Bruker BioSpin

# AVANCE Systems

Solid State NMR

Acceptance Test Procedures

Version 010

think forward

NMR Spectroscopy

This manual was written by

Jochem Struppe

This manual was edited by

Stanley J. Niles



Rheinstetten, Germany

P/N: B92999

DWG-Nr.: 1234010

For further technical assistance on the AVANCE Systems unit, please do not hesitate to contact your nearest BRUKER dealer or contact us directly at:

BRUKER BioSpin GMBH
am Silberstreifen
D-76287 Rheinstetten
Germany

Phone: + 49 721 5161 0
FAX: + 49 721 5171 01
E-mail: service@bruker.de
Internet: www.bruker.com

# Revision History List

| Index | Date | Alteration Type | Initials |
|---|---|---|---|
| 00 | 02/01/2001 | Created | JOS |
| | 06/11/2001 | Revised | HCL, JOS |
| | 03/27/2002 | Edited | ASF, JOS |
| 01 | 04/28/2003 | Revised | JOS |
| | 09/03/2003 | Revised | JOS |
| 02 | 02/24/2004 | Revised | JOS |
| 03 | 12/22/2004 | Revised | JOS, BRC |
| 04 | 11/11/2005 | Extended with DCP and HFC experiments | JOS |
| 08 | 07/07/2008 | Completely revised with JD | JOS, JD |
| 09 | 02/03/2009 | Merged with Lab companion | JOS |
| 10 | 12/01/2009 | Proofread and placed in new corporate template | NIL |
| | | | |
| | | | |

# Summary of Contents

# Summary of Contents

# Summary of Contents

# Summary of Contents

# 1 Introduction

## 1.1 Purpose

This manual describes the procedures for the NMR tests that are necessary to set up Solid State NMR MAS experiments in order to demonstrate the high performance of Bruker AVANCE instruments. It includes basic specification tests such as $^{13}C$ resolution (line width at half height) and sensitivity tests, as well as some advice on shimming MAS probes. More advanced experiments and their setup can be found in the TopSpin help menu (other topics - solids users' manual) or the NMR Guide.

**All test procedures are subject to change without notice.**

## 1.2 Area of Application

This manual is for Bruker service personnel engaged in final testing, service and installation of NMR instruments, as well as for customers. The manual is a complement to the Acceptance and Test Procedures for Avance NMR systems, ZUEP0102. The manual complements the solids part of the ATP program and can be used only for systems with the software Release XWIN-NMR patch level 11 and higher with AQS electronics and TOPSPIN 1.3 and TOPSPIN 2.0, 2.1.

**Note:** The CP pulse programs and related parameter sets do not work on systems with AQX/AQR electronics. Pulse programs for D*X systems are available in the software release under '/exp/stan/nmr/lists/pp.dsolids'. For AVANCE I and II systems, the pulse programs have the extension *.av and parameter sets need to be changed accordingly. Parameter sets are fully valid for Avance III systems. Appropriate adjustments to the parameter sets need to be done as well. When in doubt, please contact the Bruker Applications Department in case of questions regarding older versions of hardware.

**It is generally assumed and required that all amplifiers are linearized and their power outputs are measured.**

## 1.3 Referenced Documents

| | |
|---|---|
| ZUEP0102 | Acceptance test procedures for Avance spectrometers and documents referenced in ZUEP0102. |
| H9321 | Solids User Manual. |
| Z31401 | SB MAS Operation Manual. |
| B3072 | SB Wideline Probe Manual. |
| Bxxx | HR-MAS Standard Test Procedures. |

# Introduction

# 2 Basic ATP Experiments for CPMAS Probes

| Sample | Nucleus | Shift (ppm) |
|---|---|---|
| Water | $^{1}H$ | 4.7 |
| KBr | $^{79}Br$ | ~61 |
| Adamantane | $^{13}C$ | 31.5, 50.48 relative to DSS or 29.5, 38.48 relative to TMS. |
| Glycine | $^{13}C$ | 176.4 (Carbonyl line) relative to adamantane/TMS. |
| Glycine | $^{15}N$ | 33.45 cross referencing if 13C field is referenced with adamantane relative to TMS. |
| TTMSS | $^{13}C$, $^{29}S$, $^{1}H$ | 0 ppm? - 8.9 ppm, 0 ppm. |

Table 2.1 Some Chemical Shifts That Can be Used for Referencing

KBr is used to adjust the magic angle, and adamantane for shimming and pulse length determinations for $^{1}H$ and $^{13}C$. Glycine is used to measure the sensitivity of $^{13}C$ and $^{15}N$ in natural abundance. Glycine is generally a good sample for setup of experiments because it has a simple spectrum and a short relaxation time.

For the CPMAS setup a rotor filled with a mixture of adamantane and KBr is advantageous.

References:

K.W. Zilm et al. *Chemical shift referencing in MAS solid state NMR*, J. Magn. Reson. 162 (2003) 479-486

W.L. Earl, and D.L. VanderHart, *Measurement of $^{13}C$ Chemical Shifts in Solids,* J. Magn. Res. 48, 35-54 (1982).

IUPAC Recommendation from Harris et al.:
http://www.iupac.org/web/ins/2003-006-1-100

## 2.1 Magic Angle Adjustment KBr (msol)

### 2.1.1 Setting up the Experiment to Measure and Adjust the Magic Angle with KBr

**Test Sample:** KBr

**Spinning rate**: 5 kHz (all CPMAS probes)

**Experiment time**: 1 minute.

Within the ATP software:

1. Load the experiment by clicking on the appropriate line in the ATP panel for the installed experiments.
2. Click the line labeled “msol Adjust magic angle for MAS probe” to load the first experiment.

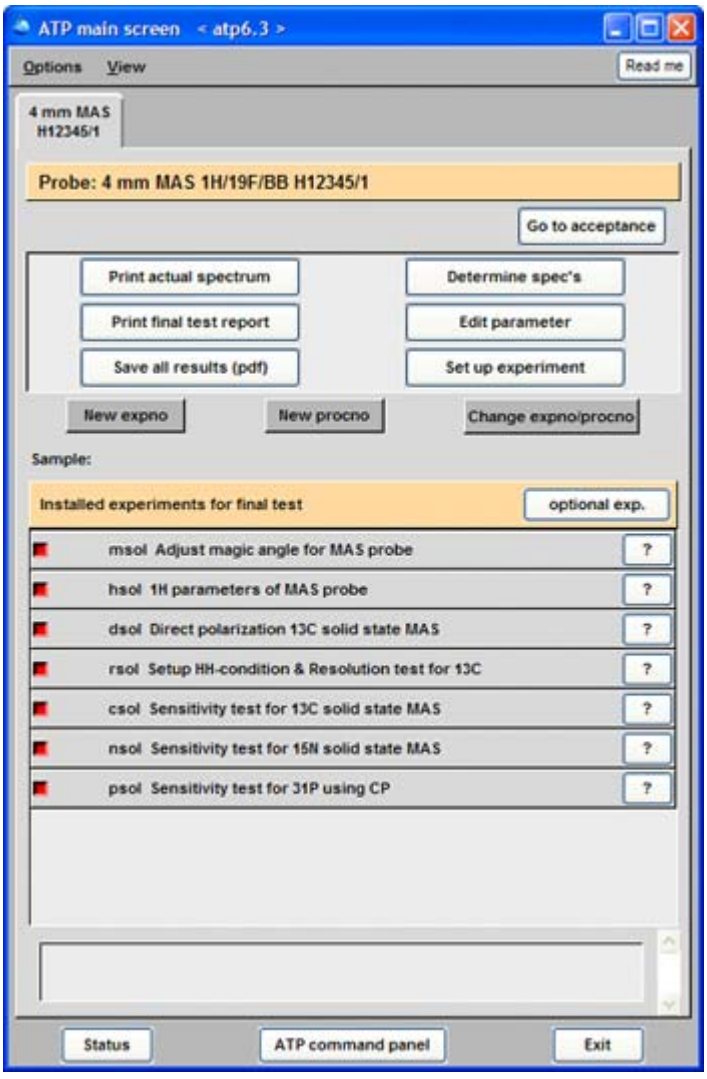



Figure 2.1 ATP Panel for Testing CPMAS Probes

NOTE: Be sure to use “*edhead*”, when the probe is not equipped with a PICS chip. We generally advise setting the maximum pulse power in “*edhead*” to the power value that was needed to achieve the specified pulse widths. Such procedures require TopSpin 2.1 or higher. If **PICS** is limiting the available RF power (which happens in some probes), whereas one cannot achieve the required pulse widths, the PICS cable should not be connected and a new probe entry for the CPMAS probe in question should be created. Please notify the Applications Department of such issues, providing the complete probe ID and system ID.

If you are not using ATP, generate new data sets using the ***edc*** command with the with appropriate names or experiment numbers to record all individual setup steps:

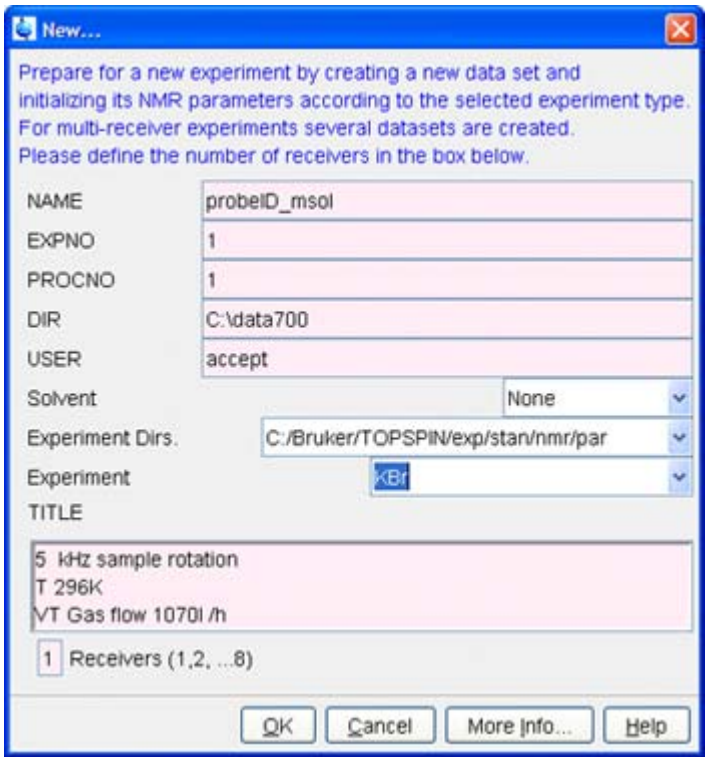



Figure 2.2 EDC Experiment Setup Window

In the EDC experiment setup window:

1. Enter a name for the experiment series.
2. Enter an experiment number.
3. Enter a process number (usually 1).
4. Use the default directory and user for DIR and USER.
5. Choose “None” for solvent from the pull down menu.
6. In the Experiment pull down menu the parameter set for the KBr experiment which is called KBr.
7. Write a appropriate title in the field called TITLE. We recommend adding parameters like T, VT gas flow rate and the spinning rate if they are of importance for the

experiment, as they are all not necessarily accurately (TE and MASR) reflected in the status parameters of the data set.

8. Check “OK”.

Enter the acquisition window by either typing ***eda*** on the command line or by checking the ***AcquPars*** tab in the experiment window (see Figure 2.2).

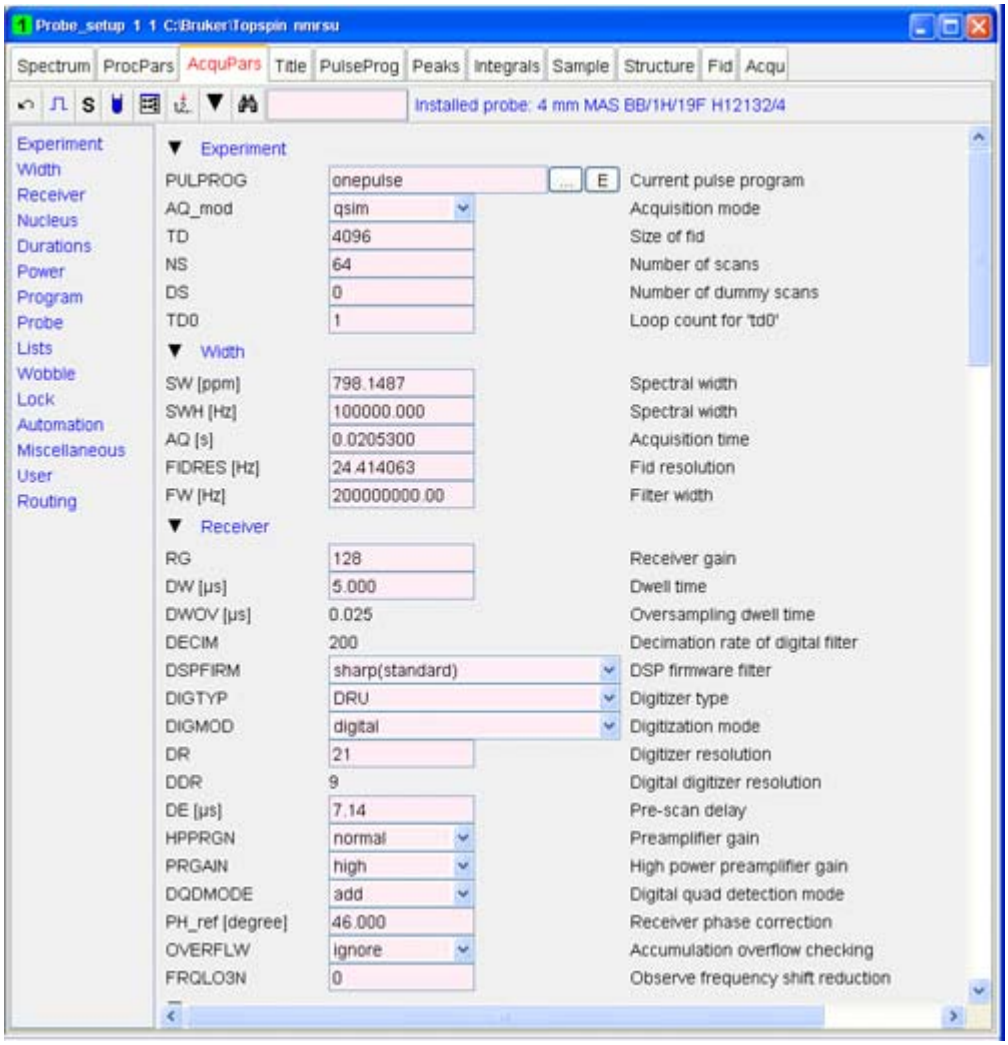



Figure 2.3 EDA Window of the KBr Experiment

### 2.1.1.1 RF Routing

To open the RF routing interface “***edasp***”, click on the routing icon in the AcquPars window (you can also type ***edasp*** into the command line).

1. Verify the appropriate RF-routing in the **edasp** window.
2. Click the default button to make sure the high power stages of the available dual stage amplifiers are selected (see Figure 2.4).

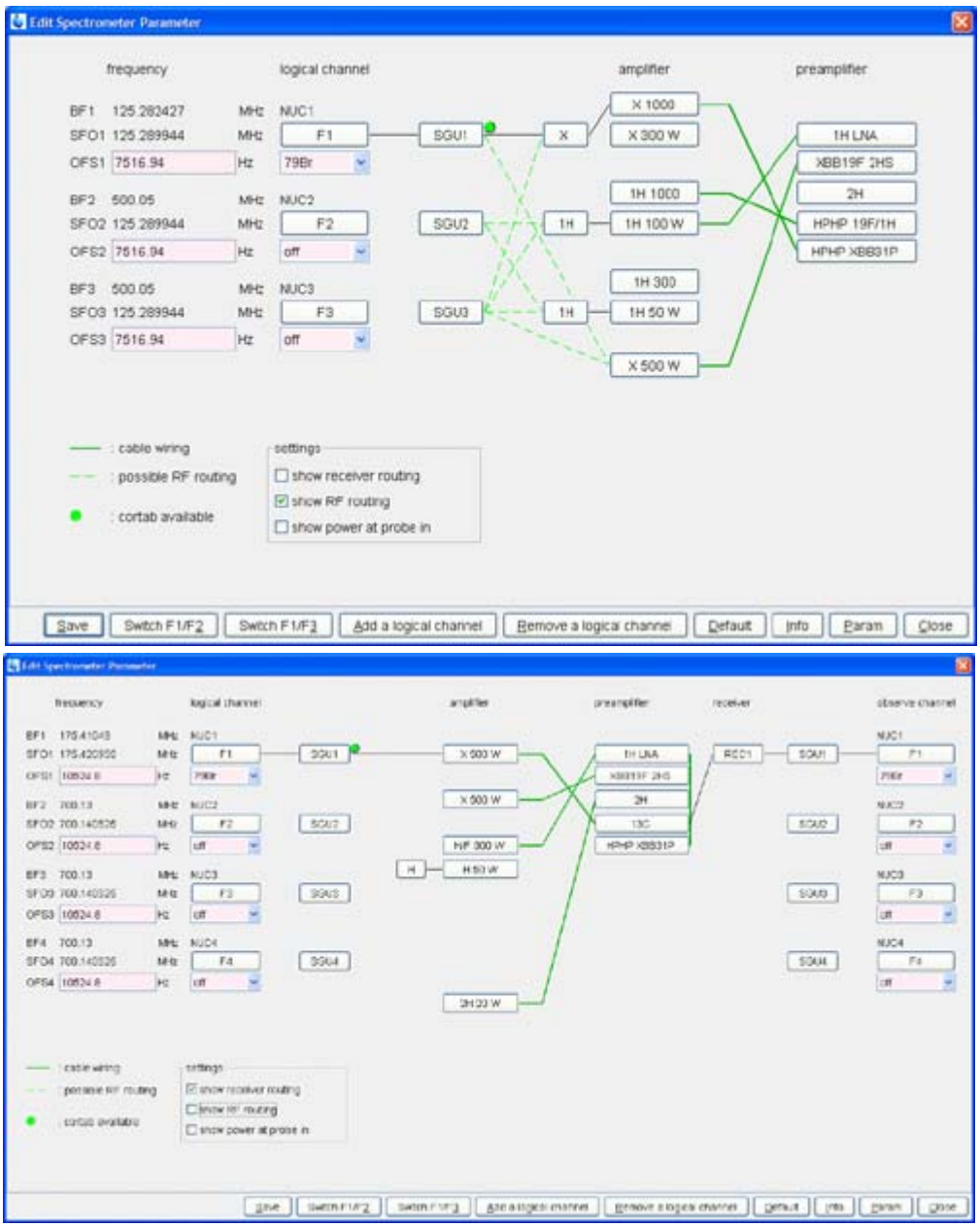



Figure 2.4 Routing Table Examples

In Figure 2.4 (**TOP**) is a routing table with the default routing for the KBr experiment. The green dotted lines show all available routing options. Note, the routing is only effective, if the parameter ***powmod* =** *high* (***powmod*** can have the values *high, low* and *linear*). The value *linear* is not used). In the **(Bottom**) is another routing example with the receiver routing open. Make sure that the receiver routing is correct! This is important in particular with some special configurations. If ***wobb*** works but you see no signal, most likely is the receiver routing incorrect.

