# China Users' Meeting – 2019
# Tips and Troubleshooting for NMR Experiments

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Service & Lifecycle Support (SLS)
Bruker Users Meeting China, July 24th 2019

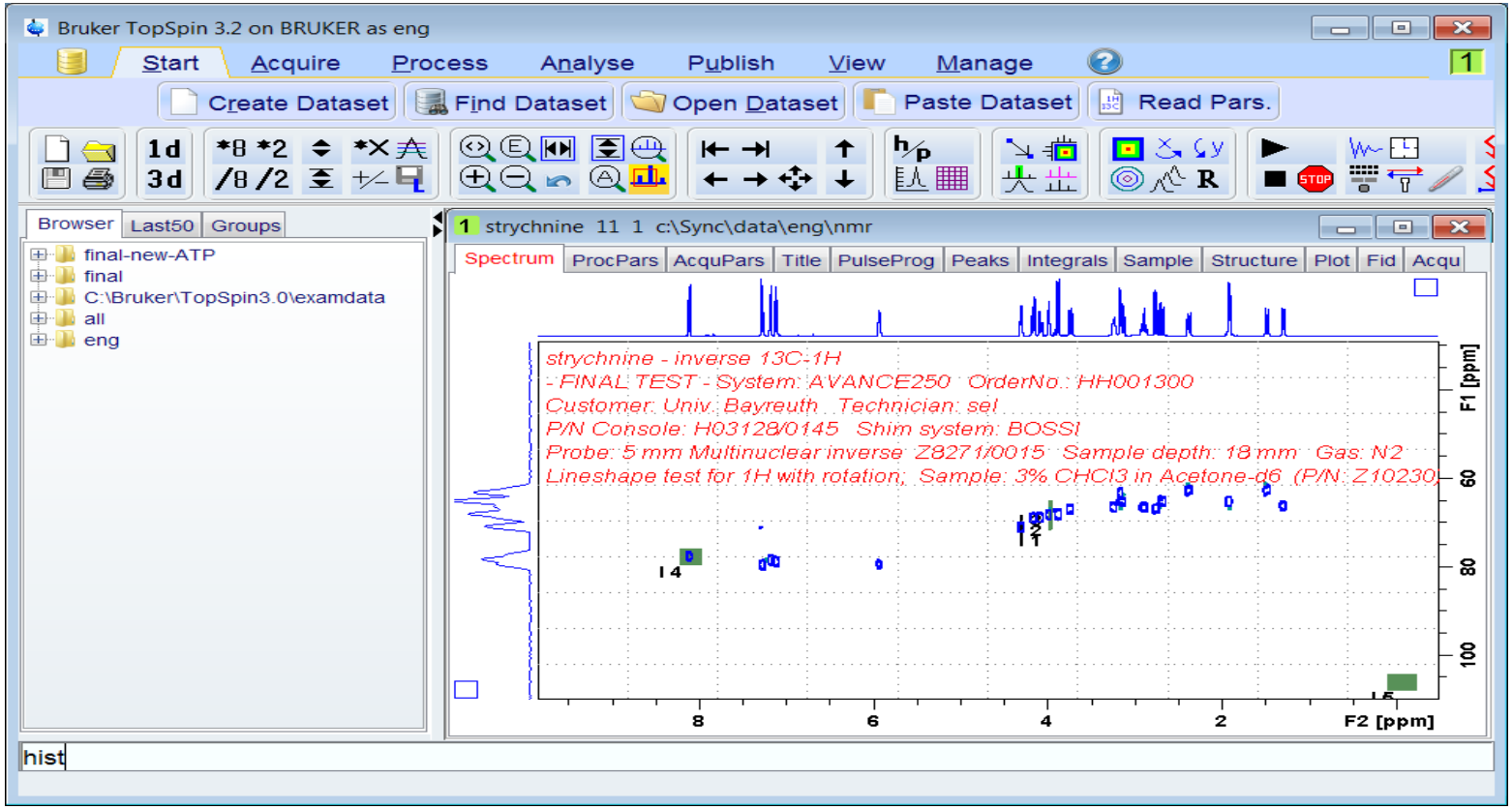
Innovation with Integrity

# General hints

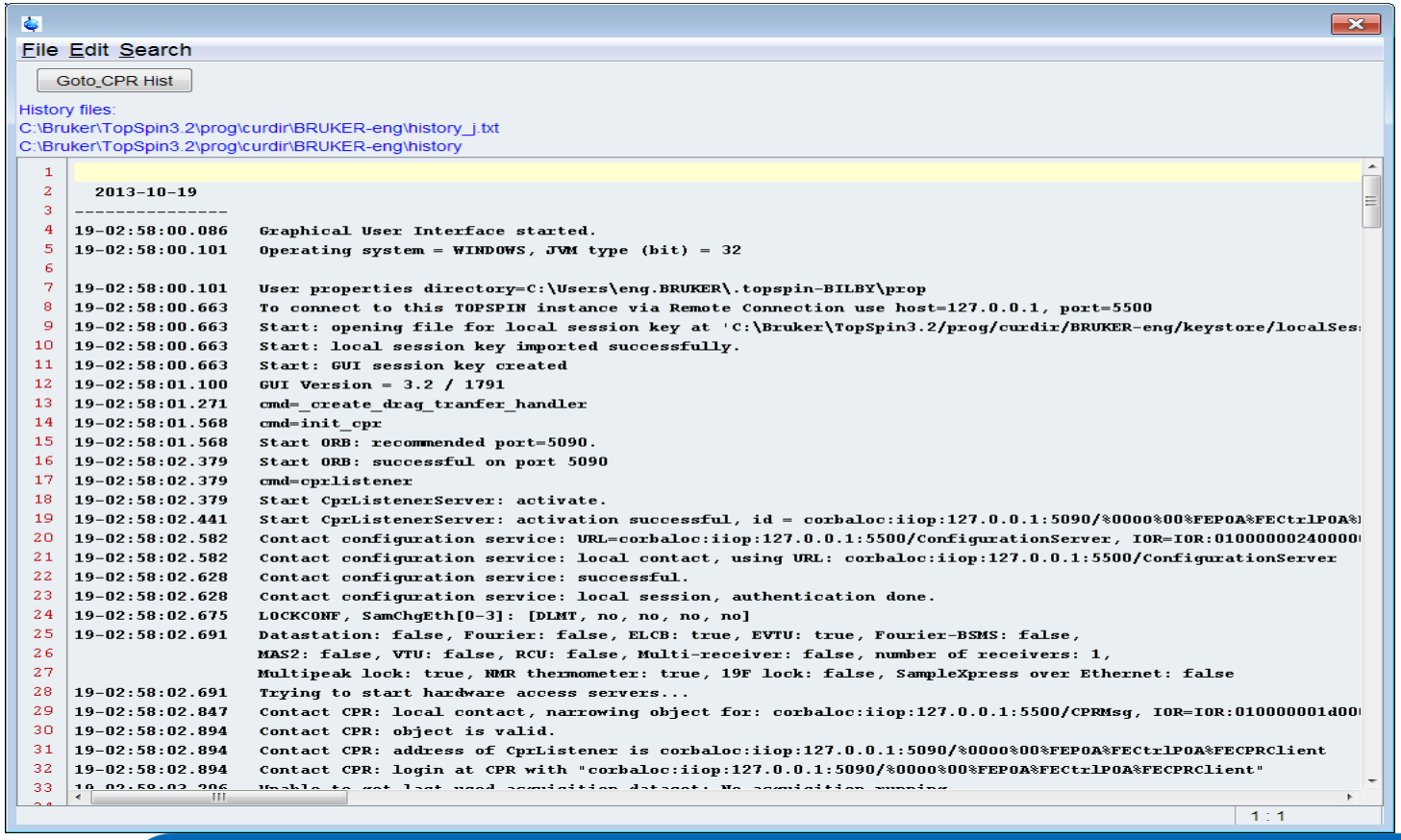
*A few hints on how to get more information from the system:*

- Read the error messages appearing in TopSpin carefully, often they help in tracking down the problem.
- Enter '**hist**' in TopSpin and check the latest error messages.
- Is it a problem which is always there or only from time to time?
- Can you reproduce the problem? E.g. the problem occurs only in a certain data set.
- Create a backup of the history files right after the problem occurred with the command '**savelogs**'. That file can be sent to Bruker if required:
  - Enter 'savelogs' in TopSpin
  - As Support Token, enter your company name and your order number, e.g. 10234567_BrukerCH

