Dynamic nuclear polarization by frequency modulation of a tunable gyrotron of 260 GHz

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Abstract

An increase in Dynamic Nuclear Polarization (DNP) signal intensity is obtained with a tunable gyrotron producing frequency modulation around 260 GHz at power levels less than 1 W. The sweep rate of frequency modulation can reach 14 kHz, and its amplitude is fixed at 50 MHz. In water/glycerol glassy ice doped with 40 mM TEMPOL, the relative increase in the DNP enhancement was obtained as a function of frequency-sweep rate for several temperatures. A 68 % increase was obtained at 15K, thus giving a DNP enhancement of about 80. By employing $\lambda/4$ and $\lambda/8$ polarizer mirrors, we transformed the polarization of the microwave beam from linear to circular, and achieved an increase in the enhancement by a factor of about 66 % for a given power.

Keywords: DNP, TEMPOL, frequency modulation, gyrotron, millimeter waves, circular polarization

1. Introduction

Dynamic nuclear polarization (DNP) has been known for a long time to enhance nuclear spin polarization by transferring electron spin polarizations to nuclear spins. The enhancement ε of nuclear spin polarization by DNP can in principle reach the value γ_e/γ_n (~ 660 for ^1H & ~ 2600 for ^{13}C), and DNP has been of great interest for improving the inherently low NMR signal to noise ratio (SNR) of low γ nuclei[1]. However, there have been many obstacles to performing DNP in a magnetic field strong enough to obtain the high-resolution NMR

required for chemical or biological materials, because at these high fields, the electron paramagnetic resonance (EPR) falls in the TeraHertz (THz, 100 GHz - 10 THz) frequency range. As the technology in this frequency range has been rapidly improving, giving access to THz generators, waveguides, and vector network analyzers (VNA), recent DNP-NMR studies have shown SNR improvement more than a 100-fold at 9.4 T[2–5].

Gyrotrons used as microwave (MW) sources, for example in MAS-DNP, are generally monochromatic (typical natural width $\Delta f/f < 100$ kHz) and cannot depolarize all electron spins, even when there is spectral diffusion. In this paper, we show how frequency-modulation of the gyrotron improves the polarization transfer. In DNP studies with nitric oxide radicals at high magnetic field, solid state MW sources have been employed for

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frequency-modulated MW. Recently, Hovav *et al.* [6] have successfully reported an increase in the DNP enhancement by modulation using a solid state MW source at 3.34 T from 10 K to 50 K. They showed the increase in ε as a function of the amplitude A_{md} and the sweep rate f_{md} of modulation and obtained an increase in ε by a factor of about 3. In their simulation, they considered the nuclear polarization enhanced by the solid effect (SE) and cross effect (CE) with frequency modulation, and showed that the number of active electrons contributing to DNP increases with increasing $A_{m.d}$ unless single quantum transitions are induced by off-resonance or spectral diffusion. They also showed that the nuclear polarization obtained by the solid effect is independent of f_{md} , while that by the cross effect is effectively enhanced provided f_{md} is higher than the electron spin-lattice relaxation rate $1/T_1^e$. Field modulation rather than frequency modulation was also shown to increase ε . Thurber *et al.* [7] performed DNP with field modulation at 9.4 T. They showed that ε can be increased by a factor of 2 at temperatures and radical concentrations suitable for the CE. ε was shown to increase with increasing f_{md} , up to the point when f_{md} exceeds the electron spin-lattice relaxation rate $1/T_1^e$. In their simulation, they considered the cross effect and assumed that the spectral diffusion of electron spins is not fast enough to spread the depolarization across neighboring spin packets during T_1^e . Frequency modulation was also reported to increase DNP signal intensity in dissolution-DNP where DNP mechanism is thermal mixing[8]. Bornet *et al.* showed an increase in ε with increasing A_{md} and f_{md} , faster build-up rate, and more efficient cross-polarization. Besides nitric oxide radicals, silicon particles with defects on the surface have been previously used for DNP with frequency modulation[9].

These frequency modulation experiments with nitric oxide radicals reported so far were only at low temperatures, presumably because of the low power of solid state MW sources.

In this study, we present the enhancement of 1H nuclear spin polarization by DNP for static samples in 9.28 T using a gyrotron MW source capable of frequency-tuning, and frequency-modulation, and ns pulsed regime[10, 11]. We obtained an increase of ε by frequency modulations at fields higher than reported previously. Further more, as gyrotrons produce higher MW power than solid state MW

sources, we were able to examine the effectiveness of frequency-modulation up to 100 K. We also show that the conversion of linearly polarized MW to circular polarization improves ε for a given MW power, as it has been shown with solid state MW sources and quasi-optical system[12, 13].