To set up for $^{79}$Br observation, click on the "**Default**" button to display the correct routing. The green dot at SGU1 indicates that for this nucleus and the selected RF-hardware path, SGU and amplifier, is calibrated for amplitude and phase linearity.

With high power transmitters, two power stages may be selected by clicking on the desired stage. High power stage requires that the parameter ***powmod*** be set to "high". Clicking the "**Default**" button in the routing editor (see section 2.1.1) selects the amplifier stage based on the ***powmod*** parameter setting. If the parameter ***powmod*** is set to "low", the routing will automatically default to the 300W stage of the dual stage 1000W amplifier. Selecting a path which is not fully routed will generate an error message.

To test the available routing, press the button "**show RF routing**" in the **settings** area of the routing editor display (see Figure 2.4). We suggest checking the receiver routing as well and make sure it is displayed properly, otherwise one needs to make the connection the usual way with mouse clicks.

3. Continue by checking the *save* button and the *ased* button in the *AcquPars* table.


Figure 2.5 Icon to activate *ased* (reduced acquisition parameter) table.

4. Fill in the pulse program parameters in the **ASED** parameter editor and check whether these parameters agree with the ones given in Table 2.2.

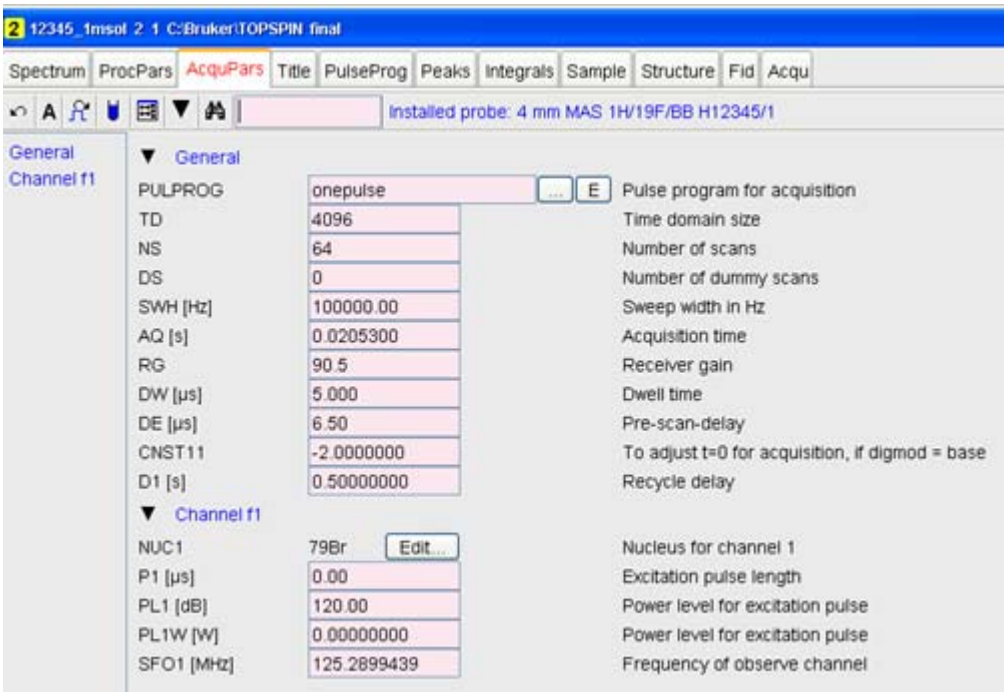



Figure 2.6 ASED table

---

**i** When selecting a nucleus where the transmitter amplitude and phase linearity were not calibrated and the green dot is not visible, the power level setting in dB will produce ≥6 dB additional power (≥4 fold power) which may lead to serious probe damage – with Powercheck enabled, the pulse program will not run. In such cases do CORTAB and linearize the RF-path.

If such calibration is impossible to achieve, use power levels starting with 10 dB less power (higher *PL(n)*-value). Reminder for engineers: with few exceptions it is expected that all systems are linearized. If you are in doubt for whatever reason, check with your supervisor or the application specialist.

If you run CORTAB, please write a README file in the CORTAB directory where you note the conditions of the power measurements, i.e. measured power at amplifier output, or measured power at preamplifier output. Note the method you chose to measure the RF-power in the same „readme“ file so that other engineers and application specialists can judge the RF-power at the probe. See note on *EDHEAD* (section 2.1.1).

Additional information on PL values and pulse widths can be found in Setting Transmitter Power on page 71.

---

5. Match and tune the probe.
6. Set the P1 value to 4 µs and the PL1 value to a reasonable value (see above) and obtain a spectrum. Print Table 2.2 and use it to enter the selected pulse parameters. Run an experiment and phase the spectrum.

7. Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | one pulse | Pulse program |
| NUC1 | 79Br | Nucleus on the F1 channel. |
| TD | 4096 | Time domain sampled complex data points |
| DW | 5 µs | Dwell time |
| Measure power level for µs 90º pulse | | |
| PL1 | | High power level F1 channel ($^{79}$Br) |
| P1 | 4 µs | 90° $^{79}$Br pulse (F1 channel) |

Table 2.2 Acquisition Parameters

## 2.1.2 Running the Experiment

1. Optimize for the magic angle in ***gs*** mode and obtain a spectrum.
2. Optimization is achieved by maximizing the spikes riding on the time signal (see Figure 2.7).

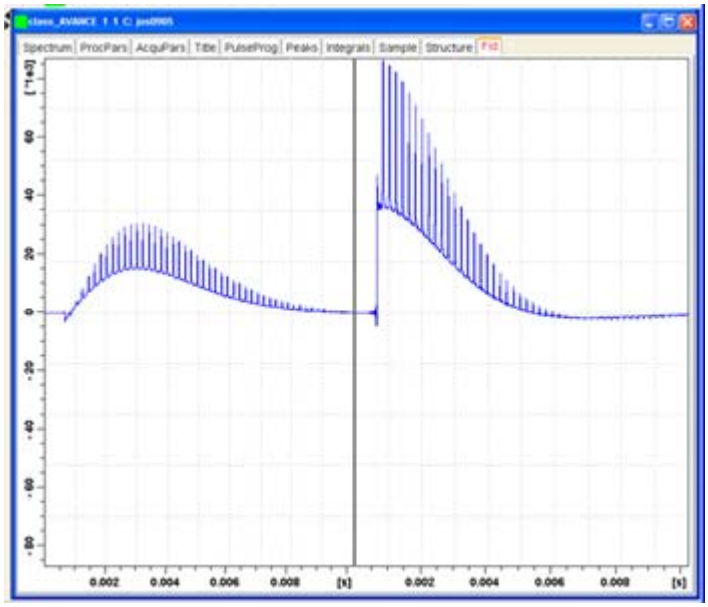



Figure 2.7 The figure shows the FID after magic angle adjustment

3. Measure the line width of the central peak and compare it with the line width of the

5th spinning sideband. If the line widths compare within ±5%, then the MA setting is acceptable. The line width comparison is conveniently achieved using the program ***peakw*** as follows.

4. Go into overview mode (click icon).
5. Center around the peak of interest.

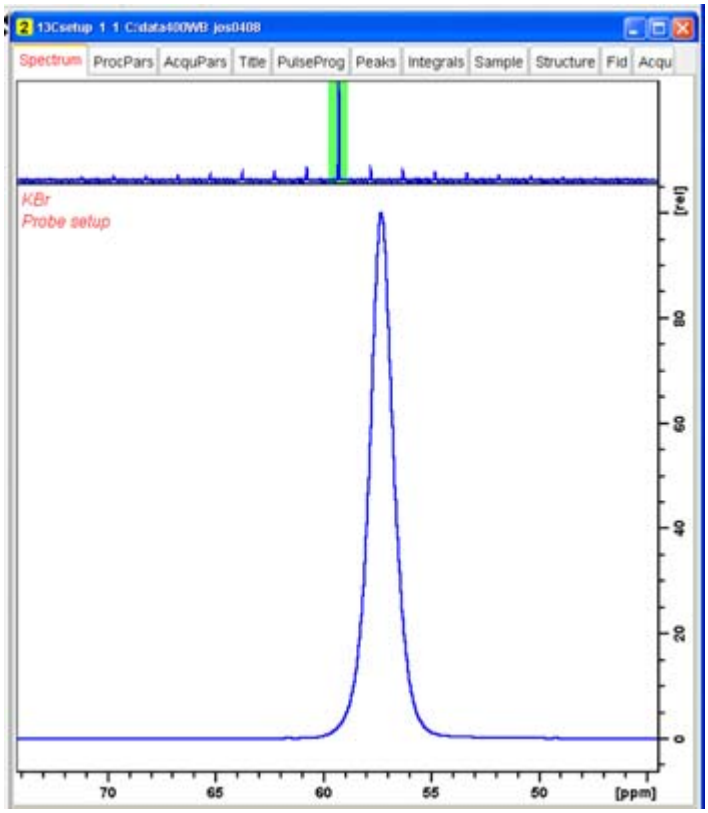



Figure 2.8 Overview mode

The green highlighted area can be moved using the mouse (left mouse, key down) to inspect different areas of the spectrum in the spectrum window.

6. Type ***peakw*** on the command line.

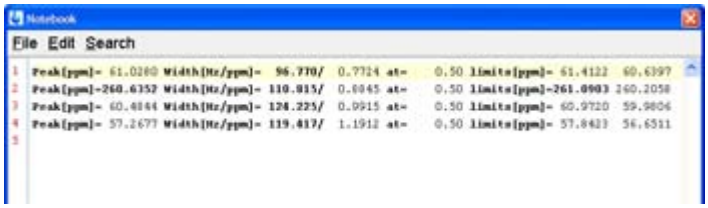
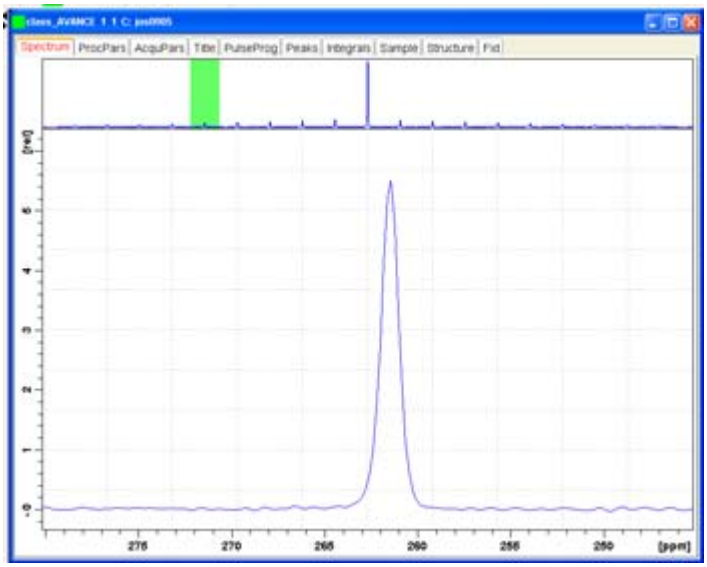



Figure 2.9 PEAKW result pane

7. Check ***save and exit***, move to the next line, then repeat the command.
8. Note that the peak widths and positions are listed in the pop-up interface.

9. Move the green bar in the overview window such that the next peak of interest is displayed in the spectrum window and reenter ***peakw***.



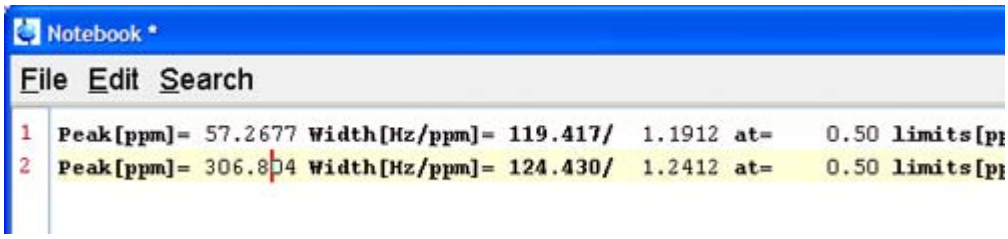



Figure 2.10 KBr spectrum and *peakw* analysis tool.

10. When more than one line is present in the ***peakw*** interface, check ***clear*** and ***save and exit***, then reenter the command ***peakw***.
11. Move the green bar in the overview window such that the next peak of interest is displayed in the spectrum window and reenter ***peakw***.

### 2.1.3 Probes with Flip-Type Stators

12. Remember to always approach the magic angle setting from the same side!
13. It is best to approach the magic angle setting by turning the adjustment **counter-clockwise**, while looking up at the probe from the bottom!
14. Check reproducibility of magic angle setting.
15. Create a new data set.
16. Stop the sample rotation.
17. Toggle the stator by ejecting and inserting the sample.
18. Spin sample up and run another experiment.

19. Change to dual display mode and compare the two data sets, or measure the line widths.

## 2.1.4 Multiple Display Mode [.md]

20. Click the multiple display icon.
21. Compare the previous spectrum with the new spectrum in multiple display mode.

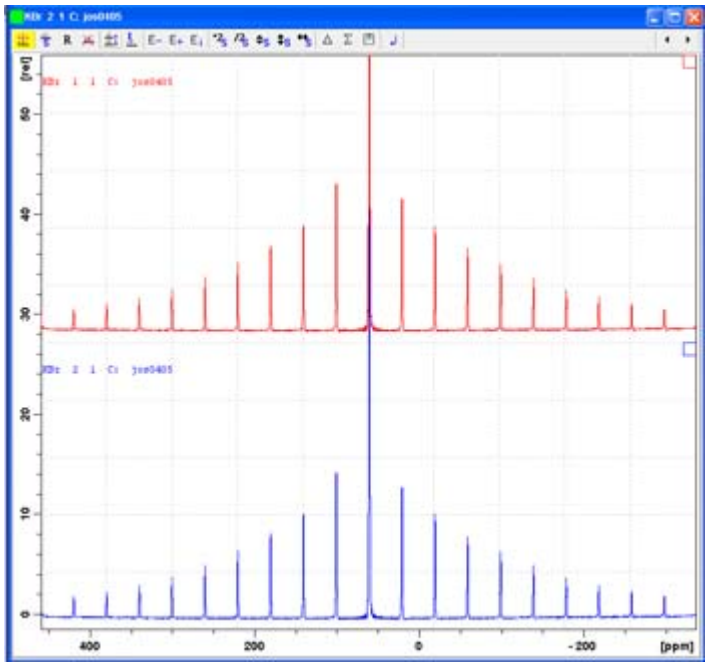



Figure 2.11 Dual Display Mode

22. Load the second spectrum by either entering "*re*" on the command line, followed by the experiment and process number, or by dragging the experiment from the browser into the multiple display window.

23. Click the *toggle display* button.
24. Compare the spectra.
25. If the new spectrum is worse, turn the adjustment dial less than 1/8$^{th}$ of a turn **counterclockwise**.
26. Get another spectrum and compare them again. Approach slowly, if you overshoot, you have to start over.
27. Plot the spectra.

## 2.2 Pulse Calibration $^{1}$H on Adamantane *(hsol)*

### 2.2.1 Experiment Setup

**Test Sample:** Adamantane

**Spinning rate**: As fast as specifications permit

**Experiment time**: 3 minutes

1. Use either the parameter set **SOLIDS1H**, or select the *hsol* experiment item line from the ATP panel experiment list (see Figure 2.1).
2. Compare the acquisition parameters from Table 2.3 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
3. Check for correct routing on the 1 kW amplifier, or for a 100W amplifier.

