KJM 5280 ^{1}H nmr introductory user manual

Version 1.5

TopSpin 1.3 patch level 10

DPX 200, DPX 300 and DRX 500

Windows XP

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Welcome to the wonderful and amazing world of Nuclear Magnetic Resonance (NMR) Spectroscopy. The first part of this document describes how to configure you nmr-user account and how you configure the nmr-program TopSpin 1.3 on the vintage Windows XP PCs at the University of Oslo NMR Center. Please locate the nmr-instrument and the associated PC you are assigned to use and sit down in front of the PC.

Press the three buttons Ctrl Alt Delete on the keyboard.
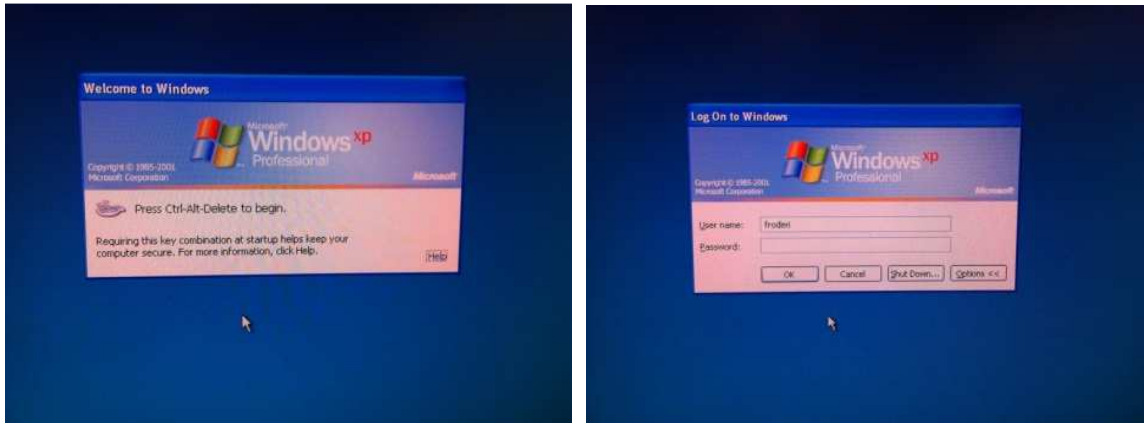
Type inn your username. The first time you use a nmr PC you have no password. Leave the password empty and click OK. You will then log in without any password by clicking on OK.

When you have logged in without any password you will start the process of defining your password by pressing the three keys Ctrl Alt Del again and select "change password".
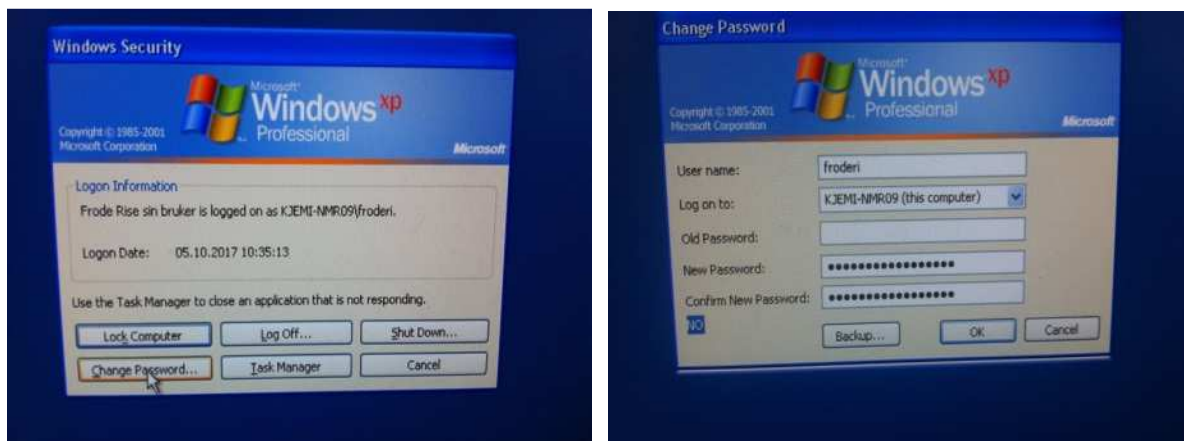

Leave the Old Password field empty and type in your New Password in the two lines. Click OK. Log out and in again – this time using your new password. The password must only contain letters and numbers. No slash or backslash or any other funny character. Locate the Topspin 1.3 icon and the data storage (R).cmd icon on your desktop. It is advised to drag them to the center of the screen so you find them more easily next time. They are usually not located in the middle of the screen.
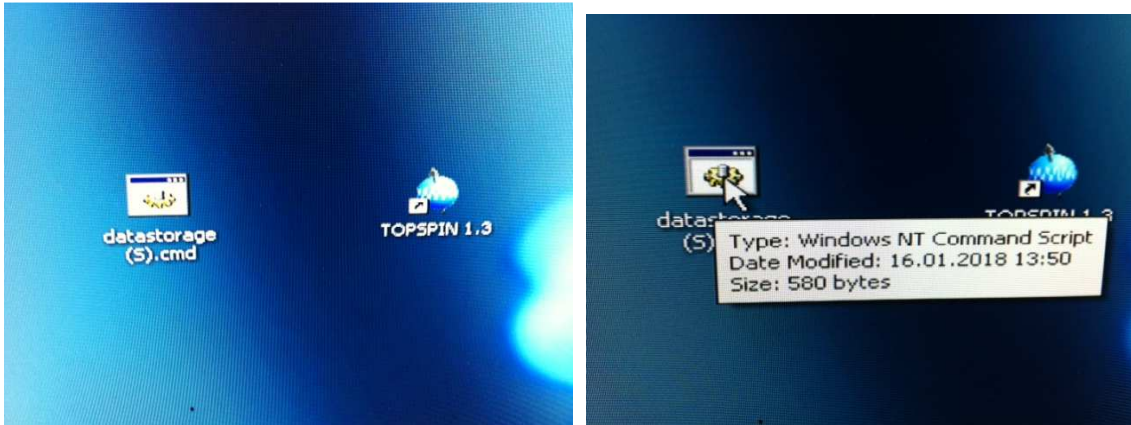
Double click on the data storage icon and a black window appears on the screen.
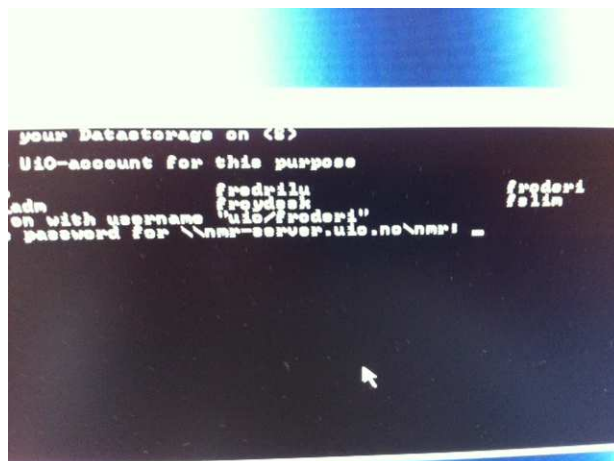
Type in your uio password (might be different from your nmr password). There is no response on the screen when you type the password and you must do it correctly. Hit enter/return and the black window disappears. If you misspelled your password the black window does not go away. You must close it and start over. You are doing this to be able to look at nmr data from other locations. More about this later.
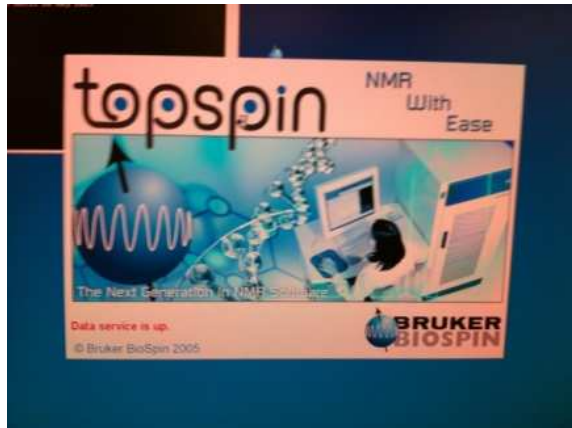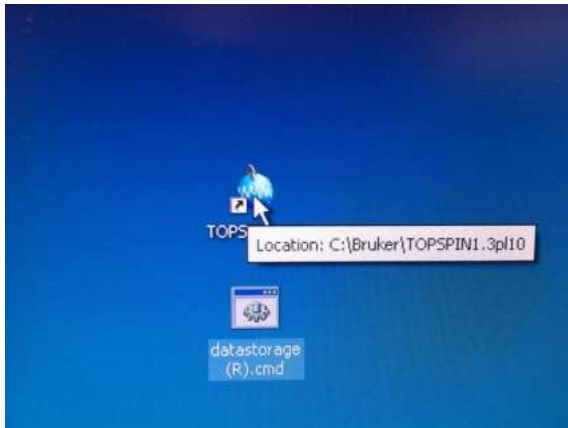
Double click on the Topspin 1.3 icon. The nmr program starts.
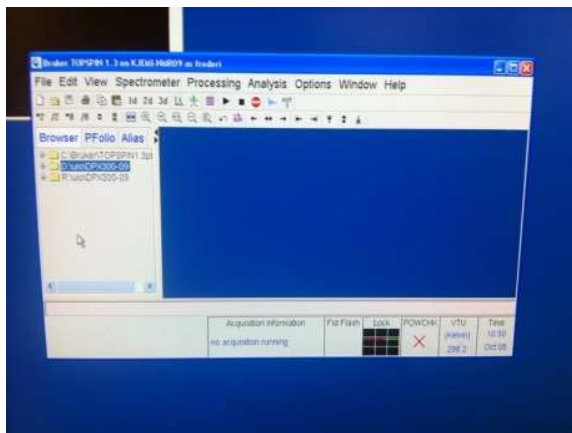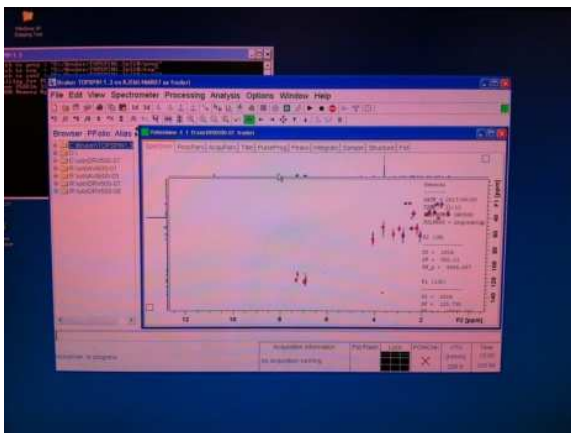
If you have run an experiment before it will appear in the main part of the program. If this is the first time for you on this nmr-instrument/PC the main Topspin window will be empty.

Before using the program, you must configure the program. You must do this once – but you must do it on all the nmr-instrument PCs and all nmr processing PCs you are using. Locate the Options button in the upper row of pull down menus. Click on Options followed by selecting Preferences. A new window pops up. You will select a bunch of options as shown in two pictures.
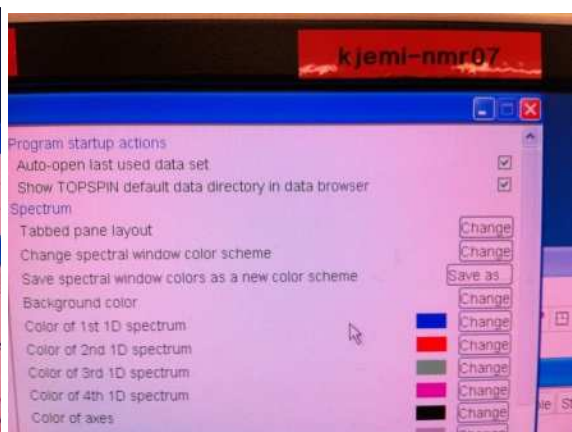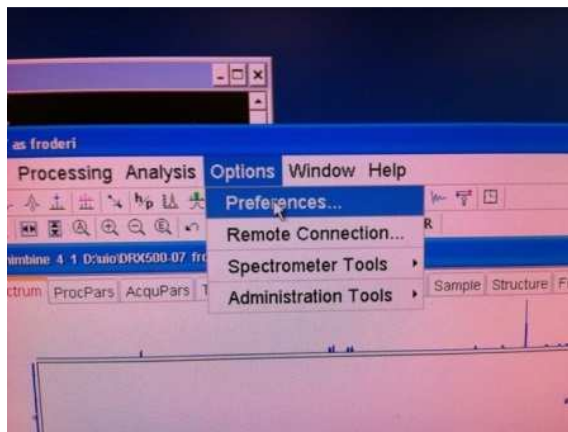
Mark the upper two options, e.g. Auto-open… and Show TOPSPIN default…
Mark all the options which are selected in the following picture. Do not select Mas spinning rate. Mas (magic angle spinning) applies only to solid state nmr instruments.
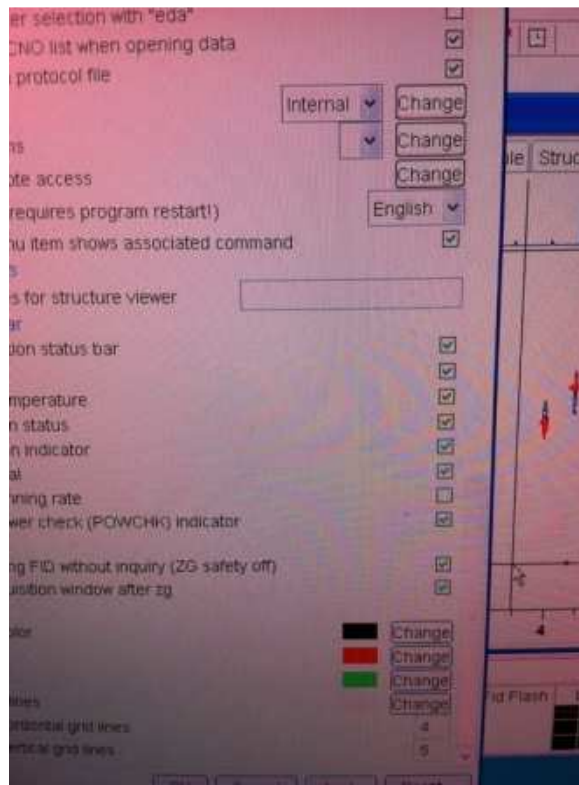
When you have selected these options, you are advised to click on Apply and OK at the bottom of the User Preferences window (not shown here).

