500-fold enhancement of in situ ^{13}C liquid state NMR using gyrotron-driven temperature-jump DNP

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Abstract

A 550-fold increase in the liquid state ^{13}C NMR signal of a 50 μL sample was obtained by first hyperpolarizing the sample at 20 K using a gyrotron (260 GHz), then, switching its frequency in order to apply 100 W for 1.5 s. so as to melt the sample, finally, turning off the gyrotron to acquire the ^{13}C NMR signal. The sample stays in its NMR resonator, so the sequence can be repeated with rapid cooling as the entire cryostat stays cold. DNP and thawing of the sample are performed only by the switchable and tunable gyrotron without external devices. Rapid transition from DNP to thawing in one second time scale was necessary especially in order to enhance liquid ^1H NMR signal.

Keywords: DNP, temperature-jump DNP, direct ^{13}C DNP, gyrotron

1. Introduction

Dynamic nuclear polarization (DNP) was proposed in the 1950s to transfer the much higher polarization of electron spins to nuclear spins by saturating the electron spins via microwave irradiation, resulting in an enhanced nuclear polarization (i.e., ~ 660 for ^1H and ~ 2600 for ^{13}C) [1]. Therefore, DNP has been considered as a means to overcome the low sensitivity of nuclear magnetic resonance (NMR) due to low gyromagnetic ratios γ of nuclei. Despite this attractive feature, for many years the applicability of DNP was limited to low fields (~ 0.3 T, ~ 9.3 GHz) as the magnetic resonance frequency of electron spins falls in the TeraHertz range in the high fields generally used for NMR. Recently,

however, there has been a renaissance of interest in DNP because this technical bottleneck has been disappearing as new technologies and methodologies have been developed. Griffin *et al.* pioneered the use of gyrotrons to carry out DNP enhanced solid-state NMR spectroscopy with magic angle spinning (MAS-DNP) near 100 K at fields above 5 T. Typically, they used frozen solutions doped with paramagnetic radicals [2–4]. Their success led to the introduction of DNP to the high fields (~ 9 T and more) which are commonly used to study structure and dynamics of biomolecules by NMR.

Alongside the developments of DNP in the solid phase, there have also been many attempts to implement DNP in liquid state NMR. Most notably, dramatic enhancements of a factor of $10^4 \sim 10^5$ have been obtained by dissolution-DNP [5, 6] where a solid sample is hyperpolarized at relatively low field at ultralow temperature, diluted with hot water, and then transferred to a room-temperature

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NMR spectrometer for signal detection. Although some loss of polarization occurs during the melting and transfer processes, this spectacular enhancement allows for single scan NMR signals with high signal to noise ratio. Another approach is to use the Overhauser effect in solutions, which had been performed for the past decades at low fields only because of the limitation due to short contact times in solution[7, 8]. However, Prisner *et al.* recently reported an enhancement of a factor of 100 at 9 T by employing a high power gyrotron and a microwave resonator with a high Q-factor of ~ 400 and a sample of about 3 nL[9–11]. Sample shuttle DNP was also suggested as an alternative approach to DNP-liquid NMR[12, 13], in which a liquid sample was polarized in a 0.35 T magnet placed over a 14 T NMR magnet, and the polarized sample was transferred to 14 T within 140 msec. Thus, an enhancement of up to 15 was obtained that depended on which nuclei they tested.

An alternative to liquid state DNP is the 'Temperature-jump DNP'[14–16] that has been recently demonstrated, where a frozen solution is polarized by DNP around 100 K, quickly melted by a CO₂ laser, followed by NMR data acquisition before the sample refreezes. In contrast to dissolution DNP, the sample keeps the same composition and in contrast to the shuttling technique, it does not move either. Hence, temperature-jump DNP is amenable to multiple scans and multi-dimensional NMR spectroscopy. These authors obtained enhancements by a factor of 100–400 for different nuclear species, and demonstrated a ¹³C-¹³C TOCSY spectrum with good resolution[15]. Hot nitrogen gas has been also suggested[17–19] instead of using laser-heating for melting a frozen solution. In these experiments(named 'rapid-melt DNP'), the bore in the NMR magnet(3.4 T) has three regions in the vertical direction: the lower region where DNP takes place at low temperature, the middle region where the sample is melted with hot nitrogen gas, and the upper region where liquid NMR signal is acquired. The sample can be transferred from the cooling region to the NMR signal detection region by a linear actuator within 20 msec, and the total experiment time from polarization to signal acquisition is about 5 sec. Furthermore, these authors succeeded in acquiring multiple scans of NMR signal with a fast rate. The signal enhancement for ¹H was estimated to be about 500 with a sample volume of 10 nL to 1 μ L using the high signal detection efficiency of a microstrip resonator.