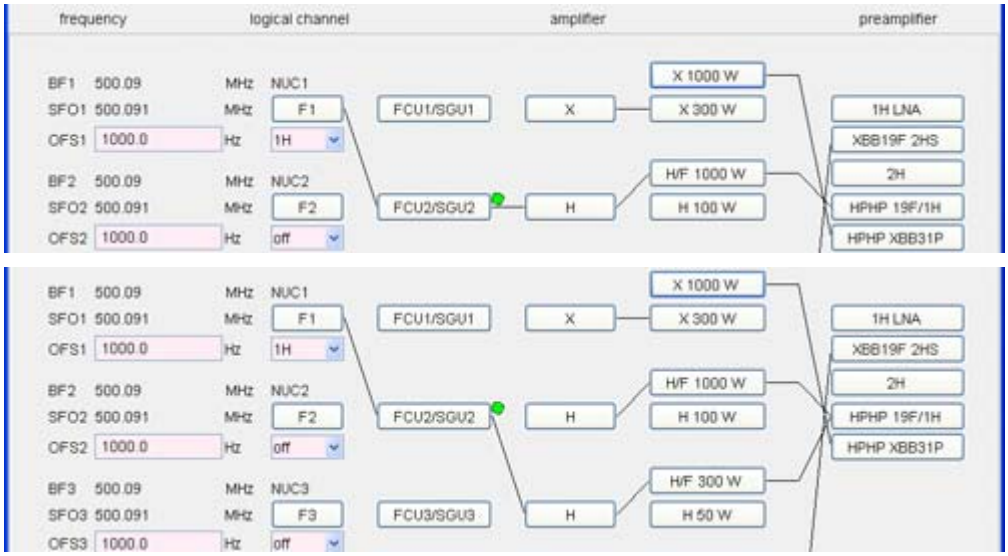



Figure 2.12 Routing suggestions for various amplifier choices.

4. Set the initial pulse parameters so that, for example, the parameter PL1W shows a value between 50 and 100W for all probes (except 1.3 mm probes, where only 10W is required) and set the P1 value to 2 µs (see Table 2.3).
5. Insert the adamantane sample, spin to the maximum specified rotation rate and document by setting up a MAS rate log file (see MAS Control on page 69).
6. Match and tune the probe.

### 2.2.2 Experiment Execution and Parameter Optimization

7. Obtain an initial spectrum.
8. Phase the spectrum and select the plotting region.
9. Measure the pulse width using POPT (if you are not familiar with POPT, please check instructions in POPT on page 65).
10. In the POPT editor enter a starting value of 1 µs for P1, and an end value of 30 µs, with an increment of 0.5 µs or 1 µs.
11. Start POPT.
12. Inspect the result, check nulls (180º, 360º …) and make a sensible choice for the 90º pulse:

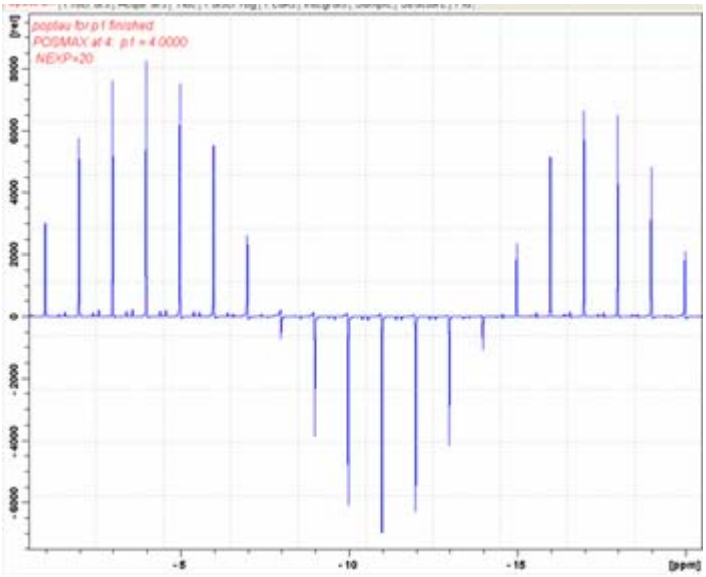


Figure 2.13 POPT nutation spectrum from run on parameter *P1*

In the figure above, the maximum is at 4 ms, the first null at almost 8 ms and the second null between 14 and 15 ms (see also POPT on page 65). For the pulses in the table choose the duration for a 360º pulse $t_{360}$ and divide by 4, i.e. $P1=t_{360}/4 \approx 3.8$ µs.

### 2.2.3 Measure Various $^{1}$H Pulse Parameters, Utilize au Program *pulse*

13. Enter the result for **P1** and calculate the power level required for a 50 kHz pulse using the command ***pulse*** in the command line.

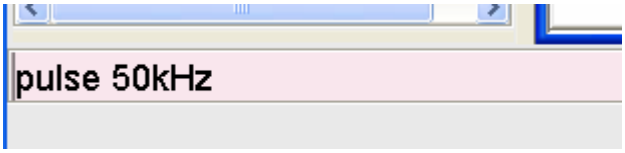



Figure 2.14 Calling the program *pulse* from the command line without any parameter

Calling the program *pulse* from the command line can also be achieved without any parameter. In this case the pulse width, power level, or field value must be entered in Hz or kHz upon request from the program. The parameter after the pulse command can be a field value as shown in the figure below, or a pulse width (e.g. 5 µs for 5 ms), or a power level (e.g. 6 dB).

14. The pulse and power level for the requested field strength are shown in the following pop-up window example:

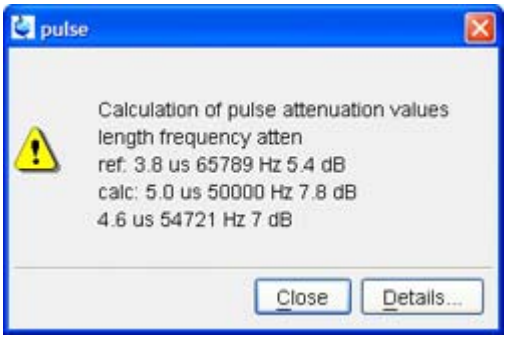



Figure 2.15 Result window from *pulse* utility.

15. Enter the result 7.8 dB for **PL1** and verify the result with another **POPT** run (run through at least two zero crossings of the nutation beyond the 360º pulse).
16. Document the values for **P1** and **PL1** in the pulse parameter table (e.g. **7.8 dB** and **5 ms**, refer to Table 2.3).
17. Calculate the required power level for the maximum decoupling specified for the probe, then back off by 1dB (to increase the attenuation by 1dB, add 1dB to the calculated power level).
18. Enter the result for **PL1** and verify the result with another **POPT** run (run through at least two zeros, beyond 360º pulse).
19. For more information on pulse width calculation and other helpful AU-programs (like ***calcpowlev***) refer to Setting Transmitter Power on page 71.

### 2.2.4 Plot Results and Prepare Documentation

20. Use a copy of Table 2.3 as a worksheet to document all the measured pulse parameters and attach the worksheet to the ATP report.
21. Plot the spectrum.
22. Plot the MAS rate log.

| Parameter | Value | Comments |
|---|---|---|
| TD | 2048 – 4096 | Number of sampled points (real and imaginary). |
| DW | 5 µs | Sweep width. |
| masr | 7000 to 15000 or 35000 | MAS spinning rate (as fast as possible). |
| Initial pulse parameters:<br>Set a safe power level for the amplifier, for example:<br>8 dB for a 1 kW or 1 dB with a 300W with 4 mm probes, and,<br>3 dB higher or lower power for 7 mm or 2.5 mm probes, respectively. | | |
| PL1 | | High power level F1 channel ($^{1}$H). |
| P1 | | 90$^{o}$ $^{1}$H pulse (F1 channel). |
| CP pulse parameters<br>Calculate the power level for the required CP pulse, for example: a 4 µs pulse on a 4 mm probe (needs to be the same pulse as for the 13C CP). Set this value and enter it in the PL1 value field. Then measure the 90 degree pulse and document it in the pulse width value field of your log. | | |
| PL1 | | High power level F1 channel ($^{1}$H). |
| P1 | | 90$^{o}$ $^{1}$H pulse (F1 channel). |
| Decoupling and P3 pulse parameters:<br>Calculate the power level for the required decoupling field, e.g. 100 kHz (or 2.5 µs) on a 4 mm probe. Enter this value in the PL1 value field and note it in the PL1 value field of the log. Measure the 90 degree pulse width P1 and document in the pulse value field of the log. | | |
| PL1 | | High power level F1 channel ($^{1}$H). |
| P1 | | 90$^{o}$ $^{1}$H pulse (F1 channel). |

Table 2.3 Parameter for 1D proton experiments

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

## 2.3 Pulse Calibration 13C on Adamantane (dsol)

### 2.3.1 Experiment Setup

**Test Sample:** Adamantane

**Spinning rate**: 5 kHz or less (all CPMAS probes)

**Experiment time**: 3 minutes.

1. Use either the parameter set DPC13, or check the *dsol* experiment in the ATP panel experiment list (see Figure 2.1).
2. Reduce the sample rotation rate to 5 kHz.
3. Compare the acquisition parameters in Table 2.4 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.

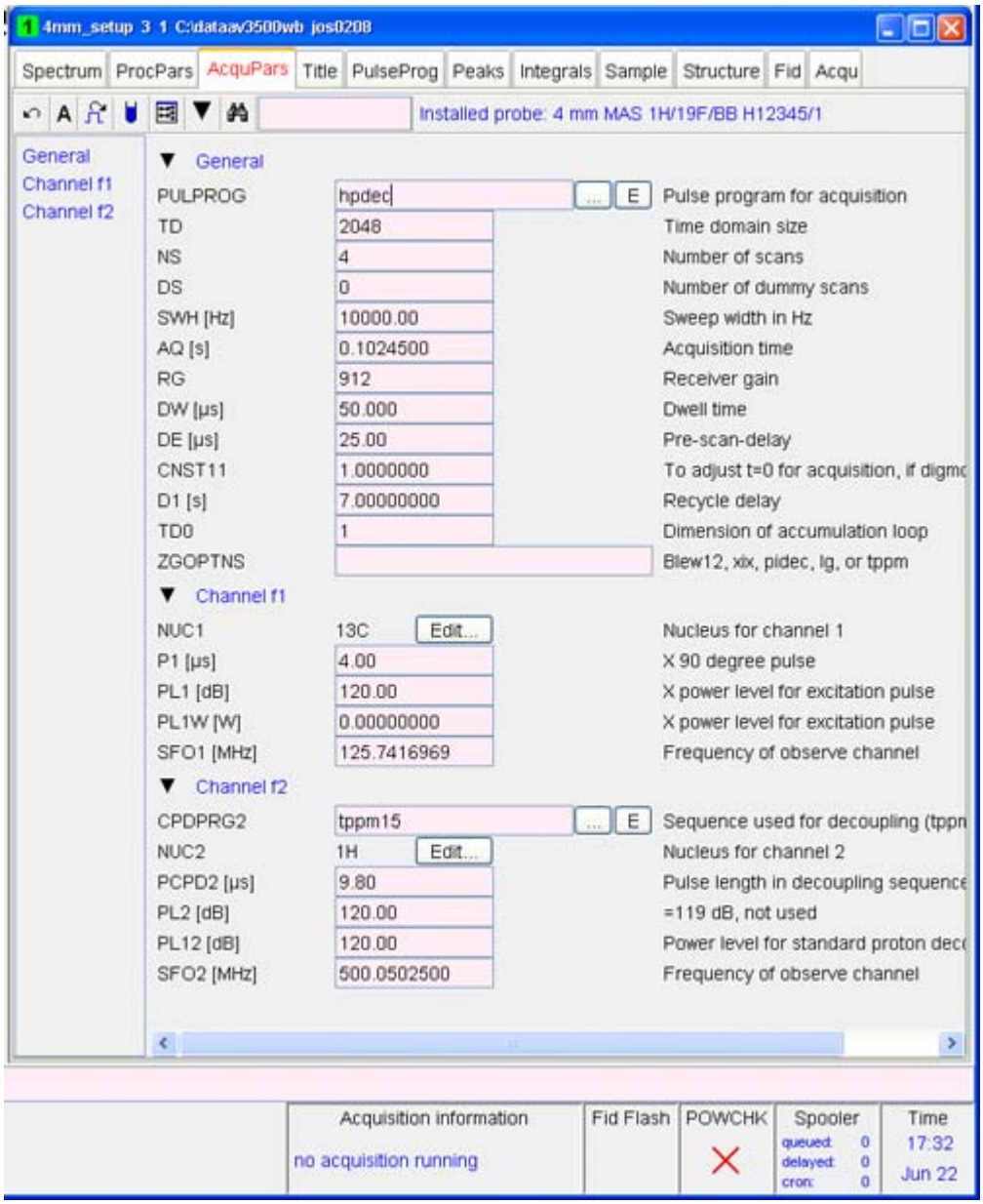



Figure 2.16 Parameter set for *dsol* experiment

4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window (see Figure 2.14).

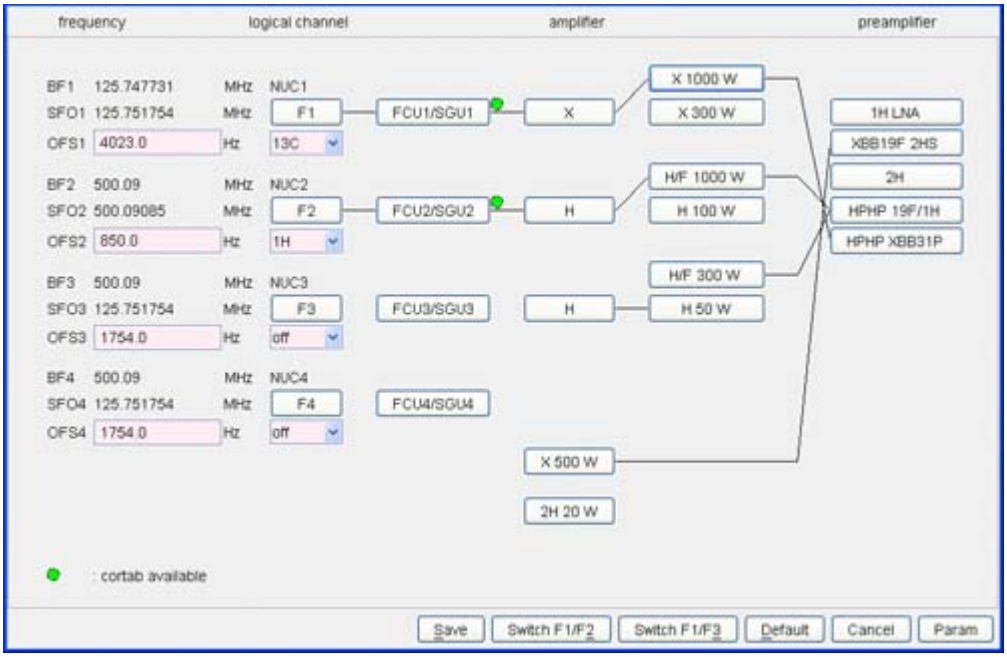



Figure 2.17 Routing for double resonance experiment using high power amplifiers.

5. Load the initial pulse parameters (see Table 2.4). For the **PL12** value, enter the 50 kHz power level obtained. For the **$^{1}$H** parameter, enter the value from the previous ***hsol*** experiment (see worksheet from Table 2.3).
6. Match and tune the probe. Make sure the $^{1}$H bandpass filter is used for this experiment. If bypassing the HPPR module, add 1dB (increase attenuation!) to account for insertion losses of the 1H HPPR module.
7. For initial values, use 2 ms for the **P1** value and the same value from the ***msol*** experiment ($^{79}$Br) for the **PL1** value.

## 2.3.2 Run Experiment, Reference Spectrum

8. Obtain an initial spectrum.
9. Process the data.
10. Make sure the processing parameter ***sr*** equals 0. Measure the position of the low frequency resonance. It should be close to 29.5 ppm.
11. If the resonance is off: measure how much it is off (e.g. 2 ppm).
12. **When this is a new installation (only)**, bring the resonance to the correct position using the **BSMS-Field** on the BSMS keyboard or the BSMS-display.

    **Otherwise**, discuss the action with the customer, do software referencing and calculate the differences. Use Table 2.4 to document all the steps taken for later use.
13. To move a resonance line which is off by 2 ppm to the correct resonance position:

- Calculate the $^{1}H$ offset by multiplying the ppm value by the MHz value of the $^{1}H$ frequency (e.g. on a 500 MHz spectrometer, 500*2 =1000Hz).
- Divide this value by 5 for a WB system, or 6.5 for a SB system.
- Change the current value for the **BSMS_field** by the calculated amount.

14. Obtain a spectrum and iterate the procedure if needed. A deviation of ± 0.1 ppm is acceptable.
15. Measure the **P1** value and adjust the **PL1** value to obtain the pulse width/spin nutation frequency required for CP in the probe specifications sheet.

### 2.3.3 Plot Spectrum and Document Parameter Measurements

16. Enter the values in the worksheet created from Table 2.4.
17. Plot the spectrum, or,
18. Shim the probe as outlined below, then plot the spectrum after shimming.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | hpdec | Pulse program. |
| NUC1 | 13C | Nucleus on the F1 channel. |
| O1P | 32 ppm | $^{13}C$ offset. |
| CPDPRG2 | tppm15 | Decoupling scheme F2 channel ($^{1}H$). |
| PCPD2 | 9.8 µs | Decoupler pulse length optimize for 50 kHz spin nutation field. |
| TD | 2048 | Time domain sampled complex data points. |
| DW | 50 µs | Dwell time. |
| Measure the P1 value using a safe power level.<br>Calculate the necessary power level for the pulse width associated with the required CP pulse width or RF field strength, as given in the probe specification (e.g. 4 µs for 4mm WB probes). Enter this value in the PL1 value parameter field and note it in the PL1 value field. Measure the 90º pulse and document it in the pulse value field. | | |
| PL1 | | High power level F1 channel ($^{13}C$). |
| P1 | | 90º $^{13}C$ pulse (F1 channel). |
| Use PL for 50 kHz B1-field, i.e. 5 µs 90º pulse from Table 2.3 PCPD2 is then 9.8 µs long. | | |
| PL12 | | High power level F2 channel ($^{1}H$). |
| PCPD2 | 2*P90 -0.2 µs | Decoupler pulse length optimize if needed. = 9.8 µs for 50 kHz $B_1$-field. |

Table 2.4 Acquisition Parameters

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state

NMR.