Then you have to add the appropriate file structure (data directory) for where your files will end up. In the left part of the topspin window you might or might not see file structures. Right Click with the right mouse button in the left part of the Topspin window. Select the "Add New Data Dir…" option with the left mouse button.
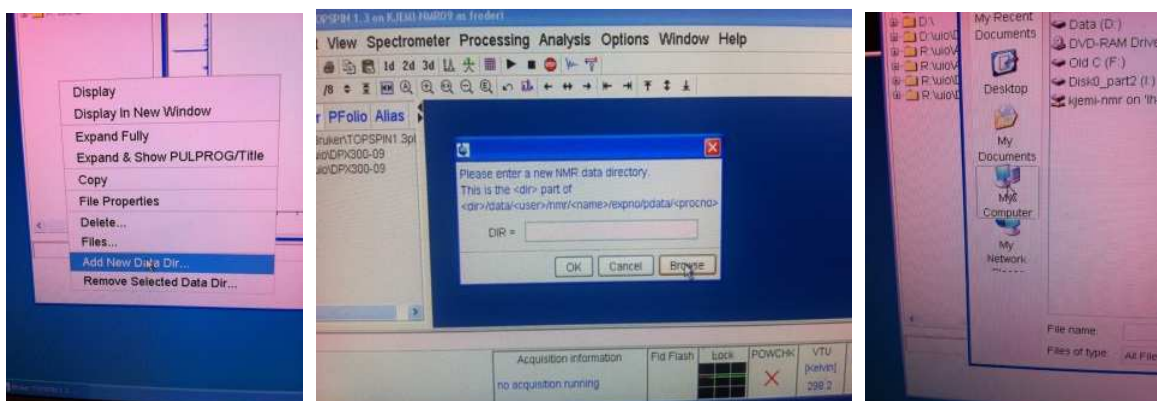
A new window pops up. Click on Browse and then click on My computer. You must now dig yourself through the file system. This is complicated. Locate the Data (D:) disk. The exact

name varies from computer to computer but the letter D is always included. Double click on it.
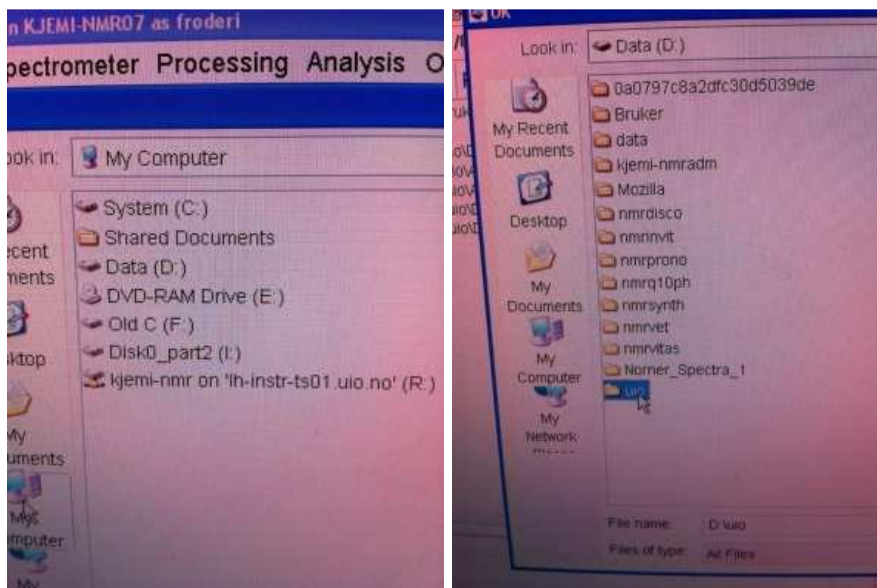
Locate the uio partition/folder and double click on it.

Click once on the DPX300-09 or the DPX200-11 or DRX500-07 folder so it becomes blue or another appropriate folder if you are on either of the following instruments: AVII400, AVIIIHD400, AVI600, AVII600 or AVIIIHD800. Then click then on the OK button located to the lower right.

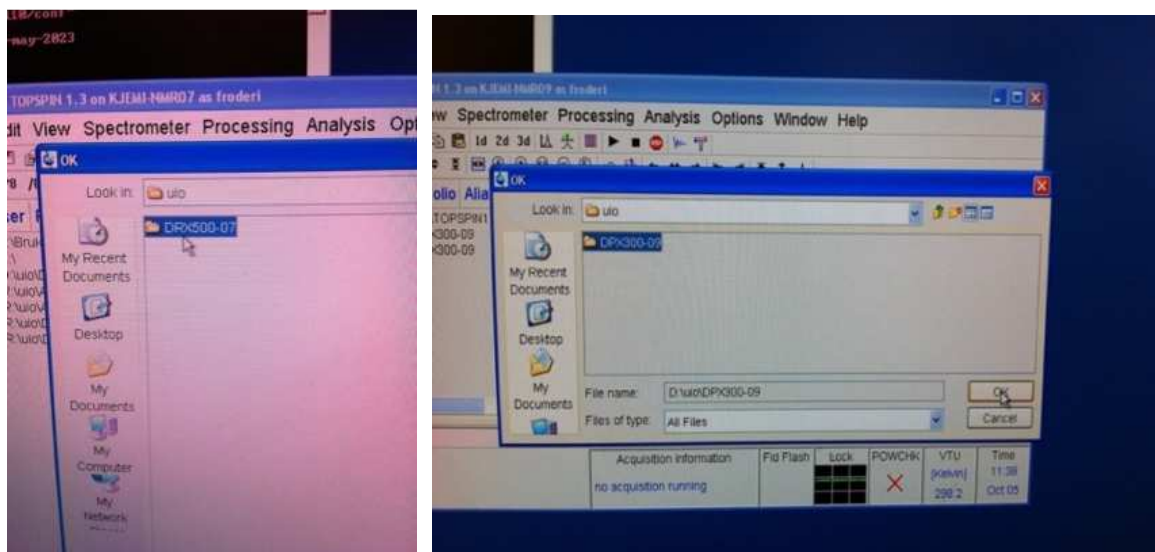Most of the file structure path for where your data ends up will now be in the left part of the Topspin program window. You are now ready to define your first nmr-experiment. The file system where your files will be located will be made when you define your first experiment. You cannot see your username among the other usernames before the first experiment is defined but it is not needed to execute the experiment.

Find somebody else´s experiment and select one of them. Be careful from now on - you can accidentally overwrite other people´s data. Double click on the other person´s experiment and it pops up inside the main window. This is the only time you are starting from someone else´s experiment (on this computer).
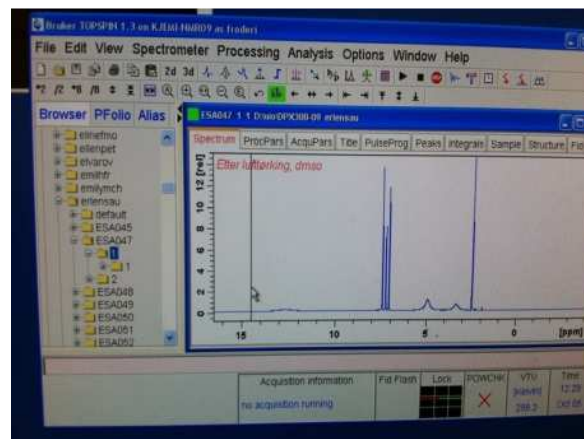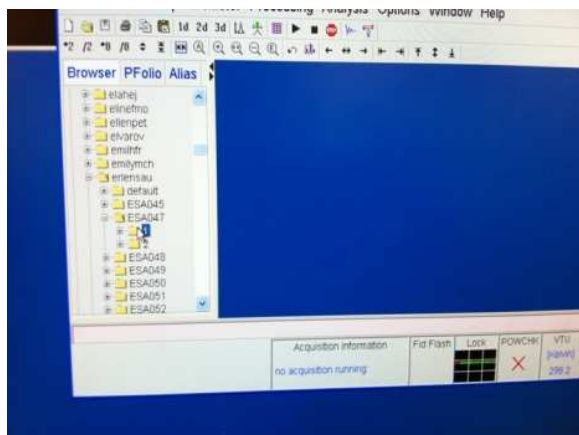

After clicking on someone´s experiment it shows up in the main Topspin window.
Type edc or new in the command line followed by enter/return and that person´s file definitions comes up. The concepts of NAME and USER are confusing. NAME relate to your lab note book experiment notation or your molecule name. USER is YOU = your username in the UIO as well in the nmr-computing system. **Here in the document is where you actually start DOING nmr.**
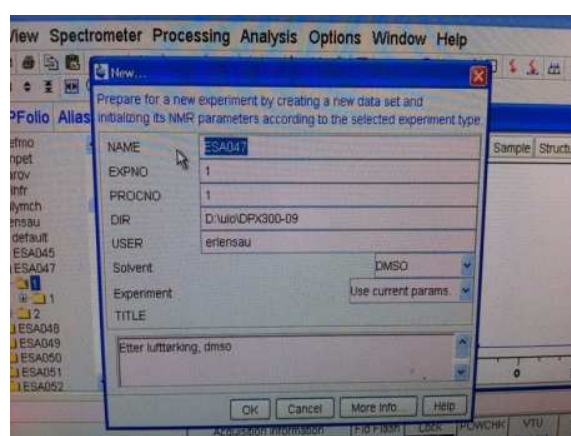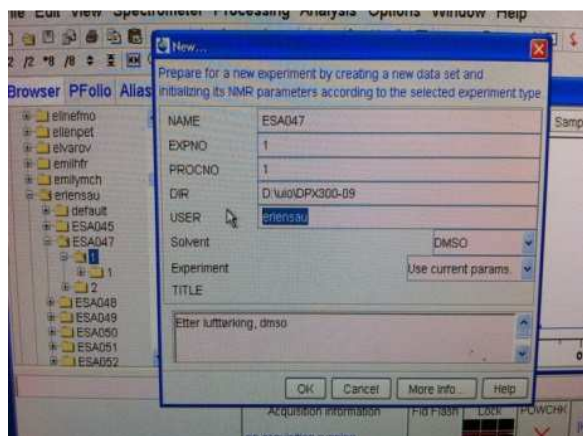
Change the USER to yourself. Change the NAME to for instance default. Be aware of EXPNO and PROCNO. They both start with 1. You can do many different experiments = EXPNO on your sample/molecule. You can process each experiment number (EXPNO) many times and the different processing results can be stored in many different processing numbers (PROCNO). Then select the correct nmr solvent. Nmr solvents are deuterated for three reasons, lock and shim – discussed later, the third reason is to avoid the solvent ^{1}H nmr signals to completely cover your nmr signals.
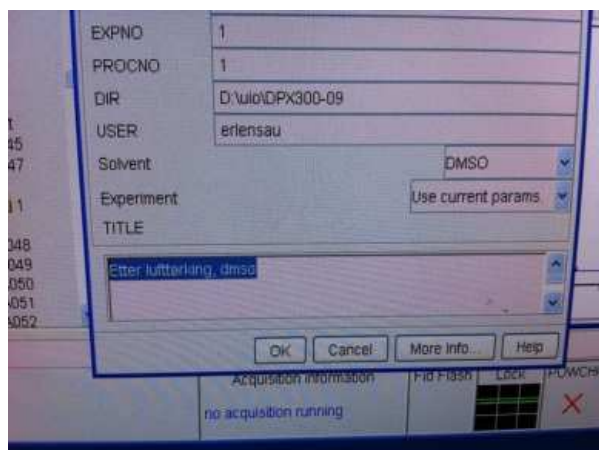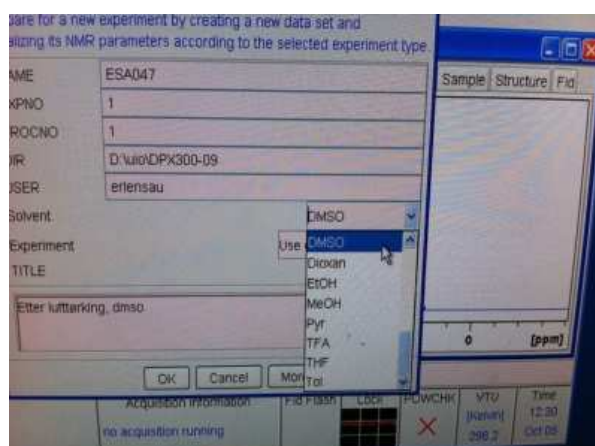
Be aware of DIR (directory). It shall look like what you see in the picture. But it is of course different if you are using another instrument. DPX300-09 is only applicable if you are working on the DPX-300 instrument. Change the text (in blue) so it has something to do with your experiment/molecule. Click on OK and you are half way in defining your nmr experiment and you are at the same time making your file structure on the windows computer as well. There are several ways of defining what your currently empty experiment shall contain. The most direct one is to type the experiment name into the command line, as below. But you must know the NAME = PROTON to do this. (You can also type RPAR proton). There are 100s to 1000s of experiments to choose from. To make life hard for you all instruments also have many experiments listed that cannot be run due to hardware limitations on the instrument you are using.

When rpar PROTON all is typed in the command line almost all that is needed to run a 1H experiment is loaded into your experiment.
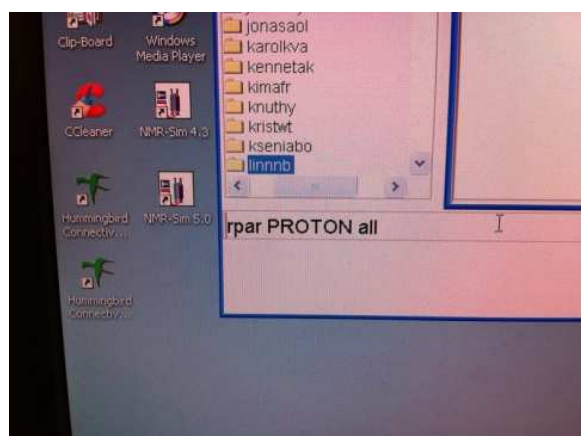

Typing RPAR (and enter/return of course) in the command line brings up all experiments present in this computer. It takes time to learn/comprehend/understand the list of experiment names. Your immediate goal in this course is to memorize up to 10-20 different experiment names to be used on a daily basis.

