Using gNMR

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gNMR is a free program that allows you to interpret and simulate your data. You can download it from http://home.cc.umanitoba.ca/~budzelaa/gNMR/gNMR.html. You have the possibility to simulate spectra optimizing chemical shifts and J-couplings, line widths, integrals etc. for different nuclei. Additionally gNMR can simulate chemical-exchange processes. You can enter data with molecular structures or from first guesses or you can have the program start with primitive shift-predictions. Being a very powerful tool, it might take a little while to get the hang of it, but then it is great! I hope this sheet helps you on your way.

To get your data to a form that gNMR can work with you will have to do the following steps, here described for Bruker XWINNMR data:

1. **Work up your data in the usual way.**
2. **Transfer the data to the PC.**
3. **Convert the data to gNMR with gCVT.**
4. **Run gNMR.**
5. **Save and Export your results.**

1. Work up your data in the usual way.

Work up your data i.e, appodize, Fourier transform and phase your spectrum. You may also do a baseline correction now, even though there is a routine in the gNMR package to do it later.

2. Transfer the data to the PC running gNMR

Dalhousie users can get advice from Ulli or Mike, if you need help with this step.

3. Convert the data to gNMR with gCVT.

To convert the data to a format that gNMR can use, you need to apply the conversion program gCVT. Double click on the icon. In the opened window choose **Convert from** *WinNMR*. Browse your way to the correct directories and files: These are

acqPar file:	…/*filename*/*exp*#/acqus
ProcPar file:	…/*filename*/*exp*#/pdata/*proc*#/procs
Spectrum file:	…/*filename*/*exp*#/pdata/ *proc*#/1r
Imag spectrum:	…/*filename*/*exp*#/pdata/ *proc*#/1i
FID file:	…/*filename*/*exp*#/fid

Choose the correct "Nucleus" from the periodic table.
For the **Target Select** you need to set the directory and type the file name you want to give the spectrum that you are creating. Finally hit **Go!** and **Exit** the program.

4. Run gNMR.

Double click on gNMR to start the program.

a) Setting the stage

Next you will be prompted into the window Molecule 1. Of course the problems you want to solve dictate what you enter here. You can simulate or fit an experimental spectrum from one compound. Alternatively you can simulate or fit spectra from several species, spectra attached to nuclei with less than 100% NMR active species, and isomers etc. with or without chemical exchange. The technical term chemical exchange describes a situation, where one nucleus changes between sites with different chemical shifts. These sites can be located at the same or at different molecules. In either case, I recommend to make a drawing of your molecule(s), and assign numbers to each nucleus or nuclei groups (for example methyl groups). These numbers are the ordering for your entries in Molecule 1. Enter the nucleus name, the number of nuclei with the specified value (n), and the ppm shift. You do not have to enter a line width but can do that later. The more nuclei you add, the more J-couplings you will be able to enter. If you plan to simulate a spectrum that has signals from different molecules, you need to set up the other one buy clicking on **Molecule**. You can click **New** for a new molecule and enter different data. Alternatively you can **Copy To New** molecule the information from another one and edit the entries (especially useful for species attached to NMR active and inactive nuclei). Under **Settings -> Molecule Settings** window you can determine intensities and specify, if you want to iterate on the concentration. Keep the intensity of one molecule at 1 to decrease the number of variables. Once you set up everything click on *the spectrum symbol*. The spectrum will appear in a plot window Spectrum 1.

b) Loading an experimental spectrum

Click in the spectrum window. Then, under **Settings → Spectrum Settings** under **Iteration** choose ***File***. Answer the question to automatically update SFO1. Clicking back onto the **Settings → Spectrum Settings** under **Iteration** under ***Display*** you can choose ***Overlapping***. I find that a more satisfying way to compare the fitting result with the experimental spectrum. Now, with the experimental and the synthesized spectrum displayed you can read out shifts and enter their values into the Molecule information windows. This way you can optimize starting values for the simulations. To read out the chemical shifts, move the cursor over the spectrum. The ppm values will be displayed. If you move the cursor just slightly below the top blue bar, you are in a shift and zoom mode. To shift the spectrum click and hold down the left mouse key and point to the destination of the starting point. To zoom into a region, hold down the shift key while

moving the mouse over the area of interest. If the vertical sizes of the two spectra are very different, enter manually some linewidths in the molecule windows. The normalization of the area under the spectra is used to adjust the vertical scale. (For later assignments, I find it easiest to start with very sharp lines, to see how many you will have to assign.)

