SUPPORTING INFORMATION

^{1}H-Detected quadrupolar spin-lattice relaxation measurements under magic-angle spinning solid-state NMR

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1. Experimental parameters

Variable	^{23}Na indirect Fig. 1c	^{23}Na direct Fig. 1b	^{14}N indirect Fig. 2a	^{81}Br indirect Fig. 2b
Spectrometer details: Field / Console / Probe	14.1 T / Bruker AVIII / 4mm	14.1 T / Bruker AVIII / 4mm	9.4 T / Bruker AVIII / 4mm	14.1 T / Bruker AVIII / 4mm
Material and source	$Na_2HPO_4 \cdot 2H_2O$ (Merck)	$Na_2HPO_4 \cdot 2H_2O$ (Merck)	Glycine (Bio-Lab Chemicals)	Tetra-n-butylammonium bromide (Chem-Impex Int'l Inc.)
Spinning speed	14 kHz	14 kHz	14 kHz	14 kHz
PM pulse power / length (τ_{PM})	33.5 kHz / 10 T_R	33.5 kHz / 10 T_R	30 kHz / 50 T_R	40 kHz / 10 T_R
*Excitation pulse power / length (τ_p)	9.9 kHz / 12.6 μs	9.9 kHz / 12.6 μs	30 kHz / 41.5 μs	51.5 kHz / 2.4 μs
CP power ^{1}H / CP power X / pulse length	39 kHz / 14.6 kHz / 1.5 ms		29 kHz / 15 kHz / 2.4 ms	45 kHz / 8.5 kHz / 3.0 ms
^{1}H decoupling		100 kHz, swf-tppm		
Recycle delay	1 s	1 s	1.6 s	1 s
Scans	32	4	512	8192
Total experimental time	1.16 hrs	8.7 min	5.71 hrs	63.4 hrs
Temperature**	~45 °C	~45 °C	18.2 °C	~45 °C
Apodization	Exponential, 100 Hz	Exponential, 30 Hz	Exponential, 200 Hz	Exponential, 500 Hz

<u>^{23}Na experiments</u>: The ^{1}H-detected $\{^{23}Na\}^{1}H$ CP experiment shown in the inset of Fig. 1c was conducted with 32 scans and all other experimental parameters were similar to Fig. 1c. The Bloch-decay ^{1}H spectrum was obtained using a 90° pulse of 100 kHz and a single scan. The ^{1}H T_1 value in this compound is ~7 min, hence a single scan was used for the Bloch-decay ^{1}H spectrum, and the measurement was performed after a long waiting period.

<u>^{14}N experiments</u>: The ^{1}H-detected $\{^{14}N\}^{1}H$ CP experiment in the inset of Fig. 2a was conducted with 128 scans, a recycle delay of 5 s, and the same experimental parameters as the saturation recovery experiment (Fig. 2a). The Bloch-decay ^{1}H spectrum was obtained using 90° pulse of 100 kHz, a recycle delay of 3 s, and a single scan.

<u>^{81}Br experiments</u>: The ^{1}H-detected $\{^{81}Br\}^{1}H$ CP experiment in the inset was conducted with the same experimental parameters used in the saturation recovery experiment. ^{1}H was saturated in the beginning of the sequence to avoid the presence of any residual signal from direct excitation. The Bloch-decay ^{1}H spectrum was obtained with a recycle delay of 35 s, and a single scan.

* ^{81}Br power levels were calibrated using the signal of KBr. ^{14}N power levels were calibrated using NH_4Cl.

** The temperature in the experiments on ^{23}Na and ^{81}Br are the values of the temperature in the room (22 °C) corrected for frictional heating at a spinning speed of 14 kHz, as determined from experiments on $PbNO_3$ (approximately 23-25 °C). The temperatures in the experiments on ^{14}N were determined by the second sensor in the probe. Temperature dependent experiments on ^{14}N are detailed below (Figs. S2, S3) with their explicit experimental values.

