Poster #1073/Doty Scientific Webinar

A Highly Versatile Switched Angle Spinning (SAS) Probe

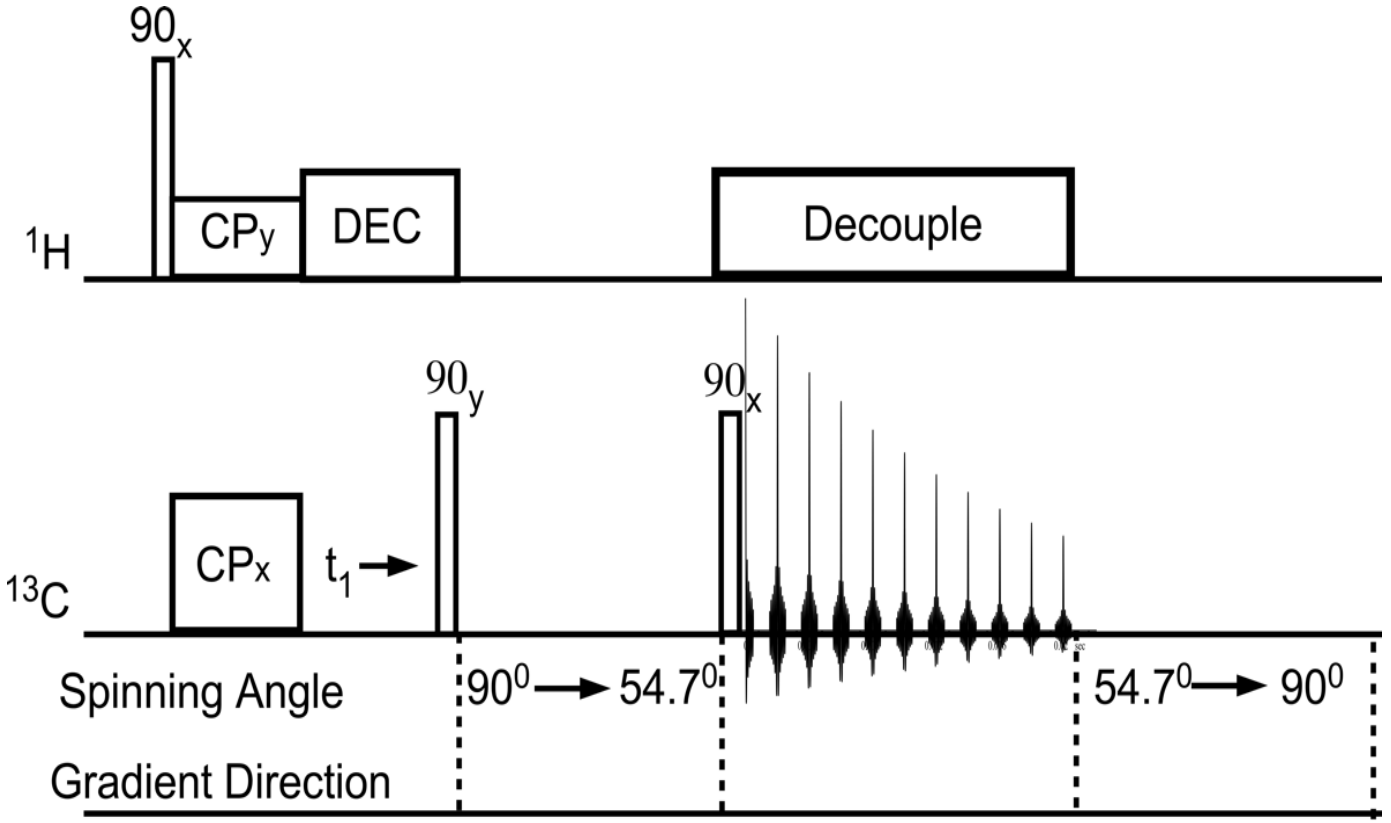
F. David Doty[a,§], Glenn Doty[a], John P Staab[a], J. B. Spitzmesser[a], Vince Cothran[a], Daniel Arcos[a], Bibhuti Das[a,b], and Paul D Ellis[a,]