### 2.3.4 Probe Shimming

1. This experiment can be used for shimming the probe. If the signal is too poor, or shimming is difficult, use the CPMAS experiment in section 2.4.
2. For shimming it might be necessary to set *aq* to higher values, perhaps up to 500 ms. In this case, use 25 kHz decoupling, equivalent to a 10 ms pulse.
3. Verify that the recovery delay D1 is 7 s.
4. **Do not** exceed a maximum of 500 ms for *aq*!

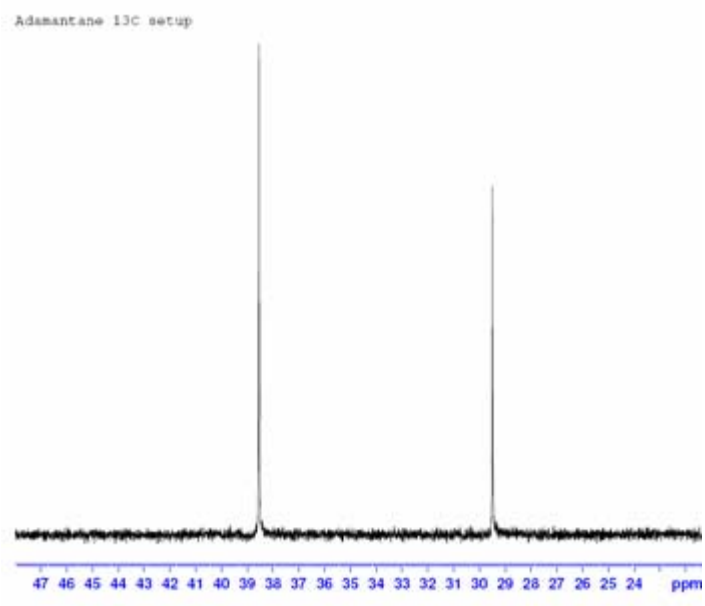



Figure 2.18 Adamantane Spectrum

## 2.4 CPMAS Experiment (*rsol*)

### 2.4.1 Experiment Setup

**Sample:** Adamantane.

**Spinning rate:** 5 kHz for Adamantane.

**Experiment time:** 3 minutes.

**Parameter set:** CPADAM.

1. Use the parameter set **CPADAM**, or check the ***rsol*** experiment on the ATP panel experiment list (see Figure 2.1).
2. Compare the acquisition parameters from Table 2.5 with the ones in ***ased*** and cor-

rect the parameters in ***ased*** if needed.

3. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window (see Figure 2.17).
4. Load the initial pulse parameters, referring to Table 2.4 (***dsol experiment***) for the values. Use Table 2.4 as a worksheet to log the parameters.
5. Match and tune the probe. Make sure the 1H bandpass filter is used for this experiment.
6. Bypass the 1H preamplifier module and adjust the PL12 value if not already done in the ***dsol*** experiment above.
7. Disable the *aq* protection feature using the flag *lacq* in ZGOPTNS: -Dlacq.

### 2.4.2 Run Experiment, Optimize CP Pulse Parameter (Hartmann Hahn Match)

8. Obtain an initial spectrum.
9. Process the data.
10. Optimize **SP0** for maximum signal intensity using **POPT**. Enter the values in the worksheet created from Table 2.5.
11. Shim the probe as outlined in Probe Shimming on page 29 if it has not been done already.
12. Use POPT to measure ***P3***, verifying and asserting the precision for **PL12**. Iterate and change the ***PL12*** value if required.

### 2.4.3 Plot Spectrum and Document Results in Table

13. Enter all the results in the pulse parameters fields of the worksheet created from Table 2.4.
14. Plot the spectrum document line width.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | cp | Start the experiment using xaua. |
| NUC1 | 13C | Nucleus on the F1 channel. |
| O1P | 32 ppm | $^{13}$C offset. |
| NUC2 | 1H | Nucleus on the F2 channel. |
| O2P | 2 ppm | $^{1}$H offset. |
| P15 | 3 ms | Contact pulse (F1 and F2 channel). |
| D1 | 5 s | Recycle delay. |
| DW | 50 µs | |
| TD | 2048 | Number of acquired complex points. |
| CPDPRG2 | tppm15 or tppm20 | Decoupling scheme F2 channel ($^{1}$H). |
| PCPD2 | 2*P3-0.2 µs | Optimized decoupling pulse. |
| ZGOPTNS | -Dlacq | LACQ stands for long acquisition. Be careful when switching protection off – remove the parameter after the experiment. |
| In the next field write the power level PL1 as measured in the previous experiment for the required CP condition (e.g. 4 µs pulse power level for 4mm WB CPMAS probes).<br>Optimize the signal by varying the SP0, then write the result for SP0 into the SP0 value field in your log. To optimize the SP0 value start with a PL from section 2.1.1, minus 3 dB to account for the ramped contact pulse. For example, if the PL was 3dB, start with a SP0 value of 0 dB. | | |
| PL1 | | High power level F1 channel ($^{13}$C) contact pulse |
| SP0 | | High power level F2 channel ($^{1}$H) contact pulse |
| Vary P3 in POPT. Set the variation from 1 to 25 µs in steps of 1 µs. Compare with results from $^{1}$H measurements above and correct PL12 or P3 if required. Note: **This is important for the next experiment, $^{13}$C CPMAS on glycine** | | |
| PL12 | | High power level F2 channel ($^{1}$H) excitation P3 and decoupling use power level for 5 µs π/2 pulse |
| P3 | Larger or equal to 5 µs | 90$^{o}$ $^{1}$H pulse at PL12 (F2 channel). |
| PCPD2 | | See Table 2.4, PCPD2 = 2*P3-0.2 µs. |

Table 2.5 Acquisition Parameters

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

## 2.5 CPMAS $^{13}$C Sensitivity on Glycine (*csol)*

### 2.5.1 Experiment Setup

**Sample:** Glycine

**Spinning rate:** Spin at N kHz where N is defined by the 1H spectrometer frequency divided by 100 MHz (e.g. for a 500.13 MHz spectrometer N=5).

**Parameter set:** CPGLY

1. Use either the parameter set **CPGLY**, or check the appropriate item line for the **csol** experiment in the ATP panel experiment list (see Figure 2.1).
2. Load the glycine sample with natural isotope $^{13}$C abundance, spin the sample to the required speed (see above). Match and tune the probe.
3. Compare the acquisition parameters from Table 2.6 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window (see Figure 2.14).
5. Load the initial pulse parameters, referring to Table 2.5 (***rsol experiment***) for the values. Use Table 2.5 as a worksheet to log the parameters.
6. Load the initial parameters for the $^{1}$H channel, **PL12**, **P3,** and **PCPD2 = (2*P3)** using the values noted from the ***hsol*** experiment. Load the parameters for maximum decoupling as outlined in the probe specification sheet.
7. Match and tune the probe. Make sure the 1H bandpass filter is used for this experiment.
8. Bypass the 1H preamplifier module and adjust the PL12 value as discussed above.

### 2.5.2 Run Experiments and Optimize CP and Decoupling Parameters

9. Obtain an initial spectrum.
10. Process the data.
11. Optimize the ***SP0*** value for maximum signal intensity on the ***aliphatic peak*** (refer to the next experiment) using **POPT**. Enter the values in the worksheet created from Table 2.5.
12. Use POPT to measure the ***P3*** value, verifying and asserting the precision for **PL12**. Iterate and change ***PL12*** if required.
13. Use POPT to measure the ***PCPD2*** value in a range of **±1 dB** around the calculated value. Use **0.1 dB** increments. If in doubt about the correct O2P setting (the decoupler carrier frequency), optimize the O2P using POPT.

### 2.5.3 Evaluate Experiment, Document Setup Results and Plot

14. Enter all the results in the pulse parameters fields of the worksheet created from Table 2.6.
15. Determine the signal to noise ratio.
16. Plot the spectrum.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | cp | |
| NUC1 | 13C | Nucleus on the F1 channel. |
| O1P | 100 ppm | $^{13}$C offset. |
| NUC2 | 1H | Nucleus on the F2 channel. |
| D1 | 5 s | Recycle delay. |
| NS | 4 | Number of scans. |
| SW | 300 ppm | Sweep width for Glycine. |
| TD | 2048 | Number of acquired complex points. |
| CPDPRG2 | SPINAL64 | Decoupling scheme F2 channel ($^{1}$H). |
| SPNAM0 | ramp.100 | For ramped CP. |
| P15 | 2 ms | Contact pulse (F1 and F2 channel). |
| Use CP parameters as obtained from above experiment with adamantane.<br>Optimize the signal at about 40 ppm by varying SP0 value. | | |
| PL1 | | High power level F1 channel ($^{13}$C) contact pulse. |
| SP0 | | High power level F2 channel ($^{1}$H) contact pulse. |
| Use the decoupling power level measured in Experiment Setup on page 32. Use corrections to this power level if results from the CP experiment on adamantane suggest it! If in doubt, use a conservative PL12 value, measure the P3 and PCPD2, then adjust the PL12 to get the maximum specified decoupling.<br><br>Example: A 4mm WB CPMAS probe is specified with 100 kHz decoupling. This is equivalent to a P3 of 2.5 µs and a best PCPD2 of 5µs (±1 µs) using SPINAL64. Use POPT and P3 variations out to 360º pulses (e.g. P3 from 1 to >10 µs in increments of 0.25 µs in POPT). | | |
| PL12 | | High power level F2 channel ($^{1}$H) excitation and decoupling). |
| P3 | | 90º $^{1}$H pulse at PL12 (F2 channel). |
| PCPD2 | | SPINAL64 decoupling pulse.<br>Starting point: for SPINAL64.<br>PCPD2 is about 2*P3 (180°Pulse). |
| O2P | 2.5 - 3 ppm | $^{1}$H offset - optimize in 400 - 500 Hz steps for maximum signal of aliphatic peak. |

Table 2.6 Acquisition Parameters

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

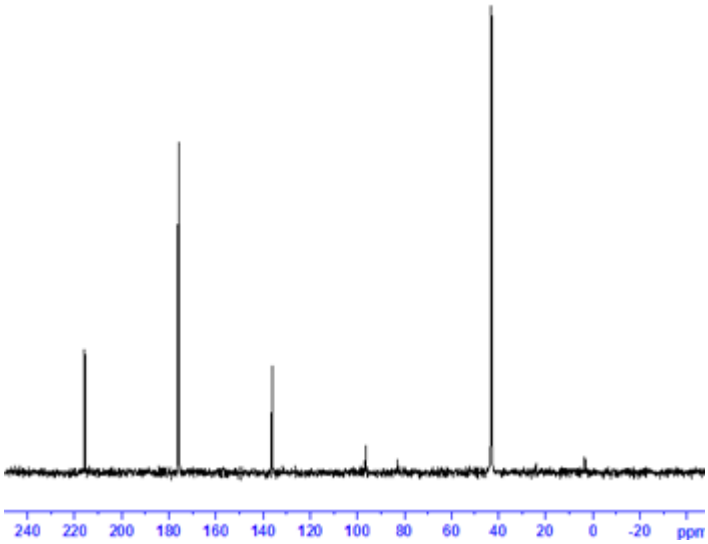



Figure 2.19 $^{13}C$ spectrum of glycine natural abundance

## 2.6 CPMAS: Measuring 13C Pulse Widths (ctsl)

### 2.6.1 Experiment Setup

**Sample:** Glycine

**Spinning rate:** Spin at N kHz where N is defined by the 1H spectrometer frequency divided by 100 MHz (e.g. for a 500.13 MHz spectrometer N=5).

**Experiment time:** 3 minutes.

1. Use either the parameter set **CPGLY**, or click on "*optional exp*" in the ATP panel (Figure 2.1) and choose the *ctsl* experiment. Spin the sample to the required speed, then match and tune the probe.
2. This experiment is in principle identical to the sensitivity experiment 2.5.1 except that the pulse program used is called ***cp90***.
3. Compare the acquisition parameters from Table 2.6 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window (see step 23.).
5. Load the pulse parameters from the **csol** experiment (see Table 2.6). Set **PL11 to 120dB** and **P1** to the required value (see specifications or the **dsol** experiment).
6. Match and tune the probe, make sure the $^{1}H$ bandpass filter is used for this experiment.
7. Bypass the 1H preamplifier module and adjust the PL12 value as discussed above.

## 2.6.2 Run Experiment and Measure Pulse Parameters

8. Obtain a reference spectrum and process the data.
9. Set the **O1P** value close to one of the resonances at 50 ppm or at 176 ppm.
10. Obtain a second spectrum and process the data.
11. Set **PL11** to **PL1** and measure **P1** using **POPT**.
12. Use **ZERO** for the optimization method in **POPT**.
13. Enter all the results in the pulse parameters fields of the worksheet created from Table 2.7.

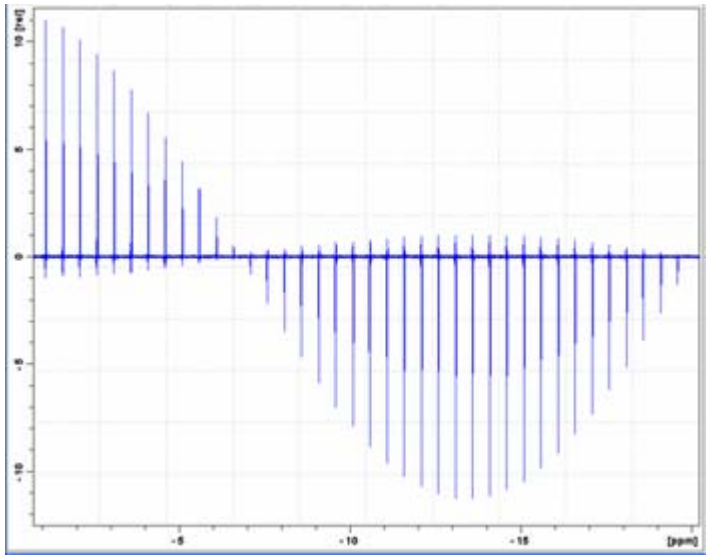


Figure 2.20 Parameter optimization for flipback pulse after CP. Note 90º pulse is at the zero crossing.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | cp90 | |
| Set all values known from previous experiments for PL1, PL2, PL12, P3 and P3. Measure P1 and adjust PL11 if required and repeat. | | |
| PL1 | | High power level F1 channel ($^{13}$C) contact pulse. |
| Leave PL11 at 120 dB set P1 to the projected value, e.g. 4 µs, then obtain and phase the spectrum. Set PL11 to the value of PL1 and optimize P1 in POPT. Set the optimization method to ZERO. Optimize by varying P1 from 1 µs to 16 µs in steps of 1 µs. The 90º pulse is at the zero intensity of the signal and the 180º pulse at the negative maximum of the signal. | | |
| PL11 | | High power level F1 channel ($^{13}$C) pulse. |
| P1 | | 90º $^{13}$C pulse at PL11 (F1 channel). |
| P1 | | 180º $^{13}$C pulse at PL11 (F1 channel). |
| Use $^{1}$H parameters from Table 2.6 | | |
| SP0 | | High power level F2 channel ($^{1}$H) contact pulse. |
| PL12 | | High power level F2 channel ($^{1}$H) excitation and decoupling. |
| P3 | | 90º $^{1}$H pulse at PL12 (F2 channel). |
| PCPD2 | | SPINAL64 decoupling pulse. |
| O2P | | $^{1}$H offset. |

Table 2.7 Acquisition Parameters

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

## 2.7 CPMAS $^{15}$N Sensitivity on Glycine (*nsol*)

**ATTENTION**! When using different amplifiers and channels for $^{15}$N experiments, e.g. as done with Biosolid probes or other triple resonance probes for DCP setup, use the following preparation experiment for a $^{15}$N pulse. Be careful if a 1kW amplifier is used for the 15N channel and 300W or 500W for the 13C channel.

### 2.7.1 $^{15}$N Sensitivity Experiment on Glycine Natural Abundance

**Sample:** Glycine natural abundance

**Spinning rate:** Spin at N kHz where N is defined by the 1H spectrometer frequency divided by 100 MHz (e.g. for a 500.13 MHz spectrometer N=5).

**Experiment time:** 3 minutes.

1. Use either parameter set **CPN15**, or check the appropriate item line for the nsol experiment in the ATP panel experiment list (see Figure 2.1).
2. Load the glycine sample with natural isotope $^{15}$N abundance; spin the sample to the required speed (see above). Match and tune the probe.
3. Compare the acquisition parameters from Table 2.9 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the *default* button in the routing window (see step 23.).
5. Load all $^{1}$H pulse parameters (**PCPD2** and **PL12**) from ***csol*** experiment; see Table 2.6.
   a) For WB probes subtract 3dB from the PL1 recorded in Table 2.6 (double the RF-power).
   b) For SB probes use the same power level as a starting point.
6. For **SP0** use a power level that is 3 dB higher (lower power) then recorded in Table 2.6 (the $^{13}$C CPMAS experiment).
7. If the setup experiment was not done, begin with a **PL1** which is 3dB lower (twice the power) than the **PL1** from the experiment ***csol*** (Table 2.6).
8. Match and tune the probe. Make sure the 1H bandpass filter is used for this experiment.
9. Bypass the 1H preamplifier module if required. This is required for most HPHP 1H/19F modules, particularly in high field systems > 500MHz.

### 2.7.2 Run Experiment, Optimize $^{15}$N{$^{1}$H} CPMAS Condition

10. Obtain a spectrum and process the data.
11. If the setup experiment was used and the pulse parameters for the 15N channel are known, optimize **SP0** using **POPT**.
12. Go to ***ntsl*** (next experiment) and measure the pulse parameters for the 15N channel. Adjust power levels to specifications and repeat ***nsol*** experiment with the correct **PL1** value.