2. Experiment set-up

2.1. Sample preparation

We prepared samples by dissolving 40 mM TEM-POL (Sigma Aldrich) in a mixture of H_2O , D_2O and d_8 -glycerol of volume ratio 10: 30: 60 (DyNuPol. Inc). The sample of about 10 μl was inserted in a sapphire tube of inner diameter 1 mm, which has a high transmission for MW frequencies and a high thermal conductivity[14]. It is well known that glass-forming of samples composed of water and radicals is vital for high enhancement. We quenched the samples by inserting the DNP-NMR probe quickly into a cryostat set at a temperature much colder than the vitrification temperature. This implies a cooling rate higher than the minimum rate for vitrification of the sample, which is about 70 K / min for 60 % glycerol[15–17]. We observed by NMR that the sample solidification is generally completed in 1 min, thus insuring glass-formed samples.

2.2. Frequency-tunable Gyrotron

The main design features of the gyrotron prototype[10, 18, 19] are: frequency stability(with long-term feedback stabilization), spectral purity, fast and slow tunability, and MW-power control over a wide range. The cavity resonator and up-taper of the gyrotron were designed with special attention in order to achieve frequency-tunability in the vicinity of 260 GHz, relying on the smooth transition between axial eigenmodes of the cavity, as it has been reported on other papers about gyrotrons[20, 21]. A high flexibility of the electron beam parameters is achieved by making use of a triode-magnetron-injection gun with an independent control of the anode-voltage, allowing a fast frequency tunability. Furthermore, as described e.g. by Barnes *et al.*[20], a slow but wide range tunability is obtained by changing the cavity magnetic field and other control parameters.

The gyrotron characterization showed a maximum power of 150 W at a frequency of $f_0 = 260.45$ GHz.

The Vlasov converter together with the internal optical system ensures a high gaussian mode content of the microwave beam at the gyrotron-window[22]. The gyrotron output frequency, which can be long-term stabilized by a feedback-control[22], can be tuned on a time scale of several tens of seconds over a range of $\Delta f = 1.2$ GHz with a power in excess of 1.5 W. Fast tuning over a frequency range of ~ 100 MHz on a minimum time scale of $\sim 30 \mu s$ can be achieved by the modulation of the anode voltage, as it has been described elsewhere using a modulation of the accelerating voltage[23, 24]. This fast tuning is illustrated in Fig. 1, showing the frequency modulation by the anode voltage modulation. As we sweep the anode voltage in the gyrotron for frequency modulation with other parameters fixed, the MW frequency follows the anode voltage while the MW power is not constant in the range of 260.82 ± 0.050 GHz; the highest power of about 1.6 W occurs at 260.8 GHz and the power keeps decreasing down to about 0.4 W at the frequency maximum of the sweep.

Figure 1. (Colour online) real-time MW-spectrum (bottom) and anode voltage control (top) with fast frequency modulation (sweep rate f_{md} and amplitude A_{md} of fast frequency modulation = 14.5 kHz and 50 MHz, respectively).

The diagnostics which are used to analyze the MW-characteristics mainly consist of a calorimeter, a VDI heterodyne detection board (Virginia Diodes, Inc) connected to a 3 GHz-oscilloscope for measuring the instantaneous frequency and of a Schottky-diode for measuring the instantaneous power[10].

2.3. Matching Optics Unit and attenuator

A matching optical unit (MOU) (Fig. 2 (a)) is composed of a plane mirror, a $\lambda/4$ polarizer mir-

ror, a focusing mirror, and a $\lambda/8$ polarizer mirror, which are designed for maximizing the coupling between the HE_{11} mode supported by the corrugated waveguide and the gaussian beam radiated from the gyrotron. The two corrugated polarizer mirrors in the MOU enable the transformation of the linearly polarized gyrotron output to a circular polarization or an elliptical polarization, after sequential reflections from the $\lambda/4$ mirror and the $\lambda/8$ mirrors[25, 26]. The $\lambda/4$ mirror is manufactured with metallic grooves of period $d = 0.500$ mm, width $c = 0.250$ mm, and depth $h = 0.310$ mm, and the $\lambda/8$ mirror with the same d and c , but $h = 0.214$ mm[27]. Based on the geometry shown in Fig. 2 (a), when the groove axis orientation angle $\phi_{\lambda/4}$ of the $\lambda/4$ mirror and the angle $\phi_{\lambda/8}$ for the $\lambda/8$ mirror are 49.1° and 0° , respectively, with respect to linearly polarized incoming MW, the MW reflected off the mirrors maintains its polarization. When both angles are at 49.1° , the MOU converts the linear polarization to circular polarization. Therefore, linearly polarized MW is able to be transformed from 100 % linear to 100 % circular polarization by rotating the $\phi_{\lambda/8}$ from 0° to 49.1° , while keeping the $\phi_{\lambda/4}$ at 49.1° .