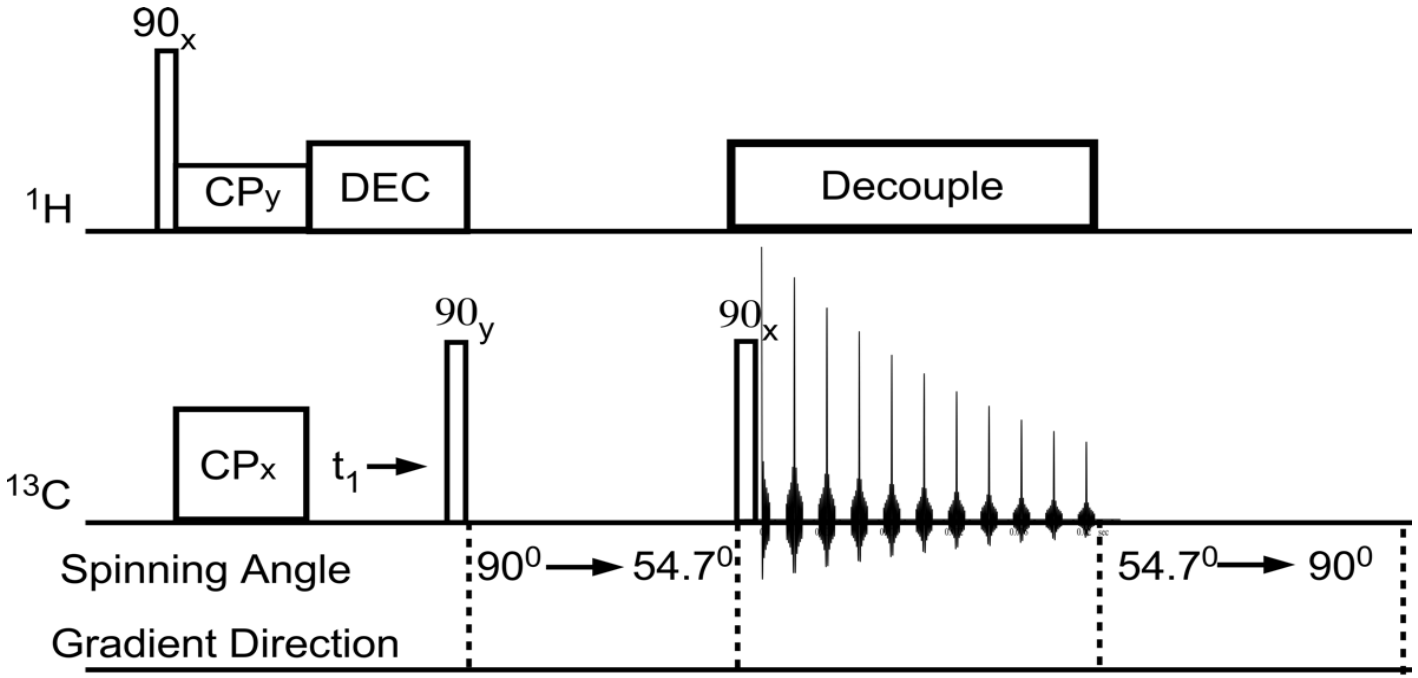
[a]Doty Scientific, Inc
700 Clemson Road
Columbia, SC 29229
Email: david@dotynmr.com
Email: paul@dotynmr.com

[b]Bibhuti Das
Current Address:
Nalco Champion (an Ecolab Company),
11177 S Stadium Drive, Sugar Land, TX 77478.
Email: bibhuti.das@ecolab.com.

Approximately thirty-five years ago, Bax, Szeverenyi, and Maciel [1, 2] (BSM) started a small revolution within the area of solid state NMR (ssNMR) spectroscopy utilizing magic angle spinning (MAS). What they accomplished was to rotate the spinning axis from θ_1 to θ_2 during the experiment. In their experiments one of the angles would be the magic angle: $\theta_m = cos^{-1}(1/\sqrt{3})$. The BSM experiments resulted in a 2D experiment where the spins would evolve under one angle and detected under a second angle. A schematic depiction of the pulse sequence is outlined in **Figure 1**. The spins after ^{13}C cross-polarization (CP) evolve under the influence of θ_1 (90° with respect to the magnetic field)

Figure 1. The basic schematic of the SAS experiment as described by BSM is depicted to the right. The exception is the inclusion of the potential gradient pulses. The durations depicted in the Figure are for information only and do not represent relative values.





With ^{1}H decoupling for a period t_1. The resulting magnetization is in turn is flipped onto the z-axis. The spinner assembly then rotates from 90° to θ_m while the magnetization remains along the z-axis. After the stator/rotor has settled, the magnetization is flipped back to the transverse plane and detected for a time t_2 while spinning at the magic angle (θ_m). This experiment separates portions of the Hamiltonian that depends on angle(s).

1. Bax, A., N.M. Szeverenyi, and G.E. Maciel, *Chemical shift anisotropy in powdered solids studied by 2D FT NMR with flipping of the spinning axis.* Journal of Magnetic Resonance (1969), 1983. **55**(3): p. 494-497.
2. Bax, A., Szeverenyi, and Maciel, G. E., *Correlation of Isotropic Shifts and Chemical Shift Anisotropies by Two-Dimensional Fourier-Transform Magic-Angle Hopping NMR Spectroscopy.* J. Magnetic Resonance, 1983. **52**: p. 147-152.

