



# Chemistry Department

## NMR/Instrumentation Facility

### *Users Guide - VNMR 6.1*

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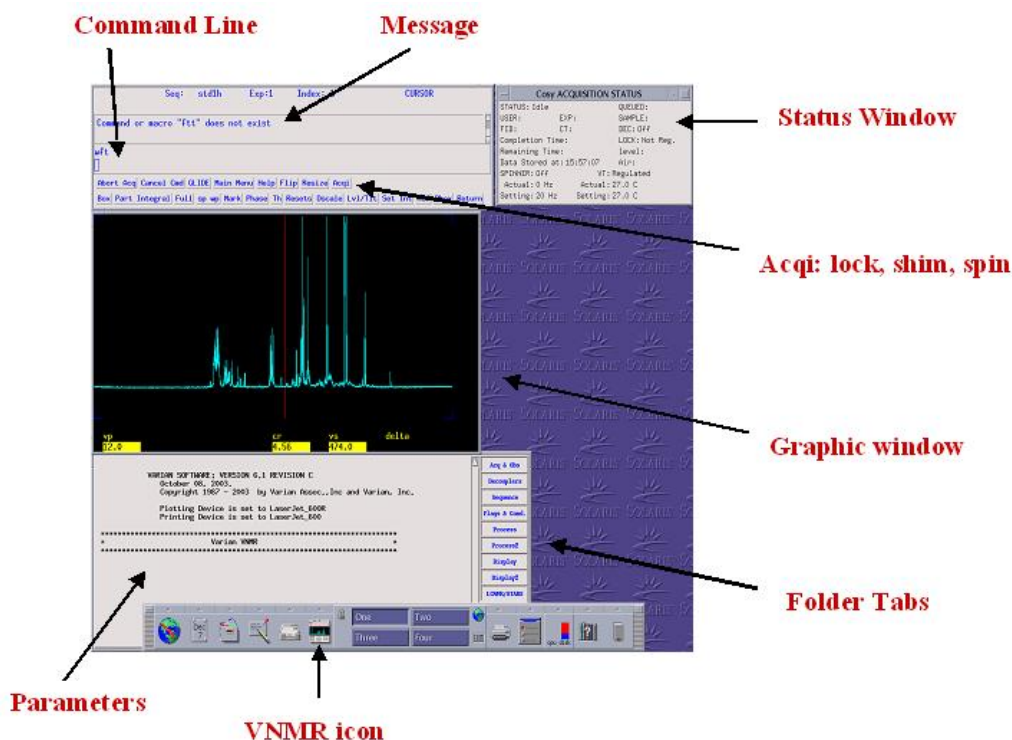
The following procedures should be used to acquire one-dimensional proton and carbon NMR data on the 200MHz NMR instrument.

The Experimental setup should be followed for any experiment.

- **Experiment setup**
  - insert/eject sample
  - spinning
  - lock
  - shimming
- **Proton spectrum**
  - integration
  - lineshape
  - digital resolution
  - coupling constant
- **Carbon spectrum**
  - <sup>1</sup>H-decoupled
  - <sup>1</sup>H-coupled
- **General commands**
  - display (pulse sequence, acquisition parameters, scale, threshold)
  - saving
  - referencing
  - phasing
  - printing

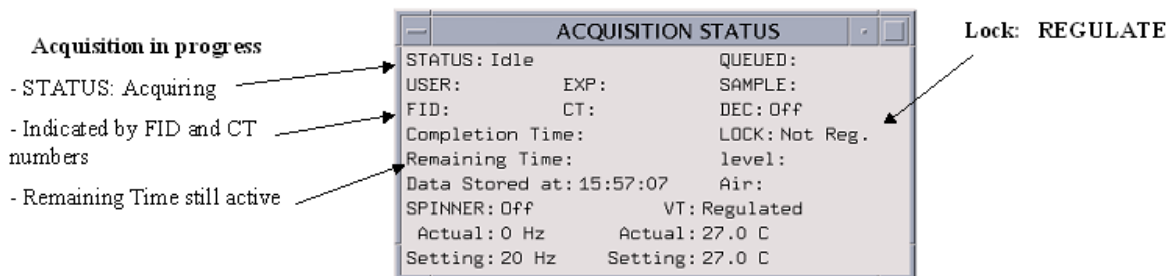
# Experiment setup

## VNMR 6.1C display



### Observe NMR computer status window

- the Status window on the desktop display allows you to check on the Acquisition progress, Spin and Lock of the system.