By typing rpar PROTON all you have defined a PROTON (^{1}H one dimensional) experiment. All parameters in the experiment are defined, but they contain NO numerical values. A radio pulse has for instance a strength/power (in Decibel or Watts) and it lasts for a period

(microseconds). The numerical values to be put into seemingly identical experiments differ between instruments. Instrument specific values are loaded by typing the command getprosol (get probe and solvent values/numbers!) in the command line.
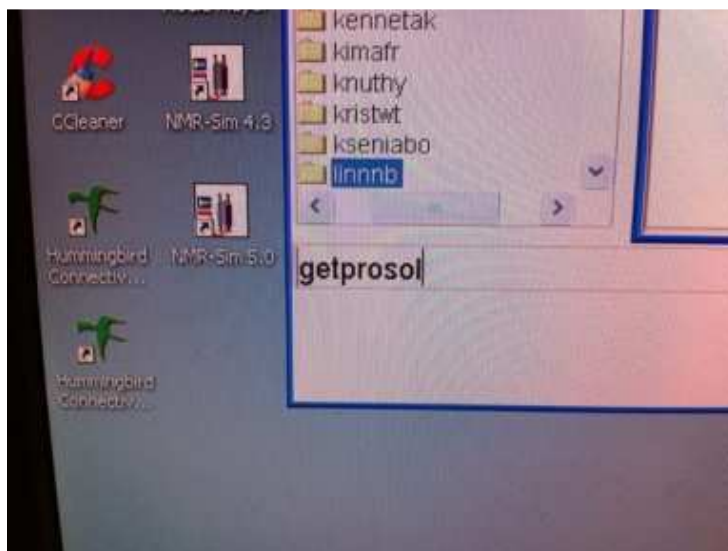
It is now time to load your sample into the magnet. But you must eject the standard sample inside the magnet before doing so. You do this with the help of buttons on the small BSMS keyboard. The name BSMS = Bruker smart magnet system is used for the small keyboard and also for a section in the electronics cabinet. The context decides what one refers to. If a light is on at the AUTOMSHIM button please turn it OFF. Similarly, if the LOCK and/or the SPIN lights are on press the buttons so there is no light anymore. Then you locate the upper left button LIFT ON/OFF (on the DPX 200 instrument the text is no longer there). Press it – it lightens up and the sample comes to the top of the magnet in 3-6 seconds. Remove your keys, wallet, mobile/cell phone from your pockets and all other iron containing items and move over to the magnet.

Remove the sample from the top of the magnet and insert your own sample after you have adjusted the height/position of the holder spinner on your nmr tube. Do NOT insert the height adjusting device into the magnet! In old times spinning of the sample tubes were used (SPIN ON/OFF), we do not spin nmr tubes anymore.

Then you lower you sample into the magnet. Guess what button to press on the BSMS key board?

Now a so-called shim file has to be loaded. This file contains a series of numeric values related to settings of many extra small shim coils used to correct the main magnetic field inside the main magnet. These currents are making the magnetic field more homogenous in your nmr tube. (Why is this needed?). Type rsh in the command line. Rsh= read shim. A list of shim files shows up. Try to locate file names containing luf = last updated file in the name. The numeric part is built up by year, month and day 170818 means 2017, august and day number

18. Just behind # the name of the probe which sits inside the magnet is given. TXI here (on the DRX 500 instrument). Ask if you are confused. Mark the file.
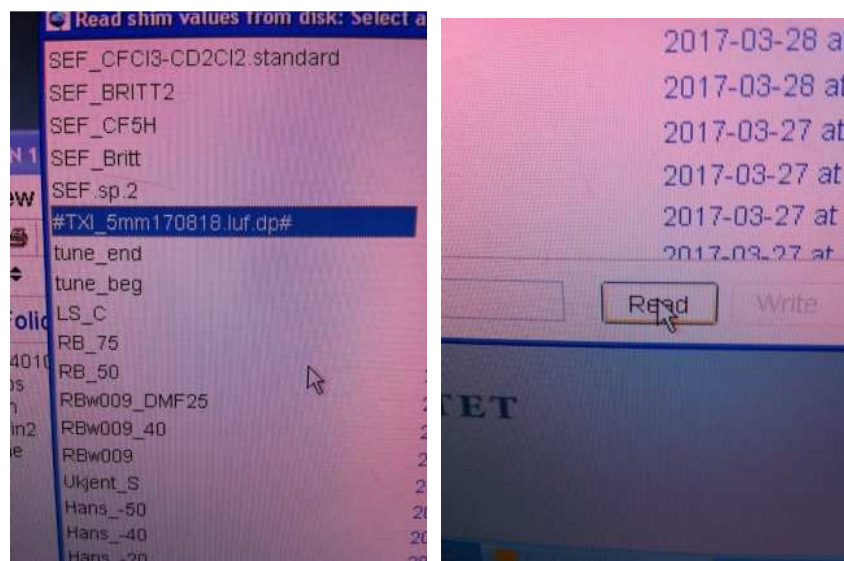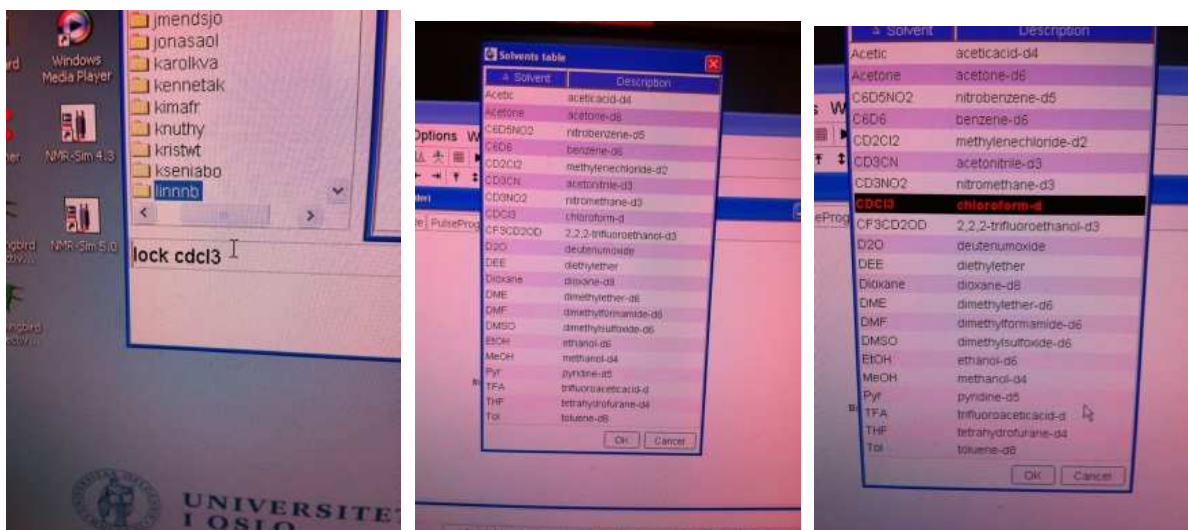

Click on Read at the bottom.

Now you need to get the lock display up. Type lockdisp in the command line.
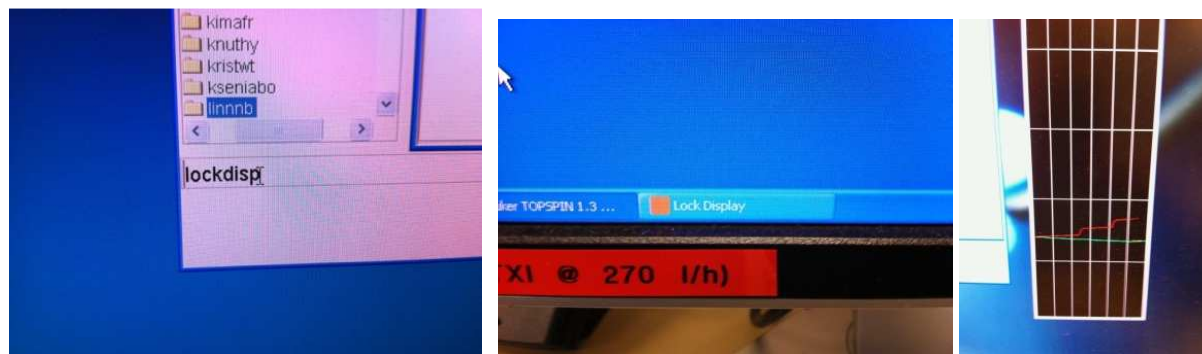
Sometimes the black lock display window shows up on desktop and sometimes it is hidden down at the bottom of the windows main screen. If so – click on it. Move the lock display to a free portion of the screen. A red and green cursor moves on the screen. Then you need to lock the magnetic field to the deuterium atoms in your solvent. Type lock solvent in the command line – where solvent is your own solvent. Be aware that the names can be strange, Chloroform = $CDCl_3$, but methanol is called MeOH.

You have no idea how to type the solvent name? Then you simply type lock in the command line. And the whole list of possible solvents pops up. Click on the correct one after consulting other people and then click on OK at the bottom in the window.

The red and green line in the black lock window starts moving as the computer is performing the lock process (see next page).
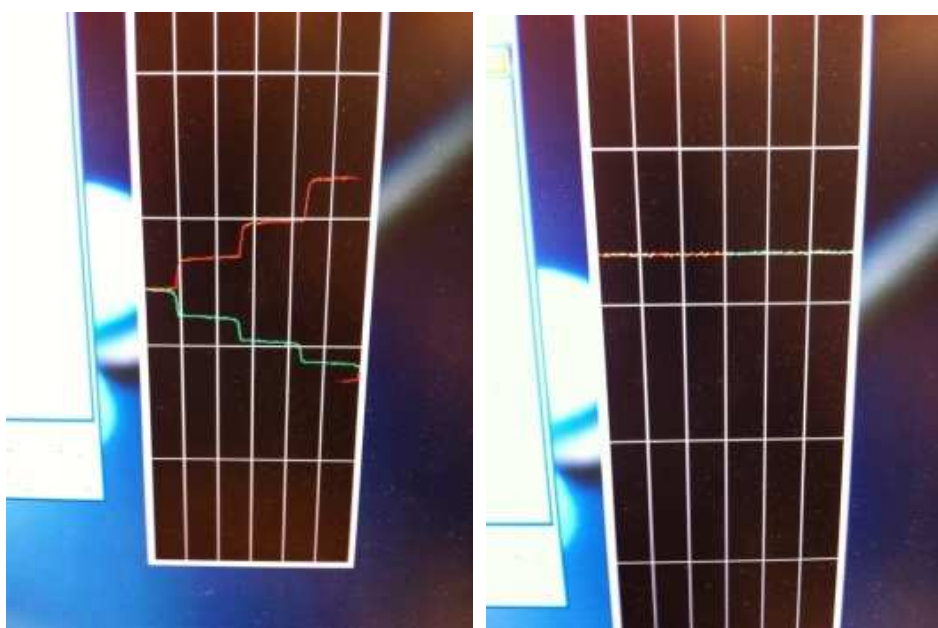
The lock line, actually the continuous wave nmr line of the deuterium atoms in the solvent ought to stabilize as a straight line in the upper portion of the window when moving back and forth. If it jumps up and down the lock power button in combination with the wheel has to be adjusted down and then you use the lock gain button and the wheel to get it up again.

The lock gain button (and many others) might have lost their white text due to tear and wear since 1994.

Be aware that the wheel you adjust the lock line with has both a coarse and a fine setting. See the picture above.

On the DRX500 instrument you will now tune and match the ^{1}H signal on the probe. On the DPX200 and the DPX300 instruments we do not perform this operation even though it is possible, but with around 50 inexperienced users doing the tuning and matching operations these instruments settings will end in disaster since the tuning and matching must be set back manually after each measurement is completed. On the AVII400, AVIIIHD400, AVI600, AVII600 and AVIIIHD800 instruments when run in the automation program ICONNMR automation the tuning and matching is done automatically by the instruments. When ran manually the command atma (automatic tuning and matching) takes care of the tuning and matching process. This functionality was not invented when the DRX500, DPX200 and DPX300 instruments were installed in 1994 and the command atma do not exist in TopSpin 1.3.
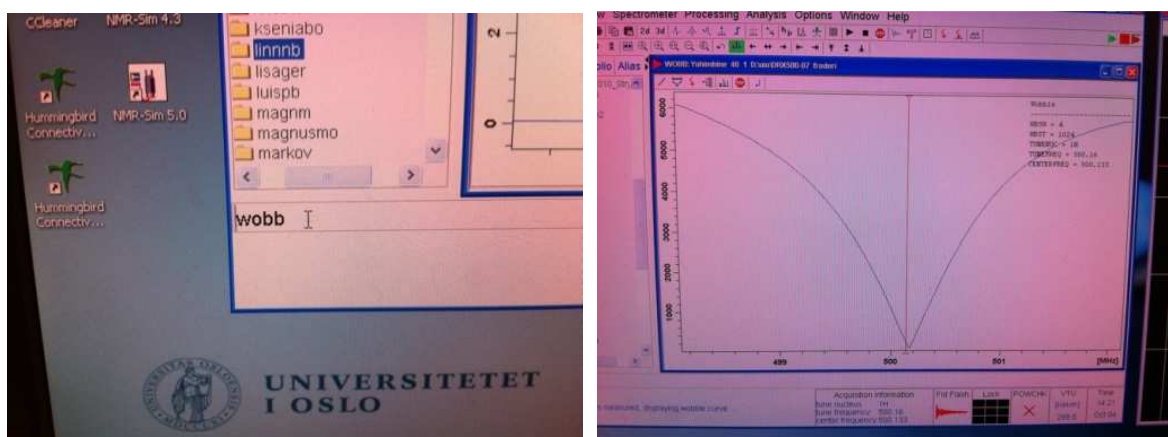

On the DRX 500 instrument you now are starting the tuning and matching (which can be compared to a 2–dimensional FM radio searching process for best FM-signal with a hypothetical two dimensional wheel on the radio) with the command wobb. The window to

the right above appears, the goal is to adjust the curve so it hits the bottom at the cursor position. It is almost OK in the above picture. The adjustment is done by turning 2 screws or moving 2 sliders up and down under the magnet while you at the same time are watching the computer screen or on the box next to the magnet leg. This process is complicated and is almost impossible to learn by reading a text. Each person must learn this on site with experienced people showing how the process of wobbing is done. No-one are allowed to do the wobbing without proper individual training.

