IMSERC User Manual for Solids

CONTENTS

INTRODUCTION

Solid state NMR is useful to the samples those are not soluble in any solvent or undergo structural changed in solution. It can provide detailed information about the local structure, whether crystalline or amorphous. Various pulse sequences can be employed to study different interactions in solid-state NMR, such as dipolar coupling, chemical shift anisotropy, and quadrupolar coupling. This manual covers basic NMR operations and provides detailed procedures for multiple solid-state NMR methods.

SAFETY

All users of IMSERC must review the general safety policies at http://imserc.northwestern.edu/about-policies.html. Plus, users should know the points below:

- Users with pacemaker are not allowed
- Emergency Exits
- Location of shower and eyewash
- No food and drink
- Dressing code
- 5-Gauss line

DATA MANAGEMENT

Your personal data folder is created during training. Please save data under your personal folder, which must be located under your supervisor's group folder. See a staff member if you do not have a personal folder on this instrument yet.

NMR data on this instrument are copied on 'imsercdata.northwestern.edu' under 'PI/AREA/INSTRUMENTNAME' within a few seconds. Please follow instructions at http://imserc.northwestern.edu/about-general-faq.html#data for details about data access.

SOFTWARE

Offline data processing and analysis can be performed with MNOVA and Topspin. Northwestern has campus wide license for MestraNova. Please refer to Mnova installation instructions at http://imserc.northwestern.edu/about-general-faq.html#software to install the program on your computer. Make sure to connect to Northwestern VPN when you work off campus. You are also encouraged to download the Topspin software from Bruker at

https://www.bruker.com/service/support-upgrades/software-downloads/nmr.html and claim your free academic license. DMfit is used for spectra simulation and deconvolution. Users can download the free DMfit from website: https://nmr.cemhti.cnrs-orleans.fr/dmfit/

PREPARATION

Spectrometer: NMR-Hg400-Solid only

Probe: Bruker 4mm HX probe or 1.6 mm HX probe. For the sample packing and experiment on 1.6 mm probe, please ask Dr. Jinlei Cui

Prerequisite: users have done the basic NMR training; also users should understand the differences between solution and solid NMR, e.g. hardware, software, T1 and T2, etc.

Sample: must be in powder form; and about 80 mg

Rotor: Bruker https://bruker-labscape.store/products/4mm-mas-rotor-kit Part# H14355

Sample tools: from Left to right: Sample filling funnel, sample packing/removing rod/drill, inserting cap gauge, removing cap blade, spatula, black Sharpie

DEFAULT INSTRUMENT STATUS

The default measurement mode of Hg400-Solids is 4mm HX probe with 1H in H channel and 13C in X channel. If you would like to run an experiment in a different mode than H/C, e.g. 31P, you need to tune back to the default setting when you finish the experiment. If you want to use the 1.6 mm HX probe, please contact Dr. Jinlei Cui.

The default working condition of INSTRUMENT-NAME is as follows:

1. Computer screen is by default deactivated. You must start your reservation through NUCore in order to be able to turn on the computer screen. If screen is already on, start your reservation through NUCore
2. Acquisition software topspin should be kept on screen. Leave the acquisition software open when you are done with the measurement.

If there is an error or problem with the instrument, please report the issue by following at least one of the steps below:

1. If you have already started your reservation using NUCore, please logoff by selecting the error reporting option and a brief description about the issue
2. If you have not started your reservation using NUCore, please report problems with the instrument at http://imserc.northwestern.edu/contact-issue.html add place the sign near the instrument computer.
3. Email or talk to a staff member

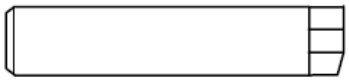
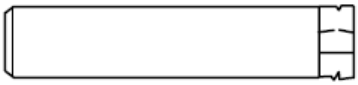
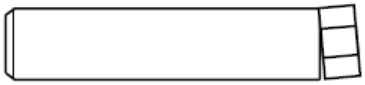
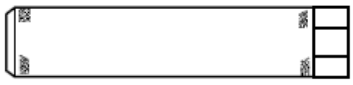
EXPERIMENT SETUP

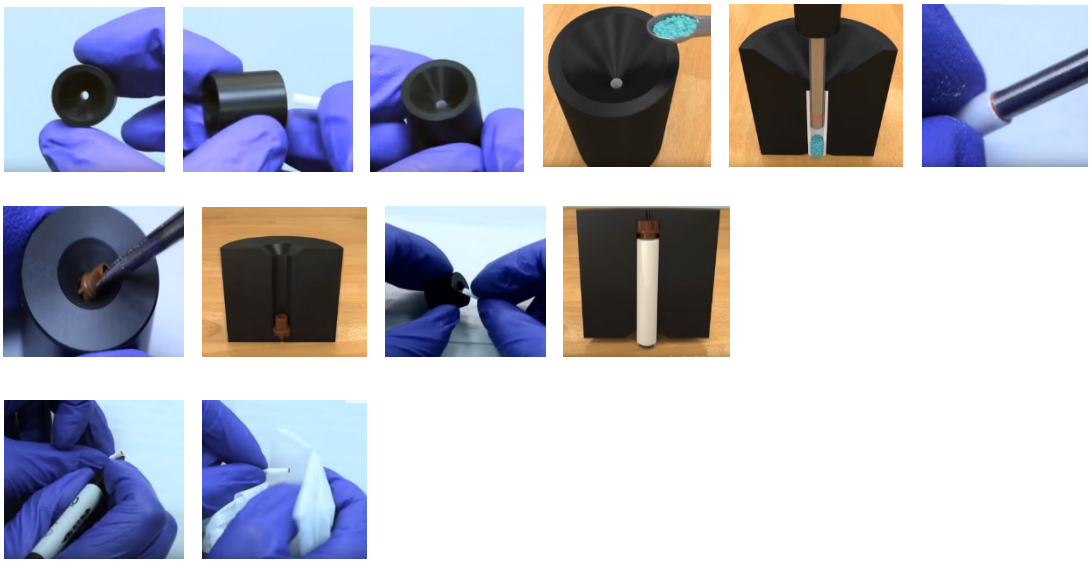
STEP 1. LOAD SOLID POWDER INTO A 4MM ROTOR

Before you start, you need to watch this Bruker video https://www.youtube.com/watch?v=bNFJj2g0UjI

By using special tools to pack sample and finally cap it (more details are shown below)

Rotor and Kel-F Cap Trouble Shooting Guide

Rotor and Cap Condition (Exaggerated)	Problem	Cause/Prevention
	Dented cap will not spin properly	Kel-F caps can be dented with excessive force. Never use a hard surface to press the cap into the rotor Change another cap
	Cut cap will not spin properly	Caps are cut by improper use of metal cap puller. Consult puller instructions or use liquid nitrogen to remove caps
	Tilt cap will not spin properly	Rotor was packed too full or not symmetrically-packed Remove excess sample or repack sample then reinsert cap
	Cap not inserted completely due to too much sample, or cap pups off during spin up (that could stop spinning abruptly)	Remove excess sample then re-cap it The cap is loose. Try another cap
	Dark smudges or marks on end of rotor indicate contact with bearing and/or drive plates during spin up	Non-symmetrically-packed rotors can ‘wobble’ during spin up Replace another rotor or use low spin-rate



Note:

- Make the rotor and cap are in good condition (see the Trouble Shoot Guide above)
- Pack sample fairly tight inside of rotor
- Use packing rod to measure height, make sure enough space for a cap inserted
- Make sure the cap is not damaged and **tightly inserted**
- Re-label the black mark at bottom of rotor if necessary

STEP 2. INSERT ROTOR INTO THE PROBE

From top of magnet, remove a special cage, black mark side down, then put cage back immediately

STEP 3. SPIN SAMPLE

Open MAS display by double click icon MAS from screen bottom, then click Insert button, then GO

Note:

- Set starting spin rate 5000, then increase to another spin-rate as you want
- Avoid using the up-limit of spin rate 15 KHz, instead, use only the spin rate you needed
- Don't keep rotor spinning when data acquiring completed, e.g. spin overnight but experiment is finished at 11 PM

STEP 4. EDIT A NEW DATA SET

Start from Data Browser panel

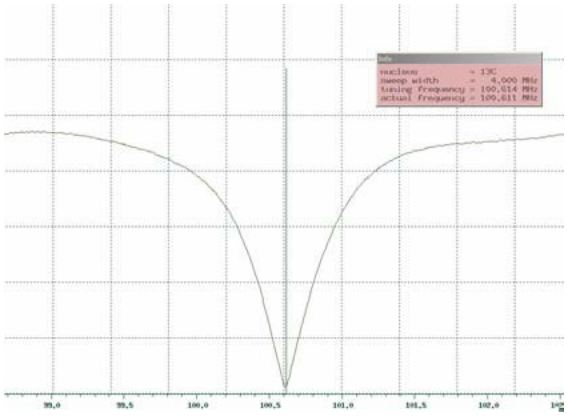
Make sure correct data saving path, i.e. /PI/netid/

You can select current parameter set or SELECT Expt

STEP 5. TUNING

Type command **wobb** or **wobb thick** to see a tuning dip (below)

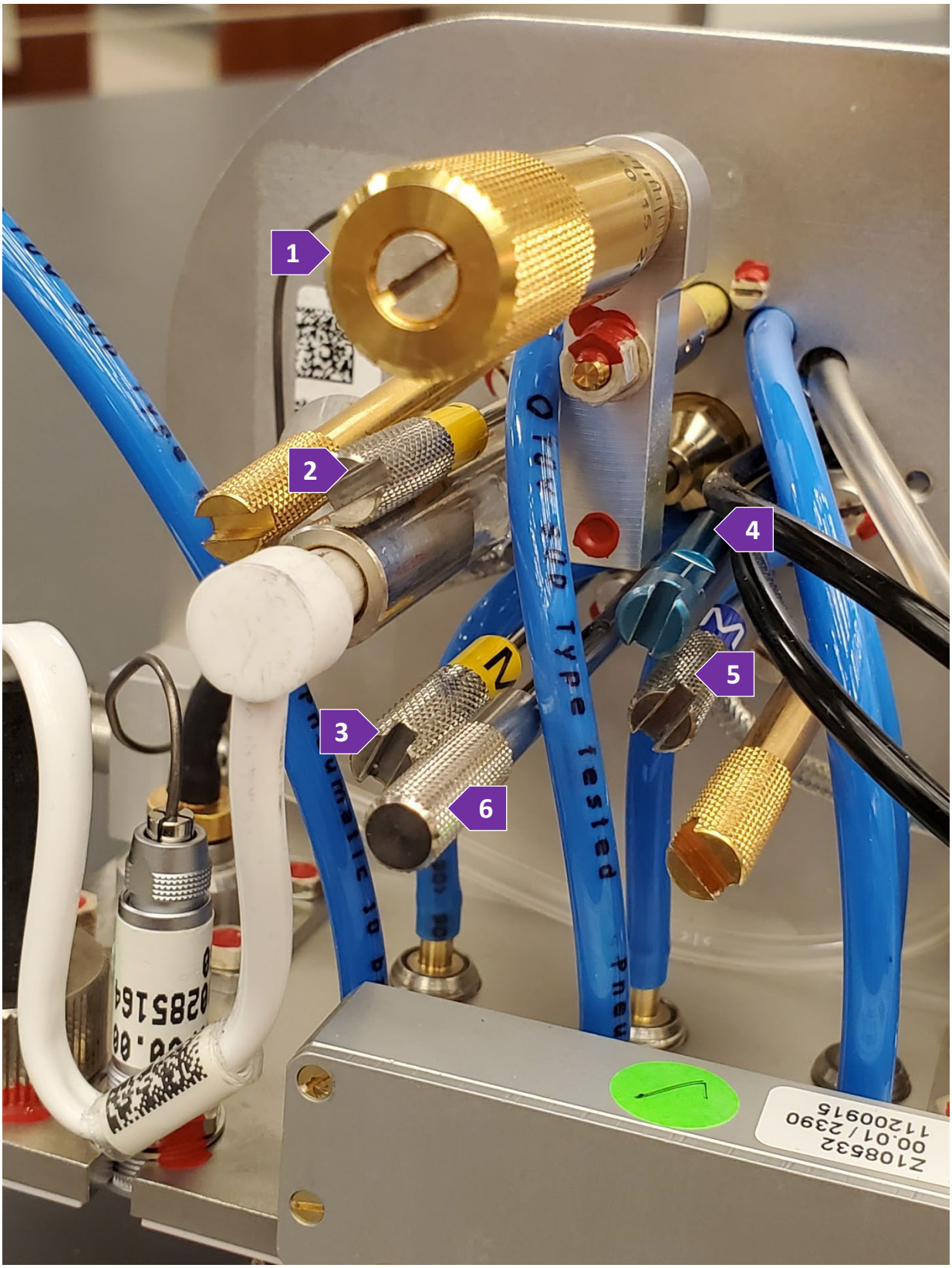
Go to the probe bottom to rotate tune/match rods for X then H (below)



- Note:
  1. It takes about 20 seconds to show the wobb signal
  2. You may change tuning scale to a large one if you don't see a tune dip
  3. Never overturned tune rods, all the moves, either rotate or up/down, should be gently
  4. For X-band switch rod (see picture below), **you may gently move it up or down**. There are three vertical positions (see chart below)

Switch Position	All the way Down	Middle	All the way Up
Freq. Range (MHz)	44 - 111	32 - 44	63 - 171
Typical Nucleus	13C	15N	31P

Diagram of 4mm Probe Tuning Rods



Note for probe tuning rods:

1. Magic Angle Adjust Rod, Golden (never touch it)
2. H-Tune Rod, yellow with a label T
3. H-Match Rod, yellow with a label M
4. X-Tune Rod, blue with a label T
5. X-Match Rod, blue with a label M
6. X-Band Switch Rod, silver color with a label X-band (move it Up or Down only)

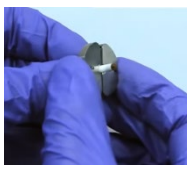
2. H-T	4. X-T
3. H-M	5. X-M

STEP 6. ACQUIRE DATA

Click AcquPar Tab to change **ns** as you want

ENDING WORK

1) Stop spinning
2) Eject rotor out of probe
3) Remove sample out of rotor by special tools and clean up the rotor
https://www.youtube.com/watch?v=bNFJj2g0UjI




-
- Note:
  a. Follow the instructions above to remove the cap

b. Use drill tool to take powder out of rotor
c. Use iso-propanol to remove powder if necessary, and dry rotor inside after

4) Keep desk top clean
5) Logout from NUcore

DATA ANALYSIS

MNova is recommended (see SOFTWARE Part). More details can be seen from the link of MNova Tutorial http://imserc.northwestern.edu/downloads/nmr-mnova_chemists8.pdf

PUBLICATION

EXPERIMENTAL SECTION

"Solid state NMR data were collected at room temperature on a Bruker Avance III 400 MHz spectrometer equipped with a 4mm HX probe." See the details of experiment section in each appendix.

ACKNOWLEDGEMENT

Add Acknowledgement info as listed under http://imserc.northwestern.edu/about-acknowledgements.html

Use was made of NMR-Hg400-solids at Northwestern University, which has received support from National Science Foundation (CHE-9871268) and International Institute for Nanotechnology (IIN).

TROUBLESHOOTING

Provide information about common mistakes users do that prevents them from starting a measurement

1. If auto-spinning fails, double check the following:
   a. Cap loose or tight
   b. Cap all the way inserted
   c. Any scratching strip on the rotor
   d. Rotor bottom black mark worn
   e. Re-pack sample

2. If auto-spinning fails and device MAS III has red lid, you can do rebooting as following:
   f. Go to the back of MAS device
   g. Switch power off and wait for 10 seconds
   h. Switch power on then wait for all lights solid green. This takes about 3 minutes.

APPENDIX A: HOW TO PACK/REMOVE SAMPLE INTO/OUT OF A ROTOR

Watch a video: https://www.youtube.com/watch?v=bNFJj2g0UjI

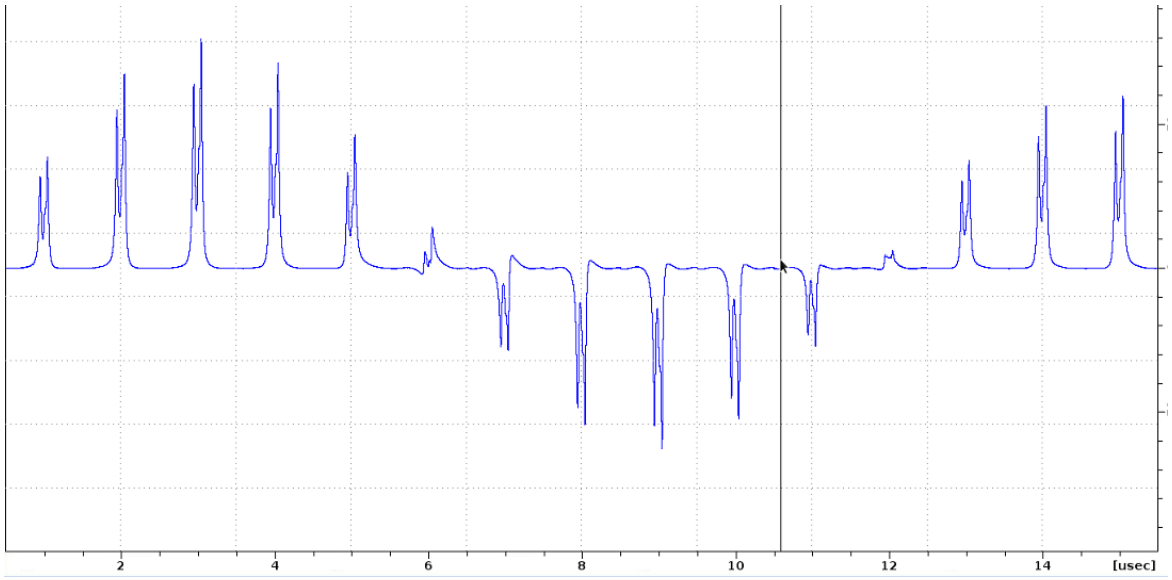
APPENDIX B: OPTIMIZATION OF PARAMETERS

Optimization of parameters in SSNMR plays a critical role in the experimental set up. The command for optimization is “popt”. Here we use an example of optimization of 90-degree pulse (nutation curve) to display the process. Similar processes can be used to optimize any parameters in experiments with command “popt”.

The calibration of 90 pulse length is important for NMR experiment, such as hahn-echo, spin quantification, recoupling pulse. It should be calibrated with the standard sample or with your sample (if your sample has significantly conductivity). The way to decide the 90-pulse length is as follows. After obtaining the 1D spectrum of standard sample or your sample, click the left mouse to select the display range of 1D spectra then type command “**dpl**”. Type command “**popt**” and open the optimization window, set the parameters as follows and click “start optimization”. You can see the optimization result from the “99X” file from the same data folder. Remember, since the power of pulse (PLW) could be different, the nutation curve is also different. For some specific NMR recoupling pulse, the power of pulse will be adjusted to find the appropriate 90 pulse.

After the determination of 90 pulse length (P90), the B_1(RF) is equal to $1/(4*P_{90})$. Here is an example of a nutation curve, the 2π pulse is about 12 μs. π/2 pulse is about 3 μs. The B_1(RF) is about 83.333 kHz.

However, if you find your nutation curve is good a good “sine” shape curve, it could be due to the insufficient recycle delay in your experiment. If so, please increase the recycling delay time.


2
4
6
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12
14
[usec]

APPENDIX C: MEASUREMENT OF T_1 AND T_2 SSNMR

INTRODUCTION

The measurements of T_1 (spin-lattice relaxation) and T_2 (spin-spin relaxation) are the basic experiment and necessary for all the SSNMR experiment. Here, we used ^1H as the example and the method could be also used for all the other nuclei.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Use adamantane as the reference sample. Run a 1D ^1H NMR spectra of the adamantane sample. Find the pi/2 pulse of ^1H NMR with adamantane.
2. Replace adamantane with your sample (Alanine as example in this manual). Run 1D ^1H NMR spectra of your sample, measure the T_1 and T_2.

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_T1_T2_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. INSERT ROTOR INTO THE PROBE AND REF THE CHEMICAL SHIFT WITH ADAMANTANE

Insert the rotor with adamantane and KBr into the probe. Spin the adamantane sample to correct spinning rate. Run a regular 1D first with “zg” file for adamantane. The major peak of adamantane should be calibrated to 1.82 ppm. Use “popt” to decide the 90-degree pulse. (see the details in Appendix B)

STEP 2. ACQUIRE THE 1D ^1H SPECTRA OF YOUR SOLID SAMPLE

Replace the adamantane rotor with your sample’s rotor (here use alanine as example). Spin your sample and open the “zg” file for solid sample, set the power “plw1” the same as in the last step for adamantane and set “P1” to the pi/2 pulse length. Then acquire a 1D ^1H spectra of your solid sample with a larger value of D1, 60s.