### Important observations:

1. Check the STATUS message:  
*An experiment can be started when the Status is shown as **Idle**.*
2. LOCK: REGULATED

**If you need to stop an experiment type aa**

### Sign in and open software

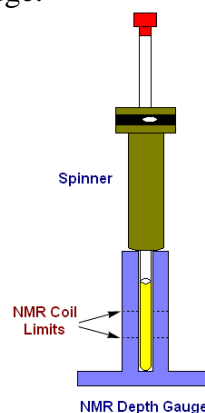
- sign in the log book
- log in
- **vnmr** is typically already open (If not click on icon  on bottom toolbar - one left mouse click)

### Remove lock sample and insert your sample

- remove Lock sample -  $\text{CDCl}_3$  - and type e

*The Lock sample will come up from the magnet. Remove it carefully!!*

- load your sample on the spinner and adjust the height using the depth gauge:



- place the sample in the magnet (it should float) and insert the sample by typing **i**

### Check your directory

- click on [Main Menu] – [File] – [Set Directory].
- find your directory, click [Change] to set the directory or on [Parent] to go up in the file structure.
- make sure you do this before saving files on your own folder, for easy access.

### Set up the experiment desired

- click [Main Menu] – [Set Up] and choose nuclei and solvent
- options are:  $^1\text{H}$ ,  $\text{CDCl}_3$   
 $^{13}\text{C}$ ,  $\text{CDCl}_3$   
*Nucleus, Solvent*
- if you are running  $^1\text{H}$  or  $^{13}\text{C}$  and your solvent is  $\text{CDCl}_3$ , just use the [1H,  $\text{CDCl}_3$ ] or [1H,  $\text{CDCl}_3$ ] options.
- if you are running  $^1\text{H}$  or  $^{13}\text{C}$  in another solvent, use the [Nucleus, Solvent] option.
- a list of solvents is next to the computer.

### Spinning

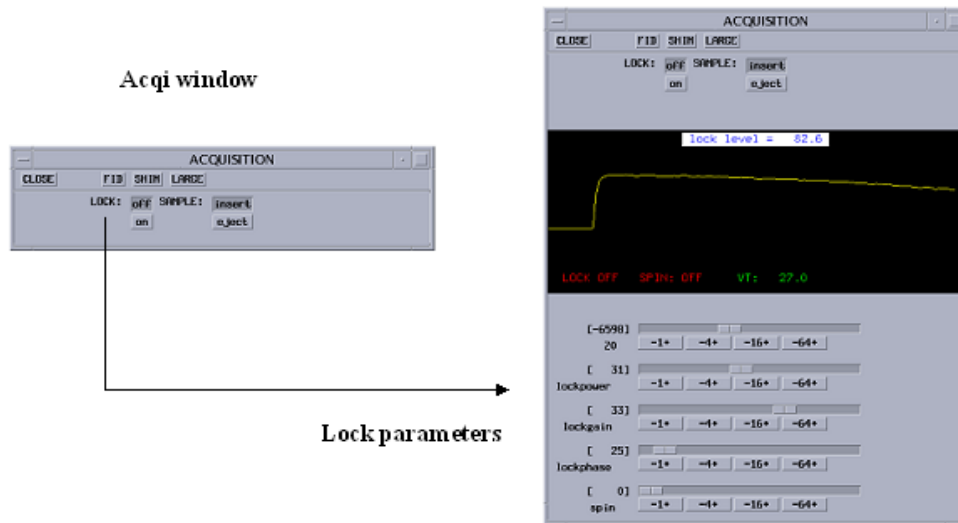
- check if sample is spinning (**green light** on left leg of magnet and on Status window **vnmr**)
- spin rate is set to **20Hz**, set by using the [Acqi] window

## Lock your sample

Click on the [Acqi] button, a new window will open.

Click on [Lock] and the window will expand showing the lock parameters: **lockpower**, **lockgain**, **lockphase**.

You should then see the wave line on the Graphic Window.