After completing the wobbing process you will optimize the magnetic field in order to get sharp and narrow nmr signals, by performing the so called shimming process.


You start manual shimming on your sample with the help of the small extra BSMS keyboard. Be aware that there are two visually different versions of the extra small BSMS key board. One version has ONAXIS in the lower left corner. Press this button and the press Z^1 afterwards (Do NOT press Z^0). If you have the rightmost version press Z^1 directly. You will now use the wheel to adjust the lock line as high up as possible. Please observe that the FINE button should be activated = have a green light on it. Move the wheel while simultaneously observing the lock line in the black window. The lock line shall move up as high as possible. Try both clockwise and counter clockwise with the wheel. There is a delay from when you make a change with the wheel to the response from the nmr-sample and the electronics is seen. Be patient. When you are not getting the line any higher please press STANDBY and then press the Z^2 button. Use the wheel again. When reaching a new maximum repeat with Z^1. Go on with Z^2 and Z^1 until you cannot get any higher. If you move above the top of the black screen get the lock line down with STANDBY then LOCK POWER and the wheel again, then STANDBY and use the Z^1 and Z^2 until you cannot get it any better. Then click STANDBY and then click AUTOSHIM.
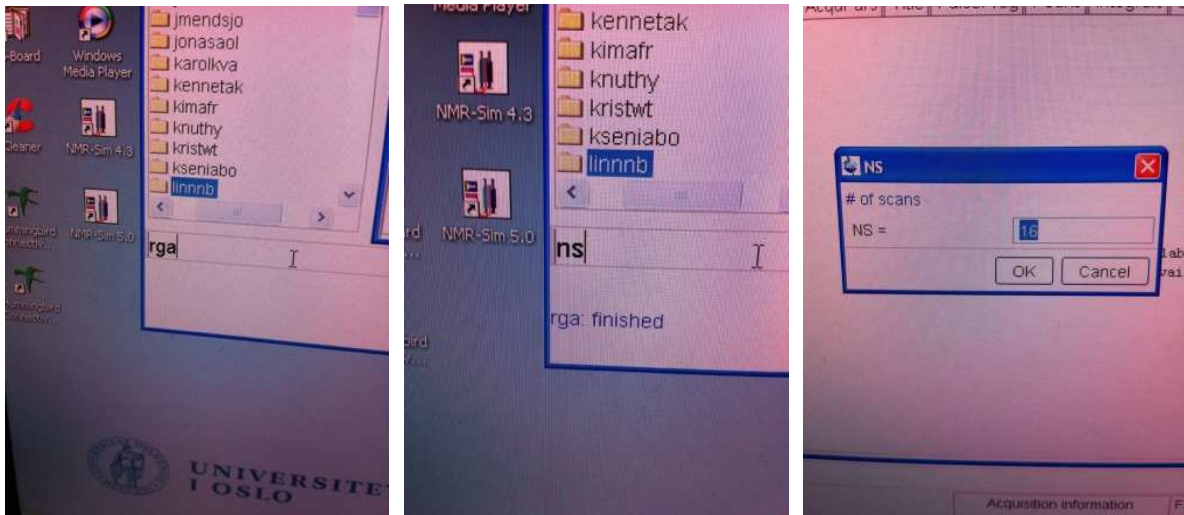
There is an analogue to digital electronic board (ADC) in the nmr electronics console. If the ADC receives a too high analogue nmr-signal from the magnet it cannot convert the continuous signal into digital format. Typing rga (receiver gain adjustment) in the command line attenuates (reduces) or increases the analogue signal to a maximum allowed level. Wait until the rga process is finished. Sit and watch what the program says. You need to know something about the number of "scans" that is included in your experiment. The lower the molarity of the solution the more scans must be run to get a useful nmr spectrum. Nmr signals are directly proportional to the molarity of each different molecule in a mixture of molecules. Nmr signal intensities are also depending upon the number of atoms at each position in the molecule, e.g. a CH_3 gives a nmr signal three times larger than a CH. Type ns in the command line and observe the response from the computer. Adjust ns up or down. If you have no idea what to choose keep 16.
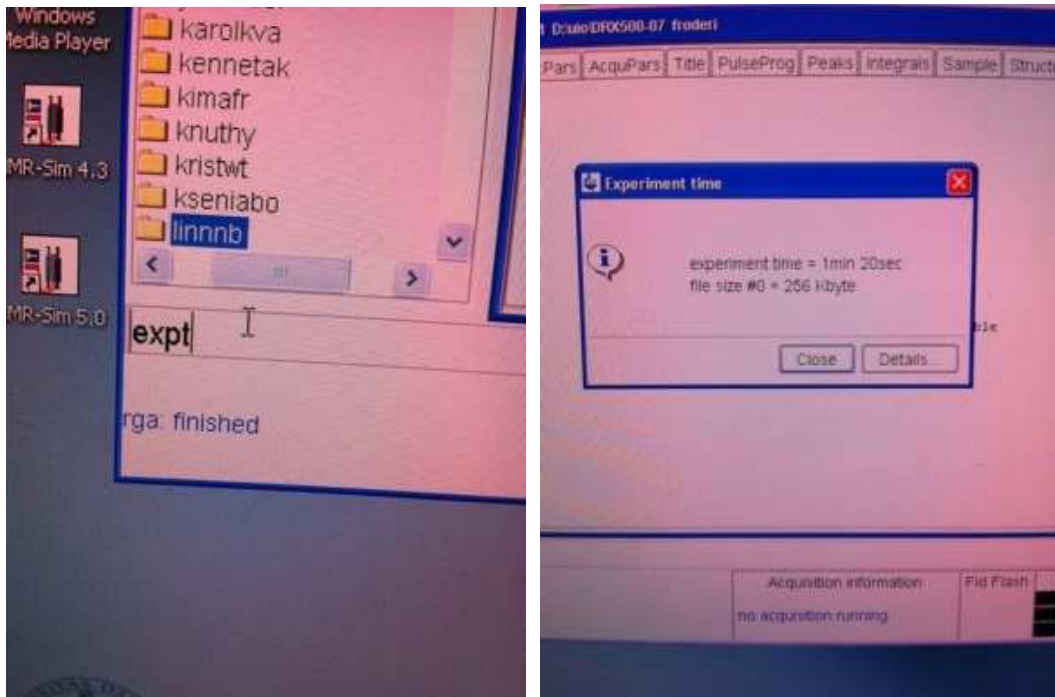
It might be good to know how long time an experiment takes. Type expt in the command line and observe the response from the program.
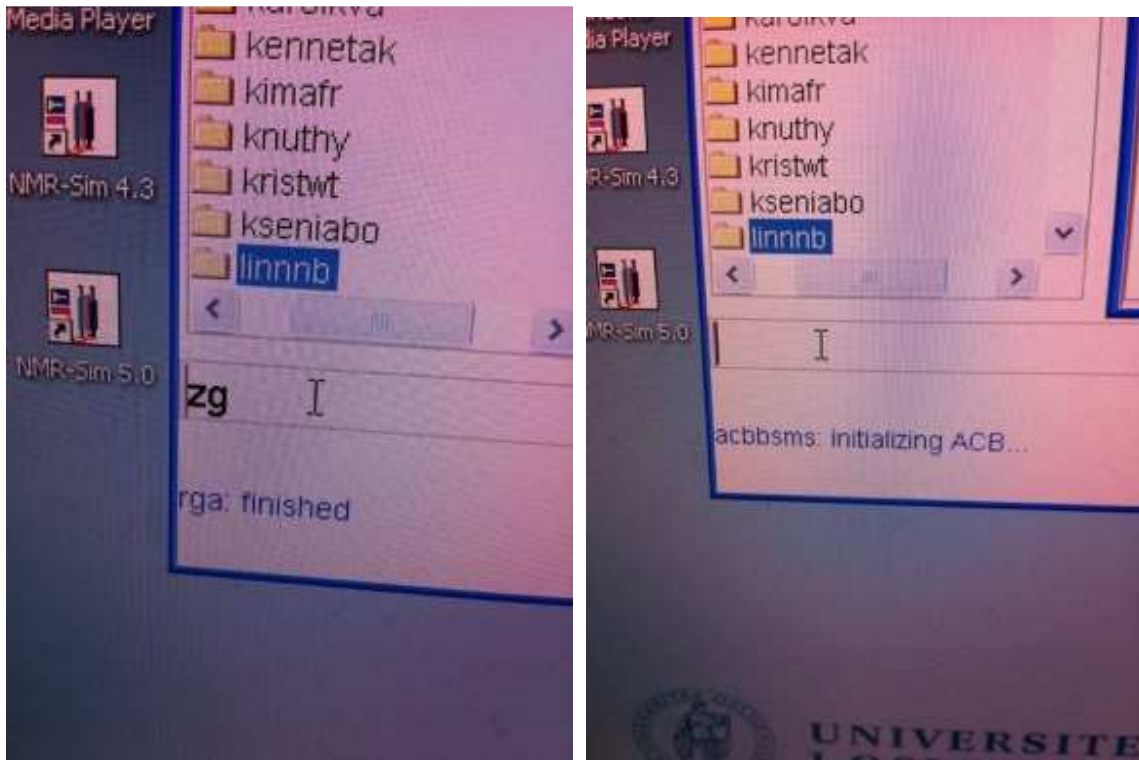
Start the experiment with the command zg (zero out whatever is in the experiment from before – usually nothing - and go ahead.) You will see other information like acbbsms (amplifier control board Bruker smart magnet system) initializing ACD... Do nothing while this happens.
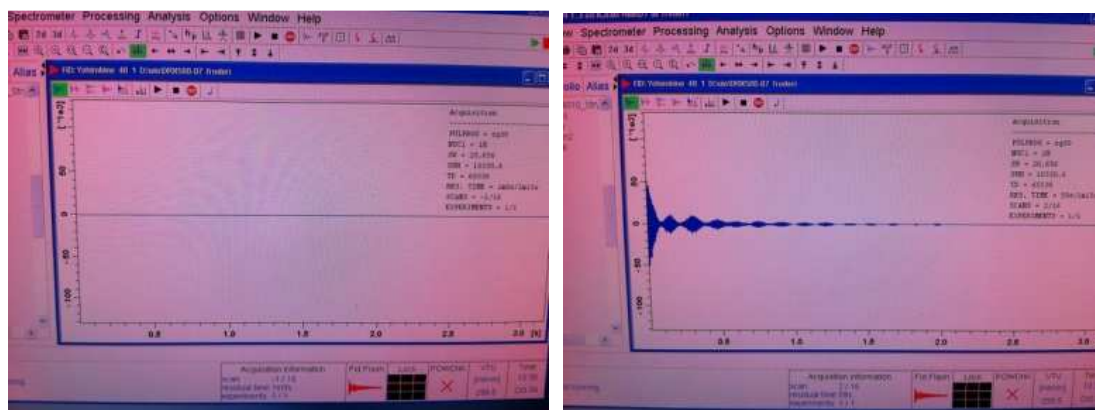
You either get the window shown above up automatically or you bring the acquisition window up by typing the command acqu in the command line. In the left window above the so called dummy scans are ongoing. Depending upon the complexity of your nmr-experiment a small or huge number of dummy scans are performed before the real experiment starts. In the right window 2 out of the real 16 scans have been performed. The signal seen is the real nmr signal. The y scale is intensity and the x scale is in time (seconds). The signal dies out with time and this process is called relaxation. Ideally the signal must die out completely before the next scan is started.

If you are impatient you might look at the result before the experiment is completed. Type the command tr (transfer) in the command line. Data stored in the electronics console is transferred to the computer. The nmr time domain data is converted to an understandable format by using the command efp (exponential multiplication - Fourier transformation processing). This can be done after the tr process is completed or after the fully completed acquisition or both, usually both. You cannot use the efp command before the so called checklockshift process is completed if you use the tr command.

