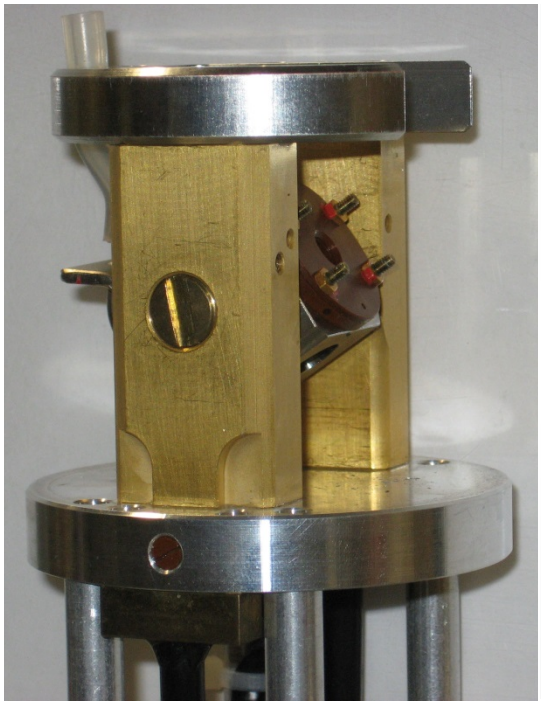

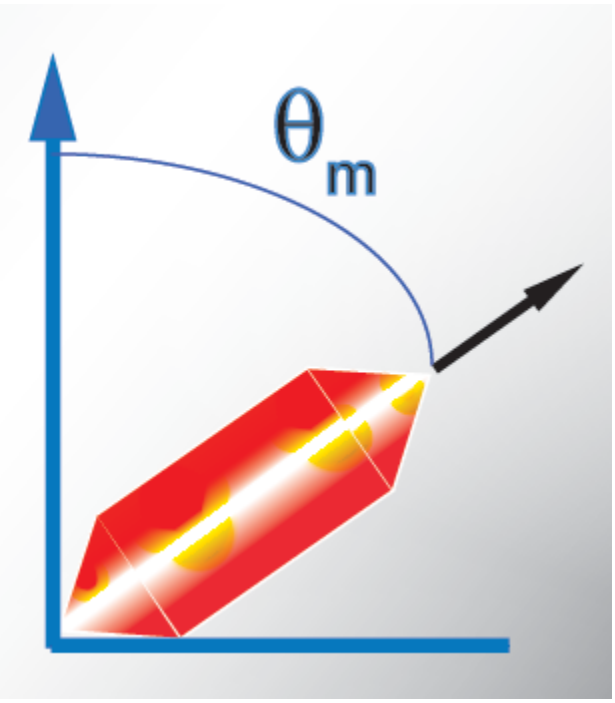

1D Solid-state NMR Procedure

(Avance III Machines running Topspin 3.1 under Windows 7)

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Spectroscopy Facility
Materials Research Laboratory
University of California Santa Barbara
Version 1.0 Last Modified Nov. 12, 2013

Safety Issues

⚠ If you, or people working with you, have magnetic metal implants, please consult your doctor for possible effects of magnetic field;
⚠ For those who have pacemakers, please stay away from NMR magnets;
⚠ Be aware of High Radio-Frequency Power in Solid-state NMR.
⚠ Remove from your pocket anything ferromagnetic or vulnerable to magnetic field:

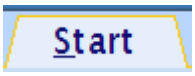
- Your wallet, bank cards, credit cards, and any cards with magnetic stripes;
- Electronics: cell phone, mp3, ipod, etc.;
- Mechanic watches;
- Keys and other magnetic items.

Table of Contents

I. Logsheet & Recharge

Enter

1. your name
2. your advisor's name and department
3. your recharge account number (in the format: 8-4xxxxx-xxxxx-3)
4. your start time
5. (**Do this at the end of experiment:** your stop time and duration of experiment)
6. (**Do this at the end of experiment:** Status of instrument and report problems if any as soon as possible)

II. 

2.1. Login and Launch TopSpin

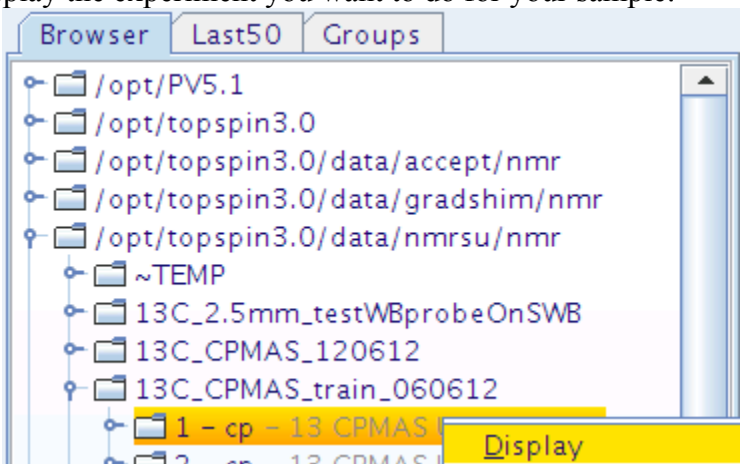
to login

Double clicks on 

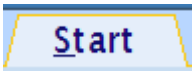
to start Topspin.

2.2. 

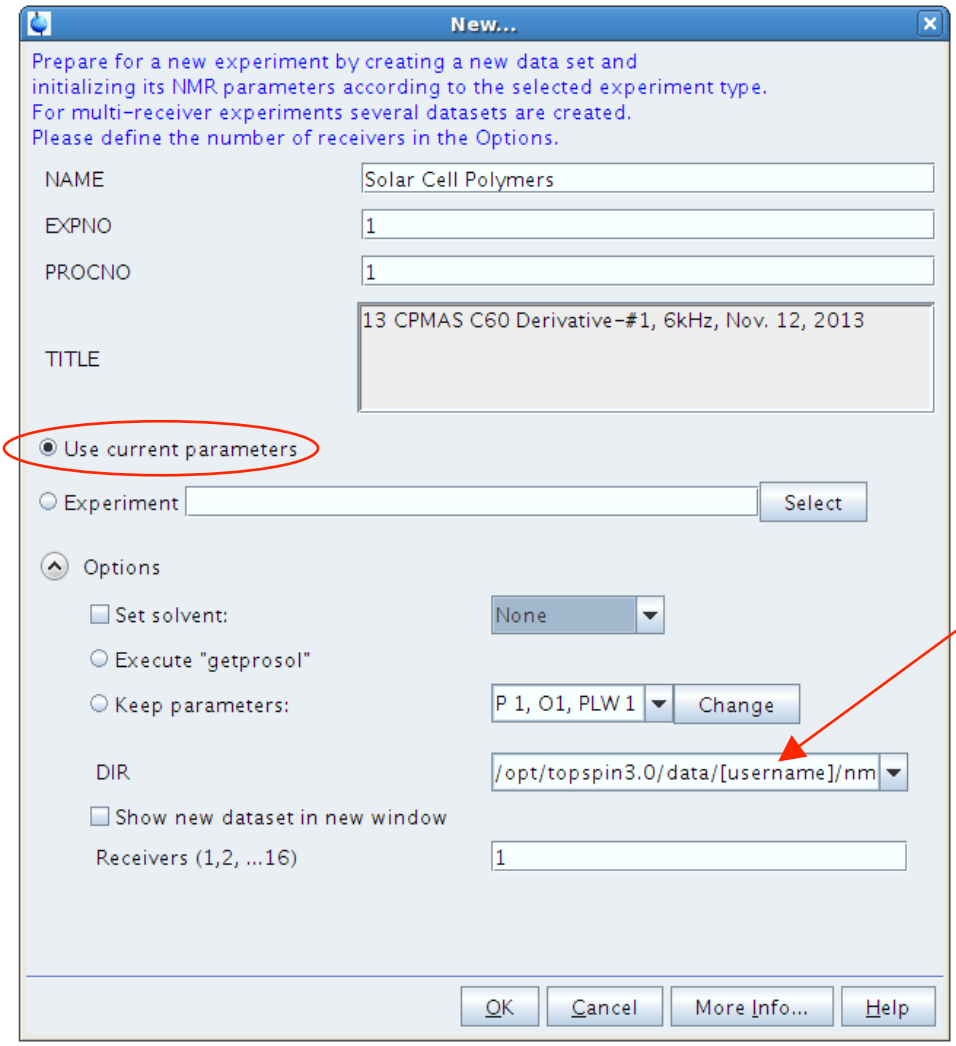
- Pull out and display the experiment you want to do for your sample:



- Create a new dataset based on the one opened above:



→ 



Name*: Solar Cell Polymers (e.g.) (meaningful or descriptive)
EXPNO*: 1 (start with 1)
PROCNO: 1 (start with 1)
Title: (any information useful for the current experiment)
Use current parameters checked to run the same experiment as the current data in display.
DIR: /opt/topspin3.0/data/[login username]/nmr
Solvent: (irrelevant)

* ⚠: IF YOU DO NOT CHANGE EITHER THE NAME OR THE EXPNO OF YOUR DATASET, YOU MAY OVERWRITE YOUR OLD DATA AND LOSE IT FOREVER.

III. Acquire

3.1. Sample

3.1.1. About Samples

- Samples feasible: Powders, Single crystals, Plastics/Rubbers, Ceramics, LT liquids, Tissues, Liquid crystals, More …
- Requirements: Dry, Pure, and small particles (smaller than table salts) for MAS.
- Sample Volume for 4mm rotors: ~100mg and ~200mg for organic and inorganic powders, respectively.

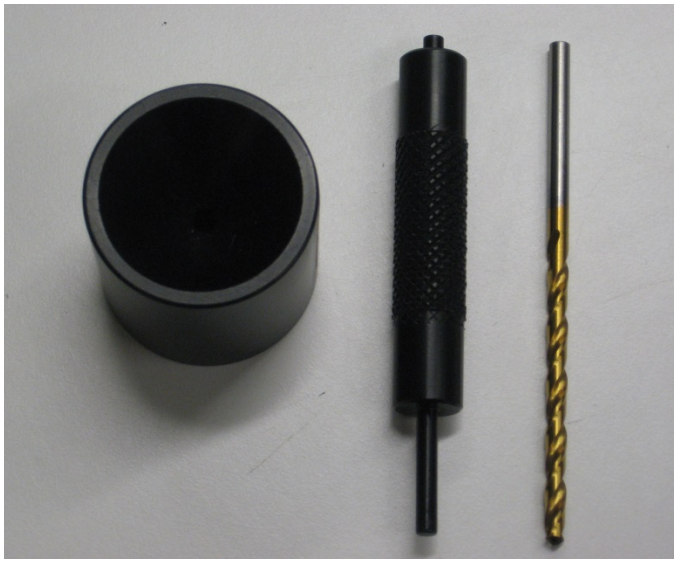
Bruker Rotor Dimensions (mm)

O.D.	Length	Depth	I.D.	Volume (mm^3)
1.3	7.68	through	0.78	3.67
2.5	12.07	through	1.23	14.34
3.2	15.36	10.90	2.17	56.81
4.0	17.97	16.21	2.98	125.33
7.0	17.95	16.41	5.59	440.53

3.1.2. Packing/Unpacking Samples

- Choose the right rotor and cap: size (4mm is the most popular), paint half of the bottom and should to black, and test the empty rotor/cap pair for good spinning.

- Pack sample with packing tools into a rotor as uniformly as possible through gentle tapping, press sample with a presser straight down (NO SIDEWAYS) for more sample (But DON'T break the presser !!!). Leave ~2mm space at the top for cap.



- Cap the rotor with bare hands only and clean the outside of the rotor with ethanol-rinsed napkin.

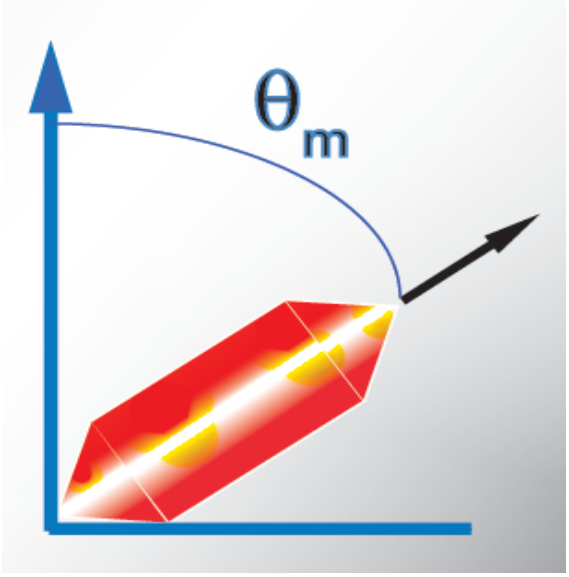
If the cap is too tight, use the multi-piece cap opener for assistance.

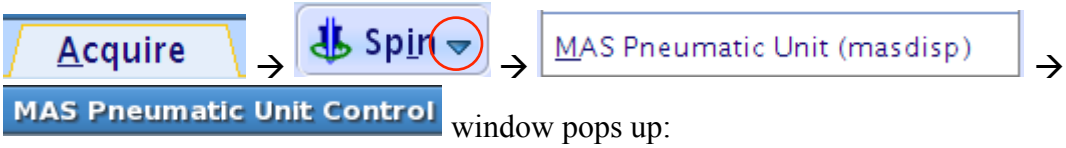
- Clean the rotor surface with an ethanol-damped kimwipe.
- Repaint with a black Sharpie half of the rotor bottom including shoulder for spinning speed detection.
- Test the spinning of the newly packed rotor on the MAS test station (in room 1414).

