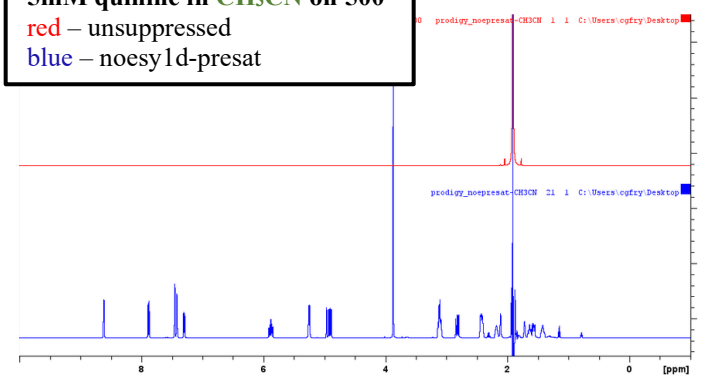
SOLVENT SUPPRESSION USING BRUKER'S LC-NMR SOFTWARE

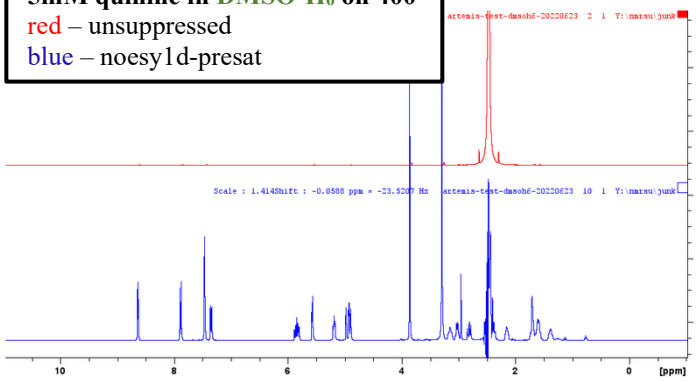
INTRODUCTION

Excellent quality ^{1}H 1D spectra can now be obtained on fully protonated solvents on Artemis (400), Eos (400), Nyx (500) and Phoebe (600) in the Chemistry NMR Facility. A few examples of spectra are shown below.

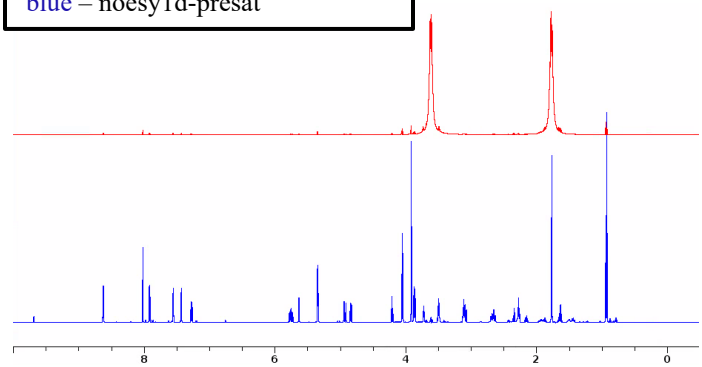
5mM quinine in CH_3CN on 500
red – unsuppressed
blue – noesy1d-presat



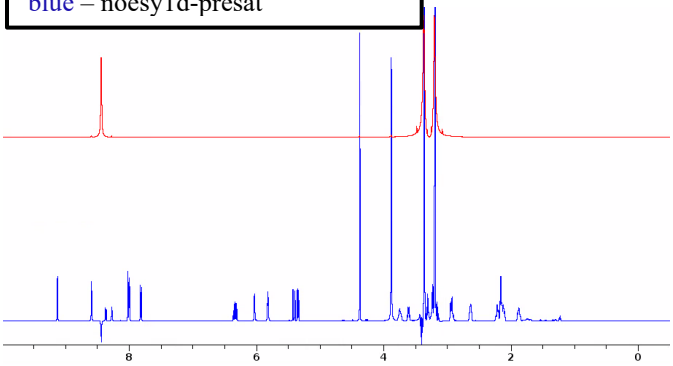
5mM quinine in DMSO-H_6 on 400
red – unsuppressed
blue – noesy1d-presat