Most of the Hamiltonians of interest to this presentation depend upon two Legendre polynomials $P_2(\cos\theta)$ or $P_4(\cos\theta)$, i.e.,

$$P_2(\cos\theta) = (½)\cdot(3\cos^2\theta - 1)$$
$$P_4(\cos\theta) = (⅛)\cdot(35\cos^4\theta - 70\cos^3\theta + 3).$$

Interactions: $P_2(\cos\theta)$ … Chemical Shielding, Dipole-Depole, and First Order Quadrupole

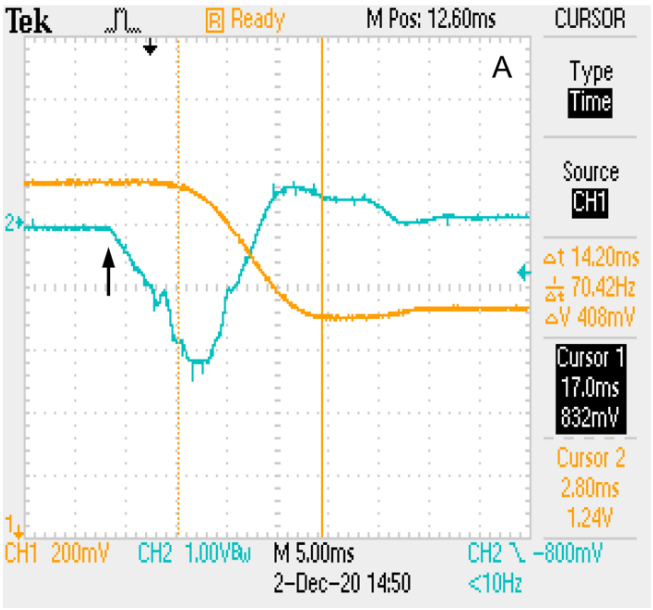
$P_4(\cos\theta)$ … Second Order Quadrupole

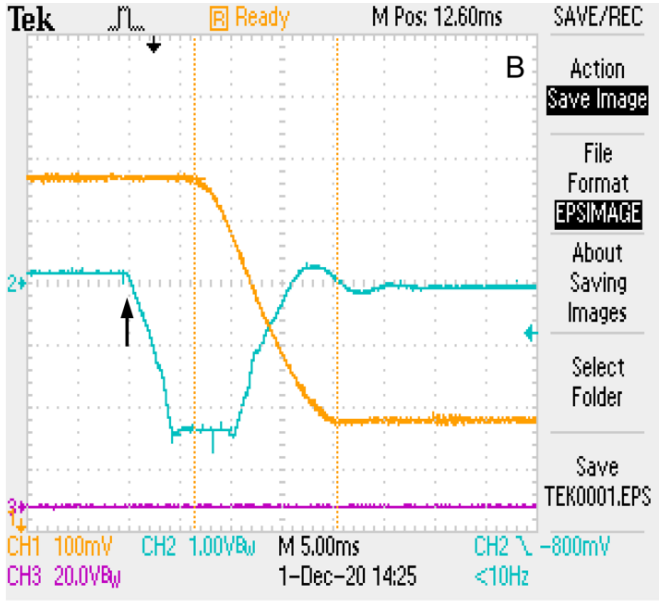
Target Capabilities of the Probe:

One of the several unique aspects of the probe described here is the ability to switch the spinning axis rapidly and accurately between two or more orientations within a single “scan” experiment, and to keep on doing that day after day, month after month, and year after year, for thousands of samples. In addition to the robustness of the design, a key attribute is the rotor assembly must switch between angles quickly. In the present case, the switching time (including settling) going from 90° to the magic angle (a change in angle of 35.26°) is 16.6 ms or 2.12°/ms. Furthermore, the switching times are symmetrical. That is, the time going between angles is independent of direction. Additionally, this probe, *via* a novel coil design, has three independent channels. In its present form, those channels are fixed tunned at ^{1}H, ^{13}C, and ^{15}N. Eventually, the high frequency channel will be either ^{1}H or ^{19}F and the mid- and low-frequency channels will be broadband tunable. The probe supports a three-axis gradient capability. Due to space limitations, the SAS probe fits inside housing which can fit into a wide bore (WB) magnet. Within the housing is a gradient system capable of 270 G/cm along each axis. Finally, this probe has a modest variable temperature capability, i.e., from -50°C to 120°C. In the future we plan to extend this temperature range.