> The lack of signal originating from direct excitation of the proton spins was verified by performing experiments without irradiation on the quadrupolar spins.

\>>Phase cycle opt. 1: Quadrupolar excitation pulse: $y, \overline{y}$; CP(^{1}H): $x, x, \overline{x}, \overline{x}, y, \overline{y}, y, \overline{y}$; CP(X): x; receiver: $x, \overline{x}, \overline{x}, x, y, \overline{y}, \overline{y}, y$. (X≡^{23}Na, ^{14}N, ^{81}Br)
\>>Phase cycle opt. 2: Quadrupolar excitation pulse: $y, \overline{y}$; CP(^{1}H): $(x)_4, (\overline{x})_4, (y)_4, (\overline{y})_4$; CP(X): $(x)_2, (\overline{x})_2$; receiver: $x, \overline{x}, \overline{x}, x, \overline{x}, x, x, \overline{x}, y, \overline{y}, \overline{y}, y, \overline{y}, y, y, \overline{y}$.

2. Temperature dependent ^{1}H-detected ^{14}N PM-saturation recovery spin-lattice (T_1) relaxation measurements in natural-abundance glycine.

Experimental variables different from the Table above are indicated explicitly.

The fit values were used to produce Figure 3 in the article.

Figs. S2.1-S2.5 were acquired with a long ^{14}N excitation pulse τ_p; Figs. S2.6-S2.9 were acquired with a short excitation pulse.

All curves were fit using the MATLAB tool 'cftools'. The errors report a confidence level of 95%.

Figure S2.1: Temperature (T)=18.2 °C.
The mono-exponential fit yields $\boldsymbol{m} = \mathbf{0.99 \pm 0.03}$; $\boldsymbol{a} = \mathbf{1.07 \pm 0.03}$; $\boldsymbol{T_1} = \mathbf{590 \pm 77}$ **ms**.
τ_{PM} = 30 T_R; τ_p=41.5 μs. Total experimental time (t_{exp}) = 5.71 hrs.

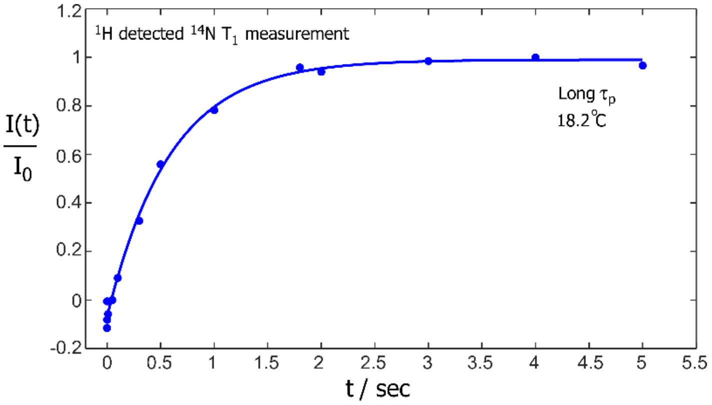


Figure S2.2: T=18.1 °C.
The mono-exponential fit yields $\boldsymbol{m} = \mathbf{0.98 \pm 0.03}$; $\boldsymbol{a} = \mathbf{1.08 \pm 0.03}$; $\boldsymbol{T_1} = \mathbf{648 \pm 74}$ **ms**.
τ_p=48 μs; CP power ^{1}H: 29.8 kHz, power ^{14}N 15 kHz, length 3ms. t_{exp} = 5.71 hrs.

