NMR FACILITY NEWSLETTER

University of Windsor, Department of Chemistry and Biochemistry

Matt Revington-Facility Manager

Introducing the New Facility Manager

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This is the first issue of a quarterly newsletter that I will be producing for users of the Departmental NMR Facility to keep everyone informed about developments in the NMR Facility and to introduce users to new experiments as they become available.

As I have recently taken over this position from Mike Fuerth I should first, briefly introduce myself. I graduated from this program in the early 1990's and received a MSc in Medical Biophysics from the University of Toronto and a PhD in Biochemistry from the University of Western Ontario . This was followed by post-doctoral stints at the University of Michigan and at UWO. Prior to taking this position I was a NMR Staff Scientist at St Jude Children's Research Hospital in Memphis, Tennessee. My background is primarily in the application of NMR to biomolecular structure and dynamics and I have extensive experience in multidimensional NMR techniques. I have enjoyed returning to my roots and thank everyone for their help and support so far.

My goals in taking this position is to first maintain the high level of service that Mike provided for the department and over the next couple of years to take initiatives in improving training in the use of the spectrometers through an upgraded website, this newsletter and workshops on beginning and advanced topics. I am open to any suggestions that you have about improvements to the facility.

Facility News

A new BBFO (broad band fluorine optimized) probe was installed on the 500 MHz in October. The probe gets about two times better signal to noise for ^{13}C than the previous probe and has the automated tuning accessory. Installation of a new probe requires new files for solvents and pulse parameters for experiments. The common experimental files have been updated, if you are unsure if the parameter set that you are using is the best just check with me. If your favourite deuterated solvent is not on the list or if a lock file is giving you problems you can also contact me. One unforeseen issue with the new probe is that making full use of the ^{19}F capabilities is going to require upgrading the 500MHz from XWINNMR to TOPSPIN software,. We anticipate that the software upgrade will occur in the next few months, until then ^{19}F experiments be run on the 300DPX or the instrument in room B82.

I now have NMR tube inserts for external locking available for loan to people who have been running unlocked due to a lack of a compatible deuterated solvent.

The most recent optimized shim files are now being saved under the easier to find name "aa_best" on all of the instruments.

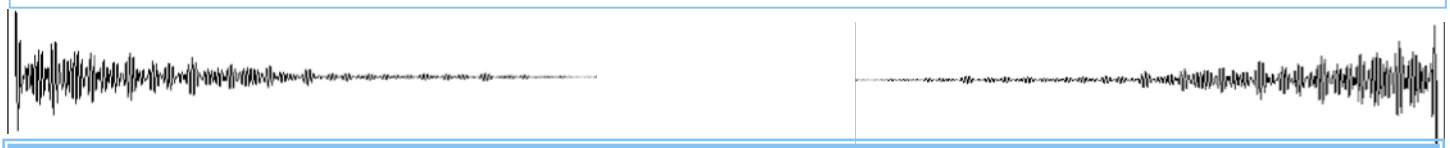
NMR Facility Website Updates

I am in the process of upgrading the NMR Facility website to be a better information source for users. Usage and scheduling guidelines for the instruments have been posted to the site. If you have any suggestions or problems with any policies that have been posted please contact me.

Updates concerning anything unusual such as equipment downtime , or longer term booking of the instruments will be also posted there ahead of time.

Simple protocols for setting up 1D experiments has been posted and in the near future protocols for VT experiments and data processing will be added. If you make use of these please don't hesitate to give me constructive criticism about them. If you want instruction sets for other aspects of NMR operation

In each addition of this newsletter I plan to introduce less commonly used NMR experiments that would be of use to some of our users, these articles will also be posted on the website.



Technical Comment-Tuning

Since I have started here it is apparent that there is a wide variety of comprehension/skill levels of the individual users of the spectrometers. Probably the most common problem I see is the failure to tune properly. To start with many users don't know the difference between shimming and tuning.

Shimming is optimizing the homogeneity of the magnetic field around the sample by adjusting the current flowing through small coils of wire (shims) near the sample. On Bruker spectrometers we do this by selecting a shim (ie Z1) then turning the knob until the line in the lock window is at its maximum position. Proper shimming results in narrow lineshapes and good resolution between signals.

Tuning is adjusting two capacitors (tune and match) in the probe circuit to minimize the impedance, on older instruments this is done directly by turning knobs on the bottom of the magnet, on newer instruments small motors controlled by software adjust the capacitors. If the tuning is bad not enough power reaches the sample to excite the spins properly resulting in poor signal to noise. This becomes especially apparent in ^{13}C experiments which have a signal on the order of 5000 times weaker than ^{1}Hs. The high sensitivity of ^{1}H experiments means that good quality spectra can usually be collected without tuning and when moving onto collect ^{13}C data users often forget to tune which result in poor or no signal even with an overnight collection. The figure below shows what the wobb window on the screen should look like for a well tuned nuclei.