Let’s turn our attention to Switching Times

One of our Problems … The Controller … The electronics can be described as “Archaic”.





The switching time as noted previously in the left panel is on the order of 14.2 ms. However, that is not the case in the panel on the right. Here the switching time is on the order of 12.6 ms.

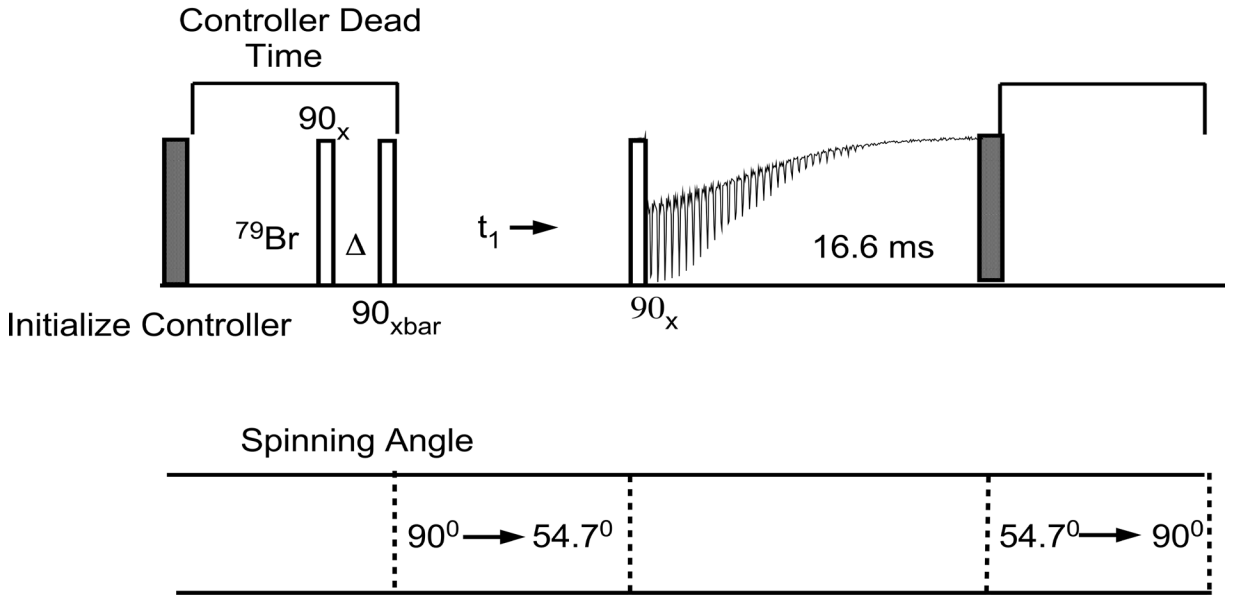
The arrow indicates when the command to “flip” begins. The upper trace represents the response of the motor. In the left panel the probe is out of the magnet. Whereas the right panel the probe is in the magnet. In both panels we have tracked the motor voltage and the movement of the stator. Note: in both panels there is a significant lag between when the motor which sees the pulse (the vertical arrow in each panel) from the spectrometer and when the stator starts to move. That delay is on the order of 7.2 ms. The cause is due to the electronics in (20+ - years-old prototype) controller.

Why not perform an NMR experiment …

Note, we have taken advantage of the controller deadtime by applying the controller pulse some 7.2 ms before we need to initiate a change in the spinning angle. During this deadtime we generate transverse ^{79}Br magnetization. The time Δ is arbitrary. In our experiments Δ was 20 μs.

The subsequent magnetization is stored along the z-axis with 90_{xbar} pulse. At this point the stator starts its motion. After some time, t_1, the stored magnetization is brought back to the transverse plane, via a 90° pulse to initiate data acquisition. The resulting FID will look normal (a collection of decaying spun echoes) only as t_1 approaches the switching time for the angle change.

In our experiments Δ was 20 μs. The subsequent magnetization is stored along the z-axis with 90_{xbar} pulse. At this point the stator starts its motion. After some time, t_1, the stored magnetization is brought back to the transverse plane, via a 90° pulse to initiate data acquisition. The resulting FID will look normal (a collection of decaying spun echoes) only as t_1 approaches the switching time for the angle change.



The pulse sequence utilized the determination of the switching time in the SAS experiment.

In this experiment we are spinning at 10 kHz. In all our experiments we utilized a DSI spinning speed controller. While the stator is stationary, the spinning speed is stable to within ±2 Hz. However, during the angle change the spinning speed changes as much as ±(5 to 7) Hz.

We summarize the results of the “Martin test” with our SAS probe.

