Electronic Supporting Information

A convenient, high-sensitivity approach to multiple-resonance NMR with inductively-coupled micro-coils.

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Experimental Methods

Glucose Solution: All experiments were performed on U-^{13}C labeled glucose. The 340 mM solution was made by dissolving 2.8 mg of U-^{13}C-labelled glucose in 55.8 mg of D_2O (99%, Spectra Isotopes). ^{1}H and ^{13}C chemical shifts are referenced using the anomeric signal for the alpha anomer. Spectra were acquired on a Bruker Avance 300 spectrometer equipped with a widebore 7 T magnet (Oxford), using a Bruker 4 mm HXY (in HX-mode) MAS probe. A spinning rate of 1.5 kHz was employed for the HMQC spectra.[1-3] The ^{1}H 90 and 180 degree pulses were of 5.5 and 11 μs, respectively and the ^{13}C 90 degree pulses were 6 μs. Decoupling of the $^{1}J(^{13}C,^{1}H)$ interaction during the acquisition was effected using the WALTZ-16[4, 5] decoupling scheme with an RF nutation frequency of 5.3 kHz. The use of a standard solid-state MAS probe necessitated the use of phase cycling rather than pulsed-field gradients for coherence selection and a long (500 ms) low-power saturation pulse for solvent suppression. The micro-coil was wound onto a quartz capillary of 700 μm o.d. (500 μm i.d.), which had been sealed with epoxy at one end. The coil was wound from 62 μm copper wire, consisted of 13 turns, had a total length of 1.6 mm and was tuned to 293 MHz (close to the ^{1}H Larmor frequency) using a 6.8 pF capacitor (Murata manufacturing Co. ltd.) The coil volume was filled with the solution using a syringe such that the sample slightly (<0.5 mm) exceeded the top edge of the coil and the capillary was sealed using paraffin wax minimizing any air bubbles. The tuned coil was positioned in a Shapal-M (machinable aluminium(II) nitride) insert and the ensemble placed inside of a standard 4 mm Bruker rotor. This coil along with the Shapal-M insert and 4 mm rotor are shown in Figure S1.

Solid Glycine: All experiments were performed on ^{13}C labeled (-CH_2-) glycine (99 atom % ^{13}C, Aldrich Chemical), used as purchased. ^{13}C chemical shifts are reported relative to tetramethylsilane (TMS) using adamantane (+29.5 and +38.6 ppm) as a secondary reference. NMR signals were acquired on a Bruker Avance II 500 spectrometer equipped with a widebore 11.7 T magnet (Bruker), using 4 mm HX and HXY MAS probes (Bruker). Spinning rates of 10,000 ± 2 Hz were achieved using the commercial automatic spinning control unit. Coils were wound onto quartz capillaries of 700 μm o.d. (500 μm i.d.), which had been sealed with epoxy at one end. A coil tuned to ^{1}H was wound using 62 μm o.d. copper magnet wire. It consisted of 10 turns, and had a total length of ~1.7 mm. The coil was tuned to 492 MHz with a 3.3pF capacitor (having dimensions of 0.4 mm x 0.2 mm x 0.2mm, Murata manufacturing Co. ltd.). A separate coil tuned to ^{13}C was wound using 62 μm o.d. coated copper wire and consisted of 16 turns, and had a total length ~2.0 mm. It was tuned to 123 MHz with a 22 pF capacitor (Murata manufacturing Co. ltd.). Final tuning of the whole circuit (probe + micro-coil: ^{1}H = 499.131 MHz and ^{13}C = 125.511 MHz) was achieved using the probe's tune and match elements. The capillary plus the tuned coils were positioned inside a Shapal-M (machinable aluminium(II) nitride) insert and the ensemble placed inside of a standard 4 mm Bruker rotor.

All solid-state spectra were processed using Topspin (ver. 1.3, Bruker), and solution spectra were processed using SpinWorks (ver. 3.1.3).[6]

Signal-to-noise and Coil Volume

A complete formulation of the S/N (including sample and coil temperature, bandwidth effects etc. may be found in the literature).[7, 8] Assuming no change in those contributions we may work with a simplified expression for S/N:

$$SNR = \frac{\text{peak signal}}{\text{RMS noise}} \propto \frac{\omega_0^2 (B_1/i) N_S}{V_{noise}} \quad \text{(S1)}$$

where B_1/i is the radio-frequency field generated by the coil per unit current N_S denotes the number of spins, V_{noise} is the voltage noise and ω_0 is the resonance frequency. Since $V_{noise} \propto \sqrt{r_{coil}}$ and the power dissipation is $P = r_{coil} i^2$, we may re-write equation S1 as the following:

$$SNR = \frac{\text{peak signal}}{\text{RMS noise}} \propto \omega_0^2 N_S \frac{B_1}{\sqrt{P}} \quad \text{(S2)}$$

