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Abstract

We describe the design and implementation of the instrumentation required to perform DNP-NMR at higher field strengths than previously demonstrated, and report the first magic-angle spinning (MAS) DNP-NMR experiments performed at H/e frequencies of 700 MHz/460 GHz. The extension of DNP-NMR to 16.4 T has required the development of probe technology, cryogenics, gyrotrons, and microwave transmission lines. The probe contains a 460 GHz microwave channel, with corrugated waveguide, tapers, and miter-bends that couple microwave power to the sample. Experimental efficiency is increased by a cryogenic exchange system for 3.2 mm rotors within the 89 mm bore. Sample temperatures \(\leq 85\) K, resulting in improved DNP enhancements, are achieved by a novel heat exchanger design, stainless steel and brass vacuum jacketed transfer lines, and a bronze probe dewar. In addition, the heat exchanger is preceded with a nitrogen drying and generation system in series with a pre-cooling refrigerator. This reduces liquid nitrogen usage from \(>400\) liters per day to \(<100\) liters per day and allows for continuous (\(>7\) days) cryogenic spinning without detrimental frost or ice formation. Initial enhancements, \(\varepsilon = -40\), and a strong microwave power dependence suggests the possibility for considerable improvement. Finally, two-dimensional spectra of a model system demonstrate that the higher field provides excellent resolution, even in a glassy, cryoprotecting matrix.

Keywords

Dynamic Nuclear Polarization; Instrumentation; Sensitivity; Magic Angle Spinning; Nuclear Magnetic Resonance; TOTAPOL

1. Introduction

Dynamic nuclear polarization (DNP) has emerged as a widely applicable technique to provide significant gains in sensitivity to NMR [1-6]. In a DNP experiment the sample is generally doped with an exogenous paramagnetic polarizing agent, and the large polarization present in the electron spin reservoir is transferred to the nuclear spins via
microwave irradiation of transitions in the electron paramagnetic resonance (EPR) spectrum. In the early 1950’s Carver and Slichter [7; 8] performed the initial demonstration of DNP, but subsequent applications to high resolution, high field NMR have been limited. In particular, there was a dearth of microwave sources operating at electron Larmor frequencies (130-660 GHz) corresponding to the magnetic fields of the superconducting magnets (200-1000 MHz 1H frequencies) used in contemporary NMR experiments. This barrier was broken in the early 1990’s by gyrotrons [3; 4] and subsequently by Gunn and Impatt diodes [4; 9] resulting in the application of the method to a wide range of chemical and biochemical problems at fields up to 9 T[10-15] with one instrument operating at 14.1 T [16].

The recent availability of commercial DNP spectrometers operating at 9.4 T (1H/e− frequencies of 400 MHz/263 GHz) [17] has greatly expanded access to DNP [18-20]. However, for many contemporary NMR experiments, 9.4 T is a relatively low field for optimal spectral resolution and it is therefore important to extend DNP to higher fields. Here, we describe the extension of magic-angle spinning (MAS) DNP to 16.4 T (1H/e− frequencies of 700 MHz/460 GHz), a nearly twofold increase in field over commonly available DNP instrumentation. Our initial experiments show that standard samples yield the expected enhancements and that the higher field provides increased resolution even for molecules embedded in glassy solvents such as glycerol/H2O.

This paper is organized as follows. Section 2 describes details of the instrumentation, including advances in MAS NMR probe technology, cryogen cooling and delivery, cryogenic sample exchange, and microwave power delivery. Section 3 presents one and two-dimensional experiments on model compounds that illustrate the improved resolution available to DNP experiments at higher magnetic fields.

2. Spectrometer Design

The spectrometer architecture is illustrated schematically in Figure 1a. Shown are a 700 MHz/89 mm magnet and a 460 GHz gyrotron. The microwave radiation from the gyrotron is coupled to the probe (Figure 1b) by a system of corrugated waveguides, tapers, and miter-bends. On the left of the figure are located the cryogenics for the system. It presently consists of a nitrogen generator in series with ballasts, pressure regulators, refrigerators, heat exchange coils, and vacuum jacketed transfer lines cool and deliver the dry ~80 K N2 gas to the sample chamber. The spectrometer console, designed by Cambridge Instruments, is in the background. We now discuss each of these components in greater detail.