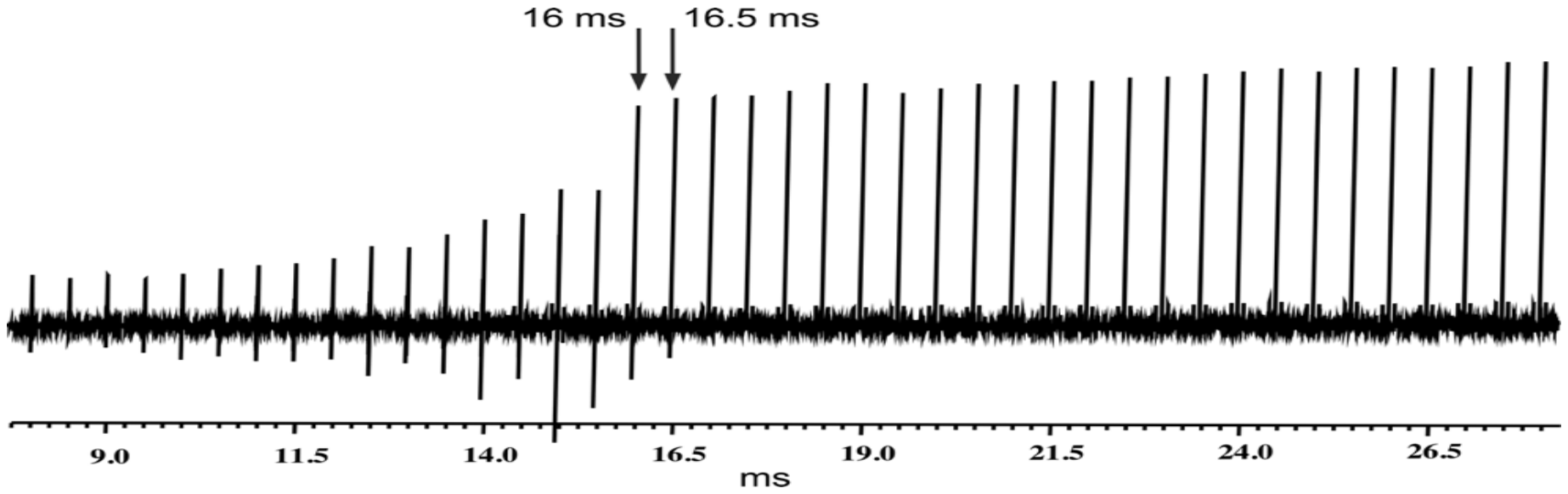
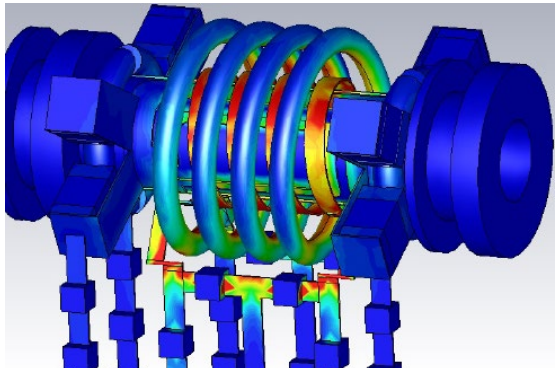


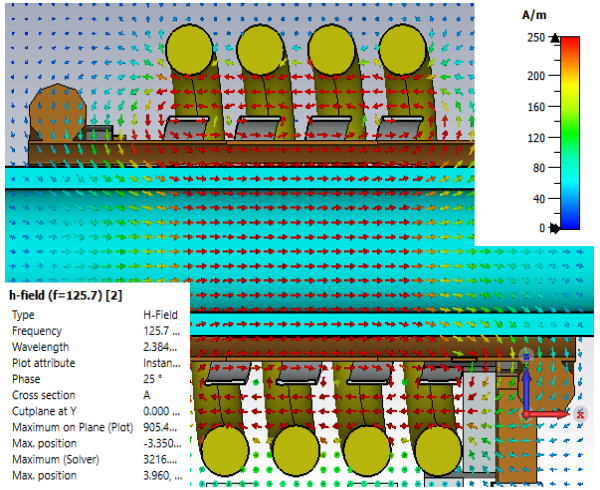
Figure 14. Here we summarize a series of experiments where we have incremented the t_1 by 0.28 ms. The t_1 values associated 16.0 to 16.5ms. A conservative estimate of 17.0 ms appears to be a reasonable value of the switching time.

Litvak, I.M., et al., *Pneumatic switched angle spinning NMR probe with capacitively coupled double saddle coil.* Journal of Magnetic Resonance, 2010. **206**(2): p. 183-189.

