

APPENDIX 1

Version of 8/24/05 11:01 AM

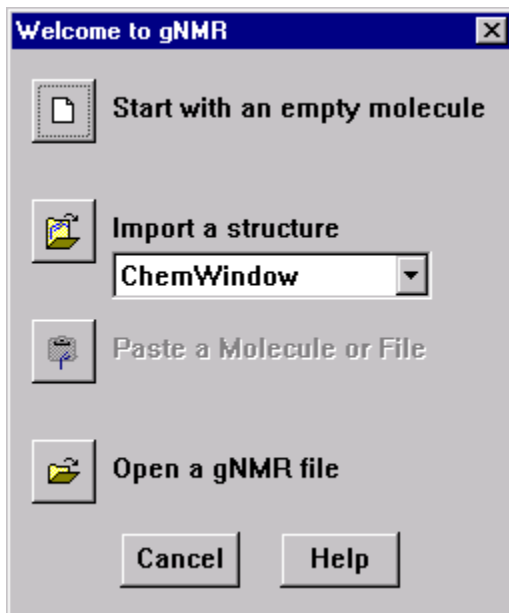
Simulation of ^1H -NMR without a structure*:

Mircea D. Gheorghiu

*Because the gNMR program has been updated, the figures in the text may appear slightly different on the computer.

A. Without iteration.

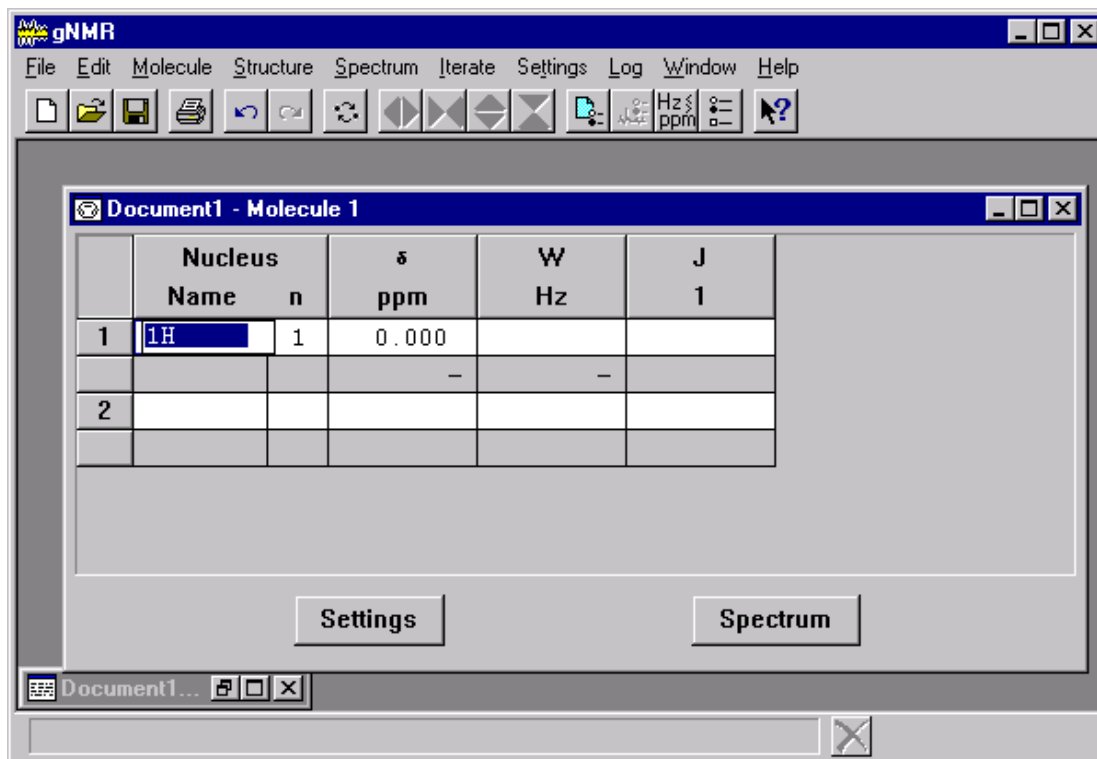
1. Click on the on the icon that is displayed on the Dell OptiPlexGX1 PC.
2. The **Welcome to gNMR** window pops-up. If the **Molecule** window automatically opens instead, then skip to the next step.