### 2.7.3 Evaluate Experiment, Document Optimization, Print Spectrum

13. Determine the signal to noise ratio.
14. Enter all relevant parameters into copy of Table 2.9.

15. Plot the spectrum.

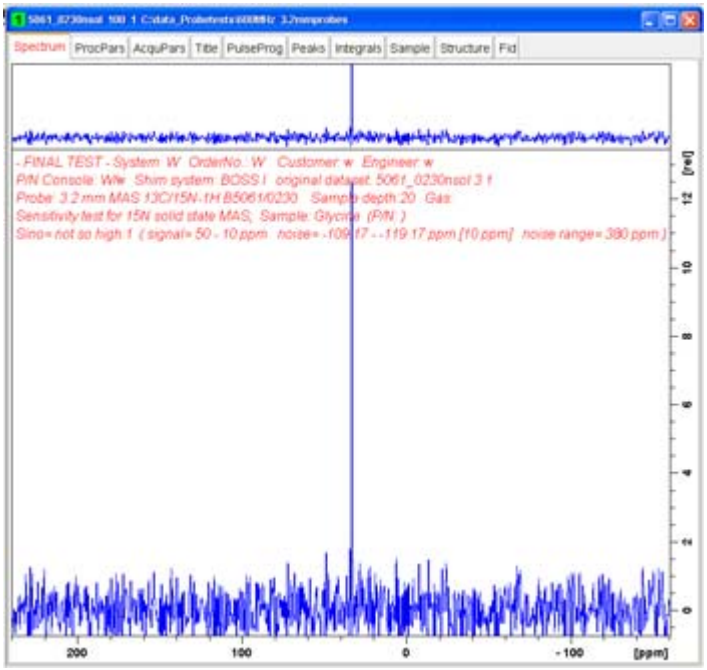



Figure 2.21 $^{15}$N CPMAS on glycine at natural abundance level

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | cp | |
| NUC1 | 15N | Nucleus on the F1 channel. |
| O1P | 40 ppm | $^{15}$N offset |
| NUC2 | 1H | Nucleus on the F2 channel. |
| D1 | 5 s | Recycle delay. |
| NS | 2 to 4 | Number of scans. |
| SW | 400 ppm | Sweep width for Glycine. |
| TD | 1024 | Time Domain complex points. |
| CPDPRG2 | SPINAL64 | Decoupling scheme F2 channel ($^{1}$H). |
| AQ_MOD | QSIM | |
| SPNAM0 | ramp.100 | For ramped CP. |
| P15 | 2 ms | Contact pulse (F1 and F2 channel). |
| Use the PL1 value from the setup experiment. If you do not use the setup experiment value, use a conservative PL1 value in order to get an acceptable CP to work such that the signal is acceptable. Then use the ntsl experiment to find the appropriate power level for PL1 (see CPMAS: Measuring 15N Pulse Widths: (ntsl) on page 41). | | |
| PL1 | | From previous $^{15}$N experiment. |
| Use the SP0 value from the 13C experiment and reduce it by 3dB. If, for example, the SP0 was 3 dB, set the SP0 value to 2-6 dB, then optimize the PL1 value. Note that this works only if the same transmitter and SGU are used for $^{13}$C and $^{15}$N CPMAS experiments. If this is not the case, use caution and the setup described at the beginning of this experiment. The SP0 value then needs to be optimized and the PL1 value set! | | |
| SP0 | | High power level F2 channel ($^{1}$H) contact pulse. |
| For the following: Use all PL and P values from the $^{13}$C experiment *csol*. | | |
| PL12 | | High power level F2 channel ($^{1}$H) excitation and decoupling. |
| P3 | | 90$^{o}$ $^{1}$H pulse at PL12 (F2 channel). |
| PCPD2 | | SPINAL64 decoupling pulse. |
| O2P | 2.5 – 3.5 ppm | $^{1}$H offset. |

Table 2.8 Acquisition Parameters

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

## 2.8 CPMAS: Measuring $^{15}$N Pulse Widths: (*ntsl)*

### 2.8.1 Experiment Setup

**Sample:** Glycine

**Spinning rate:** Spin at N kHz where N is defined by the 1H spectrometer frequency divided by 100 MHz (e.g. for a 500.13 MHz spectrometer N=5).

**Experiment time:** 3 minutes.

1. Use either the parameter set **CPN15**, or click on "*optional exp*" in the ATP panel (Figure 2.1) and choose the *ntsl* experiment.
2. Load the glycine sample with natural isotope $^{15}$N abundance, spin the sample to the required speed (see above). Match and tune the probe.
3. Compare the acquisition parameters from Table 2.9 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window (see step 23.).
5. Load the pulse parameters from the ***nsol*** experiment (see Table 2.8). Set **PL11** ***to*** **120dB** and **P1** to the required value (see specifications or the **dsol** experiment)**.**
6. Match and tune the probe. Make sure the 1H bandpass filter is used for this experiment.
7. Bypass $^{1}$H preamplifier module if needed and adjust **PL12** as discussed above.

### 2.8.2 Run Spectrum, Measure Flip-back Pulse Parameters

8. Obtain a reference spectrum for phasing.
9. Process the data.
10. Set **PL11** to **PL1** and measure **P1** using **POPT**.
11. Use **ZERO** for the optimization method in **POPT**.

### 2.8.3 Print Spectrum, Document Result from Parameter Optimization

12. Enter all the results in the pulse parameters fields of the worksheet created from Table 2.10.
13. Plot the spectrum.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | cp90 | |
| Set all values known from previous experiments for PL1, SP0, PL12, P3 and PCPD2. Measure P1 and adjust PL11 if required and repeat. | | |
| PL1 | | High power level F1 channel ($^{15}$N) contact pulse from the previous experiment. |
| Leave PL11 at 120 dB set P1 to the projected value, e.g. 4 µs, then obtain and phase the spectrum. Set PL11 to the value of PL1 and optimize P1 in POPT. Set the optimization method to ZERO. Optimize by varying P1 from 1 µs to 25 µs in steps of 1 µs. The 90° pulse is at the zero intensity of the signal and the 180° pulse at the negative maximum of the signal. | | |
| PL11 | | High power level F1 channel ($^{15}$N) pulse. |
| P1 | | 90° $^{15}$N pulse at PL11 (F1 channel). |
| P1 | | 180° $^{15}$N pulse at PL11 (F1 channel). |
| Use all parameters from Table 2.8 | | |
| SP0 | | High power level F2 channel ($^{1}$H) contact pulse. |
| PL12 | | High power level F2 channel ($^{1}$H) excitation and decoupling. |
| P3 | | 90° $^{1}$H pulse at PL12 (F2 channel). |
| PCPD2 | | SPINAL64 decoupling pulse. |
| O2P | | $^{1}$H offset. |

Table 2.9 Acquisition Parameters

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

## 2.9 CPMAS: Measuring $^{31}$P Pulse Parameters: (*psol)*

### 2.9.1 $^{31}$P Sensitivity Experiment on Glycine Natural Abundance

**Sample:** Ammonium dihydrogen Phosphate (hereafter ADP)

**Spinning rate:** Spin at N kHz where N is defined by the 1H spectrometer frequency divided by 100 MHz (e.g. for a 500.13 MHz spectrometer N=5).

**Experiment time:** 3 minutes.

1. Use either the parameter set **CPP31**, or check the appropriate item line for the **psol**

experiment in the ATP panel experiment list (see Figure 2.1).

2. Load the rotor with ADP and spin the sample to the required speed (see above). Match and tune the probe.
3. Compare the acquisition parameters from Table 2.11 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the *default* button in the routing window (see Figure 2.17).
5. Make sure that the correct receiver path is selected (see Figure 2.4).
6. Load all the $^{1}$H pulse parameters (**PCPD2** and **PL12**) from the ***csol*** experiment (see Table 2.6).

a) Add 3dB from the PL1 recorded in Table 2.6 (half the RF-power).

7. For **SP0** use the same power level as recorded in Table 2.6 (the $^{13}$C CPMAS experiment).
8. Match and tune the probe. Make sure the 1H bandpass filter is used for this experiment.
9. Bypass the 1H preamplifier module if required. This is required for most HPHP 1H/19F modules, particularly in high field systems > 500MHz.

### 2.9.2 Run Experiment, Optimize $^{15}$N{$^{1}$H} CPMAS Condition

10. Obtain a spectrum and process the data.
11. The resonance should be around 2.5 ppm.
12. Optimize **PL1** using **POPT** to get an optimum HH match.

### 2.9.3 Evaluate Experiment, Document Optimization, Print Spectrum

13. Determine the signal to noise ratio.
14. Enter all relevant parameters into copy of Table 2.11.
15. Plot the spectrum.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | cp | |
| NUC1 | 31P | Nucleus on the F1 channel. |
| O1P | 0 ppm | $^{31}$P offset. |
| NUC2 | 1H | Nucleus on the F2 channel. |
| D1 | 5 s | Recycle delay. |
| NS | 2 to 4 | Number of scans. |
| SW | 300 ppm | Spectral width for ADP. |
| AQ | 50ms | Acquisition time. |
| CPDPRG2 | SPINAL64 | Decoupling scheme F2 channel ($^{1}$H). |
| AQ_MOD | QSIM | |
| SPNAM0 | ramp.100 | For ramped CP. |
| P15 | 5 ms | Contact pulse (F1 and F2 channel). |
| Use the PL1 value from the setup experiment. If you do not use the setup experiment value, use a conservative PL1 value in order to get an acceptable CP signal. Then use the ntsl experiment to find the appropriate power level for PL1 (see CPMAS: Measuring 15N Pulse Widths: (ntsl) on page 41). | | |
| PL1 | | |
| Use SP0 from $^{13}$C experiment then optimize PL1. Note: This works only if the same transmitter and SGU is used for $^{13}$C and $^{31}$P CPMAS experiments. Otherwise use the above setup experiment, but proceed with caution. Optimize the SP0 and set the PL1 value. | | |
| SP0 | | High power level F2 channel ($^{1}$H) contact pulse. |
| In the following: Use all PL an P values from $^{13}$C experiment *CSOL*. | | |
| PL12 | | High power level F2 channel ($^{1}$H) excitation and decoupling. |
| P3 | | 90$^{o}$ $^{1}$H pulse at PL12 (F2 channel). |
| PCPD2 | | SPINAL64 decoupling pulse. |
| O2P | 2.5 – 3.5 ppm | $^{1}$H offset. |

Table 2.10 Acquisition Parameters

Print and use the table above, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

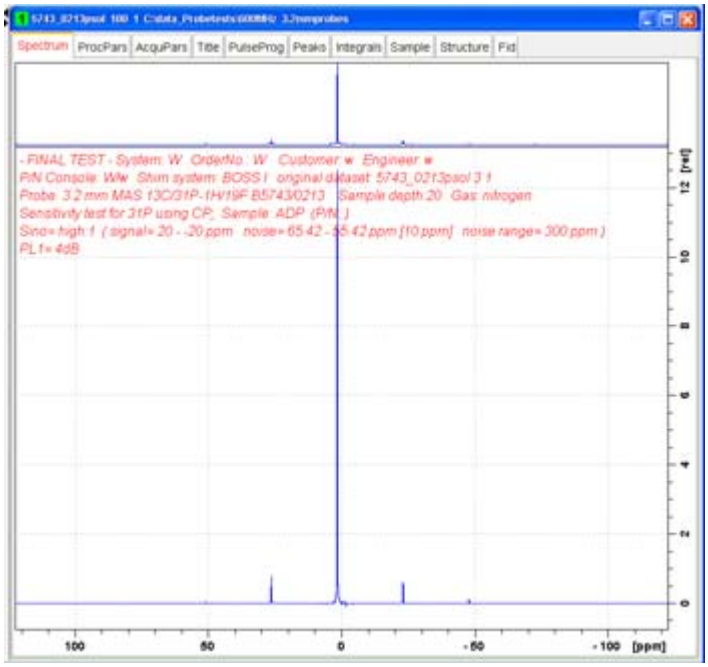



Figure 2.22 $^{31}$P CPMAS on ADP

The **sensitivity** is determined by measuring the signal level of the peak and noise over a 20-ppm wide region. Use the au program **sinocal**. Signal region = 15 ppm to -15 ppm, whole spectrum 125 ppm to -125 ppm and noise bandwidth is 20 ppm.

After this the program will look for the best noise region and return the values for noise region, signal region and S/N.

## 2.10 CPMAS: Measuring $^{31}$P Pulse Widths: (*ptsl*)

### 2.10.1 Experiment Setup

**Sample:** ADP

**Spinning rate:** Spin at N kHz where N is defined by the 1H spectrometer frequency divided by 100 MHz (e.g. for a 500.13 MHz spectrometer N=5).

**Experiment time:** 3 minutes.

1. Use either the parameter set **CPP31**, or click on "*optional exp*" in the ATP panel (Figure 2.1) and choose the *ptsl* experiment.
2. Load the ADP sample and spin the sample to the required speed (see above). Match and tune the probe.
3. Compare the acquisition parameters from Table 2.11 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.

4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window (see Figure 2.17).
5. Load the pulse parameters from the ***psol*** experiment; see Table 2.10. Set **PL11** to **120dB** and **P1** to the required value (see specifications or the dsol experiment)
6. Match and tune the probe. Make sure the 1H bandpass filter is used for this experiment.
7. Bypass the $^{1}$H preamplifier module if needed and adjust **PL12** as discussed above.

### 2.10.2 Run Spectrum, Measure Flip-back Pulse Parameters

8. Obtain a reference spectrum for phasing.
9. Process the data.
10. Set **PL11** to **PL1** and measure **P1** using **POPT**.
11. Use **ZERO** for the optimization method in **POPT.**

### 2.10.3 Print Spectrum, Document Result from Parameter Optimization

12. Enter all the results in the pulse parameters fields of the worksheet created from Table 2.11.
13. Plot the spectrum.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | cp | |
| Set all values known from previous experiment for PL1, SP0, PL12, P3 and PCPD2. Measure P1 and adjust PL11 if required and repeat. | | |
| PL1 | | High power level F1 channel ($^{31}$P) contact pulse from previous experiment |
| Leave PL11 at 120 dB set P1 to the projected value, e.g. 4 µs, then obtain and phase the spectrum. Set PL11 to the value of PL1 and optimize P1 in POPT. Set the optimization method to ZERO. Optimize by varying P1 from 1 µs to 25 µs in steps of 1 µs. The 90º pulse is at the zero intensity of the signal and the 180º pulse at the negative maximum of the signal. | | |
| PL11 | | High power level F1 channel ($^{31}$P) pulse. |
| P1 | | 90$^{o}$ $^{31}$P pulse at PL11 (F1 channel). |
| P1 | | 180$^{o}$ $^{31}$P pulse at PL11 (F1 channel). |
| Use all parameters from Table 2.10 | | |
| SP0 | | High power level F2 channel ($^{1}$H) contact pulse. |
| PL12 | | High power level F2 channel ($^{1}$H) excitation and decoupling. |
| P3 | | 90$^{o}$ $^{1}$H pulse at PL12 (F2 channel). |
| PCPD2 | | SPINAL64 decoupling pulse. |
| O2P | | $^{1}$H offset. |

Table 2.11 Acquisition Parameters

Print and use the following table, or use a laboratory notebook, to keeping track of pulse widths and power levels. It is ***essential*** to keep track of pulse and power parameters during the setup until appropriate parameter tables become available for solid state NMR.

# 3 HFX ATP Experiments for CPMAS Probes

## 3.1 Basic HF, HFC Setup

### 3.1.1 General HFC Hardware Routing

General channel setup for HFC experiments benefit from $^{19}F$ preamplifier modules, for example the XBB19F 2HS module:

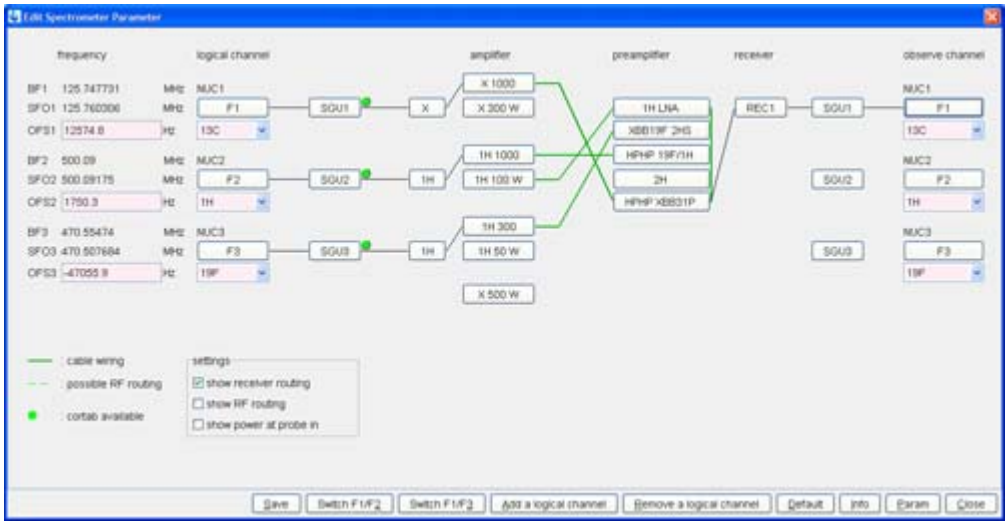



Figure 3.1 HFC Experiment Setup Example with Routing Table and Preamplifier Selection.

### 3.1.2 Probe Setup and Tuning

Once the normal $^{13}C$ sensitivity is measured on this probe, the $^{1}H$ band pass filters are replaced by the HF filter set. This configuration uses two high power filters on each $^{1}H$ and $^{19}F$ channel. The diplexer couples the two amplifier outputs coming through the band-pass filters into the probe and splits the RF-signal coming back from the probe into the correct preamplifier module (see Figure 3.2).