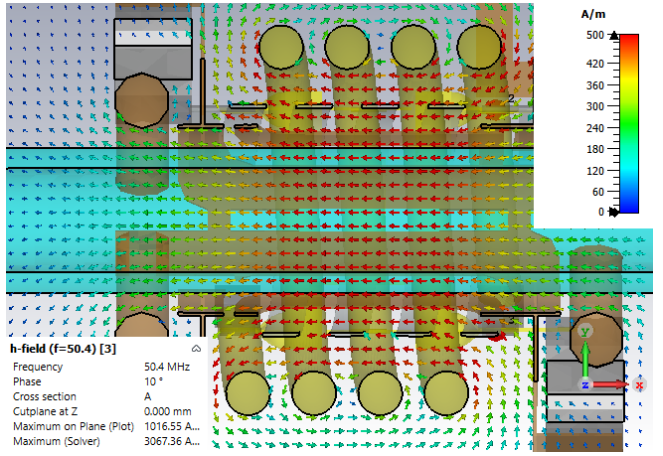
Multinuclear Capability: High Frequency Channel (^{1}H or ^{19}F) the Mid and Low Frequency Channels are broadband tunable.

Getting two magnetically orthogonal coils to work efficiently in MAS is not too difficult – we showed how that could be done using our XC coil for the ^{1}H channel and a solenoid for the LF channel 23 years ago. The challenge is to get *three* magnetically orthogonal coils that can each be locally tuned close to the needed frequencies and thus permit triple resonance with leads that will survive tens of millions of flips.



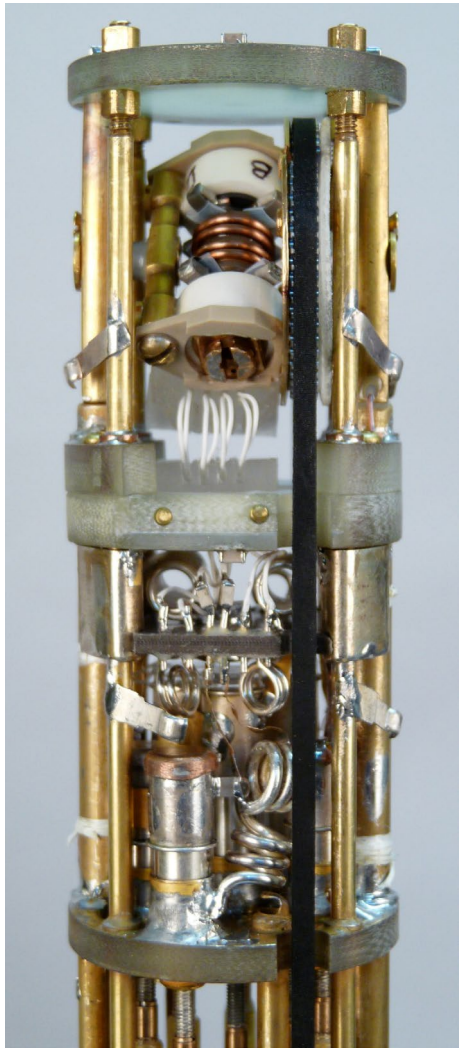


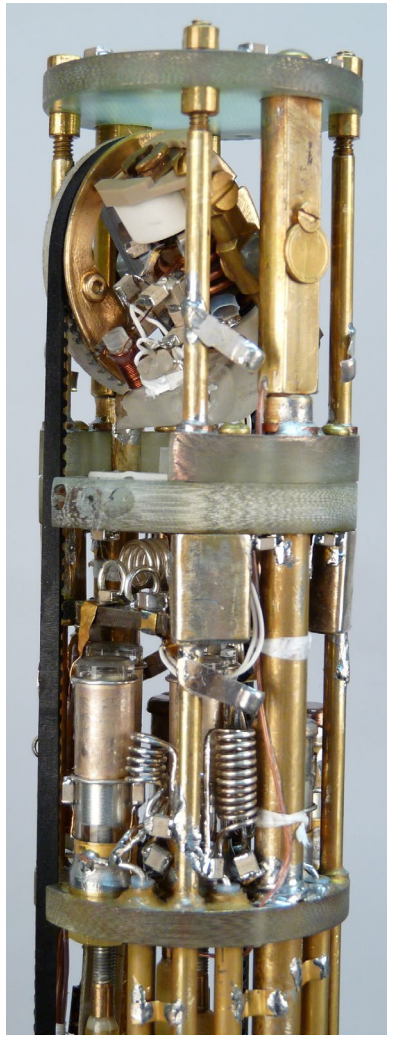
The H field from the inner 13C coil on *The H field from the outer ^{15}N coil on an axial plane.* Here, the Si3N4 rotor is seen in blue.