In this paper, we report temperature-jump ¹³C and ¹H DNP using a switchable gyrotron for ice-melting instead of laser-heating or hot nitrogen gas. The gyrotron serves both as a microwave source for DNP, and also as a melting device. Therefore, the sample stays fixed and no additional device is needed. The sample is hyperpolarized at 20 K, then 100 W of microwave power is applied just long enough to melt the sample so liquid NMR can be performed. We thus obtained a 550-fold increase in ¹³C NMR signal intensity. The increase in ¹H NMR was only 40-fold, because of the shorter nuclear spin-lattice relaxation time of ¹H spins.

2. Sample preparation

Samples were prepared by dissolving 40 mM TEMPOL(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl) radicals in a mixture of solvents (H₂O:D₂O:d₈-glycerol=10:30:60). The sample is placed in a teflon tube of 5mm in diameter and 15 mm in height. Teflon has a thermal shock resistance high enough for repeated rapid temperature transitions between 20 K and room temperature. We observed that boron-silicate glass tubes with thin walls are unable to withstand the thermal shock, and break into fragments after melting and refreezing. Glassy samples, generally obtained by a fast freezing rate, are essential to distribute radicals homogeneously and yield a high enhancement. One disadvantage of using a teflon tube is its lower thermal conductivity relative to sapphire or boron-silicate tubes, which might result in a poor glass phase and thereby lower enhancement. We compared the ¹H enhancement at low temperatures of the samples filled in the teflon tube with that in a sapphire tube, as an indirect indicator of vitrification. We obtained the same enhancement regardless of the type of tube, implying good glass-formation.

3. Experiment schemes

Our DNP-NMR probe is described in reference[20]. In the present experiment, we used a saddle coil instead of a solenoid coil. This coil was selected to gain from both a high microwave transmission and a good NMR sensitivity, as described in the simulation results of reference [21]. A high microwave transmission is required to reduce melting time, so that the least nuclear

relaxation occurs during melting. Although all results in this article were obtained with a teflon tube and a saddle coil, we also succeeded in obtaining similar enhancements with a solenoid coil and other kinds of sample tubes.

All DNP-NMR experiments were performed in a conventional wide-bore superconducting NMR magnet fixed at 9.29 T(395.7 MHz for ^1H , and 99.5 MHz for ^{13}C) using a home-built spectrometer. DNP experiments below were conducted at 20 K, which is the minimum temperature attainable in our cryostat. As described earlier([20, 22, 23]), the gyrotron can be switched on and off by an external trigger, and set at frequencies within a range of 1 GHz. The maximum power is 150 W and the power versus frequency dependence is steep at these high power levels. For the temperature-jump DNP, it is required to irradiate the sample during DNP with a moderate microwave power (1 ~ 5 W), a very accurate frequency and a high spectral purity. For melting process, only a high power (> 50 W) is necessary regardless of the frequency.

The transition from DNP to melting process can be accomplished in two ways: on a long time scale (several minutes) by tuning the gyrotron magnetic field at fixed electron beam energy or, on a short time scale (one second or shorter) at fixed magnetic field, by changing the electron beam kinetic energy together with the electron pitch angle (i.e. the ratio between perpendicular to parallel velocity). This is only possible with a triode electron gun. This shorter time scale is limited by the external high-voltage power supplies capabilities and the gyrotron control system.

The transition from DNP to melting process is required to be accomplished before the hyperpolarized nuclear spins relax back to thermal equilibrium. Therefore the transition time Δt has to be shorter than nuclear spin-lattice relaxation T_1^n at low temperature. For temperature-jump ^{13}C DNP, the transition from DNP to melting process was achieved by changing the value of the magnetic field of the gyrotron, taking place on a 2 min time scale, which is much shorter than T_1^n of ^{13}C at low temperature. Since the relaxation of ^1H is of about 100 sec at low temperature, we needed a fast transition ($\Delta t \simeq 1$ sec). So the gyrotron needs to be controlled via its internal parameters, as described above, while its magnetic field stays constant. The two gyrotron operating points, corresponding to the DNP and melting processes, have been determined by numerical simulations([24, 25]) and afterwards

validated on the experiment. It is important to stress the fact that the fast transition from DNP to melting process can only be done with a triode gun. An example of the gyrotron parameters is given in table 1. The time evolution of the anode and cathode voltages, as well as the microwave power measured with a Schottky diode are given in Fig. 1 around the transition between the two phases.

Phase	B field [T]	I_b [mA]	U_k [kV]	U_a [kV]	P_{mw} [W]	f [GHz]
DNP	9.43	100	10	5.5	2	260.63
melting	9.43	100	14	8	100	260.42

Table 1: Main gyrotron parameters for the fast power transition ($\Delta t \simeq 1$ sec) used for temperature-jump ^1H DNP. I_b , U_k , U_a , and P_{mw} are electron beam current, cathode voltage, anode voltage, and microwave power, respectively.