We used an attenuator (Tydex) to reduce MW power, which is composed of 5 silicon wafers with different transmissions (70 %, 30 %, 10 %, 3 %, and 1 %). Combinations of the wafers in the attenuator enables us to adjust the MW power while keeping the gyrotron parameters constant. The attenuator is inserted between the entrance of the wave guide and the $\lambda/8$ mirror, as shown in Fig. 2 (a).

2.4. DNP-NMR probe and NMR measurement

The NMR probe (Fig. 2 (b) & (c)) is composed of a corrugated waveguide (Swisstol12) and an NMR resonator circuit. The NMR coil is a solenoid of 4-6 turns with 1 mm spacing. It is placed close to the open end of the waveguide. Two variable capacitors are used for tuning and matching at 1H NMR frequency = 395.2 MHz. The quality factor Q of the NMR resonator is about 60. A demountable miter bend is used to couple the probe to the waveguide that brings the MW beam from the MOU to the NMR probe.

1H NMR signal intensity is acquired by a saturation-recovery pulse sequence as described in Fig. 3. The saturation pulse, which is a comb pulse composed of a train of 90° pulses, is used to set

Figure 2.

(a) **MOU:** MW window (1) of the gyrotron, plane mirror (2), $\lambda/4$ mirror (3), focusing mirror (4), $\lambda/8$ mirror (5), attenuator (6) composed of 5 silicon wafers whose transmissions are 70 %, 30 %, 3 %, and 1%, and waveguide (7). The short and long lines in the $\lambda/4$ and $\lambda/8$ mirrors (the radius and diameter of the disks, respectively) represent the groove axes and the electric field axis of MW, respectively. The relative angles between those two lines are defined as $\phi_{\lambda/4}$ and $\phi_{\lambda/8}$, respectively, (b) **top of the NMR probe:** waveguide (8) (same as (7)), side section of the miter bend (9), waveguide going to the NMR resonator circuit(10), (c) **bottom of the NMR probe:** waveguide (11) (same as (10)), variable capacitor (12), sapphire tube (13), solenoid coil (14).

a constant initial state of the nuclear polarization. After the saturation pulse, the nuclear polarization grows during the time τ with or without MW and is detected by a solid echo pulse sequence composed of $90_x^\circ - \tau_{echo} - 90_y^\circ$ [7, 28]. Since our gyrotron is fast-switchable, MW is rapidly turned on at the end of the saturation comb pulse, and is turned off right before the solid echo pulse. A duty cycle of 25 % is maintained to allow the sample to cool and return to the initial temperature before every acquisition. The NMR signal intensity is obtained by integrating the solid echo signal in the time domain. The 90° pulse width is about $5 \mu\text{sec}$ and τ_{echo} is $100 \mu\text{sec}$ at 70 K or $250 \mu\text{sec}$ at 20 K. Long τ_{echo} is used in this study to eliminate background signals not coming from the sample.

The enhancement ε in this study is defined as the gain in nuclear polarization obtained with DNP at a temperature T normalized to the thermal-equilibrium nuclear polarization at the same temperature. It can be expressed as :

$$\varepsilon = \frac{S_{DNP} - S_0}{S_0}, \quad (1)$$

where S_{DNP} and S_0 represent NMR signal intensities with and without MW. S_{DNP} and S_0 are obtained with and without MW during the time $\tau_{b,d}$ allocated for letting the DNP signal build up. As the growth rate of S_{DNP} with $\tau_{b,d}$ is known to be

Figure 3. Solid echo 90_x° and 90_y° pulse sequence preceded by the saturation comb composed of 50– 90° pulses. The MW is turned on during $\tau_{b,d}$ and turned off during $\tau_{off} = 3 \times \tau_{b,d}$.

similar to that of S_0 in the CE [6, 7, 29], we also obtained similar growth rates when MW power is attenuated to an appropriate level so as not to induce large dielectric heating of the sample. Therefore, we took the same $\tau_{b,d} = 5T_1^n$ for obtaining both S_{DNP} and S_0 , where T_1^n is nuclear spin-lattice relaxation time without MW.