STEP 3. CHECK THE PAPAMETER FOR T_1 EXPERIMENT

Open the file "satrect1" with blue color, which uses saturation recovery for T_1 measurement. Set "p1" to the pi/2 pulse length and the plw1 to the same power from step 1. To ensure it works, set L20 about 50. Set D20 to be about 0.01s. Set D1 to 0.5s. You can set "ns" to the same number in step 3 for a quick experiment.

Click the left mouse to select the "E" button in the VDLIST. A window of Vd list will show up. Vd file is the file of recovery time in saturation recovery experiment.

First, save the current vd file to a new file. Second, delete everything in the new file. Third, input the first number as 0.000010 and second number as 30 in the new file. Then save the file and close edit.

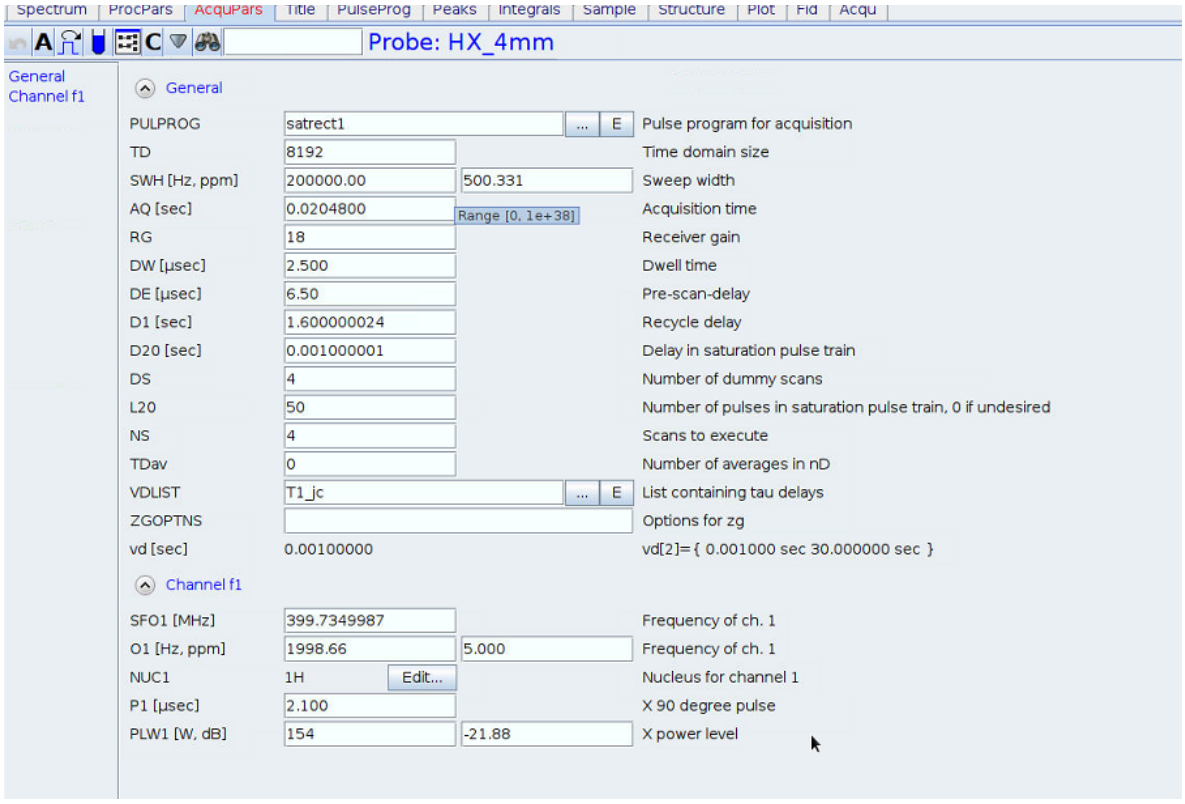
After that, click the "…" button in the vdlist. Pick the file that you just edited, chose the "set selected item in editor". Then change the number in F1 dimension to "2". After that, run the experiment.

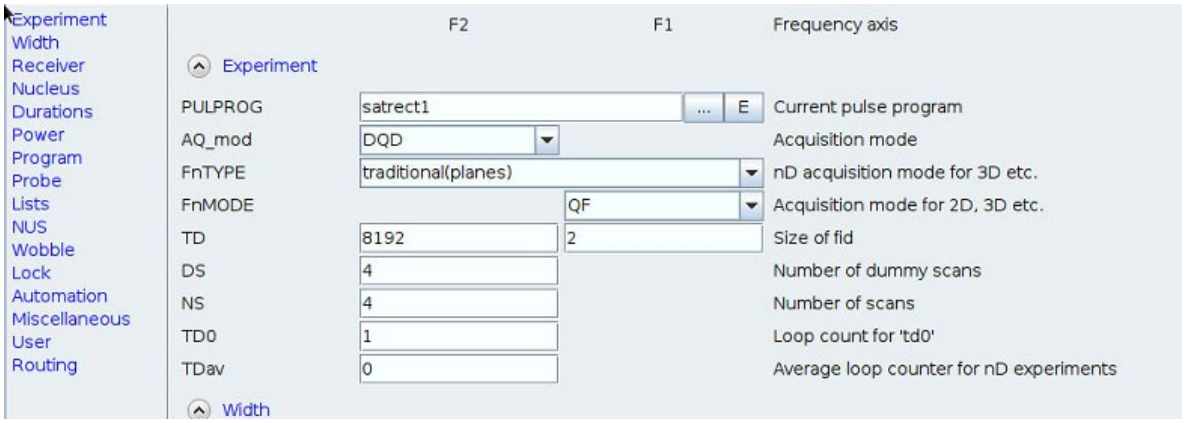
The experiment should give you two experiment data, one is for 10 us and other for 30s. Make sure there is almost no signal for 10 us spectra. If there is still significant signal, increase the L20 number and re-run.

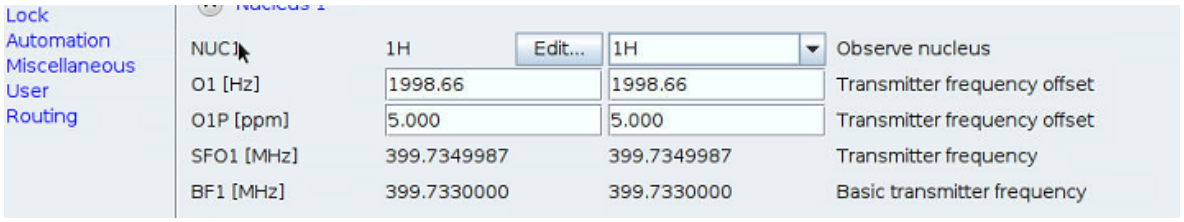
STEP 4. MEASUREMENT OF ^{1}H T_1 FOR YOUR SAMPLE

After checking step 3, you can edit the vdlist file and add a series number. From 10 us to the required long time, for example 100s. The series number in vdlist could provide a series data point in the saturation recover T_1 curve. You can change the series number in vdlist for different nuclei in different samples. Then change the number in F1 dimension to number of points in your newest vdlist.

Here is the final parameter set up of ^{1}H T_1 measurement of alanine for 4 mm probe.



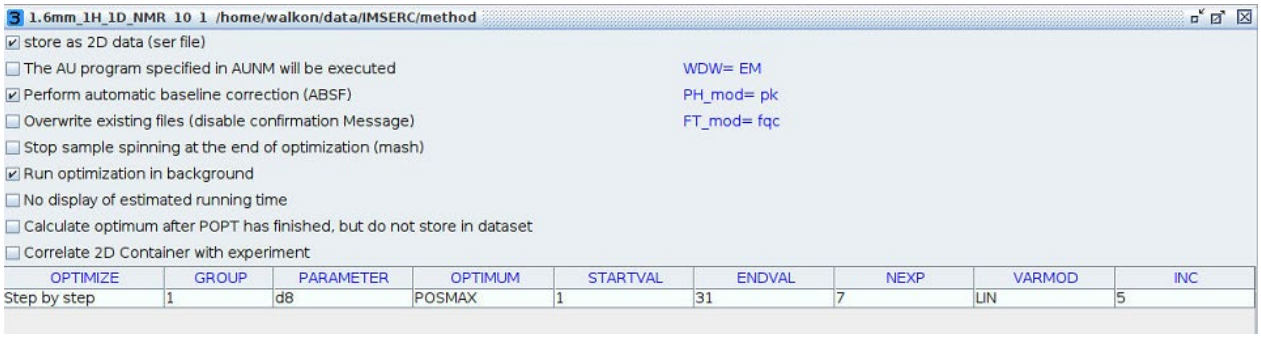




For the 1.6 mm probe, if your sample's signal is weak compared to the background, you can use the file "satrect1_echo_jc". Command type "cnst31" and set the cnst31 valve to the spinning rate. Check the

power set PLW1 to be correct valve from step 1. Set “p1” to the pi/2 pulse length and the “p2” to “pi” pulse length. Acquire the 1D 1H NMR spectra.

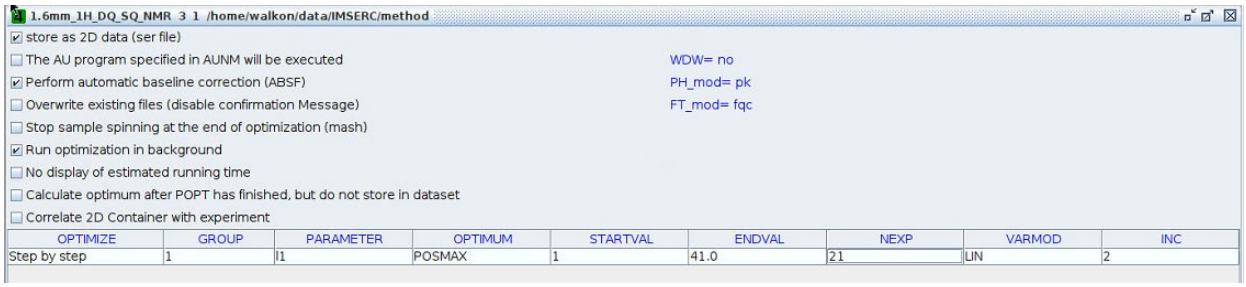
Click the left mouse to select the display range of 1D spectra then type command “**dpl**”. Use “**popt**” to observe the signal’s intensity changing with increasement of d8 valve. The 5*T1 time is the valve of d8 when the signal’s intensity almost becomes flat. You can see the optimization result from the “99X” file from the same data folder.



STEP 5. MEASUREMENT OF ^{1}H T_2 FOR YOUR SAMPLE

T_2 is the spin-spin relaxation time. Open the “hahnecho_dec_half” file for the solid sample. Type command “cnst31” and set the cnst31 valve to the spinning rate. Set “L1” to “1” and the D1 to 1.3*T1 (T1 was determined previously). Check the power set PLW1 from step 1. Set “p1” to the pi/2 pulse length. Acquire the 1D NMR spectra.

Click the left mouse to select the display range of 1D spectra then type command “**dpl**”. Type command “**popt**” to observe the signal’s intensity changing with increasement of L1 valve. The T_2 time is the valve of 2*d6 when the signal’s intensity decay around 66%. You can see the optimization result from the “99X” file from the same data folder.



STEP 6. PROCESSING T_1 AND T_2 NMR

After the acquisition of T_1 and T_2 NMR, the spectra will be saved in a topspin file format. You will need to read the T_1 and T_2 relaxation mechanism to fit the data and extract the T_1 and T_2.

https://en.wikipedia.org/wiki/Relaxation_(NMR)

APPENDIX D: $^{13}C\{^{1}H\}$ CROSS-PALARIZATION (CP) MAS NMR

INTRODUCTION

Due to the low sensitivity and long relaxation time, the direct acquisition of X nuclei is time consuming, such as ^{13}C or ^{29}Si. ^{1}H nuclei are extremely sensitive, and cross-polarization (CP) MAS NMR is a solid-state NMR experiment that transfers magnetization from ^{1}H nuclei to X nuclei through dipolar coupling. Here, we use ^{13}C as the example in the manual. It can also be used for other ½ nuclei, such as ^{31}P, ^{113}Cd, ^{77}Se, ^{29}Si etc.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Use adamantane as the ref sample. Run a 1D ^{1}H NMR spectra of the adamantane sample. Find the pi/2 pulse of ^{1}H NMR with adamantane.
2. Run 1D ^{13}C NMR spectra of adamantane. Reference the ^{13}C adamantane to 38.48 ppm.
3. Use adamantane as the standard sample. Optimize the PLW1 to find the best CP HH-matching conditions.
4. Change the sample. Run a regular 1D ^{1}H MAS NMR of your sample at a certain spin rate.
5. Run the saturation T_1 experiment and find the ^{1}H T_1 time of your sample.
6. Run $^{13}C\{^{1}H\}$ CPMAS NMR using the previously determined valve from step 3 and step 5.
7. Optimize the contacting time for your solid sample
8. Check all parameters (see detailed procedures below)
9. Acquire data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_1H_13C_CPMAS_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. INSERT ROTOR INTO THE PROBE AND REF THE CHEMICAL SHIFT WITH ADAMANTANE

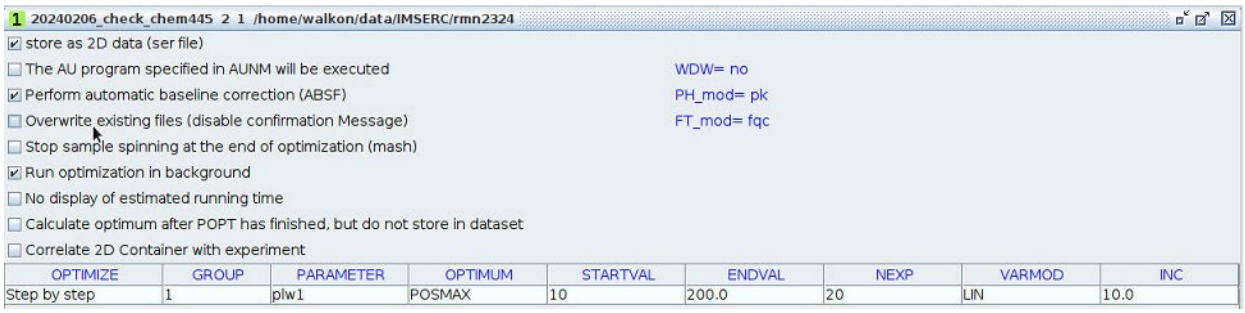
Insert the rotor with adamantane and KBr into the probe. Spin the adamantane sample to correct spinning rate. Run a regular 1D first with “zg” file for adamantane.

The major peak of adamantane should be calibrated to 1.82 ppm. Run a nutation curve (changing P1 pulse length) to find the pi/2 pulse of ^{1}H nuclei with appropriate power. Please read Appendix B.

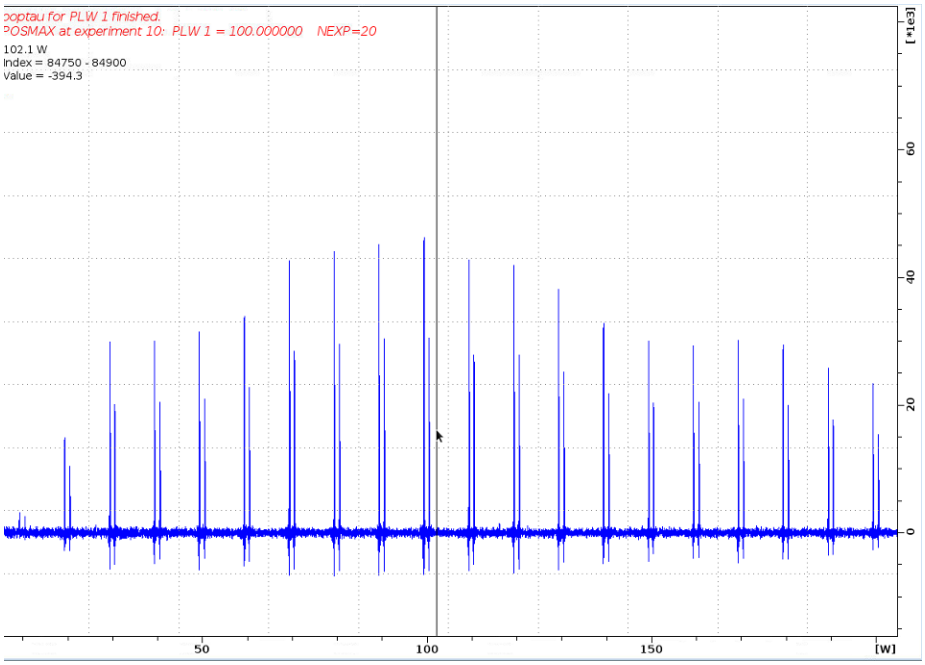
STEP 2. GET 1D $^{13}C\{^{1}H\}$ CPMAS SPECTRA AND OPTIMIZE THE CP CONDITIONS

After the 1H pi/2 pulse is determined and the adamantane is referenced, open the file "cp" file for adamantane. After tuning the probe, set the P15 to "5000" and then quickly run the spectra with 4 scans without any other optimization. Calibrated the left peak of adamantane spectra to 38.48 ppm.

After obtaining the 1D $^{13}C\{^{1}H\}$ CPMAS NMR of adamantane, you need to optimize the HH-matching conditions by changing PLW1. Click the left mouse to select the display range of 1D spectra then type command "**dpl**". Use the "popt" command to optimize PLW1. See the details in Appendix B. You can see the optimization result from the "99X" file from the same data folder.



Here is an example of optimization of PLW1 for CPMAS NMR of alanine with 4 mm probe. The best PLW1 valve should be 100.



Once your CP matching condition is optimized, you can use the CP condition repeatedly.

STEP 3. ACQUIRE THE 1D ^{1}H SPECTRA OF YOUR SOLID SAMPLE

Replace the adamantane rotor with your sample's rotor. Spin your sample and open the "zg" file for solid sample. Set the power "plw1" the same as last step for adamantane" and "P1" to the pi/2 pulse length. Then acquire a 1D ^{1}H spectra of your solid sample.

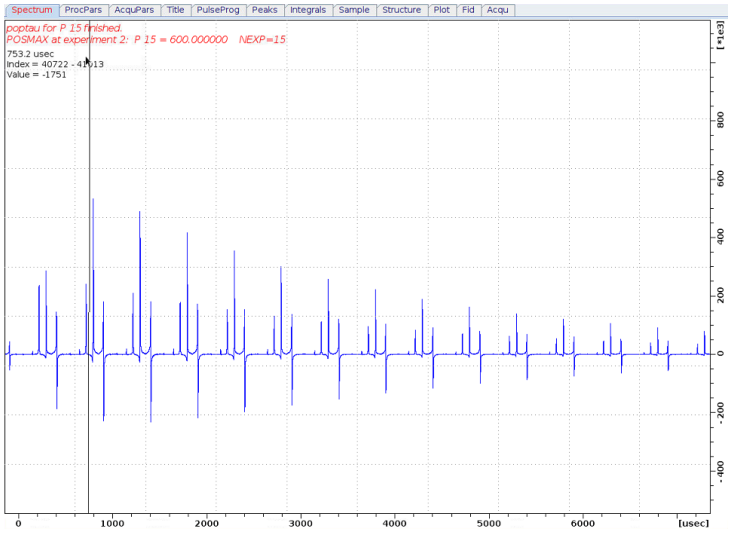
STEP 4. DETERMINE THE T_1 TIME OF YOUR SAMPLE

Read the manual for T_1 measurement and measure the ^{1}H T_1 value of your sample

STEP 5. ACQUIRE 1D ^{13}C{^{1}H} CPMAS NMR OF YOUR SAMPLE

After the determination of T_1 valve, Open the 1D cp file "cp" file for solid sample. Set the PLW1 from optimization of step 3. Set "D1" to "1.3*T_1", where T_1 is determined from step 5. Set PLW12 and P3 for ^{1}H as determined in Step 2. Set p15 to 1000 and quickly run the 1D ^{13}C{^{1}H} CPMAS for your sample with reasonable scans number. After that, click the left mouse to select the display range of 1D spectra then type command "**dpl**". Type command "**popt**" to optimize p15 (see the details of "popt" optimization in Appendix B). By optimization, you should find the signal's intensity should increase with increasement of p15 valve. You can see the optimization result from the "99X" file from the same data folder.

Here is an example of optimization of p15 for the alanine. From this optimization, p15 is chosen as the strongest signal intensity.



Here is the final parameter set up of $^{13}C\{^{1}H\}$ CPMAS of alanine after p15 optimization for 4 mm probe.

