1D Selective NOESY / ROESY for Small Molecules (VnmrJ ChemPack)

IU NMR Facility – *September, 2010*

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 provide valuable positional information that may otherwise only be obtained with X-ray crystallography.

The NOESY experiment 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 experiment will always give positive peaks. The 1D ROESY experiment typically has less S/N and is less clean than 1D NOESY but is still useful, obviously mostly for intermediate sized molecules that give null enhancements in NOESY experiments.

The 1D NOESY provides equivalent information to the 1D nOe difference experiment with no subtraction errors and no saturation delay so it is the preferred method. Transient nOe is measured in the 1D 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 1D NOESY, but the nOe buildup rate can be determined if desired.

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. Both experiments use Z filtering (on by default as opposed to 2D versions) to minimize unwanted peaks.

The selective 1D NOESY or ROESY experiment is effectively the same as one "slice" of a 2D experiment, using selective excitation of the peak of interest to isolate the "slice". Our implementations of 1D NOESY and ROESY are pre-calibrated for the instrument with 40 Hz wide selective pulses so all you need to do is use a 1D ^{1}H spectrum to set the value for selective excitation.

Experiment Procedure:

1) Lock, shim, setup a 1D proton experiment, choose solvent, acquire a quick 1D proton spectrum, reference and save it. You can also optionally calibrate the 90 degree **pw** for your sample to get best results. See the VnmrJ 2D Guide for this procedure.
2) Center cursor on the peak or multiplet of interest and type "**dsel**" to display the frequency to be used in the 1D selective experiments. You will need to manually enter this frequency so might want to write it down. Keep in mind the selective pulses are preset to about 40Hz wide windows. If desired you can repeat this step and make a list of all frequencies you want to use.
3) Move to another experiment ("**jexp2**" for example) and type "**iunoesy1D**" or **"iuroesy1D"** to setup an optimized selective 1D experiment.
4) If you ran a standard Proton experiment in step 1 make sure the solvent is the same, and possibly transfer the reference settings (**rfl** and **rfp**). Otherwise it's also a good idea to confirm **sw** and **tof** are also the same.

5) Enter the selective frequency from step 2 to use as "**selfrq =** *value*". Multiple frequencies can be separated by commas ("**selfrq =** *value, value, etc.*") to create multiple experiments that will be stored and saved together as an arrayed experiment.
6) For longer experiments increase **nt** by multiples of 4.
7) The selective excited peak or multiplet will be the largest one in the spectrum and is typically phased upside down for plotting so that NOESY and ROESY peaks are positive. If you arrayed **selfrq** values, use **ds(1)**, **ds(2)**, etc. to access spectra.
8) To create a plot with both the 1D reference spectrum and a 1D selective NOESY or ROESY:
   a) Make sure the same expansion is shown in both - you can use **sp** and **wp** to do this. For example "**sp=1p wp=9p**" will show from 1 to 10 ppm.
   b) Raise one of the spectra. If your proton reference spectrum is in Experiment 1, try "**jexp1 vp=80**" for example.
   c) Plot both, typing "**page**" at the end. For example "**jexp1 pl pscale jexp2 pl pscale page**".
9) Save your data.

Additional Information on 1D NOESY and ROESY:

It is helpful to purify, filter and degass your sample to maximize nOe's.

Mix time can be changed using **mix**, **mixN** or **mixR**. The default NOESY mix time is **mixN=0.8** seconds, optimal for small molecules. For less than optimal situations (i.e. larger molecule, more viscous sample, faster relaxation from other sources) you can set **mixN=0.2 -0.6** seconds**.** The default ROESY mix time is **mixR=0.2** seconds. You will rarely need to change this.

You may occasionally see peaks with opposite intensities to the NOESY peaks (same as the diagonal). These can be indirect NOESY peaks (looks like A->C but is really from A->B->C), residual zero quantum COSY-like peaks or can be from chemical exchange.

The Z filtering is on by default for both of these experiments. Zero quantum filtering reduces all signal slightly but can reduce or eliminate COSY and other unwanted zero quantum correlations. It also results in cleaner results particularly with these 1D versions so it's suggested that you leave it on with both.