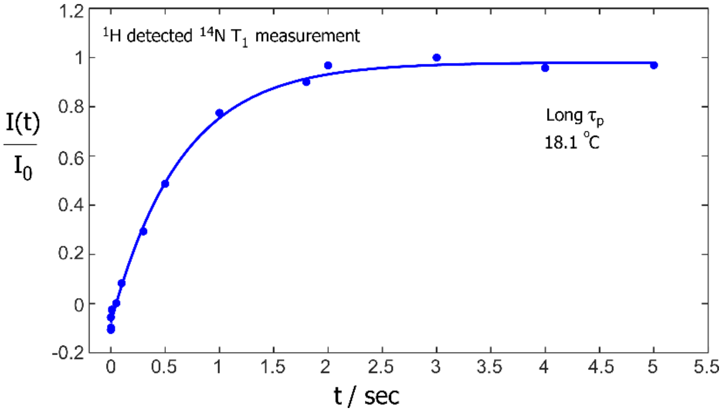


Figure S2.3: T=-28.3 °C.
The mono-exponential fit yields $\boldsymbol{m = 0.98 \pm 0.02}$; $\boldsymbol{a = 1.01 \pm 0.03}$; $\boldsymbol{T_1 = 255 \pm 25}$ **ms**.
τ_p=48 μs; recycle delay = 9.6 s. t_{exp} = 21.63 hrs.

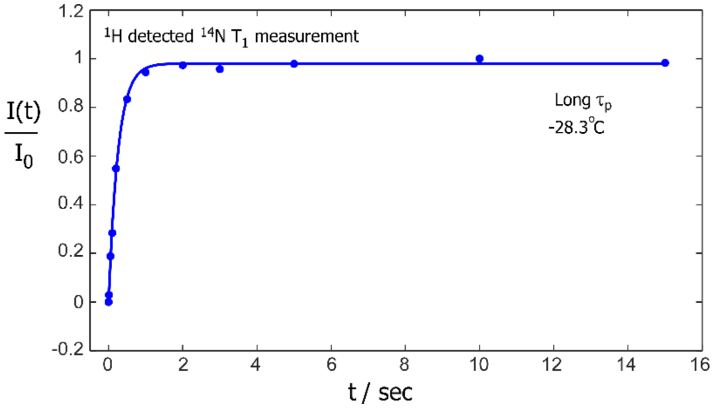


Figure S2.4: T = 47.2 °C.
Fit: $\boldsymbol{m = 0.97 \pm 0.04}$; $\boldsymbol{a = 1.07 \pm 0.05}$; $\boldsymbol{T_1 = 839 \pm 143}$ **ms**.
τ_p = 48 μs; recycle delay = 1.3 s; 1024 scans. t_{exp} = 11.85 hrs.

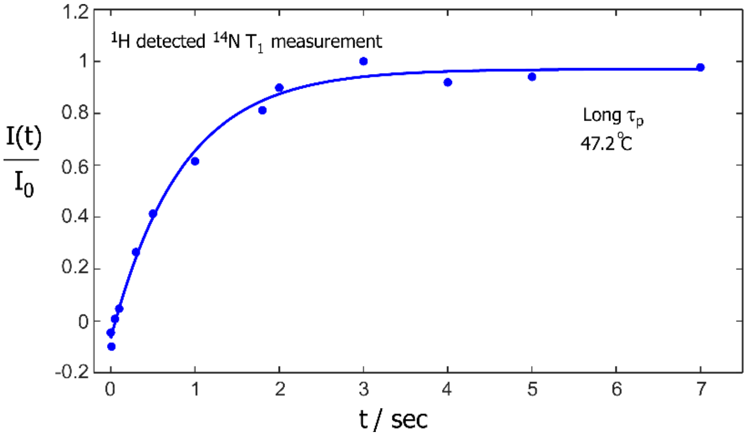


Figure S2.5: T = -3.8 °C.
Fit: $\boldsymbol{m = 0.98 \pm 0.03}$; $\boldsymbol{a = 1.01 \pm 0.04}$; $\boldsymbol{T_1 = 349 \pm 51}$ **ms**.
τ_p = 48μs; recycle delay = 3.2 s. t_{exp} = 6.82 hrs.