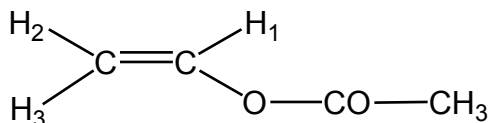
Click on: **Start with an empty molecule** to view the **Molecule** window . This window is a spreadsheet with the following columns:

- (1) **nucleus name** (^1H , ^{13}C , ^{19}F , ^{31}P , etc)
- (2) n, **number of magnetically equivalent nuclei** For example n=3 for the methyl protons)
- (3) **chemical shift** (in ppm)
- (4) **individual line width** (not applicable for 5.311 cases)
- (5) **coupling constant(s)** (in Hz – will appear after data is entered on the chart).

Experiment #2: Nuclear Magnetic Resonance



4. Assume that you want to simulate the three-proton spin system (H_1 , H_2 and H_3 , respectively,) of vinyl acetate (the methyl group is isolated and does not interact with the vinyl protons):

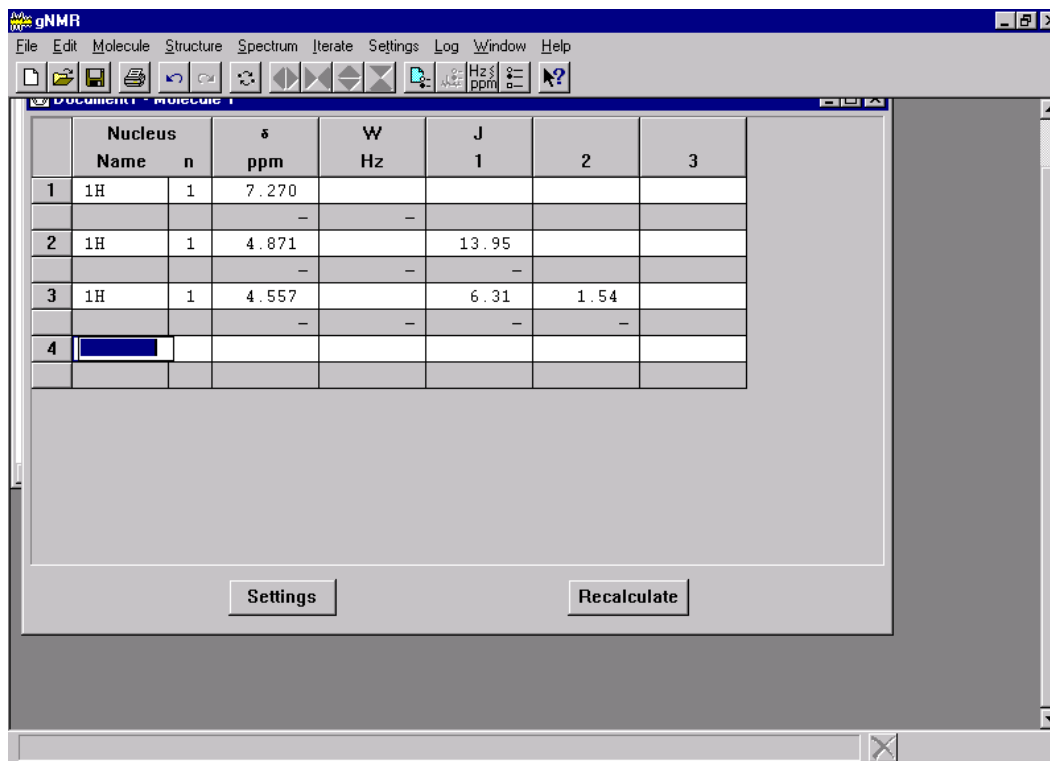


Using the print-out from the Varian Mercury Plus, identify the ppm value that is in the middle of each of the three quartets. . This value is the chemical shift for the respective proton (e.g. δ_1 , δ_2 , and δ_3 , respectively). The distance in Hz between the quartet lines provides the coupling constant ($J_{1,2}$, $J_{1,3}$, $J_{2,3}$)