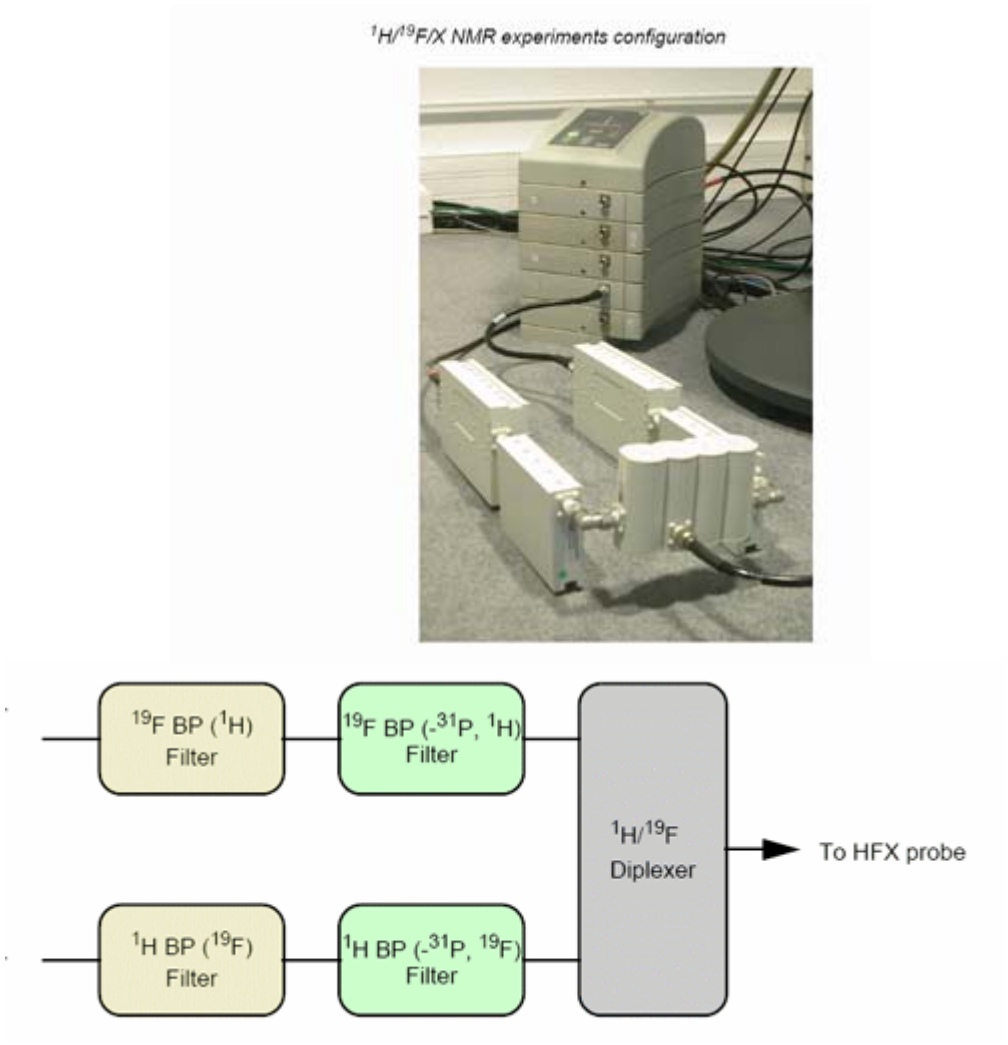



Figure 3.2 HFX Band-pass Filter Cascade and Diplexer Setup.

This filter configuration should be used for the first setup, however can be varied if satisfying simultaneous matching and tuning conditions cannot be met.

If the system has only one pre-amplifier capable of $^{19}F/^{1}H$, then only the observe nucleus should be routed through the pre-amplifier. Care must be taken that the same cabling is always used, as probe tuning will most likely change if different cables are used. Note: add approximately 1 dB to the power level setting to compensate for pre-amplifier insertion losses when in a bypass configuration.

There are three wands used for tuning the 1H and 19F channels. To tune the probe:

1. First tune and match $^{1}H$ using the $^{1}H$ tune and $^{1}H$ match.
2. Note the direction you've turned the $^{1}H$ match.
3. Switch to $^{19}F$ and adjust the $^{19}F$ tuning (wand with red label).
4. Adjustment of the match will also most likely be needed (for matching only the $^{1}H$

matching wand can be used). A compromise between the matching of the $^{1}H$ and the $^{19}F$ channels is needed. Neither will be perfect, however, proper tuning should be maintained.

To improve simultaneous matching conditions you can play with the order of the two band pass filters of each channel, by swapping the connections and cables which connects them to the pre-amplifier module. For example, you can try and connect one band-pass filter to the pre-amplifier module and then use the short N-cable to connect to the other module, which in turn is connected to the diplexer.

## 3.2 FH Experiment (*fhdp) – (hfdp)*

### 3.2.1 Experiment Setup

**Measure $^{19}F$ pulse widths:** (*fhdp)*

**Sample:** PVDF

**Spinning rate:** Spin as fast as possible (35, 24 or 15 kHz).

**Experiment time:** 3 minutes.

1. Use either the parameter set **F19HPDEC**, or check the appropriate item line for the *fhdp* experiment in the ATP panel experiment list (see Figure 3.1).
2. Load the PVDF sample and spin the sample to the required speed (see above). Match and tune the probe (see "Probe Setup and Tuning" on page 49).
3. Compare the acquisition parameters in Table 3.1 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.

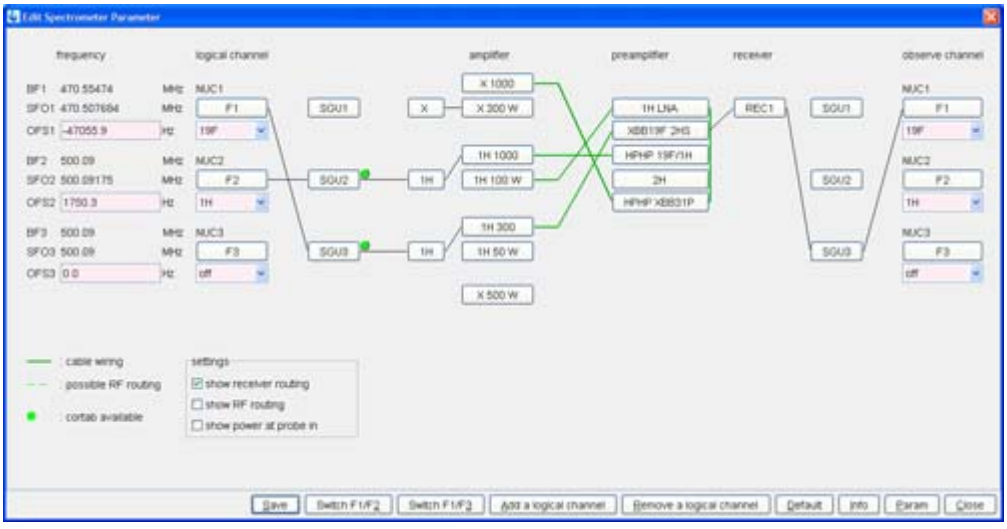



Figure 3.3 Example of routing for *fhdp* experiment.

**The ideal situation is when all hardware channels remain the same for ALL HF (*hfdp*), FH (*fhdp*), CF (*cfsl*), CH (*chsl)* and CFH (*cfhsl*) experiments!**

Other routing choices are possible and one can also use X amplifiers for systems up to 400MHz $^{1}$H resonance. For higher field instrumentation, a second $^{1}$H amplifier is required. If available, it is possible to use an XBB19F preamplifier module for the $^{19}$F channel. Systems with HPLNA need either such an amplifier or the HPHP 19F/1H module. The latter is a poor choice as it is a passively switched preamplifier module and does not permit the use of shaped pulses. When uncertain about the appropriate routing, please contact you local solid state NMR applications scientist.

4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window, then change the **$^{19}$F routing goes through SGU3** (see Figure 3.3).
5. Load the pulse parameters, using parameters from the ***hsol*** experiment as guidance (see Table 2.3). Set **PL12 = 120dB** and **P1** to the required values (see specifications).

### 3.2.2 Run Experiment, Measure Pulse Parameters

6. Obtain a reference spectrum for phasing.
7. Process the data.
8. Measure **P1** using **POPT**.

### 3.2.3 Plot Spectrum and Document Results

9. Enter all the results in the pulse parameters fields of the worksheet created from Table 3.1.
10. Plot the spectrum.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | hpdec | |
| TD | 1024 | Number of sampled points (real and imaginary) |
| DW | 5 µs | Dwell time |
| masr | 15000, 24000 or 35000 | MAS spinning rate (as fast as possible) |
| Starting pulse parameters:<br>Set a safe power level, for example:<br>• 8 dB on 1 kW or 1 dB on 300 W amp for 4mm probe<br>• 3 dB higher or lower power for 7 mm or 2.5 mm probes. | | |
| PL1 | | High power level F1 channel ($^{19}$F) |
| P1 | | 90$^{o}$ $^{19}$F pulse (F1 channel) |
| CP pulse parameters:<br>Calculate the power level for required CP pulse, e.g. 4 µs pulse on 4 mm probes (needs to be the same pulse as for $^{13}$C CP). Set this and note it in the PL1 value field. Then measure the 90 degree pulse and document it in the pulse value field. | | |
| PL1 | | High power level F1 channel ($^{19}$F) |
| P1 | | 90$^{o}$ $^{19}$F pulse (F1 channel) |
| Decoupling and P3 pulse parameters:<br>Calculate power level for required decoupling field, e.g. 80 kHz (or 3.1 µs) on 4mm probe. Set this value into PL1 and note it in the PL1 value field. Then measure the 90 degree pulse and document in the pulse value field. | | |
| PL1 | | High power level F1 channel ($^{19}$F) |
| P1 | | 90$^{o}$ $^{19}$F pulse (F1 channel) |

Table 3.1 Acquisition Parameters

## 3.3 Measure $^{1}$H Pulse Widths

### 3.3.1 Experiment Setup

**Sample:** PVDF

**Spinning rate:** Spin as fast as possible (35, 24 or 15 kHz).

**Experiment time:** 3 minutes.

1. Use either the parameter set **F19HPDEC**, or the previous experiment.
2. Create a new experiment using edc and change F1 and F2 in the ***EDASP*** display

(Figure 3.4).

3. Match and tune the probe (see "Probe Setup and Tuning".

4. Compare the acquisition parameters from Table 3.1 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.

5. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window. Then change such that **$^{19}$F routing goes through SGU3:**.

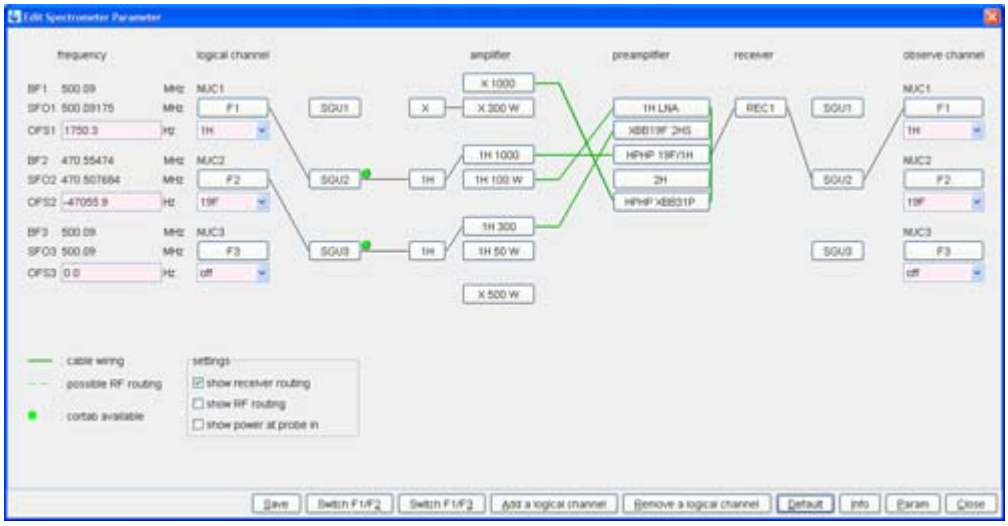



Figure 3.4 Example of routing for *hfdp* experiment.

**The ideal situation is when all hardware channels remain the same for ALL HF (*hfdp*), FH (*fhdp*), CF (*cfsl*), CH (*chsl)* and CFH (*cfhsl*) experiments!**

Other routing choices are possible and one can also use X amplifiers for systems up to 400MHz $^{1}$H resonance. For higher field instrumentation, a second $^{1}$H amplifier is requried. If available, it is possible to use an XBB19F preamplifier module for the $^{19}$F channel. Systems with HPLNA need either such an amplifier or the HPHP 19F/1H module. The latter is a poor choice, as it is a passively switched preamplifier module and would not permit the use of shaped pulses. When uncertain about the appropriate routing, please contact you local solid state NMR applications scientist.

6. Load the pulse parameters using parameters from the ***hsol*** experiment as guidance (see Table 2.3). Set **PL12 = 120dB** and **P1** to the required values (see specifications)**.**

### 3.3.2 Run the Experiment and Measure the Pulse Parameters

7. Obtain a reference spectrum for phasing.

8. Process the data.

9. Measure **P1** using **POPT**.

### 3.3.3 Plot Spectrum and Document Results

10. Enter all the results in the pulse parameters fields of the worksheet created from Table 3.2.
11. Plot the spectrum.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | hpdec | |
| TD | 512 | Number of sampled points (real and imaginary). |
| DW | 5 µs | Sweep width. |
| masr | 15000, 24000 or 35000 | MAS spinning rate (as fast as possible). |
| Starting pulse parameters:<br>Set a safe power level, for example, for a 50 kHz pulse as obtained in the *hsol* or *rsol* experiment. | | |
| PL1 | | High power level F1 channel ($^1$H). |
| P1 | | 90° $^1$H pulse (F1 channel). |
| CP pulse parameters<br>Cross check with *hsol, rsol or csol* verifying the appropriate pulse parameters (see instructions for *hsol* Table 2.3). | | |
| PL1 | | High power level F1 channel ($^1$H). |
| P1 | | 90° $^1$H pulse (F1 channel). |
| Decoupling and P3 pulse parameters:<br>IN HFX mode, MAX. DECOUPLING REDUCED<br>Calculate the power level for the required decoupling field, e.g. 80 kHz (or 3.1 µs) on 4 mm probe. Set this value into PL1 and note it in the PL1 value field. Then measure the 90 degree pulse and document it in the pulse value field. | | |
| PL1 | | High power level F1 channel ($^1$H). |
| P1 | | 90º 1H pulse (F1 channel). |

Table 3.2 Acquisition Parameters

## 3.4 Measure $^{19}F$ ($^{1}H$) Decoupled Spectrum: (*fhdp*)

### 3.4.1 Experiment Setup

**Sample:** PVDF

**Spinning rate:** Spin as fast as possible (35, 24 or 15 kHz).

**Experiment time:** 3 minutes.

1. Use either the parameter set **F19HPDEC**, or check the appropriate item line for the *fhdp* experiment in the ATP panel experiment list (see Figure 2.1) or increment from experiment in section 3.2.
2. Compare the acquisition parameters from Table 3.3 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
3. Load the appropriate pulse and power level values for $^{19}F$ and $^{1}H$ (**PL12**) using Table 3.1 and Table 3.2 for reference.

### 3.4.2 Run experiment

4. Obtain a spectrum.
5. Note the pulse parameters used for the experiment in Table 3.2**.**
6. Process the data.

### 3.4.3 Plot spectrum document results

7. Plot the spectrum and compare with the **$^{19}F$** spectrum without **$^{1}H$** decoupling.

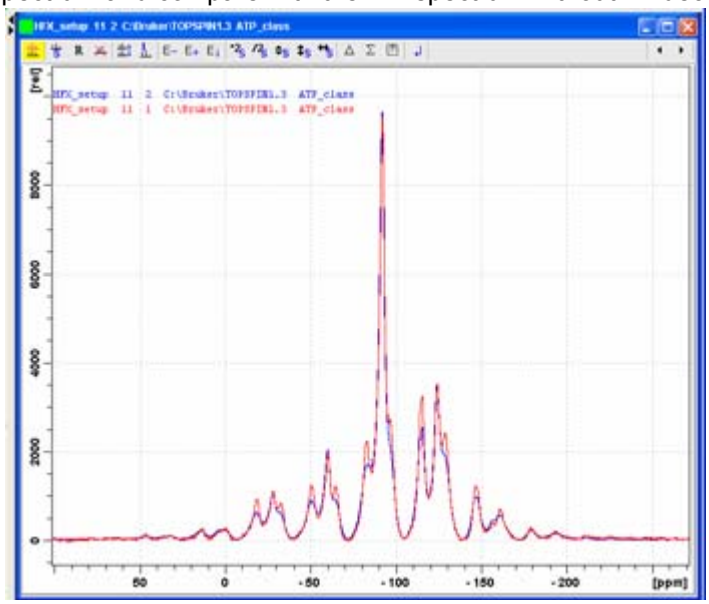



Figure 3.5 Direct 19F spectra of PVDF 15 kHz MAS, blue no decoupling, red 80 kHz 1H TPPM decoupling.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | hpdec | |
| TD | 512 | Number of sampled points (real and imaginary) |
| DW | 5 µs | Sweep width |
| masr | 15000, 24000 or 35000 | MAS spinning rate (as fast as possible) |
| Pulse Parameters from Table 2.11 | | |
| PL1 | | High power level F1 channel ($^{19}$F) |
| P1 | | 90$^{o}$ $^{19}$F pulse (F1 channel) |
| Heteronuclear Decoupling Pulse Parameters from Table 3.1 | | |
| PL12 | | High power level F2 channel ($^{1}$H) |
| CPDPRG2 | TPPM15 | Heteronuclear decoupling program for $^{1}$H decoupling use PCPD2 = value for 180$^{o}$ pulse minus 0.2 µs |
| PCPD2 | | Almost 180$^{o}$ $^{1}$H pulse (F2 channel) |

Table 3.3 Acquisition Parameters

## 3.5 $^{13}$C{$^{19}$F} CPMAS Experiments

### 3.5.1 Setup $^{13}$C{$^{19}$F} CPMAS Experiment: (*cfsl*)

**Sample:** PVDF

**Spinning rate:** Spin 15 kHz.

**Experiment time:** 3 minutes.

1. Use either the parameter set **CPC13F19**, or check the appropriate item line for the *cfsl* experiment in the ATP panel experiment list (see Figure 2.1).
2. Load the PVDF sample, then spin the sample to required speed (see above). Match and tune the probe, as described previously.
3. Compare the acquisition parameters from Table 3.3 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
4. Check for correct routing on the 1 kW amplifiers. If the routing is incorrect, click the ***default*** button in the routing window (see Figure 2.14) and adjust it such that the hardware section of the routing (SGU's, amplifiers and HPPR's) for the decoupler channel ($^{19}$**F**) is identical to the routing selected for $^{19}$**F** in the ***fhdp*** experiment.

