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NMR/Instrumentation Facility

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NMR Data Processing

NMR data

The raw NMR data (time domain - FID) consists of a list of numbers, usually negative and positive integers, as function of time in equal time increments. There are two types of data values: real and imaginary, which reflect the two channels of the NMR receiver. Varian samples both channels simultaneously. The data is saved as a directory (extension **.fid**), which contains the files: **fid** - actual binary data file; **log** - history of the experiment; **text** - file user can create describing sample; and **procpar** - list of parameters used.

Sensitivity and resolution

These terms are used to characterize the quality of a spectrum:

- **resolution** - ability to distinguish components of the signal that are close in frequency
 - digital frequency resolution measures how closely the discrete frequencies are spaced.
- **sensitivity** - ability to distinguish signal from noise
 - S/N ratio - number giving the ratio of highest peak in the spectrum to the height corresponding to the noise level.
- Higher field gives better S/N and separates signals better, making coupling patterns simpler.
- Probes optimized for a particular nucleus give the best S/N for that nucleus. The Inova 400 with the indirect detection probe is most sensitive to proton. The switchable and broadband probes will give better S/N for other nuclei, e.g. carbon, nitrogen, phosphorus

Measuring digital resolution on vnmr and vnmrj

- place cursor on a peak and on the command line type **nl dres**
- a value for linewidth (at half height $LW_{1/2}$, in Hz) and resolution (in Hz/pt) will be shown on the Message window

Notes:

- ^1H digital resolution for ethylbenzene standard was below 0.2Hz/pt
- linewidth is dependent on relaxation time and will be specific to each peak in the molecule. CHCl_3 has $\text{LW}^{1/2}$ below 0.5Hz

Measuring S/N ratio on vnmr and vnmrj

- place cursor on largest peak in spectrum and type **nl**
- then use both cursors to select a noise region and type **dsn**
- a value for the S/N will be shown in the Message window

Note:

- higher S/N values indicates that the instrument is more sensitive:
 - 200MHz SW probe has 30:1 for proton
 - 400MHz ID probe has 345:1 for proton

1D NMR data processing on VNMR and VNMRJ

Processing parameters can be viewed using folder tabs:

- **vnmr** - [Process]
- **vnmrj** - [Process] - [Process] and [Process] - [Linear Prediction]

AUTOMATIC PROCESSING

wft aph - standard zero filling, apodization, FT and autophasing are applied

Starting with an FID, the following operations need to be performed. Some of which will improve sensitivity and resolution:

1) Zero filling the FID

- adding zeroes to the end of the FID to increase the number of data points before FT, increasing digital resolution
- has no effect on peak positions, intensities or linewidth
- **fn=2*np** - define the data size (**fn**) before FT to a larger number than the acquired data (**np**)
- **fn** must be a power of 2 ($16384=2^{14}$, $32768=2^{15}$)

2) Linear prediction

- improve quality of FID and corresponding spectra. Used to repair distorted parts of an FID caused by mis-set acquisition parameters, or spectrometer perturbation.
- mainly used for multidimensional NMR experiments:
 1. **backward linear prediction** - repairs few first points of FID, and t reconstruct and FID back to $t=0$

2. **forward linear prediction** - applied to complete non-decayed 1D FID, which occurs when the **at** is too short, causing baseline distortions.

3) **Multiplying FID by a window function - *apodization or windowing***

- the FID consists of exponentially decaying sinusoids. In theory, each transition in the spectrum is represented by a Lorentzian lineshape, since Lorentzian functions are related to decaying sine and cosine waves, which are experimentally detected.
- application of window functions enhance quality of spectra, by emphasizing certain parts of the FID
- apodization functions change the S/N ratio, resolution and shape of peaks:

i) exponential multiplication

- specify the linebroadening (**lb**, in Hz)
- a good value to use is the digital resolution of the spectrum (**dres**, Hz/pt)
- trial and error may be needed to discover the optimum value for **lb**
- positive values of **lb** increase S/N at the expense of resolution
- negative values of **lb** increase resolution at the expense of S/N
- proton spectra **lb**=0.2Hz
- carbon spectra **lb**=1.0Hz (weak signals may become more visible using **lb**=3.0 or 5.0Hz)

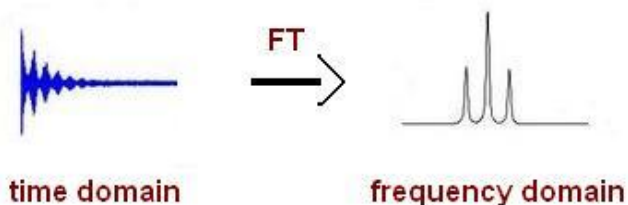
ii) gaussian multiplication

- changes peaks from Lorentzian to gaussian shapes
- proper selection of **gf** and **gfs** to achieve best S/N and resolution

iii) sine bell multiplication

- changes peaks from Lorentzian to sinc shapes
- proper selection of **sb** and **sbs** to achieve best S/N and resolution

4) **Fourier Transformation**



- the FT is the central step in NMR data processing, which transforms the time domain signal into a frequency domain signal.
- typing **wft** (weighed Fourier transform) applies the window function to the FID

5) **Phasing**

- after FT peaks may be upside down or have a dispersive lineshape, the spectrum needs to be phased to give the correct absorptive peak

- **aph** - automatic phasing, often works well for 1D experiments

6) Referencing

- place cursor on center of the reference peak and type **nl rl(#p)**, where # is the value in ppm.

7) Integration (optional)

- refer to VNMR and VNMRJ manuals

8) Baseline correction

- caused by external perturbations or spectrometer imperfections. More pronounced with dilute samples and give problems with integrations of 1D and 2D spectra.

If the baseline is not flat, or if you plan to integrate, apply baseline correction:

- Type **dc** to apply a linear drift correction.
- Type **cz** to clear the list of baseline points.
- Type **region** to automatically create the list of baseline points.
- Type **bc** to apply a baseline correction.