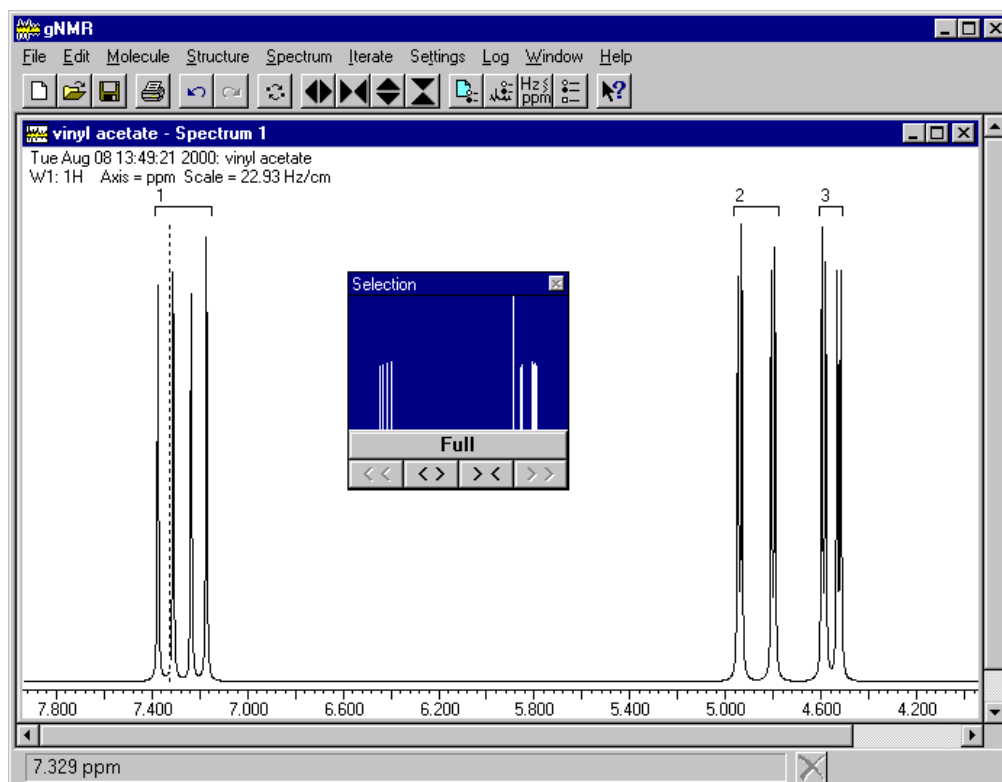
Note that the matrix of coupling constants is symmetric because $J_{1,2}=J_{2,1}$; $J_{2,3}=J_{3,2}$; etc). Therefore, only the lower triangle is filled in the **Molecule** window spreadsheet.