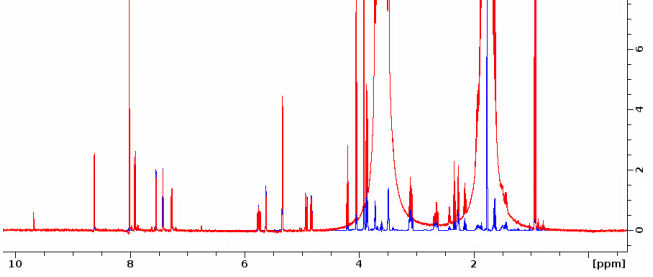
5mM quinine in THF-H_8 on 600
red – unsuppressed
blue – noesy1d-presat



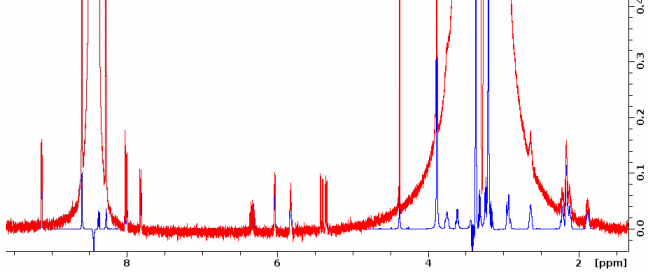
5mM quinine in DMF-H_7 on 600
red – unsuppressed
blue – noesy1d-presat



5mM quinine in THF-H_8 on 600
overlay of above with red ×100



5mM quinine in DMF-H_7 on 600
same as above with red ×150



These new noD experiments use noesy1d-presaturation. Minimal loss of spectral information close to the solvent peaks is the primary advantage of the technique (see Figure 1 below), which also usually produces flat baselines.

→ ^{13}C decoupling is performed to minimize the satellite peaks, but some may still be present (more common with multiple-peak suppression, as in the THF-H_8 and DMF-H_7 examples above).

→ Presaturation techniques reduce the intensity of protons that are exchanging with the solvent (e.g., amide protons in water). Other solvent suppression methods may be better in these cases, such as wet or watergate.

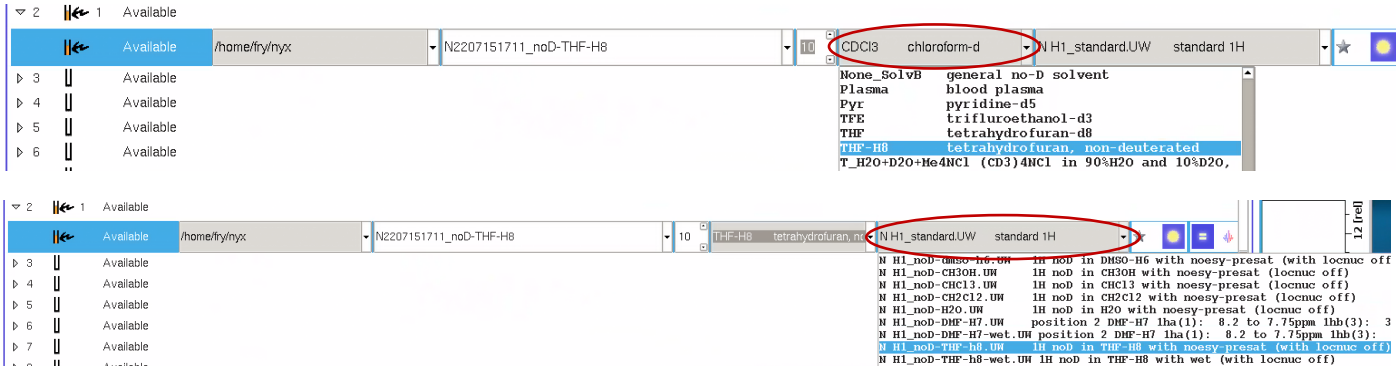
→ Quantitative data can be obtained, but with important caveats. See below for details.