Nitrogen generation for MAS

To achieve operating temperatures down to ~80 K, we and others have traditionally used dry N2 produced from liquid boil-off to drive the MAS rotors. After evaporation, the N2 is first warmed to ambient temperature, to allow precise control of the pressure, and then cooled directly to ~80 K with a custom pressurized can heat exchanger [21; 22]. While boil-off N2 has the advantage of very low H2O vapor content, which prevents ice formation, this strategy leads to high operational costs, due not only to the N2(l) required for generation of the dry gas, but also the N2(l) needed to re-cool the gas from 300 K to 80 K. To reduce costs and allow for continuous long-term operation of the spectrometer, we now employ a N2 generation and pre-cooling strategy similar to that described previously [16] and illustrated schematically in Figure 1c. Compressed air that initially has a dew point of 253 K is first processed through a series of two pressure swing activated (PSA) dryers (Parker-Balston, Haverhill, MA). The dry air then passes through a PSA nitrogen generator (Parker-Balston, Haverhill, MA) that removes oxygen and argon and further reduces the H2O dew point to <77 K, as is crucial to prevent ice formation in the heat exchange coils. The pressure of the dry N2 gas is stabilized by another ballast and controlled precisely with pressure regulators.

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From there it enters a Polycold PGC-152 gas chiller shown in Figures 1a and 2 for pre-cooling (Brooks Automation, MA) from 300 K to ~150-200 K, depending on the flow rate. Bayoneted connectors and vacuum jacketed transfer lines connect the output of the refrigerators (one for bearing and one for drive) to the input of a custom pressurized-can heat exchanger [21] described below. This strategy allows for continuous operation for periods longer than one week without detrimental ice formation while reducing the nitrogen consumption rate from ≥400 L N$_2$(l) per day to ≤200 N$_2$(l) per day. In addition, the liquid that was vaporized and used to drive the rotor is no longer used, saving an additional ≥100 liters/day. Therefore the system saves ≥4 in nitrogen cost.

**Heat Exchanger**

Following cooling to T=150-200 K by the Polycold chillers, the N$_2$(g) is routed via vacuum jacketed transfer lines to the heat exchanger which further cools the gas to ∼85 K (Figure 2). This device is designed in a manner similar to the one we described some time ago [21; 22], but with several modifications. Specifically, it consists of two independent 7 turn, 7″ cooling coils made of 0.375″ o.d. nickel-plated copper tubing, which independently cool the drive and bearing gas and permit the two to be adjusted independently. The large cooling capacity of the coils allows a relatively low N$_2$(l) level (resulting from condensation of N$_2$(g) at <5 psi in the can) to effectively cool the spinning gases to ∼85 K, and yields stable, long-term cryogenic MAS without liquefaction of the spinning gases. Less than 1 K temperature stability over a period of days is achieved as described previously [22] with heating elements and Cernox temperature sensors that are engineered into the flexible transfer lines (Precision Cryogenics, Indianapolis, IN) near the probe interface and are controlled by 50 and 100 W heating units under PID feedback (Lakeshore Cryogenics, OH). A further modification of the heat exchanger that is under development will use a third chamber and permit the drive and bearing to operate at higher temperatures while independently cooling the center of the rotor containing the sample.

**Metal Composite Transfer Lines**

In large 127 mm bore magnets [22; 23], it is possible to use fiberglass in the dewar and vacuum jacketed transfer lines to avoid magnetic materials. However, although fiberglass is an excellent thermal insulator, it must be thick for use in transfer lines and dewars. It also requires a relatively large vacuum space between the inner and outer vessels, as its emissivity can otherwise lead to substantial radiative heat transfer to the outer vessel. Furthermore, the epoxy required to connect the fiberglass to other pieces of the assembly complicates fabrication and is prone to forming leaks that compromise the vacuum space. Meanwhile, gases (especially helium) can permeate the fiberglass itself.