# If you feel like it, have a look at the history file …



# There are two parts to the history file …



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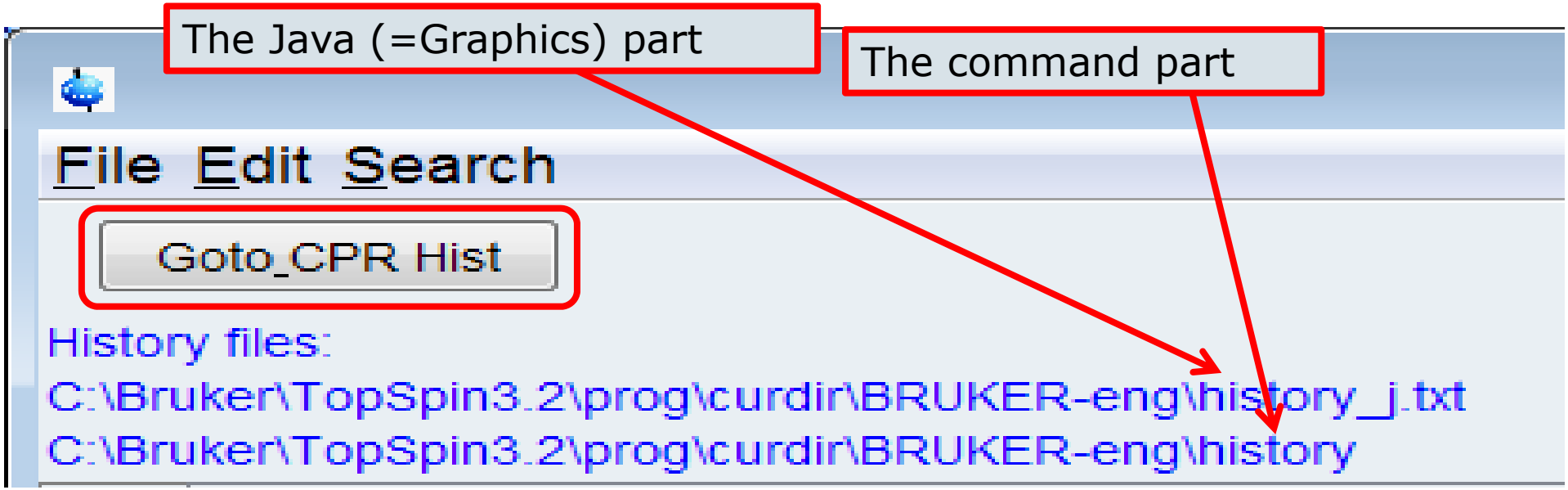
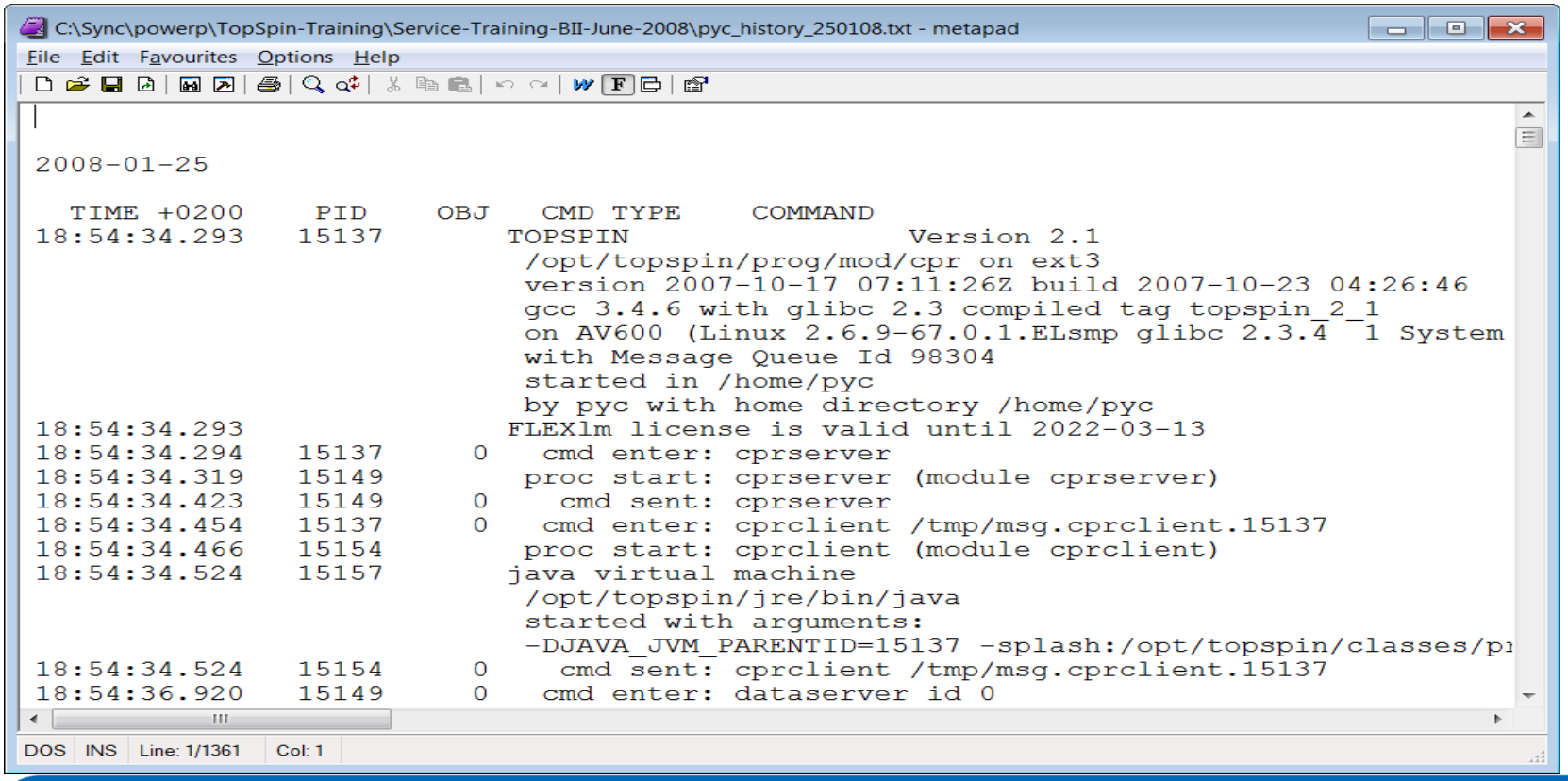
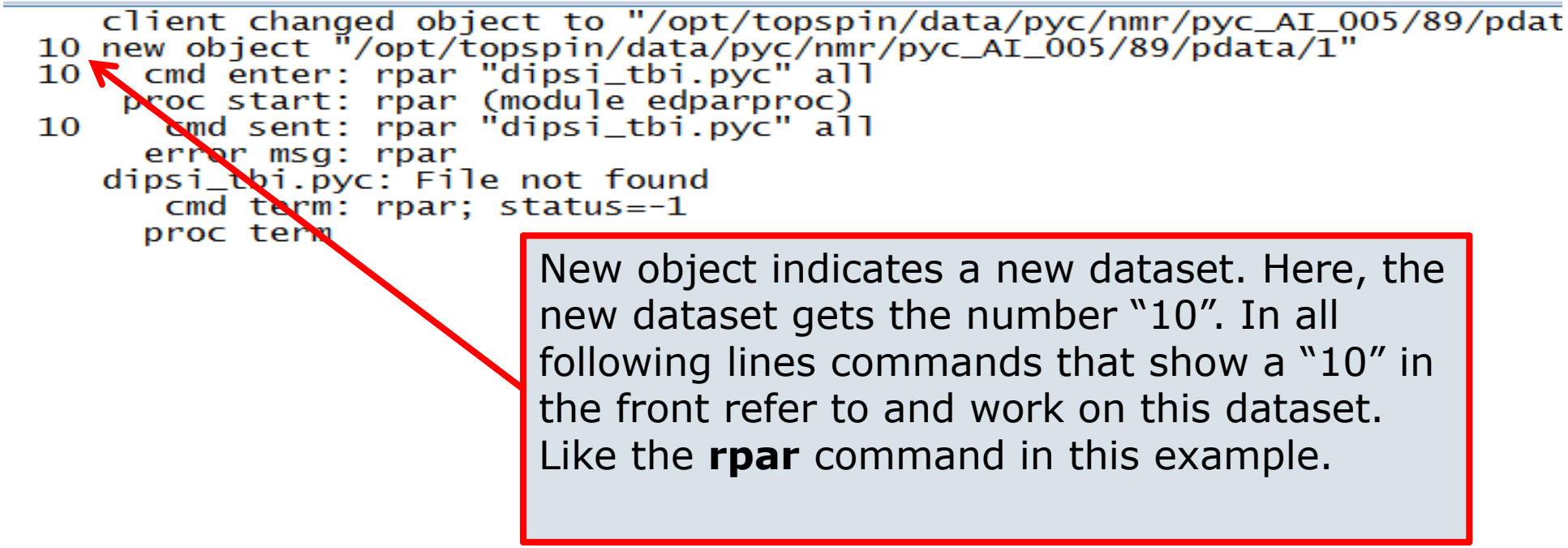