Channel f1			
SFO1 [MHz]	100.5229943		Frequency of ch. 1
O1 [Hz, ppm]	10051.29	100.000	Frequency of ch. 1
NUC1	13C Edit...		Nucleus for channel 1
P15 [µsec]	600.000		Contact time at PLW1(f1) and SPW0(f2)
PLW1 [W, dB]	100	-20.00	X power level during contact
Channel f2			
SFO2 [MHz]	399.7349987		Frequency of ch. 2
O2 [Hz, ppm]	1998.66	5.000	Frequency of ch. 2
NUC2	1H Edit...		Nucleus for channel 2
CNST21	1.0000000		on resonance, usually = 0
CPDPRG 2	spinal64 ... E		E.g. cw, spinal64 (at PLW12)
P3 [µsec]	2.100		Proton 90 at power level PLW12
PCPD2 [µsec]	4.00		Pulse length in decoupling sequence (e.g. 180deg)
PLW2 [W, dB]	154.07	-21.88	=0W, not used
PLW12 [W, dB]	154.07	-21.88	Decoupling power level (if not PLW13)
SPNAM 0	ramp50100.100 ... E		Use e.g. ramp.100 or ramp90100.100 for variable amplitude CP
SPOAL0	0.500		Phase alignment of freq. offset in SP0
SPOFFS0 [Hz]	0		Offset frequency for SP0
SPW0 [W, -dBW]	100	-20.00	Proton power level during contact

STEP 6. ACQUIRE DATA

After setting up everything, run the 1D CPMAS NMR with more scans.

APPENDIX E: $^{13}C\{^{1}H\}$ MULTIPLECP NMR

INTRODUCTION

CPMAS NMR is an advanced solid-state NMR Experiment. However, CPMAS is not quantitively due to the different dipolar coupling among different ^{1}H-X nuclei spin pair. To get a quantitative CPMAS, multiple CPMAS NMR is developed. Here, we used ^{13}C as the example in the manual.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Follow the CPMAS NMR manual to optimize the parameters for the CPMAS. Find the pi/2 pulse of ^{13}C nuclei.
2. Check all parameters for your samples with multiple CPMAS.
3. Acquire data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_1H_13C_multipleCP_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. BASIC 1D $^{13}C\{^{1}H\}$ CPMAS NMR

Read the 1D $^{13}C\{^{1}H\}$ CPMAS NMR manual and optimize the parameters for $^{13}C\{^{1}H\}$ CPMAS with adamantane.

STEP 2. FIND THE PI/2 PULSE OF ^{13}C

After step 1, use adamantane sample to find the pi/2 pulse of ^{13}C. Run the file of “zg” file for ^{13}C. Set the power of p1 pulse (PLW1) to almost the maximum power of the probe. Use “popt” to decide the 90-pulse of ^{13}C, see the details in Appendix B.

STEP 3. MEASURE THE ^{1}H T1 VALVE OF YOUR SAMPLE

Replace the adamantane rotor with your sample's rotor, spin your sample. Follow the manual for T_1 measurement and measure the ^{1}H T_1 value of your sample.

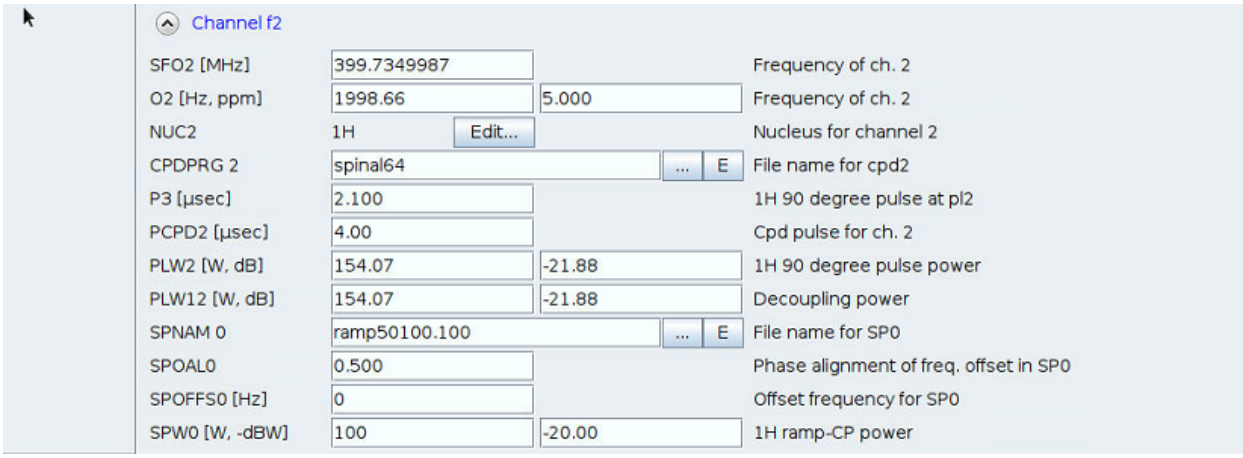
STEP 4. SET THE PARAMETERS FOR THE 1D ^{13}C{^{1}H} MULTIPLE CPMAS NMR

Open the "multicp.jc" file. Confirm the HH matching condition, set D1 to 1.3*T1 from step 3. Set D11 to 2*T1 from step 3. Set PLW11 and p1 to pi/2 from step 2. Set P15 to be either 500 us or 1000 us.

There is an also saturation pulse in the beginning of the pulse. To ensure it works, please set L5 to be larger than 20.

Here is an example of parameters about 1D ^{13}C{^{1}H} multiple CPMAS NMR when spinning rate is 14000 Hz with 4 mm probe.

TD	4096		Time domain size
SWH [Hz, ppm]	100000.00	994.797	Sweep width
AQ [sec]	0.0204800		Acquisition time
RG	203		Receiver gain
DW [µsec]	5.000		Dwell time
DE [µsec]	6.50		Pre-scan-delay
D1 [sec]	1.000000000		Recycle delay
D11 [sec]	1.000000000		Inter-CP delay
DS	4		Number of dummy scans
L0	7		Number of CP loops prior to the final contact
L5	10		Number of presaturation pulses
NS	1024		Scans to execute
d11d2 [sec]	0.50000000		d11d2=d11/2
Channel f1			
SFO1 [MHz]	100.5229943		Frequency of ch. 1
O1 [Hz, ppm]	10051.29	100.000	Frequency of ch. 1
NUC1	13C Edit...		Nucleus for channel 1
P1 [µsec]	3.650		X 90 degree pulse at pl11
P15 [µsec]	500.000		Contact time
PLW1 [W, dB]	100	-20.00	X CP power
PLW11 [W, dB]	100	-20.00	X 90 degree pulse power



After setting up the initial parameters, run an optimization of L0. You will find the signal intensity almost constant when you achieve the appropriate L0 number.

If possible, a 90 pulse MAS NMR of your sample will be also performed and compared with the multiple CPMAS spectra. This will confirm the successfully set up of multiple CPMAS NMR.

STEP 5. ACQUIRE DATA

After the optimization of L0 number, use the command “wrpa #” (# is the experiment number) to create a new file. Set the L0 with the optimized number in the new file and run the 1D $^{13}C\{^{1}H\}$ multiple CPMAS NMR.

APPENDIX F: ^{29}SI{^{1}H} CPMAS WITH CPMG NMR

INTRODUCTION

CPMAS NMR is an advanced solid-state NMR Experiment. However, the low sensitivity of certain nuclei, such as ^{29}Si, could be still a challenge for the common CPMAS acquisition. Thus, Carr-Purcell-Meiboom-Gill (CPMG) could be used to boost the signal-to-noise (SNR) and save experiment time.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Follow the CPMAS NMR manual to optimize the parameters for the CPMAS. Find the pi pulse of ^{29}Si nuclei.
2. Check all parameters for your samples with CPMG.
3. Acquire data
4. Process data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_1H_29Si_CPMG_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. BASIC 1D ^{29}SI{^{1}H} CPMAS NMR

Spin the standard ^{29}Si standard sample rotor, TKS (tetrakis(trimethylsilyl)silane, $Si(Si(CH_3)_3)_4$). Use the current existing ^{29}Si{^{1}H} CPMAS file to optimize the parameters for ^{29}Si{^{1}H} CPMAS, such as HH matching conditions. Run the 1D ^{29}Si{^{1}H} CPMAS NMR of the TKS sample. The peak of TKS is at -9.8 ppm.

STEP 2. FIND THE PI PULSE OF ^{29}SI

After step 1, use TKS sample to find the pi pulse of ^{29}Si. Run the “zg” file for TKS. Use “popt” to decide the 90-pulse of ^{29}Si. See the details in Appendix B.

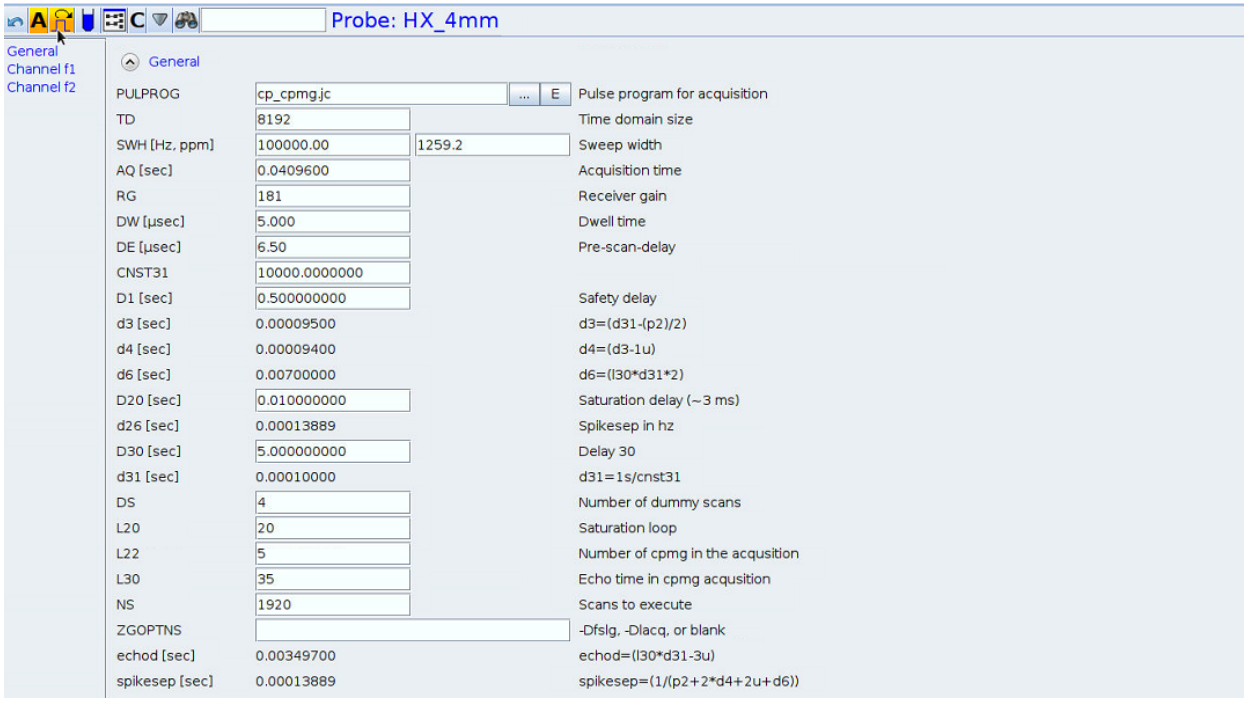
STEP 3. SET THE PARAMETERS FOR THE 1D ^{29}SI{^{1}H} CPMAS CPMG NMR

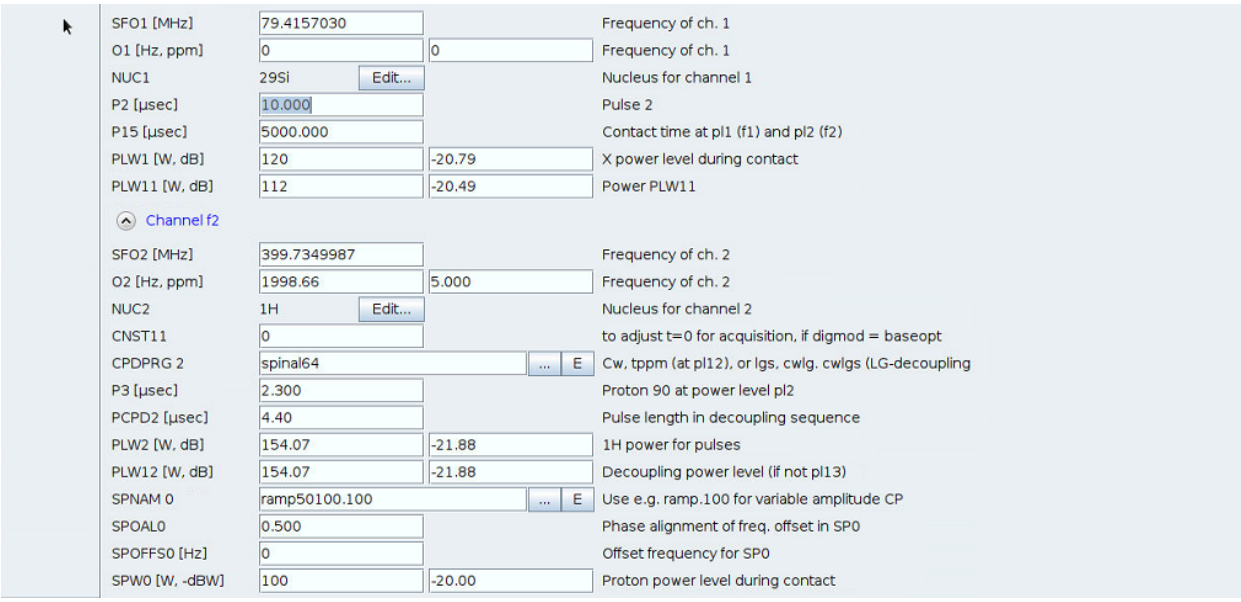
Replace the TKS rotor with your sample's rotor, and spin your sample. Open the previous "cp_cpmg.jc" file. Confirm the HH matching condition to be same as step 1. Change the p15 valve to 5 ms, change D30 to 5s. change cnst31 to the spinning rate, set D1 to 0.5s.

To successfully run CPMG, change L30 to ensure d26 is about 100 Hz. Then change the L22 to ensure the L22* (1/d26) < AQ. Meanwhile, check the plw11 and p2 for the pi pulse (180 degree) pulse from step 2.

There is an also saturation pulse at the beginning of the pulse. To ensure it works, please set L20 to be larger than 20 and D20 to be around 5 or 10 ms.

Here is an example of parameters about 1D ^{29}Si{^{1}H} CPMAS CPMG NMR of silicate when spinning rate is 10000 Hz with 4 mm probe.





SFO1 [MHz]	79.4157030		Frequency of ch. 1
O1 [Hz, ppm]	0	0	Frequency of ch. 1
NUC1	29Si Edit...		Nucleus for channel 1
P2 [µsec]	10.000		Pulse 2
P15 [µsec]	5000.000		Contact time at pl1 (f1) and pl2 (f2)
PLW1 [W, dB]	120	-20.79	X power level during contact
PLW11 [W, dB]	112	-20.49	Power PLW11
Channel f2			
SFO2 [MHz]	399.7349987		Frequency of ch. 2
O2 [Hz, ppm]	1998.66	5.000	Frequency of ch. 2
NUC2	1H Edit...		Nucleus for channel 2
CNST11	0		to adjust t=0 for acquisition, if digmod = baseopt
CPDPRG 2	spinal64 ... E		Cw, tppm (at pl12), or lgs, cwlg. cwlgs (LG-decoupling
P3 [µsec]	2.300		Proton 90 at power level pl2
PCPD2 [µsec]	4.40		Pulse length in decoupling sequence
PLW2 [W, dB]	154.07	-21.88	1H power for pulses
PLW12 [W, dB]	154.07	-21.88	Decoupling power level (if not pl13)
SPNAM 0	ramp50100.100 ... E		Use e.g. ramp.100 for variable amplitude CP
SPOAL0	0.500		Phase alignment of freq. offset in SP0
SPOFFS0 [Hz]	0		Offset frequency for SP0
SPW0 [W, -dBW]	100	-20.00	Proton power level during contact

STEP 4. ACQUIRE DATA

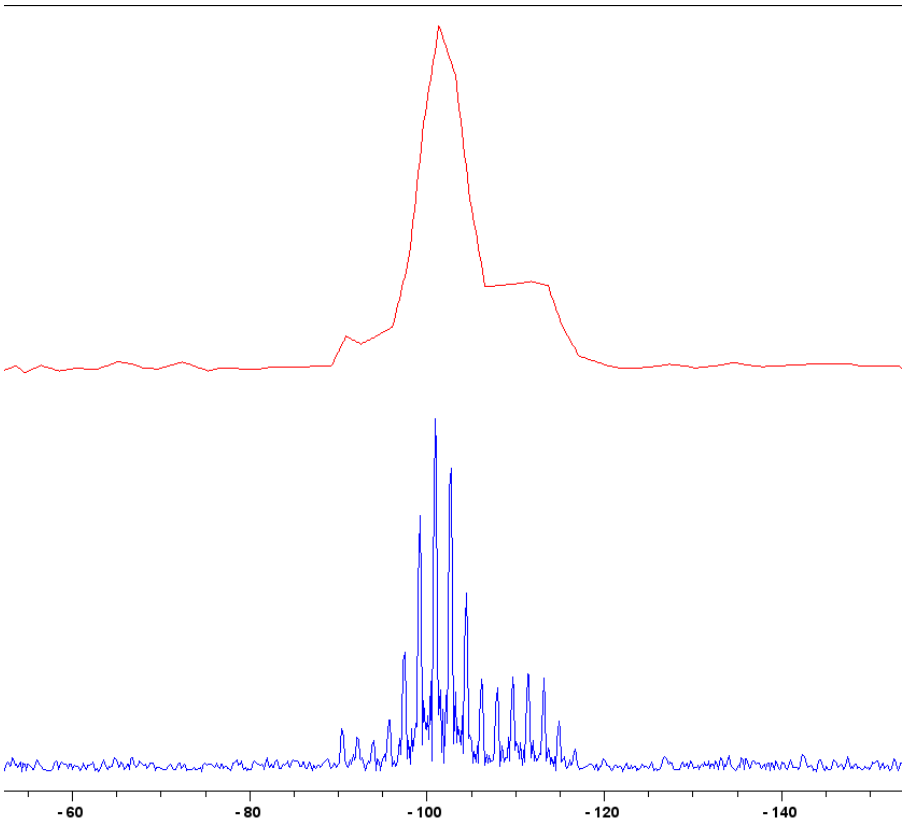
After setting up everything, run the 1D $^{29}Si\{^{1}H\}$ CPMAS CPMG NMR.

STEP 5. PROCESSING CPMG NMR

After the acquisition of CPMAG CPMG NMR, the spectra will be saved in a topspin file format.

You need to regenerate the spectra by UWNMRSpectraShape. The software can be downloaded from the following: https://www.imc.cas.cz/en/research/research-departments/structure-and-dynamics-of-macromolecules/structural-analysis/software. The regenerated spectra can be saved as topspin data format.

Here is an example of parameters about 1D $^{29}Si\{^{1}H\}$ CPMAS CPMG NMR of silicate when spinning rate is 10000 Hz with 4 mm probe before (blue) and after spectra regeneration by UWNMRSpectraShape (red).


-60
-80
-100
-120
-140

APPENDIX G: $^{13}C\{^{1}H\}$ HETERONUCLEI CORRELATION (HETCOR) MAS NMR

INTRODUCTION

In addition, the correlation 2D NMR between ^{1}H and X nuclei will provide more information to elucidate the local structure. HETCOR is one of those 2D NMR based on CPMAS.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Follow the ^{1}H-^{13}C CPMAS NMR manual. Optimize all the parameters for the CPMAS and obtain the 1D CPMAS NMR spectra of your solid sample.
2. Check all parameters for 2D HETCOR NMR (see detailed procedures below)
3. Acquire data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_1H_13C_HETCOR_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command "edc" to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. BASIC 1D $^{13}C\{^{1}H\}$ CPMAS NMR FOR ALANINE

Spin the standard ^{13}C enriched alanine sample rotor. Read the 1D $^{13}C\{^{1}H\}$ CPMAS NMR manual and optimize the parameters for CPMAS, such as HH matching conditions. Run the 1D $^{13}C\{^{1}H\}$ CPMAS NMR of the alanine sample.

