A Reliable Switched Angle Spinning (SAS) Probe for Solid-State NMR

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INTRO In this update to an ongoing project, we report on optimizations to a triple-resonance H/X/Y SAS-NMR circuit for higher fields (up to at least 800 MHz); improvements to probe mechanics, and development of a high-performance SAS angle controller.

In the landmark paper by Bax, Szeverenyi, and Maciel, they described seminal work on a "Magic Angle Hopping Probe", published over 40 years ago. Over the years, the probe has transformed into what we describe here, known as a Switched Angle Spinning or SAS probe, capable of re-orienting the spinning axis (including RF coils) rapidly and accurately through arbitrary angles. SAS methods, while challenging, have the significant advantage of being able to determine structures in near-native environments on large dilute samples.

A major problem with most earlier SAS probe designs was that the leads to the sample coils would fail after a few tens of thousands of flips.

The objectives of this project included:

- Fast (10-ms) accurate, bi-directional flipping for arbitrary angle sequences.
- Robust operation for millions of flips between services.
- Fast, stable spinning during fast flipping.
- Extremely low vibration and noise, for compatibility with 2D and 3D NMR methods.
- Efficient triple-resonance multi-nuclear performance at high fields.
- Fitting the probe in a mid-bore magnet, or inside a commercially available 3-axes gradient insert for WB magnets.

METHODS

- Devise ***three magnetically orthogonal sample coils***, one for each channel, so they can be individually tuned and matched locally to the desired frequency, thereby permitting the use of fine leads for compatibility with flexing millions of times without failure.
- Use two outer solenoids for the X and Y channels and the classic XC inner resonator with its transverse rf magnetic field as the inner coil for the ^{1}H channel.
- Use multiple parallel wires of ultra-fine-stranded hard-copper for the flexible leads to the coils.
- Use detailed 3D CST simulations – that include the stator, the coils, the lumped elements, and the long flex leads to the tune/match variables – to refine a detailed fully coupled rf circuit model to permit rf circuit optimization in a reasonable time frame.
- Develop a new high-speed modern controller with webserver, internet, and wi-fi connectivity.

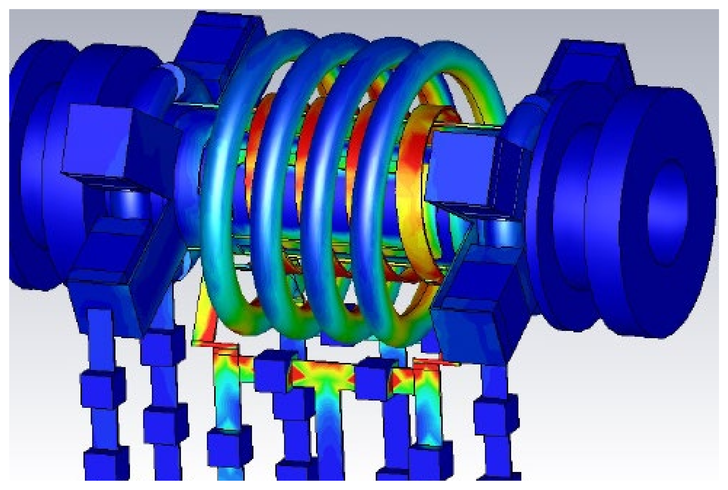

Fig. 1. The novel coil geometry using two concentric solenoids for ^{13}C (middle foil) and ^{15}N (outer wire) respectively, with ^{1}H on the inner XC. Seen here is a rainbow plot of absolute surface current density for the case where the ^{13}C circuit is driven at 126 MHz.

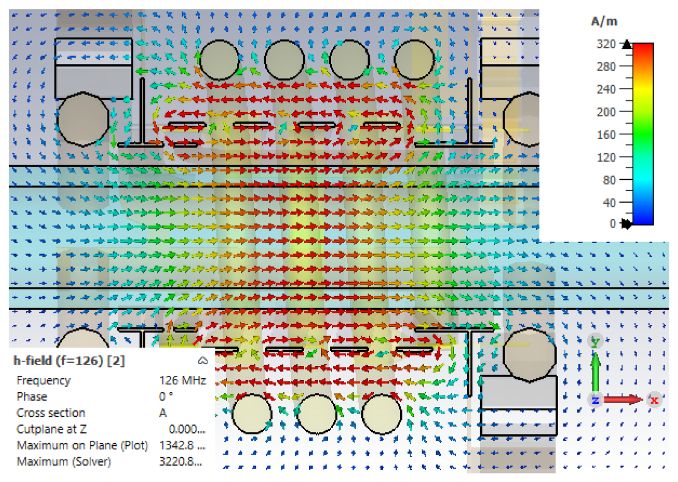

Fig. 2. The **H** (rf magnetic) vector field from the inner ^{13}C foil coil on the z=0 plane for the case where it is tuned at driven at 126 MHz. The outer wire solenoid (not driven) is tuned for ^{15}N, and the XC (innermost foil) is tuned to 500 MHz.