The value $B_1/\sqrt{P}$ varies with the volume and geometry of the coil. For a solenoid of given aspect ratio (ratio of length to diameter) we can use the relation $B_1/\sqrt{P}$ given by Clark[9] :

$$\frac{B_1}{\sqrt{P}} \propto \sqrt{\frac{Q}{V_{coil}\omega_0}} \quad \text{(S3)}$$

where, Q is the quality factor of the coil and V_{coil} is the volume of the coil and substitute into equation S2 to yield the following:

$$SNR = \frac{\text{peak signal}}{\text{RMS noise}} \propto \omega_0^{3/2} N_S \sqrt{\frac{Q}{V_{coil}}} \quad \text{(S4)}$$

Equation S4 allows a direct assessment of the impact of the coil volume and number of spins present on the signal-to-noise obtainable. It should be noted that in the case of

inductively-coupled micro-coils additional factors such as the regime of the coupling (i.e., under-, critically- or over-coupled) and the effects of resonance offset from the *exact* resonance frequency of the spins also play important roles and have been examined in detail elsewhere.[10, 11]

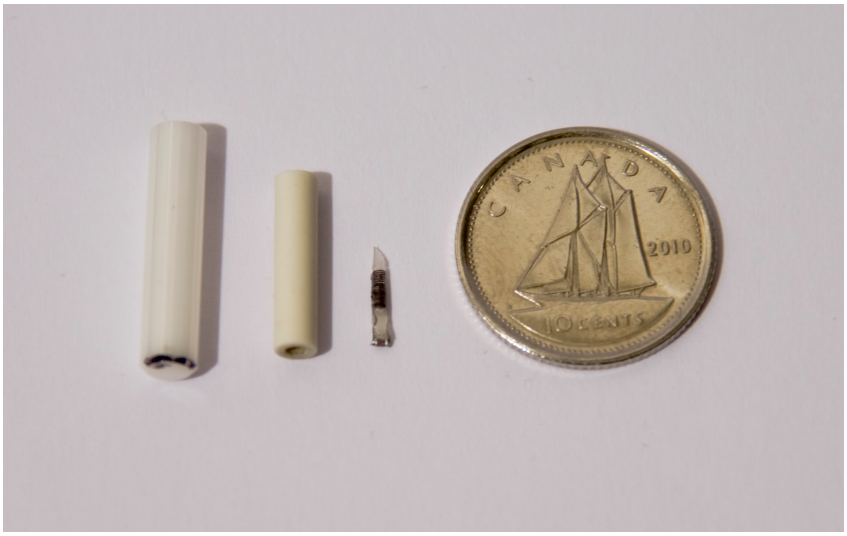

Figure S1: A typical 4 mm MACS setup. Shown from left to right alongside a Canadian 10 cent piece (∅=18mm) for comparison are: a standard 4 mm Bruker MAS rotor, an AlN centering insert, and the 700 μm o.d. micro-coil employed for the $^{1}H\{^{13}C\}$ HMQC experiment.