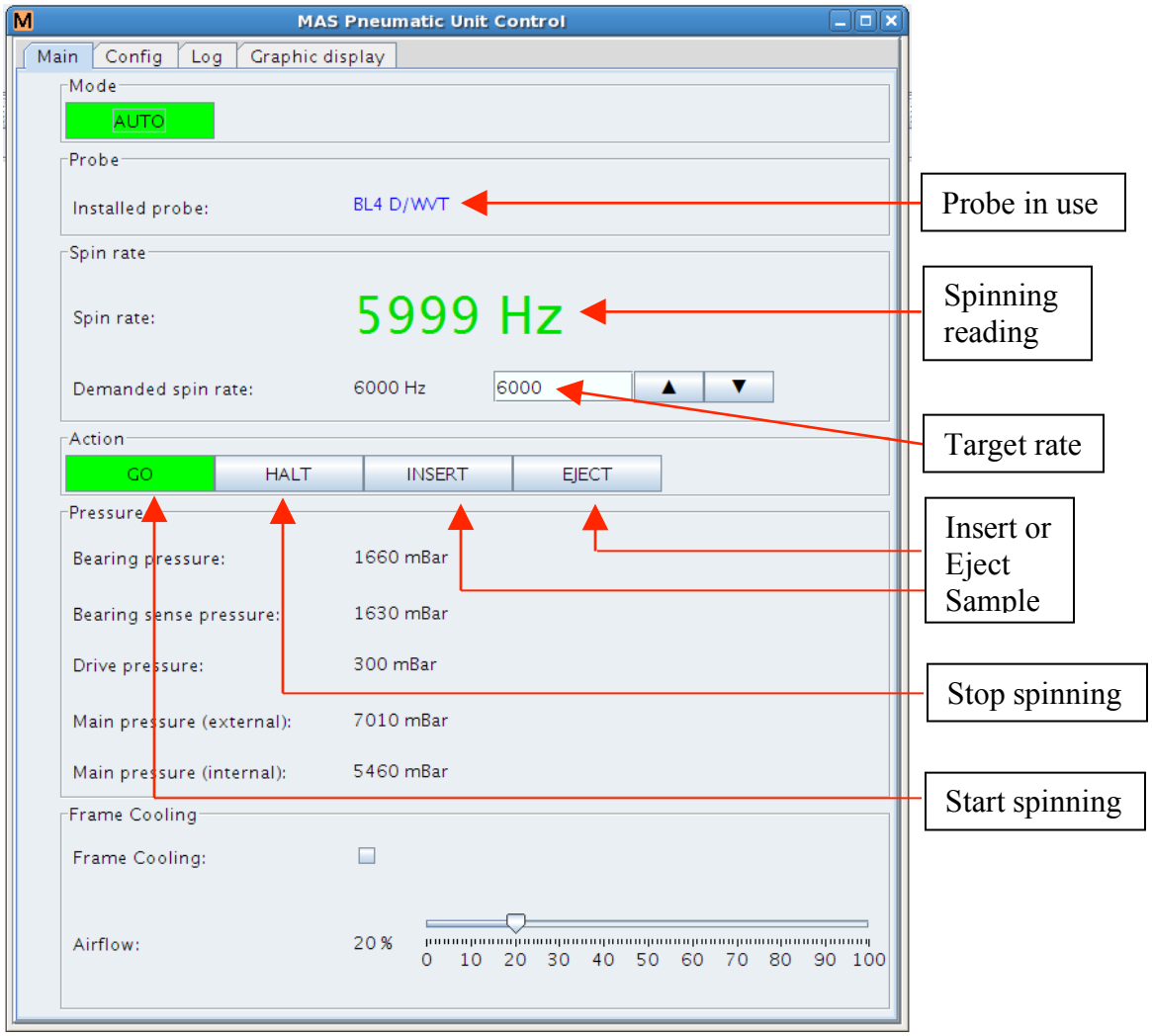
- After NMR experiments, remove the cap, unpack sample with a matched drill bit and spatula.
- Clean the inside of rotor/cap with brushes, cotton swabs, kimwipes, etc. and get the rotor/cap ready for next use.

3.1.3. Magic Angle Spinning (MAS)

- Magic Angle (θm=54.7°) between rotor axis and magnetic field



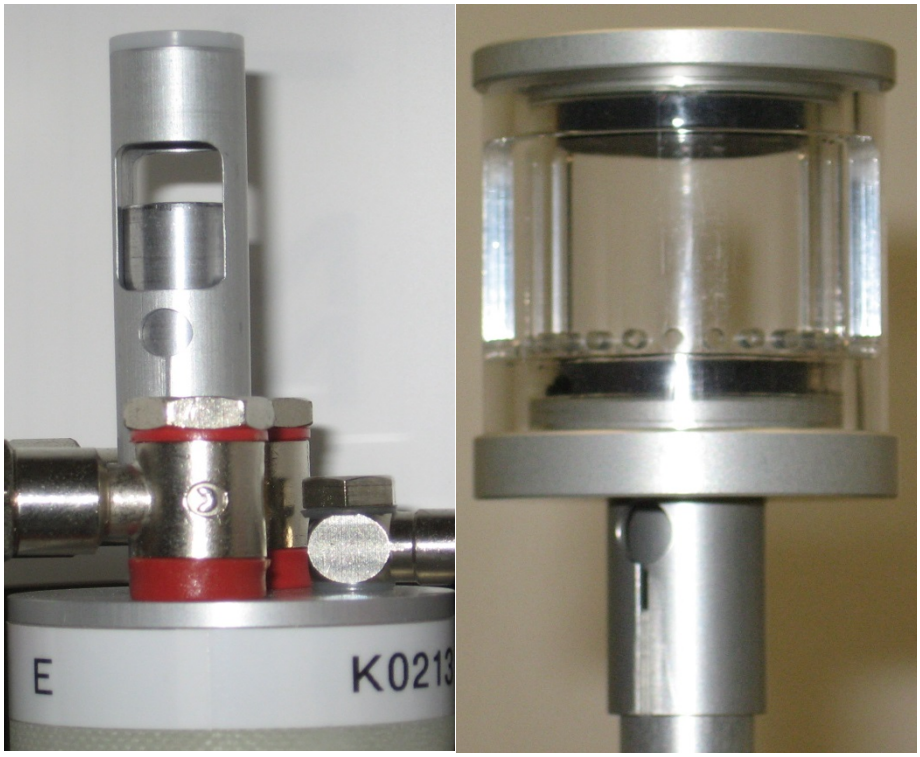
-  window pops up:



- (Important: It is important to make sure there is no sample already inside the magnet.) In the pop up window, see if the reading Spin rate: is zero first. Click EJECT if it is, otherwise HALT and wait for spinning to go down to zero, and then click on EJECT.

  Direct click on a button performs the default function of the button, while LMB click on the triangle on the right of a button displays other functions of the button.

- Load the sample from the top of the magnet by removing the sample catcher and dropping the sample in the hole of the transfer line with the painted end down;



4mm Sample Catchers (left: 4mm; right: 3.2mm & 2.5mm)

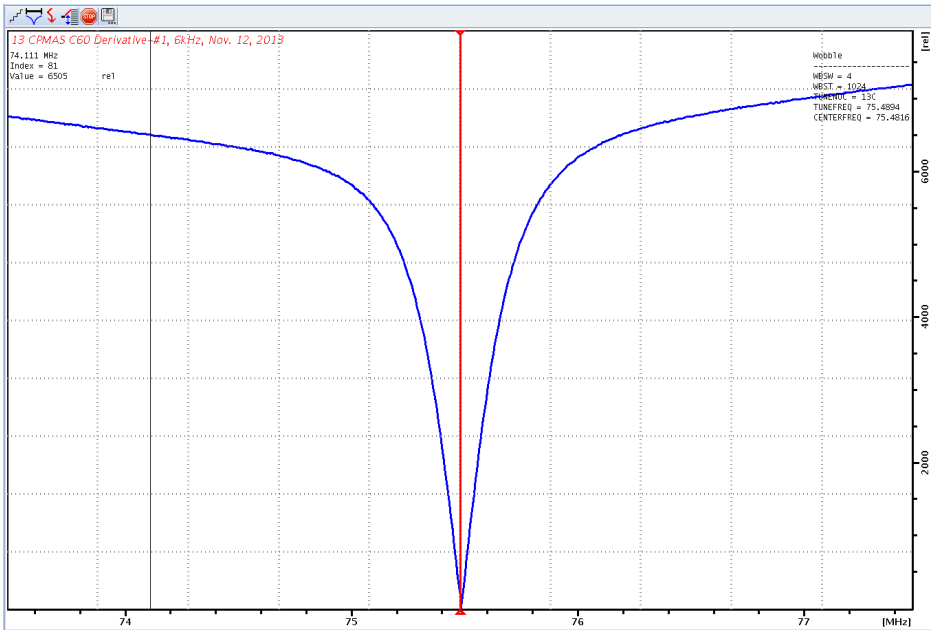
- Click on INSERT to push sample down to the probe.
- Use the Demanded spin rate: box to set the target spinning rate: type in the number and hit return. For a newly packed sample, start with a low spinning, e.g. 3kHz.
- Click GO button to start spinning and wait for the spinning to stabilize (which normally takes half a minute).
- If spinning is stable at a low rate, increase the Demanded spin rate: in an increment of 2 – 3kHz, and hit return. Repeat the process until the final desired rate is set.