Figure 1: Time evolution of the anode and cathode voltages and microwave power during the fast power transition used for temperature-jump ^1H DNP.

Figure 2 illustrates the temperature-jump DNP sequence. It starts with a train of saturation comb, composed of 90° pulses, in order to initialize the nuclear magnetization in a reproducible way. After the end of the saturation comb, frequency-modulated microwave for DNP is turned on during the build-up time τ_{dnp} . After the frequency-modulated microwave is turned off, the gyrotron is retuned to an operation point capable of producing P_{melt} in the transition time Δt . After the retuning, P_{melt} is turned on for 1.5 sec (^{13}C) or 0.5 sec (^1H), finally the NMR signal is acquired. T_1^n of ^1H in the liquid state is much shorter than that of ^{13}C , so it requires faster melting to maintain hyperpolarized ^1H . Thus, we reduced the sample volume to 15 μL and also shortened the melting time to 0.5 sec. The enhancement ε by temperature-jump DNP in this study is defined as the relative ratio of the signal intensity obtained by temperature-jump DNP

Figure 2: From top to bottom : cycling schematics, rf pulse sequence, microwave for DNP, microwave for melting. Δt is about 2 min and 1 sec for ^{13}C and ^1H DNP, respectively. t_{melt} is about 1.5 sec and 0.5 sec for ^{13}C and ^1H DNP, respectively.

with respect to that obtained by the liquid NMR at room temperature. The NMR signals obtained after rapid melt as reported below are the result of a single acquisition.

The frequency-modulated microwave was used for DNP at 20 K, because it has been reported to produce an increase in enhancement[26–28]. We recently reported that the frequency-modulated microwave produced by our gyrotron increases the enhancement by more than 60 % [20]. As reported previously, the electron spin-lattice relaxation time in our sample is expected to be about a few tens of msec, thus the sweeping rate of a few of kHz is fast enough to saturate electron spins within the amplitude of the frequency modulation before the electron spins relax to thermal equilibrium.

The melting method used in this study is a dielectric heating by microwave, which is generally effective for polar frozen solutions. Since MW can penetrate into the entire sample, dielectric heating is relatively homogeneous throughout the sample, and enables rapid melting. Provided that the sample is glassy, we can expect a weak temperature dependence of its dielectric properties at the sub-THz frequencies we use [29, 30]. Therefore, we can expect that dielectric heating would also work at the much lower temperatures used in dissolution DNP.

4. Results

In order to determine the DNP frequency, we obtained the direct ^1H DNP enhancement profile us-

Figure 3: Enhancement for ^1H as a function of microwave frequency. DNP and NMR signals were obtained with a build-up time of 150 sec.

ing a solid state microwave source (Virginia Diodes, Inc.) as shown in Fig. 3. The microwave frequency for maximum enhancement in our ^{13}C DNP experiment was deduced from Fig. 3, based on the theory of the cross effect according to which the positive and negative enhancement peaks occur $\omega_n/2$ away from the center of the electron paramagnetic resonance (EPR) spectrum [31]. In contrast to the case of direct ^{13}C DNP as in our experiment, in the case of ^{13}C DNP with ^1H - ^{13}C cross polarization (CP), the maxima of positive and negative enhancements are near those of ^1H DNP enhancement profile due to the indirect transfer [2]. Fig. 3 has the zero enhancement around 260.9 GHz, roughly corresponding to the center of the EPR spectrum, so 260.85 GHz was selected for the DNP frequency. Furthermore, frequency-modulation around this frequency with an amplitude of 50 MHz and a sweeping rate of 3 kHz was performed in order to increase the enhancement.

Figure 4 shows a temperature-jump gyrotron-driven ^{13}C DNP spectrum with $\tau_{\text{dnp}} = 3$ hours at 20 K, and a liquid NMR spectrum at room temperature obtained by signal averaging over 17 hours. The sample volume was about 50 μL , which can be completely melted by P_{melt} with the duration 1.5 sec. In the liquid NMR spectrum at room temperature, the two peaks at 62 and 73 ppm (referred to g_1 and g_2 , respectively) correspond to the two chemical shifts of glycerol in the mixed solvent. The errors in the chemical shifts and the broadening come from the inhomogeneity of our NMR

Figure 4: (Color online) Temperature-jump ^{13}C DNP spectrum with $\tau_{dnp} = 3$ h (red line, top), and liquid ^{13}C NMR spectrum at room temperature multiplied by a factor of 50 (black line, bottom). The NMR magnet used in this study has a field homogeneity of about 10 ppm, which causes large inhomogeneous broadening in liquid state NMR spectra. The broad spectrum (*) at around 115 ppm comes from the teflon tube.