To circumvent these issues the probe transfer lines shown in Figure 3 are made exclusively of non-magnetic brass and austenitic steel. This provides excellent insulation of the cryogens while passively holding a vacuum for extended periods of operation. We emphasize that insulating the cryogens until they enter the sample chamber is crucial for attaining the sample temperatures of ∼85 K that significantly increase DNP enhancements, as described in the results section.

**Dewar**

A vacuum jacketed dewar thermally isolates the cryogenic sample chamber from the magnet bore. Excellent insulation is required not only to establish ∼85 K at the sample, but also to protect the O-ring on the bore tube of the NMR magnet from freezing, compromising the insulating vacuum of the magnet, and leading to a quench. The inner vessel is machined from 2.25″ i.d., 3″ o.d. silicon bronze tubing (National Bronze, Lorain, OH). We elected to use bronze rather than stainless steel because the inner vessel of the dewar surrounds the
sample in close proximity, and even a weakly ferromagnetic character can lead to a field inhomogeneity across the sample that cannot be effectively compensated for by shim coils. Although austenitic stainless steel (i.e., 316, 321 series) is commonly referred to as “non-magnetic”, it actually becomes quite magnetic by NMR standards after mechanical work or thermal cycling due to martensite formation[23].

Because it is prohibitively difficult to machine the full 30″ length of the inner surface to the final 0.015″ wall thickness, the inner vessel is first cut into three sections to turn down the material, and then soldered together with vacuum tight joints (see Figure 3c).

There is a bellowed port on the top of the dewar to accommodate the sample exchange tube similar to that described previously.[23] In this dewar we also include a port to accept the cryogen exhaust line. Utilizing the space above the probe to exhaust the cryogens out of the top of the system frees space at the bottom of the probe, making it easier to fit the fiber optics, magic-angle adjustment assembly, and transfer and transmission lines into the lower assembly.

700 MHz MAS DNP Probe

The custom designed probe, shown in Figure 1b and Figure 4, has over 11 ports for the diverse functions required of a DNP MAS probe. Fiber optic channels monitor the MAS frequency, the sample temperature, and provide a pathway for in situ illumination of the sample with visible light for photochemical experiments. The fiber optics in the sample chamber are shown in Figure 4a,b. In-situ irradiation of the sample with visible light, in conjunction with temperature control from 80–300 K, facilitates cryo-trapping of photoreaction intermediates as in bacteriorhodopsin.[24] The temperature is continually monitored at four points using fiber optic temperature sensors (Neoptix, Canada): a sensor several millimeters away from the sample (the yellow fiber optic in Figure 4a) provides a close measure of the sample temperature, one in the probe box near the tuning elements is needed to maintain long-term radiofrequency tuning and stability, and sensors at the top and bottom of the magnet bore near the O-rings protect the superconducting magnet system.

Three vacuum jacketed composite metal transfer lines provide an insulated pathway for delivery of the cold bearing, drive, and variable temperature gas. A high-flow vacuum jacketed port at the top of the probe exhausts the cold cryogens during operation, but is switched to input high pressure ejection gas during sample exchange (see below).

A Schaefer-McKay transmission line circuit[25; 26] generates RF fields at the $^{13}\text{C}$ and $^1\text{H}$ Larmor frequencies of 175 MHz and 698 MHz, respectively. The Rabi frequencies are $\gamma B_{1f}/2\pi=105$ kHz and 90 kHz for $^1\text{H}$ and $^{13}\text{C}$, respectively. The transmission line (1.125″ outer conductor, 0.25″ inner conductor) allows the temperature sensitive and more bulky tuning and matching capacitors to be physically, and thermally, isolated from the cryogenic sample chamber, while providing efficient coupling to the 5-turn RF transmit/receive solenoid. The 460 GHz channel of the probe delivers the microwave power to the sample as a Gaussian beam (see below).

