NMR New User Workshop (3)

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Conte A328 (7-1428)

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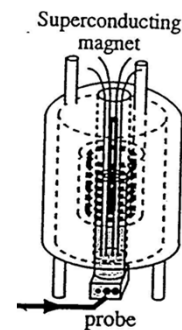
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Magnet Safety

▪ Very strong magnetic field!
  – ca. 100,000 times stronger than earth magnetic field
  – Never get iron object close to magnet
    ▪ Wrenches, heat gun, etc could fly to the magnet
  – Keep credit cards, cell phone, watches, etc. away
  – Pregnant women should stay away
  – People with pacemakers should stay away

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Sample Handling Safety

- What would happen if you insert tube without spinner?
- NMR tubes are brittle; handle with care
  - Report to me if the spinners are too loose/too tight
- Measure the correct sample depth
  - Incorrect depth makes lock and shim difficult
  - too much depth will get the sample stuck
  - If you have less than 4cm sample, center your sample around the thin black line rather than push it to the bottom
- If reusing NMR tubes, only wash with mild solvent and drive at ambient T; check for cracks under light

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NMR Facility Overview

- Avance500 (B622 Conte): 1H, 19F, and everything else
- Avance400 (075 LGRT): 1H, 19F, and everything else
- Agilent700 (082 LGRT) and Bruker 600 (B342): 1H and 13C
  - 2.5x stronger signal than 400. Excellent for low concentration samples
  - Must have justified need and pass additional training
- 600 solid-state (B342)
  - insoluble materials

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400 and 500 Operation

- Please read "400500 Instructions" thoroughly
- IconNMR mode
- Manual mode

- To go from manual to Icon mode: type *icona*
- To go from Icon to manual mode:
  - Click "cancel" on the IconNMR login screen
  - If you have logged in Icon and are on the Automation screen, you need to click Stop on top right of the screen, then exit. Otherwise you won't be able to use the manual mode.

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Phase Correction

- Phase distortions cannot be corrected by baseline correction
- *apk* often does not do an ideal job
- Manual phase correction:
  - 0th order: correct phase of all peaks to the same degree
  - 1st order : correction amount $\propto$ distance to the pivot line
- Objective of phase correction: to make baseline visually continuous
  - So that baseline correction can work

Before apk

After apk

After apk amplified

After manual pk amplified
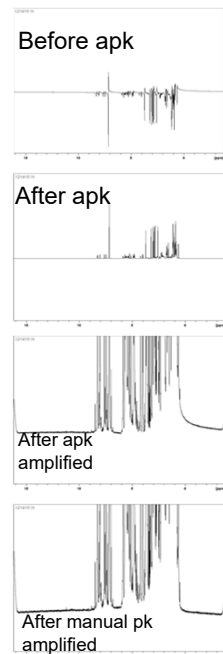
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Advanced 1D and 2D NMR

- Gives a lot of information and is often fairly quick
- DEPT and HMQC are faster than regular 13C spectra
- HSQC combines the power of DEPT and HMQC
- HMBC: 1H-13C multi-bond correlation
- 1D and 2D NOESY: through-space 1H-1H correlation
- My blog has the setup instruction for these experiments.
- Many more techniques can be done.
- Many good resources available in print and online.

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Fast and Quantitative NMR

- If you want to do quantitative 13C, or you want to run 13C faster, use $Cr(acac)_3$ and follow instructions on my blog.
  - Paramagnetic chromium speeds up $\underline{T_1}$ relaxation
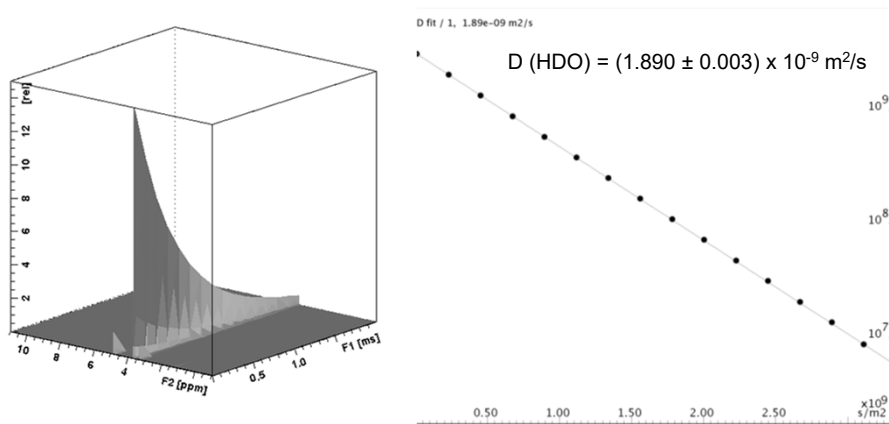 - This technique also works well for 29Si