3.2. Tune

Acquire → Tune → Tune/match ATM probe manually (atmm) / Display wobble curve (wobb)

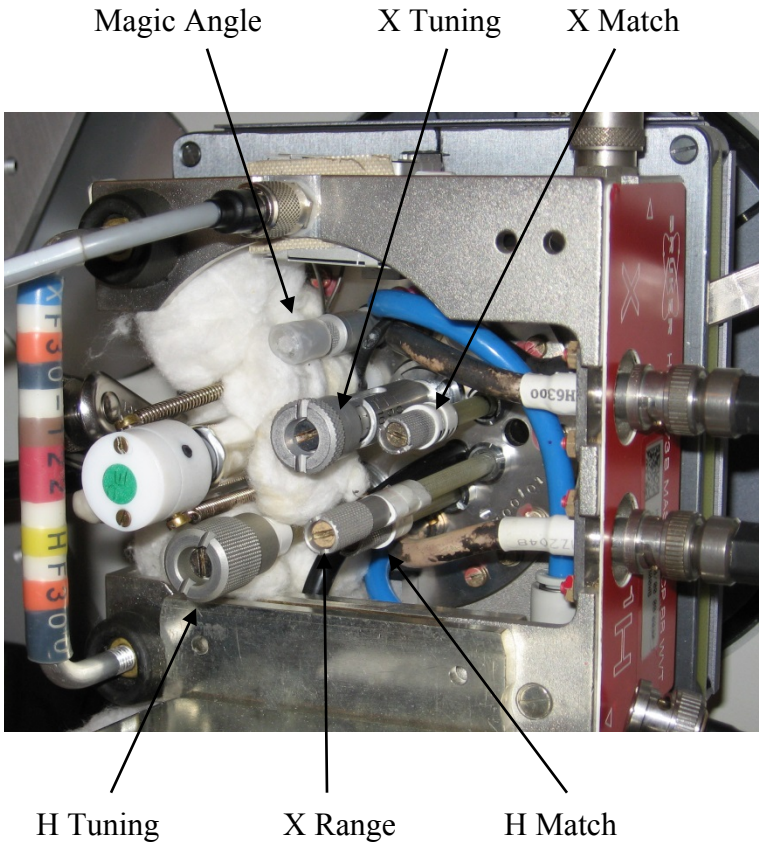
(or click on WOBBT for a thick curve display)

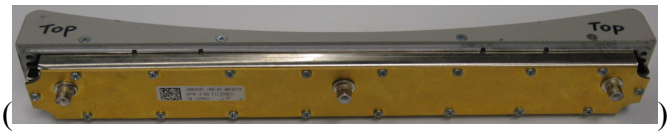
→ After ~20s, you will see a WOBB window showing the tuning/matching curve, the horizontal position of which corresponds to tuning and the depth to matching.



❖ Go to the probe.

This is a piece of equipment which goes into the magnet from the bottom. It has cables and hoses attached.



- On the IPSO 500MHz and 800MHz NMR instruments, the RF filter (

) on the side of X preamplifier of the HPPR box has to match the nucleus to be observed and be replaced as necessary. So is the range rod on the probe.

  To tune probe from nucleus X (e.g. ^{13}C) to Y (e.g. ^{29}Si), filter on the HPPR box, tuning rod and range rod on the probe have to be set correctly according to the tuning table given to the probe (if available). Use a large WBSW (e.g. 60MHz) in WOBB at first for coarse tuning and 4MHz at the end for fine tuning.

- With the supplied tool, turn the tuning rod (with T) so that the curve aligns with the vertical red line and the matching rod (with M) to make the curve reach all the way to the zero line of Y axis. Go back and forth between tuning and matching for optimization.

  You can also look at the preamplifier box called HPPR (a small box with cables next to the magnet) and minimize the number of LEDs lit on the horizontal (tune) and the vertical (match) LED arrays, normally 3 green LEDs lit for match and 1 green LED (and maybe a yellow one) lit for tune.

  .

- Tune and Match ^{1}H channel:

  After the ^{13}C channel is optimized, click on  , or press the F2 button on HPPR twice, to switch to ^{1}H and wait until the ^{1}H curve occurs (takes ~20s). Adjust the Tuning and Matching Rods for ^{1}H to optimize ^{1}H.

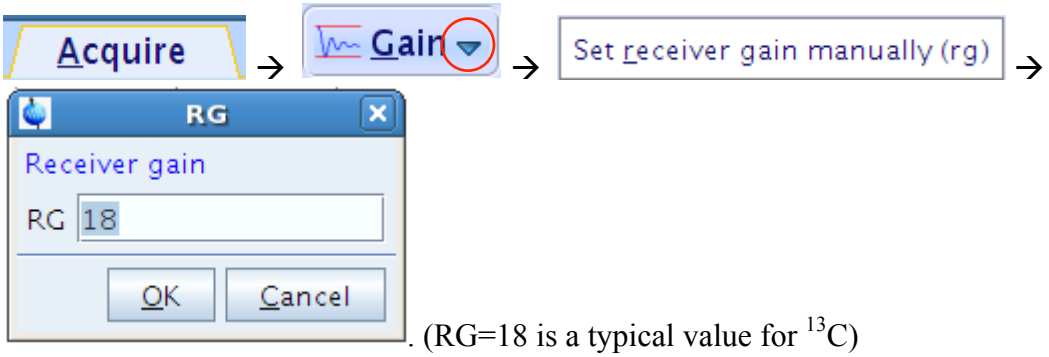
  To tune ^{1}H on the IPSO 500Mhz and 800MHz, the cable from the ^{1}H port on

the probe has to be connected to the HPPR box.

- If ^{1}H tuning have changed significantly, go back to ^{13}C by clicking on  , or pressing the F2 button on HPPR twice, and check its tuning. Make adjustment if necessary.
- Click on  to quit the probe tune/match process.

 On the IPSO 500MHz and 800MHz NMR machines, make sure that after ^{1}H tuning the cable from the ^{1}H port on the probe is connected to a ^{1}H filter to bypass the HPPR box for a better S/N ratio for X nuclei NMR with ^{1}H used for CP, decoupling, etc.