### Select Lock OFF:

*You should see a sine wave if the lock is off resonance.*

*When the lock approaches resonance, a flat step line will be seen (figure above).*

For the initial value, set the **lockgain** at its maximum (30 db)

For the initial value of **lockpower**, set it to ~30. The power you need to lock depends on your solvent and the concentration of the sample. Setting the power value too high will saturate the lock signal, and you will not be able to find the lock. At the same time the **lockpower** will need to be higher than the normal setting for locking.

Change Z0 until the signal changes from a sine wave to a flat line (with some noise).

***Lock must be off in order to change Z0.***

After establishing the lock, click on Lock **ON**.

If the lock value exceeds 100%, reduce the **lockpower** or **lockgain**; making sure the lock is still on.

Optimize the **lockphase**, until a maximum lock level is reached.

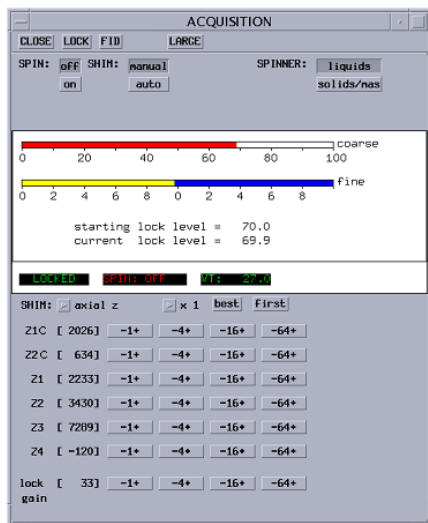
Return the lock level to 40-60 range by decreasing **lockpower** or **lockgain**.

Always minimize **lockpower** – the lock level should not significantly fluctuate if the power is set correctly.

**Check if Lock is ON.**

## Shimming

Click on [Shim] and the window will change to:



Optimize Z1C and Z2C, and then Z1 and Z2 observing the increase in the lock level, start with [-1+] or [-4+].

Reduce **lockpower** and **lockgain** if lock level reaches 100.

- shim (test lineshapes by running a standard 1D  $^1\text{H}$  spectrum)

## Loading data

- click on [Main Menu] – [File] – [Set Directory].
- find your directory, click [Change] to set the directory or on [Parent] to go up in the file structure.
- select the experiment (*.fid* extension) you wish to load, and click on it to highlight the file.
- select the icon [Load], type **wft aph** to process and display the spectrum

## Proton spectrum

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The proton experiment is used for solving simple structural problems, to check the progress of synthetic work and for setting up more sophisticated experiments. The chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) may be estimated; and the integration of proton resonances gives the number of corresponding protons. This information is useful for peak assignments and quantitative analysis.

The basic one-dimensional proton NMR experiment consists of a very simple pulse sequence, **s2pul** available in Varian systems. The first pulse is when the radio frequency (**rf**) is turned on for a few  $\mu$ s and then turned off. The first delay (relaxation delay) allows the spin systems to relax back to equilibrium. This is important for achieving the maximum signal-to-noise ratio. If the spin system doesn't relax sufficiently the relative intensity of the observed peaks will be affected. Generally **d1** is set to 1-3 times the longest T1 in the molecule (0.1-10s).

For quantitative measurements the 90° pulse should be used with an appropriate **d1** value.

### PROCEDURE

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- insert sample, lock and shim

Word in **bold** are to be typed on the **vnmr** command line

Word/phrase in square brackets [ ] are icons that can be accessed by a left mouse button click

#### Acquisition

- select [Main Menu] - [Setup] - [Nucleus, solvent] - [H1] - [solvent]
- if your solvent is not listed select [Other] and type the solvent name on the command line when prompted.
- parameters that can be changed by user:
  - [Acq & Obs]
  - **nt** = number of scans/transients (multiple of 4)
  - **ss** = steady state scans (dummy scans) (necessary for NOE experiments)
  - **np** = number of data points acquired (at least 2\***sw**, best resolution with 4\***sw**)
  - **sw** = sweep width of spectrum (to change use **movesw**) (**tof** and **np** will be changed)
  - **d1** = relaxation time (1-3\*T1) If integrals don't make sense, increase **d1** and re-run experiment
  - **gain** - depends on sample concentration (**gain='n'** - ensures that a suitable gain is used, auto-gain)
- **go** or **ga**