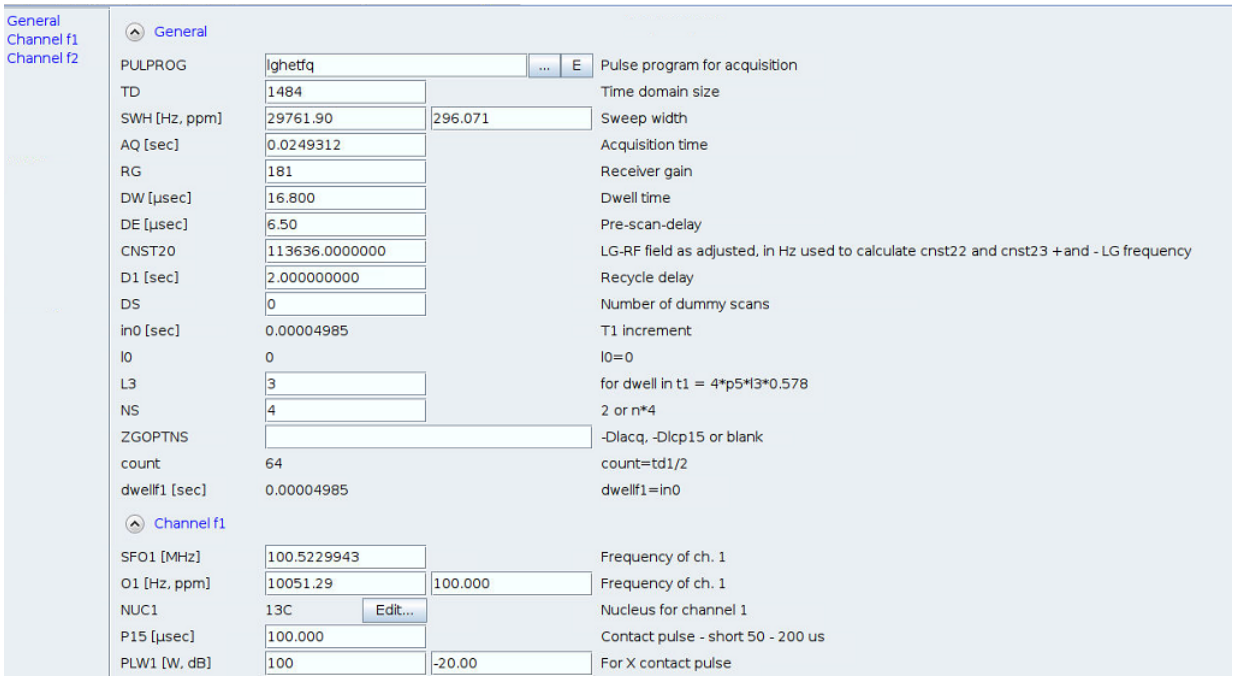
STEP 2. SET THE PARAMETERS FOR THE 2D HETCOR NMR

After acquiring the 1D $^{13}C\{^{1}H\}$ CPMAS NMR spectra of alanine, Open the 2D HETCOR file "lghetfq" with blue color. Set "D1" to "1.3*T_1". (2s is enough). Set L3 to a number between 2 and 4 (here we use 3). Set p15 to 100 µs. Ensure that plw1, spw0, and plw12 are the same as the 1D CPMAS NMR. Set plw13 to be same as plw12. **Set cnst20=1/4/p3, this is very important. If the cnst20 is not set correctly, a scale factor will show and interfere with the ^{1}H chemical shift.** Set cnst24: -2000.

Set the F1 dimension window increment to be same as in0. Set the F1 dimension step as 128 steps. Set Fnmode to "States-TPPI."

Click "ProcPars." Set the F1 dimension WDW to "EM," set PH_mod to "ph," and set MC2 to "states-TPPI."

Here is an example of parameters about 2D $^{13}C\{^{1}H\}$ HETCOR NMR of alanine when spinning rate is 15000 Hz with 4 mm probe.



General
Channel f1
Channel f2

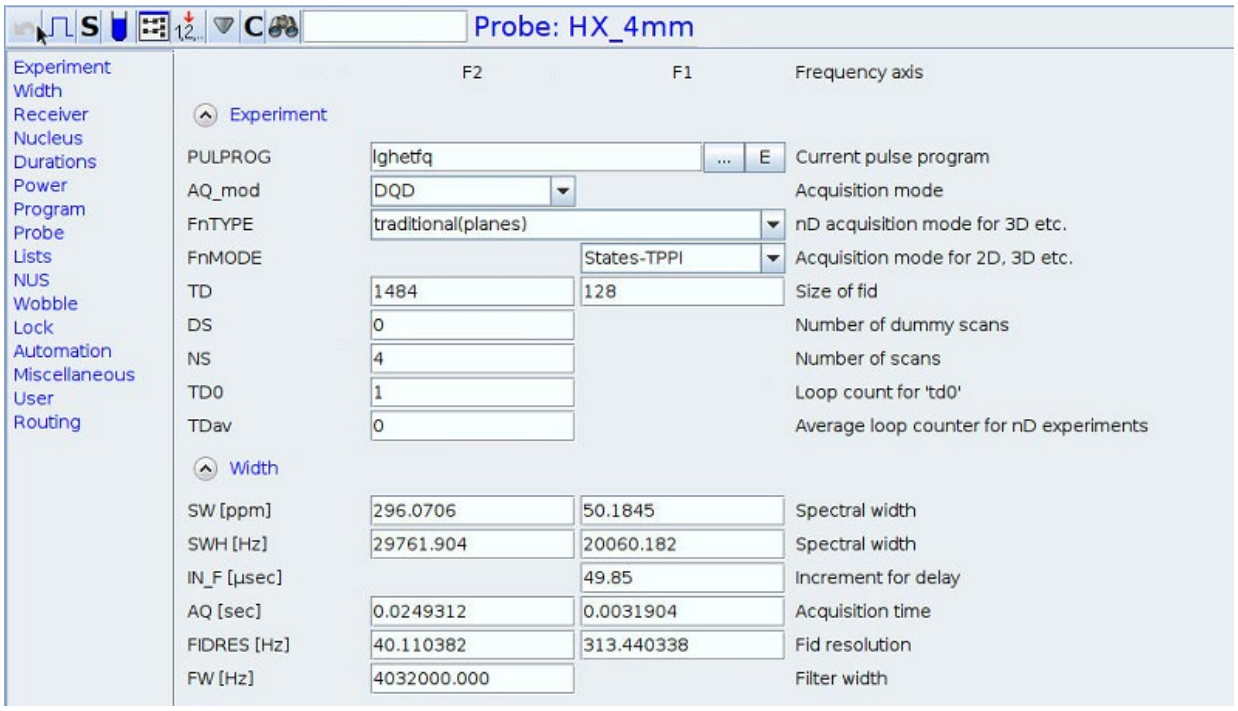
General

PULPROG	lghetfq ... E		Pulse program for acquisition
TD	1484		Time domain size
SWH [Hz, ppm]	29761.90	296.071	Sweep width
AQ [sec]	0.0249312		Acquisition time
RG	181		Receiver gain
DW [µsec]	16.800		Dwell time
DE [µsec]	6.50		Pre-scan-delay
CNST20	113636.0000000		LG-RF field as adjusted, in Hz used to calculate cnst22 and cnst23 +and - LG frequency
D1 [sec]	2.000000000		Recycle delay
DS	0		Number of dummy scans
in0 [sec]	0.00004985		T1 increment
l0	0		l0=0
L3	3		for dwell in t1 = 4*p5*l3*0.578
NS	4		2 or n*4
ZGOPTNS			-Dlacq, -Dlcp15 or blank
count	64		count=td1/2
dwellf1 [sec]	0.00004985		dwellf1=in0

Channel f1

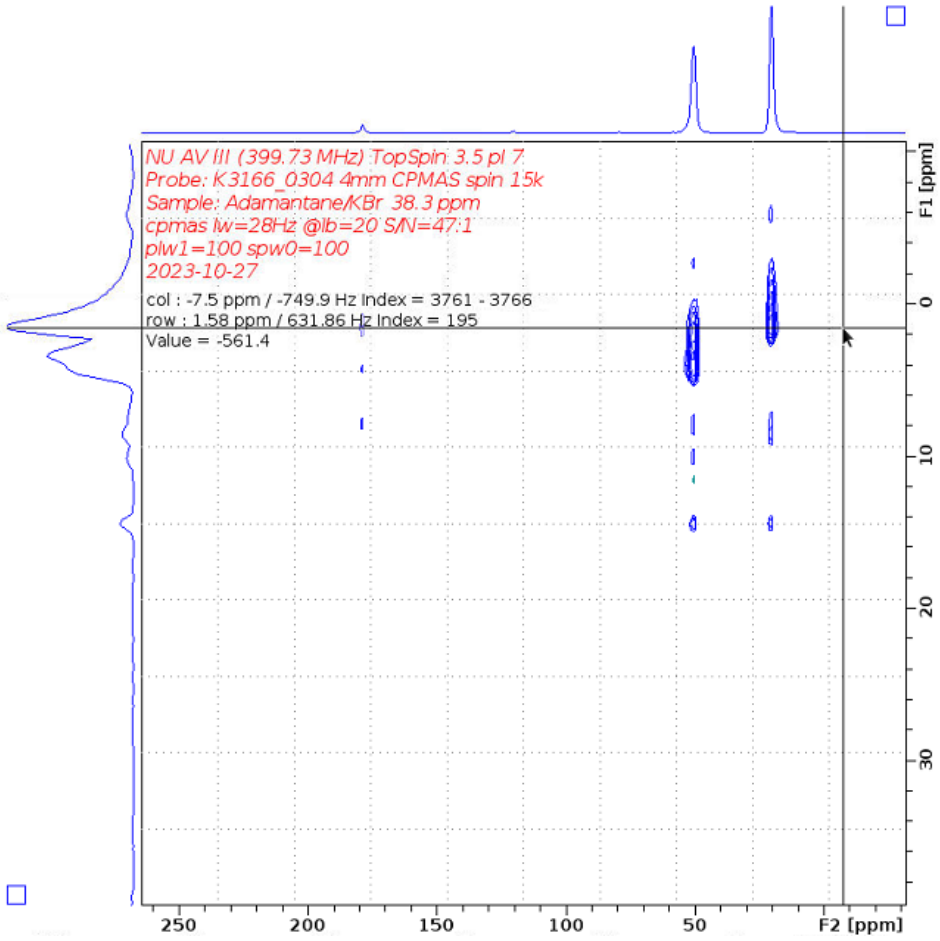
SFO1 [MHz]	100.5229943		Frequency of ch. 1
O1 [Hz, ppm]	10051.29	100.000	Frequency of ch. 1
NUC1	13C Edit...		Nucleus for channel 1
P15 [µsec]	100.000		Contact pulse - short 50 - 200 us
PLW1 [W, dB]	100	-20.00	For X contact pulse

SFO2 [MHz]	399.7374774		Frequency of ch. 2
O2 [Hz, ppm]	4477.41	11.201	Frequency of ch. 2
NUC2	1H Edit...		Nucleus for channel 2
CNST11	0		to adjust t=0 for acquisition, if digmod = baseopt
cnst21	0		cnst21=0
cnst22	78352.789062		+LG frequency offset
cnst23	-82352.789062		-LG frequency offset
CNST24	-2000.0000000		Offset for proton evolution under LG, usually 0 - -2000
CPDPRG 2	spinal64 ... E		Tppm15, SPINAL64
P3 [µsec]	2.200		90 degree 1H pulse excitation
p5 [µsec]	7.19		FSLG 2pi pulse set by lgcalc.incl
PCPD2 [µsec]	4.20		Pulse length in decoupling sequence
PLW2 [W, dB]	0	1000.00	=120dB, not used
PLW12 [W, dB]	180	-22.55	For decoupling and excitation 1H
PLW13 [W, dB]	180	-22.55	For homonuclear decoupling
SPNAM 0	ramp70100.100 ... E		Shape for contact pulse ramp.100
SPOAL0	0.500		Phase alignment of freq. offset in SP0
SPOFFS0 [Hz]	0		Offset frequency for SP0
SPW0 [W, -dBW]	115	-20.61	Proton power level during contact
pul54 [µsec]	1.34		pul54=(p3*547)/900



STEP 3. ACQUIRE THE 2D $^{13}C\{^{1}H\}$ SPECTRA OF ALANINE

After setting the parameters for the 2D $^{13}C\{^{1}H\}$ spectra of alanine, run a quick 2D NMR spectrum. Adjust the ^{1}H offset, to move the proton spectra to the upper half of the F1 dimension. The contour in the center of F1 dimension is an article signal from imperfect phase cycle or pulse. Here is an example of the 2D $^{13}C\{^{1}H\}$ HETCOR spectra of alanine with previous set up in step 2.



STEP 4. ACQUIRE THE 1D ^{1}H SPECTRA OF YOUR SOLID SAMPLE

Replace the alanine rotor with your sample's rotor and spin your sample. Open the previous 1D CPMAS NMR file of alanine after the optimization, run the 1D $^{13}C\{^{1}H\}$ CPMAS NMR of your sample. After that, optimize the contacting time p15 for your sample with "popt".

STEP 5. MEASURE THE ^{1}H T1 VALVE OF YOUR SAMPLE

Follow the manual for T_1 measurement, and measure the ^{1}H T_1 value of your sample.

STEP 6. ACQUIRE THE 2D $^{13}C\{^{1}H\}$ SPECTRA OF YOUR SAMPLE

After the previous step, you can quickly set up 2D NMR for your sample. Open the previous 2D $^{13}C\{^{1}H\}$ spectra file of alanine and use command "wrpa #" to create a new file with same parameters (# is the

number of experiment file). Go to the new 2D file, change the p15 valve from step 4, change D1 to 1.3*T_1 from step 5. Change scans times (ns) according to your sample's sensitivity.

STEP 7. ACQUIRE DATA

After setting up everything, run the 2D $^{13}C\{^1H\}$ HETCOR NMR.

To better understand the correlation between ^1H and ^{13}C, experiments with different contacting times are important. For example, if p15 is set to 25 us, you will only find the correlation with direct sigma bond length. If p15 is set to longer time, such as 2000 us, you will observe longer distance correlations. **Usually, 2D NMR with two different correlation time should be obtained: one with the optimal p15 time from step 4 and another with a short correlation time, such as 100 or 50 us.**

After the acquisition of 2D NMR, the spectra will be saved in a topspin file format. You can process the data in topspin by "xfb".

Since the 2D HETCOR spectra of alanine and your solid sample use same parameters, you can use the alanine ^1H as a reference. The first ^1H peak of alanine is about 1.46 ppm. You can use the calibrate function to calibrate the chemical shift in F1 diememsion.

APPENDIX H: ^{13}C-{^{1}H} HETERONUCLEI MULTIPLE QUANTUM COHERENCE (HMQC) NMR

INTRODUCTION

2D HETCOR NMR between ^{1}H and X (s=1/2) nuclei will provide more information to elucidate the local structure. However, due to the nature of quadrupolar nuclei, applying CP to quadrupolar nuclei is challenging. Heteronuclear Multiple Quantum Coherence (HMQC) with ^{1}H detection is a powerful technique to detect the correlation among nuclei, complementing the normal HETCOR. Here, we used ^{1}H-^{13}C as the example in the manual. However, this technique can be applied to multiple nuclei.

PREPARATION

1. Probe: 1.6 mm probe is preferred due to its fast spinning and the high resolution in ^{1}H spectra.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Use Alanine as the standard sample to set up the HMQC. Optimize the parameters for the 1D HMQC, especially the RF power of recoupling pulse
2. Run 2D HMQC of alanine to confirm that everything is correct.
3. Follow the T_1 measurement manual and get the ^{1}H T_1 value of your solid sample
4. Optimize the RF power for X nuclei in your sample
5. Set up the 2D HMQC parameters for your solid sample
6. Acquire data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_1H_13C_HMQC_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. REF THE CHEMICAL SHIFT WITH ALANINE AND POWER OPTIMIZATION

Insert the rotor with ^{13}C enriched alanine. Spin the sample to correct spinning rate, for example 35 kHz. Run a regular 1D ^{1}H spectra first with “zg” file for alanine.

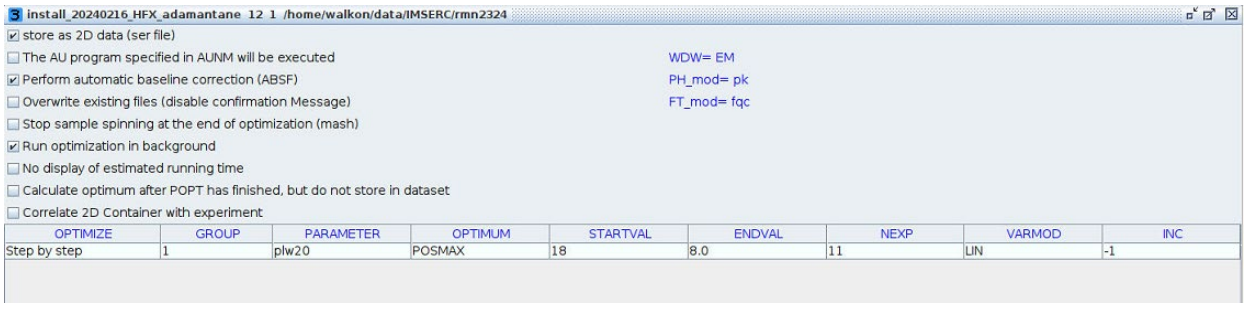
The right peak of the alanine should be calibrated to 1.46 ppm. After obtaining the 1D spectrum of alanine, run a nutation curve (changing P1 pulse length) to find the pi/2 pulse of ^{1}H nuclei. Set the power of p1 pulse (PLW1) to almost the maximum power of the probe. See the details of nutation curve in Appendix B.

STEP 2. OPTIMIZATION OF THE SR4 RECOUPLING

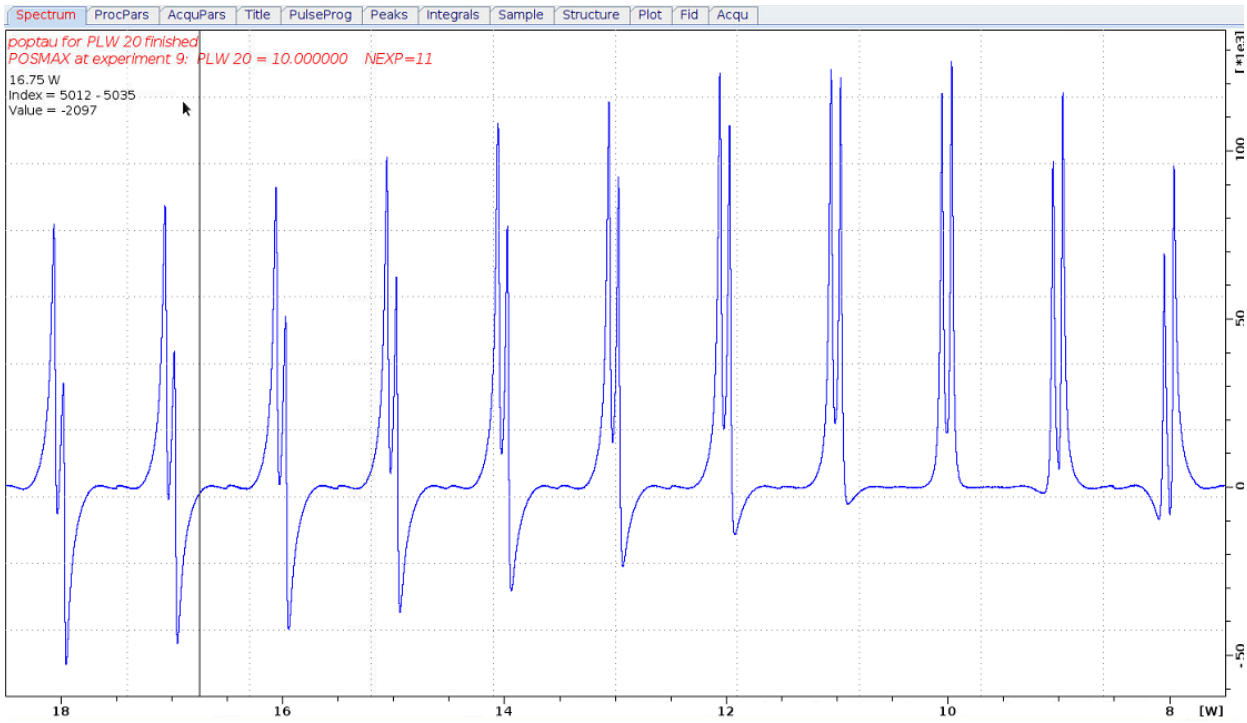
Open the file "1H.SR4.spinlock.jc" for the alanine. Set the determined plw1 and p1 from step 1. Type command "cnst31" and set it to the spinning rate, for example 35 kHz. Then the P4 should be 7.14 us. (0.25*1s/cnst31). P4 is the pi pulse for the SR4 recoupling.

To achieve the recoupling successfully, you need to set the power PLW20 correctly to achieve a pi pulse of 7.14 us for ^{1}H nuclei. Thus, you need to get back to step 1. Use the "zg" file for alanine. Decrease the PLW1 to a much lower power and re-run the nutation curve until you find the appropriate power for ^{1}H recoupling pulse.

After you found the rough power, return to the "1H.SR4.spinlock.jc" file, set the plw20 and quickly run the experiment. After that, Click the left mouse to select the display range of 1D spectra then type command "**dpl**". Type command "**popt**" and open the optimization window, set the parameters as follows and click "start optimization" to find the best plw20 for SR4 recoupling.



Here is an example of the optimization of plw20 for alanine spinning at 35 kHz.