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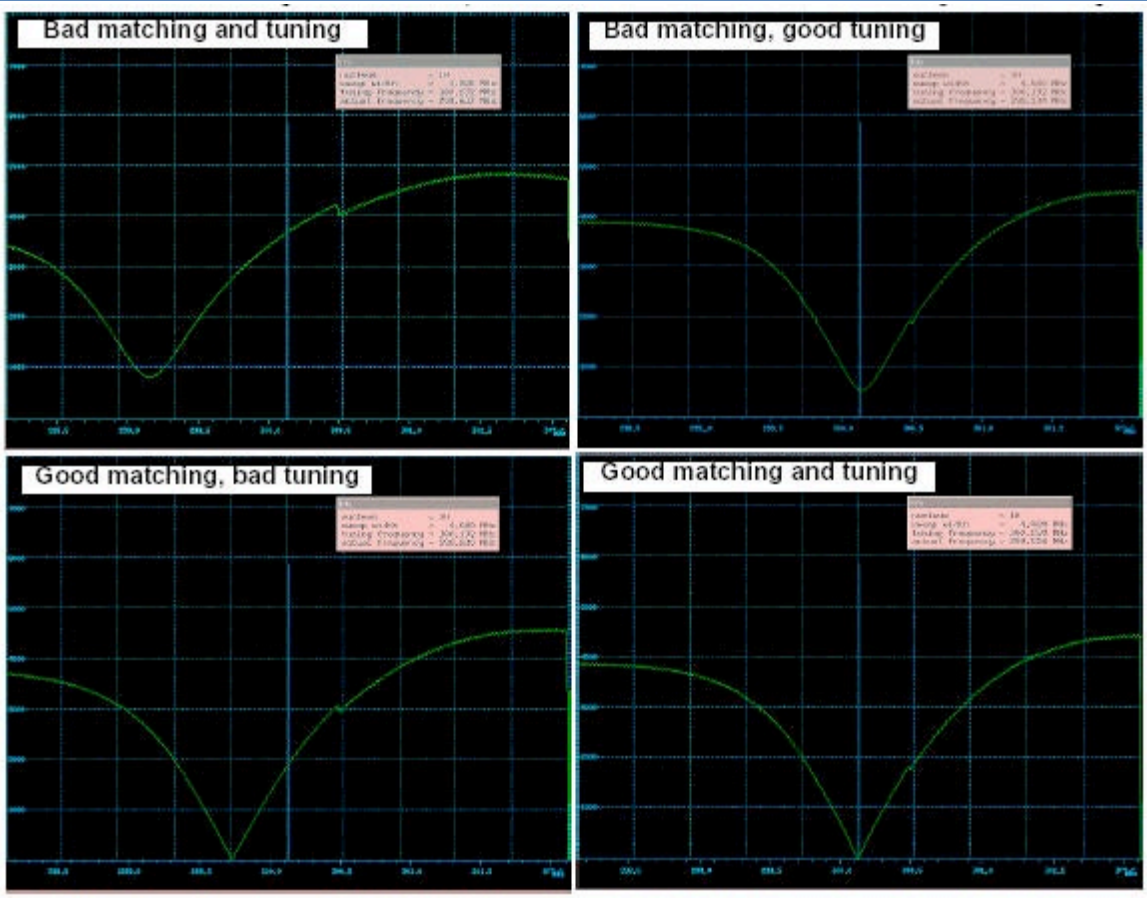
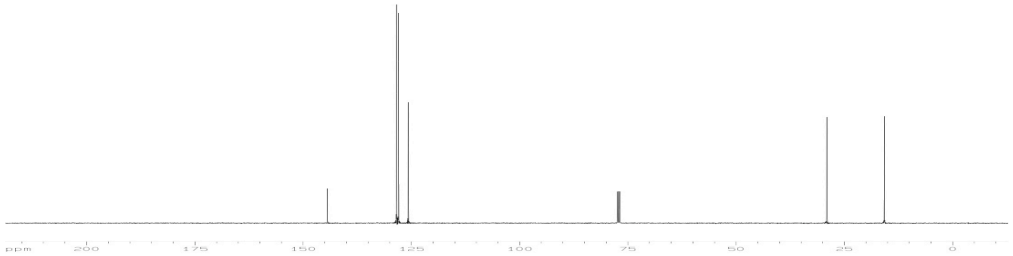


Optimal values for both shimming and tuning will vary with different samples and show some temperature dependence therefore they should be checked each time a sample or the temperature is changed.