#### Processing

- **wft aph** (weighted Fourier transform with autophasing)
- parameters such as **fn** (at least 2\***np**) and **lb** can be changed
- see general notes on phasing, reference, saving and printing a spectrum

## NOTES

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### Integration

- **cz**
- click on [Int] to set integrals, a green integral line is displayed
- the middle mouse button will adjust the vertical scale of the integral (**isadj**)
- click on the [lvl/tlt], drag line up and down with left (coarse) or right (fine) mouse buttons
- click on [Box] to get out of level-tilt mode
- click on [Resets]. The left mouse button is now used to select where to break the integral. If you make a mistake, use the right button to remove the nearest reset.
- click on [Box] to get out of resets mode
- to display integrals type **dpir** or **dpirn** (normalized)
- to set a specific peak to a number, place cursor on that region and select [Set Int], then type number desired at the prompt. Use **dpir** to display values

### Lineshapes and shimming

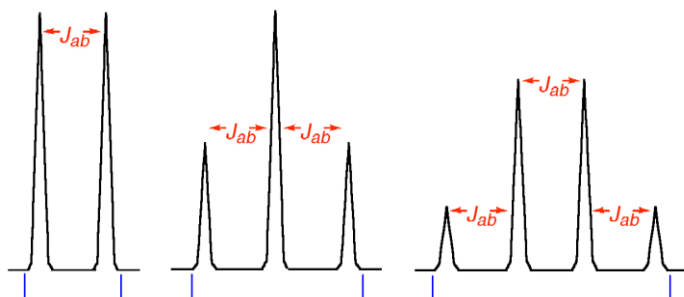
- inspect your spectrum and observe the lineshapes - this will give you indication on the shimming: if there are any humps or unusual splitting on **all** peaks it means you need to shim again.

### Digital Resolution

- place cursor on a peak and on the command line type **dres**
- a value for linewidth and digital resolution will be shown on the Message window (over command line on **vnmr**)
- typically proton NMR will show resolution below 0.2Hz/pt
- optimal linewidth will vary with molecular weight of compound and solvent
- for small molecules in non-viscous solvents, linewidth should be less than 1Hz.

### Measuring coupling constants and integration

- coupling patterns: doublet, triplet, quartet, etc - measure the distance between the peaks to get **J** values
- when selecting the area of the peak to be integrated you should select the point at the base line, before and after the peak (marked below)



## Carbon spectrum

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The naturally abundant carbon-12 does not have a nuclear spin, and therefore no NMR. When performing a carbon NMR, only the 1% naturally occurring carbon-13 is being acquired. The sensitivity is thus much lower than proton NMR and the spectrum takes more time for acquisition.

Protons attached to a carbon atom will cause splitting of the carbon signal, lowering the signal-to-noise ratio. The routine  $^{13}\text{C}$  experiments are performed using proton decoupling and NOE conditions (see **Acquiring  $^1\text{H}$ -decoupled  $^{13}\text{C}$  spectrum**). The carbon spectrum of a compound will display a single sharp signal for each structurally distinct carbon atom in a molecule.

In order to produce a spectrum where carbons are coupled to adjacent protons the proton-decoupler is turned off (see **Acquiring  $^1\text{H}$ -coupled  $^{13}\text{C}$  spectrum**).

Carbon atoms with long T1 experience saturation and result in reduced intensity, which is the case of quaternary carbons, *i.e.* carbons with no directly bonded protons. A long **d1** can be helpful when trying to observe quaternary carbons.

### Acquiring $^1\text{H}$ -decoupled $^{13}\text{C}$ spectrum (**dm='yyy'** - decouple + NOE)

#### PROCEDURE

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- insert sample, lock and shim

Word in **bold** are to be typed on the **vnmr** command line

Word/phrase in square brackets [ ] are icons that can be accessed by a left mouse button click