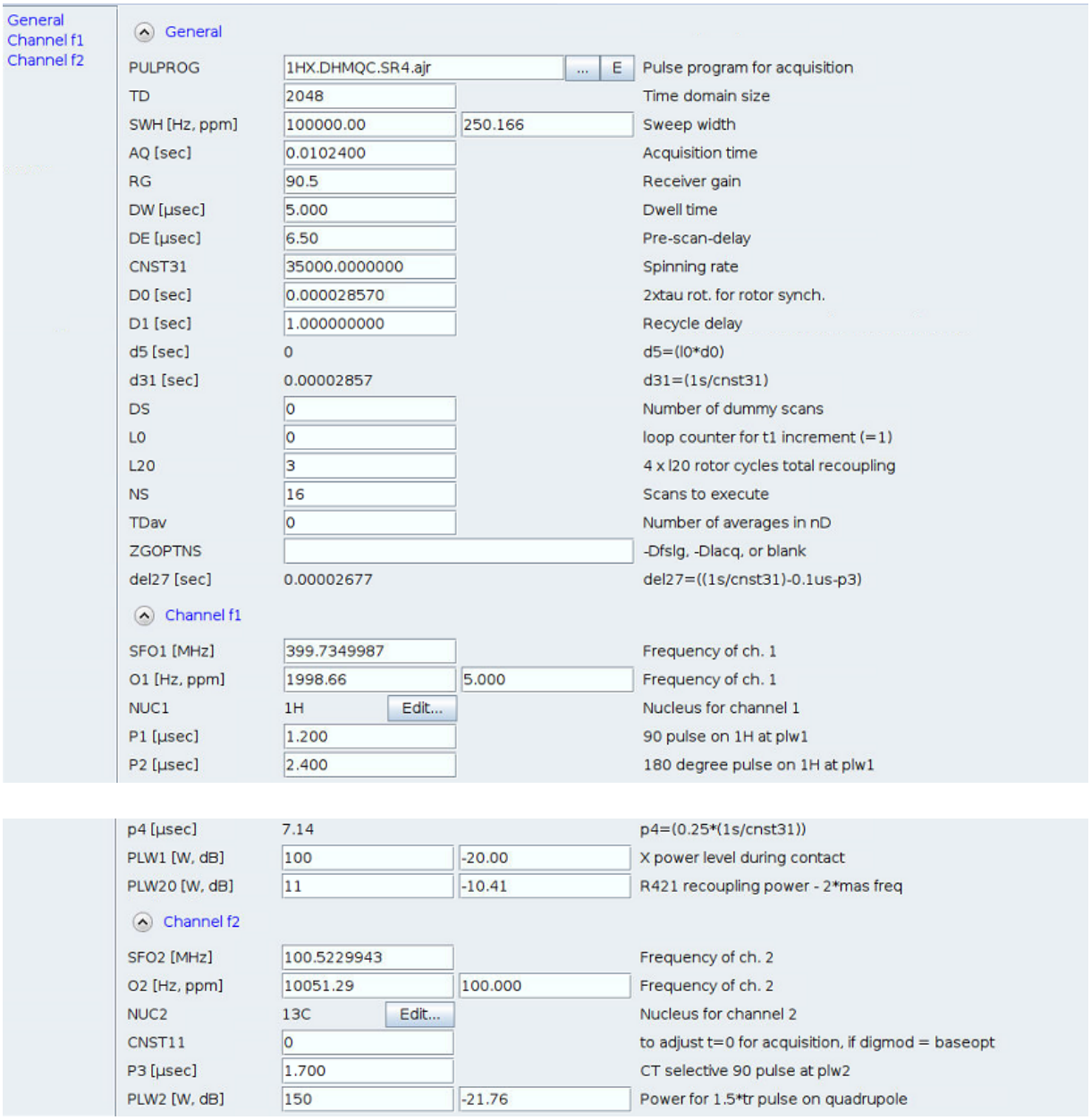
STEP 3. SET THE PARAMETERS FOR 2D ^{1}H-^{13}C HMQC NMR

Open the 2D HMQC file "1HX.DHMQC.SR4.jc" with blue color for alanine. Set plw1, p1 and p2 value from step 1. Set plw20 value from step 2. Set cnst31 to the spinning rate. Set D0 to 2*1s/cnst31 or 1s/cnst31.

Set the F1 dimension window increment to be same as d0. Set the F1 dimension step as 128 steps. Set Fnmode to "States-TPPI."

Click "ProcPars." Set the F1 dimension WDW to "EM," set PH_mod to "ph," and set MC2 to "states-TPPI."

Here is an example of parameters about 2D ^{1}H-^{13}C HMQC NMR of alanine when spinning rate is 35000 Hz with 1.6 mm probe.



General
Channel f1
Channel f2

General

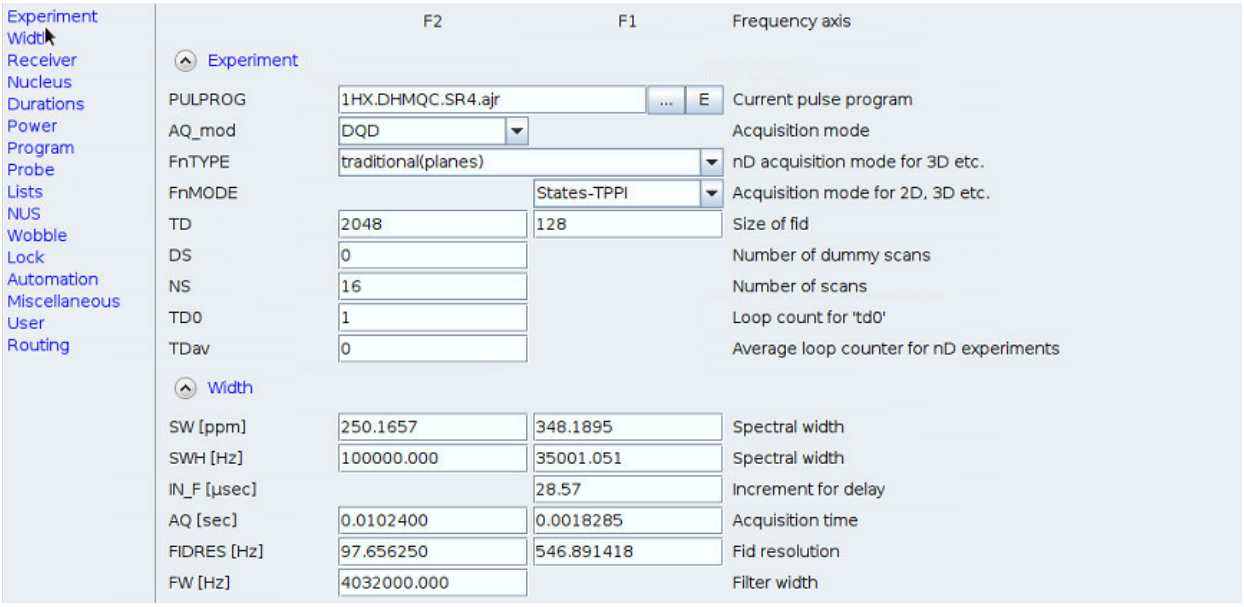
PULPROG	1HX.DHMQC.SR4.ajr ... E		Pulse program for acquisition
TD	2048		Time domain size
SWH [Hz, ppm]	100000.00	250.166	Sweep width
AQ [sec]	0.0102400		Acquisition time
RG	90.5		Receiver gain
DW [µsec]	5.000		Dwell time
DE [µsec]	6.50		Pre-scan-delay
CNST31	35000.0000000		Spinning rate
D0 [sec]	0.000028570		2xtau rot. for rotor synch.
D1 [sec]	1.000000000		Recycle delay
d5 [sec]	0		d5=(l0*d0)
d31 [sec]	0.00002857		d31=(1s/cnst31)
DS	0		Number of dummy scans
L0	0		loop counter for t1 increment (=1)
L20	3		4 x l20 rotor cycles total recoupling
NS	16		Scans to execute
TDav	0		Number of averages in nD
ZGOPTNS			-Dfslg, -Dlacq, or blank
del27 [sec]	0.00002677		del27=((1s/cnst31)-0.1us-p3)

Channel f1

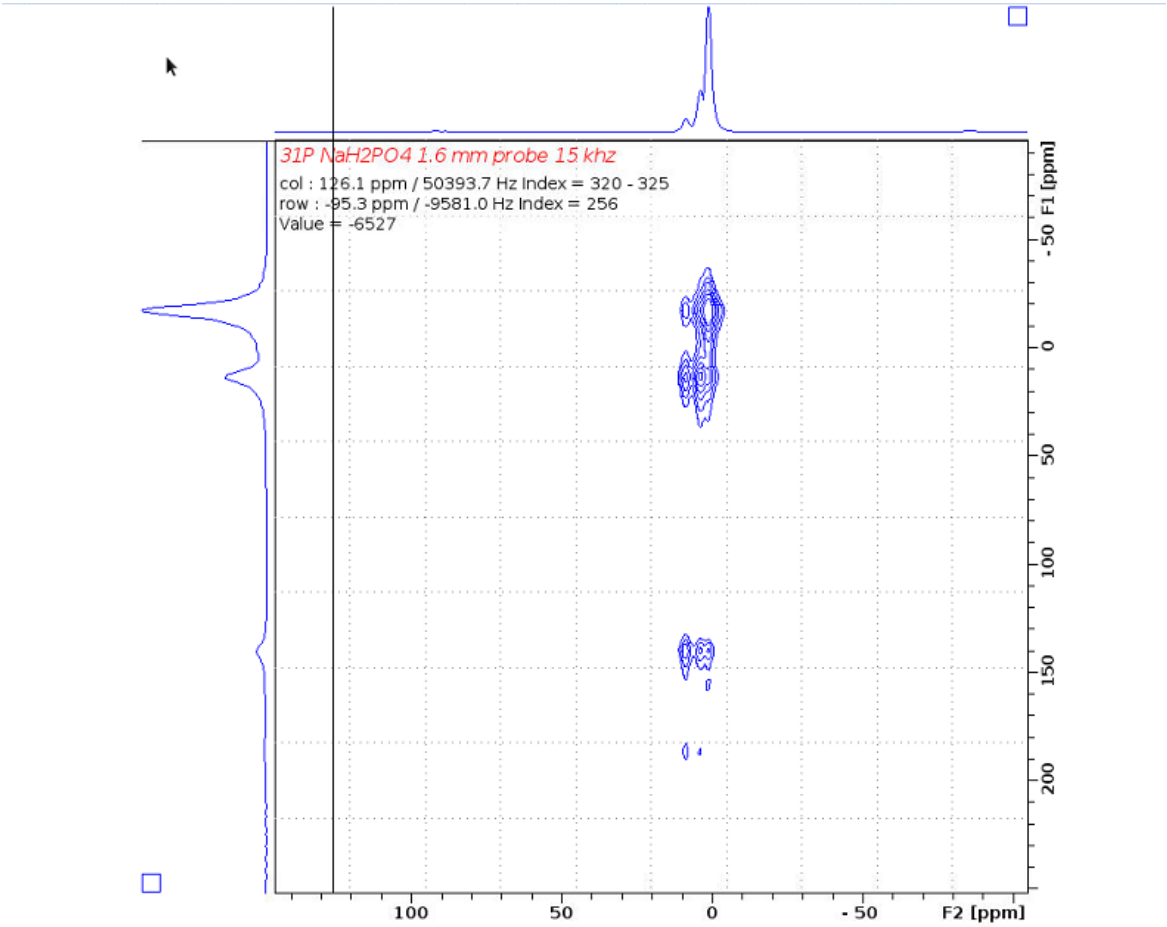
SFO1 [MHz]	399.7349987		Frequency of ch. 1
O1 [Hz, ppm]	1998.66	5.000	Frequency of ch. 1
NUC1	1H Edit...		Nucleus for channel 1
P1 [µsec]	1.200		90 pulse on 1H at plw1
P2 [µsec]	2.400		180 degree pulse on 1H at plw1
p4 [µsec]	7.14		p4=(0.25*(1s/cnst31))
PLW1 [W, dB]	100	-20.00	X power level during contact
PLW20 [W, dB]	11	-10.41	R421 recoupling power - 2*mas freq

Channel f2

SFO2 [MHz]	100.5229943		Frequency of ch. 2
O2 [Hz, ppm]	10051.29	100.000	Frequency of ch. 2
NUC2	13C Edit...		Nucleus for channel 2
CNST11	0		to adjust t=0 for acquisition, if digmod = baseopt
P3 [µsec]	1.700		CT selective 90 pulse at plw2
PLW2 [W, dB]	150	-21.76	Power for 1.5*tr pulse on quadrupole



Here is one example of HMQC results of alanine



STEP 4. OPTIMIZE THE RF PULSE FOR X NUCLEI

You need to prepare a liquid sample with the target nuclei as salts. Use a capillary to seal the liquid. Please ask Dr. Jinlei Cui for those operations if you are not familiar with this operation. Insert the capillary into the probe and run a regular 1D first with "zg" file for X nuclei. (The outside of capillary with liquid sample should be clean by Kim wipe paper carefully, as any remaining liquid will contaminate the probe.)

The RF power for X nuclei should be calibrated. For quadrupolar nuclei, you need to use a soft pulse (details about soft pulse for quadrupolar nuclei are included in the MQMAS manual, Appendix k, setup 3).

STEP 5. ACQUIRE THE 1D ^{1}H SPECTRA OF YOUR SOLID SAMPLE

Replace the alanine rotor with your sample's rotor, spin your sample. Run a 1D "zg" file for your sample to get the ^{1}H spectra.

STEP 6. MEASURE THE ^{1}H T_1 TIME OF YOUR SAMPLE

Follow the manual for T_1 measurement and measure the ^{1}H T_1 value of your sample.

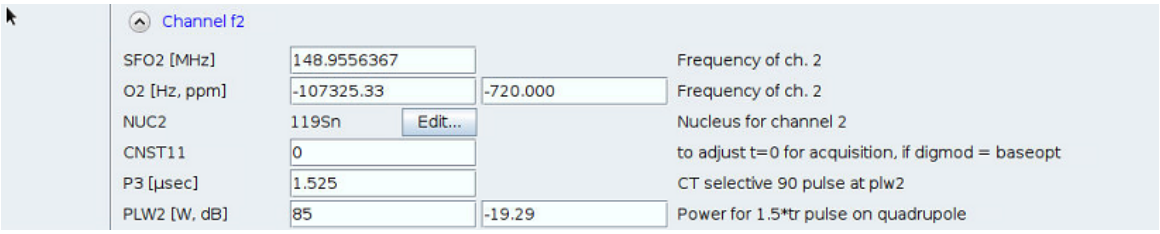
STEP 7. SET THE 2D ^{1}H-X HMQC SPECTRA FOR YOUR SAMPLE

To acquire the 1H-X HMQC spectra of your sample, spin your sample at same spinning rate as alanine. Open the previous 2D 1H-13C HMQC spectra of alanine, use command "wrpa #" (# is the file number) to create a new file. Open the new file, change the nuclei in F2 channel to the desired X nuclei.

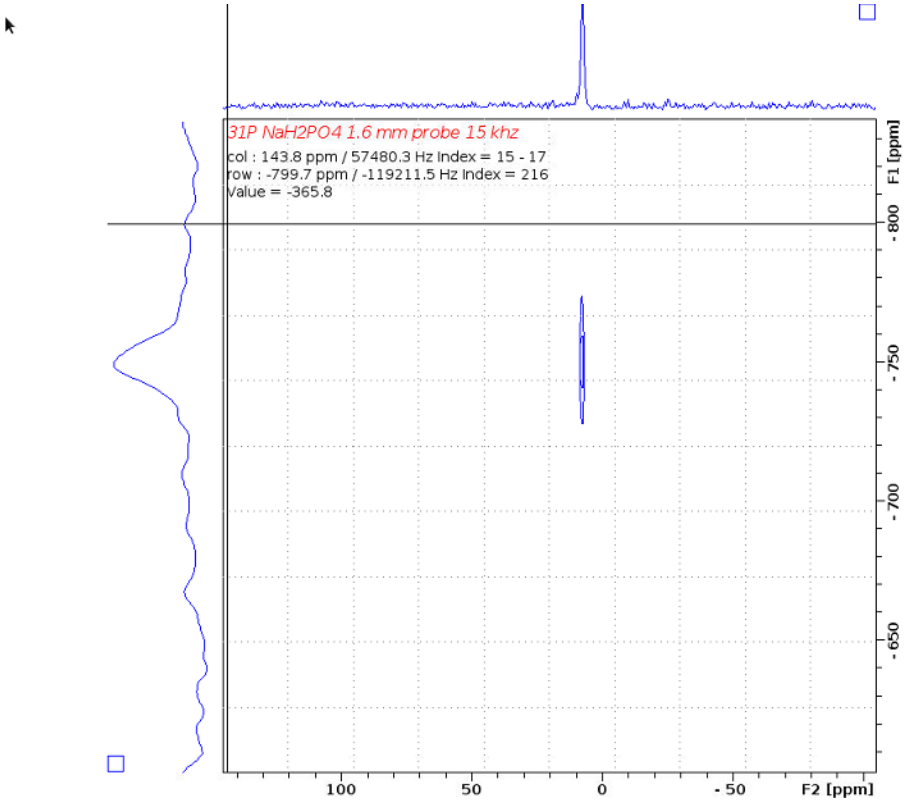
For S=1/2 nuclei, just input determined the p3 and PLW2 from step 4. For quadrupolar nuclei, you need to set the p3 by the following equation: $\pi/2/(I+1/2)$ μs, where I is the spin number of nuclei (e.g., for ^{27}Al, I is 5/2). For instance, if the soft pulse $\pi/2$ is 25 μs (solution sample), then you should set p3 to 25/(5/2+1/2) = 8.33 μs.

Set D1 to 1.3*T1, T1 is determined in step 5. Change the L3 to adjust the recoupling time. You can also change the "ns" to increase the scan time.

Then run the 2D 1H-X HMQC spectra of your sample.



Here is one example of ^{1}H-^{119}Sn HMQC NMR.



STEP 8. ACQUIRE DATA

After setting up everything, run the 2D ^{1}H-X HMQC NMR.

To better understand the correlation between ^{1}H and ^{13}C, recoupling time experiments are important. For example, **Usually, 2D NMR with two different correlation time should be obtained. One with the best long recoupling time and another with the short correlation time (different L3 value)**

STEP 9. PROCESSING 2D ^{1}H-X HMQC NMR

After the acquisition of 2D NMR, the spectra will be saved in a topspin file format. You can process the data in topspin by “xfb”.

APPENDIX I: ^{1}H-^{1}H DOUBLE QUANTUM-SINGLE QUANTUM (DQ/SQ) MAS NMR

INTRODUCTION

^{1}H nuclei are extremely sensitive nuclei, and DQ (double quantum) - SQ (single quantum) ^{1}H NMR is a 2D solid state NMR Experiment used to understand the spatial distribution of terminal group through dipolar coupling. It can also be used for other ½ nuclei, such as ^{19}F, ^{31}P etc.

PREPARATION

1. Probe: 1.6 mm HX probe is preferred due to its fast spinning rate and high resolution ^{1}H spectra.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Use adamantane as the ref sample. Run a 1D ^{1}H NMR spectra of the adamantane sample. Find the pi/2 pulse from the nutation curve of ^{1}H NMR with adamantane.
2. Run a regular 1D ^{1}H MAS NMR of your sample at a certain spin rate. Increase the spinning rate to improve the resolution of ^{1}H spectra.
3. Run the saturation T_1 experiment with your sample.
4. Run the T_2 echo experiment to find the ^{1}H T_2 time of your sample.
5. Run 2D DQ/SQ NMR from previous determined valve from step1, step 3 and step 4.
6. Check all parameters (see detailed procedures below)
7. Acquire data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/1.6_1H_DQ_SQ_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. INSERT ROTOR INTO THE PROBE AND REF THE CHEMICAL SHIFT WITH ADAMANTANE

Insert the 1.6 mm rotor with adamantane and KBr into the probe. Spin the adamantane sample to 35 kHz. Run a regular 1D experiment first with “zg” file for adamantane. The major peak of adamantane should be calibrated to 1.82 ppm. After obtaining the 1D spectrum of adamantane, run a nutation curve

(changing P1 pulse length) to find the pi/2 pulse. Set the power of p1 pulse (PLW1) to almost the maximum power of the probe. Check the details in Appendix B for nutation curve.

STEP 2. ACQUIRE THE 1D SPECTRA OF YOUR SOLID SAMPLE

After the 1H pi/2 pulse is determined and the adamantane is referenced, stop the spinning. Replace the adamantane rotor with your sample's rotor. Spin your sample and open the "zg" file for solid sample, set the power "plw1" the same as in the last step for adamantane and set "P1" to the pi/2 pulse length. Then acquire a 1D spectra of your solid sample.

