

Fall 2014 Chem 636 – HW #7

Automation: IconNMR and VNMRJ

Assignment due at beginning of lab, week 8 (Oct 21 – Oct 24).

Use Artemis and Hermes (Mercury-300) for this week's HW #7.

Although you may work in groups, each of you should setup and acquire your own data, and process and hand in that individual set of data.

In this week's lab you will learn how to use spectrometers under automation. Artemis and Callisto use IconNMR. When you are using a spectrometer in TopSpin mode — anytime on Persephone, and Callisto on Wed and Sundays — IconNMR can be started up and used to automate a set of your samples. The Varian Mercury-300, named Hermes, uses a different program called VNMRJ.

The setup of experiments on these instruments is simple, but also restricts what can be done compared to acquisitions in TopSpin. For most 1D experiments, automation provides a convenient method to acquire data. Restrictions become more apparent with 2D experiments, and most selective-1D experiments (we'll see a couple at the end of the class) are best not done in automation.

Two User Guides (on the User Guides main page) assist with the use of automation:

For IconNMR: “Avance 400 – Automation using IconNMR and the SampleJet robot”
(https://www.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/Av400UG_IconNMR.pdf)

For VNMRJ: “Introduction to the Use of Hermes (Varian Mercury-300)”
http://www.chem.wisc.edu/~cic/nmr/Guides/VUG/Use_of_Hermes.pdf

IconNMR and VNMRJ make acquiring data almost too easy a task: it would be a very bad habit to not *think* about your data when setting up experiments. If you queue up the sample to the wrong holder position, as (unhappily a not infrequent) example, the queue will stop and other users (and the staff) will not be pleased with your mistake. Note also the issue that has caused many problems recently with 400: please insure that you are using only the older PAT PENDING labeled Norell caps. The new caps swell in the presence of CDCl₃, and the tubes drop away when the robot picks a sample up with a swollen and therefore loose-fitting cap.

Even if it seems simple, please ask questions! And document and report — email is usually best — any problems you observe with the instrument. Don't assume staff will already be aware of the problem.

Note: There are no recommendations made for NS for the spectra below. All the samples are at relatively high concentration ($\geq 30\text{mM}$).

I. IconNMR on the Avance-400 (Artemis)

1. Acquire ^1H and ^{19}F (^1H -coupled) 1D spectra of 3-amino-2-chloro-6-fluoroquinoxaline in $\text{DMSO-}d_6$, using the default parameter setups (check **NS** on the ^{19}F). It is important to get these spectra queued immediately. You'll need them for setting up the other experiments in section III below.

Now go to the Mercury-300 and submit spectra there. Then come back to the 400.

II. VNMRJ on the Mercury-300 (Hermes)

On Hermes, you will each be given a login name and a temporary password; you should have changed your password during you demo lab session.

To setup your sample in automation:

- Insert the sample into the spinner and check the depth using the gold depth gage
- Check the sample height by using the 9" scale on the front of the sample table (the NMR tube should not be longer than 9", and no shorter than 7")
- **Do not use the following slots:**
 - a) slot 0 – the robot will use this slot after a power out or other troubleshooting
 - b) slot with robot arm above it – sample in the magnet will come back to this slot
 - c) slot 99 – reserved for the CDCl_3 standard
 - d) slot 100 – a bug in the software prevents use of this slot
- Below is a brief list of important parameters used on NMR spectrometers:

Bruker	Varian	description
NS	nt	number of scans or transients
DS	ss	number of dummy scans
D1	d1	relaxation or recycle delay
AQ	at	acquisition time
TD	np	number of data points
TD1	ni	number of increments

A more complete list providing Bruker and Varian parameters and commands is given at:

http://www.chem.wisc.edu/~cic/nmr/Guides/VUG/AMAC_tab.pdf

1. Acquire a ^1H 1D spectrum of quinine in benzene- d_6 .
2. Setup and acquire a standard $^{13}\text{C}\{^1\text{H}\}$ and DEPT-135 spectra. For a 30mM concentration, the number of transients (**nt**) need not be too high (i.e., ~10 minutes should be enough for each experiment).

→ When considering the parameters for these two experiments, suppose the quaternary carbons showed up on a previous $^{13}\text{C}\{^1\text{H}\}$ spectrum at $< 1/4$ the intensity of the protonated

carbons. Change **d1** by reducing or increasing it by 50% (you decided which is right) such that the new value will assist in getting better relative intensity on the quats.

1☞ Plot the ^1H 1D in the normal manner. Note the differences in the way the data are stored, compared to Bruker data; remember that Hermes data is stored (currently) on Apollo. Note also the difference baseline characteristics. Hermes uses analog filters, similar (but not identical) to those on the AC-300.

2☞ Plot the $^{13}\text{C}\{^1\text{H}\}$ and DEPT-135 spectra as a stack plot.

Q1 From discussion in lecture concerning sensitivity between these two experiments, which should be more sensitive for protonated carbons? Explain briefly why?

III. IconNMR on the Avance-400

3☞ Plot the ^1H and ^{19}F 1D spectra acquired in Section I (as two separate plots).

- Based on the information provided in these two spectra,
 - acquire a $^1\text{H}\{^{19}\text{F}\}$ spectrum
 - acquire a $^{19}\text{F}\{^1\text{H}\}$ spectrum.

Q2 For which spectrum does the O2p have to adjusted? Why?

- Acquire a ^1H 1D spectrum of sucrose in D_2O .
 - Acquire another ^1H spectrum having an obtainable resolution of 0.1 Hz.
 - Acquire a 3rd spectrum with an optimized spectral window (this is not as easy as with TopSpin, as there is no way to graphically use the spectrum; you will have to figure out values of **SW** and **O1p** to enter).

4☞ Plot the spectra up as a stack plot.

- Acquire $^{13}\text{C}\{^1\text{H}\}$ on rotenone. This sample is $> 2\times$ as concentrated as the quinine sample.

Q3 How many scans should be asked for? How can you tell?

- Acquire a ^1H -coupled ^{13}C spectrum of rotenone.

Q4 Again, how many scans? More or fewer than in the standard $^{13}\text{C}\{^1\text{H}\}$ spectrum? By how much more would you estimate? Why?

- Acquire a DEPT-135 and DEPT-90.

Q5 Yup, NS again (last time)... Should the NS be smaller than $^{13}\text{C}\{^1\text{H}\}$, or larger? Why?

5☞ Plot the $^{13}\text{C}\{^1\text{H}\}$ spectra up, and annotate NS values on each.

Turn in 5 (or more) plots, and answers to 5 questions.