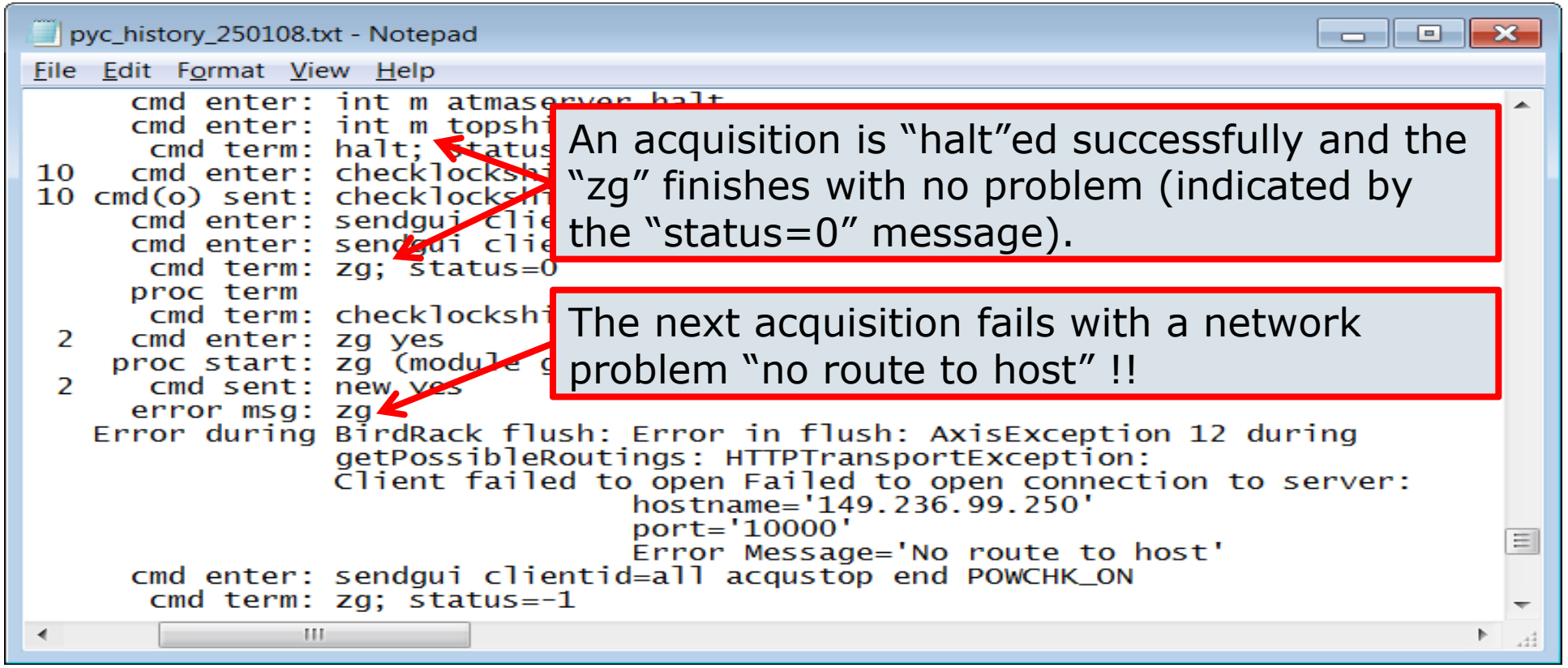
# A real life example:



A real life example:



# A real life example:

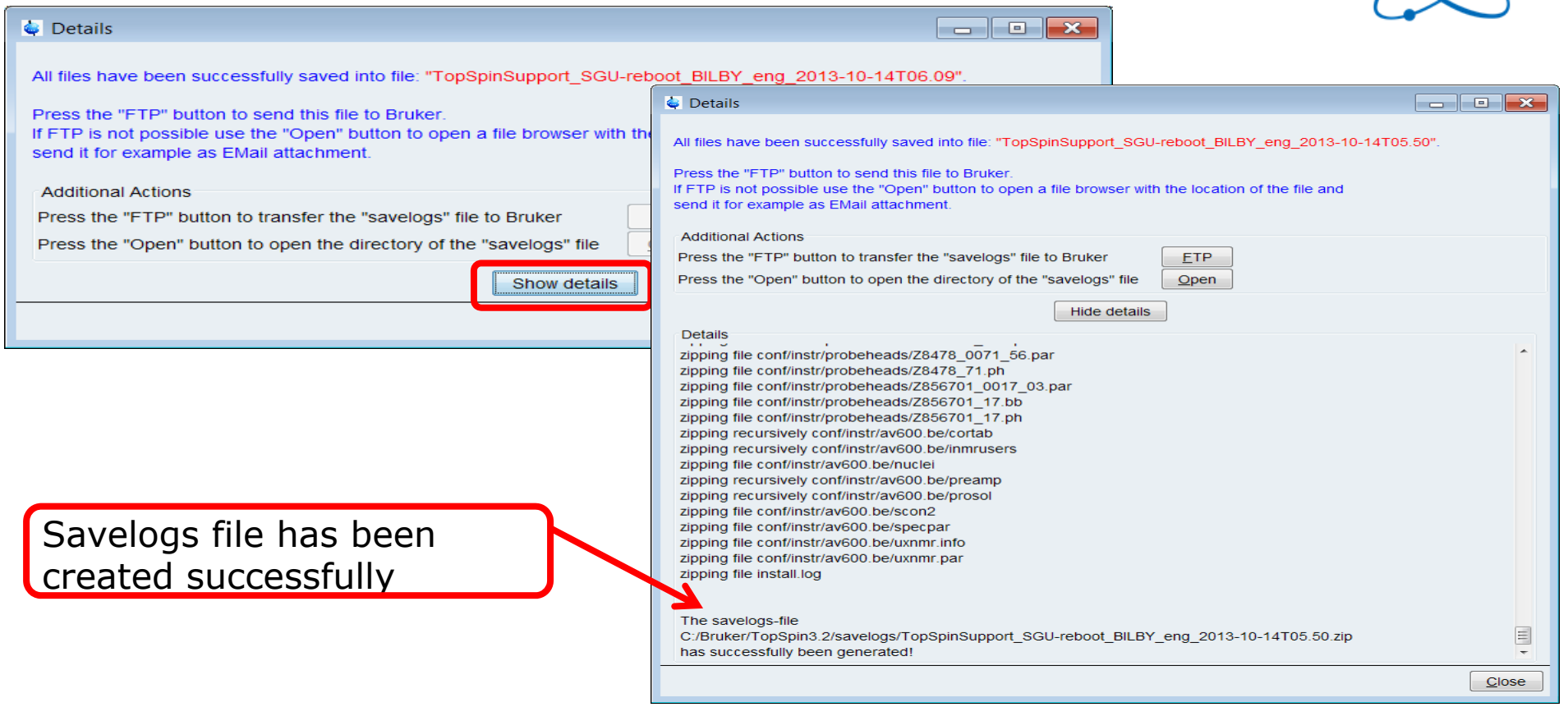


And the solution was:


Firmware update on the BLAXH amplifier !!