Efp usually ends up with a spectrum with peaks/resonances pointing both up and down. We want them all pointing up. The command apk (automatic phase korrection – the Germans making this program forgot that correction is with the letter c when they made the predecessor of the Topspin program in the 1950s and 1960s) usually fixes this. apk seemed to work here ☺
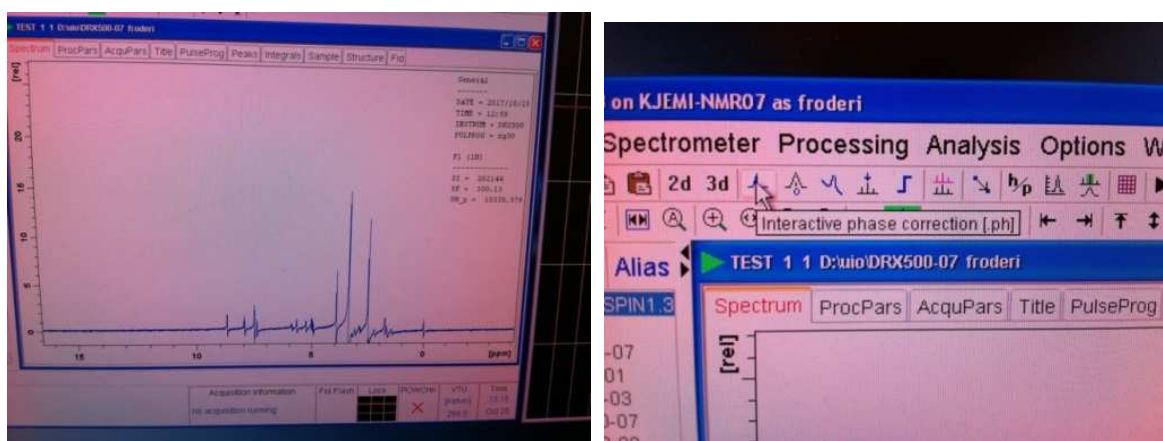
In some rare cases apk will not flatten your baseline. Locate the Interactive phase button and click on it.
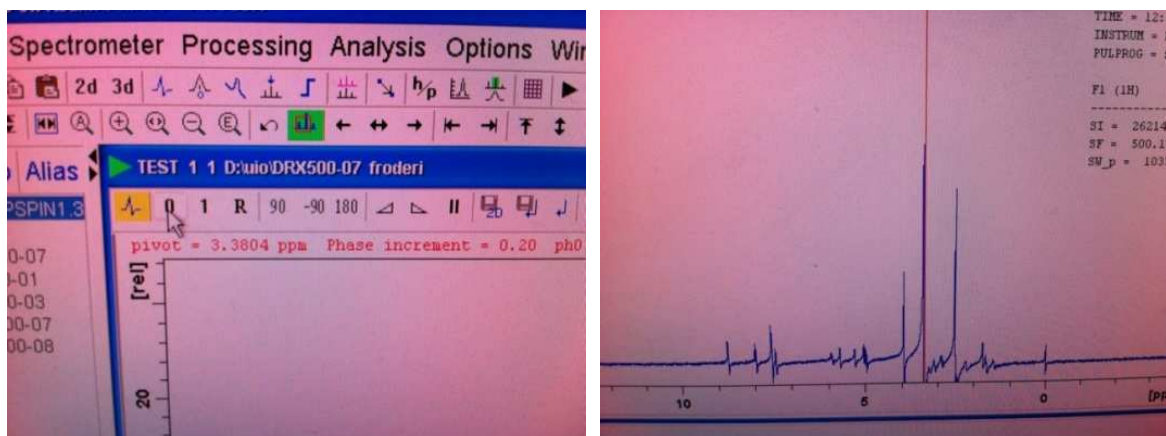
The appearance of the main window changes and you see a 0 and 1 in the left corner. Click on the 0 with left mouse button and hold the button in while you move the mouse up or down while you simultaneously look at the spectrum. Please also observe the red line located at the most intensive nmr resonance. The 0 (zero order) phasing is happening mostly around the red line. You then click on the 1 (first order) with the left mouse button and keep it pressed in while phasing the rest of the spectrum. You might have to switch between zero order and first order phasing a couple of times. When you are performing this interactive phasing, you are actually composing the resulting spectrum from two distinct parts of the datasets. Each raw nmr signal/dataset is composed of two Free Induction Decay signals (FIDS) which are 90 degrees out of phase relative to each other.
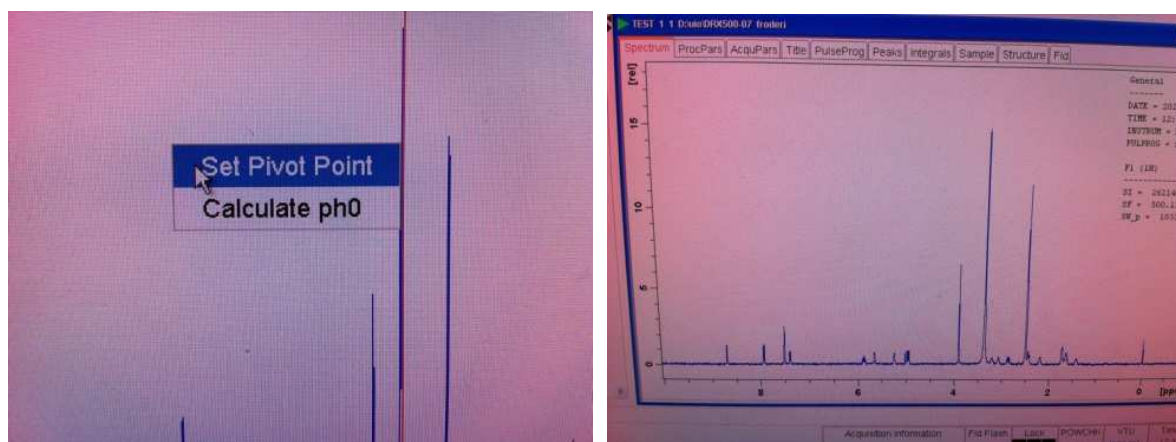
If the phasing does not work properly you might move the red cursor to another position. Use the right mouse button on the main screen and set the pivot point to another place and do the phasing again.
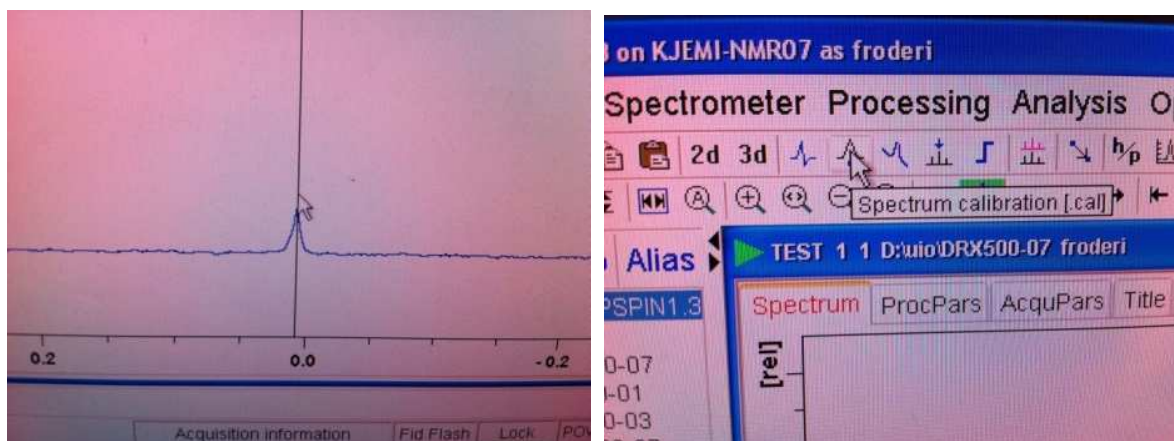
Calibration of the ppm scale is often necessary. Either the solvent peak is used or TMS is used (as here). Most of the times the scale is referenced to the residual ^1H signal in the deuterated solvent, e.g. $CHCl_3$ in $CDCl_3$. There are tables of these values on sheets of paper taped to the tables in the nmr-labs. In the example used here TMS is the reference. Locate the "Spectrum calibration button" and click on it. Then click on the TMS or solevent peak and enter the desired ppm-value.
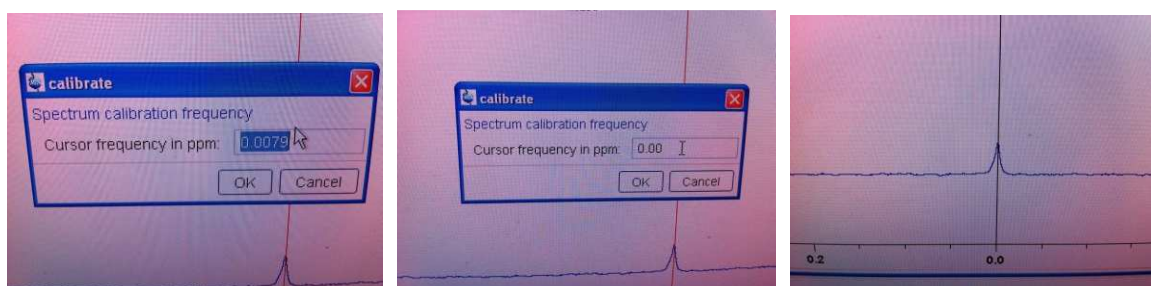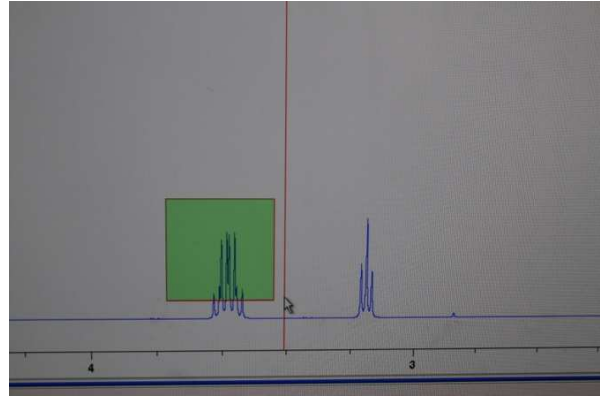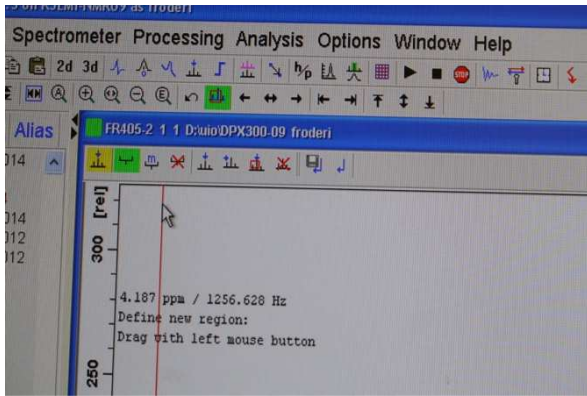

Ta da ☺

Often it is required to have exact numerical values of the chemical shifts, either in ppm or in Hz or both.
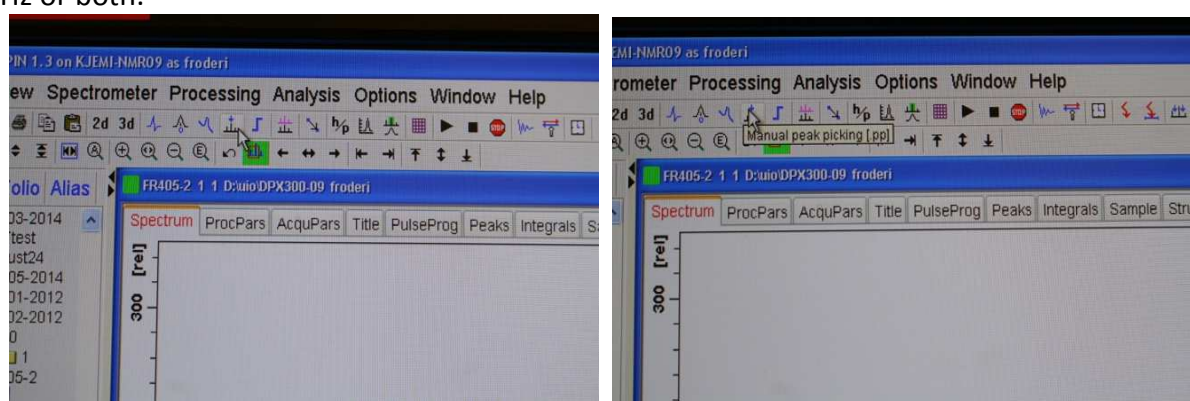
Locate the manual peak picking button and click on it.

Observe that the top line in the main window changes. Mark the symbol shown above so it becomes green. Use the mouse to select the areas where there are peaks of interest to you.
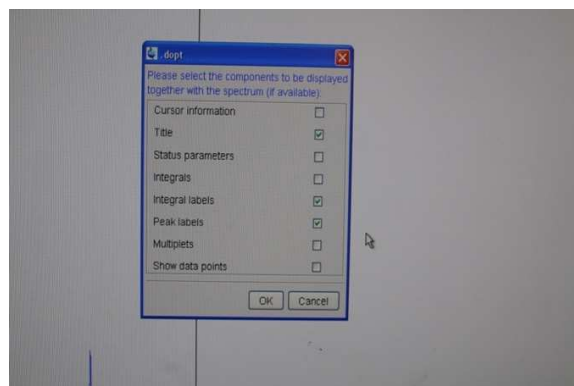

Then you make the discovery that there are no visible numbers. You have to exit the peak picking sub menu followed by right clicking in the TopSpin main window and green mark Peak labels. Click on OK and enter the peak picking routine again.
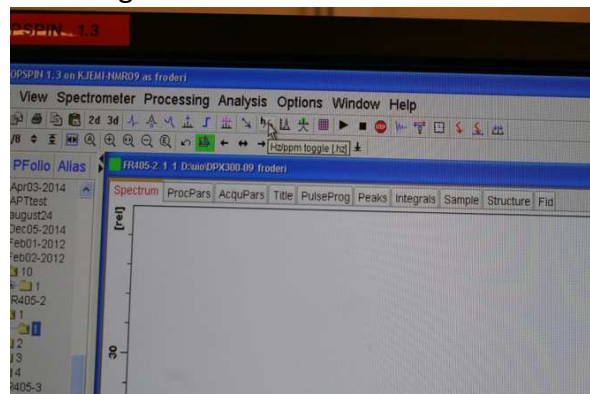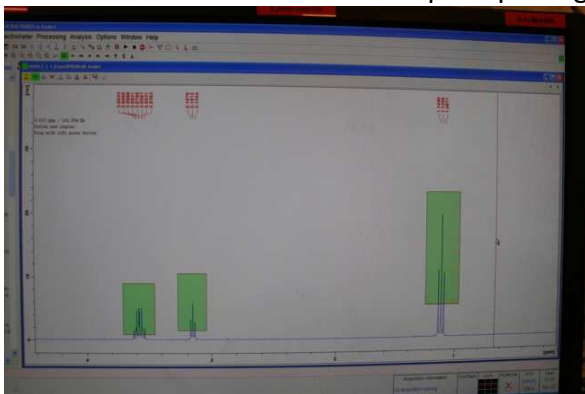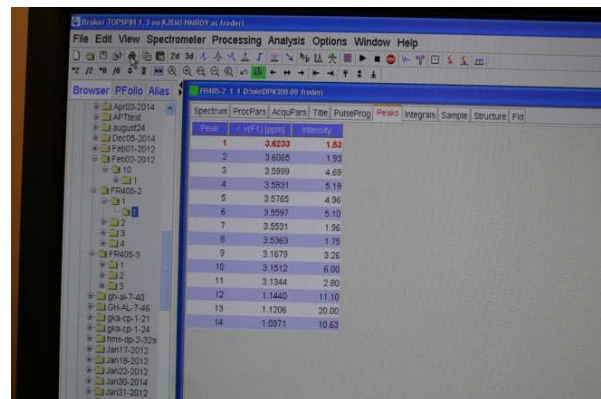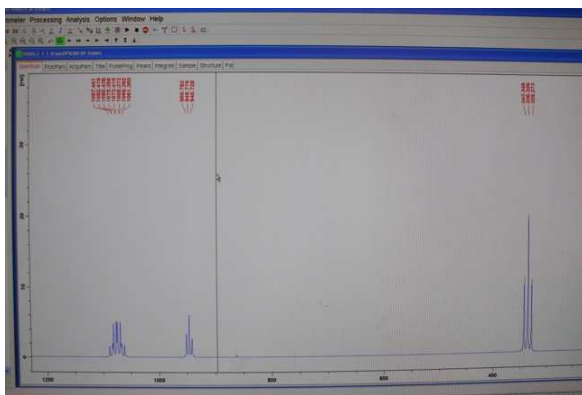

This time the numbers show up. Print the spectrum after first saving the peaks using the diskette symbol. If your supervisor wants the numbers in Hz locate the h/z button on the top of the TopSpin window and click on it.
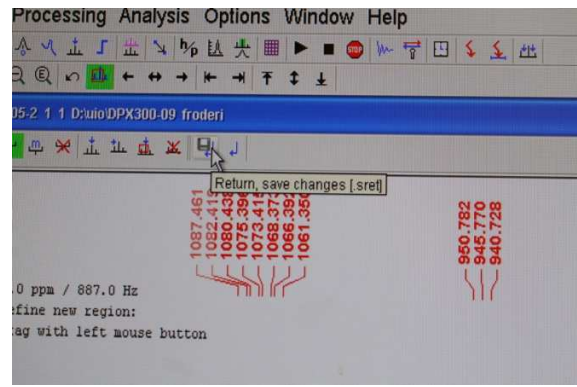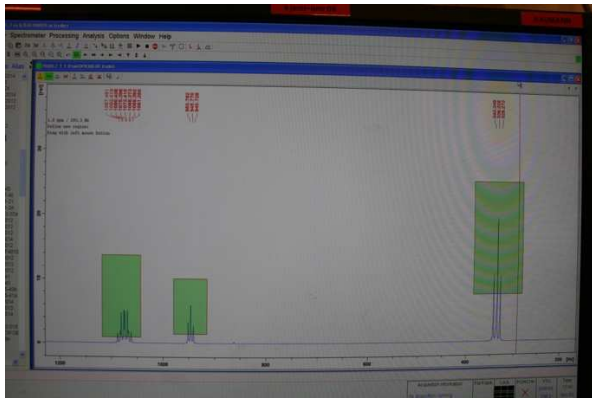
Enter the peak picking routine again and you have your Hertz numbers. Return and save changes.