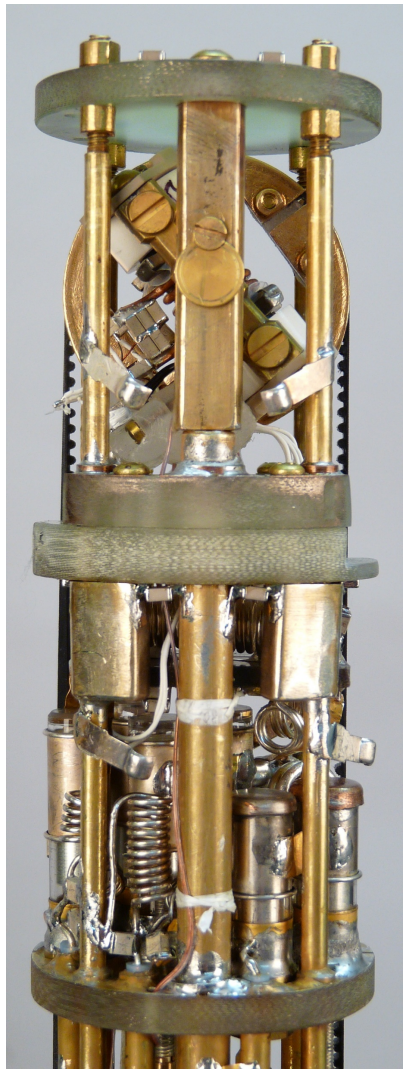


The H field from the outer ^{15}N coil on an axial plane.

The experimentally measured $\pi/2$ pulse widths for each channel for a given power is: 3.35 μs for ^{1}H at 62 W, 6.85μs for ^{13}C at ~300 W, and 10 μs for ^{15}N at ~300 W.







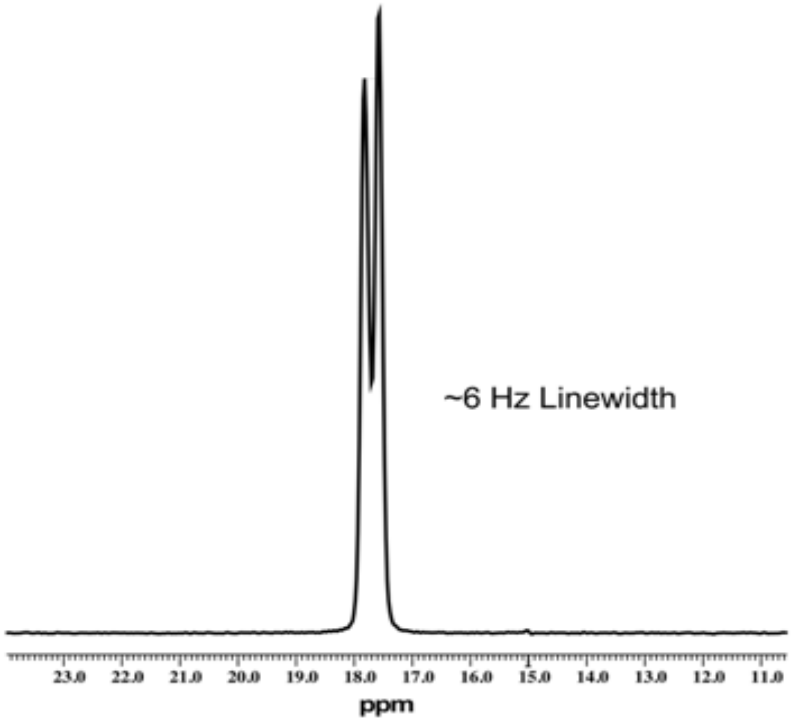
An enhanced Switched Angle Spinning (SAS) probe was designed and manufactured. Three views of the WB 500 MHz, triple-resonance probe shown above.

The photo shows the completed 3 axis PFG gradient stack on the left and the triple-resonance SAS probe on the right. The gradient coil fits inside standard WB high-field magnet shim bores (73 mm ID). The probe (46.5 mm OD) slides inside the gradient coil.

There is a lot of stuff between the sample and the shims … what about the resolution?