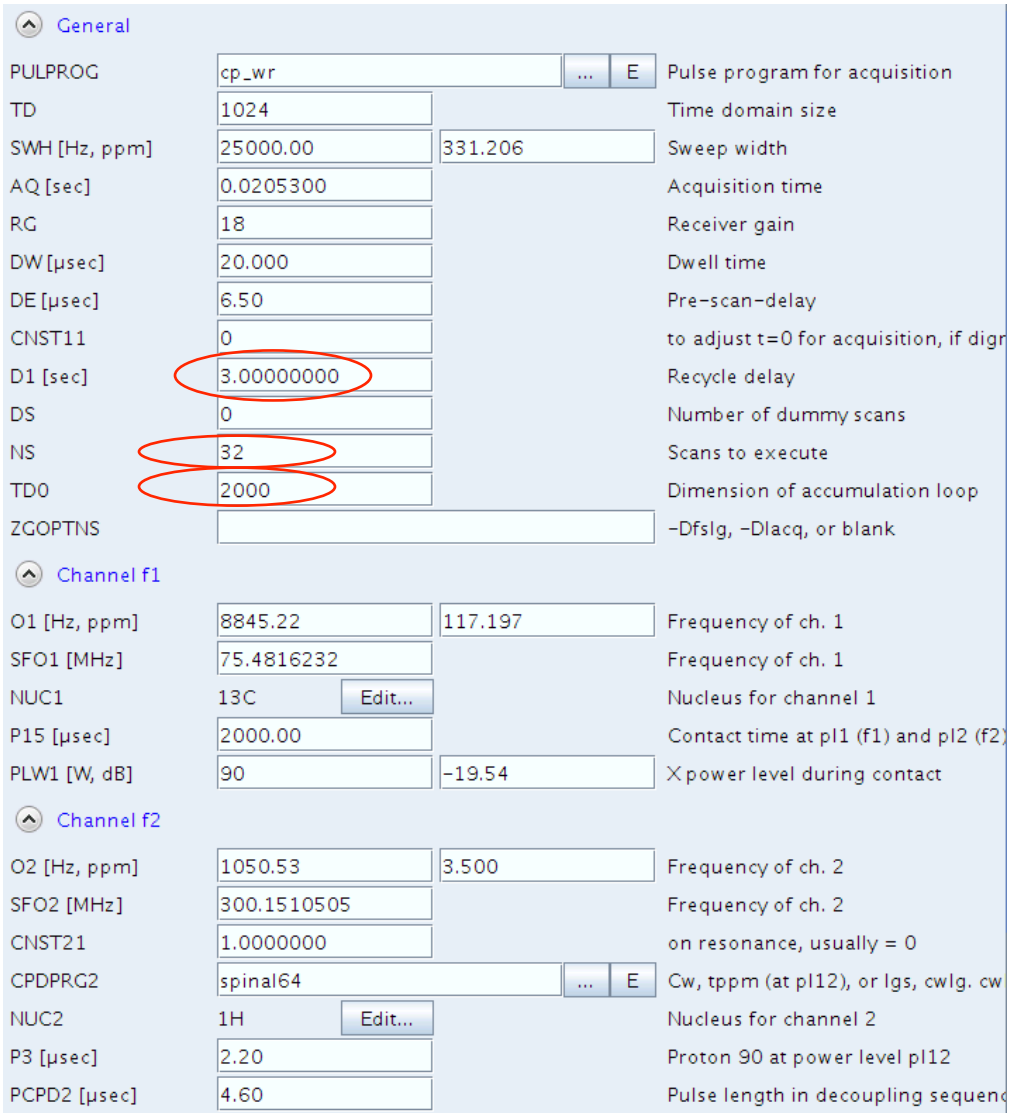
3.3. 



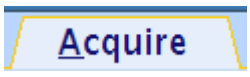
. (RG=18 is a typical value for ^{13}C)

 If the RG value is too high, i.e. the first scan is clipped vertically, reduce RG until the first scan intensity is half of the display window.

3.4. Set Key Parameters under 



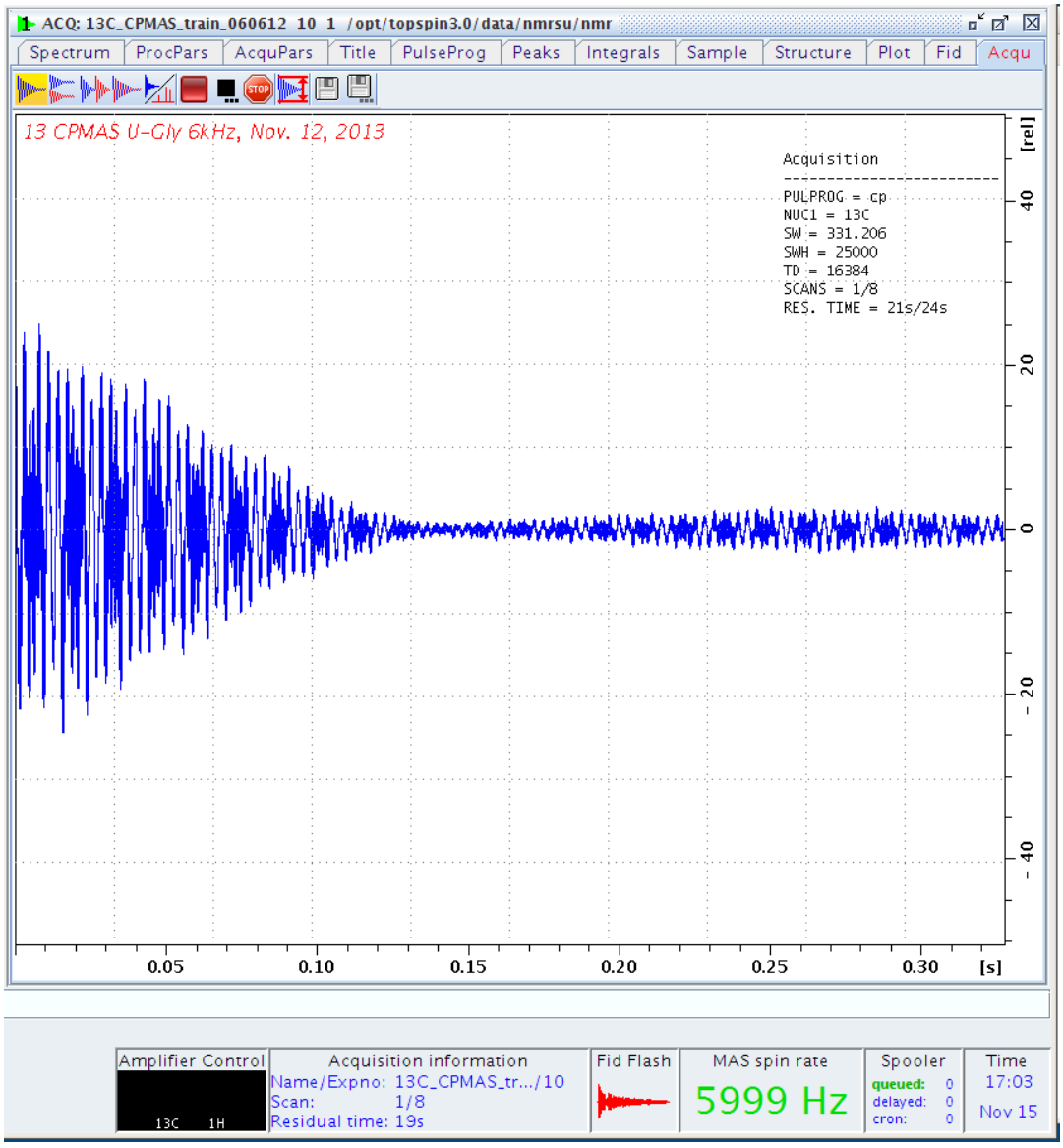
3.5. 