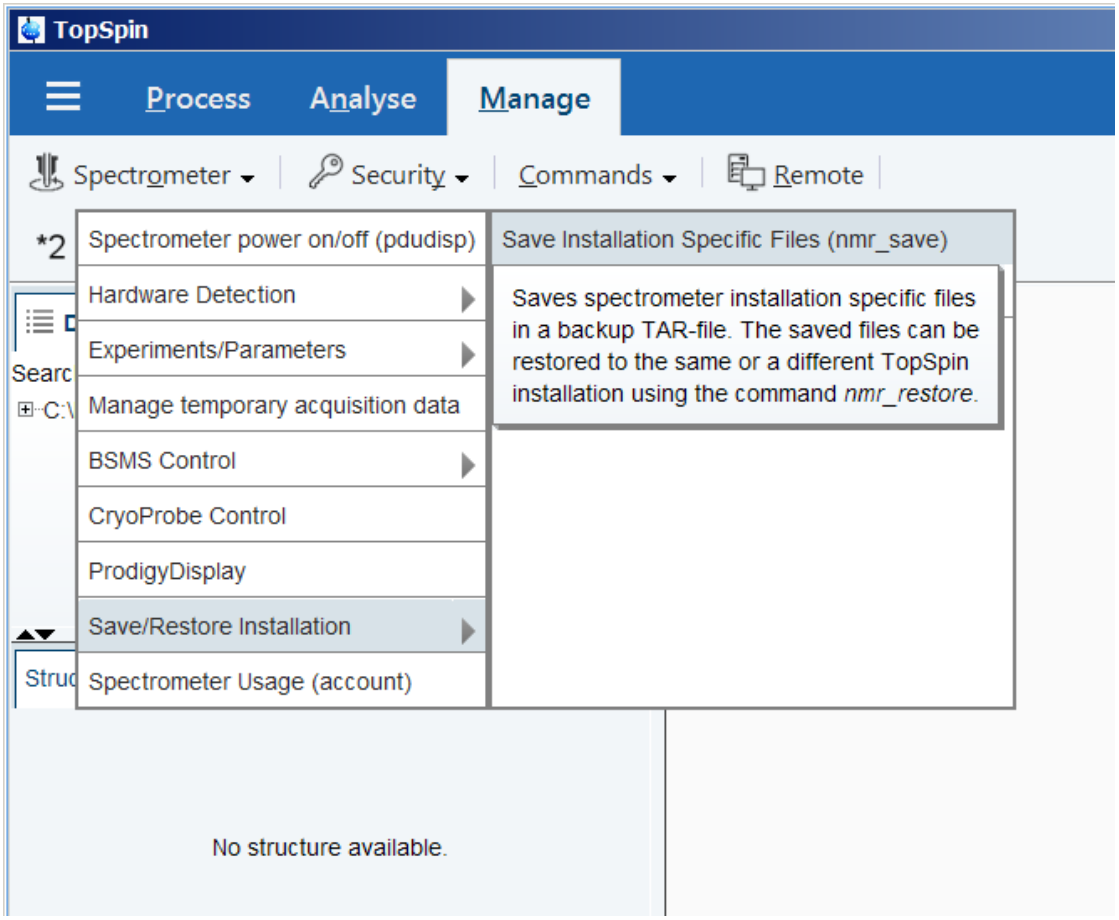
The amplifier occasionally lost its Ethernet connectivity due to a race conflict in the firmware.

# **savelogs** details



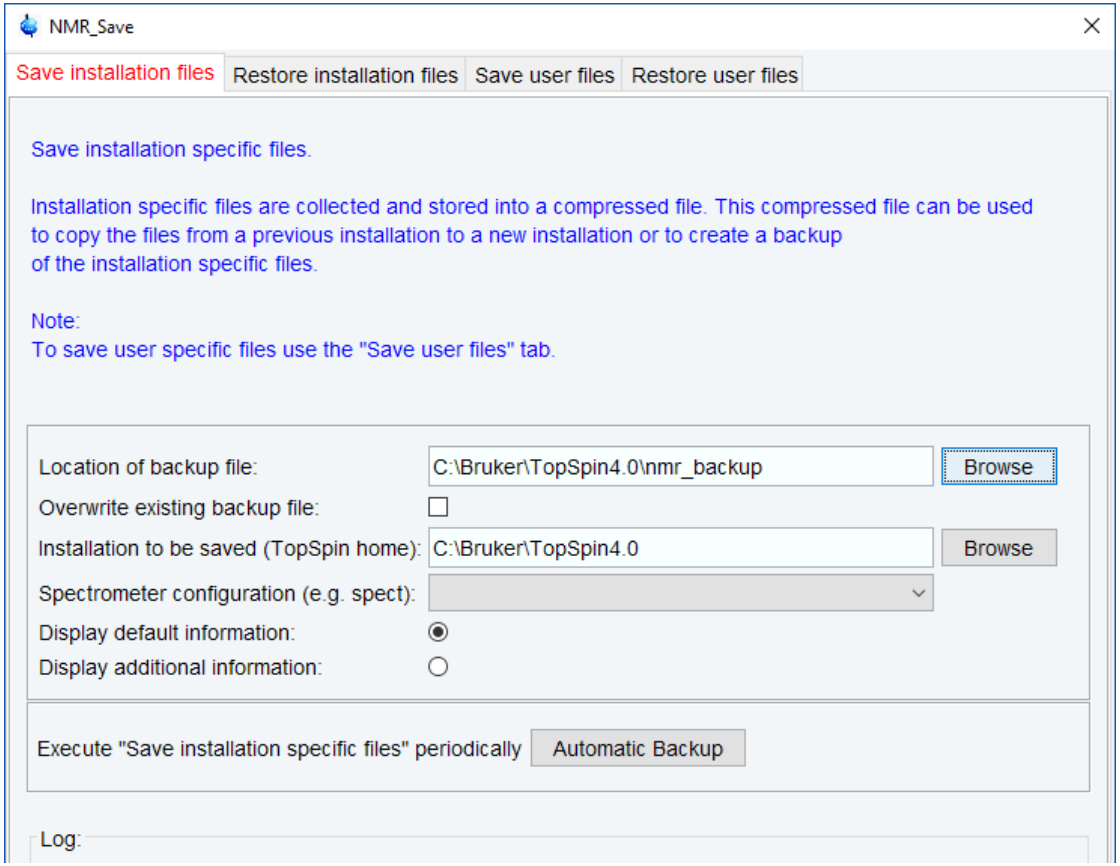

Savelogs file has been created successfully

# nmrsave




nmrsave:
VERY IMPORTANT !!!

# nmrsave




nmrsave:
Archives AVANCE NEO Configuration !!!

# General hints

- Is it a hardware failure?
  Check the power supply voltage LEDs in the console.
- SampleChanger is not running?
  Check the input pressure from the SampleChanger.
- Do other systems in the lab also have problems?
  It could be a power issue.

# Tracking the problem

**Here are some questions you could ask yourself**

- Is the magnet on field?
- Is there ice on the magnet?
- Can we communicate with the spectrometer?
- Does tuning and matching work (‘wobb’, ‘atma’)?
- Is there a lock? Does it look normal?
- Can you run TopShim? (on 1H and 2H)
- Do we get a spectrum? On more than one channel?

# Is the magnet on field?

**If there is neither a lock nor a spectrum can be acquired, the magnet could have quenched or the main switch could have opened and the magnet either lost field or is still discharging.**

- Try feeling the magnetic field by using a magnetic tool.
  Be careful!
- If there is ice on top of the magnet, or the magnet is wet, this could indicate a severe problem! Contact Bruker immediately!

# Can you communicate with the hardware?


- Try to run ‘ii’ and ‘ii restart’
- Use ‘ha’ to check which units are available in the spectrometer network

What could help?

