Supplementary Information

Rapid NMR Relaxation Measurements Using Optimal Non-Uniform Sampling of Multi-Dimensional Accordion Data Analyzed by a Sparse Reconstruction Method

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Pulse Sequence

The constant-time accordion pulse sequence follows closely the R_1 accordion sequence published by Mandel & Palmer[1] and is shown in Figure S1. The present implementation differs from the previous one in that z-axis pulsed field gradients were used for artifact suppression and gradient-enhanced PEP reverse polarization-transfer. The order of the ^{15}N and ^1H 180° pulses in the constant time period was reversed compared to Figure 1C in Mandel & Palmer, so in our case we apply the ^{15}N pulse before the ^1H pulse. We have also added a water flip-back pulse at the start of the sequence and allowed for the use of selective pulses on H_2O during the relaxation period T_κ, to aid in solvent suppression.
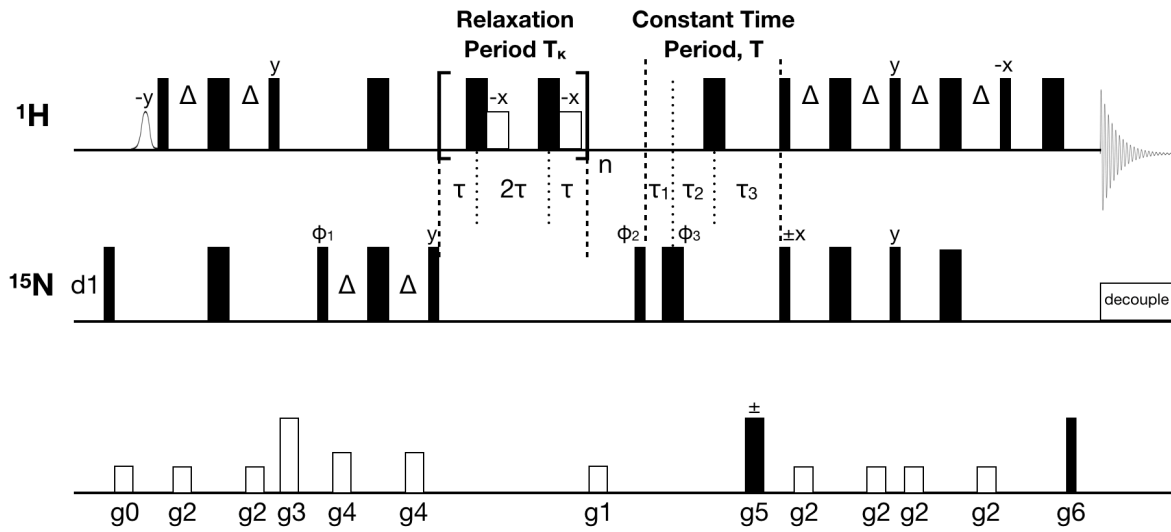

Figure S1. Pulse sequence for proton detected ^{15}N inversion recovery experiment used for accordion NUS. Thin (thick) black bars correspond to 90° (180°) non-selective pulses. All pulses have phase *x*, unless otherwise indicated. The open bell-shaped pulse at the beginning of the sequence and the open bars in the relaxation period are selective pulses on the water resonance. $\Delta = 1/(4J_{HN})$, where J_{HN} is the one-bond scalar coupling constant. The phase cycle is $\varphi_1 = (x\ -x)$, $\varphi_2 = (y)$, $\varphi_3 = (x\ x\ y\ y\ -x\ -x\ -y\ --y)$, receiver = ($x\ -x\ -x\ x$). Gradient enhanced PEP polarization transfer is achieved by acquiring a second data set with inversion of the phase of the ^{15}N 90° pulse indicated with ±x, and gradient g5. The gradients g5 and g6 are used for coherence selection. The phase φ_2 and the receiver phase are inverted for each t_1-increment. The gradient times and levels are g0: 1 ms, 8.9 G cm^{-1}; g1: 1 ms, 8.9 G cm^{-1}; g2: 0.5 ms, 7.1 G cm^{-1}; g3: 1 ms, 44.4 G cm^{-1}; g4: 0.5 ms, 14.2 G cm^{-1}; g5: 1.25 ms, 53.2 G cm^{-1}; g6: 0.125 ms, 53.8 G cm^{-1}.

The total relaxation delay $T_\kappa = n \cdot 4 \cdot \tau$, where *n* is the sampled point number, and

$$\tau = \frac{\kappa \cdot \Delta t_1}{4}$$

The total constant-time delay $T = \tau_1 + \tau_2 + \tau_3$, where

$$\tau_1 = \frac{T - t_1}{2}$$

$$\tau_2 = \frac{T}{2} - \Delta$$
$$\tau_3 = \Delta + \frac{t_1}{2}$$

The experiment was performed on an Agilent Varian VNMRS 600 MHz instrument using a 5 mm HCN triple resonance room temperature probe. The uniformly sampled data were acquired with a spectral width of 8012.8 Hz, sampled over 1920 complex data points, in the direct dimension (t_2). The forward and reverse accordion experiments were acquired interleaved, with the two experiments for each t_1 increment acquired in pairs.