The **Molecule** window spreadsheet will look like:

Experiment #2: Nuclear Magnetic Resonance

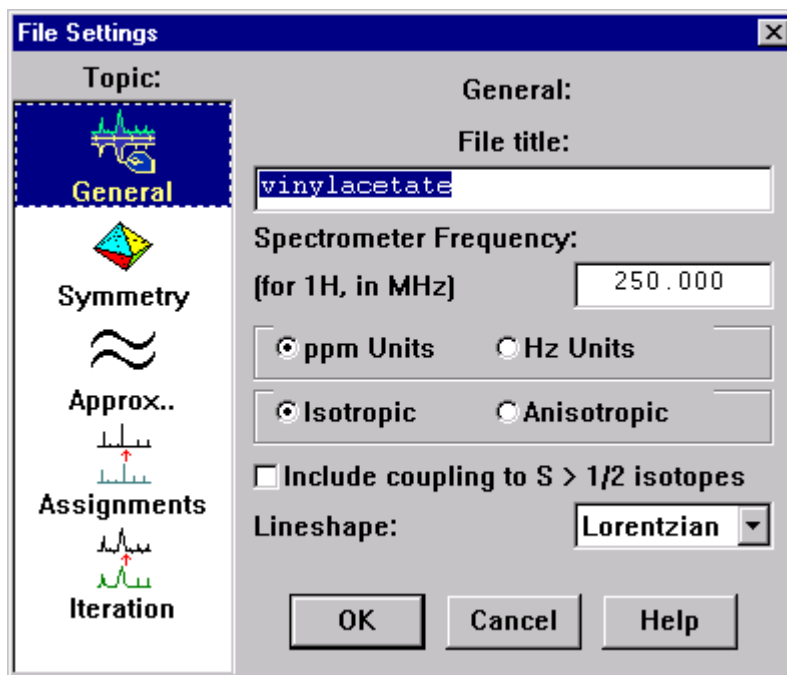


5. Click on **Spectrum** (see the figure above) or **Recalculate** (if you have done some changes in the **Molecule** window). The full spectrum of the three vinyl protons system (calculated with the spectral parameters provided) is then displayed.