- Restart TopSpin
- Reboot the spectrometer
- Reboot the workstation
- Disable the firewall on the workstation

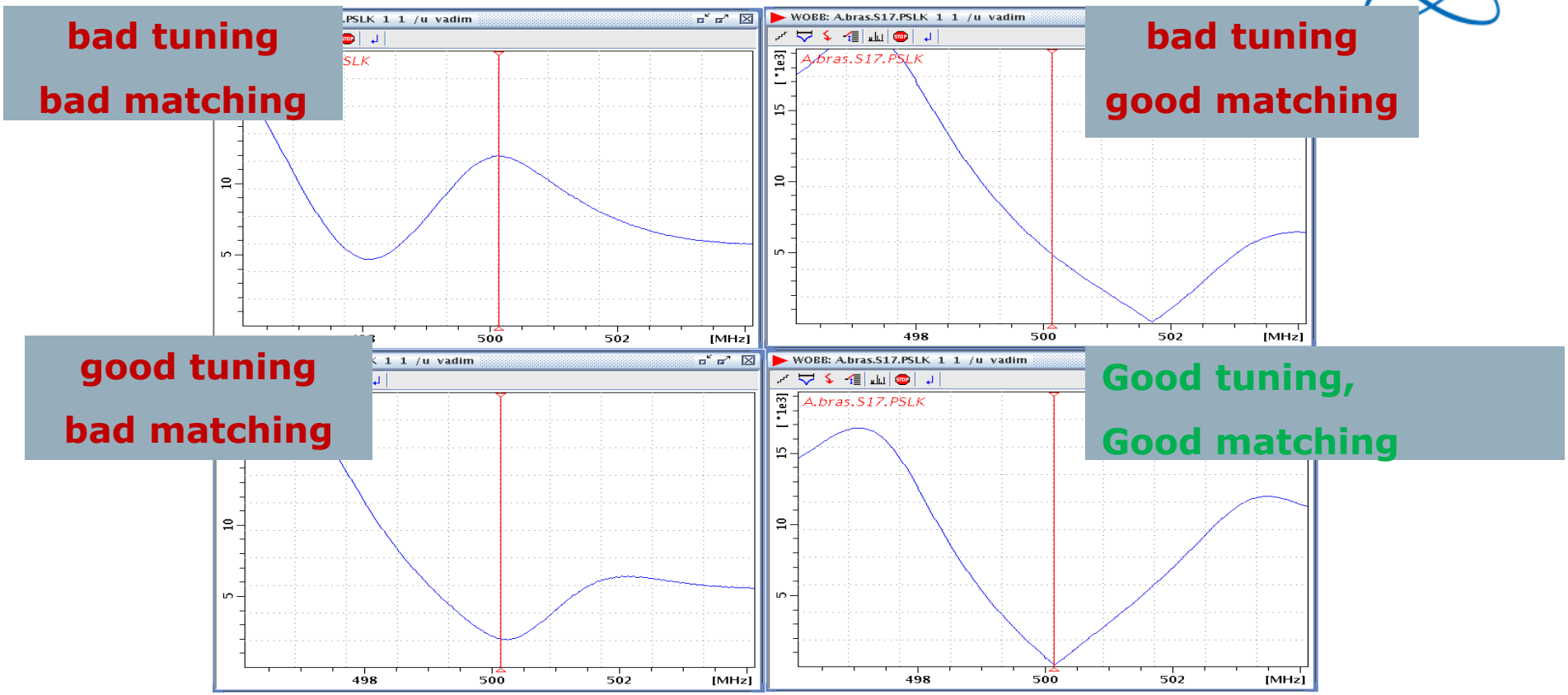
# Can you acquire a spectrum?

- If you cannot acquire a spectrum, try a different nucleus, usually 13C.
- A different nucleus requires probably a different channel (SGU/TRX) and a different HPPR slice.
- A cable might not be connected or a frequency might not be produced by the REF unit.
- You can also try to use a different SGU, if your spectrometer is SGU based (change routing in ‘edasp’).

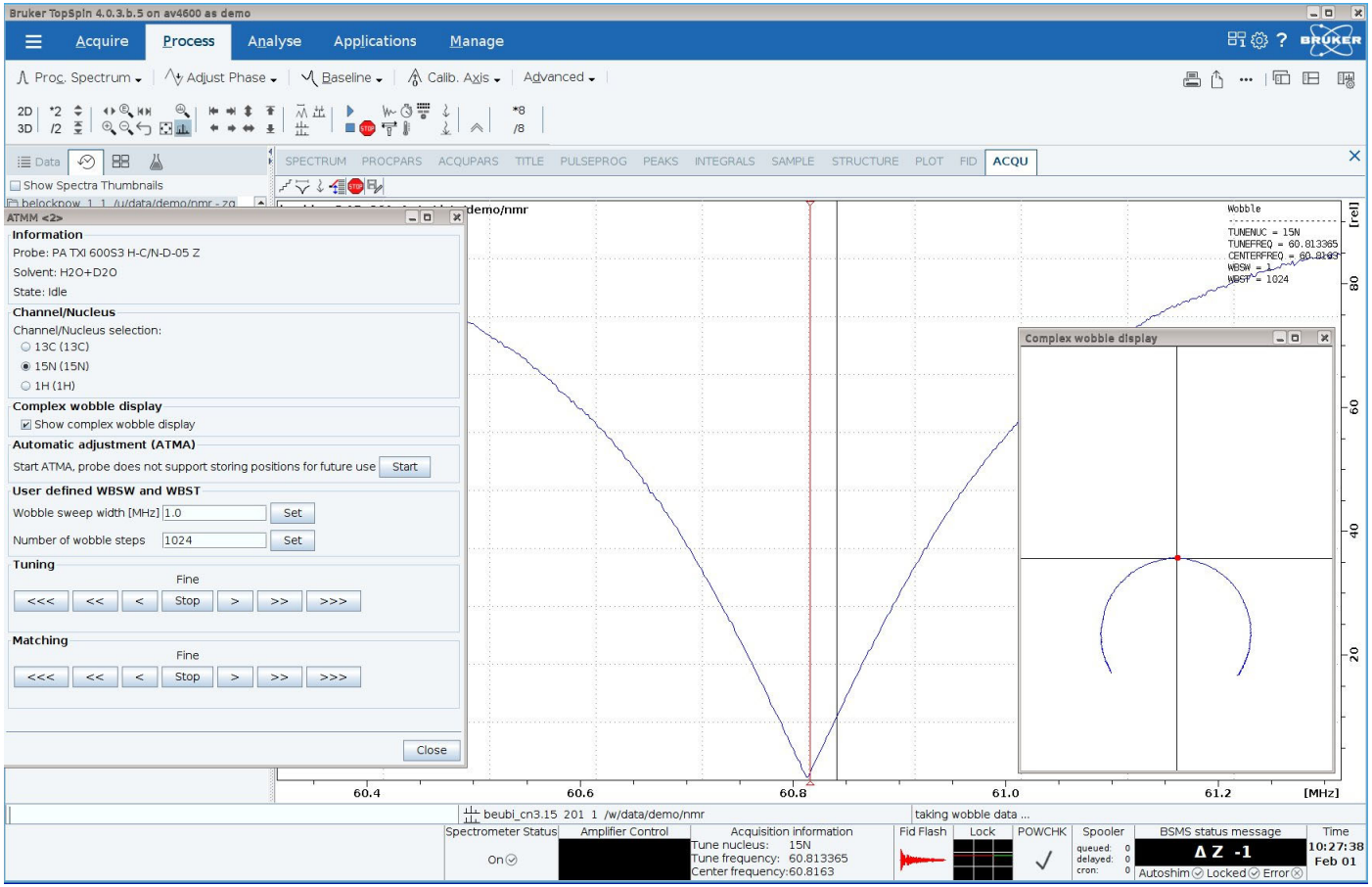
# Can you run ‘wobb’ / ‘atma’?

- The ‘wobb’ routine uses many components of the spectrometer and is therefore generally a good test. If it runs fine, it means that the receiver as well as parts of the frequency generation works fine.
- If ‘wobb’ does not run, try a different nucleus.
- Do ‘atma’ or ‘atmm’, does it work?