magnet (~ 10 ppm). The broad peak (*) shifted by about 50 ppm away from the two peaks of glycerol comes from the teflon tube which contains a large amount of carbon. The Teflon signal, visible in the room temperature NMR spectrum, disappears in the temperature-jump DNP spectrum due to its negligible intensity in comparison to the sample signal intensity enhanced by DNP. The enhancement ϵ with $\tau_{dnp} = 3$ h is estimated to be about 550. The maximum enhancement attainable by temperature-jump DNP is given by $\epsilon^* T_{obs}/T_{DNP}$, where ϵ^* , T_{obs} , and T_{DNP} are DNP enhancement at low temperature, temperatures for observing liquid NMR signals and for doing DNP, respectively. Since ^{13}C DNP enhancement at 20 K cannot be determined due to the extremely long measurement time this would require, we cannot measure how much the hyperpolarized nuclear spins relaxes toward thermal equilibrium. Assuming that the enhancement for direct ^{13}C DNP is about two-fold larger than that for ^1H DNP ($\simeq 75$ with frequency modulation)[20, 32], we roughly expect that about 25 % of the hyperpolarized ^{13}C spins remained after melting.

The growth of the temperature-jump ^{13}C DNP spectrum as a function of τ_{dnp} is shown in Fig. 5. The τ_{dnp} dependence of ϵ fits to an exponen-

Figure 5: Enhancement ϵ as a function of τ_{dnp}

tial function with a growth time constant of about 40 min. This slow growth rate of the enhancement is an intrinsic property of direct ^{13}C DNP due to its low natural abundance and slow spin diffusion. Since the build-up time constant of the enhancement for ^1H is about 25 sec, ^{13}C DNP with cross polarization would polarize the ^{13}C faster[26].

As applying P_{melt} for a long duration might cause the sample to boil away, the temperature-jump DNP signal might not be repeatable if the irradiation time is not properly calibrated. We cycled through the temperature-jump sequence (Fig. 2) repeatedly and obtained the same signal amplitude each time, within 5 %. This suggests the feasibility of multiple scanning and multi-dimensional NMR.

We also demonstrated temperature-jump ^1H DNP using a fast transition of the gyrotron operation mode from DNP to melting, as described earlier. Monochromatic MW at the positive maximum in Fig.3 was irradiated during $\tau_{dnp} = 120$ sec for DNP, followed by P_{melt} for 0.5 sec. ^1H DNP enhancement at 20 K is estimated to be of a factor of 50. Thus, the maximum enhancement for temperature-jump ^1H DNP is estimated to be of a factor of 750 (DNP+Boltzmann factor) with $T_{obs} \simeq 300$ K.

Figure 6 shows a temperature-jump ^1H DNP spectrum and a liquid ^1H NMR spectrum at room temperature. ϵ is estimated to be around 40, which shows that about 5 % of the hyperpolarized nuclear spins survived after melting. This fast relaxation comes from the short T_1^n of about 100

Figure 6: Temperature-jump ^1H DNP spectrum and room temperature ^1H NMR spectrum. The two bumps (*) at around 75 ppm and 165 ppm in the temperature-jump ^1H DNP spectrum are due to artifacts, and would vanish after averaging.

msec in the liquid state due to the high viscosity of glycerol. We can think of ways to improve the temperature-jump ^1H DNP. The melting time could be reduced by using a smaller volume or higher microwave power. Changing the radical from TEMPOL to BDPA could also be an alternative, as discussed in the reference[17].

5. Conclusion

We performed temperature-jump DNP for ^{13}C and ^1H using a gyrotron. The signal intensity of ^{13}C DNP was increased by around 550 with $\tau_{\text{dnp}} = 3$ h. This signal intensity was reproduced consistently, which shows a feasibility of temperature-jump DNP for multiple scanning and multi-dimensional NMR. The direct ^{13}C DNP was slow in conformity with published literature. This problem can easily be alleviated by cross polarization between ^1H and ^{13}C [32, 33]. Temperature-jump ^1H DNP was also possible with the gyrotron enable to transit the power in about 1 sec.

Our temperature-jump DNP experiment uses the dielectric heating of the sample, while the whole cryostat remains cold. The melting time per volume is about $0.03 \text{ sec}/\mu\text{L}$ for temperature jump from 20 K to room temperature, while we estimated the previous results to be about $0.11 \text{ sec}/\mu\text{L}$ [14] and $0.6 \text{ sec}/\mu\text{L}$ [17] for going from about liquid nitrogen temperature to room temperature.

In this study, temperature-jump DNP by dielectric heating was shown to achieve large enhancement with a convenient sample volume of $15\text{--}50 \mu\text{L}$, and be repeatable without losing any part of the sample. This temperature-jump DNP set-up can be improved in performance by going to even lower temperature, by implementing cross polarization in order to avoid the long build-up time of ^{13}C , and by using solutions of lower viscosity.

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