Figure 4. Enhancement ε with MW power at 260.84 GHz as a function of MW power at 20 K with linear polarization. The MW power is measured at the gyrotron window, and adjusted using the attenuator.

3. Experimental result

3.1. Enhancement versus MW polarization

If MW is linearly polarized, it can be decomposed into clockwise and counterclockwise circular polarizations, and magnetic resonance will occur by absorbing only one appropriate handedness, while the other handedness does not contribute to the magnetic resonance. Thus, in principle, circular polarization with appropriate handedness can increase the effective B_1 field of MW by a factor of 2. Armstrong *et al.* reported previously that DNP signal intensity can be increased by 28 % with the same MW power by transforming linearly-polarized MW to circularly-polarized MW using their quasi-optical units[13]. Thurber *et al.* also showed that ε can be increased by about 25 % by going from linear to circular polarization[12].

In order to show the polarization dependence of ε , we attempted to exclude the effect of dielectric heating on ε by attenuating the MW power to a certain low level, which is in a range that ε is proportional to MW power. Therefore, we obtained the DNP signal at 260.83 GHz as a function of the MW power. It shows that ε increases rapidly with increasing MW power, and reaches an asymptote above 70 mW. Thus, we measured ε as a function of $\phi_{\lambda/8}$ with 10 mW (Fig. 5).

Figure 5. Enhancement ε at 260.84 GHz as a function of $\phi_{\lambda/8}$ from 0° to 49.1° at 20 K. The MW power is about 10 mW at all angles.

We set the $\theta_{\lambda/8}$ at positive values to produce elliptical or circular polarization. We find that the enhancement changes by as much as 60 % as we move away from the linear polarization. The maximum in ε occurs at 40° . This value is different by about 10° from our expectation, possibly due to practical imperfections, such as the misalignment of the mirrors, and the MW scattering in the NMR coil.

3.2. DNP by frequency modulation

Here, we present an increase in the enhancement ε by frequency-modulated MW produced by the gyrotron, as shown in Fig. 6. Figure 7 shows the DNP frequency profile, which shows the enhancement versus MW frequency, obtained by tuning the MW frequency at fixed magnetic field. The maximum negative enhancement occurs about 260.7 GHz and zero enhancement is found at 260.55 GHz, which is close to the center of the EPR spectrum. From Fig. 7, we chose 260.84 GHz as the center frequency for the frequency modulation because this frequency-swept band is close to where the maximum enhancement occurs, so the electron spin packets within the amplitude A_{md} of frequency modulation and neighboring packets saturated by spectral diffusion also can contribute to the enhancement. The A_{md} is 50 MHz, and the sweep rates f_{md} of frequency modulation are 770 Hz, 2.3 kHz, 6.3 kHz, and 14 kHz. As depicted

Figure 6. (Colour online) ^1H NMR spectrum at 20 K without MW (top, black), with monochromatic MW at 260.84 GHz (middle, red), and with frequency-modulated (14 kHz) MW (bottom, blue). The power levels of monochromatic and frequency-modulated MW are about 70 mW. The center frequency of frequency-modulated MW is coincident with the monochromatic MW.

Figure 7. DNP frequency profile at 20 K: ε as a function of MW frequency at 20 K with MW power of 70 mW. The DNP signal and NMR signals are obtained during the build-up time of 150 sec ($T_1^n \sim 30$ sec) with and without MW, respectively. DNP spectrum in the range of positive enhancements is uncompleted because the minimum tuning frequency of the gyrotron is 260.48 GHz.

in Fig. 1, the modulation as a function of time is nearly triangular in shape.

Figure 8 shows ε obtained by monochromatic MW and frequency-modulated MW at temperatures from 15 K to 100 K. Since MW power with frequency modulation is 10 % larger than that without frequency modulation, we used a large enough MW power at each temperatures to reach the maximum DNP signal in order to obtain enhancements independent of these changes of power levels. This 10 % difference of the MW power is not expected to induce a significant change in dielectric heating of the sample. In Fig. 8, ε shows initially a rapid increase with f_{md} , but the increase rate becomes smaller with increasing f_{md} , as reported by others[6, 8]. The increase of ε by frequency modulation is defined as the gain η described by,

$$\eta(\%) = 100 \times \frac{\varepsilon(f_{md}) - \varepsilon(0)}{\varepsilon(0)}, \quad (2)$$

where $\varepsilon(f_{md})$ and $\varepsilon(0)$ are the enhancements with and without frequency modulation, respectively. We find that we were able to obtain a significant

increase η with $f_{md} = 14$ kHz even at 100 K, although ε is small with the MW power of about 1 W at this temperature perhaps due to a high electron spin-lattice relaxation rate $1/T_1^e$.

