Electronic Supplementary Material (ESI) for Chemical Communications

A convenient method for the measurements of accurate transverse relaxation rates in homonuclear scalar coupled spin systems

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Electronic Supplementary Information

1 Experimental parameters

Experiments were performed on a 9.4 T Bruker Avance II NMR spectrometer using a 5 mm $^{13}C/^{1}H$ probe. The sample was prepared dissolving 5 mg of uracil into 500 μL of DMSO-d_6 and 100 μL of D_2O. The dissolved oxygen was not removed. For the results shown in Fig. 2 and 3, the recycle delay was adjusted to ensure full recovery of the magnetization and was set to 18 s. The ^{1}H 90° pulse length was 9 μs.

In all cases, the experimental ^{1}H signal amplitudes were estimated by integrating the spectral peaks. These amplitudes were normalized against the peak integral for $\tau = 4$ μs. The confidence limits on the determined relaxation rates R_2 were determined by non-linear fitting to the mono-exponential decay formula.

2 Phase Cycling

The ZQ- and DQ-filtered signals are obtained from separate experiments. The same result can be obtained with a unique experiment multiplied by appropriate weights. The pulse phases are given in the following table:

ϕ_1	90°
ϕ_2	0°
ϕ_3	90°
ϕ_4	0° 90° 180° 270°
ϕ_5	0°
$\phi_{R_{ZQF}}$	0° 270° 180° 90°
$\phi_{R_{DQF}}$	0° 90° 180° 270°

Table 1: Phase cycling for ZQ- or DQ-filtered pulse sequence shown in Fig. 1. Phases are given for the 5 radiofrequency pulses, in order from left to right, and for the receiver phase. A four-step phase cycle can be added to ϕ_3 and ϕ_5 to ensure the sign change of the coherences order, giving rise to a 64-step phase cycle. Data shown in Fig. 2 and 3 were obtained using the 4-step and 64-step phase cycles, respectively.

3 Impact of diffusion on R_2 measurements

In the presence of background gradient g_b, due to magnetic field inhomogeneity ΔB_0, the signal intensity does not only depend on the relaxation rate but also on the molecular self-diffusion coefficient.

The signal loss induced by molecular diffusion can be estimated by measuring the NMR signal line width at half height $\Delta\nu_{1/2}$. Considering the worst case scenario, where the signal line width is only due to the magnetic field inhomogeneity, we can write:

$$\Delta\nu_{1/2} = \frac{\gamma \Delta B_0}{2\pi} \tag{1}$$

In addition, the background gradient is given by:

$$g_b = \frac{\Delta B_0}{L} \tag{2}$$

with L being the length of the coil active region. Thus, the background gradient can be rewritten according to:

$$g_b = \frac{1}{L}\frac{2\pi}{\gamma}\Delta\nu_{1/2} \tag{3}$$

Typically, for standard solution-state NMR probes we have $L = 1$ cm and

$\Delta\nu_{1/2} = 0.5$ Hz.

In a spin-echo experiment, the amplitude of the signal at the echo is given by:

$$\exp\left(-\tau R_2\right)\exp\left(-\frac{1}{12}\gamma^2 g_b^2 D\tau^3\right) \tag{4}$$

With $D_{uracil} = 3.10^{-10}$ m^2.s^{-1}, the term related to diffusion is equal to 0.997 at the largest τ value (10 s) which basically means that the influence of diffusion can be neglected.

4 Strongly coupled spin system

A citric acid sample was used to illustrate the case of a strongly coupled spin system. 10 mg of citric acid were dissolved in D_2O. Each of the two CH_2 groups forms a diastereotopic proton pair. If the labile-OH protons are ignored, the spin system classification is AA'BB'.

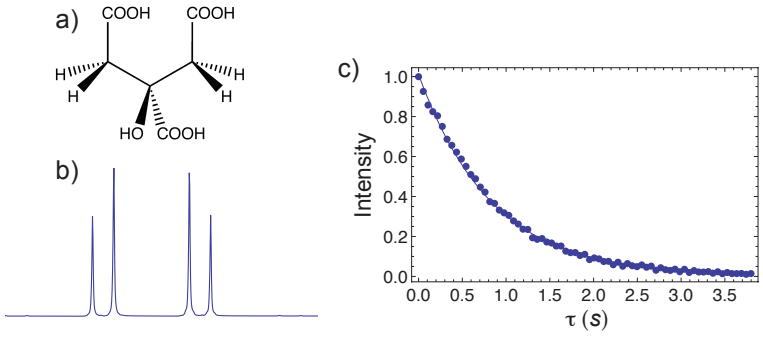

Figure 1: a) Citric acid molecular structure b) Experimental ^{1}H NMR spectra of citric acid c) Experimental ^{1}H ZQF+DQF signal amplitudes obtained as a function of τ for a citric acid sample dissolved in D_2O mixture; The solid curve represents the best fit to the mono-exponential decay.

5 Uracil CPMG and Hahn-Echo curves

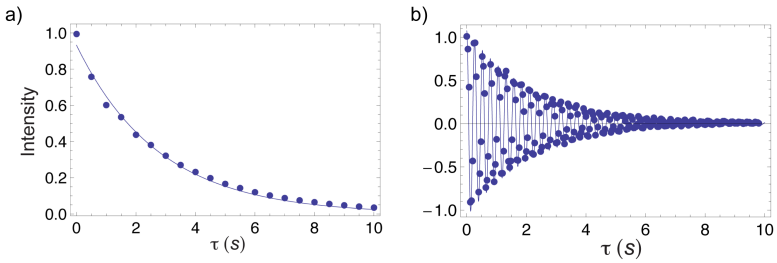

Figure 2: Experimental evolution as a function of τ of the ^{1}H signal amplitude of a uracil sample (proton H_1) dissolved in a DMSO-d_6/D_2O mixture obtained with: a) The CPMG pulse sequence. The solid curve represents the best fit to the mono-exponential decay. b) The Hahn-Echo pulse sequence. The solid curve represents the best fit to the analytical function: $\cos(\pi J\tau)\exp(-\tau R_2)$.