STEP 3. DETERMINE THE T_1 AND T_2 VALVE OF YOUR SAMPLE

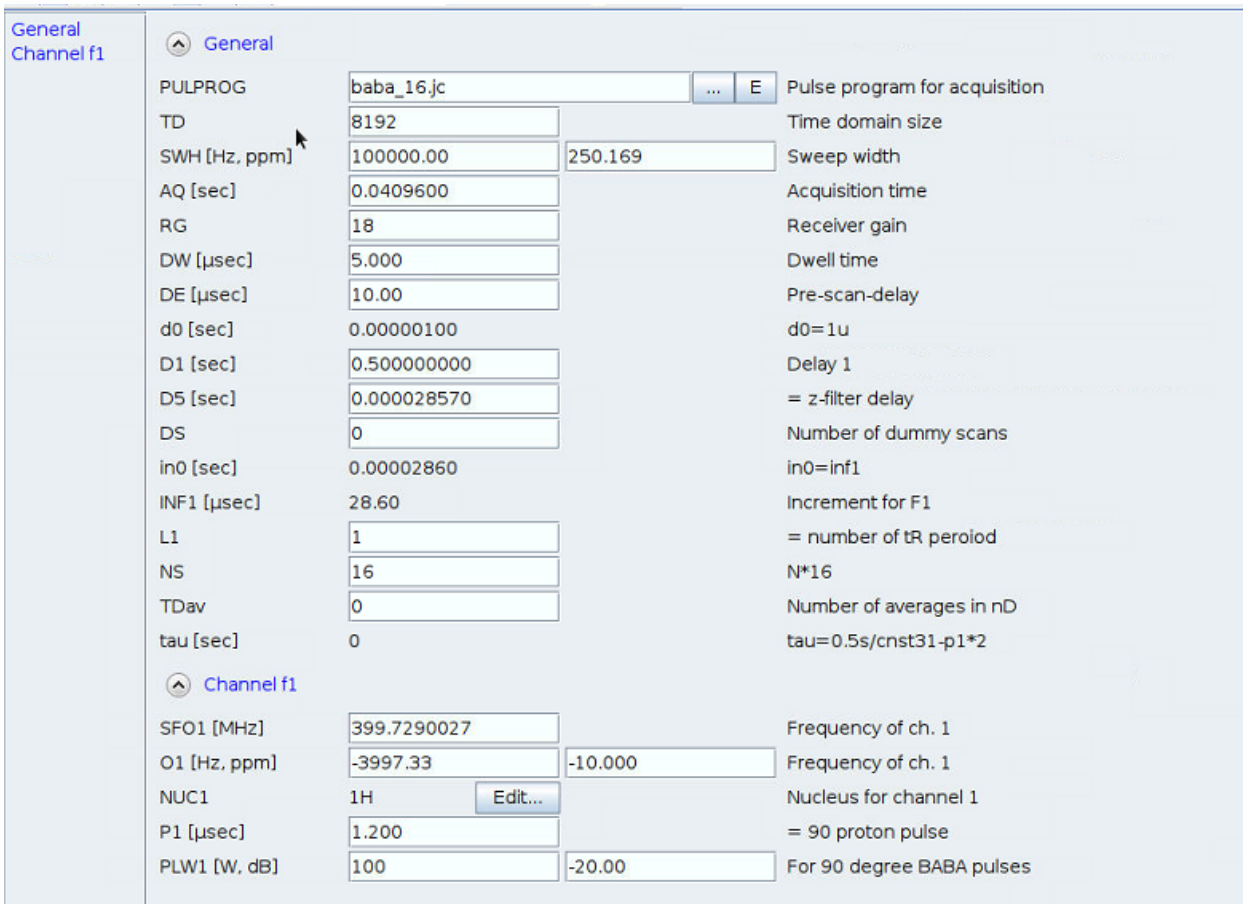
Read the manual for T_1 and T_2 measurement. Use the provided files to measure the ^1H T_1 and T_2 values.

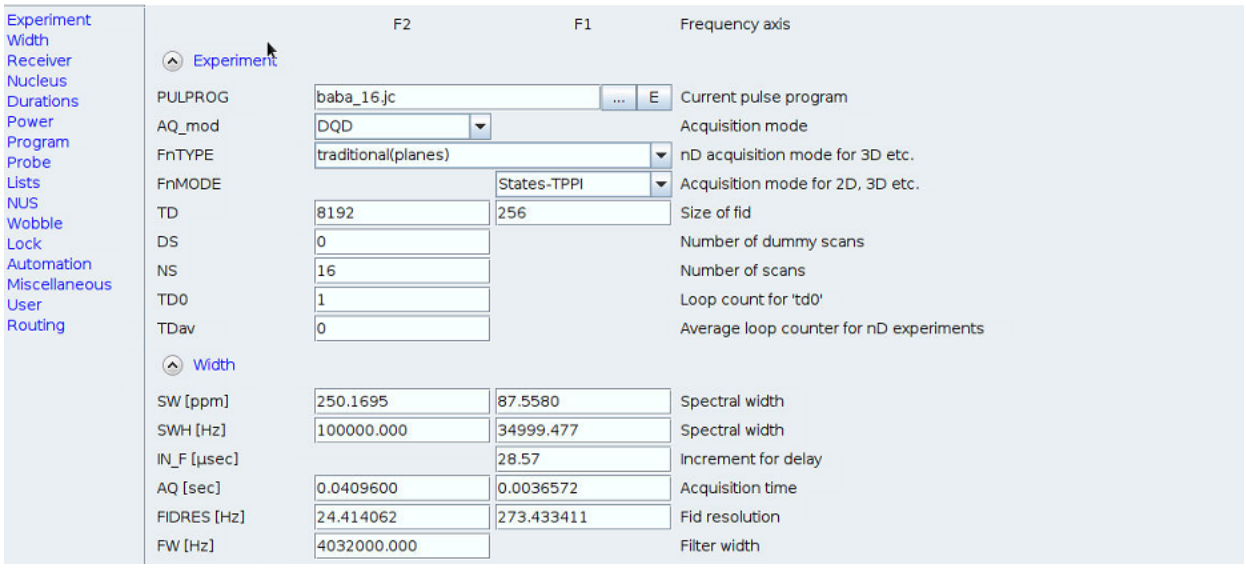
STEP 4. ACQUIRE 2D DQ/SQ MAS NMR

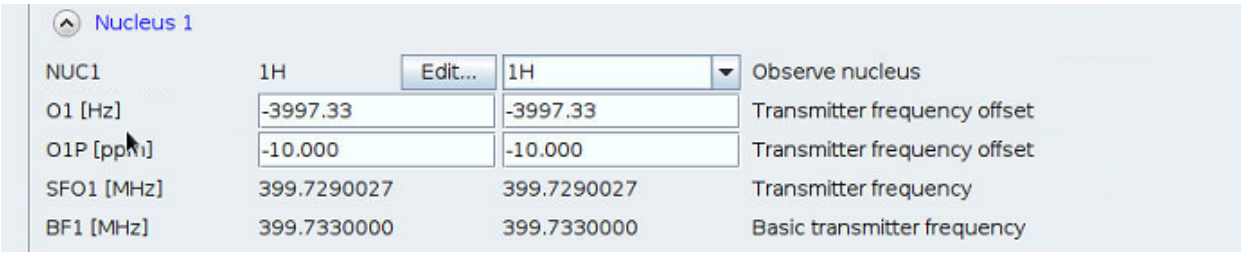
After the determination of T_1 and T_2 valve, Open the 2D file "baba_16.jc" with blue color. Set the "PLW1" from step 2 and "P1" to the valve of "pi/2" pulse length. Set "D1" to "1.3*T_1". Set D5 to one spinning rotor cycle time (1/spinning rate). The F1 dimension nuclei is the same as the F2 dimension. Set the F1 dimension window to the spinning rate. Set the F1 dimension step as 256 steps. Set Fnmode to "States-TPPI." The "AQ" time in F1 dimension should be similar to the T_2 time determined previously.

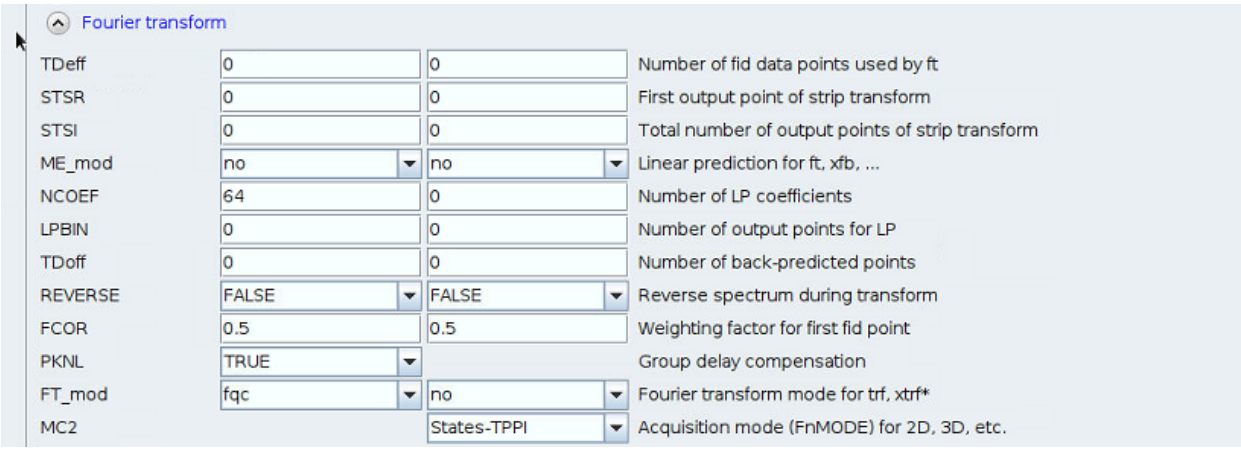
Click "ProcPars." Set the F1 dimension WDW to "EM," set PH_mod to "ph," and set MC2 to "states-TPPI." Set the F1 dimension SR valve the same as the F2 dimension.

Here is an example of parameters for 2D ^1H-^1H DQ/SQ MAS NMR experiment when the spinning rate is 35000 Hz.


General
Channel f1
General
PULPROG baba_16.jc ... E Pulse program for acquisition
TD 8192 Time domain size
SWH [Hz, ppm] 100000.00 250.169 Sweep width
AQ [sec] 0.0409600 Acquisition time
RG 18 Receiver gain
DW [µsec] 5.000 Dwell time
DE [µsec] 10.00 Pre-scan-delay
d0 [sec] 0.00000100 d0=1u
D1 [sec] 0.500000000 Delay 1
D5 [sec] 0.000028570 = z-filter delay
DS 0 Number of dummy scans
in0 [sec] 0.00002860 in0=inf1
INF1 [µsec] 28.60 Increment for F1
L1 1 = number of tR peroiod
NS 16 N*16
TDav 0 Number of averages in nD
tau [sec] 0 tau=0.5s/cnst31-p1*2
Channel f1
SFO1 [MHz] 399.7290027 Frequency of ch. 1
O1 [Hz, ppm] -3997.33 -10.000 Frequency of ch. 1
NUC1 1H Edit... Nucleus for channel 1
P1 [µsec] 1.200 = 90 proton pulse
PLW1 [W, dB] 100 -20.00 For 90 degree BABA pulses


Experiment
Width
Receiver
Nucleus
Durations
Power
Program
Probe
Lists
NUS
Wobble
Lock
Automation
Miscellaneous
User
Routing
F2 F1 Frequency axis
Experiment
PULPROG baba_16.jc ... E Current pulse program
AQ_mod DQD Acquisition mode
FnTYPE traditional(planes) nD acquisition mode for 3D etc.
FnMODE States-TPPI Acquisition mode for 2D, 3D etc.
TD 8192 256 Size of fid
DS 0 Number of dummy scans
NS 16 Number of scans
TD0 1 Loop count for 'td0'
TDav 0 Average loop counter for nD experiments
Width
SW [ppm] 250.1695 87.5580 Spectral width
SWH [Hz] 100000.000 34999.477 Spectral width
IN_F [µsec] 28.57 Increment for delay
AQ [sec] 0.0409600 0.0036572 Acquisition time
FIDRES [Hz] 24.414062 273.433411 Fid resolution
FW [Hz] 4032000.000 Filter width



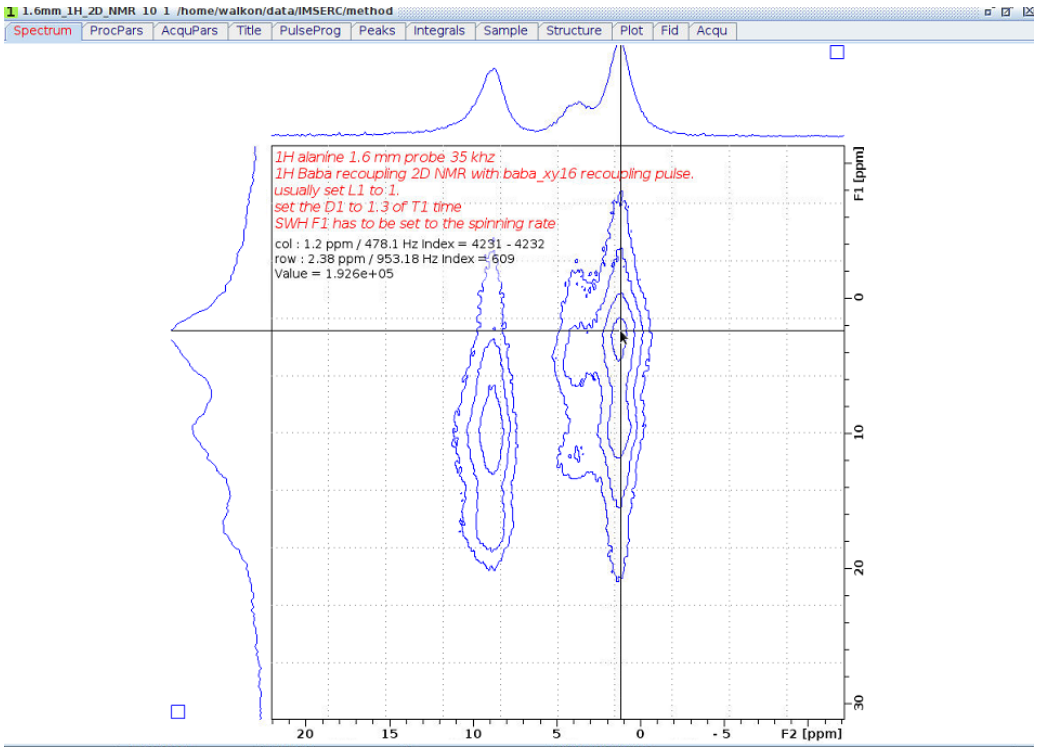


STEP 5. ACQUIRE DATA

After setting up everything, run the 2D NMR. While the 2D NMR is running, type the command "**xfb**" to process the 2D NMR.

After processing the 2D DQ/SQ NMR, check the contour in the 2D spectra. The F2 dimension chemical shift should be twice the F1 dimension. You can calibrate the F2 dimension using the calibration function.

Here is an example of a 2D DQ/SQ ^{1}H MAS NMR of Alanine when the spinning rate is 35000 Hz.


1.6mm_1H_2D_NMR_10_1 /home/walkon/data/IMSERC/method
Spectrum
ProcPars
AcquPars
Title
PulseProg
Peaks
Integrals
Sample
Structure
Plot
Fid
Acqu
1H alanine 1.6 mm probe 35 khz
1H Baba recoupling 2D NMR with baba_xy16 recoupling pulse.
usually set L1 to 1.
set the D1 to 1.3 of T1 time
SWH F1 has to be set to the spinning rate
col : 1.2 ppm / 478.1 Hz Index = 4231 - 4232
row : 2.38 ppm / 953.18 Hz Index = 609
Value = 1.926e+05
F1 [ppm]
0
10
20
30
20
15
10
5
0
- 5
F2 [ppm]

APPENDIX J: ^{1}H-^{1}H NOESY MAS NMR

INTRODUCTION

^{1}H nuclei are extremely sensitive, and NOESY of ^{1}H NMR is a 2D solid state NMR Experiment where the transfer of magnetization among the spins occurs through dipolar coupling or chemical translocation. It can help the researchers understand the spatial distribution of nuclei or spin diffusion. It can also be used for other ½ nuclei, such as ^{19}F, ^{31}P etc.

PREPARATION

1. Probe: 1.6 mm HX probe is preferred due to its fast spinning rate and high resolution ^{1}H spectra.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Use adamantane as the ref sample. Run a 1D ^{1}H NMR spectra of the adamantane sample. Find the pi/2 pulse from nutation curve of 1H NMR with adamantane.
2. Change sample. Run a regular 1D ^{1}H MAS NMR of your sample at a certain spin rate. Increase the spinning rate to improve the resolution of ^{1}H spectra.
3. Run the saturation T_1 experiment with your sample.
4. Run 2D ^{1}H NOESY NMR from previous determined valve from step1 and step 3.
5. Check all parameters (see detailed procedures below)
6. Acquire data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_1H_NOESY_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. INSERT ROTOR INTO THE PROBE AND REF THE CHEMICAL SHIFT WITH ADAMANTANE

Insert the 1.6 mm rotor with adamantane and KBr into the probe. Spin the adamantane sample to the wanted spinning rate. Run a regular 1D first with “zg” file for adamantane.

The major peak of adamantane should be calibrated to 1.82 ppm. After obtaining the 1D spectrum of adamantane, run a nutation curve (changing P1 pulse length) to find the pi/2 pulse. Set the power of p1 pulse (PLW1) to almost the maximum power of the probe. Check the details in Appendix B for 1H nutation curve

STEP 2. ACQUIRE THE 1D SPECTRA OF YOUR SOLID SAMPLE

After the 1H pi/2 pulse is determined and the adamantane is referenced, stop the spinning. Replace the adamantane rotor with your sample's rotor. Spin your sample and open the "zg" file for solid sample, set the power "plw1" the same as in the last step for adamantane" and "P1" to the pi/2 pulse length. Then acquire a 1D spectra of your solid sample.

STEP 3. DETERMINE THE T_1 VALVE OF YOUR SAMPLE

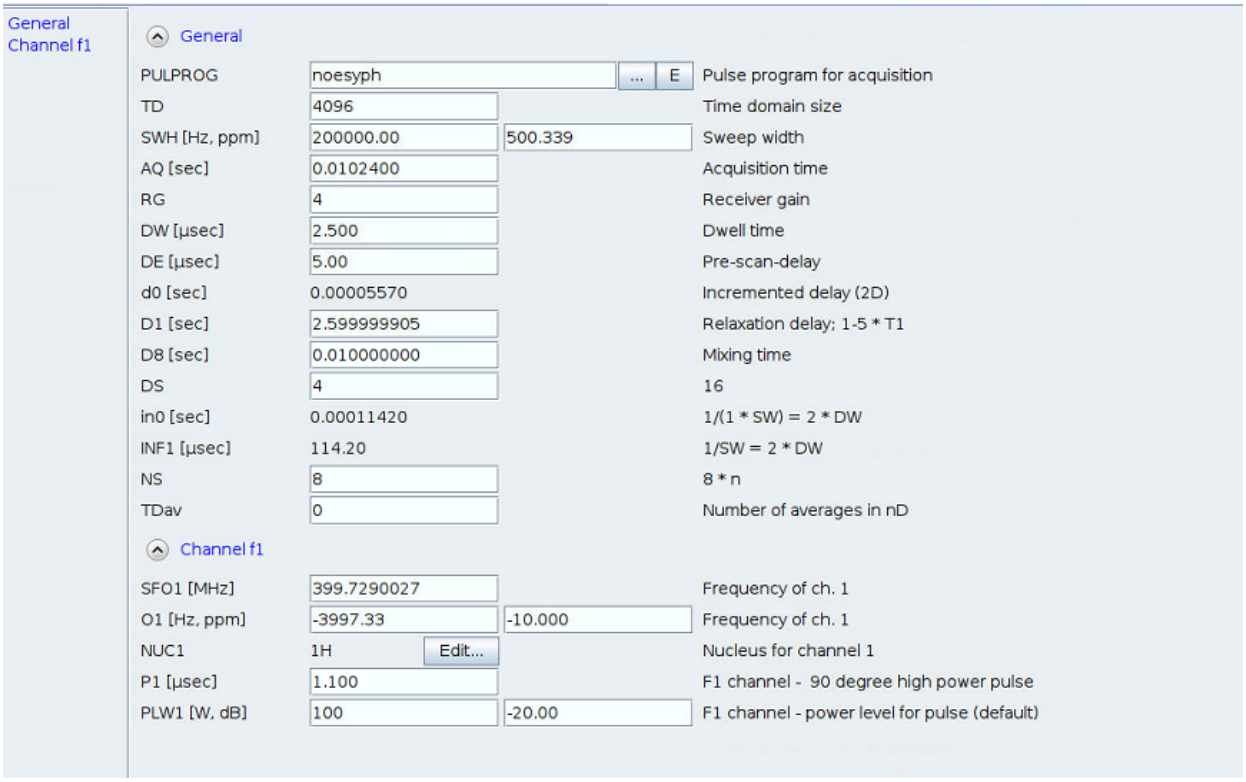
Read the manual for T_1 measurement and measure the ^1H T_1 value of your sample

STEP 4. ACQUIRE 2D ^1H NOESY MAS NMR

After the determination of T_1 valve, Open the 2D ^1H-^1H NOESY file "noesyph" with blue color. Set the "PLW1" from step 2 and "P1" to the "pi/2" pulse length. Set "D1" to "1.3*T_1". The F1 dimension nuclei is the same as the F2 dimension. Set the F1 dimension window to the spinning rate. (or you can set the F1 dimension window to 1/n of spinning rate, n =2,3, 4) Set the F1 dimension step to 256 steps. Set Fnmode to "States-TPPI." D8 is the mixing time for NOESY, you can set it between ms to us. Long mixing time allows more exchange among different spins.