RESULTS A key attribute of the **probe** (Fig. 3) is its mechanical stability and longevity. It demonstrated stable tuning and spinning, as measured multiple times over a period of >1 year in which the stator underwent ~500,000 flips. Additionally, the probe has VT range of -15 °C to +80 °C.

Equally important to the performance of the probe is the user's ability to guide the setup and control of the experiment.

The new **controller** (Fig. 3) has:

- Reduced switching/settling times, to 15 ms, with 16 kHz MAS (4 mm rotor);
- Uses a Magellan MC58113 motor controller chip with its controller board and a Raspberry PI4 single-board computer with webserver, ethernet, and wi-fi capabilities.
- A touch screen on the front of the controller can also serve as an operating interface.

CONCLUSION All the new capabilities permit an unparalleled level of stability with respect to settling time, without loss of magic angle stability, NMR lineshape as reflected in the resolution, and S/N, as seen in Fig. 2. With fast settling and reduced noise, acquisition of 2D NMR data is enabled.

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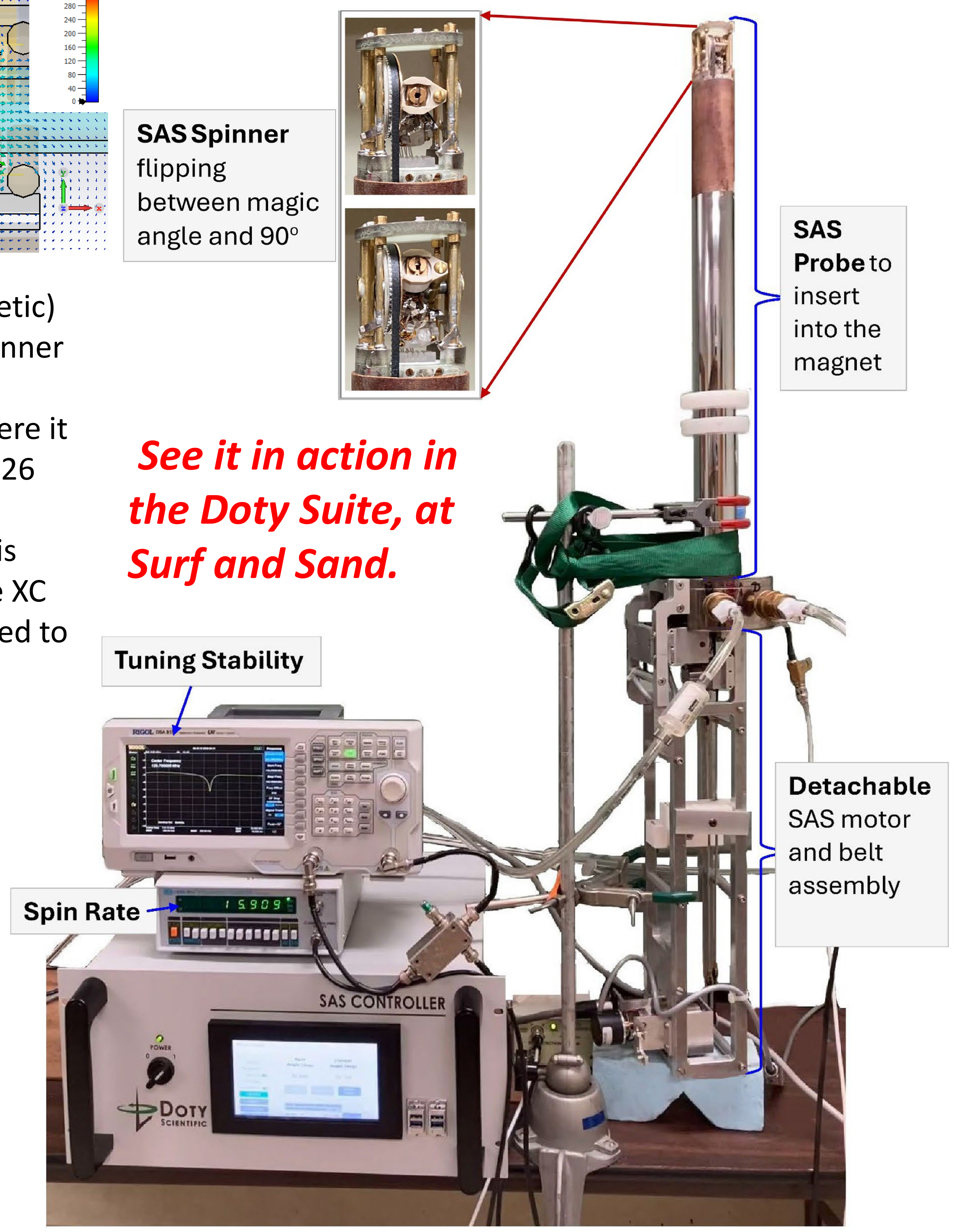

Fig. 3. The 4 mm HXY SAS probe and SAS controller in operation.