Spinning detection is performed on the rotor body with the detection fiber optics protruding into the stator housing as indicated in Figure 4a. A support block is attached to the stator housing and is required to lock the detection optics in place during cryogenic operation and extreme temperature cycling. Two PEEK screws, orthogonal to the holes in the Kel-F support block that guide the fiber optics, are threaded through the support block and gently pinch the spinning detection fiber optics to keep them securely in place. The support block also houses a pathway for a variable temperature gas-stream (nitrogen or helium) to blow directly on the rotor, although this is not yet fully implemented.
3.2 mm Cryogenic Sample Exchange

Previous DNP probe technology in our lab has been designed for use in 127 mm (5″) bore magnets. Even with the longer 4 mm diameter rotors employed in those probes, there is sufficient space in the bore for the rotor to turn from the magic angle to an orientation parallel with the bore for sample insertion and ejection. However, the smaller 89 mm bore magnets present a greater challenge. In order to implement a cryogenic sample exchange system, we optimized the ejection trajectory in the sample eject pipe, and maximized the space available in the dewar.

After the rotor makes the turn in the sample eject pipe, it must couple to the long straight ejection tube leading to the top of the magnet. This is accomplished by two overlapped cones, which maintain the ability to adjust the magic angle[23]. However, the cone requires space that is difficult to accommodate in the 89 mm bore. Whereas previous designs simply mounted the cone on the vertical end of the sample eject pipe, the present design introduces a curved pathway to first bend the rotor trajectory back toward the center of the bore. This complicated geometry is fabricated by 3D printing (Accelerate Global Sourcing, Cedar Park, TX). Extrusions on the surface of the eject pipe flush with the front bearing mount ensure proper alignment of the insertion pathway in the ejection pipe with the inner surface of the front bearing. Care is taken to ensure that the guiding pathway is well aligned and extremely smooth (<0.2 μm roughness), to allow the rotor to slide into the front bearing of the stator. The robust plastic ejection pipe survives dozens of temperature cycles and hundreds of sample ejections.

460 GHz Microwave Transmission

Substantial efforts in the development of microwave sources for DNP have resulted in the availability of robust, continuous wave gyrotrons with 10-35 W power levels capable of generating electron nutation frequencies of 1 MHz across microliters of lossy sample volume[18; 27-31]. A gyrotron operating in the second cyclotron resonance harmonic with a TE_{11,2} whispering gallery interaction mode was specifically developed for DNP at 16.4 Tesla. This design offers greater than 1 GHz of tuning range while maintaining 12 W of stable microwave power output for extended periods. [32; 33]

The output beam of the gyrotron reflects off the last surface of the mode converter and into the corrugated waveguide that protrudes into the cross bore of the gyrotron magnet. Alignment of the output beam is crucial to maintaining a high purity HE_{11} mode in the transmission line. After exiting the crossbore of the gyrotron magnet, the microwave power traverses 4.7 m to the probe in a 19 mm wide corrugated waveguide (see Figure 5a), and then travels 0.8 m up the magnet bore. Altogether the radiation travels 5.5 m passing through 6 miter-bends and two tapers, so any distortion in the beam quality (in the form of the presence of higher order modes) leads to a cumulative loss of the microwave power and significant decrease in DNP performance.

To precisely align the output of the mode converter mirror with the probe inside the NMR magnet across the room, we utilize two sets of double 90 miter-bends. Each employs small gaps between the waveguide pieces connecting the miter-bends, as shown in Figure 5b. Generally, gaps in overmoded corrugated waveguides that are shorter than the i.d. of the guide have very low transmission loss. This allows us to add more degrees of freedom during the alignment process by implementing a ‘flexible’ GHz transmission line. Evidence for the excellent coupling into the transmission line from the gyrotron and proper alignment of the system is shown in Figure 5c. The pyroelectric image of the beam recorded from the bidirectional coupler (Figure 5a) shows an excellent beam with >90% Gaussian content. The bidirectional coupler[34] permits continuous monitoring of the microwave power either with
a calorimeter or a diode. The output can be fed back into the LabView control system of the gyrotron to stabilize the power output via PID control of the electron beam current.