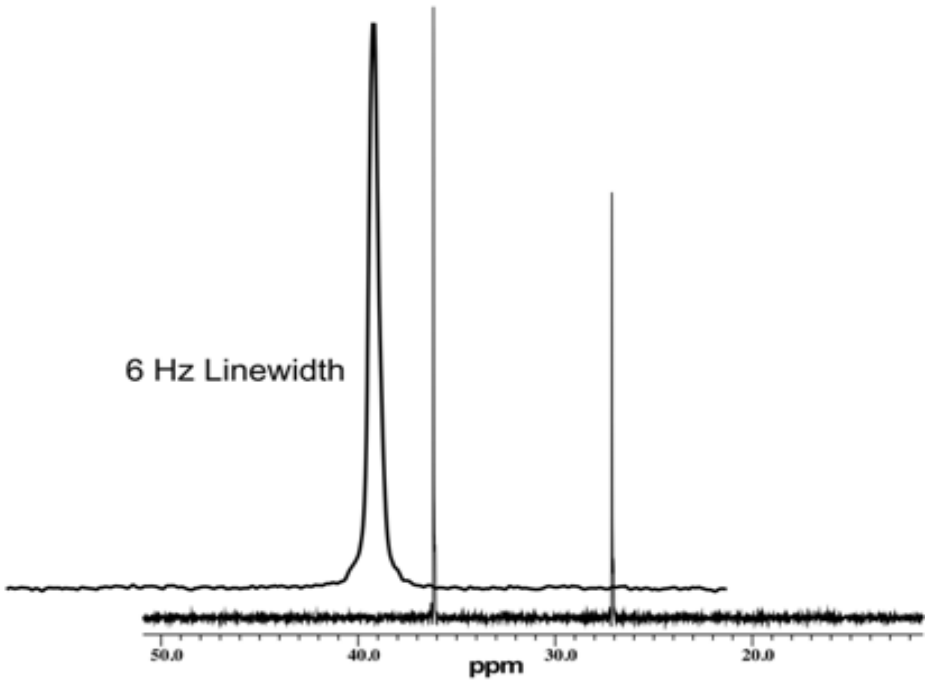
Resolution in the DSI SAS Probe

The Chemical Shift of 0.2735 ppm
Corresponds to a Shift of ~14 Hz.



4 Scans of ^{15}N NMR of ^{15}N labelled (100%) Ammonium Sulfate, Spinning at 5 kHz Illustrating the crystallographic nonequivalent sites.

Expansion of the Deshielded
Resonance of Adamantane



^{13}C NMR of Adamantane at 11.7T
Spinning at 5.2 kHz, 4 scans

What needs to be finished …

More than a year ago (pre COVID) DSI ordered a new console and shim set for our 11.75T spectrometer. After many delays (COVID in nature) about 2 months ago the console arrived was installed and then the vendor turned their attention to the magnet. ***Due to a significant ice buildup in the magnet (great filling techniques over the ~20-year period), it was necessary to remove the ice. This was done in a dramatic fashion … the magnet quenched.*** We are back up and running with a new system, but we are behind. Now that we have improved the magnet homogeneity, we want to repeat some of the resolution experiments. Further, we have a "new" gradient amplifier, so we must reexamine the recovery time for the pulsed gradient. Typically, that recovery time is on the order of a few hundred micro-seconds. Clearly, those numbers must be checked.

Finally, *we are going to utilize our current SAS controller as a boat anchor* and replace it with one utilizing modern electronics with the aim of improving its reliability, significantly reducing the switching time, while at the same reducing the amount of noise the controller sends to the probe.

As they say stay tuned to this DSI station …

Summary

A novel 4 mm Switched Angle Spinning (SAS) probe is described. The probe has 3-channels. Presently, the channels are fixed tuned for ^{1}H, ^{13}C, and ^{15}N. In subsequent versions of the probe, the proton channel can be either ^{1}H or ^{19}F, while the mid- and low-frequency channels on either version will be broadband tunable. The experimentally measured $\pi/2$ pulse widths for each channel for a given power is: 3.35 μs for ^{1}H at 62 W, 6.85μs for ^{13}C at ~300 W, and 10 μs for ^{15}N at ~300 W. Full Computer Simulation Technology (CST) simulations of the probe yielded 3.90 μs for ^{1}H at 62W, 9.69 μs at 300 W, and 9.00 μs for ^{15}N for the same powers utilized in the experiments. The $^{1}H/^{19}F$ channel can handle 200 W, whereas the low frequency channels can handle powers more than 600 W. The probe fits inside an assembly which houses a 3-axis gradient coil set. Each axis within the gradient set is capable of 270 G/cm. This outer probe body fits into a standard wide bore magnet. The construction of the probe is such that it can perform in excess of 10^{6} flips without damage to the coil leads. We illustrate the probes capabilities by demonstrating it switching speed from 90° to the magic angle. The switching speed in this version is 16.6 ms (in either direction). Resolution is important parameter. The probe has achieved a 6Hz on the deshielded resonance in Adamantane and a ~6 Hz resolution on *both* resonances in Ammonium Sulfate Dihydrate.