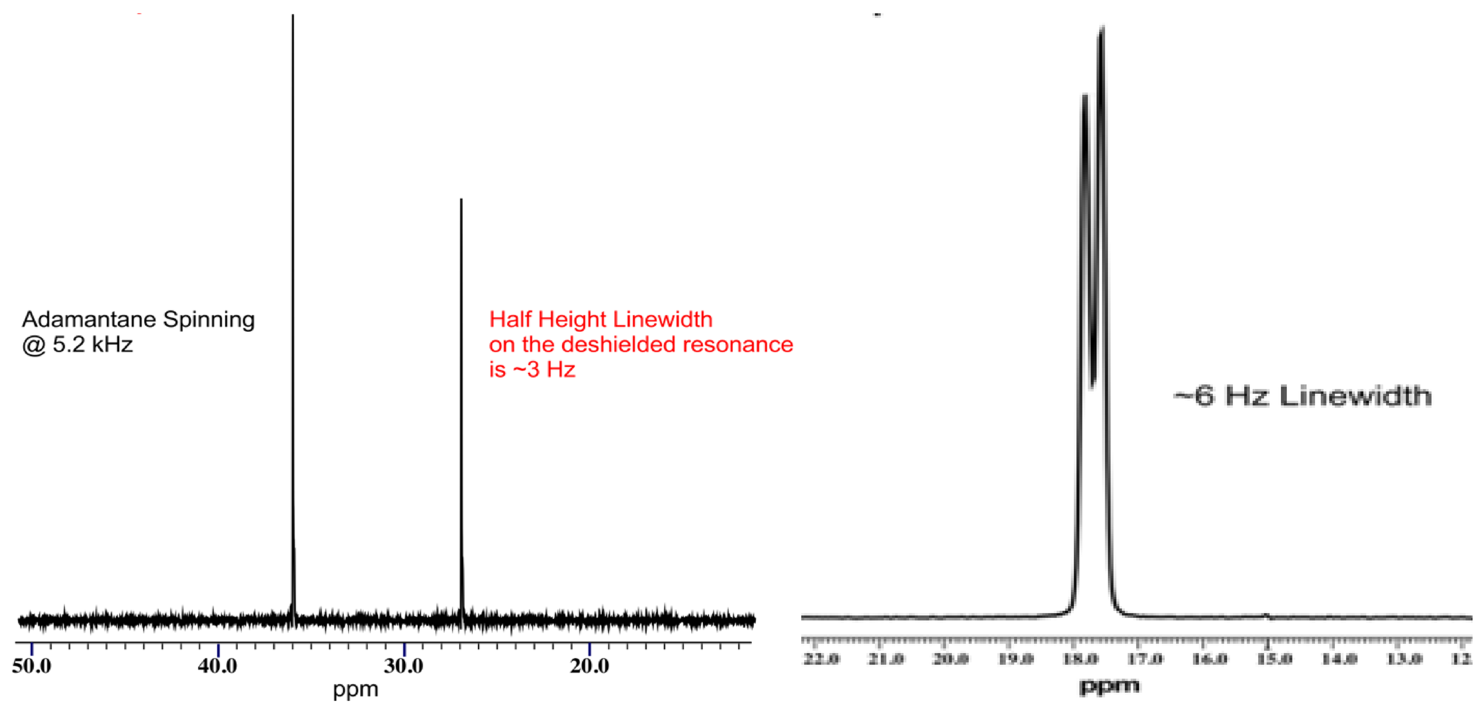

Fig. 4. To demonstrate the NMR lineshape, shown here at left is resolution on ^{13}C in adamantane, 4 scans, spinning at 5.2 kHz, at 11.7 T. On the right, are 4 scans on ^{15}N labeled (100%) ^{15}N in ammonium sulfate, at 5 kHz, illustrating the crystallographic nonequivalent sites. The chemical shift splitting of 0.2735 ppm corresponds to ~14 Hz.

References:
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3. Doty FD, Kulkarni J, Turner C, Entzminger G, Bielecki A, "Using a cross-coil to reduce RF heating by an order of magnitude in triple-resonance multinuclear MAS at high fields", JMR., 182, 239-253, 2006.