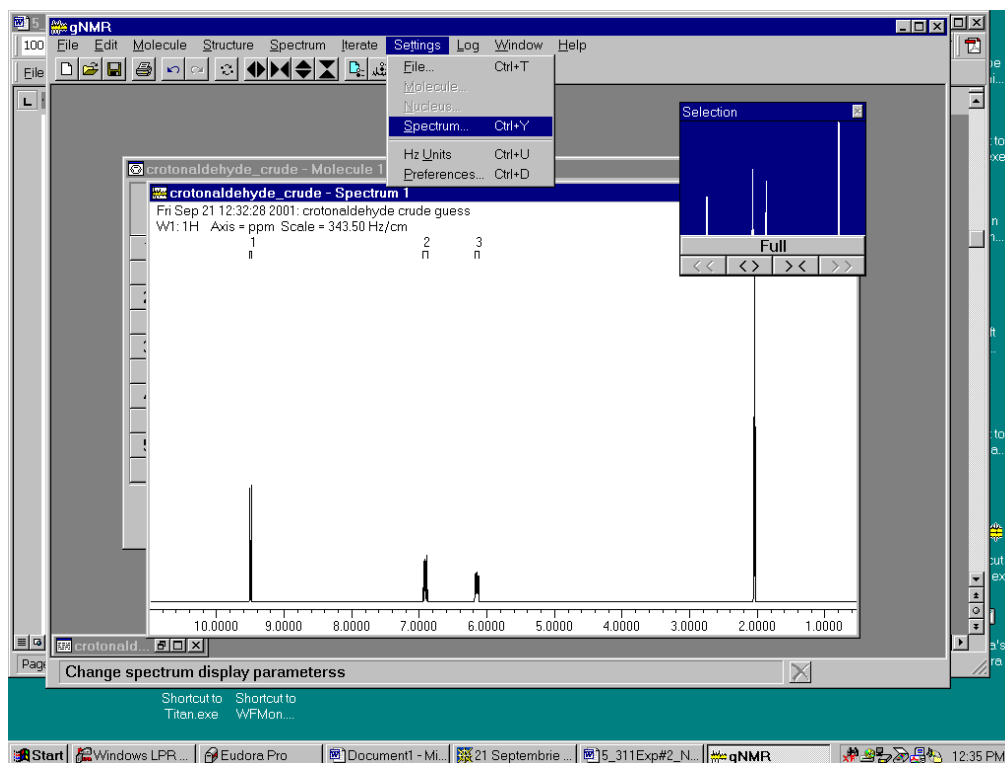


Experiment #2: Nuclear Magnetic Resonance

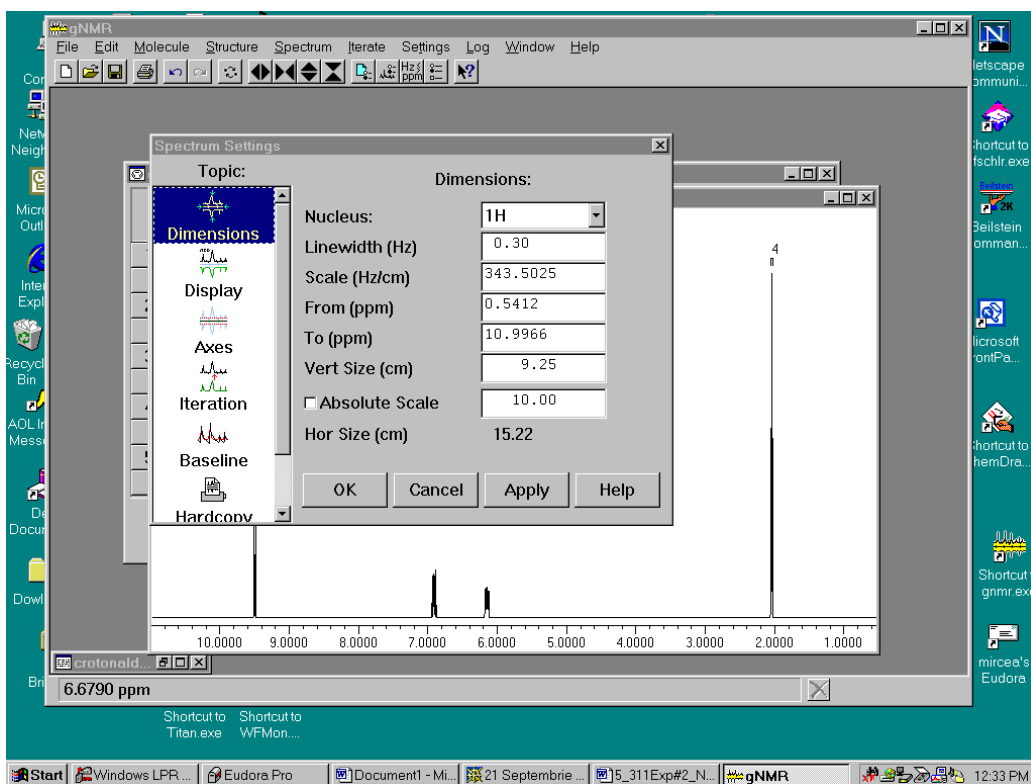
5a. Next check that the spectrometer frequency is correctly set by clicking on **Settings|File...** and setting the spectrometer frequency to 300 MHz for Varian Mercury Plus NMR. Click Apply.