Click "ProcPars." Set the F1 dimension WDW to "EM," set PH_mod to "ph," and set MC2 to "states-TPPI." Set the F1 dimension SR valve the same as the F2 dimension.

Here is an example of parameters about 2D DQ/SQ ^1H MAS NMR when spinning rate is 35000 Hz and the F1 window is set to the quarter of spinning rate, which can save the 2D experiment time. In addition, if the in_F1 is not the n*1/spin rate (n=1,2,3,4…), use the "sine" window function in the F1 dimension for data processing.



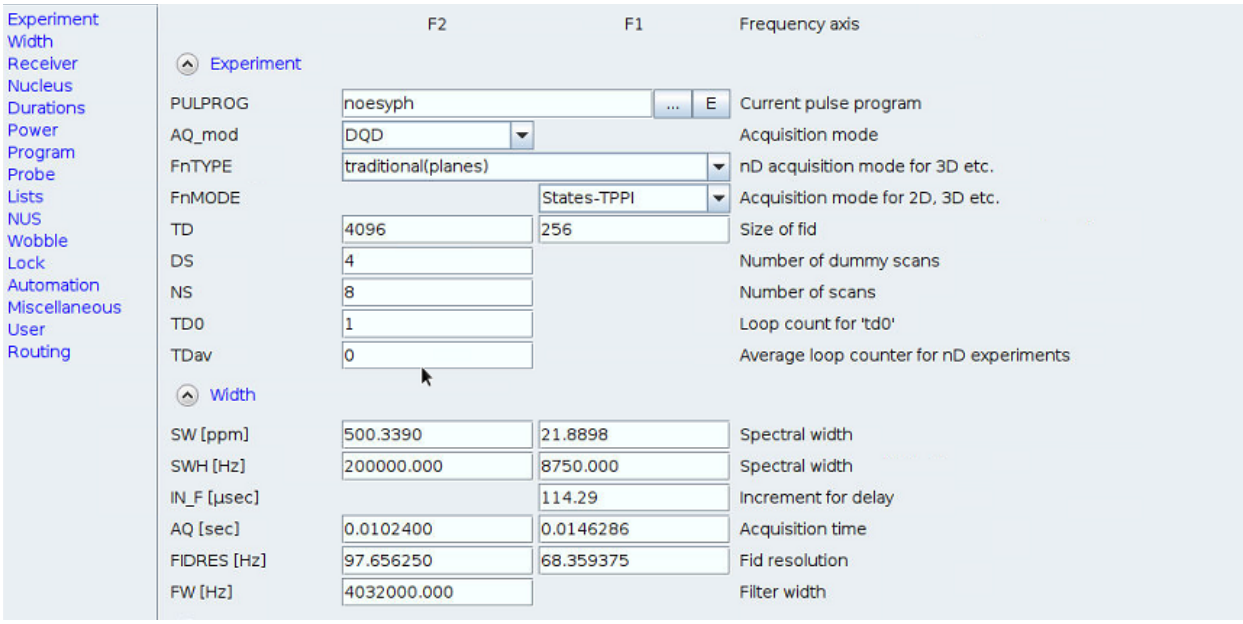
General
Channel f1

General

PULPROG	noesyph ... E		Pulse program for acquisition
TD	4096		Time domain size
SWH [Hz, ppm]	200000.00	500.339	Sweep width
AQ [sec]	0.0102400		Acquisition time
RG	4		Receiver gain
DW [µsec]	2.500		Dwell time
DE [µsec]	5.00		Pre-scan-delay
d0 [sec]	0.00005570		Incremented delay (2D)
D1 [sec]	2.599999905		Relaxation delay; 1-5 * T1
D8 [sec]	0.010000000		Mixing time
DS	4		16
in0 [sec]	0.00011420		1/(1 * SW) = 2 * DW
INF1 [µsec]	114.20		1/SW = 2 * DW
NS	8		8 * n
TDav	0		Number of averages in nD

Channel f1

SFO1 [MHz]	399.7290027		Frequency of ch. 1
O1 [Hz, ppm]	-3997.33	-10.000	Frequency of ch. 1
NUC1	1H Edit...		Nucleus for channel 1
P1 [µsec]	1.100		F1 channel - 90 degree high power pulse
PLW1 [W, dB]	100	-20.00	F1 channel - power level for pulse (default)



Experiment
Width
Receiver
Nucleus
Durations
Power
Program
Probe
Lists
NUS
Wobble
Lock
Automation
Miscellaneous
User
Routing

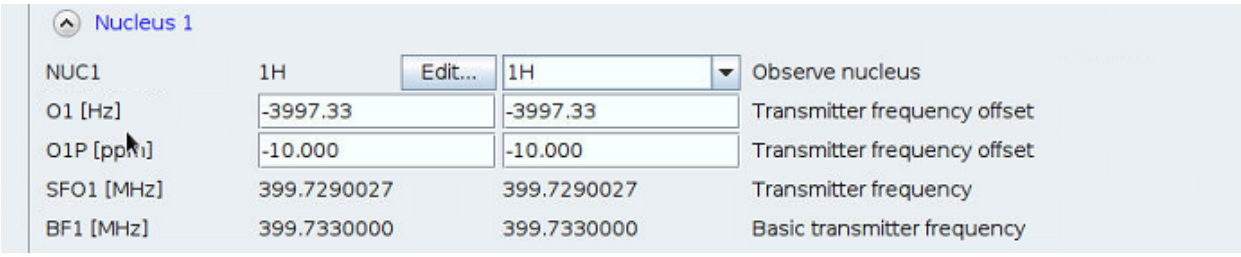
	F2	F1	Frequency axis

Experiment

PULPROG	noesyph ... E		Current pulse program
AQ_mod	DQD		Acquisition mode
FnTYPE	traditional(planes)		nD acquisition mode for 3D etc.
FnMODE		States-TPPI	Acquisition mode for 2D, 3D etc.
TD	4096	256	Size of fid
DS	4		Number of dummy scans
NS	8		Number of scans
TD0	1		Loop count for 'td0'
TDav	0		Average loop counter for nD experiments

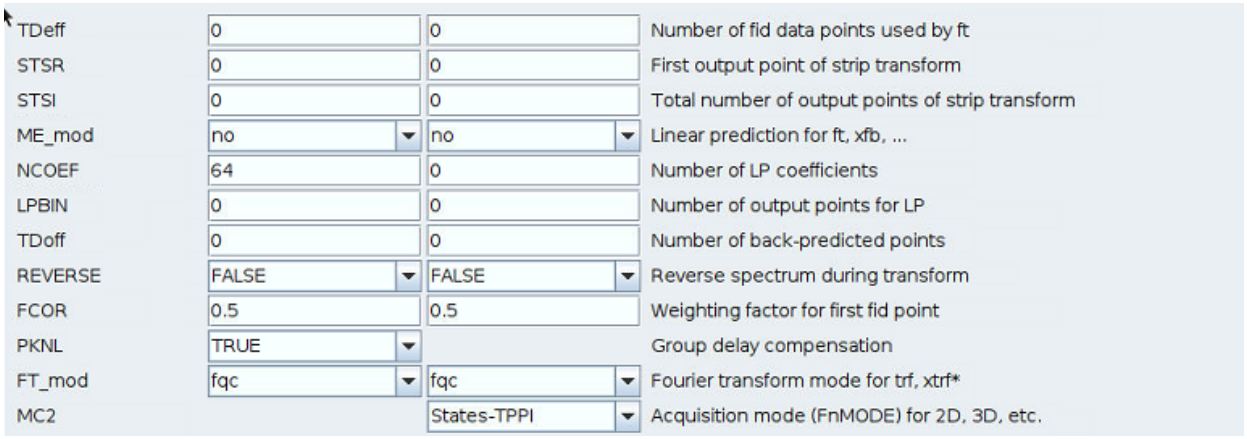
Width

SW [ppm]	500.3390	21.8898	Spectral width
SWH [Hz]	200000.000	8750.000	Spectral width
IN_F [µsec]		114.29	Increment for delay
AQ [sec]	0.0102400	0.0146286	Acquisition time
FIDRES [Hz]	97.656250	68.359375	Fid resolution
FW [Hz]	4032000.000		Filter width



Nucleus 1

NUC1	1H	Edit...	1H	Observe nucleus
O1 [Hz]	-3997.33		-3997.33	Transmitter frequency offset
O1P [ppm]	-10.000		-10.000	Transmitter frequency offset
SFO1 [MHz]	399.7290027		399.7290027	Transmitter frequency
BF1 [MHz]	399.7330000		399.7330000	Basic transmitter frequency



TDeff	0	0	Number of fid data points used by ft
STSR	0	0	First output point of strip transform
STSI	0	0	Total number of output points of strip transform
ME_mod	no	no	Linear prediction for ft, xfb, ...
NCOEF	64	0	Number of LP coefficients
LPBIN	0	0	Number of output points for LP
TDoff	0	0	Number of back-predicted points
REVERSE	FALSE	FALSE	Reverse spectrum during transform
FCOR	0.5	0.5	Weighting factor for first fid point
PKNL	TRUE		Group delay compensation
FT_mod	fqc	fqc	Fourier transform mode for trf, xtrf*
MC2		States-TPPI	Acquisition mode (FnMODE) for 2D, 3D, etc.

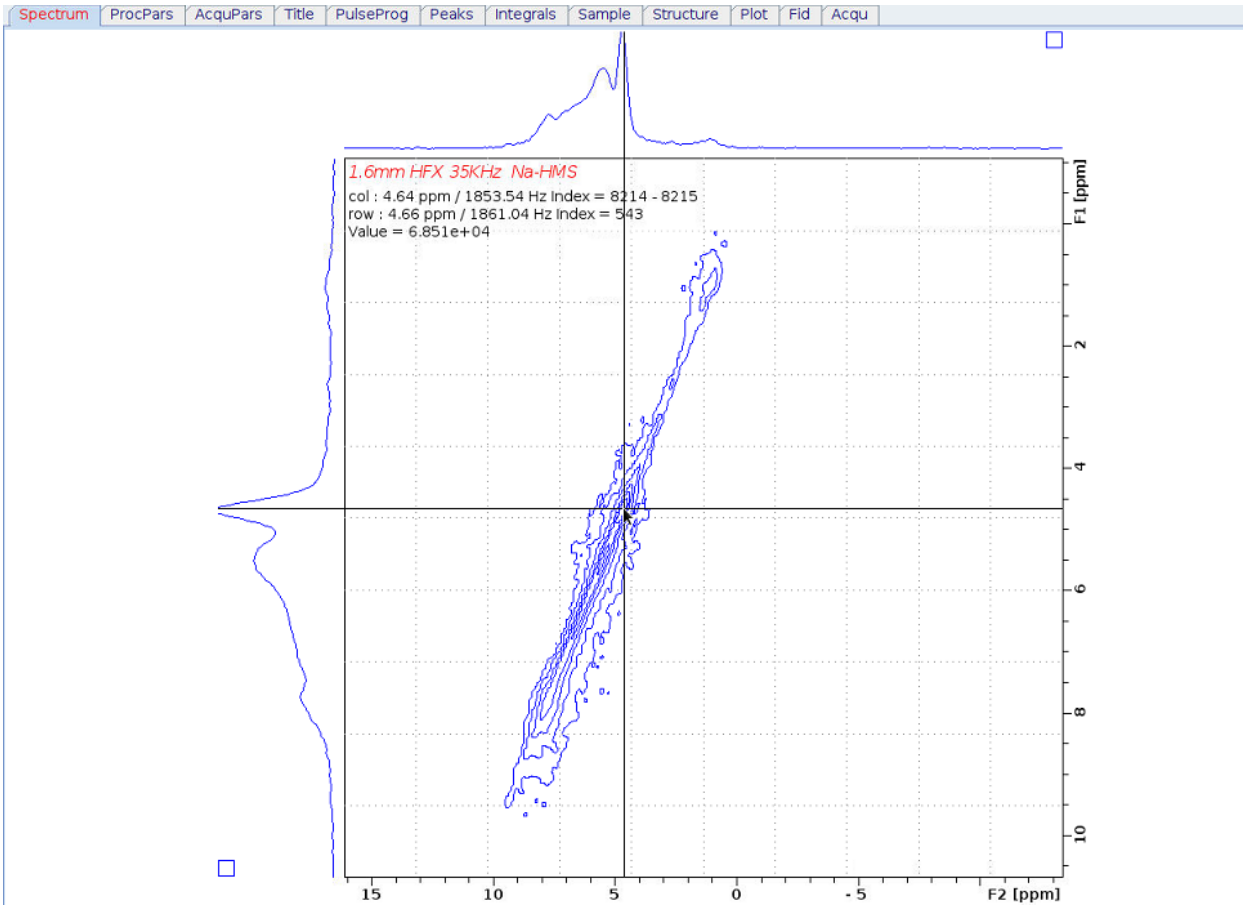
STEP 6. ACQUIRE DATA

After setting up everything, run the 2D NMR. While the 2D NMR is running, type the command "**xfb**" to process the 2D NMR.

After processing the 2D ^{1}H NOESY NMR, check the contour in the 2D spectra. The F2 dimension chemical shift should be same as the F1 dimension. You can calibrate the chemical shift in F2 dimension using the calibration function.

Run multiple 2D ^{1}H NOESY NMR with different mixing time d8 (for instance, 10 us, 5 ms, and 30 ms). These series of 2D NMR will provide information on spatial proximity.

Here is an example of 2D ^{1}H NOESY NMR of metal sulfide when spinning rate is 35000 Hz.


Spectrum
ProcPars
AcquPars
Title
PulseProg
Peaks
Integrals
Sample
Structure
Plot
Fid
Acqu
1.6mm HFX 35KHz Na-HMS
col : 4.64 ppm / 1853.54 Hz Index = 8214 - 8215
row : 4.66 ppm / 1861.04 Hz Index = 543
Value = 6.851e+04
F1 [ppm]
2
4
6
8
10
15
10
5
0
- 5
F2 [ppm]

APPENDIX K: ^{27}AL MQMAS MAS NMR

INTRODUCTION

MQMAS stands for Multi Quantum Magic Angle Spinning, which is a 2D solid state NMR Experiment for quadruple nuclei, such as ^{11}B (spin 3/2), ^{27}Al (spin 5/2), ^{87}Rb (spin 3/2), etc. Due to the quadrupole effect, the 1D spectrum peaks are usually very broad. MQMAS 2D spectrum helps to separate the overlapping peaks in the second dimension. Here, we use ^{27}Al nuclei as an example.

PREPARATION

1. Spectrometer: NMR-Hg400-Solid only
2. Probe: Bruker 4mm HX probe or 1.6 mm HX probe

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Use ^{27}Al as an example. Run a 1D ^{27}Al NMR spectra of a liquid standard sample, find the power set for non-selective (hard pulse) and selective (soft pulse).
2. Run a regular 1D MAS of ^{27}Al for solid sample at a certain spin rate, e.g. 14000 Hz
3. Edit a new data set with a pulse program “mp3qzqf”
4. Keep 1D mode first and run a quick ^{27}Al
5. Optimize p1, p2, p3 back and forth with a powerset from step 1
6. Edit another new data set and convert it to 2D
7. Check all parameters (see detailed procedures below)
8. Acquire data
9. Process data by **xfshear ratio**

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_27Al_MQMAS_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command “edc” to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. LOAD LIQUID SAMPLE INTO THE ROTOR

You need to prepare a liquid sample, with the target nuclei as the salts. For ^{27}Al, we used 0.5 M $Al(NO_3)_3$ as the liquid sample. For 4 mm HX probe, you can add the liquid sample directly into the rotor or you can use a 4 mm Bruker rotor insert. For 1.6 mm HX probe, you should use a capillary to seal the liquid. Please ask Dr. Jinlei Cui for those operations if you are not familiar. The liquid sample is not just used for optimizing the pulse but also as the chemical shift reference.

STEP 2. INSERT ROTOR INTO THE PROBE AND TUNING THE PROBE

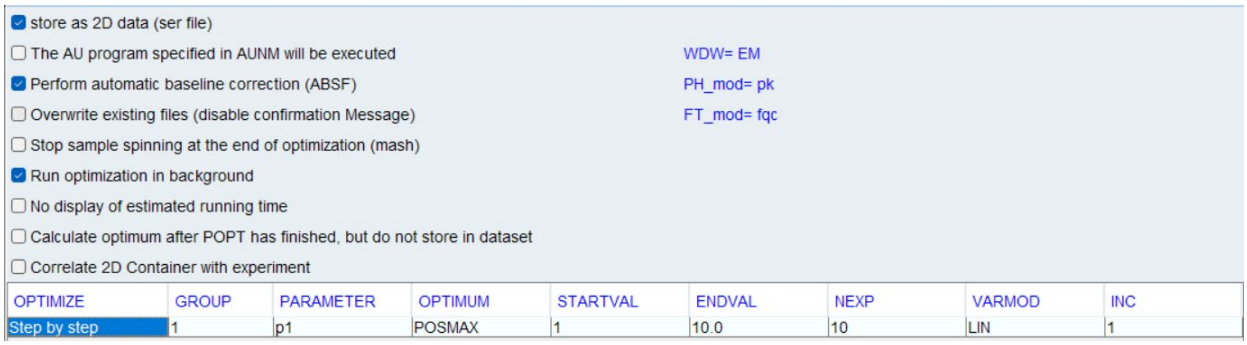
Run a regular 1D first with "zg" file for AlNO3. You can use pulse program "zg" without proton decoupling.

STEP 3. OPTIMIZE THE POWERSET FOR NON-SELECTIVE AND SELECTIVE PULSE

After obtaining the 1D spectrum of liquid sample, run a nutation curve (changing P1 pulse length) to find the non-selective (hard pulse) and selective (soft pulse). Set the power of p1 pulse (PLW1) to almost the maximum power of the probe. Use the "popt" to decide the nutation curve, see the details in Appendix B. If the π/2 pulse is short, please adjust the "startval", "endval" and "inc" values. This establishes the non-selective pulse with maximum allowed power within the probe.

After that, reduce the pulse power and re-run the nutation curve until the π/2 pulse length is about 32 μs. It means the B1 of RF pulse is about 7.8 kHz and this will help you to obtain the selective pulse (soft pulse).

If the pulse has been optimized before, you can skip this step.



STEP 4. CHNAGE THE SAMPLE WITH SOLID SAMPLE ROTOR

After you have done the liquid sample, replace the solution sample with the solid sample. Here we use γ-Al_2O_3 as the demo sample. Spin up the solid sample rotor to the almost maximum allowed spinning rate for the probe (e.g., 4 mm is 14 kHz).

Run a 1D NMR of the solid sample using the "zg" pulse sequence with the soft pulse power obtained in step 3 with experiment "zg" file for Al2O3. Adjust the pulse length (p1) to $\pi/2/(I+1/2)$ μs, where I is the spin number of nuclei (e.g., for ^{27}Al, I is 5/2; for ^{51}V, I is 7/2). For instance, if the soft pulse $\pi/2$ is 32 μs, then you should set p1 to 32/(5/2+1/2) = 10.67 μs. This will give you 1D central transition selective ^{27}Al MAS NMR.

STEP 5. MEASURE THE ^{27}AL T1 VALVE OF YOUR SAMPLE

After obtaining the 1D spectrum of solid sample, you need to find the T_1 of ^{27}Al nuclei. Open the "satrect1" file for solid sample. Set the power of p1 pulse (PLW1) to hard pulse. And then use the manual for T1 to measure the T_1 of 27Al nuclei

STEP 6. RUN THE 1D MQMAS SPECTRA AND OPTIMIZE THE PARAMETERS

After regular 1D is done, edit a new data set for mqmas preparation. Open the 1D experiment file "mp3qzqf".

Set the power for P1 and P2 for MQMAS pulse sequency with the hard pulse determined in step 3. Divide the $\pi/2$ length (hard pulse from step 3) by (I+1/2) and set the calculated value to pulse P2. Set the P1 pulse length as three times that of P2. Set pulse P3 power and pulse length as same as in step 4.

Set ns to 12*n, and set D4 to 20 us and D0 to 1 us. Run the 1D MQMAS spectra, and then zoom in the peak region, then type **dpl.** Type "**popt**" to open the optimization windows, optimize the p1 pulse length while keeping P2 and P3 fixed. The optimization range will be 3 μs around the set valve and with a step of 0.2 μs.

After the P1 is optimized, optimize P2 with P1 and P3 fixed. Typically, optimized P1 pulse length should be around three times that of P2 pulse length.

