup for a high-power cw microwave for O-DNP at 1.6 T. (c) Overview of the constructed O-DNP NMR system.

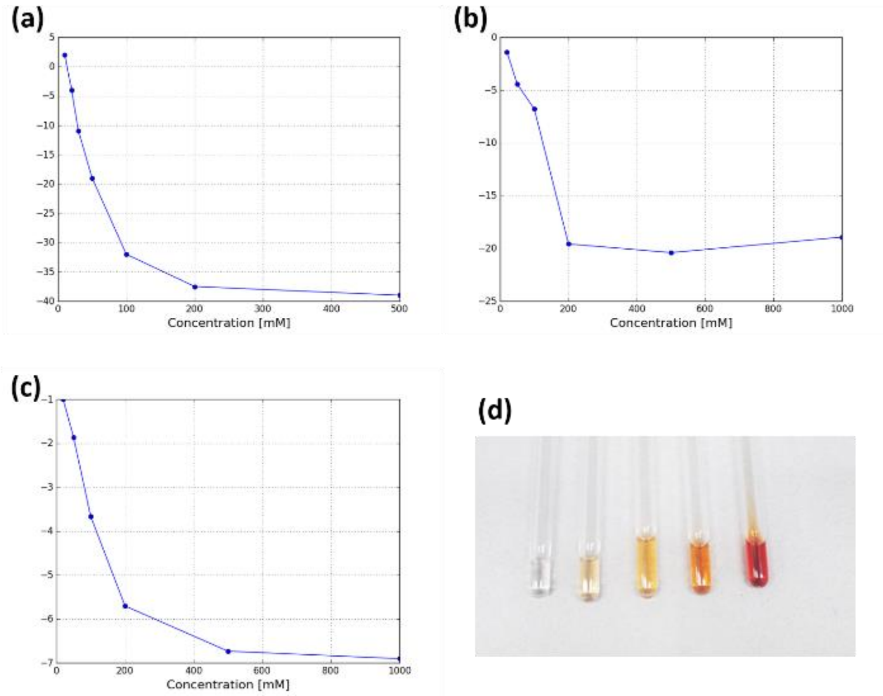

Figure 2. Concentration dependences of O-DNP enhancements for water (a), acetone (b), and ethanol (c). (d) Variation of color of water with respect to the concentration of TEMPOL (20 mM, 100 mM, 200 mM, 500 mM, 1000 mM)

Experimental methods

The most important part of a benchtop NMR is magnet. In our system, the magnetic field was produced by a permanent magnet and is approximately 1.6 T at the center. The magnet has the dimensions of 26*25*20 cm^3, and its weight is 60 kg. In the simulation, the magnetic field at the center was 1.87 T, while it turned out 1.56 T after construction. (Fig. 1 (a))

For O-DNP, microwave frequency should match with electron spin resonance (ESR). At 1.56 T, the ESR frequency is approximately 43.68 GHz. For that, a synthesizer (Anapico, Apin 12G) generated a frequency of ~11 GHz. Afterwards the output was quadrupled with a multiplier (Sage millimeter, SF-373453420-22SF-S1). Finally, a Q-band solid-state amplifier (RF Rambda, RFUPA39G48GB) used for a higher power output of 6 W. The amplifier was protected against the power refection by a Faraday isolator (Sage millimeter, STF-22-S1). The output port of the amplifier was connected to the antenna via Q-band waveguides, straight and 90 deg. bent. To launch the high-power microwave to liquid samples, we adopted an open-type antenna. Antenna has a low Q value, compared with resonators. Q-value is a

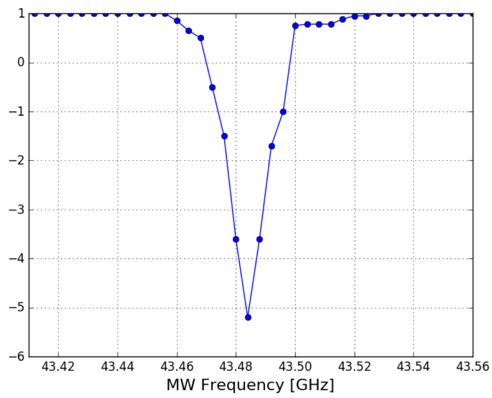

Figure 3. O-DNP enhancement of water (500 mM) as a function of mw frequency.