Print again. Locate the Peaks button in the main TopSpin window and click on it. The list show up. Find the printer symbol in the upper part of the Topspin window and print the list.

Now it is time to figure out how many protons there are under each signal/resonance. This process is called integration. 1D nmr signals are directly proportional to the molarity of each atom or atom group they represent.
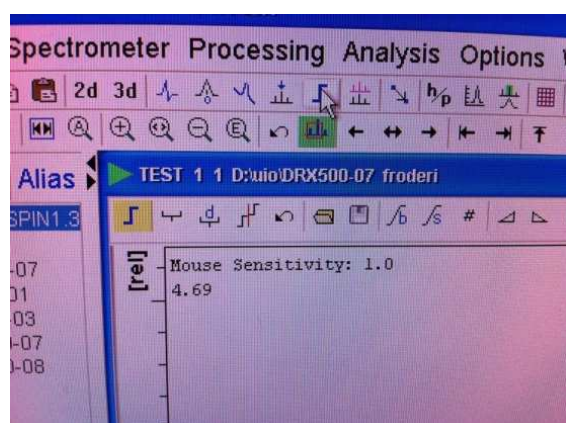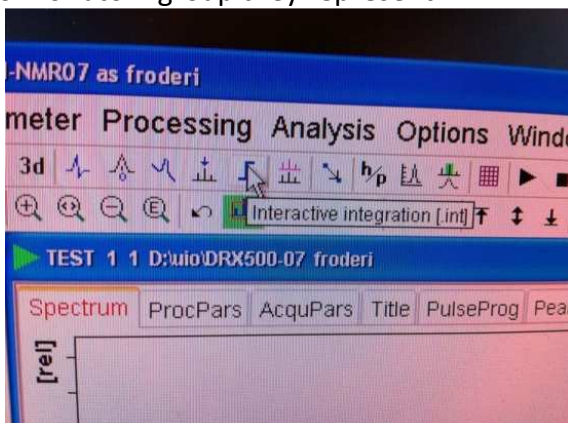

Locate the integration symbol and click on it. Observe that the top line in the main TopSpin window changes. The integration clickable symbols are showing up.
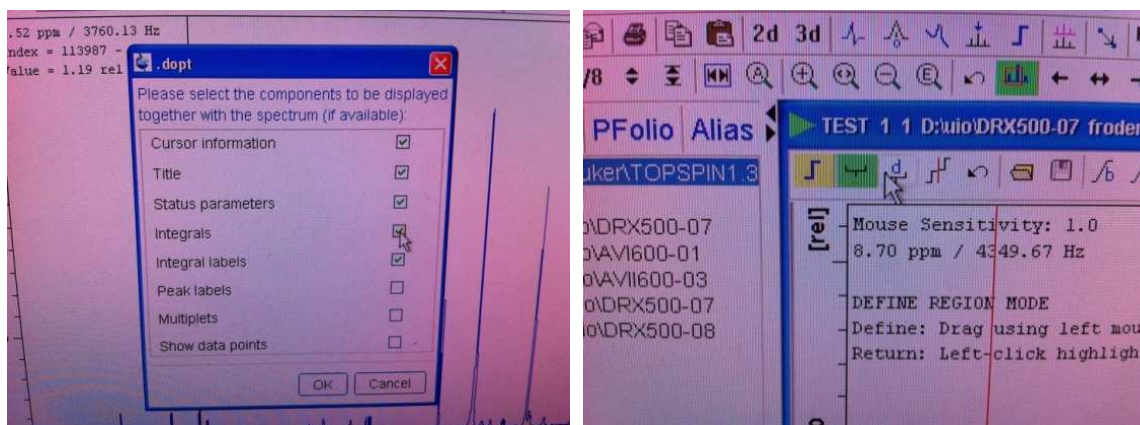
But before starting the integration you must assure yourself that the integrals are actually shown. Right click on the main window and select Integrals to be visible in the pop up window. Click then on OK in the pop up window.

You will then initially integrate all signals together (see below). You are doing this by clicking on the symbol that is shown in green above. It becomes green when you click on the symbol. Then you get a cursor on the screen, you click on the leftmost side of all peaks and drag until reaching to the right of the rightmost peak and then let go of the left mouse button. The result is seen under here.
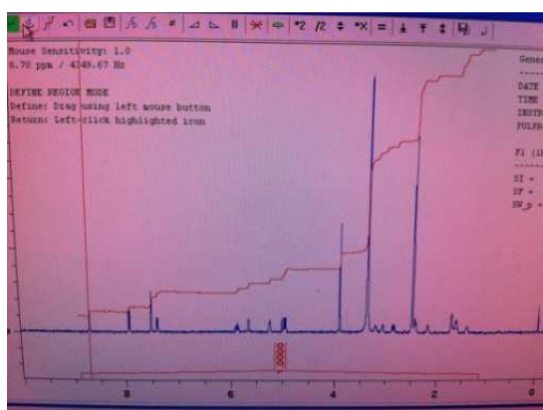

Observe that the horizontal parts of the integral are not absolutely flat. They must be horizontal. Your job is to make them absolutely flat.
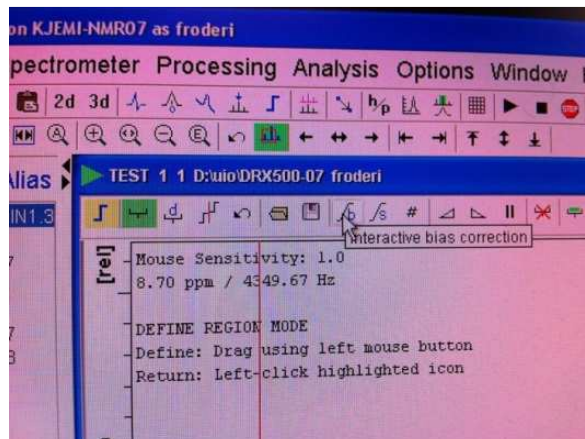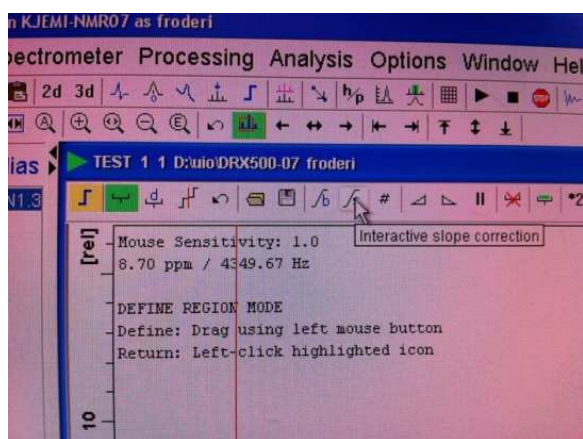
You are using the two buttons indicated in the pictures above, "Interactive bias correction" and "Interactive slope correction". Before using them, however you must define the integral you want to correct by having the vertical cursor inside the integration area, clicking the right mouse button and select "Select/Deselect" with the right mouse button. The integral is then marked with a colour, see to the right below here. Then you successively hold in the bias and slope buttons while moving the mouse up and or down. Make the integral lines flat. Use bias on the left and slope on the right.
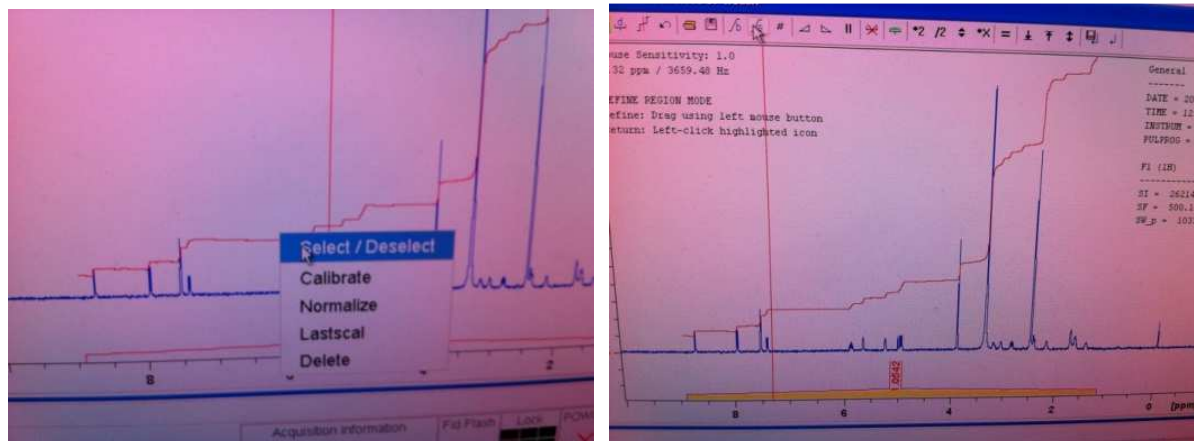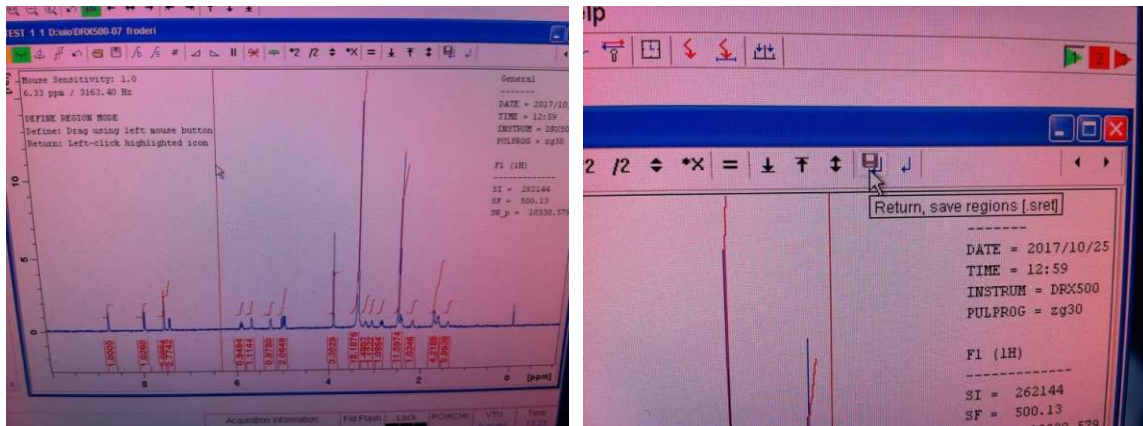

Then you delete the big integral (see below).
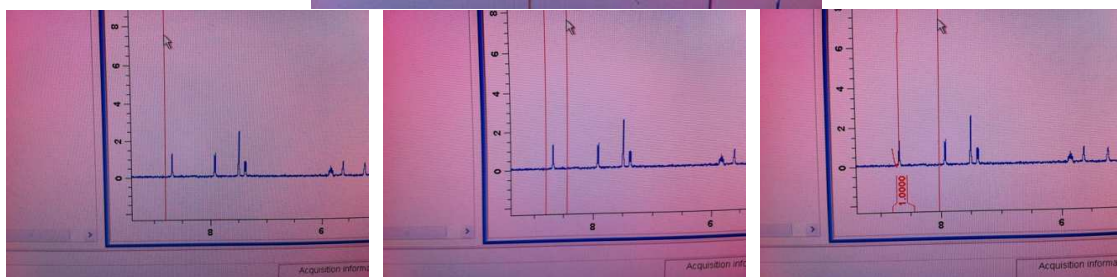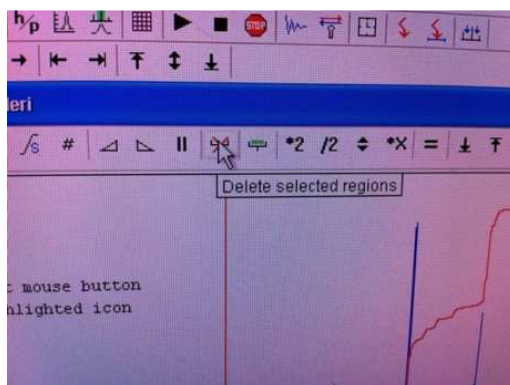
Integrate each peak alone with the cursor and the mouse.