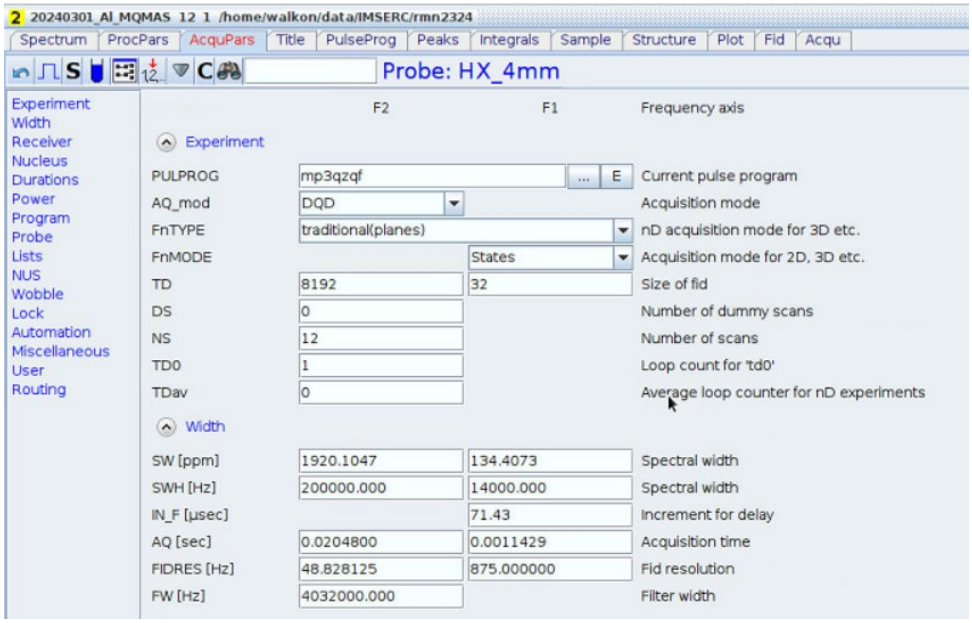
After the optimization of P1 and P2, you can either optimize P3 or not. If your previous optimization of soft pulse is correct, you can skip it.

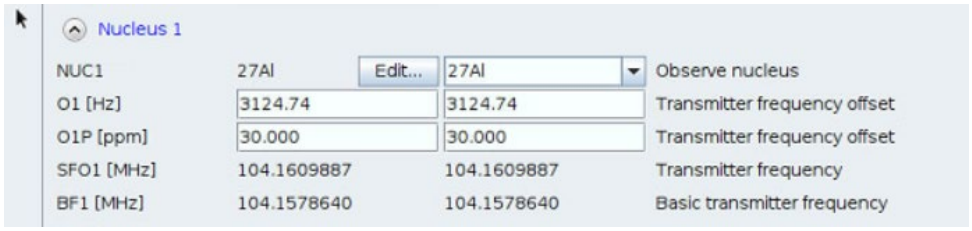
STEP 7. RUN 2D ^{27}AL MQMAS NMR

Edit another new data set for 2D. Open the 2D MQMAS file “mp3qzqf” with blue color. The F1 dimension nuclei is the same as the F2 dimension. Set the F1 dimension window to the spinning rate. Set the F1 dimension step as 32 steps. Set Fnmode to "States." Set D1 to the 1.3*T1 from step 5.

Click "ProcPars." Set the F1 dimension WDW to "EM," set PH_mod to "ph," and set MC2 to "states." Set the F1 dimension SR valve as same as the F2 dimension.

Here is an example of parameters about 2D ^{27}Al MQMAS of Al_2O_3 sample spun at 14 kHz.





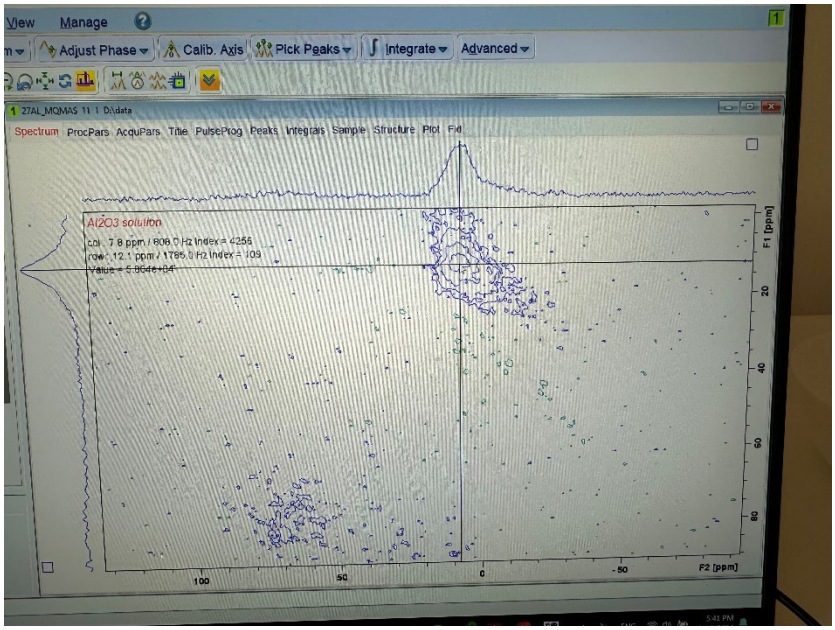
TDeff	2048	0	Number of fid data points used by ft
STSR	0	0	First output point of strip transform
STSI	0	0	Total number of output points of strip transform
ME_mod	no	no	Linear prediction for ft, xfb, ...
NCOEF	64	0	Number of LP coefficients
LPBIN	0	0	Number of output points for LP
TDoff	0	0	Number of back-predicted points
REVERSE	FALSE	FALSE	Reverse spectrum during transform
FCOR	0.5	0.5	Weighting factor for first fid point
PKNL	TRUE		Group delay compensation
FT_mod	fqc	no	Fourier transform mode for trf, xtrf*
MC2		States	Acquisition mode (FnMODE) for 2D, 3D, etc.

STEP 8. ACQUIRE DATA

After setting up everything, run the 2D NMR. While the 2D NMR is running, type the command “xfb” to process the 2D NMR. Then make sure the F1 dimension SR is the same as F2 if the chemical shift in F1 dimension does not make sense. Then type "**xfshear ratio**" to process the “**shear**” 2D MQMAS NMR. Answer "yes" for "apply abs2," enter 0 for "F1 shift in ppm," and enter the correct number for the shearing ratio, dependent on the nuclei (see table).

Spin I	R(p=3)
3/2	-7/9
5/2	19/12
7/2	101/45
9/2	91/36

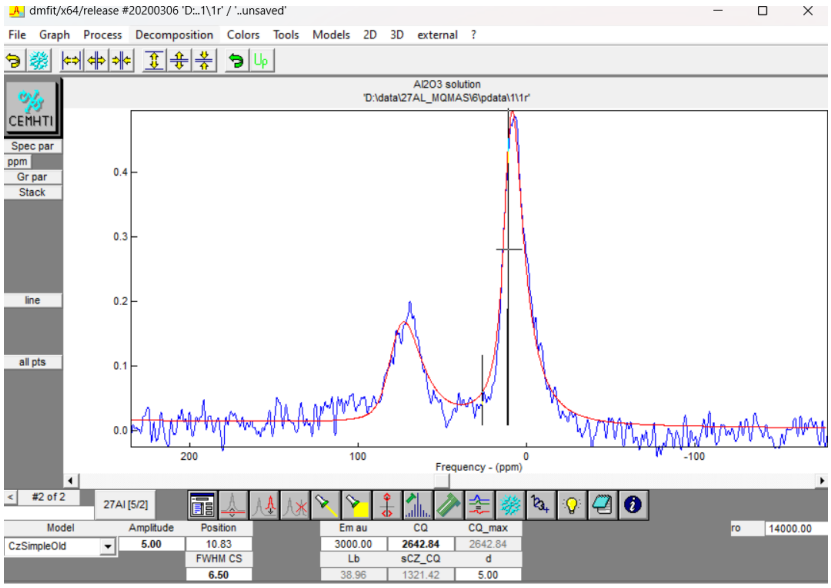
After processing the 2D MQMAS NMR, please check the contour in the 2D spectra. If the F1 value (chemical shift) is smaller than the F2 dimension, adjust the center of the windows (O1p).

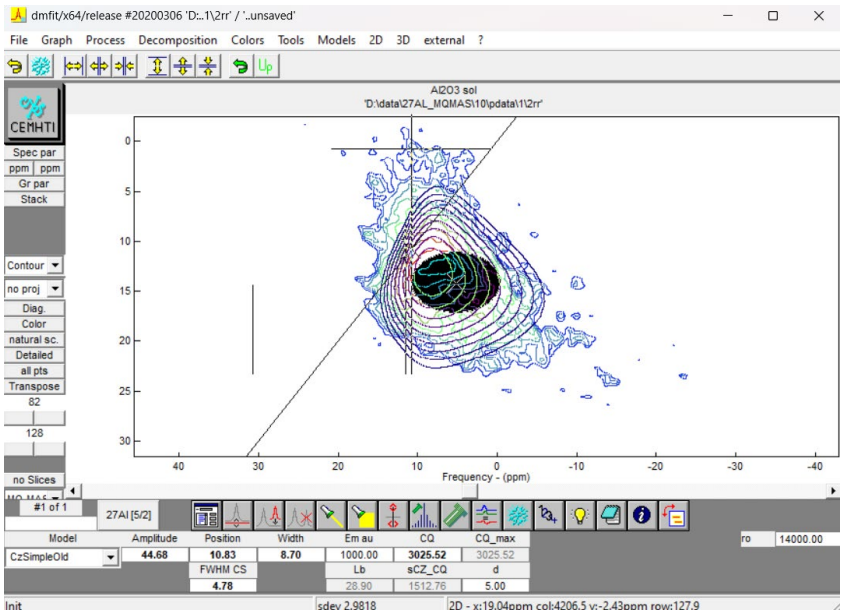


Also check a parameter MASR is the same value of your spinning rate

STEP 9. PROCESSING 1D MAS NMR AND 2D MQMAS NMR WITH DMFIT

After the acquisition of 1D MAS NMR and 2D MQMAS NMR, the spectra will be saved in a topspin file format. To deconvolute and simulate the spectra, you will need to import the data to the DMfit software. The fitting process of 1D and 2D MQMAS can be found in the DMfit website under the tab "how to do". Please read it carefully. Here, we show a 1D ^{27}Al MAS NMR and 2D ^{27}Al MQMAS NMR of Υ-Al_2O_3




dmfit/x64/release #20200306 'D:..1\2rr' / '..unsaved'
File Graph Process Decomposition Colors Tools Models 2D 3D external ?
CEMHTI
Spec par
ppm ppm
Gr par
Stack
Contour
no proj
Diag
Color
natural sc.
Detailed
all pts
Transpose
82
128
no Slices
#1 of 1
27Al [5/2]
Al2O3 sol
'D:\data\27AL_MQMAS\10\pdata\1\2rr'
Frequency - (ppm)
Model Amplitude Position Width Eq au CQ CQ_max
CzSimpleOld 44.68 10.83 8.70 1000.00 3025.52 3025.52
FWHM CS Lb sCZ_CQ d
4.78 28.90 1512.76 5.00
ro 14000.00
Init
sdev 2.9818
2D - x:19.04ppm col:4206.5 y:-2.43ppm row:127.9

APPENDIX L: ^{1}H-^{27}AL TRAPDOR NMR

INTRODUCTION

TRAnsfer of Population in Double Resonance pulse (TRAPDOR) is a very important tool for dipolar coupling between ½ nuclei and quadrupolar nuclei. Usually, it was applied before the 2D correlation NMR to ensure the presence of dipolar coupling or can provide the relative dipolar coupling's strength among different spin-pairs. Here, we used ^{1}H-^{27}Al as the example in the manual. This method could be also used for other ½ nuclei and quadrupolar nuclei, such as ^{31}P, ^{113}Cd, ^{77}Se, ^{19}F and ^{27}Al, ^{59}Co, ^{17}O etc.

EXPERIMENT SETUP (QUICK PROCEDURES)

1. Use adamantane as the reference sample. Run a 1D ^{1}H NMR spectra of the adamantane sample. Find the pi/2 pulse of ^{1}H NMR with adamantane.
2. Use the gamma-Al_2O_3 as the standard sample, run 1D ^{1}H NMR spectra of Al_2O_3.
3. Run the saturation T_1 experiment and find the ^{1}H T_1 time of Al_2O_3.
4. Set up ^{1}H-^{27}Al TRAPDOR NMR from previous determined valve from step 3.
5. Acquire data
6. Process data

EXPERIMENT SETUP (DETAILED PROCEDURES)

Open the topspin and navigate to the /home/walkon/data/IMSERC/method/#_1H_27Al_TRAPDOR_NMR/. (# is the probe, either 4 mm or 1.6 mm). Open each file and use command "edc" to generate a new experiment file to your folder with current parameters.

Do not change the files under the method folder. You should use the newly generated files under your folder.

STEP 1. INSERT ROTOR INTO THE PROBE AND REF THE CHEMICAL SHIFT WITH ADAMANTANE

Insert the rotor with adamantane and KBr into the probe. Spin the adamantane sample to correct spinning rate. Run a regular 1D first with "zg" file for adamantane. The major peak of adamantane should be calibrated to 1.82 ppm. After obtaining the 1D spectrum of adamantane, run a nutation curve (changing

P1 pulse length) to find the pi/2 pulse of ^{1}H nuclei. Set the power of p1 pulse (PLW1) to almost the maximum power of the probe. Check the details in Appendix B for nutation curve.

STEP 2. ACQUIRE THE 1D ^{1}H SPECTRA OF AL_2O_3

Replace the adamantane rotor with the Al_2O_3 rotor. Spin your sample and open the "zg" file for solid sample, set the power "plw1" as same as last step for adamantane" and "P1" to the pi/2 pulse length. Then acquire a 1D ^{1}H spectra of your solid sample.

STEP 3. DETERMINE THE T_1 TIME OF YOUR SAMPLE

Read the manual for T_1 measurement and measure the ^{1}H T_1 value of your sample

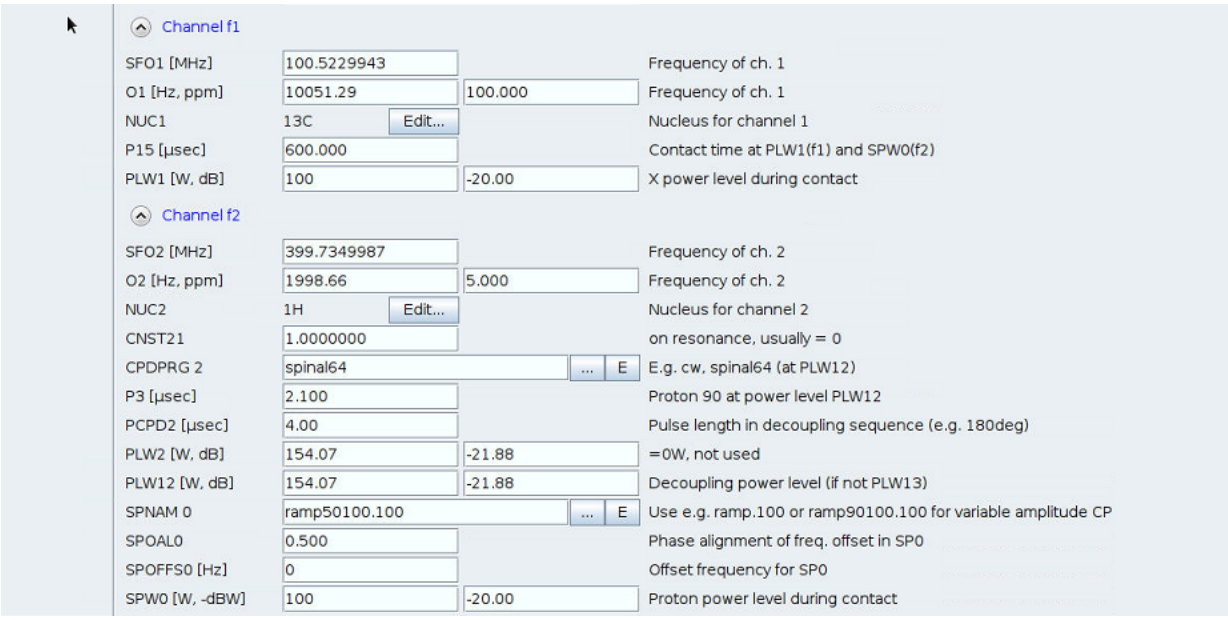
STEP 4. SET UP OF ^{1}H-^{27}AL TRAPDOR NMR

After acquiring the ^{1}H T_1 valve, Open the 1D file "TRAPDOR_HX" file for solid sample without recoupling. Set the PLW1 from optimization of step 2. Set P1 to pi/2 from step 2. Set "D1" to "1.3*T_1", where T_1 is determined from step 4. Set "cnst31" to the spinning rate. Set L1 to a reasonable number (echo time)

Open the 1D file "TRAPDOR_HX" file for solid sample with recoupling. Set the PLW1 from optimization of step 2. Set P1 to pi/2 from step 2. Set "D1" to "1.3*T_1", where T_1 is determined from step 4. Set "cnst31" to the spinning rate. Set the PLW2 to the maximum allowed power of the probe for X nuclei (here is the Al).

All the parameters in above two files should be the same. The only difference is whether the RF power is on or off for 27Al nuclei.

Here is one example for the parameter of ^{1}H-^{27}Al TRAPDOR NMR for 4 mm probe.



Channel f1			
SFO1 [MHz]	100.5229943		Frequency of ch. 1
O1 [Hz, ppm]	10051.29	100.000	Frequency of ch. 1
NUC1	13C Edit...		Nucleus for channel 1
P15 [µsec]	600.000		Contact time at PLW1(f1) and SPW0(f2)
PLW1 [W, dB]	100	-20.00	X power level during contact
Channel f2			
SFO2 [MHz]	399.7349987		Frequency of ch. 2
O2 [Hz, ppm]	1998.66	5.000	Frequency of ch. 2
NUC2	1H Edit...		Nucleus for channel 2
CNST21	1.0000000		on resonance, usually = 0
CPDPRG 2	spinal64 ... E		E.g. cw, spinal64 (at PLW12)
P3 [µsec]	2.100		Proton 90 at power level PLW12
PCPD2 [µsec]	4.00		Pulse length in decoupling sequence (e.g. 180deg)
PLW2 [W, dB]	154.07	-21.88	=0W, not used
PLW12 [W, dB]	154.07	-21.88	Decoupling power level (if not PLW13)
SPNAM 0	ramp50100.100 ... E		Use e.g. ramp.100 or ramp90100.100 for variable amplitude CP
SPOAL0	0.500		Phase alignment of freq. offset in SP0
SPOFFS0 [Hz]	0		Offset frequency for SP0
SPW0 [W, -dBW]	100	-20.00	Proton power level during contact

STEP 5. ACQUIRE DATA

Run the above two experiments and compare two experiment results to find out whether the ^{1}H signal is weaker when the RF of ^{27}Al is on.

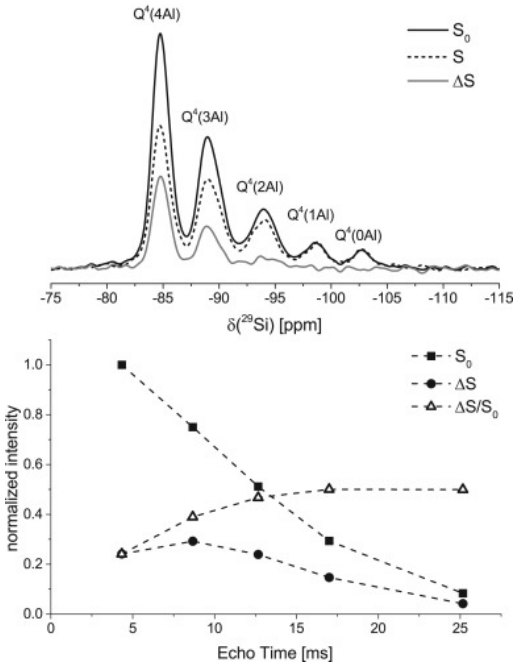
If there is no difference, try to increase the L1 and re-run the two above experiments. When you find the difference in the ^{1}H spectra, you can set up a series experiment files with different L1 value by “wrpa” command.

STEP 6. PROCESSING 1D MAS NMR

After the acquisition of 1D MAS NMR, the spectra will be saved in a topspin file format. You can process the data in topspin or DMfit. The fitting process of 1D NMR can be found in the DMfit website under the tab “how to do”.

The difference of 1H spectra with or without RF pulse of 27Al should be plotted against the TRAPDOR dephasing time 2*L1*1/cnst31.

Here is an example of how to plot the TRAPDOR curve for ^{29}Si-^{27}Al in Zeolite. So is the spectra without ^{27}Al RF pulse, S is the spectra with ^{27}Al RF pulse. ΔS is the difference between So and S (So-S).



https://doi.org/10.1016/j.ssnmr.2016.10.004

STEP 7. DETERMINE THE RF POWER OF ^{27}AL IN TRAPDOR

After the acquisition of TRAPDOR MAS NMR, you need to determine the RF power of ^{27}Al in your TRAPDOR NMR experiment. To do it, please refer to steps 1 to 3 in ^{27}Al MQMAS NMR manual. Determine the RF pulse strength with the same power set up through the 0.5 $Al(NO_3)_3$ solution sample.

REVISIONS

V2.0 2021-06-29	Added MQMAS and HETCOR into the main manual
V3.0 2024-7-19	Added and revised multiple pulse sequency in Appendix, such as CPMAS, multiple CP, CPMAS with CPMG, HETCOR, HMQC, 1H-1H DQ/SQ, 1H-1H NOESY, MQMAS, TRAPDOR