IMPLEMENTATION IN ICONNMR

Proteo-solvents now available under IconNMR automation:

a) $CHCl_3$, CH_2Cl_2, DMSO-H_6, H_2O, CH_3CN
b) CH_3OH, THF-H_8, DMF-H_7

When setting up the experiments, select *both* the correct solvent and experiment from their respective dropdowns:



→ use NS = 8×i
→ if the baseline is "odd", re-Fourier transform the spectrum in MNova or in Topspin (use **efp;absn**)

If you use one particular solvent, NMR staff can move that experiment up in your experiment list to make it easier to find.

QUANTITATION WITH NOESY1D-PRESAT EXPERIMENTS

Direct measurements of quantitative behavior can be made by observing the intensity of a standard water sample for multiple experiments where the frequency for the water is moved in constant steps. A horizontal stack of the resulting spectra forms an excitation profile. In the profile shown in Figure 1, 40 Hz frequency steps were used with 10 spectra as indicated on the abscissa equaling 1 ppm. The water signal is diminished as it moves through the saturation pulse, with:

good signal recovery of >50% within ±0.1 ppm
>90% within ±0.3 ppm
>95% within ±0.4 ppm.

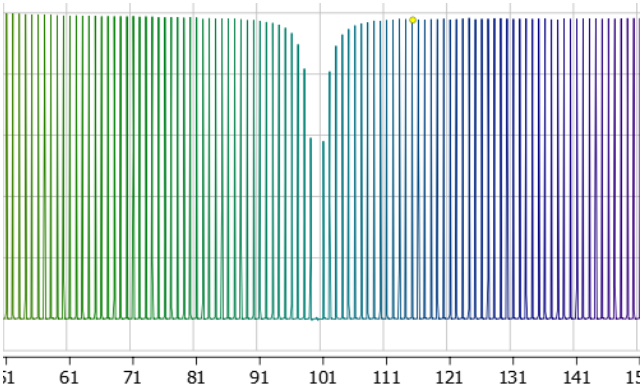
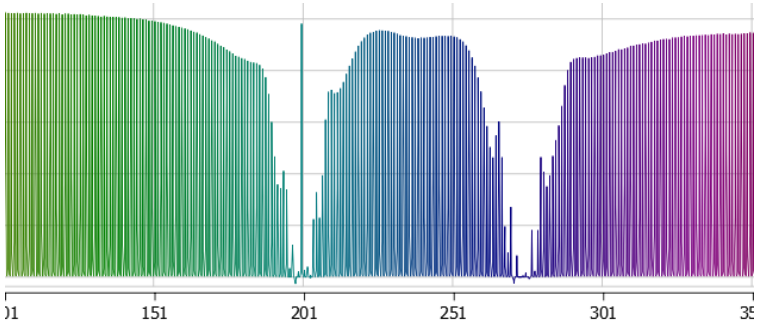


Figure 1: Excitation profile for noesy1d-excitation taken on Eos at 400 MHz with a single-peak suppression using 58 µW power. Spectra are stacked horizontally, with 40 Hz frequency differences per step (10 steps = 1 ppm).

Noesy1d-presaturation experiments of one solvent peak, taken at a saturation power of 58 µW, are quantitative outside ±0.5ppm of the solvent peak, and show good peak characteristics as close as ±0.1ppm from the solvent peak. In general, ^{13}C satellites of the solvent peak will be removed to high quality for all one peak suppression.

The quality of the suppression degrades when more solvents peaks are suppressed. For 2 peaks, as occurs for CH_3OH or THF-H_8, an excitation profile would look similar to that shown below. 50% recovery now takes ±0.25 ppm on each peak, and significant deviations from quantitative (>95%) intensities occurs more than ±1 ppm from each suppressed solvent peak.

Figure 2: Excitation profile for noesy1d-presaturation taken on Eos at 400 MHz with a double-peak suppression for THF-H_8 using 58 μW power. Spectra are stacked horizontally, with 10 Hz frequency differences per step (50 steps = 1.25 ppm).



Quantitative behavior is significantly degraded in any multi-peak suppression experiment. Excitation profiles can be obtained to verify the behavior for any specific experiment.