Sometimes the peaks are so close that you have to lump them together in collective integrals. There are buttons in the main button line on the top of the program that you can use to expand and get the whole spectrum back again. When expanding in the horizontal dimension it is easier to integrate. Now you should have used this program so much that you on your own can to figure out what buttons to use and how to use them? ☺ Remember to save the integral before leaving the integration sub menu.
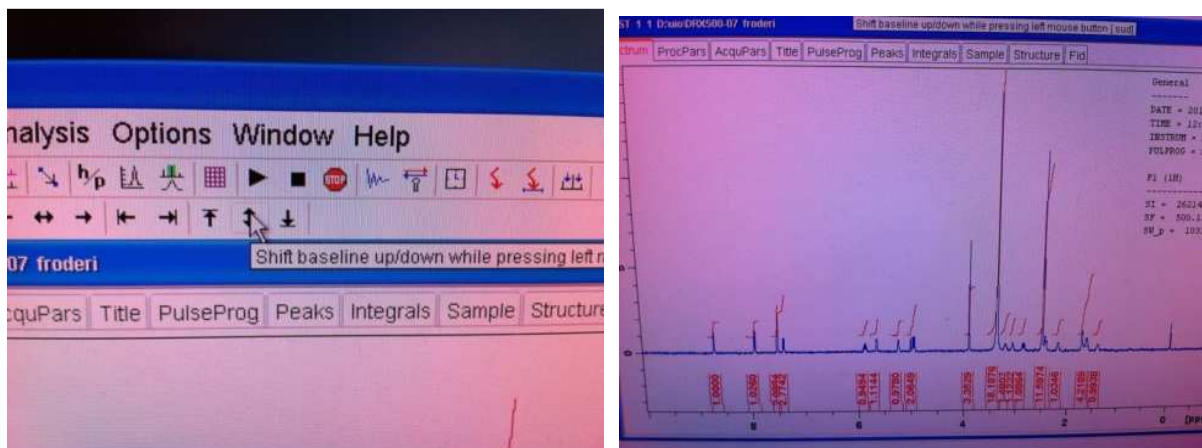

Sometimes the spectrum and the integrals are coming on top of each other. That can be fixed by using the "Shift baseline up/down while pressing the left mouse button" and moving the mouse button up/down.
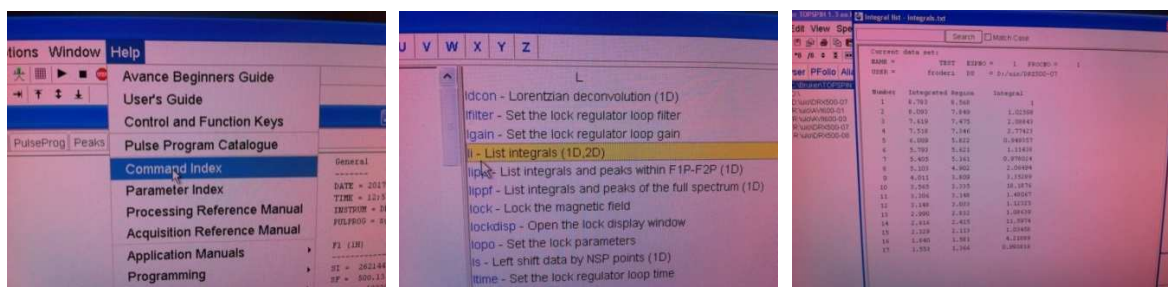

You are now becoming proficient in using this program. Have you realized how the interaction is happening between you and the program? Typing commands in the command line is one way. Clicking on a button and using the mouse simultaneously is another way. There are also buttons with numerical values on them *8 = multiply by 8, /2 = dividing by 2 and so on. If you

need a command and you do not know if it exists or what it is called you can look for it in the command listing. Locate Help in the upper line and then subsequently the Command index. Here the li command (list integrals) command is located, after executing this command in the command line the result is shown above to the right above.
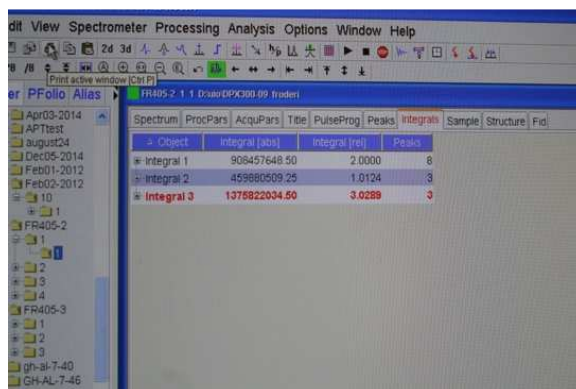

If you want to print the integrals however you must click on Integrals in the min TopSpin window followed by selecting the printer button (Print active window) in the upper line.
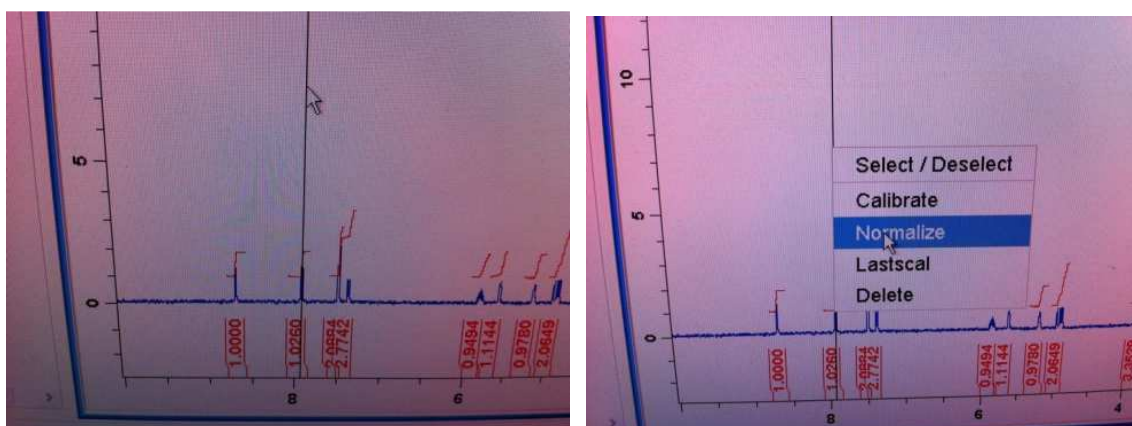
Beware that integrals are only relative. Looking at the integral above you realize that they are mostly defined as 1 (hydrogen atom) or 2. This is only an assumption, it could just as well be groups of 2 and 4 hydrogens. Your knowledge about the sample must help you in this respect. You can normalize integrals to other values. Above the second peak from left has a value of 1.0260. You place the cursor on this integral and click on Calibrate (not Normalize) and put in a new value, e.g. 1 this time and click OK.
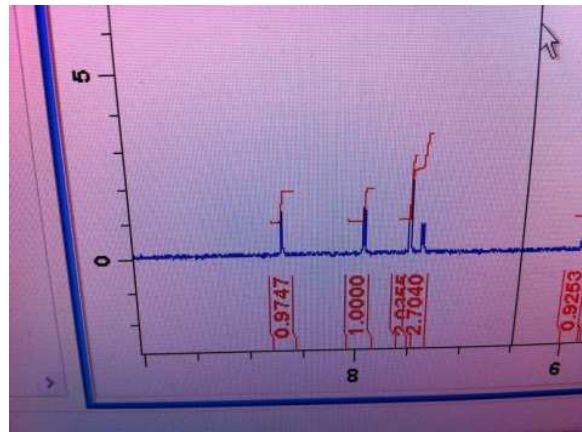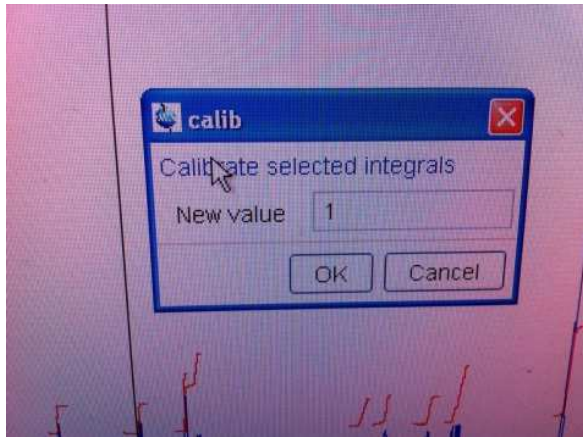
Now this peak has the value 1 and everything is calibrated relative to this peak.
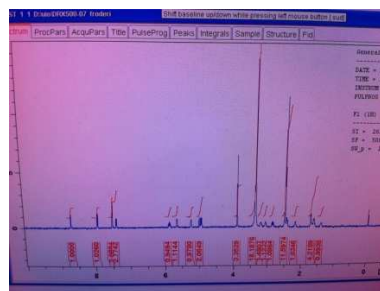
It is time to get a paper copy of your spectrum. Bring back the whole spectrum in the main window with the help of the button "Show full spectrum, leave intensity…" and locate the printer symbol/button and click on it. You will now have to work yourself through a bunch of windows on the way to obtain the actual printout.
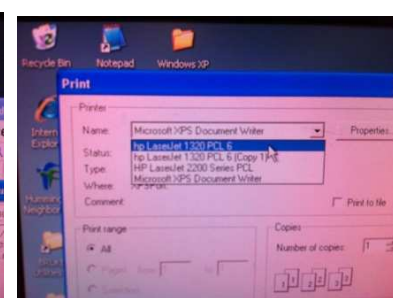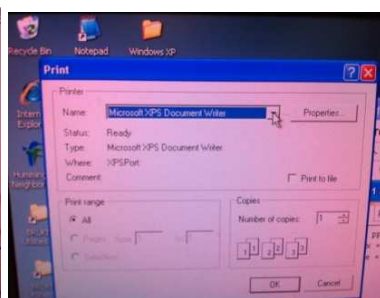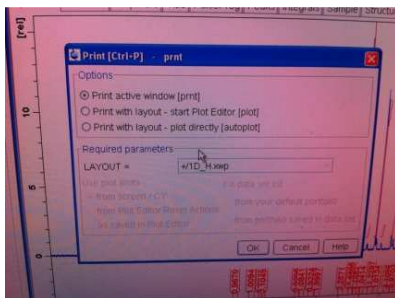
Click OK, exchange Microsoft XPS Document Writer with for instance hp LaserJet 1320 PCL 6.
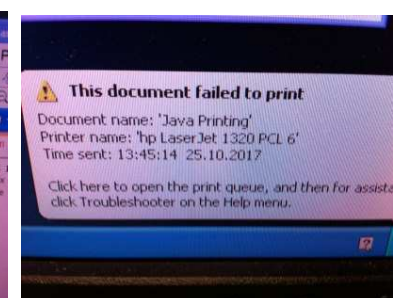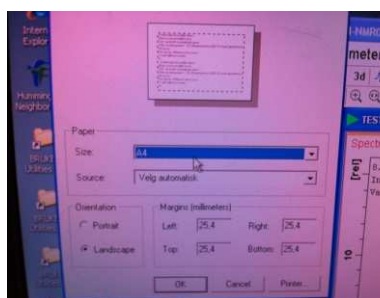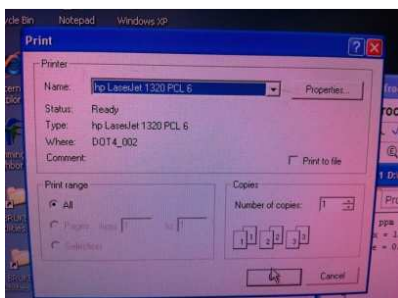
Click on the OK button. Change the US letter format to A4 and click OK again and realize that are not getting a printout since you selected a non-existing printer. Locate the printer symbol on the bottom line on the main computer screen and bring it up. You are solely responsible to delete your own failed printing/plotting jobs. No other regular users can delete your failed jobs. When the nmr personnel discover hanging print jobs you might lose your nmr access if the hanging jobs are not removed within 30 minutes after an e-mail notification is sent you.

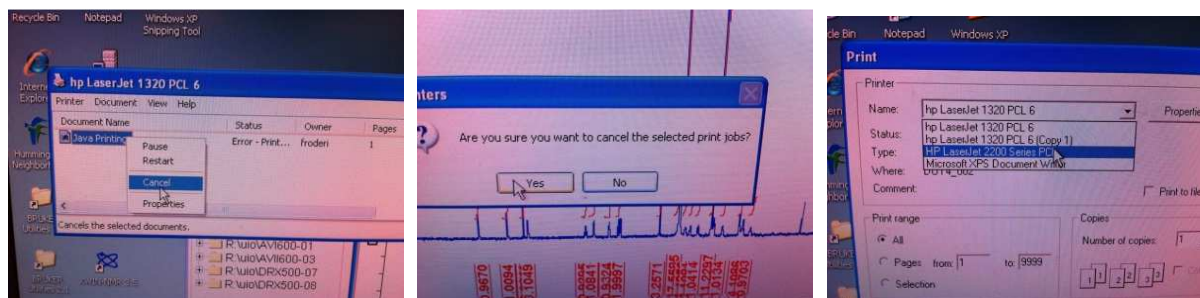Then you are more careful next time in selecting a printer that is actually connected to the PC you are using.

The print job is coming out!