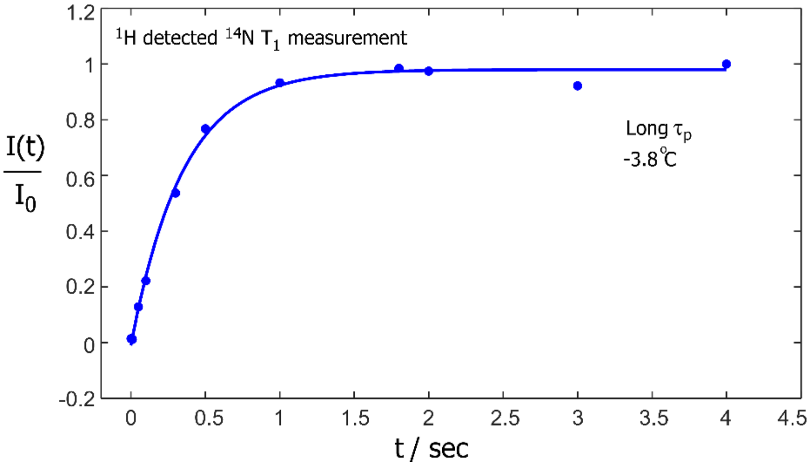


Figure S2.6: T = -3.9 °C.
Fit: $\boldsymbol{m = 0.99 \pm 0.05}$; $\boldsymbol{a = 1.15 \pm 0.06}$; $\boldsymbol{T_1 = 449 \pm 82}$ **ms**.
τ_p = 8.3 μs; recycle delay = 3.2 s; 1280 scans. t_{exp} = 17.05 hrs.

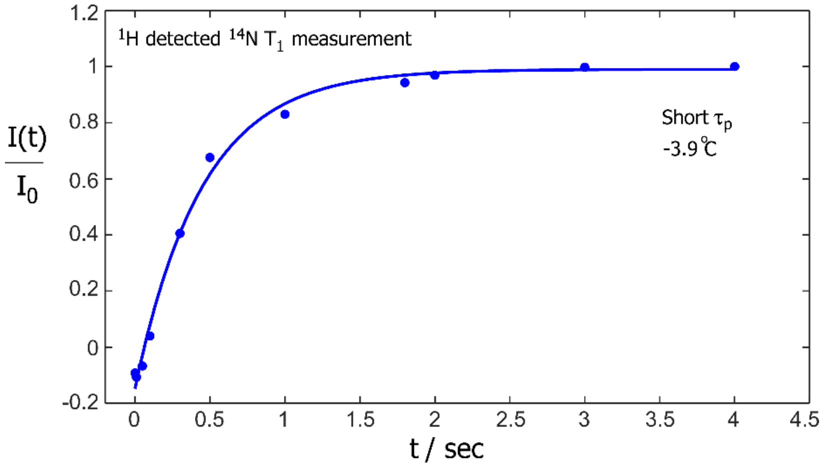


Figure S2.7: T = 18.3 °C.
Fit: $\boldsymbol{m = 1.00 \pm 0.03}$; $\boldsymbol{a = 1.01 \pm 0.03}$; $\boldsymbol{T_1 = 517 \pm 64}$ **ms**.
τ_p = 8.3 μs; recycle delay = 1.6 s; 2048 scans. t_{exp} = 17.16 hrs.