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Diffusion NMR

- Diffusion of molecules and aggregates in liquids can be studied by NMR
  - Similar to the principle of MRI
  - Diffusion through a magnetic field gradient causes decay of NMR signal, which can be monitored and modeled

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D fit / 1, 1.89e-09 m2/s

$D\ (HDO) = (1.890 \pm 0.003) \times 10^{-9}\ m^2/s$

- Diffusion Coefficients and thus particle size can be accurately determined
- Diffusion of each molecule/assembly in the sample can be probed

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Variable Temperature NMR

- We can do from ca. -30C to +70C (on 400)

- Experiments involve potential hazards – solvent boiling, explosion, and contamination etc. So all VT-NMR users need to be individually trained by Dr. Hu

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Customize Processing Parameters

- Manual phase correction

- Manual baseline correction

- Auto baseline correction for selected regions

- Line broadening to balance between resolution and S/N

- These changes only affect the processed spectrum and will not affect the raw data (FID)

lb = 15 Hz

lb = 1 Hz
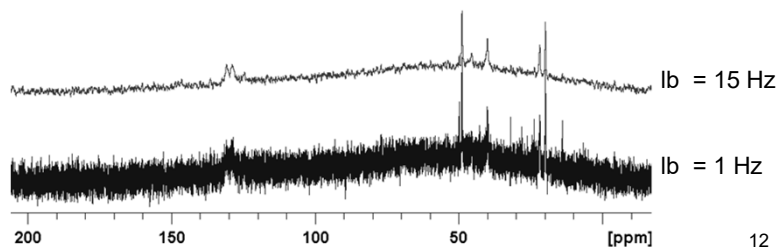
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Spectrum Plotting Options

- File -> Export, then choose a path and give a file name. You must specify the file extension.

- Click "Plot" tab, adjust settings as needed, then click Print. If you choose "Print to File", you can export to a higher-resolution vector graphic format (.ps)

- On the command line, type *convbin2asc*. You will export the spectrum to an ASCII file named "ascii-spec" in the same folder that contains the processed spectrum file.

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NMR Facility Policies

- Reservation
  - please follow the reservation rules on top of the FOM calendars.
  - If you arrive 10 minutes later than scheduled starting time (5 min later for a 15-min slot), you forfeit your slot and may be charged for the length of the reservation.
  - 3 overbooking violations will face suspension of their accounts for 3 weeks.
- The only internet access is data transfer via gFTP.
- Data storage: The NMR computer gets full quickly. You need to transfer out data and delete them from the NMR computer asap.
  - Don't use flash drive; it could contaminate
  - If you have too many data files, Topspin will load very slowly
  - click Internet -> gFTP. 128.119.71.99. Username = nmrusers.
  - folder that stores your data:
    - /opt/topspin3.2/data/[username]/nmr
    - [username] = IconNMR acct name (if you belong to a large NMR using group) or Linux acct name (all others)

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- Reporting of problems and incidents
  - Report instrument problems to Czar if your group has one, otherwise report to me.
  - Never attempt to fix problem or reboot computer
  - Report incident caused by you (standard sample breakage etc.) to Dr. Hu
- You are responsible for the act of anybody using your account (junior grad students, summer students etal)
  - When you feel your trainees can comfortably run simple nmr experiments themselves, ask them to contact me to obtain their own accounts
- Please keep the workplace clean
- Please acknowledge the NMR Facility in your papers and presentations

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Further Learning

- Use the information on my NMR blog
  - blogs.umass.edu/weiguoh
  - Under Training Materials category, find "400500-instructions.docx". It has detailed instructions on running most popular NMR experiments
- Special experiments need to be trained by Dr. Hu

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Rules for Tubes

- Wiping tube wall before inserting sample into spinner will improve your spectrum resolution
- Reuse of tubes
  - Cleaning should be done promptly. Solid deposits will be hard to remove
  - Dry with N2 gas. <u>Never bake the tube!</u> It will deform
  - Never use strong base for cleaning. It will etch the surface and deteriorate your resolution.
- Tube condition will deteriorate over time
  - Discard when cracks develop
  - Discard it when it does not freely roll on your table
  - Sample breaking inside the probe will be a bad accident
- Tubes should be graded at or higher than the instrument frequency
- Avoid paramagnetic species such as iron and chrome. These residues will severely broaden your peaks

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Common Experimental Problems

- Difficulty locking:
  - Bad shimming (2H signal is broad and low)
    - Did not do *rsh* shims.best
    - Sample does not spin
    - Sample depth not correct
    - If less than full sample, did not center sample around black line
  - Instrument may be "Fatigued"… try typing the command again
- Spectrum has a poor resolution:
  - Indications of a shimming problem:
    - Every peak has the same peak shape
    - Peak shapes are often asymmetric

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Sample quiz questions (understanding why is much more important than remembering commands)

- What should you do if you want to stop expt early and save data?

- What does *rsh shims.best* achieve? Why do you still have to further shim afterwards?

- If you don't do baseline correction, what kind of error it might cause?

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