1-D NOESY and 1-D ROESY for Small Molecules

IU NMR Facility – *November 15, 2004*

Summary:

The ^{1}H to ^{1}H nOe effect is through-space (as opposed to through-bond) and can be detected for protons up to about 5 Angstroms apart with the NOESY and ROESY experiments. These experiments can then provide valuable positional information that may otherwise only be obtained with X-ray crystallography.

The 1-D NOESY experiment provides equivalent information to nOe difference experiments but with no subtraction errors, so that in practice weaker nOe enhancements can be more reliably determined. 1-D NOESY theoretically yields less S/N per scan than nOe difference but the cleaner results and no saturation delay for 1-NOESY make it the preferred method.

Note that transient nOe is measured in the 1-D NOESY versus static (saturated) nOe in the nOe difference experiment. This is important only in that the traditional determination of percent enhancement is not possible with 1-D NOESY, but the nOe buildup rate can be determined if desired.

The NOESY pulse sequence will give positive peaks for small molecules (opposite in sign to the selectively excited peak), negative peaks for large molecules and can give null results for intermediate sized molecules. In contrast the ROESY pulse sequence will always give positive peaks.

Exchange peaks and COSY-type peaks can appear in the NOESY experiment, and will be negative (same phase as selectively excited peak). Exchange and TOCSY peaks can appear in the ROESY experiment and will also be negative.

The 1-D ROESY experiment typically has less S/N and is less clean than 1-NOESY but is still useful for confirming enhancements, particularly for intermediate sized molecules.

Our implementations of 1-D NOESY and ROESY are pre-calibrated for the instrument with a 40 Hz wide selective pulse so all you need to do is use a 1-D ^{1}H spectrum to set dof or an array of dof values for the selective pulses.

Procedure:

1) Turn spinning off. Acquire a ^{1}H spectrum, phase and reference it.
2) Use **sd** and cursor to set a dof value for the center of the selective pulses. Use **sda** to add more dof values for multiple runs. Keep in mind that the selective pulses are 40 Hz wide. Note that dof values can easily be added or changed later.
3) Move the parameters to another experiment if you want to preserve the original, with **mp(1,2)** and **jexp2** for example.

4) Type **iunoesy1d** (**iuroesy1d**) or select **noesy1d** (**roesy1d**) from the Other/2D menu under Setup.
5) That's it! You can usually use gain=60 for both 1-D selective experiments and vary nt and d1 as needed.

Notes:

1) Pure, clean, not-too-concentrated samples will give the best results. In addition it is usually worth degassing your sample by at least bubbling N_2 through it or doing a freeze, pump thaw cycle under N_2 and sealing the NMR tube and also being careful about allowing the sample to come to thermal equilibrium before starting the experiment.
2) For small molecules NOESY mixing times of about 0.4 to 0.8 seconds are desirable. Try lower values than the default of 0.8 s if expected NOESY peaks are not seen.
3) For ROESY shorter mixing times are typical due to the need for a spin lock during this period. The default is 0.2 s. The spin lock is somewhat demanding on the instrumentation, be careful about increasing the mix time too much.