Our results give some information about the spin lattice relaxation time of electron spins T_1^e by assuming that η saturates if f_{md} exceeds over $1/T_1^e$. As shown in [6], the polarization of nuclei near electrons oscillates if the frequency sweep rate is low, $f_{md} < 1/T_1^e$. If the sweep rate is high, $f_{md} > 1/T_1^e$, this polarization is constant, and the polarization of bulk nuclei is greater. We assume that the sweep rate, $f_{md} \sim 10/T_1^e$, is fast enough to average these oscillations. To show the growth of η with f_{md} more clearly, we show (Fig. 9) η normalized to $\eta(14 \text{ kHz})$, for several temperatures. η at 15 K and 20 K are shown to be almost at the maximum even for f_{md} as low as 2.3 kHz, which can be explained by assuming that 2.3 kHz is faster than that electron spin relaxation rate $1/T_1^e$ at these temperatures. Values of η below 70 K are seen to saturate at 14 kHz, while η at 100 K seems to still grow even beyond 14 kHz, indicating a much shorter T_1^e . Therefore, we expect that T_1^e is of about a few msec at temperatures below 20 K, and is shorter than 700 μsec at 100 K. By following the previously reported temperature and

Figure 8. (Colour online) The ε with and without frequency modulation at temperatures of 15 K (closed circle), 20 K (open circle), 30 K (closed triangle), 50 K (open triangle), 70 K (closed square), and 100 K (open square). The MW power levels at the sample position are about 70 mW at 15 K and 20 K, 153 mW at 30 K, 470 mW at 50 K, 720 mW at 70 K, and 1 W at 100 K.

Figure 9. (Colour online) Normalized η to $\eta(14 \text{ kHz})$ as a function of f_{md} .

Figure 10. $\eta(14 \text{ kHz})$ as a function of temperature.

magnetic field dependence of $1/T_1^e \propto B_0^4 T$ [7, 30–32], we roughly estimated $T_1^e \simeq 5 \text{ msec}$ at 15 K and $T_1^e \simeq 750 \mu\text{sec}$ at 100 K, which is consistent with the values estimated from Fig. 9. These values of $1/T_1^e$ are also approximately consistent with those previously reported [28, 33]. This also supports the assumption that the drop in ε at 100 K is due to a small MW B_1 field in comparison with $1/T_1^e$. Thus, a high ε at 100 K requires high B_1 field overcoming T_1^e or a f_{md} whose period is much shorter than T_1^e . In this study, however, we were unable to increase the MW power at 100 K beyond 1 W as our cooling power was not sufficient to overcome any higher dielectric heating.

The temperature dependence of $\eta(14 \text{ kHz})$ is depicted in Fig. 10. $\eta(14 \text{ kHz})$ increases from about 68 % to about 92 % with increasing temperature from 15 K to 30 K, but decreases with further increase in temperature. However, $\eta(14 \text{ kHz})$ remains above 60 % even at 100 K, which might be interesting to those who use MAS-DNP at 100 K. The temperature dependence of $\eta(14 \text{ kHz})$, which has a maximum at 30 K, is consistent with that obtained at 95 GHz [6]. In the paper, η increases with increasing temperature up to 50 K. Further studies, such as temperature dependence of spectral diffusion rate and T_1^e , are required to understand the temperature feature.

4. Conclusion

In this study, we have shown DNP obtained using a fast frequency-tunable, amplitude-switchable 260 GHz gyrotron with 40 mM TEMPOL, at various temperatures. We obtained a DNP frequency profile by a step-wise sweep of the MW frequency over 500 MHz, at fixed NMR frequency. By sweeping the anode voltage of the gyrotron, we were able to perform a frequency modulation at sweep rates f_{md} up to 14 kHz, covering a frequency band of electron spin resonance of 100 MHz. Frequency modulation was shown to be effective in producing a gain in enhancement of more than 60 % from 15 K to 100 K. Thanks to the high power of the gyrotron, we were also able to show the effectiveness of the frequency modulation even at 100 K. We achieved a small enhancement of about -8 and -5 with and without frequency modulation, respectively, at 100 K because the enhancement saturates after about 1 W probably due to our poor cooling power. However, the effectiveness of frequency modulation at high temperature, even at 100 K, would be still valuable to those who are able to apply high power frequency-modulated MW without much dielectric sample heating, as in MAS-DNP.

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Gyrotron

DNP SIGNAL

260 GHz

> 60 % increase
(15 K ~ 100 K)

400 MHz ^1H NMR