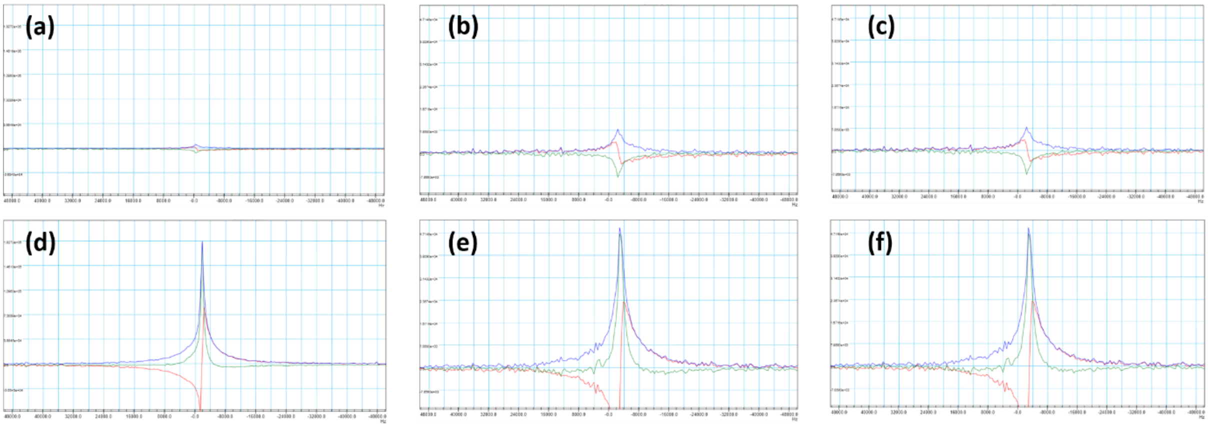

Figure 4. NMR Spectra of water (left), acetone (middle), and ethanol (right) before (top) and after O-DNP (bottom).

crucial parameter for generating a high-power microwave, since the amplitude of the microwave is proportional to $\sqrt{Q}$.[5] However, there are several advantages of using antenna. First, the volume of the sample space is significantly larger than that of the resonators. Second, antenna does not need tuning. Thus, performing O-DNP with antenna should be investigated in order to make O-DNP practically feasible for benchtop NMR.

NMR probe was constructed with a solenoid coil and two variable capacitors (Voltronics, NMTM120CE). Matching capacitance was increased with an additional SMD cap of 150 pF. The position of the NMR probe was controlled with a XYZ manual stage in order to locate the sample at the highest microwave-power area. The samples were TEMPOL (4-Hydroxy-TEMPO) solutions with several solvents, such as water acetone, and ethanol. The proton ^{1}H NMR signals from the solvents were obtained with a commercial NMR spectrometer (tecmag, SCOUT). By comparing ^{1}H NMR signals with mw on and off, the enhancement factors were estimated.

Results

For the three chemicals, i.e., water, acetone, and ethanol, we measured the O-DNP enhancements. To find the optimal conditions, first we investigated the concentration and frequency dependences. As shown in Fig.2, the enhancement factor becomes higher as the concentration of the radical increases. The negative value of the enhancement indicates that the dipolar coupling is dominant, which results in a positive coupling factor. We found that, to reach a meaningful enhancement, the concentration of the radical should be higher than 500 mM, which seems relatively high, changing the color of the solution to a significant extent (Fig. 2 (d)). The frequency dependence of water (500 mM, TEMPOL) revealed no three hyperfine lines of ^{14}N in TEMPOL, because of the line broadening caused by the high concentration of the TEMPO radical.[6]

The total results of the highest enhancements are summarized in figure 4 and table 1.

Table 1. Summary of results

Chemical	Enhancement
Water	40
Acetone	20
Ethanol	7

Discussion

As expected, the water exhibited the highest enhancement due to its low molecular weight, which improves the coupling factor. Since NMR signal intensity is proportional to the square of field strength, 40-fold enhanced signal corresponds to applying a magnetic field of 9.87 T, higher than 400 MHz NMR system. For other chemicals, however, the enhancement values are not as promising as water (Table 1).

According to the theory[6], diffusion coefficient is proportional to the inverse of the correlation time, which significantly influences the coupling factor. The fact that the diffusion coefficient of acetone is higher than that of ethanol may qualitatively explain the enhancement factor we measured. But, unfortunately, the quantitative comparison is not feasible since the temperature of the solutions vary and are unknown.

During the experiments, we found that the degree of the O-DNP enhancement strongly depends on the sample temperature[6]. This effect is associated with the dielectric loss of aqueous sample, in the range of microwave frequency, 1 – 50 GHz. The absorbed energy through dielectric loss transforms to heat dissipation. Therefore, under the exposure to a strong microwave field, the sample's temperature increases rapidly, just as a microwave in kitchen. A higher temperature leads to a faster the molecular motion, which increases the coupling factor eventually. In practice, one can increase the sample temperature by repeating O-DNP shots several times. After a couple of runs, we observed that the enhancement becomes saturated.

The linewidths shown in figure 2 are larger than 1000 kHz, i.e. 1500 ppm. This is mainly due to the intrinsic field inhomogeneity stemming from the permanent magnet we used. In order to improve spectral resolution, passive shimming technique[7] in combination with room-temperature shimming[8] should be implemented in future, making chemical studies feasible with enhanced signal via O-DNP.

Conclusion

In the present work, we report that O-DNP can effectively boost the sensitivity of benchtop NMR which is based on a permanent magnet producing 1.56 T. For the protons in water, 40-fold enhanced signal was observed. For other chemicals, acetone and ethanol, the enhancement showed less efficiencies. Although this work demonstrates the potential application of O-DNP on benchtop NMR system, further improvements, such as shimming, are still required to perform chemical analysis with Overhauser-enhanced signals. In addition, hyperpolarization of other nuclei, like ^{13}C, with O-DNP is highly required to expand the application of the benchtop DNP-NMR system.

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