# Tuning/matching and wobble curve



# Tuning/matching and wobble curve

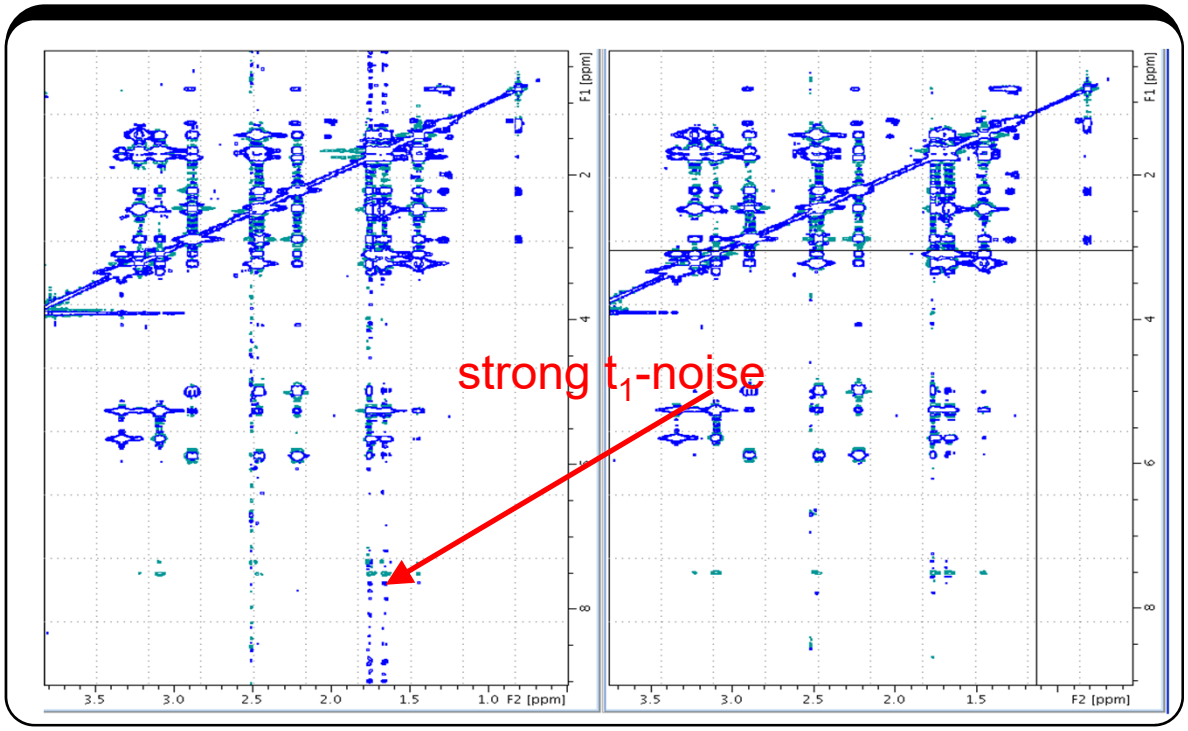


# Does the lock signal look fine?

- Check the LOCK signal carefully in the swept mode and check whether it is locking-in normally for the correct solvent and whether the lock is stable.
- It is not locking?
  - Is a sample in the magnet?
  - Is the sample depth ok?
  - Use a Bruker test sample, e.g. the Lineshape sample or the Sucrose sample for your tests.
  - Create a new data set, read a standard parameter set, e.g. ‘rpar PROTON’, do ‘ii’ and try to lock again, e.g. ‘lock acetone’.
  - Is the 2H tuning ok?
    Can be checked with: ‘rpar gradshim1d2h’ – ‘wobb’

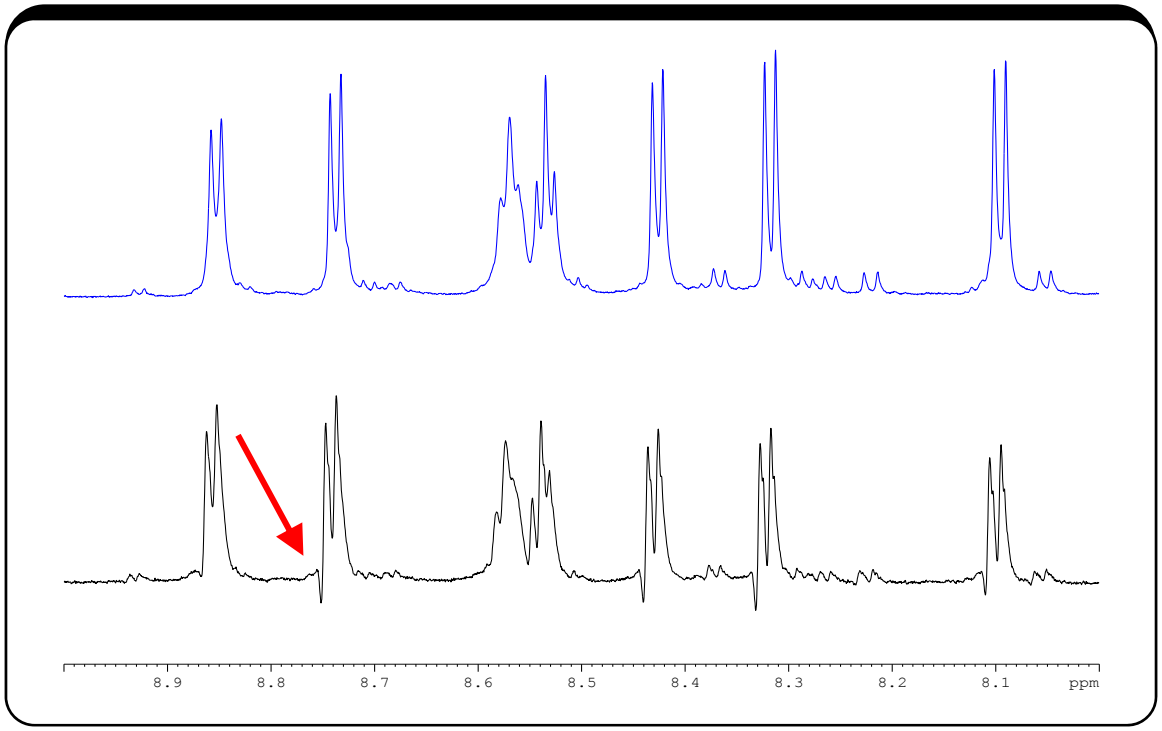
# TOCSY without gradients: $t_1$-noise

- TOCSY:
  - AUTOSHIM during acquisition can influence t1-noise
  - Especially while measuring salty aqueous Samples



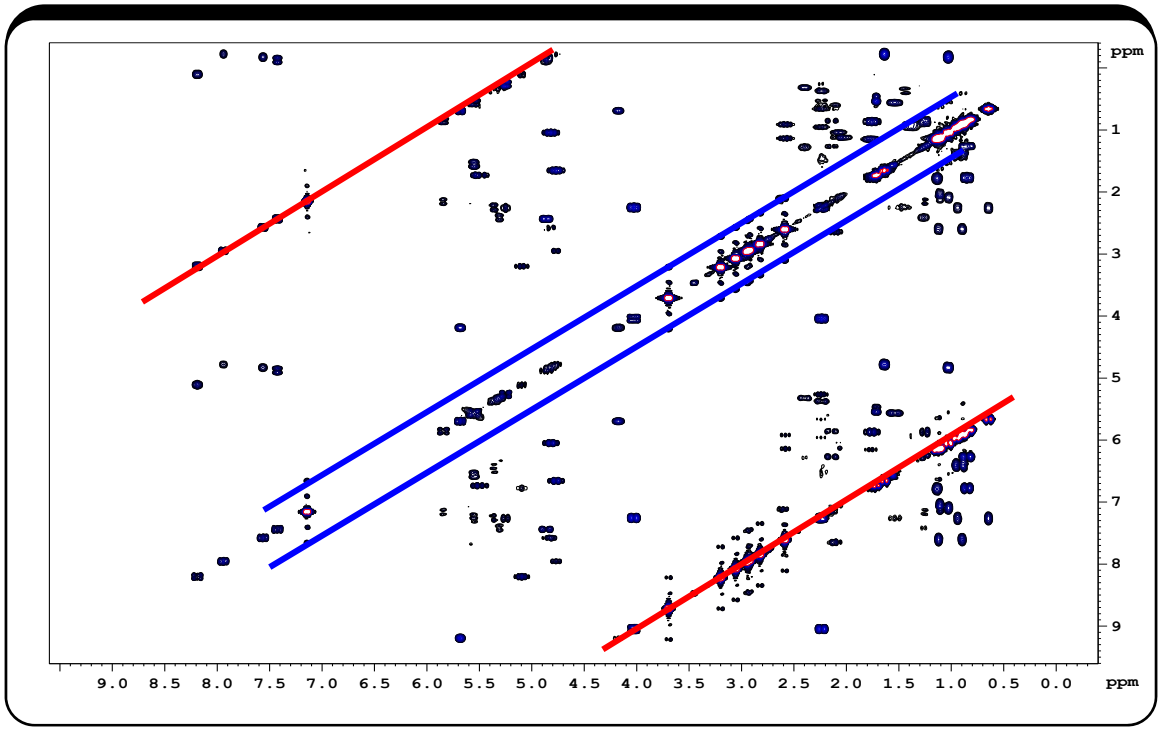
# WATERGATE experiment: gradients

- WATERGATE:
  - Lock phase wrong approximately 30°
  - Depending on the sign of the error the artifacts appear on the right or left side of the signal