The HE_{11} mode maintained in the 19 mm corrugated waveguide, whose cross section is illustrated in Figure 5d, is accepted by the 460 GHz channel of the probe. The microwave beam is then focused into a 12.7 mm i.d. tapered smooth-wall dielectric (Macor) waveguide. After a 90° miter-bend to direct the radiation up the bore of the magnet, the beam is further focused with a tapered corrugated Al waveguide that couples to the ~0.6 m long vertical helically corrugated (tapped) 4.6 mm i.d. copper waveguide. The radiation then reflects off of a final miter-bend at the inverse magic angle, travels through a short section of corrugated waveguide, and illuminates the sample as shown in Figure 5e. The beam quality is maintained through these tapers and miter-bends, as can be seen by the >90% Gaussian content of the experimental beam in Figure 5f.

### 3. Results

Figure 6a shows an enhancement of $\varepsilon = -40$ on $^{13}$C-Urea dissolved in a 60/30/10 glycerol/D$_2$O/H$_2$O glass forming matrix containing 10 mM of the biradical polarizing agent [35] TOTAPOL[36]. As was the case at lower fields, the enhancements have a strong dependence on temperature[17]. Thus, we have found that it is important to operate at temperatures in the 80-85 K range to achieve enhancement values that agree well with the expected $\sim \omega_i^{-1}$ scaling of the cross effect. [22; 36-39] The power dependence shown in Figure 6b, recorded at 6.7 kHz spinning frequency and $T = 90$ K, reaches $-20$ enhancement with 11 W output power, whereas the enhancement shown in Figure 6a increases to $-40$ by reducing the spinning frequency to 4.8 kHz, cooling the sample to 80 K, and using 12 W of output power. We note that there is still a linear dependence of the enhancement on microwave power, as shown in Figure 6b. Thus, further increases $\gamma B_1$ will likely lead to further increases in $\varepsilon$.

Finally, it is essential that the system be sufficiently stable to record multidimensional spectra. Figure 7a shows one bond correlations recorded in a 2D fashion with RFDR $^{13}$C-$^{13}$C recoupling[37], and Figure 7b employs DARR mixing for short and long-range contacts[37-39]. Each of these two-dimensional spectra took 2.6 hours to record. The ability to record these 2D spectra demonstrates the long-term stability of the DNP instrumentation and spectrometer. We note that the resolution of the 2D spectrum is sufficient to assign all of the proline resonances.

### 4. Conclusions and Outlook

Significant DNP enhancements of $\varepsilon = -40$ have been demonstrated at a field strength of 16.4 T (700 MHz for H). If the gain in Boltzmann polarization due to the lower temperature (300 K/85 K=3.53) is taken into account, then the total enhancement is $\varepsilon^\dagger \sim -140$ which is a significant improvement in sensitivity. Thus, these experiments provide a convincing demonstration of the gains that DNP can provide at high magnetic fields. At present this is to our knowledge the highest frequency DNP spectrometer in operation, and importantly takes DNP to a regime of considerable significance for studies of biological samples.

The gyrotron frequency of 460.5 GHz presently irradiates the portion of the nitroxide lineshape leading to negative enhancements. Typically for CPMAS DNP experiments with nitroxide radicals, the magnitude of enhancement is smaller on the negative side of the enhancement profile, so we expect still higher magnitude positive enhancements when the NMR field is further optimized. The strong dependence of the DNP enhancement on
microwave power suggests that improvements to the microwave transmission line, gyrotron output power, or both, could also lead to significant improvement in the enhancements.