One pair (forward and reverse) of accordion experiments was acquired at 25 °C with a spectral width of 2000 Hz in the indirect dimension (t_1), 220 t_1 points, 56 transients, recycle delay d1 = 2 s, constant time delay T = 110 ms, and with κ = 18, giving ΔT_κ = 9 ms (τ = 2.25 ms). The total acquisition time was 44.5 hours.

Another pair was acquired at 28 °C with a spectral width of 1823.4 Hz in the indirect dimension (t_1), 128 t_1 points, 8 transients, recycle delay d1 = 2 s, constant time delay T = 70 ms, and with κ = 32, giving ΔT_κ = 17.55 ms (τ = 4.39 ms). The total acquisition time was 3h 49 min. This experiment was used in the comparison with results from the conventional experiment.

Designed NUS Scheme

DSURE analysis of column 1580 of the forward accordion inversion recovery experiment for galectin-3C results in identification of seven signals. Three residues (Tyr247, Asn229 and Phe159) have their maximum intensity in this column, and it is used for determination of the R_1-values for these residues. The decay rates and RMSE for Tyr247 are presented in the main text, and Figure S3 shows results for Asn229 and Phe159.
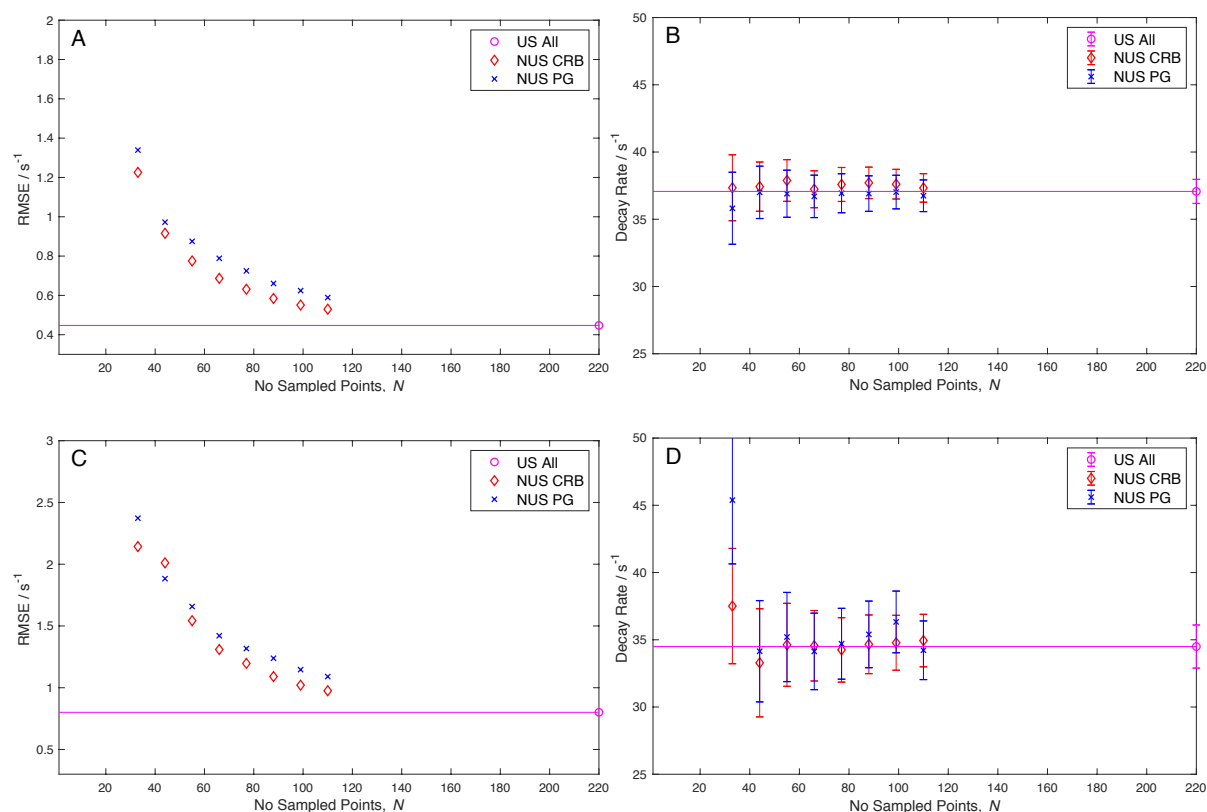

Figure S2. Performance comparison of designed and standard NUS schemes. (A) RMSE of the decay rate constants for Asn229 as a function of N for designed (CRB) and Poisson-gap (PG) NUS schemes. (B) estimated decay rate constant for Asn229 as a function of N. (C) RMSE of the decay rate constants for Phe159 as a function of N for designed (CRB) and Poisson-gap (PG) NUS schemes. (B) estimated decay rate constant for Phe159 as a function of N. Error bars correspond to the 95% confidence interval, 2·RMSE.