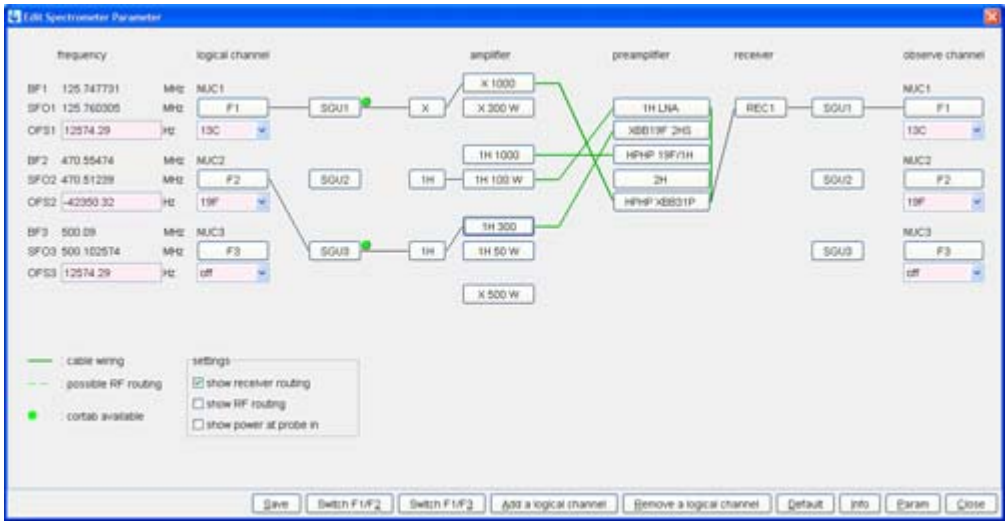



Figure 3.6 Example of routing for *cfsl* experiment.

In the figure above, it is ideal when all hardware channels remain the same for **ALL HF (hfdp), FH (fhdp), CF (cfsl), CH (chsl) and CFH (cfhsl) experiments!**

5. Load the pulse parameters using parameters from the ***csol*** and ***fhdp*** experiments as reference (see Table 2.6 for $^{13}$C, **PL1**, Table 2.11 for $^{19}$F **PL2**, and Table 3.2 **for PL12 and P31** on $^{19}$F.

### 3.5.2 Run Experiment and Optimize HH-Match

6. Obtain a reference spectrum.
7. Process the data.
8. Optimize **PL2** for maximum signal intensity using **POPT**.
9. Obtain a spectrum.

### 3.5.3 Document Results and Print Spectrum

10. Enter the values in the worksheet created from Table 3.4.
11. Process the data and plot the spectrum.

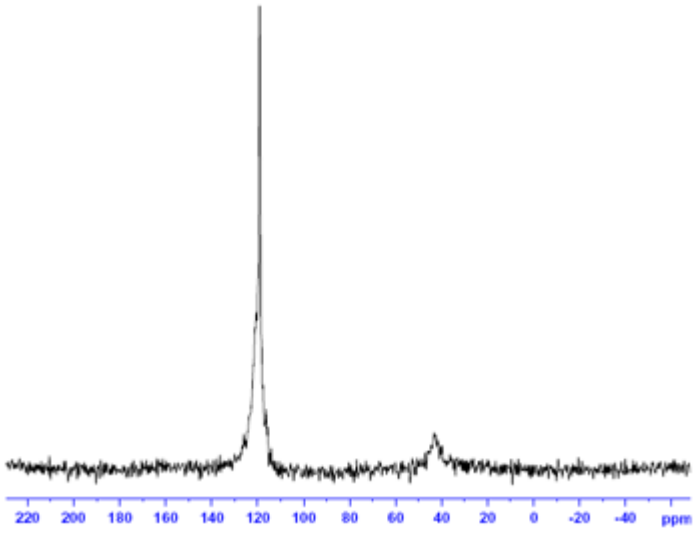



Figure 3.7 $^{13}C\{^{19}F\}$ spectra of PVDF 15 kHz MAS, 80 kHz $^{19}F$ PIDEC12 decoupling.

# HFX ATP Experiments for CPMAS Probes

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | vacp | |
| NUC1 | 13C | Nucleus on the F1 channel. |
| O1P | 100 ppm | $^{13}$C offset |
| NUC2 | 19F | Nucleus on the F2 channel. |
| O2P | -120 ppm | $^{19}$F offset |
| D1 | 5 s | Recycle delay |
| NS | 32 | Number of scans |
| SW | 300 ppm | Sweep width for PVDF |
| TD | 1024 | Number of acquired complex points |
| CNST31 | | Spinning speed in Hz |
| CPDPRG2 | PIDEC12 | Decoupling scheme F2 channel ($^{19}$F) |
| SPNAM0 | ramp.100 | For ramped CP |
| P15 | 2 ms | Contact pulse (F1 and F2 channel) |
| Use the $^{13}$C CP parameter PL1 from the *csol* experiment. For optimization of PL2, start with a PL from above (direct $^{19}$F, 4 µs [62.5 kHz]) minus 3 dB to account for the ramped contact pulse. If, for example, PL was 3dB, start with PL2 = 0dB, then optimize the 120 ppm signal (CF2) by varying the PL2 value in increments of 0.5 dB. | | |
| PL1 | | High power level F1 channel ($^{13}$C) contact pulse |
| For optimization of PL2 start with a PL from above (Direct $^{19}$F, 4 µs [62.5 kHz]) minus 3 dB to account for the ramped contact pulse. If e.g. PL was 3dB, start with PL2 = 0dB. Optimize 120 ppm signal (CF2) by variation of PL2 in 0.5 dB steps. | | |
| PL2 | | High power level F2 channel ($^{19}$F) contact pulse |
| Use the decoupling power level from ***fhdp*** based on the probe specifications, e.g. 80 kHz. If in doubt, use a conservative PL12 value, measure P3 and P31, then adjust PL12 to get the maximum specified decoupling. For example: a 4 mm WB CPMAS probe is specified with 80 kHz decoupling. This is equivalent to a P3 of 3.1 µs and a best P31 or 6.2 µs (±1 µs) using SPINAL64. Use POPT and P3 variations out past a 360 degree pulse (e.g. P3 from 1 to 14 µs in increments of 0.25 µs in POPT. | | |
| PL12 | | High power level F2 channel ($^{19}$F) excitation and decoupling |
| P3 | | 90$^{o}$ $^{19}$F pulse at PL12 (F2 channel) |
| P22 | | PIDEC12 decoupling pulse, P22 is 2*P3 |
| O2P | -120 ppm | $^{19}$F offset - optimize in 0.5 - 1 ppm steps for maximum signal of CF2 peak (120 ppm) |

Table 3.4 Acquisition Parameters

## 3.6 $^{13}C\{^{19}F\text{-}^{1}H\}$ CPMAS Experiments

### 3.6.1 Setup $^{13}C\{^{19}F\text{-}^{1}H\}$ CPMAS Experiment: (*cfhsl)*

**Sample:** PVDF

**Spinning rate:** Spin 15 kHz.

**Experiment time:** 3 minutes.

1. Use the parameter set **CPC13F19H1DEC**, or check the appropriate item line for the *cfhsl* experiment in the ATP panel experiment list (see Figure 2.1).
2. Load the PVDF sample, then spin the sample to required speed (see above). Match and tune the probe as described previously.
3. Compare the acquisition parameters from Table 3.5 with the ones in ***ased*** and correct the parameters in ***ased*** if needed.
4. Check for the correct routing on 1 kW amplifiers. If needed, adjust such that the hardware section of the routing (SGU's, amplifiers and HPPR's) for the decoupler channel ($^{19}$**F**) is identical to the routing selected for $^{19}$**F** in the ***fhdp*** experiment:

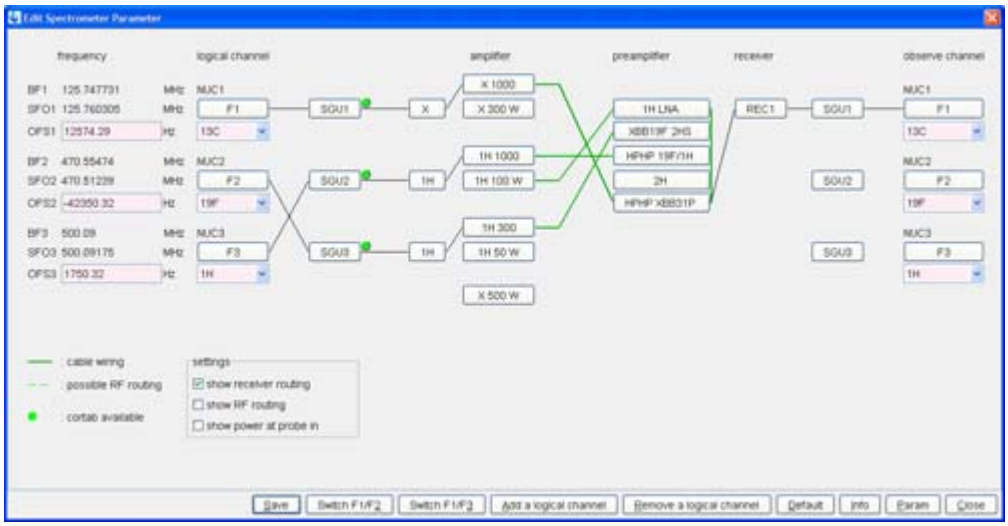



Figure 3.8 Example of routing for *cfhsl* experiment.

**NOTE: All hardware channels remained the same for ALL HF (*hfdp*), FH (*fhdp*), CF (*cfsl*), CH (*chsl*) AND CFH (*cfhsl*) experiments!**

5. Load pulse parameters use parameters from ***cfsl*** and ***fhdp*** experiment as guidance; see Table 3.3 (for $^{13}$C, **PL1**) and (for $^{19}$F **PL2**, **PL12, P3** and **P22)** and Table 3.2 (for $^{1}$H decoupling with **PL13**).
6. Set **CNST31**to15000 and **P22** to **2*P3**.

### 3.6.2 Run Experiment, Process and Document Parameter Used in Table

7. Run an experiment, process and print the spectrum. Compare the spectrum with the figure below:

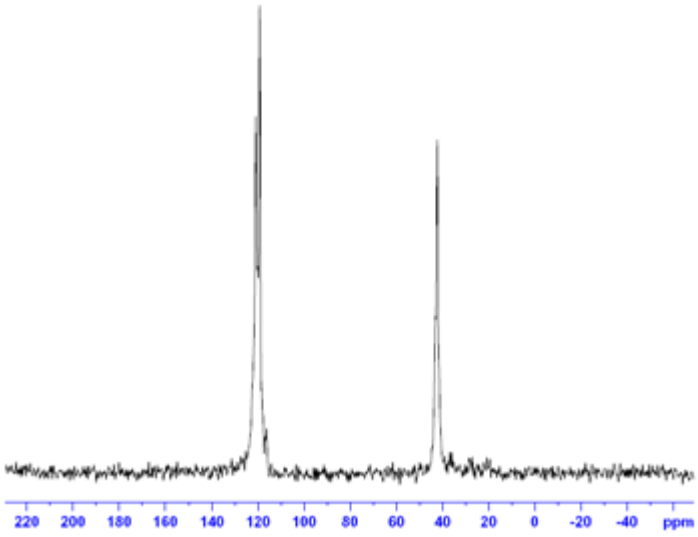



Figure 3.9 $^{13}C\{^{19}F\text{-}^{1}H\}$ spectra of PVDF 15 kHz MAS, 80 kHz $^{19}F$ Pi decoupling and $^{1}H$ 80 kHz TPPM decoupling with PL13.

| Parameter | Value | Comments |
|---|---|---|
| PULPROG | vacpF2F3 | |
| NUC1 | $^{13}C$ | Nucleus on the F1 channel. |
| O1P | 100 ppm | $^{13}C$ offset. |
| NUC2 | $^{19}F$ | Nucleus on the F2 channel. |
| NUC3 | $^{1}H$ | Nucleus on the F3 channel. |
| D1 | 5 s | Recycle delay. |
| NS | 32 | Number of scans. |
| SW | 300 ppm | Sweep width for PVDF. |
| TD | 1024 | Number of acquired complex points. |
| CNST31 | 15000 | Spinning speed in Hz for rotor sync. |
| P15 | 2 ms | Contact pulse (F1 and F2 channel). |
| SPNAM0 | ramp.100 | For ramped CP |
| ZGOPTNS | -Dpidec | Load Pi-decoupling rotor sync. |
| CPDPRG2 | PIDEC12 | Decoupling scheme F2 channel ($^{19}F$). |
| CPDPRG3 | TPPM13 | Decoupling scheme F3 channel ($^{1}H$). |
| Use $^{13}C$ $^{19}F$ CP and decoupling parameters from the *cfsl* experiment, Table 3.4. | | |
| PL1 | | High power level F1 channel ($^{13}C$) contact pulse. |
| PL2 | | High power level F2 channel ($^{19}F$) contact pulse. |
| PL12 | | High power level F2 channel ($^{19}F$) excitation and decoupling. |
| P3 | | 90$^{o}$ $^{19}F$ pulse at PL12 (F2 channel). |
| P22 | | PIDEC12 decoupling pulse, P22 = 2*P3. |
| O2P | -120 ppm | $^{19}F$ offset - optimize in 0.5 - 1 ppm steps for maximum signal of CF2 peak (120 ppm). |
| Use $^{1}H$ decoupling parameters from Table 3.4. | | |
| PL13 | | = The PL12 value from Table 3.3 *fhdp* experiment (usually 80 kHz – see specification sheet). |
| PCPD3 | | = The PCPD2 value from Table 3.3. |

Table 3.5 Acquisition Parameters

# 4 Contact

**Manufacturer:**
Bruker BioSpin NMR
am Silberstreifen
D-76287 Rheinstetten
Germany
Phone: +49 721-5161-0
http://www.bruker-biospin.com

### NMR Hotlines

Contact our NMR service centers.

Bruker BioSpin NMR provide dedicated hotlines and service centers, so that our specialists can respond as quickly as possible to all your service requests, applications questions, software or technical needs.

Please select the NMR service center or hotline you wish to contact from our list available at:

http://www.bruker-biospin.com/hotlines_nmr.html

# Contact

# Appendix A

## A.1 POPT

POPT is the replacement program for “paropt” used for parameter optimization. The program offers automatic optimization of several parameters. POPT writes each parameter found back into the parameter set and uses the value during the upcoming optimization of the next parameter in the list. The optimum value is taken from the resonances within the defined spectral region “plotreg” (see below). A protocol file of the optimization is created and can be inspected by checking the “read Protocol” button (see Figure A.1).

The parameter optimization saves the processed data to the “pdata” directory, in files named from consecutive “processing” numbers beginning at processing number 999 and descending for each optimized parameters, i.e. 998, 997, etc. Despite the automatic parameter determination, it is recommended that the inspection of the processing numbers for agreement with the computer be done by the operator, as it is the operators responsibility to decide on the optimum value, not the computers.

When inspecting the data, one can use negative ppm values of the axis if the parameter values were increased during the optimization (if they were decreased, the ppm value is correct). These values represent the values of the parameters incremented. (different units are not specifically considered.

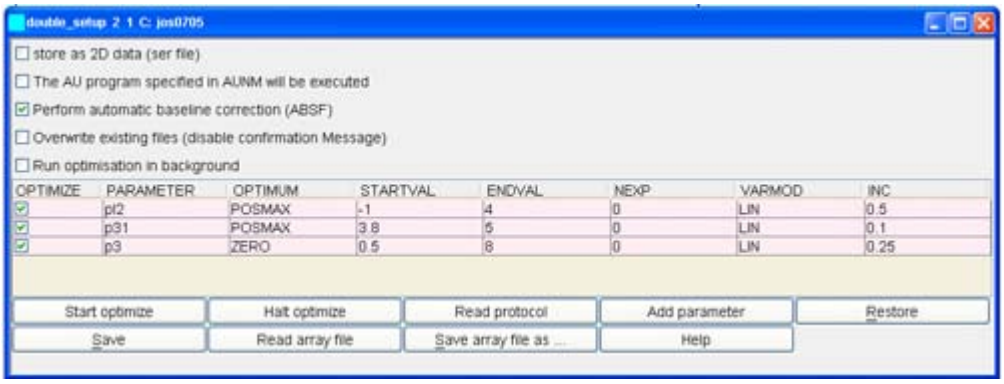



Figure A.1 POPT Interface Window

The figure above uses the parameter PL2 incremented from:

- -1dB in steps of 0.5 dB up to 4 dB using maximum intensity in the chosen plotting region;
- Parameter P31 varied from 3.8 µs in increments of 0.1 µs up to 5 µs;
- Parameter, pulse width P3 varied from 0.5 µs in 0.25 µs increments up to 8 µs where POPT optimizes for a zero transition of the signal in the selected plotting region.