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Highlights

DNP at 700 MHz/460 GHz.
Magic angle spinning enhancements of |40|.
Instrumentation for 460 GHz (\(\lambda =0.65\) mm) and low temperatures.
Figure 1.
700 MHz DNP instrumentation. a) Schematic showing the physical layout of the NMR magnet, heat exchanger, gyrotron, microwave transmission lines, and Cambridge Instruments spectrometer console with RF power amplifiers from Ophir (Los Angeles, California) at 700 MHz and Herley Industries (Lancaster, Pennsylvania) at 175 MHz. b) Custom MAS probe capable of delivering microwave, radiofrequency, and visible radiation to the sample while also enabling stable long-term MAS at 80 K and cryogenic sample exchange. c) System architecture showing the serial and parallel layout of the nitrogen gas as it is purified, cooled, and transferred to the sample chamber. Cryogen exhaust and sample exchange lines are connected to the probe from the top of the magnet.
Figure 2.
Photographs of the cryogen cooling apparatus. a) The inlet ports of the refrigerators (black units in upper corners) are connected to the precisely controlled bearing and drive gas regulators. Vacuum jacketed lines connect the refrigerators, heat exchanger, and NMR probe. b) The nickel-plated copper coil of the heat exchanger with 7 turns. c) The cold heat exchange assembly showing the 8″ copper can.
Figure 3.
Cryogenic isolation strategies. a) The vacuum jacketed transfer lines inside the probe employ brass tubing inside the bore of the magnet that can be soldered to the stainless steel (s.s.) components at the bottom of the assembly. b) The vacuum jacketed dewar features an inner bronze vessel and an aluminum outer vessel that are connected via a fiberglass thermal break and brass bellows to allow for transport of the cryogen exhaust and the rotor during sample exchange. c) CAD rendering show the three sections of the dewar inner vessel that are soldered together. d) Photograph of the dewar.
Figure 4.
Upper assembly of the 700 MHz MAS DNP probe. a) Photograph of the fiber optics and the GORE-TEX® seal required for cryogenic sample exchange. b) Solid CAD model. c) Cut-away showing the microwaves being directed at the sample and surrounding RF coil. The sample eject pathway is curved to fit the assembly into the bore while still allowing for adjustment of the magic angle.
**Figure 5.**
460 GHz microwave transmission and beam quality. a) The corrugated transmission line contains miter-bends, a bidirectional coupler for power monitoring and efficiently couples the microwave output of the gyrotron to the probe. b) The probe contains smooth-wall Macor and corrugated aluminum tapers to focus the microwave beam into the 4.6 mm i.d. vertical waveguide leading to the sample chamber. c) Thermal image recorded with a pyroelectric camera (Spiricon, Logan Utah) of the beam taken from the middle of the 3 m stretch of the 19 mm i.d. corrugated waveguide showing a high Gaussian content 10 cm from the waveguide aperture d) Schematic showing the $\frac{1}{4} \lambda$ depth and spacing of the corrugations e) Cross-section of the stator with the rotor and waveguide f) Image of the high-quality beam being launched from the end of the waveguide in panel e toward the sample 4 cm from the waveguide aperture.
Figure 6.
DNP at 700 MHz. a) enhanced $^{13}$C CPMAS spectrum of 1 M $^{13}$C-Urea in 60/30/10 (d8-glycerol/D$_2$O/H$_2$O, 10 mM TOTAPOL, showing an enhancement of -40. The spinning frequency is $\omega_r/2\pi = 4.8$ kHz, the sample temperature is 80 K, and the gyrotron output power is 12 W. b) The DNP enhancement as a function of gyrotron output power. The spinning frequency is $\omega_r/2\pi = 6.7$ KHz, sample temperature is 90 K, the gyrotron cathode potential is 12.1 kV, the microwave output frequency is 460.5 GHz, and the $^1$H NMR frequency is 697.8 MHz.
Figure 7.
$^{13}\text{C},^{13}\text{C}$ Correlation spectra at 700 MHz. a) one-bond radio frequency driven recoupling (RFDR) correlation showing the one-bond cross-peak assignments. The spinning frequency is $\omega_r/2\pi=9.8$ kHz, and the sample temperature is 85 K b) Short and long-range correlations with dipolar assisted rotary resonance (DARR) and long-range correlation assignments. The spinning frequency is $\omega_r/2\pi=7.8$ kHz, and the sample temperature is 85 K.