# COSY with gradients

- COSY with gradients:
  Lock phase wrong by approximately 40°



# Also check the other lock parameters …

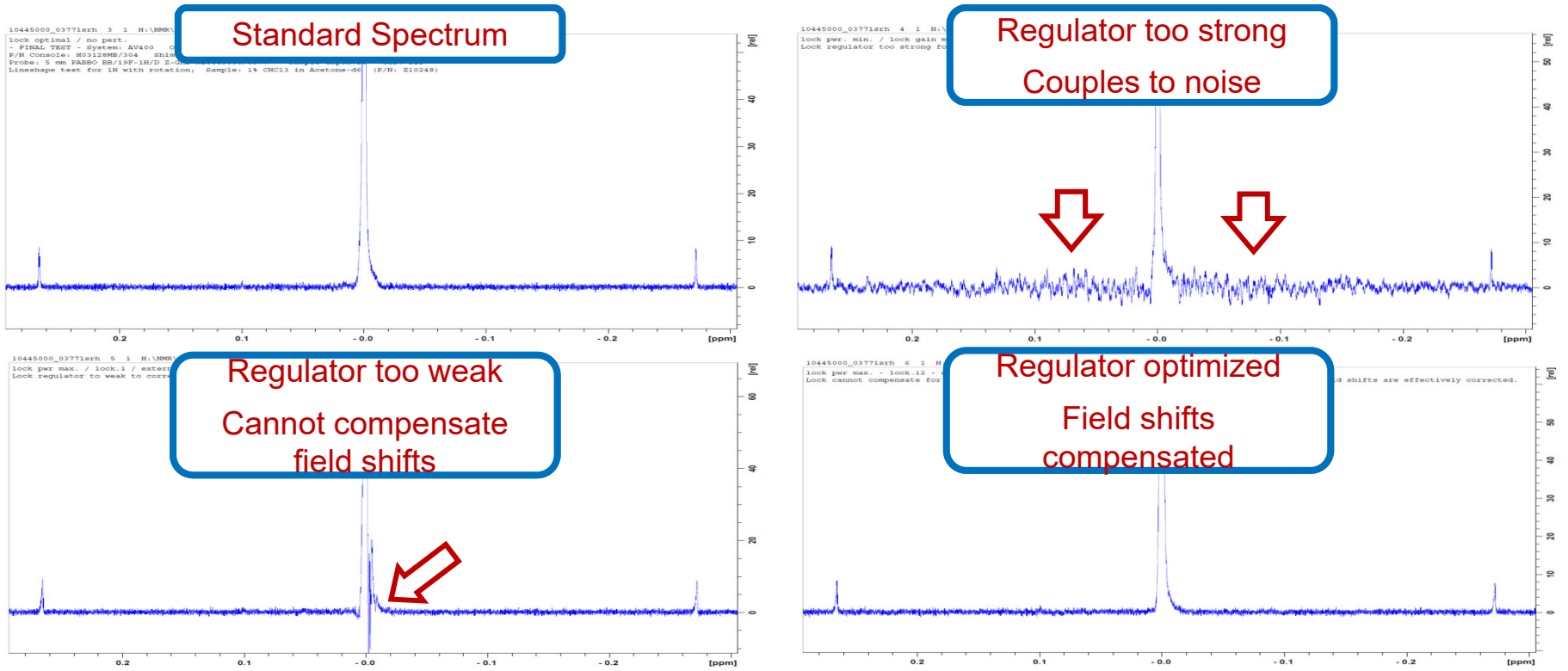
- The "Loop Gain", "Loop Phase" and "Loop filter" values are the control parameters relative to the lock current regulation loop. These values have an important influence on time average lock level stability. Their accurate setting is important when recording 2D homo-nuclear or hetero-nuclear experiments in the absence of Pulsed Field Gradients.
- A bad setting of these parameters will increase the t1 noise in these 2D experiments.
- The best way to set them is to adjust as good as possible the "Lock Power" (find the 3dB limit before solvent deuterium nucleus eigenstates saturation occur). If this value of the "Lock Power" is found you can use the automation routine "loopadj". This is an AU program that calculates the "Loop Gain", the "Loop Filter", the "Loop Time" and adjusts the "Lock Gain" and the "Lock Phase" parameters.

Also check the other lock parameters …

- The "loopadj " command does not work if the "Lock Gain" is higher than 120.0.
- A "Lock Gain" value higher than 120.0 does not match with the "Loop Gain" table

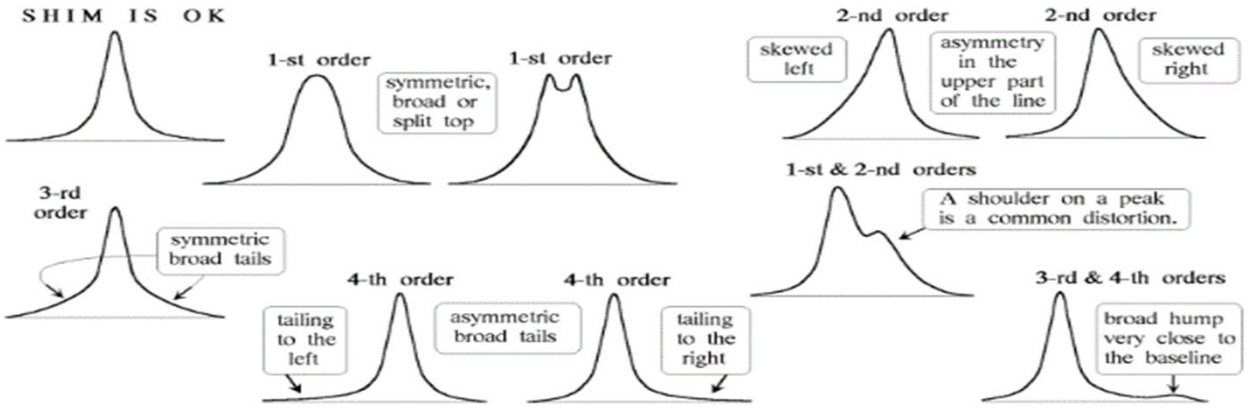
| Lock parameters | | | |
|---|---|---|---|
| Macro | Loop Filter Hz] | Loop Gain [dB] | Loop Time [s] |
| lock.1 | 20 | -17.9 | 0.681 |
| lock.2 | 30 | -14.3 | 0.589 |
| lock.3 | 50 | -9.4 | 0.464 |
| lock.4 | 70 | -6.6 | 0.384 |
| lock.5 | 100 | -3.7 | 0.306 |
| lock.6 | 160 | 0.3 | 0.220 |
| lock.7 | 250 | 3.9 | 0.158 |
| lock.8 | 400 | 7.1 | 0.111 |
| lock.9 | 600 | 9.9 | 0.083 |
| lock.10 | 1000 | 13.2 | 0.059 |
| lock.11 | 1500 | 15.2 | 0.047 |
| lock.12 | 2000 | 16.8 | 0.041 |