Advanced Techniques-DEPT

For most NMR users the 1D, one pulse ^{1}H NMR experiment is very quick, easy to setup and informative. Often the 1D ^{13}C (^{1}H decoupled) experiment seems like a logical next step, however, in practice it takes much longer (usually overnight) to collect (due to the low natural abundance of the ^{13}C nucleus and its lower gyromagnetic ratio) and contains much less information since neither ^{13}C-^{13}C J-coupling or meaningful integrals can be measured. There are many alternative NMR experiments that can be run in the same overnight timeframe that will give more information and that can be set up relatively easily. The simplest is probably the DEPT type of experiments that allow identification of the ^{13}C chemical shifts and of the number of ^{1}H's bound to those carbons

Figure 1 1D ^{13}C spectrum 10% Ethylbenzene in $CDCl_3$



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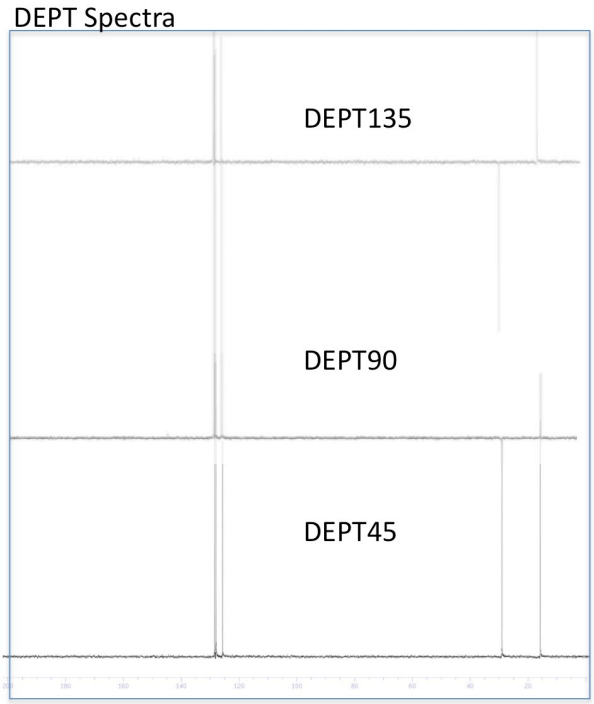
The DEPT (Distortionless enhancement by polarization transfer) experiments, which have been in use since the early 1980's (Bendall et al, JACS, 1981, 103, 4603-4605), use multiple proton and carbon pulses to produce a 1D ^{13}C spectrum where the intensities of the signals are either positive or negative depending on the number of protons bound to the carbon. Three versions of the DEPT were developed with the final carbon pulse set to 45, 90 or 135 degrees. The DEPT135 shows the CH(pos),CH_2(neg) and CH_3(pos), the DEPT45 shows all 3 states as positive and the DEPT90 shows only the CH (pos)(although small residual siganls are visible due to imperfectly calibrated pulses). It is usually sufficient just to record the DEPT135 experiment to determine the multiplicities since the CH and CH_3 nuclei in most cases have distinct chemical shift ranges. In the case of ambiguities all 3 experiments can be collected and appropriate addition and subtraction of the spectra will select for each of the ^{1}H multiplicities. Example spectra are shown in Figure 2. Parameter sets for all three DEPT experiments come with all Bruker instruments (type in "rpar" and look for DEPT45 etc). All spectra on this page were collected with 256 scans with an acquisition time of about 10 minutes.

Figure 2. DEPT spectra of 10% ethylbenzene in $CDCl_3$.



More recently Burger and Bigler (J Magn Res 1998, 135,529-534, link) developed an experiment that produced spectra with similar characteristic to the DEPT experiment but which also detected quaternary carbons. This DEPTQ experiment is somewhat less sensitive than the 1D, one pulse ^{13}C experiments but good signal to noise spectra can usually be acquired in an overnight run. As with the standard DEPT experiment in most cases only the DEPT135 is necessary where along with the positive CH and CH_3 signals and negative CH_2 signals there are also negative signals for the quaternary C. The deuterated solvent signal is seen in these experiments as a quaternary signal. As with all ^{13}C detected experiments it is crucial to set up the experiment properly including careful tuning of ^{13}C. I have coded a version of the DEPTQ pulse sequence and good parameter sets for this experiment are available on 3 all spectrometers in Rm 394-5 EH(type in "rpar" and look for deptq_45 etc). Example spectra are for ethylbenzene are show in Figure 3.

Figure 3.DEPTQ spectra of 10% ethylbenzene in $CDCl_3$.