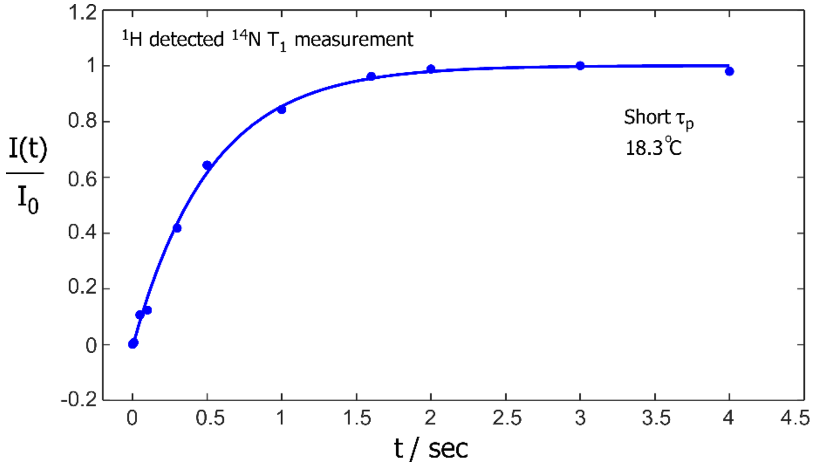


Figure S2.8: T = 47.3 °C.
Fit: $\boldsymbol{m = 0.99 \pm 0.06}$; $\boldsymbol{a = 1.27 \pm 0.06}$; $\boldsymbol{T_1 = 862 \pm 160\ \mathrm{ms}}$.
τ_p = 8.3 μs; recycle delay =1.3 s; 2048 scans. t_{exp} = 18.86hrs.

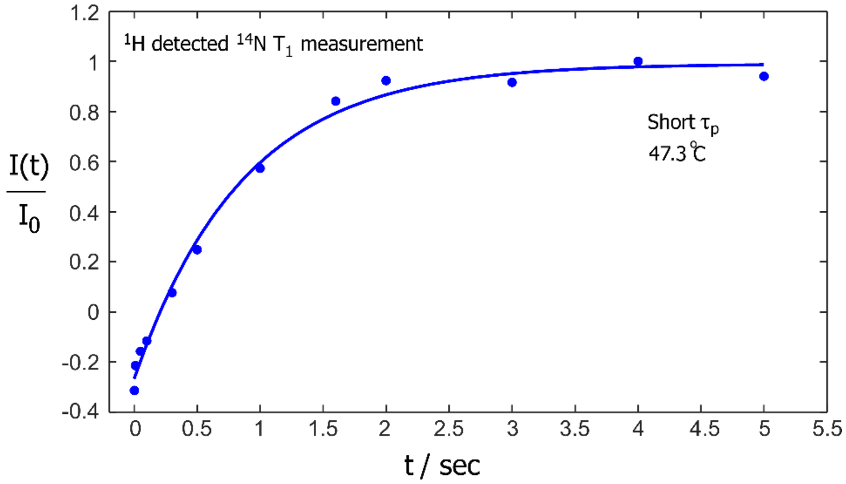
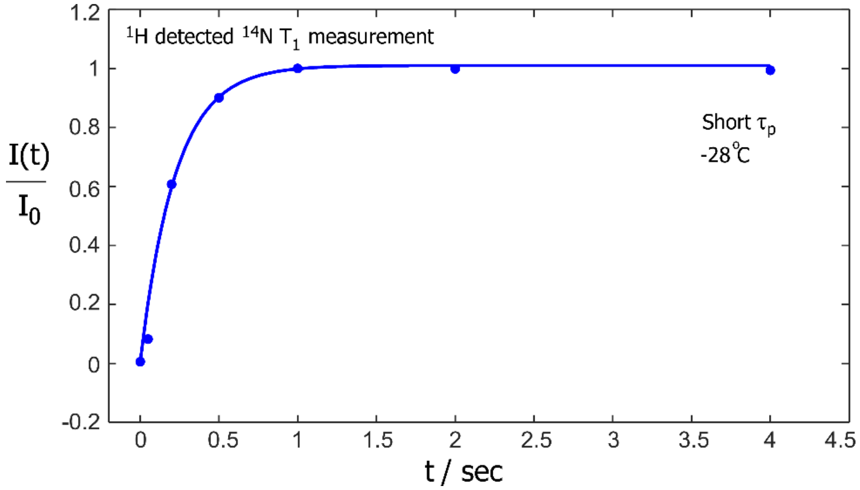


Figure S2.9: T = -28 °C.
Fit: $\boldsymbol{m = 1.01 \pm 0.08}$; $\boldsymbol{a = 1.0 \pm 0.1}$; $\boldsymbol{T_1 = 223 \pm 85\ \mathrm{ms}}$.
τ_p = 8.3 μs; recycle delay = 9.6 s; 768 scans. t_{exp} = 15.99 hrs.



