Ultra-wideline ^{14}N NMR spectroscopy as a probe of molecular dynamics

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Submitted to Chemical Communications

Electronic Supplementary Information

1. Symmetry of ultra-wideline ^{14}N NMR powder patterns: urea at 21.1 T

^{14}N NMR powder lineshapes from samples with sizeable quadrupolar interactions such as urea are dominated by the first-order quadrupolar interaction (QI). This first-order interaction results in equal and opposite perturbations to the two ^{14}N Zeeman transitions, thus resulting in powder lineshapes that are perfectly symmetric. Two other common interactions can break this symmetry; the second-order QI and chemical shielding anisotropy. The former interaction decreases in magnitude with increasing field strength, and at the high field used in this study results in a change in the ^{14}N powder pattern that is negligible compared with the full width of the spectrum. The latter interaction increases with field strength, however, the effects of CSA on the ^{14}N spectrum of urea are also negligible in size compared with the first-order QI broadening. Thus, the spectrum can be considered as being symmetric, and one half of the experimental spectrum can be used to reconstruct the other side by reflection about the isotropic shift (a value obtained from the literature).

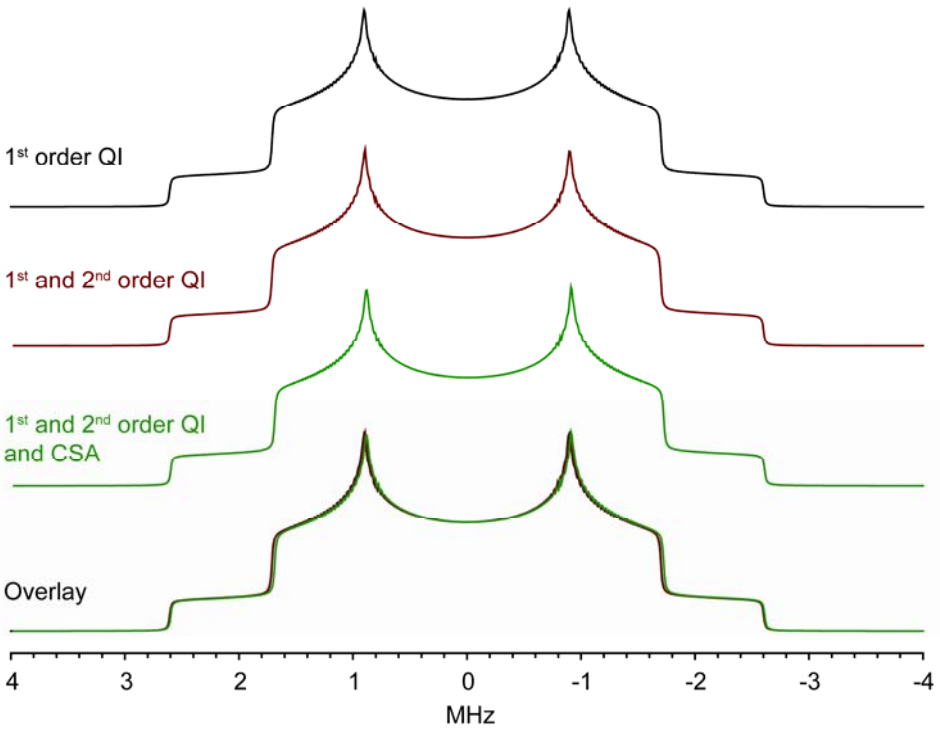

Figure S1 - Numerical simulations made using SIMPSON (Bak M., Rasmussen J.T. and Nielsen N.C., *J. Magn. Reson.* 147 (2000) 296-330) showing that the departure of the ^{14}N lineshape from symmetry due to the second-order QI and CSA interactions is negligible compared with the first-order QI broadening. Simulations were made using the following parameters: C_Q = 3.47 MHz, η_Q = 0.31, Ω = 125 ppm, κ = 0.15, α = 85°, β = 90°, γ = 270°. Definitions of these parameters, which describe the magnitudes and relative orientations of the EFG and CSA tensors, can be found in reference 11. The CSA parameters were obtained from plane-wave DFT calculations made using the CASTEP software (reference 13).

2. Relative experimental uncertainties for jump rates measured by ^{14}N NMR and CODEX experiments

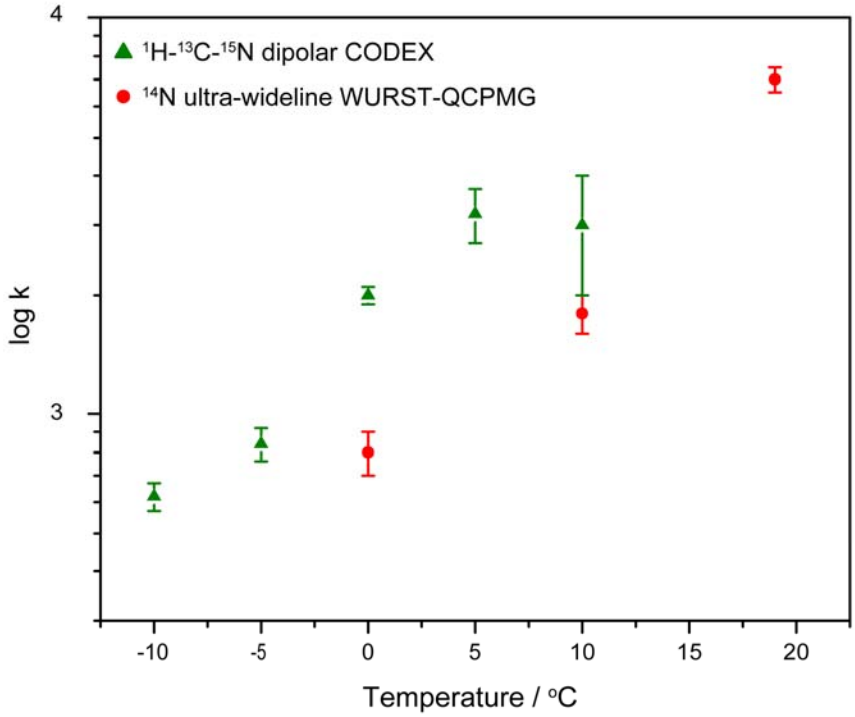

Figure S2 - An expansion of Figure 3 showing the relative experimental uncertainties for jump rates measured by the ^{14}N ultra-wideline method and by CODEX experiments (reference 15). Uncertainties for the ^{2}H experiments are not given, but are expected to be significant, especially at higher temperatures where the second dynamic mechanism (NH_2 group rotation) begins to affect the ^{2}H NMR lineshape.