The above mentioned procedure does not contain or save any raw data. If one would like to save raw data for later inspection, the field “store as 2D data (ser file)” must be

checked. POPT then creates an experiment number 899 for the whole optimization procedure (this means for all optimizations, if more then one optimization is checked). This means that all 1D experiments for the entire POPT rune are concatenated into a 2D data set. If experiment number 899 already exists, the program prompts the operator to decide whether the existing experiment number 899 should be overwritten or a new experiment should be created with the number 898, descending.

The 2D data set can be inspected in TOPSPIN using the usual processing strategies for pseudo 2D data sets.

### A.1.1 Optimization of Parameters

Optimization of parameters in experiments requiring Au programs for running the experiment can be achieved by checking the appropriate field in the parameter list.

Before starting POPT, one needs to make sure that POPT processes the data properly. This can only be achieved, if the processing parameters circled in Figure A.2 are set properly. In order to check whether all the parameters are set correctly:

1. Type the command “trf” into the command line.
2. Check whether the spectrum is properly processed.
3. Type the command “plotreg” to check whether the correct plotting region is displayed.

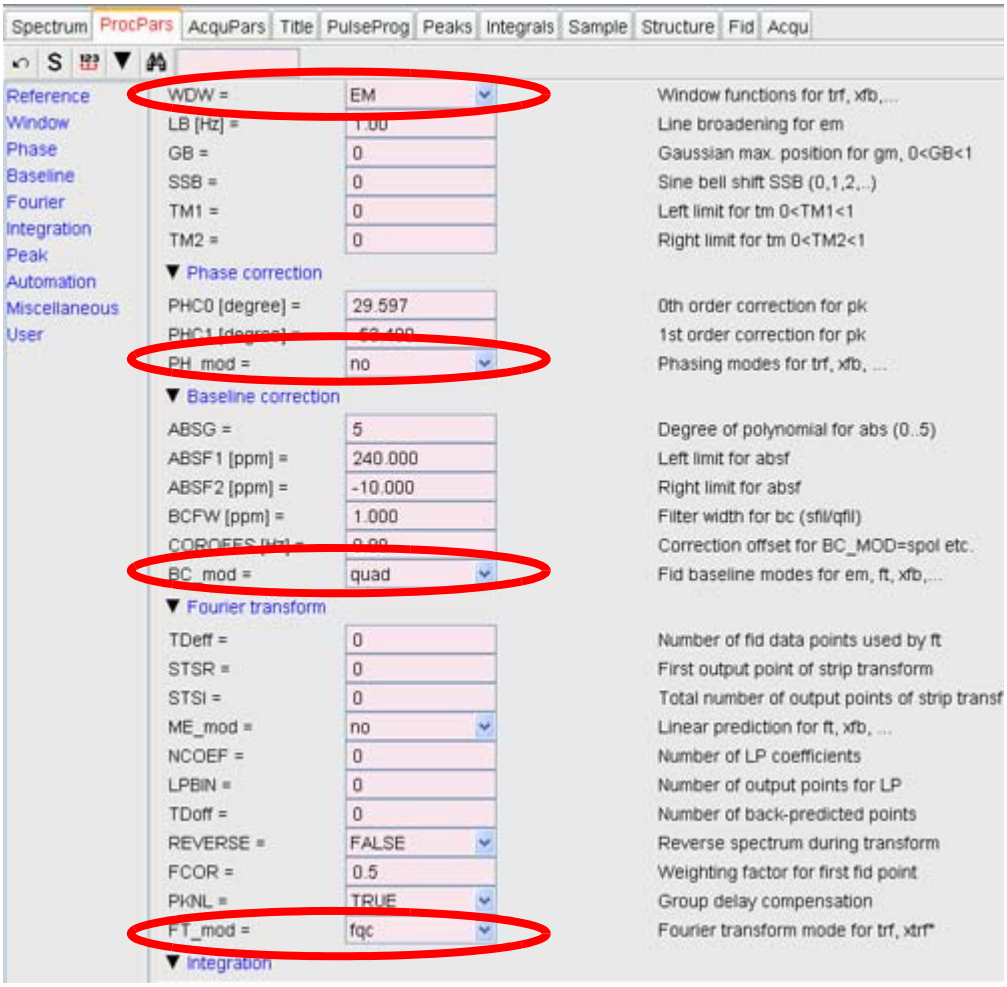



Figure A.2 Processing Parameters Important for trf

The figure above illustrates processing parameters important for *trf*: WDW, PH_mod, BC_mod and FT_mod. For example:

- When PH_mod has the value „pk“, then *trf* executes the phase correction using the values of PHC0 and PHC1.
- When the PH_mod value is „no“, no phase correction is applied.
- When the FT_mod has the value „no“, no Fourier-transformation is performed and „he“ time domain data are displayed.

## A.1.2 Selecting and Saving the Correct Plotting Region

The correct plotting region is selected by:

1. Choosing the appropriate area in the spectrum. This is accomplished by holding down the right mouse button on one side of the spectral region of interest and dragging it over the desired spectral region. The mouse button is then released.

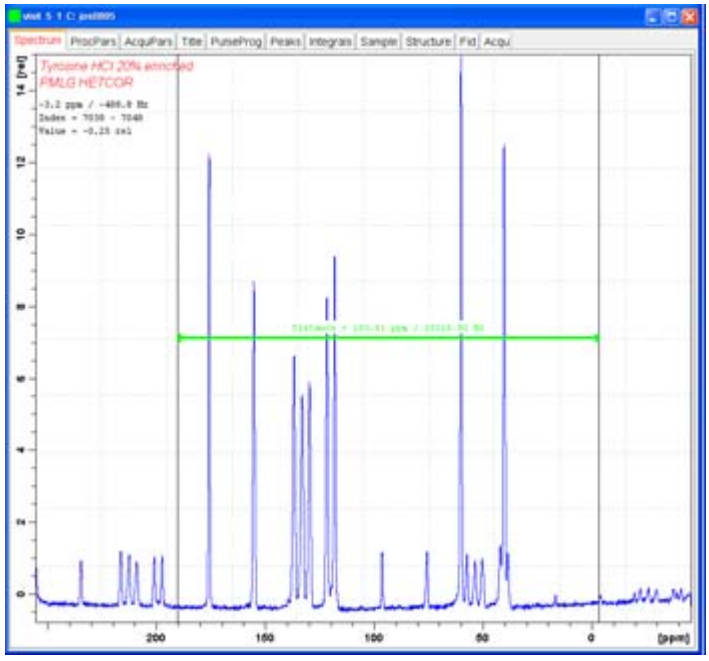



Figure A.3 Zooming into spectral region of interest

2. Zooming into spectral region of interest is achieved by placing the curser to the left or right outer side of the desired spectral region, pressing the left mouse button and dragging the cursor to the other side of the spectral region.
3. To save the display region, click the right mouse button while in the spectral window and check the second item on the pop up menu “Save Display Region To …”.

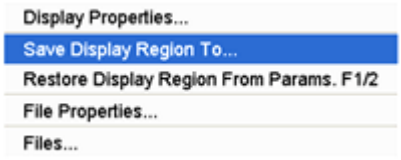



Figure A.4 Saving the Display Region.

4. Check the radio button in the upcoming list (Parameters F1/2) and click “ok”.

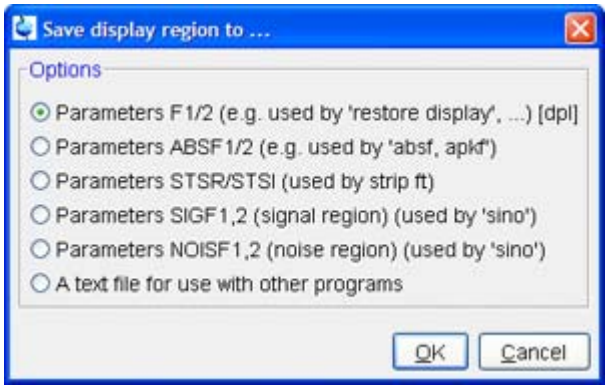



Figure A.5 Pop-up list when choosing the “save display…” option.

## A.1.3 Starting POPT and Choosing Parameter Options

1. Start POPT with the command POPT.
2. Check the boxes for the desired options in the top of the window
3. Check the box for the first parameter and fill appropriate information into the fields. Nothing needs to be entered into the field NEXP, but the following field VARMOD, *lin* or *log* must be selected. The last field contains the increment of the parameter, either positive or negative number, depending on whether the parameter is incremented or decremented.

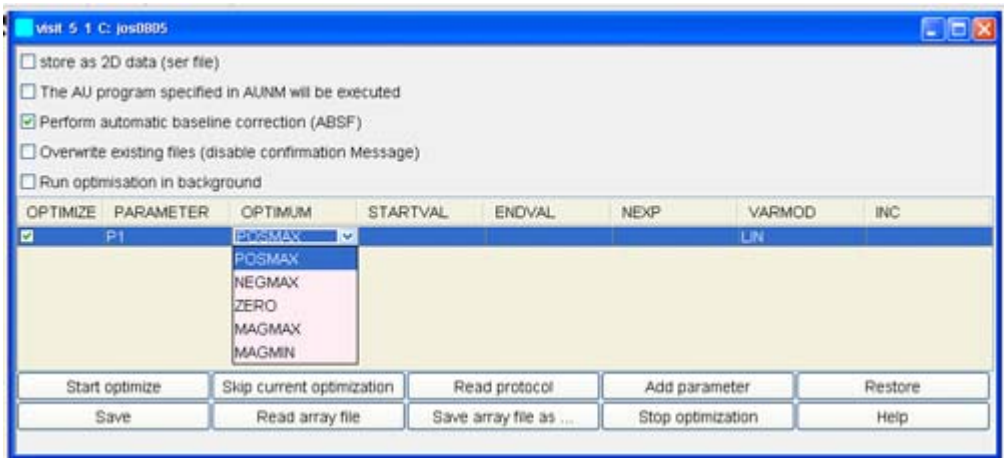



Figure A.6 POPT interface with the first parameter being about to be entered.

4. Parameter values must be entered considering the default units of these\ parameters, i.e. for pulses units are in µs, for delays units are in s for power levels, units are in dB and for the offset frequencies O1 the units are in Hz or for the O1P value in ppm, whereas SFO1 would be in MHz.
5. If everything is filled out properly, check the “**save**” field and start the optimization by checking “**Start optimize**”.

### A.1.4 Manipulating or Stopping the Optimization

- The process of the optimization can be manipulated in a controlled fashion using the “**Stop optimization**” or “**skip current optimization**” button.
- **Read protocol** enables to inspect a table with optimization values.
- From the command line the optimization can be halted by typing “POPTHALT”.
- Using “**stop**” only stops the current experiment and copies previously obtained data on the place of the stopped experiment and POPT continues with the next parameter value.

At the end of the optimization, POPT writes the obtained value into the acquisition parameter set of the experiment.

## A.2 MAS Control

Remote operation of the MAS II unit is handled from TopSpin using the program ‘mascontrol’. Mascontrol can be used for sample insert and eject, changing spinning speed, and generating a log file of the actual MAS spin rate to monitoring MAS-speed over time.

1. Type ‘**mascontrol**’ in the Topspin command line. The following window will open.


Figure A.7 Window for probe selection.

The information entered in the probe selection window is NOT fed back to the MAS II unit!

2. In this window select the type of probe that is currently in the magnet. The MAS spin rate display will open. For 3.2 mm probes, select the 2.5 mm option. **Note**: This does not change the probe selected in the MAS II unit.

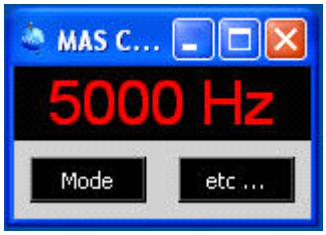



Figure A.8 MAS Control Window with spinning speed indication.

Checking the mode button yields more switches for stopping and starting sample rotation and for sample insert and eject.

3. Clicking on '**Mode**' will expand the display and provide buttons for rotor insert and eject, MAS start and stop operations.


Figure A.9 MAS Control Window - extended

- **MODE** toggles the switch display and
- **ETC ...** opens a menu for further options like MAS-rate log, update speed, new MAS rate setting, etc.

4. The 'etc…' button provides additional functionality. The spin rate log can be started and stopped by using the radio button at the top. The rate at which *mascontrol* updates the current speed can be changed from the default of 12 seconds, to a value as fast as every 4 seconds, by double-clicking the desired rate in the pop-up window. A similar option exists for writing to the log file.

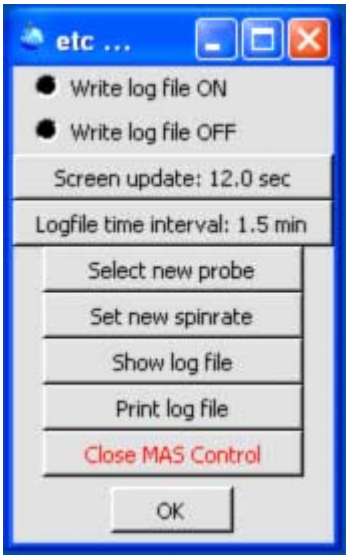



Figure A.10 ETC … menu for further options like MAS-rate log, update speed, new MAS rate setting.

5. To change the MAS rate, click on the 'Set New Spin Rate'. A new window will open that will allow the speed to be changed.

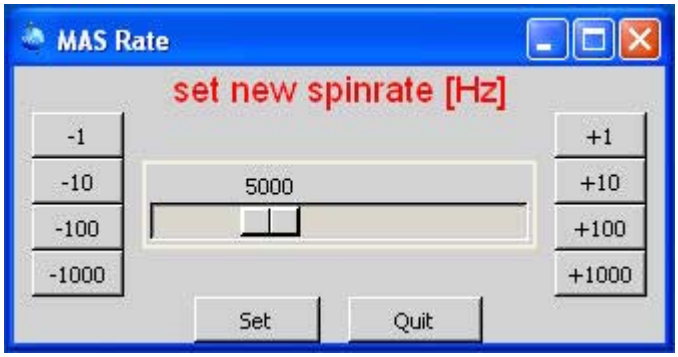



Figure A.11 Window for changing the MAS rate setting.

6. Consult the appropriate hardware manual for MAS II hardware operation.

## A.3 Setting Transmitter Power

If the correct power level for the X-channel is not already known, begin operation using 25% of the maximum power for the channel selected. This information is available on the power handling data sheet that comes with each probe, and may be used if the amplifiers are linearized and the maximum output power is available. Make sure to find out where the output power was measured – at the transmitter output directly, before the HPPR modules, or after the HPPR modules. Such differences can account for up to 3dB differences in output. If you measure the power, make sure you write a README file into the CORTAB directory reporting important details on how the power was measured.

If CORTAB was not done, e.g. with older systems, use 50% of the nominal transmitter power for the power level 0.

For linear amplifiers one can use the following relations for changing power levels in dB:

- To half or double the RF output power one needs to add or subtract 3dB from the existing power level value.

This is generally valid above 0dB and below 0dB only if **CORTAB** has been done.

**Example**:

As an example, use 75W on a 2.5 mm CPMAS probe with a linearized (**CORTAB** done) 1000W transmitter. The maximum output at the probe is 650W, reported in the CORTAB directory by Johnny Perfect. Thus we know that we have 162.5W at 0 dB, 81.25W at 3 dB and 46 W at about 5.5 dB. The dB value is defined as follows, whereas „**y**“ is a change in power level value PL2 – PL1 in dB attenuation:

Equation A.1: $$y = \text{powerlevel}_2 - \text{powerlevel}_1$$

Then using the definition of dB we find for „**y**“ the following expressions for ratios of RF-power output on W, or RF-field (or voltage) output.

Equation A.2: $$ydB = 10 \bullet \log\left(\frac{\text{power}_1(\text{Watt})}{\text{power}_2(\text{Watt})}\right)$$

That can then be used to calculate the power level change for a certain change of the pulse width or a nutation frequency, however as you are using amplitudes and not power, the equation changes to:

Equation A.3: $$ydB = 20 \bullet \log\left(\frac{pulsewidth_2}{pulsewidth_1}\right)$$

In order to find a new pulse width for a given power level we can then calculate:

Equation A.4: $$pulsewidth_2 = pulsewidth_1 \bullet 10^{\frac{(powerlevel2 - powerlevel1)}{20}}$$

As an example if $PL_1$ = 0dB and $P_1$=5 µs, then the pulse width at $PL_2$= -4 dB will be $P_2$= 3.2 µs.

## A.4 Calculating Pulse Parameters with Au Programs

Power level and pulse values can be calculated using the AU-program ***calcpowlev***. The *calcpowlev* program asks for a new pulse width ($P_2$), in our case as a first input, whereas we will choose 3.2 µs. The program then requests a reference pulse width $P_1$, which in our example is 5 µs, and returns -4dB as the change in the power level setting.

The AU-program ***pulse*** uses $PL_1$ and $P_1$ of the foreground data set to calculate either $B_1$-fields in units of Hz, pulse widths, or power levels depending on the data input. If no unit, such as Hz, dB, or µs is specified, then ***pulse*** uses ms as default, which can lead to unexpected results.

# Appendix

## A.5 Figures

## A.6 Tables

# Bruker BioSpin
# your solution partner

Bruker BioSpin provides a world class, market-leading range of analysis solutions for your life and materials science needs.

**Bruker BioSpin Group**

info@bruker-biospin.com
www.bruker-biospin.com



B92999