c) Starting an Iteration

If you can identify the correlations between the simulated and experimental spectrum set an assignment. Under **Iterate → Assignments** define the window, i.e. the spectrum that is to be fitted. Following **OK** a dotted line will appear on the most right peak of the simulated spectrum. Move the cursor to a peak in the experimental spectrum that you think agrees best with that of the synthesized spectrum and click. Work your way across the spectrum until you hear a ping and have all lines assigned. Finish by hitting **Esc**. Before you can start the iteration, you still need to specify which parameters you want to iterate on. You do that by assigning names to the variables and keep (or reenter) "-" for fixed values. Any letter will do as name. You can use, for example, a, a', x, x', Jax etc. for AA'XX' systems. If you give the same name to two values, they will be made and kept equal even between molecules.

(The following paragraph applied to an older version of gNMR, you may use it as guidance). If you defined several molecules in your system, I found that some iterations do not work unless you have the exchange permutations defined even if no exchange takes place. Under **Molecule → Exchange** the window Exchange will appear. Here you define the exchange **Rate: Iterate**, and the assignments. **Iterate** will display *inc.* until you have entered all information. For all nuclei you defined, an entry will appear in the permutation. M(1), M(2), etc. specifies the molecule the nucleus is located at. The numbers to the right are the identification numbers (#) used in the Molecule windows. You are supposed to enter the jump designation of that specified nucleus in the form 2-1, for example. This would indicate, that the nucleus specified in that line jumps to molecule 2, nucleus 1. For example, let's assume molecule 1 has one distinct site and molecule 2 has two distinct sites. Let's further assume that only the nuclei specified with 1 on each molecule do exchange with each other. Then the permutation matrix would look like:

M(1)	1	2-1
M(2)	1	1-1
	2	2-2

Once you entered all these data the box **Interate** changes to *Fixed* or your choice of *Variable*. Keep it at F*ixed* to start with. At the same time a second column will appear that would allow you to specify additional exchange processes.

Two words of warning: 1.You need to keep track that you do not exchange nuclei of different types, for example a proton with a phosphorous. 2. There is a bug in the program: Even though the window displays numbers, it does not allways mean they are entered. You may have to type them in again so that the program takes them until you get the entry *Fixed*.

Now you can start the iteration with **Iterate → Go**. The Log window will appear and contain all the iteration information. Among other values the start parameters, and the final fitted values will be displayed. (Tip: the Log window will be overlaying all other windows. If you want to watch the spectrum evolve with the iteration, make sure it is not covered up by the Log window.)

d) Exchange Calculations.

(The following paragraph applied to an older version of gNMR, you may use it as guidance) In principle, you can initiate the fitting of the exchange rate by setting the **Iterate** value to *Variable* in the Untitled1 - Permutations window and start the iteration with **Iterate → Go**. However, I found, that the Iteration does not converge to a result, when you have too many parameters, because often the spectrum does not contain sufficient information. For example, the line width is influenced by the intrinsic line width of the resonances and by the exchange rate. Also, in the coalescence region, the peak position is defined from the peak positions of the contributing lines, their intensity ratio and the exchange rate. Therefore, you need to determine and fix (replace name of variable with "-") those parameters as good as you can from spectra resulting from no or slow exchange processes at low temperatures. If you let the parameters roam freely you might get a good fit, but useless numbers. Once you developed an impression about those values, the exchange simulation should work fine. I found it worth while to start the simulations with different rates. Not always are the final fitted values identical. I recommend copying the relevant parts of the log file into an independent file (for example with Word) to keep track of your results.

6. Save and Export your results.

Finally save your data in the right directory (not necessarily the default!). You can for example use the copy/paste to document your results.

Good luck for your simulations.