→ 

to start data acquisition

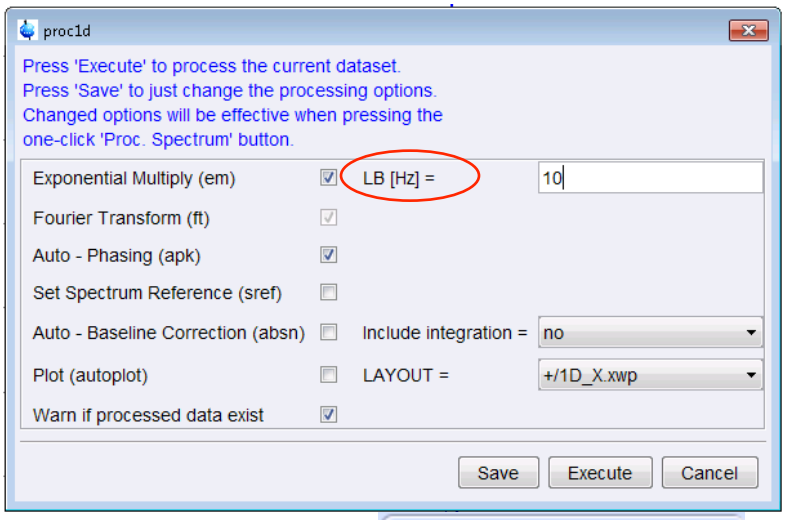
in the options can be used to estimate the experimental time.


ACQ: 13C_CPMAS_train_060612 10 1 /opt/topspin3.0/data/nmrsu/nmr
Spectrum
ProcPars
AcquPars
Title
PulseProg
Peaks
Integrals
Sample
Structure
Plot
Fid
Acqu
13 CPMAS U-Gly 6kHz, Nov. 12, 2013
Acquisition
PULPROG = cp
NUC1 = 13C
SW = 331.206
SWH = 25000
TD = 16384
SCANS = 1/8
RES. TIME = 21s/24s
[rel]
40
20
0
- 20
- 40
0.05
0.10
0.15
0.20
0.25
0.30
[s]
Amplifier Control
13C 1H
Acquisition information
Name/Expno: 13C_CPMAS_tr.../10
Scan: 1/8
Residual time: 19s
Fid Flash
MAS spin rate
5999 Hz
Spooler
queued: 0
delayed: 0
cron: 0
Time
17:03
Nov 15

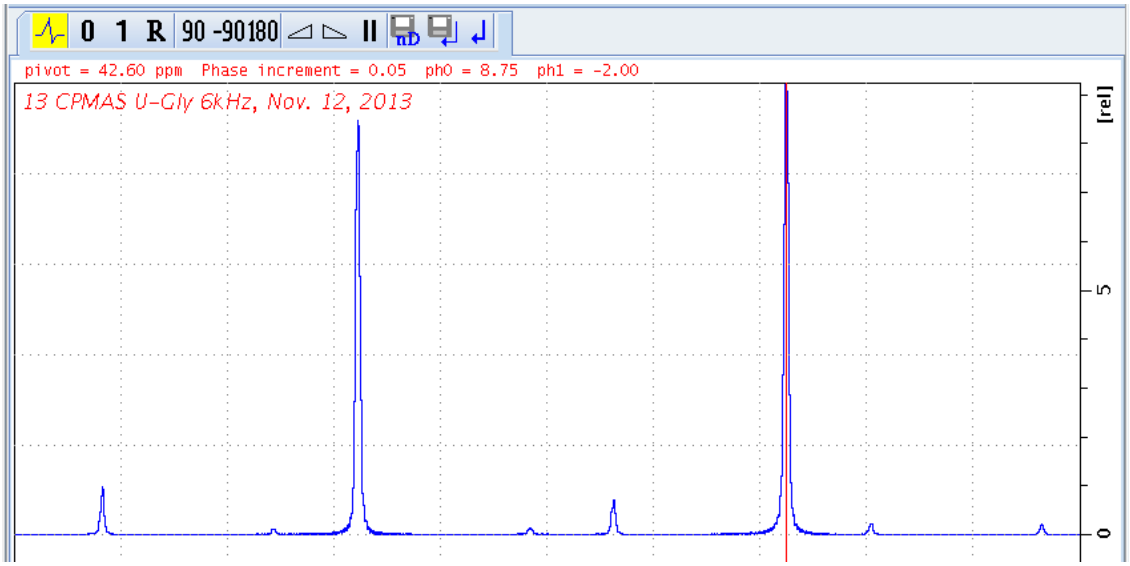
IV. Process

4.1. Proc. Spectrum

Proc. Spectrum → Configure Standard Processing (proc1d) →



Set LB = 5 – 25 and click on Proc. Spectrum →

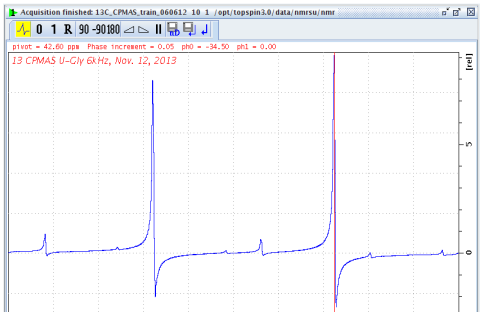


4.2. Adjust Phase

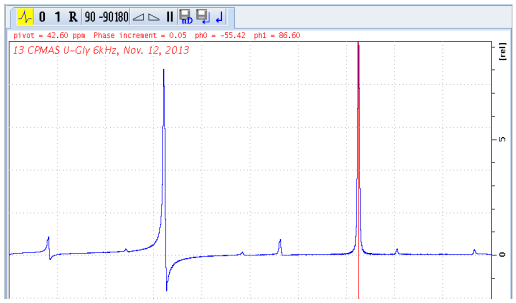
When there are broad peaks on the spectrum, which is normally the case for solid-state NMR, manual phase correction may be necessary.

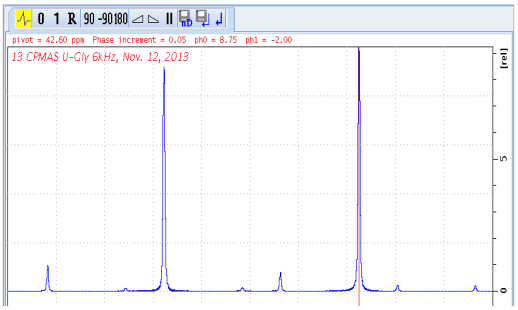
Process → Adjust Phase → use 0 for the peak at the redline

and 1 for other peaks with LMB clicked-and-held on them and moved up or down (to see phase clearly, scale up intensity 8x).



→ 0 →





→ 1 →

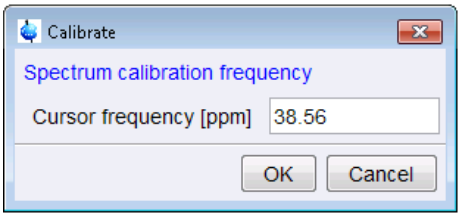
→ to save phase values.

4.3. Calib. Axis

It is necessary to calibrate the chemical shift in solid-state NMR because of the lack of solvents.

- Run a reference sample (e.g. adamantane for ^{13}C) under the same conditions as for your samples.
- Zoom in to a peak of known chemical shift → Calib. Axis → C →

Click on the top of the peak →



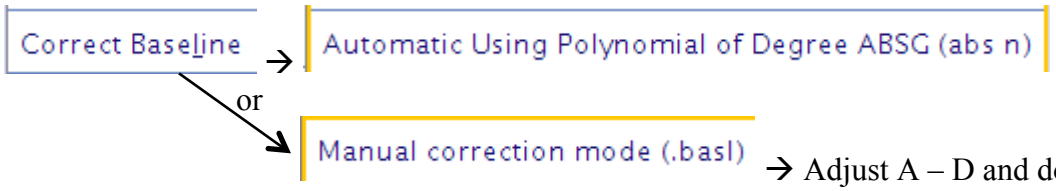
→ OK → Take the SR value to your spectrum.