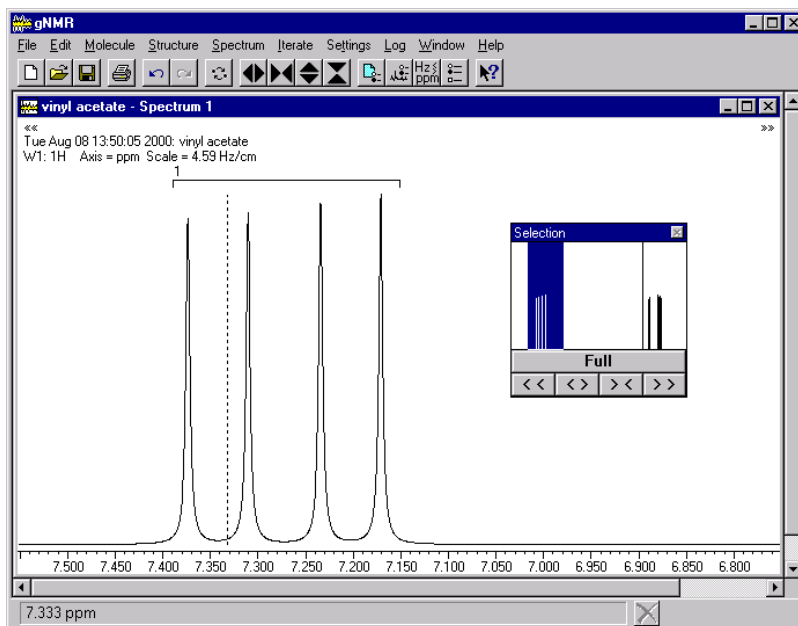
5b. Check if the line width is approximately 0.5 Hz. Click on **Settings|Spectrum...**, enter the correct value and press OK.



Experiment #2: Nuclear Magnetic Resonance



To expand the spectrum, select the desired sub-range by dragging the vertical line in the spectrum representation window that is stacked on top of the calculated spectrum. Two vertical dotted lines are visible around the selection. Click once between them, and the selected part will fill the window. To restore the whole spectrum, click on **Full**, which is the first button that is displayed in the toolbar of that window.



B. With iteration.

The iteration step is necessary because the hand guessed chemical shifts and coupling constants do not necessarily provide a calculated spectrum that fits with the peak positions and/or intensities of the experimental NMR. By iteration, a least-squares procedure is triggered that optimizes the shifts and coupling constants to produce the best fit among the observed (experimental) and calculated spectra. **Remember: before running iteration, set up first a normal simulation as described above.**

1. Go to **Molecule** window. Define variable names (letters such as a, b, c under the chemical shifts and combination of letters such as ab, ac, bc under coupling constants) for each spectral parameter that you want to optimize. Spectral parameters with the same name will be kept equal during iteration. A hyphen (“-”) at the beginning of the name means that the respective parameter will be **NOT** optimized.

The screenshot shows the gNMR software interface. The main window is titled 'Document1 - Molecule 1' and contains a table with the following data:

	Nucleus Name	n	δ ppm	W Hz	J 1	2	3
1	1H	1	7.267				
			a	-			
2	1H	1	4.871		13.95		
			b	-	ab		
3	1H	1	4.555		6.31	1.54	
			c	-	ac	bc	
4						0.00	

Below the table are two buttons: 'Settings' and 'Spectrum'.

2. Click on **Iterate|Assignments of 1H** and enter manually the peaks position (12 lines) from the output list resulted by printing the line position of the experimental spectrum.

Experiment #2: Nuclear Magnetic Resonance

		Frequency		Intensity	
		calc	obs	calc	obs
1	12	7.308	7.310	0.2419	
2	11	7.283	7.285	0.2464	
	10	7.252	7.254	0.2534	
3	9	7.227	7.229	0.2582	
	8	4.902	4.904	0.2509	
4	7	4.896	4.898	0.2608	
	6	4.846	4.848	0.2394	
	5	4.840	4.842	0.2489	
	4	4.571	4.575	0.2572	
	3	4.564	4.569	0.2474	
	2	4.545	4.550	0.2525	
	1	4.539	4.544	0.2428	

3. Click on **Iterate|Go**. The refined spectral parameters are displayed in the **Molecule** window.

	Nucleus Name	n	δ ppm	W Hz	J 1	2	3
1	1H	1	7.269				
			a	-			
2	1H	1	4.873		14.00		
			b	-	ab		
3	1H	1	4.560		6.25	1.50	
			c	-	ac	bc	
4						0.00	

Experiment #2: Nuclear Magnetic Resonance

The calculated (iterated) spectrum is:

