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Supporting Information

Ultrafast Multidimensional Laplace NMR Using a Single-Sided Magnet

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Supporting Information

Samples

Samples include water doped with 15 mM $GdCl_3$ and (undoped) glycerol (Sigma-Aldrich, St. Louis, MO). Materials were used as received from the supplier. First, the doped water and glycerol were measured individually, then put side-by-side in separate sample containers to make a "double sample."

Magnet details

All data were collected using a single-sided PM25 magnet (Magritek, New Zealand) and Scout spectrometer (Tecmag, TX). The spectrometer operates at 13.24 MHz and the magnet produces a linear field gradient of 6.59 T m^{-1}. Hard π and $\pi/2$ pulses were calibrated to 6 μs with the power of the π pulse twice that of the $\pi/2$ pulse.

Frequency-swept CHIRP pulses

The CHIRP pulses used in ultrafast experiments were entered into the spectrometer software as tables of phase and amplitude points that were generated using a script written in MATLAB (The Mathworks, Natick, MA). The CHIRP pulse power was changed depending on the length of the CHIRP pulse—shorter pulses require higher peak power. In addition, the pulse power was linearly ramped from zero to the set power level during the first 5% of the pulse (and from the set level to zero during the last 5%) to avoid Fourier artifacts from abrupt changes in pulse power. The maximum power of the π-CHIRP pulse was determined empirically; in most cases it was approximately one-tenth that of the hard π-pulse. The length of the CHIRP pulse was chosen to be on the order of the T_1 of the sample of interest, between 15 and 60 ms.

The frequency of the CHIRP pulse was input as phase modulation of the pulse. In our Matlab script, the user input a desired slice thickness in mm, from which a bandwidth in Hz was calculated using:

$$\Omega = \text{sliceheight} \cdot G \cdot \frac{\gamma}{2\pi} \cdot 1000, \tag{1}$$

where "sliceheight" is the thickness of the region of interest in millimeters, G is the gradient of the B_0 field, and $\frac{\gamma}{2\pi}$ is the gyromagnetic ratio of the nucleus being examined; their numerical values were 0.350 mm, 6.59 T m^{-1}, and 42.576 MHz T^{-1}, respectively, in these experiments. The frequency sweep of the CHIRP pulse ranged from $-\frac{\Omega}{2}$ to $+\frac{\Omega}{2}$. Given a temporal resolution of dt for the spectrometer (in our case, 100 ns), one would first determine the bandwidth per waveform point as:

$$\alpha = \frac{\Omega}{N-1} \tag{2}$$

and the number of waveform points in the overall pulse as:

$$N = \frac{\text{CHIRPpw}}{dt}. \tag{3}$$

Given these, a vector (ω_N) can be set up as the sequence:

$$\omega_N = \left[-\frac{\Omega}{2}, -\frac{\Omega}{2} + \alpha, -\frac{\Omega}{2} + 2\alpha, ..., -\frac{\Omega}{2} + (N-1)\cdot\alpha\right] = [\omega_1, \omega_2, ..., \omega_n]\,. \tag{4}$$

The final phase table in degrees was generated by taking the cumulative sum of ω_N, multiplying by dt, and taking the 360 modulo of the vector:

$$\phi = \left([\omega_1, \omega_1 + \omega_2, ..., \omega_1 + \omega_2 + ... + \omega_n] \cdot dt\right) \ \%\ 360. \tag{5}$$

Ultrafast T_1-T_2 pulse sequence and acquisition parameters

The pulse sequence was constructed as shown in Figure 1B in the main document. The CHIRP pulse and was followed by a 20 μs wait time to allow for coil ringdown. The time between the $\frac{\pi}{2}$ pulse and the first π pulse corresponded to one-half of an echo time to keep the echoes centered, and one-half the echo time separated the π pulse from the acquisition period. The echo time during the acquisition period was 700 μs, and a sufficient number of echoes was collected to observe the decay of magnetization to the level of noise (16 echoes for doped water, 64 echoes for the double sample, and 128 echoes for glycerol).

A dwell time of 8 μs per complex point (125 kHz bandwidth) was used and 76 complex points were collected per echo for an acquisition time of 608 μs per echo. The number of accumulated scans was 1024. A recovery period of 300–500 ms was appended to each scan. The reference experiments were conducted with identical parameters as the ultrafast ones, though the amplitude of the CHIRP pulse was set to zero.

Traditional T_1-T_2 pulse sequence and acquisition parameters

Traditional T_1-T_2 measurements were made using an inversion-recovery sequence with a CPMG detection scheme.[1] The experimental parameters were similar to those used in the ultrafast experiments. However, to accommodate the inhomogeneous field, the magnetization was inverted at the beginning of the sequence using a 50 μs, adiabatic iBURP pulse.[2] Also, 21 points were collected in the indirect dimension for the inversion recovery time (time delay τ) ranging from 50 μs to 60 ms; these points were linearly spaced.

Data processing

Each echo collected in ultrafast experiments was zero-filled (one level) and Fourier transformed. In order to compensate for field inhomogeneities, the transformed profiles were divided by a measured coil excitation-detection profile as described in the main document (see also Figure 2A). Though the compensation should correct inhomogeneities in the first echo well, cumulative effects of B_1 inhomogeneities in subsequent π-pulses during the CPMG loop may lead to imperfect correction. However, multiple pulses in a CPMG train quickly compensate for imperfections in flip angle,[3] so this may not be a serious issue. An example of such a coil-corrected profile is shown schematically as the solid line in Figure 1E in the main text, and shown experimentally as Figure 1 in this document. Points included within the temporal duration of the CHIRP pulse were included in the data used for Laplace transformation. However, because the signal after Fourier transform is in amplitude mode while inversion recovery requires signal of both positive and negative sign, the minimum of the coil-corrected point was set as an inflection point about which the sign of half of the data was inverted. This produces an inversion-recovery curve like the one shown in Figure 1E in the main text. The need for a sign change in the negative regions of the magnitude in the inversion-recovery curve is one inconvenience of the current ultrafast T_1-T_2 method. This could be avoided by measuring phase-sensitive data or by supplanting the inversion-recovery encoding with saturation-recovery encoding, implemented with a

$\frac{\pi}{2}$-CHIRP pulse.[4]

The Fourier transformation, coil compensation, and inversion procedure was repeated for each of the acquired echoes to produce a series of inversion-recovery curves. The recovery curves for all echoes were then concatenated into a 2D dataset, which was normalized by scaling the entire dataset to the highest magnitude reference scan. The final reconstructed 2D dataset was subjected to an inverse Laplace transformation, yielding T_1-T_2 correlation maps. The traditional T_1-T_2 datasets were transformed similarly. In order to demonstrate the increased sensitivity per square root of time provided by the ultrafast method, the SNR for each measurement was calculated in MATLAB.

Signal-to-noise

The signal-to-noise ratio (SNR) for these experiments was determined as a ratio of the maximum intensity of the echo peaks to the average noise level within the acquisition window. To determine the average noise during the acquisition window, the first four and last four acquired points from each acquisition period were concatenated, for a total of $2*4*n_{Echoes}$ noise points. The ratio of the maximum signal intensity for that measurement to the root-mean-squared value of the noise points gave the SNR.

References

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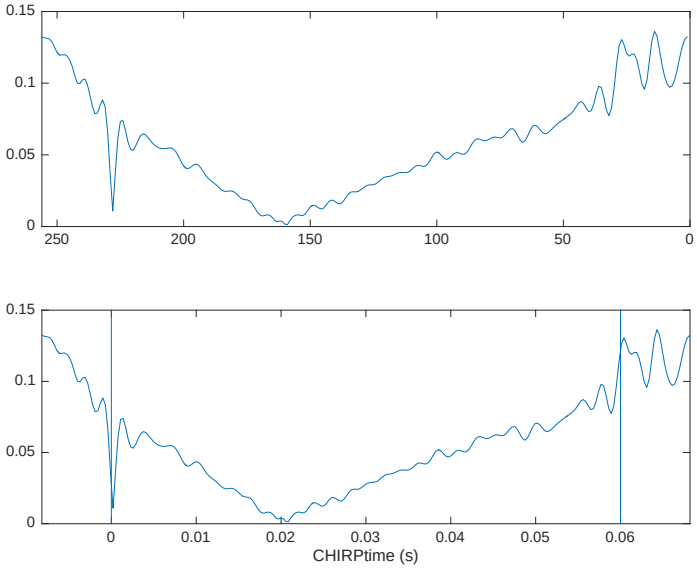

Figure 1: A coil-corrected profile for ultrafast T_1-T_2 data. The top frame shows the points that constitute the data, while the bottom frame shows how those points correspond with the timing of the CHIRP pulse. To produce an inversion-recovery curve, the data within the vertical lines (corresponding to the length of the CHIRP pulse) were used, and the points to the left of the minimum (approximately points 220–155) were negated. (Note the the sequence of points in the top panel is reversed, as a result of how the processing script was written.)