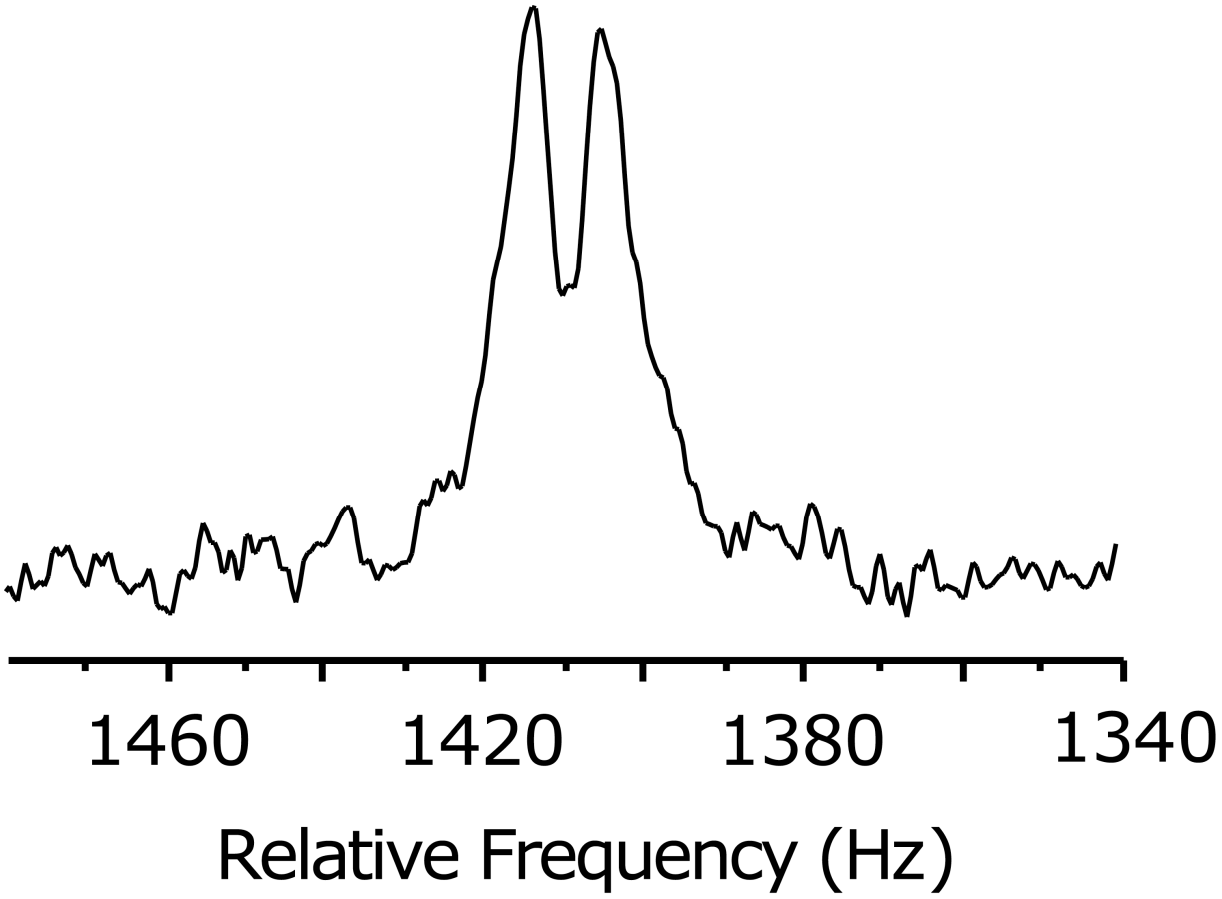

Figure S2: Slice taken from HMQC showing the anomeric ^{1}H signal of the alpha anomer of glucose. The $^{3}J(^{1}H,^{1}H)$ coupling (~7.3 Hz) is discernable despite the ~8 Hz linewidth. The signal-to-noise from this slice was found to be ~30.

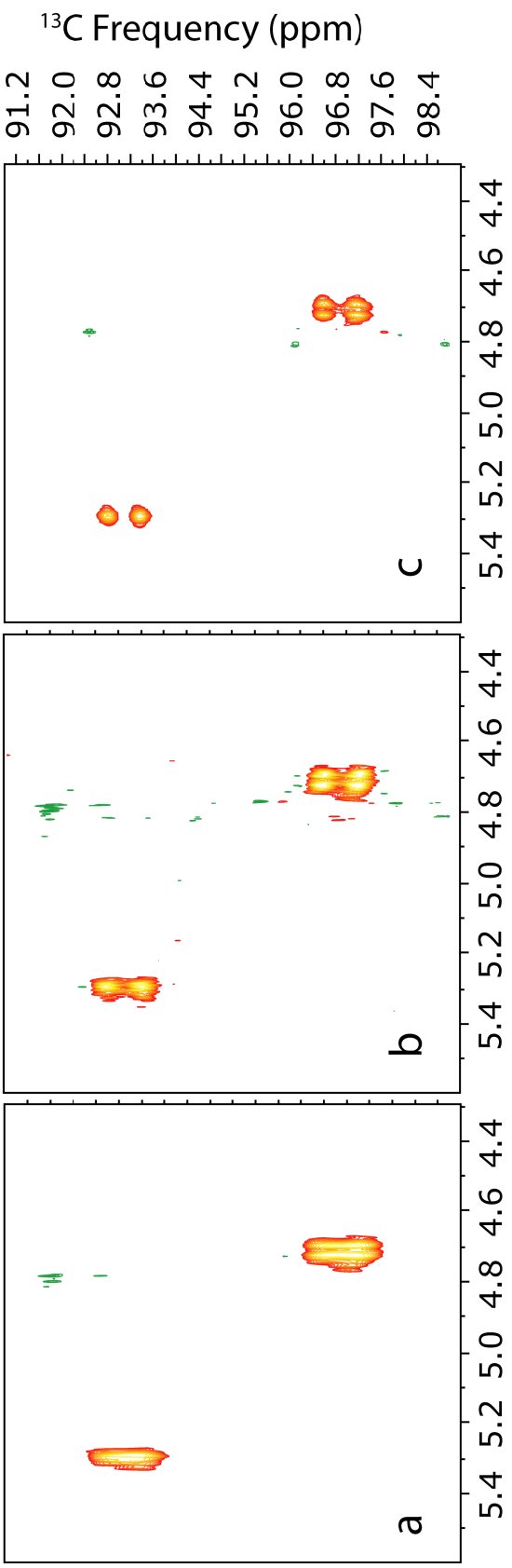

Figure S3: Anomeric region of ^{1}H{^{13}C} HMQC. (a) 128 increments, no linear prediction 2.5 hour acquisition < 5 s processing. (b) 128 increments, additional 80 points (increments) linear predicted, 2.5 hour acquisition ~90 s processing. (c) 256 increments, no linear prediction 5 hour acquisition < 5 s processing.

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