4.4. Pick Peaks

→ Activate  with LMB if necessary (Yellow means active) → Click-Hold-Drag LMB to pick peaks →

→ If necessary, use  to modify the green boxes →  to save the picked values.

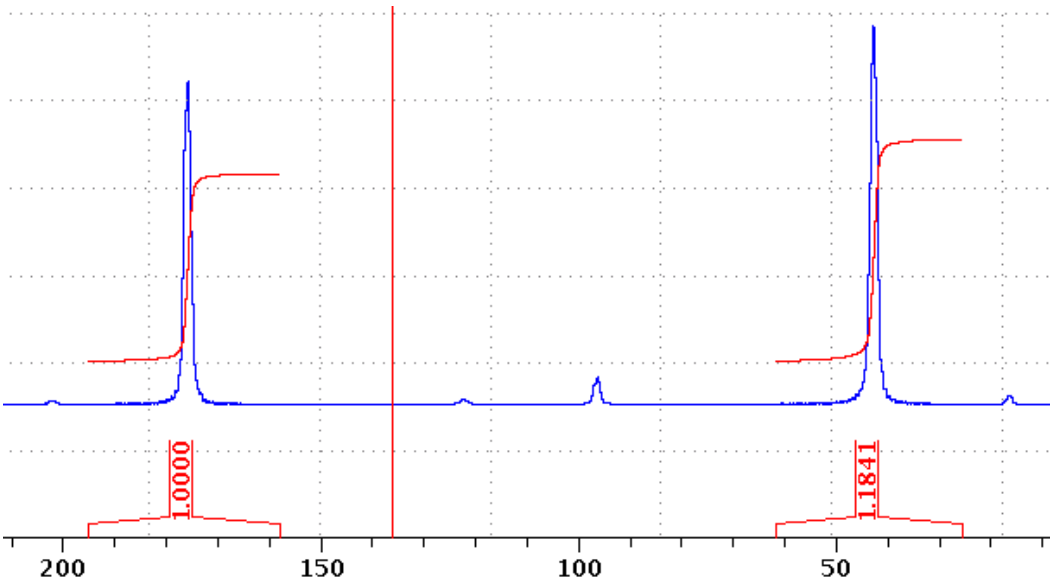
4.5.



→ Adjust A – D and do subtraction.

4.6.

→ Activate  with LMB if necessary (Yellow means active) → Click-Hold-Drag LMB over regions to be integrated →



→ If necessary, calibrate integrals: RMB click on an integral to be used as reference, select Calibrate Current Integral, and input a calibration value →  to save the integral values.

V. Publish

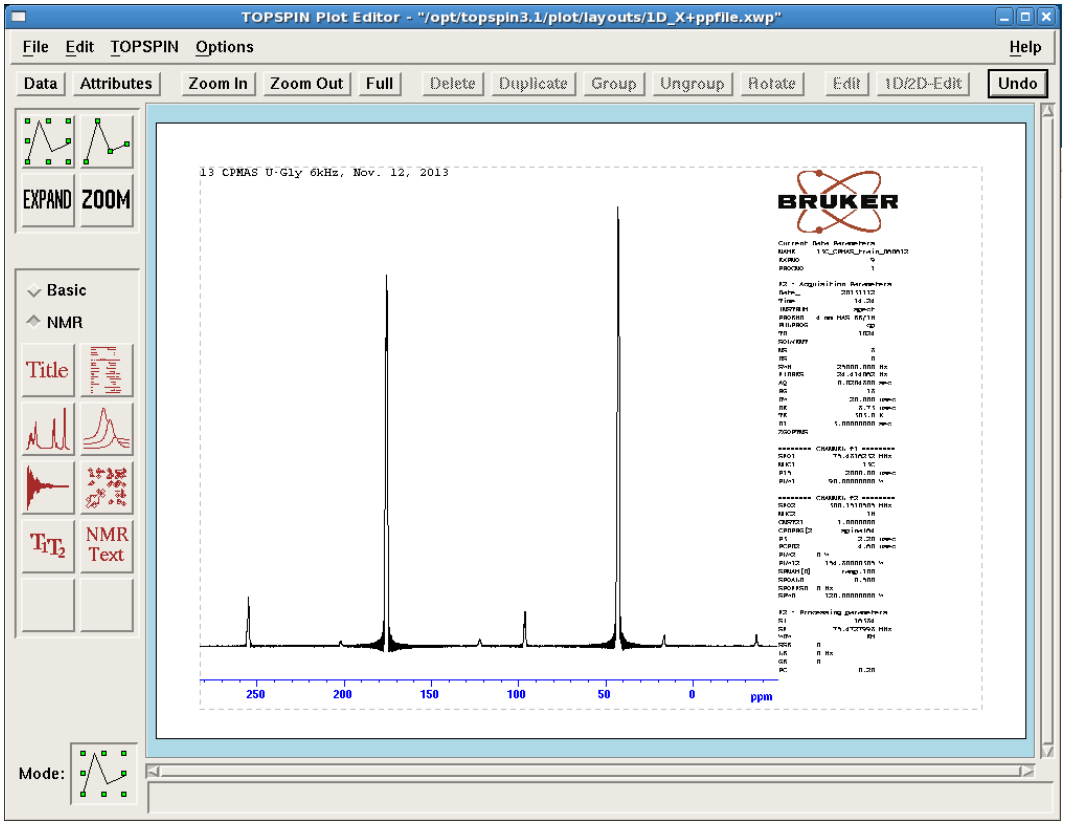
5.1. Print

Print the active window, WYSIWYG.

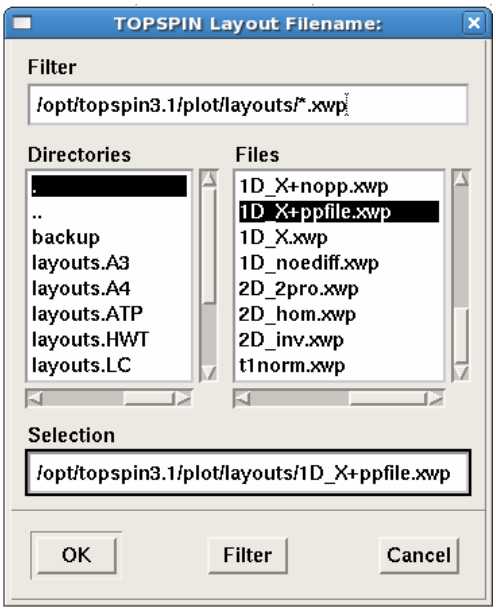
5.2. Plot Layout

Use the Plot Editor for more controlled printing.

Open Plot Editor And Modify Layout → Plot Editor opens:



To change layouts, File → Open... →



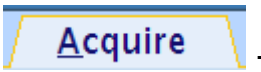
→ OK

5.3. 

Save spectrum in .pdf, .png, and other formats.

VI. Wrap-up

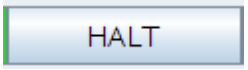
6.1. Eject your sample

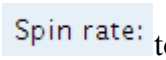


→


→


→

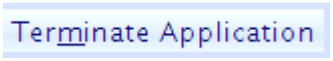

→


→ wait for


to be zero
→


→ Go to magnet to remove sample (within 10s for 4mm MAS probes).

6.2. Exit Topspin


→


6.3. Logoff your account

Click on  on the top or bottom of screen and then on 

.

6.4. Complete the logsheet

Stop time, duration of experiments, and status of instrument.