Early in this document the notion of the R disk drive was mentioned. R is the location where all new nmr-data is copied every 20-30 minutes. The R disk is also called instrument-ts.uio.no/kjemi-nmr. Sometimes it is good to look at data located on R acquired on another nmr-instrument while you are doing a nmr-experiment. You have to make the locations visible in the left part of the TopSpin program window.
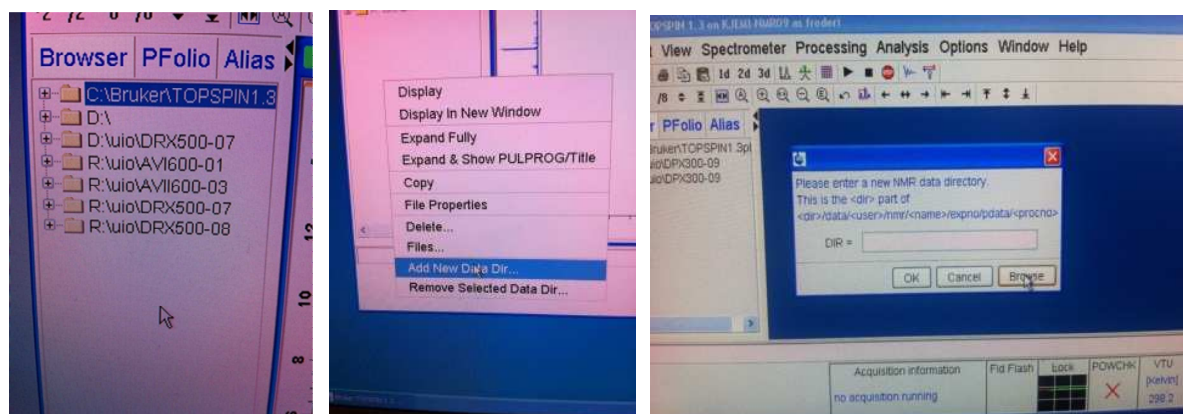
Right click in the left window. Select Add New Data Dir… Click on Browse in the window coming up. Find nmr on "nmr-server.uio.no" (S) and open it. Be aware that pictures below containing the letter R and not S. The reason for this is that USIT destroyed the connection to S in 2017 and the substitute R server had to be set up at Department of Chemistry as a replacement. Find uio at the bottom and click on it. Select the wanted nmr-instrument/computer – here AVI600-21 and click once on it.
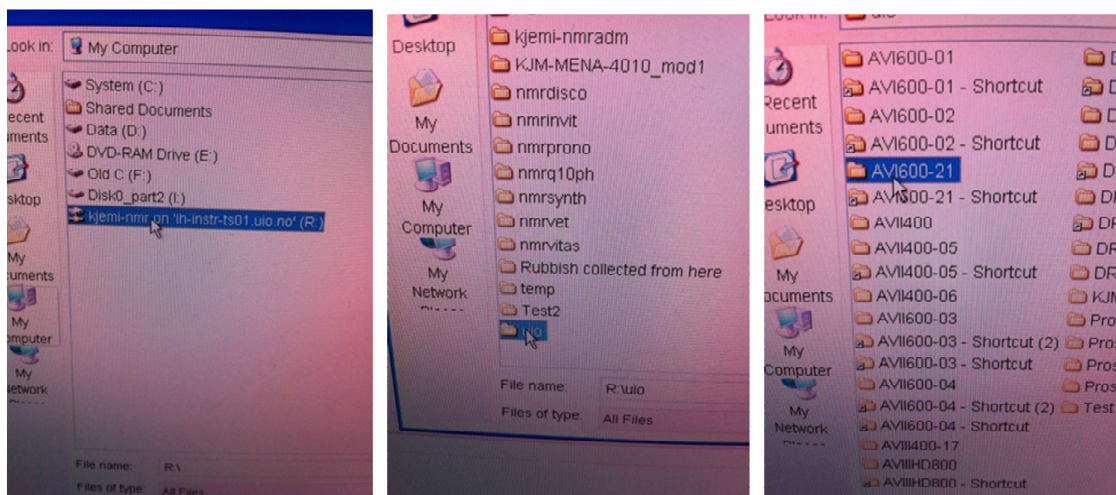

S:\uio\AVI600-21. Click then on OK in the left picture below (OK not shown) and the S:\uio\AVI600-21 location comes up. All of this depends however upon that you did connect to the UiO network by activating the S desktop icon as shown in the beginning of this document. You can now watch spectra obtained on the nmr instrument AVI600 while you run an nmr-experiment. This is however a bit dangerous. If you type zg og go in the command line with a dataset from another instrument open in TopSpin you are actually trying to run an experiment defined on another nmr-instrument and you can do a lot of damage to the electronics.
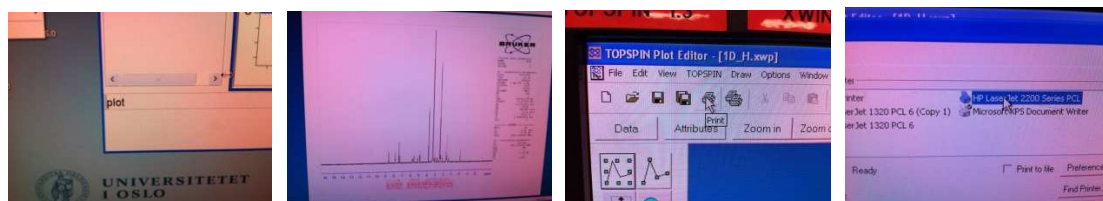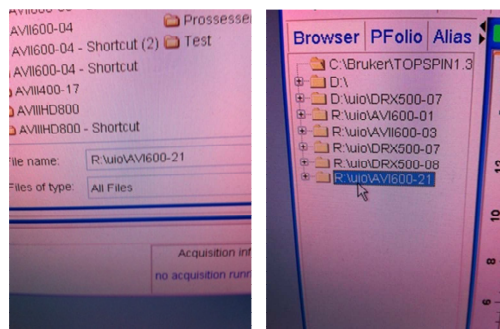
There is an extra plotting tool on inside Topspin. You can start that program with the command plot. The Topspin plot editor, in earlier versions called Xwinplot is extremely complicated to

use and very non-intuitive. In newer versions (3.2 and 3.5) of TopSpin some people actually like the program. Avoid it for all means in TopSpin 1.3 unless you want to spend a week figuring out how it works. You can make extremely complicated figures for publication purposes, but the program is worthless for quick and fast daily use.

The time is now come to remove the sample and inserting a standard sample and leaving the instrument, unless of course you want to do other experiments like for instance ^{13}C experiments. The process of leaving an nmr-instrument involves many steps. Click on AUTOSHIM so the light is not on. Click on LOCK ON/OFF so the ligt is OFF. Then you press LIFT ON/OFF so that the sample moves to the top of the magnet. Exchange your sample with a standard sample – observe what solvent is in the the nmr-tube before moving the sample down in the magnet by pressing LIFT ON/OFF again.

Observe that the light for SAMPLE UP changes to DOWN (previous page).
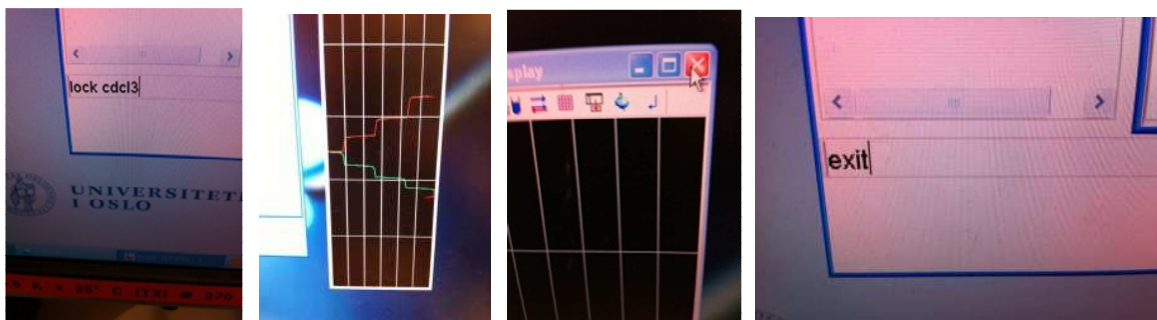
Then you lock on the solvent in the test sample either as shown in the left picture above or with the lock command in the command line. A list of solvent comes up and you select the correct one. You are patiently waiting for the lock process to be completed in the black lock window. Click on the X in the upper right corner of the lock window or type exit in the command line.
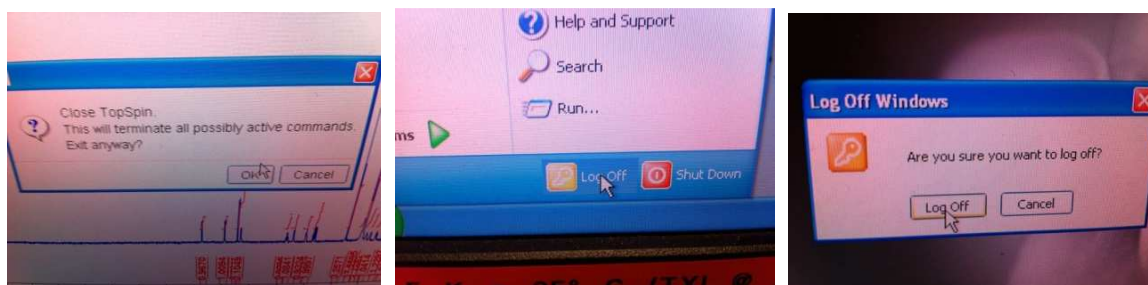
Then you click on OK in the pop up window. TopSpin closes. You look for the Log Off symbol in the lower left corner on the screen and you click on it. Then you wait for a new window to come up and click on Log Off. If you move away before doing this last step the screen eventually closes and no one can use the instrument.

A very short and handy manual to use when you have become a little experienced is written by Karoline Gangestad Primdahl at the School of Pharmacy UiO. It is shown here:

User manual for 1D experiments on DPX300 and DPX200

There is always a sample inside the NMR-instrument, to get this sample up you have to press button 1 on the control panel (Sample up/down, figure 1). Remove the standard sample and replace it with your sample (add a blue holder to the nmr tube and adjust the height with the device used for this) before you press the same button to lower your sample into the instrument.

Before you start running your experiment, make sure the light over button 2 is lit (figure 1). (Karoline and Frode are not agreeing about this). If not, press the button and wait until the light stops blinking.

1. When your sample is inside the instrument you write the command "new" ↵ in the typing line, this command will open a window where you must fill in the parameters.
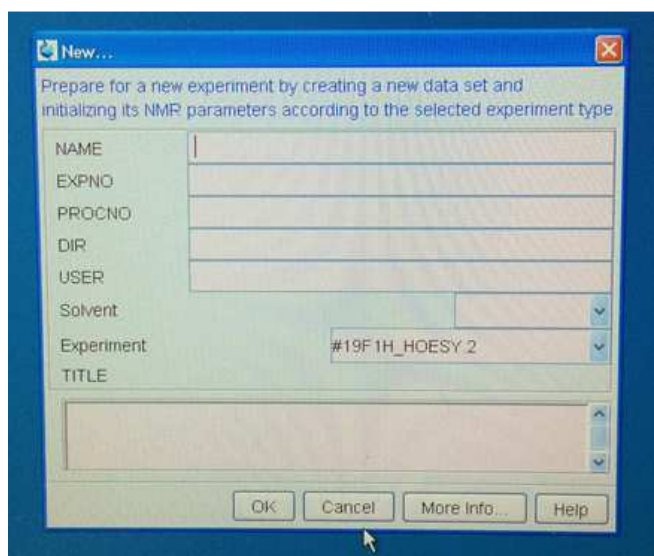
Name: Is the name of your sample.

EXPNO: 1

PROCNO: 1

DIR: D:\uio\DPX200-11 for the

DPX 200 instrument and

D:\uio\DPX300-09 for the DPX 300

instrument.

USER: Your username.

Solvent: choose the one you have

used.

Experiment: Choose the experiment

you want to run.

2. Type "getprosol"↵

Before you type a new command you must wait until the previous task is finished.

3. Type "ii"↵

4. Type "lockdisp"↵. This command will open a new window shown in figure 2.

5. Type "rsh"↵ and choose the shim file "QNP. 051019.luf" on both instruments. If the QNP probe is not in the magnet select another shim file with the name BBI/TXI/BBO/BBI in the file name.

6. Type "lock"↵ and choose the solvent that you have dissolved your sample in.

7. Next, you need to shim the instrument. Start by pressing "Z^1" on the control panel and then turn the wheel. The lines in figure 2 will then move up or down (right picture in figure 2), the purpose is to get the green and red lines as high in this window as possible. If the lines go over the top of the window you need to press "lock gain" on the control panel, turn the wheel until the lines are approximately in the middle of the window and then press "standby" before you start over again, by pressing "Z^1". After you get the lines as high as possible press "Z^2" and repeat what you have just done by turning the wheel and then finish the shimming process by pressing "standby".

8. Type "rga"↵ and wait until it is finished.

9. Type "zg".↵ This will start the experiment.

10. When the experiment is done type "efp" ↵ followed by "apk"↵ to see the spectra. If you want to see the spectra before the experiment is done you can type "tr"↵ followed by "efp" ↵ and "apk"↵.

When you are done remove your sample from the instrument and insert the sample (including correctly adjusted blue holder/spinner) you took out in the start and lower it into the instrument by pressing button 1. Type "lock"↵ and wait for it to finish before you close the program.

1. **Sample up/down**
2. **Spin on/off**
3. **Lock gain**
4. **Z^1**
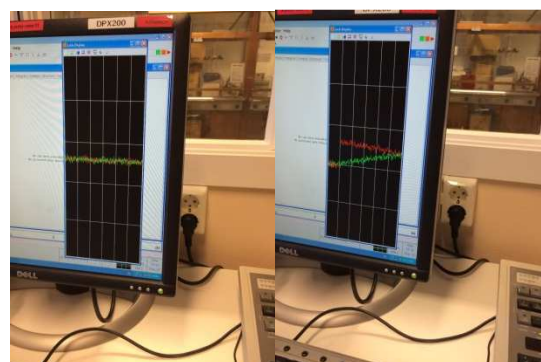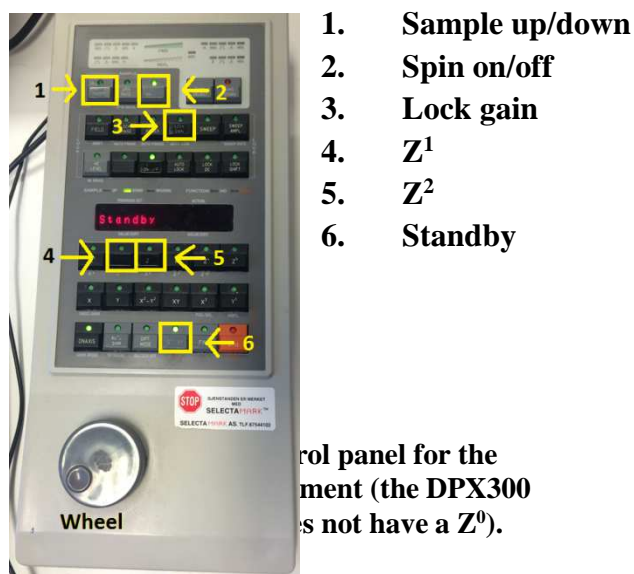5. **Z^2**
6. **Standby**

...rol panel for the ...ment (the DPX300 ...s not have a Z^0).

Figure 2: Shimming window.