3. Direct-excitation ^{81}Br spectrum and phase-modulated T_1 saturation recovery curve.

Figure S3.1: Single excitation pulse spectrum of ^{81}Br in TBAB, Tetra-n-butylammonium bromide. The spectrum was acquired with an excitation pulse of 2.4 µs, rf power level of 51.5 kHz, a spinning speed of 14 kHz, 512 scans, and a recycle delay of 1 s. Proton decoupling of 100 kHz (swf-tppm) was applied. The spectrum was processed with an exponential apodization function with a value of 500 Hz. t_{exp} = 9 min.

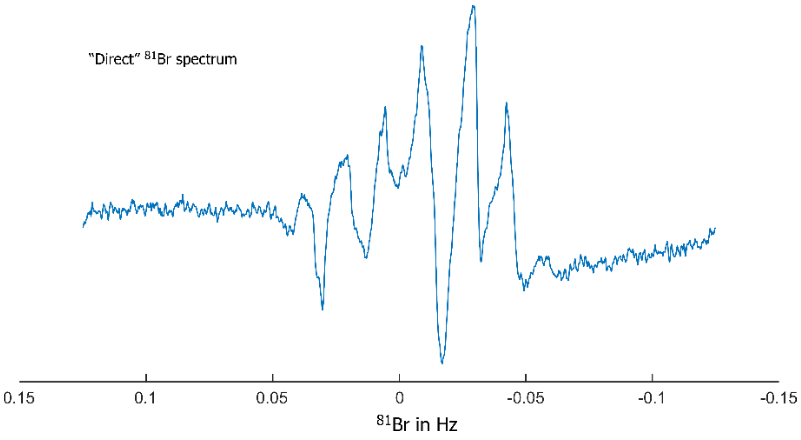
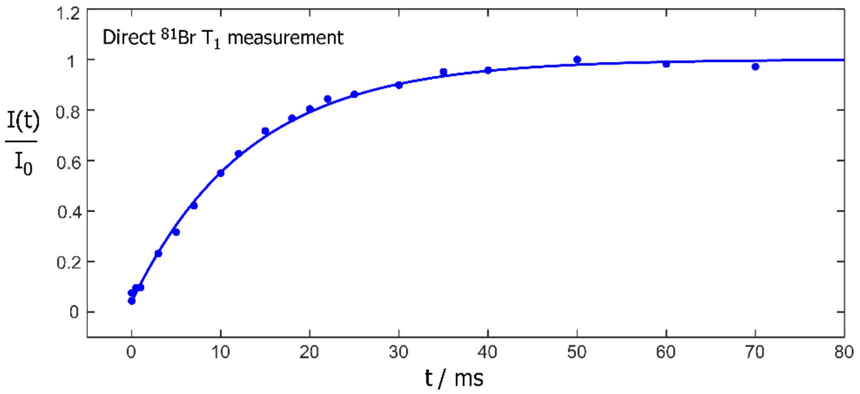


Figure S3.2: Direct ^{81}Br-detected phase-modulated saturation recovery experiment. Each data point was extracted by integrating the directly-detected spectrum. The saturation recovery sequence is given in [1] and the PM pulse lasted 10 rotor periods. The spinning speed was 14 kHz. The T_1 relaxation time is 13±1 ms. t_{exp} = 2.9 hrs.



4. References

[1] M. Makrinich, R. Gupta, T. Polenova, A. Goldbourt, Saturation capability of short phase modulated pulses facilitates the measurement of longitudinal relaxation times of quadrupolar nuclei, Solid State Nucl. Magn. Reson. 84 (2017) 196-203.