VII. Appendices

7.1. Appendix 1: Introduction to Solid-State NMR

a. What is solid-state NMR ?

NMR spectroscopy is performed directly on the samples in solid states or in oriented pseudo-solid phases, for example:

Solid-state samples

Solid-state	Example Materials
Powder	Anything powderable: Amino acids, Organic compounds, Inorganic materials, …
Single Crystal	Anything forming single crystals: Organic, Inorganic, Biological, …
Chunk Solid Materials	Machinable to cylindrical shapes to fit into MAS rotors: polymers (plastic, …)
Film	Stand-alone films or supported on substrates
LT Liquid and Slurry Materials	Anything which can be solidified: solvent, dissolved solute, protein, etc.

Oriented pseudo-solid phases: Liquid crystal, Lipid, etc.

b. Why Solid-state NMR ?

It is desirable to run NMR experiments in solid-states when

- Samples are not dissolvable.
- Properties change after dissolution.
- local structures are to be measured accurately:

c. Differences between conventional solution NMR and Solid-state NMR:

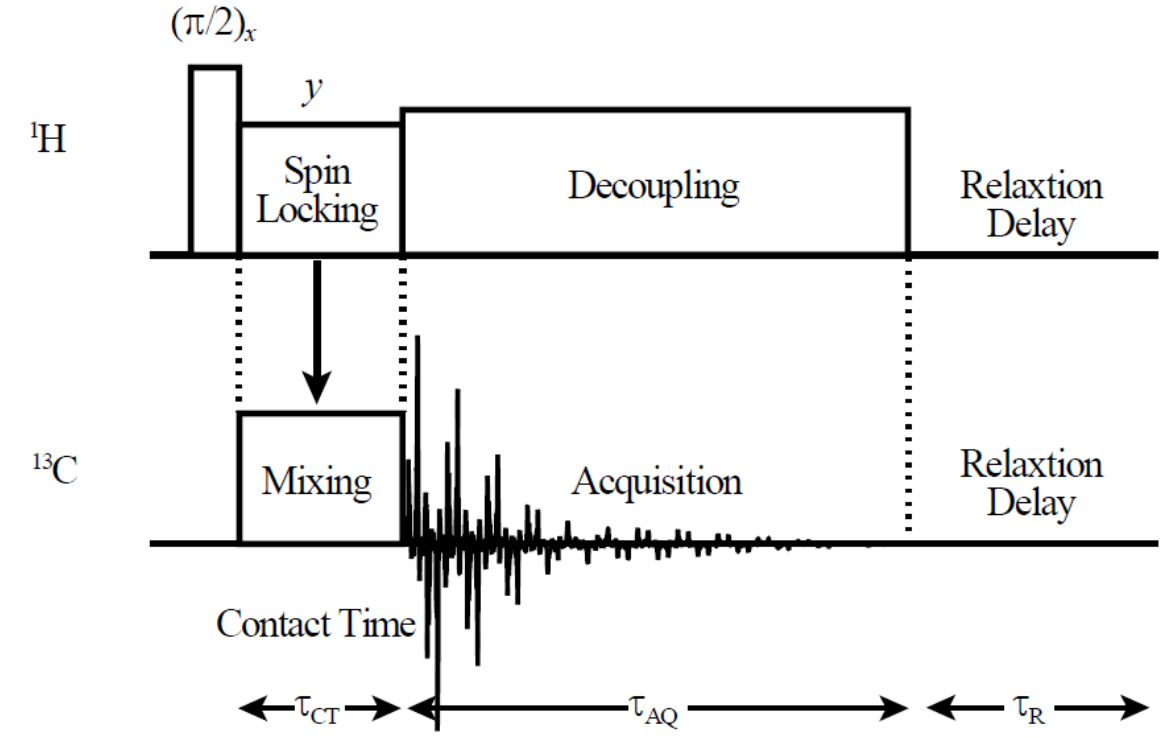
In solution: J-coupling, in the order of a couple of hundred Hz at most, dominates under fast tumbling of molecules, and high resolution spectra prevail in most cases.

In Solid-state: Other than J-coupling, there are other overwhelmingly dominating interactions intra- or inter- molecularly:

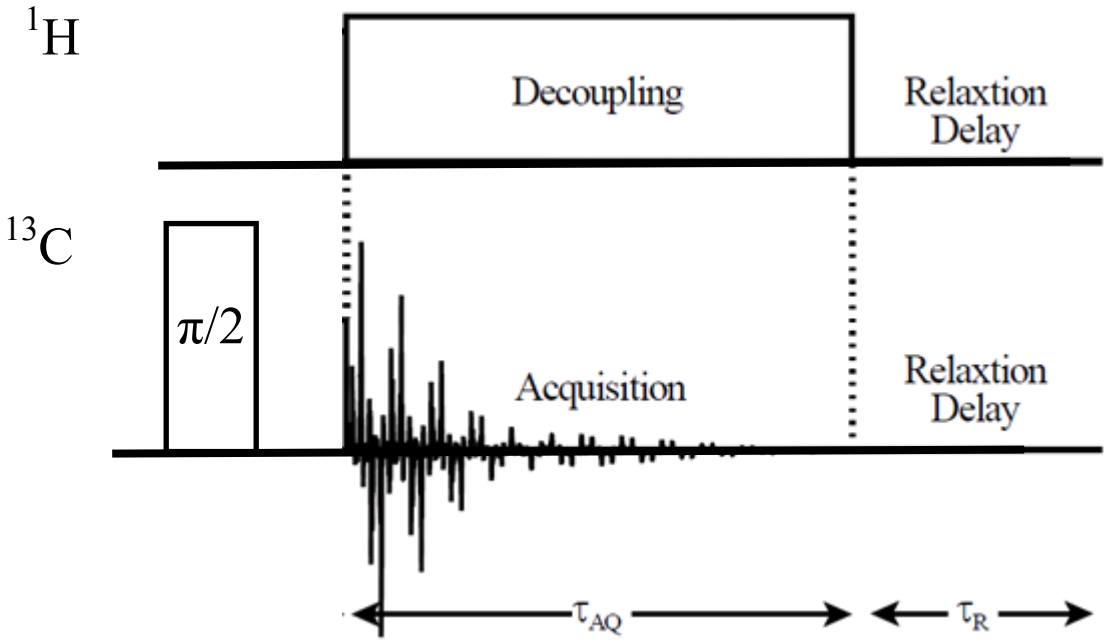
Interaction	Strength
J	Hz
CSA	Up to ~2000 ppm
Dipolar	Up to tens of kHz
Quadrpolar	Up to tens of MHz

7.2. Appendix 2: CPMAS (Cross Polarization under MAS)

Cross-Polarization under MAS (CPMAS):



Single Pulse MAS (also BD or HPDEC):



7.3. Appendix 3: Online NMR Book and Bruker NMR Encyclopedia

1) NMR Book: http://www.cis.rit.edu/htbooks/nmr/
Introduction to NMR concepts and practical issues.
2) NMR Guide & Encyclopedia: http://www.bruker.de/guide/
All you want to know about NMR.

7.4. Appendix 4: Requirements for CNSI Access

You have to pass the mini quiz within one month after training in order to be qualified for access to the NMR facility of MRL, which includes:

- Key Card for Lab & Building:
    1. Pass the MRL safety training;
    2. Fill out the CNSI access form: http://www.cnsi.ucsb.edu/facilities/building_services/access/access_application.pdf
    3. Take the form to Sylvia in 2066G, MRL
- Web Scheduling Account
- NMR Account

These requirements apply to both on- and off-campus users.