#### Acquisition

- run a proton spectrum
- select [Main Menu] - [Setup] - [Nucleus, solvent] - [C13] - [solvent]
- if your solvent is not listed select [Other] and type the solvent name on the command line when prompted
- parameters that can be changed by user:
  - [Acq & Obs]
  - **nt** = number of scans/transients (multiple of 4)
  - **ss** = steady state scans (dummy scans) (necessary for NOE experiments)
  - **np** = number of data points acquired (at least  $2*sw$ , best resolution with  $4*sw$ )
  - **sw** = sweep width of spectrum (to change use **movesw**) (**tof** and **np** will be changed)
  - **d1** = relaxation time (1s, no integration is performed)
  - **gain** - depends on sample concentration (**gain='n'** - ensures that a suitable gain is used, auto-gain)
- **go** or **ga**

## Processing

- **wft aph** (weighted Fourier transform with autophasing)
- parameters such as **fn** (at least **2\*np**) and **lb** can be changed
- see general notes on phasing, reference, saving and printing a spectrum

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## NOTES

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If incomplete decoupling is observed:

- acquire a proton spectrum of the sample
- place cursor in the center of the proton region and type **movetof**
- **tof?** - a message on the bottom right of **vnmr** will give an approximate **tof** value
- on the carbon acquisition type **dof=#** (# obtained for **tof**)

### Acquiring <sup>1</sup>H-coupled <sup>13</sup>C spectrum (**dm='yyn'** - couple + NOE)

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## PROCEDURE

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- insert sample, lock and shim

Word in **bold** are to be typed on the **vnmr** command line

Word/phrase in square brackets [ ] are icons that can be accessed by a left mouse button click

## Acquisition

- Run a <sup>1</sup>H-decoupled <sup>13</sup>C spectrum
- Change decoupler parameters:
  - **dm='yyn'**
- **go** or **ga**

## Processing

- **wft aph** (weighted Fourier transform with autophasing)
- parameters such as **fn** (at least **2\*np**) and **lb** can be changed
- see general notes on phasing, reference, saving and printing a spectrum

### “Quantitative” <sup>13</sup>C spectra

The normal carbon spectra are qualitative and integrations do not give the corresponding number of carbon present in each peak. The main reasons are due to NOE and the different relaxation times of carbon atoms (T1).

If you wish to take a quantitative spectrum, NOE and decoupling need to be removed from the pulse sequence (**dm='nny'**; assuming **d1=5\*T1**). A very long relaxation delay needs to be used as well. *The integration will still have large errors.*

# GENERAL COMMANDS

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## Create and join experiments

VNMR allows you to acquire data in several workplaces

- **cexp(#)** - # is an integer number, creates an experiment
- **jexp(#)** - # is an integer number, joins an experiment

If the message “*Experiment locked*” appears on the Message window:

- **unlock(#)** - # is the experiment number

## Acquisition parameters

- click on [Acq & Obs] on Folder tabs

## Processing parameters

- click on [Process] on Folder tabs

## View and change parameters

- type the name followed by a question mark, e.g. **np?**
- the **np** value would be shown in the Message window
- to change parameters use **name=**

OR

- locate parameters in Folder tabs and change them directly on window

## Spectral width

- the spectral width can be changed by selecting the regions where the peaks are located (with ~1ppm margins) and typing **movesw**
- all peaks should be included to avoid folded peaks in your NMR spectrum

## To stop acquisition

- **aa**

## Saving a spectrum

- **svf**
- when prompted type the name desired on the command line

## Scale in ppm or Hz:

To view scale:

- **dscale**

Change scale unit:

- by typing **axis='h'** for Hz or **axis='p'** for ppm

## Reference

Place cursor on peak to be set as reference:

- **nl rl(##.##p)**

## Threshold

- use [**Th**] button

### Peak picking

- **vsadj** - automatic vertical adjustment
- **dll** - display peaks on text window
- **dpf** - display frequencies on peaks

### Phasing

- reset phasing by using **rp=0** and **lp=0**
- **aph** for auto phasing

OR

- [Phase] button to do this manually using the left mouse button
- after manual phasing type **ds**

### Printing

- **pll pscale pir page**
- **pexpl page** - to plot the graph display
- **pl('all) pscale ppa page** - to plot spectra array

**pl** - plots spectrum  
**pscale** - plots scale  
**pir** - plots integral areas  
**pirn** - plots normalized integral regions  
**ppf** - plots peak frequencies  
**pap** - plot all parameters  
**ptext** - plots text label  
**page** - send to printer