# Also check the other lock parameters …

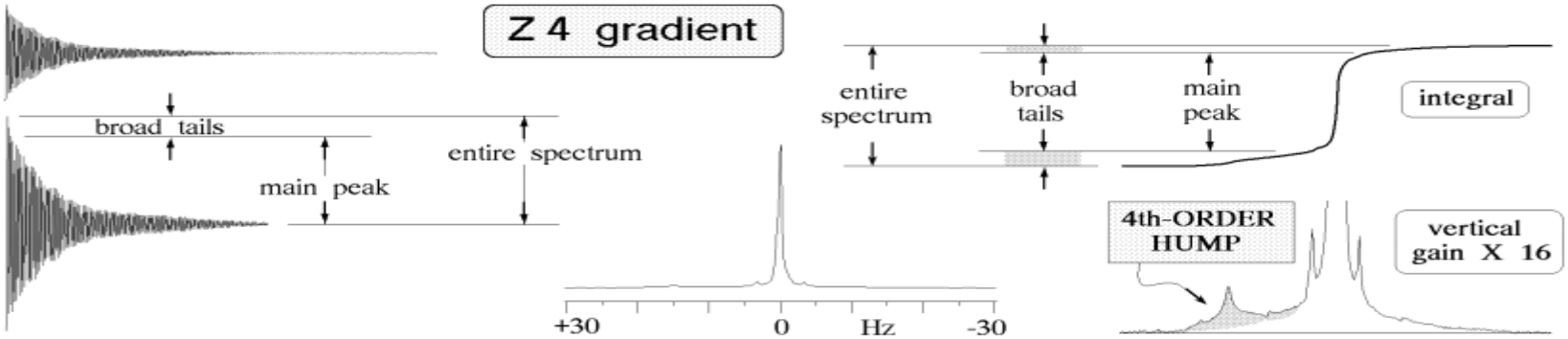



*Courtesy of Dr. Christoph Freudenberger BRUKER BIOSPIN Fällanden*

# Principles of shimming and shim errors




SKETCHES OF LINE DISTORTIONS CAUSED BY VARIOUS GRADIENTS

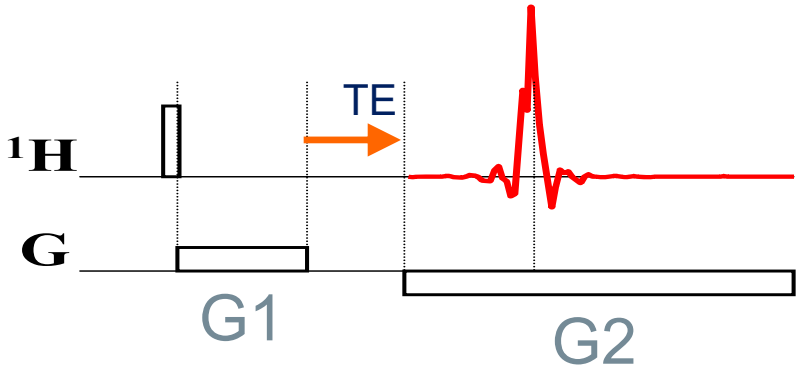



**From «Shimming an NMR Magnet» by G. A. Pearson. Highly recommended!**

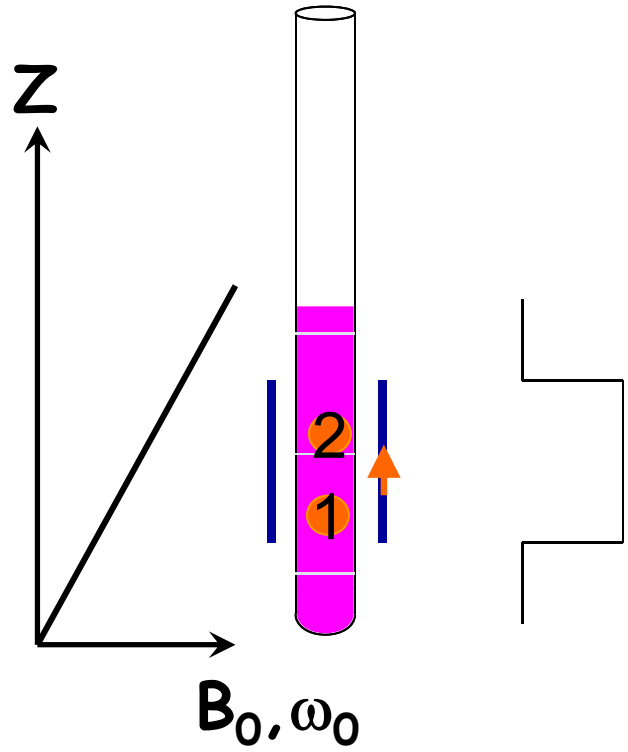
# Shimming: Preparation


- Manual Shimming:
  - Adjust the LOCK PHASE to maximize the lock level
  - Adjust the LOCK POWER according to the solvent
  - Lock level is the criterion for evaluation of magnet homogeneity

# Gradient shimming: Convection




1. Convection causes a wrong information according to the position in the sample.
2. Lost of the signal because of a incomplete focusing caused by the second gradient.



# Gradient shimming: Convection

Counteractions:

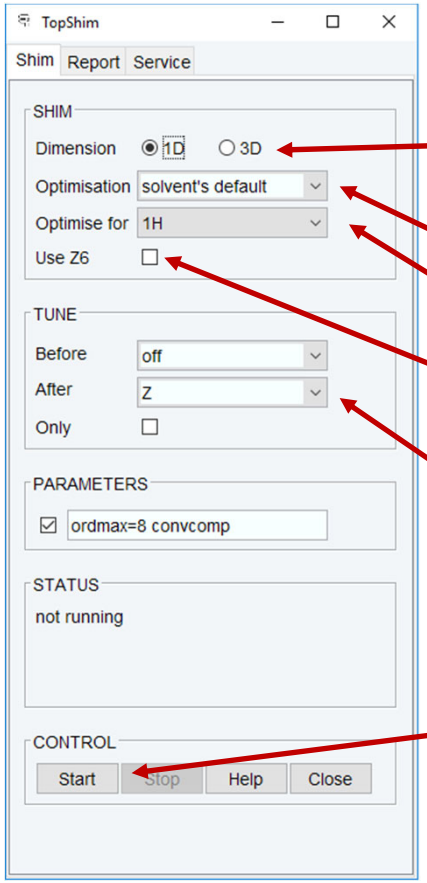
1. Avoid convection:
   - Sample filling height of 40 mm.
   - Increase the airflow.
   - Rotate the Sample.
   - Lower the temperature (if possible).
   - Use a solvent with a higher viscosity (if possible).
2. Version of TopShim with convection compensation:
   - TopShim in TopSpin 2.1 patch level 5 (or higher)
3. Version of Gradshim with convection compensation:
   - Pulse programs on request

# Gradient shimming: Convection

Common problems with TopShim:

- Situation:
  - bad result — without sample rotation
  - Good result — with sample rotation
- Reason:
  - Convection

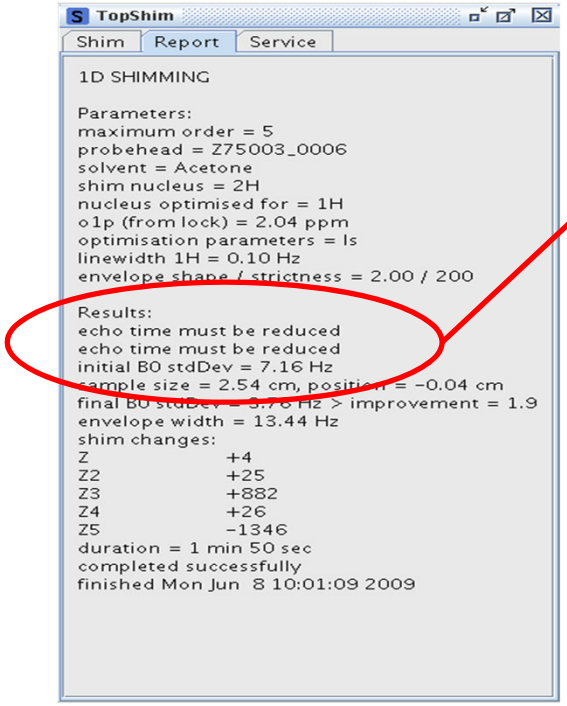
# Topshim window [topshim gui]

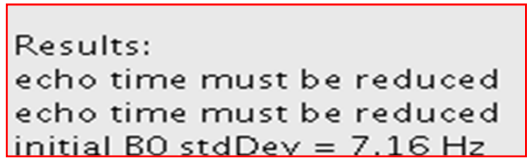



- 1D shimming (Z-Z5 only, on every sample) 3D (all shims, only 90% H2O sample using LOCK H2O+D2O)
- Optimization criterium
- For which coil optimize
- Z6 also (usually no)
- Shimming of Z,X,Y,XZ,YZ by lock before and after gradient shimming (before makes real sense)
- Start button

# TopShim: Remarks during shimming

Remark: echo time must be reduced




Reason and solution:

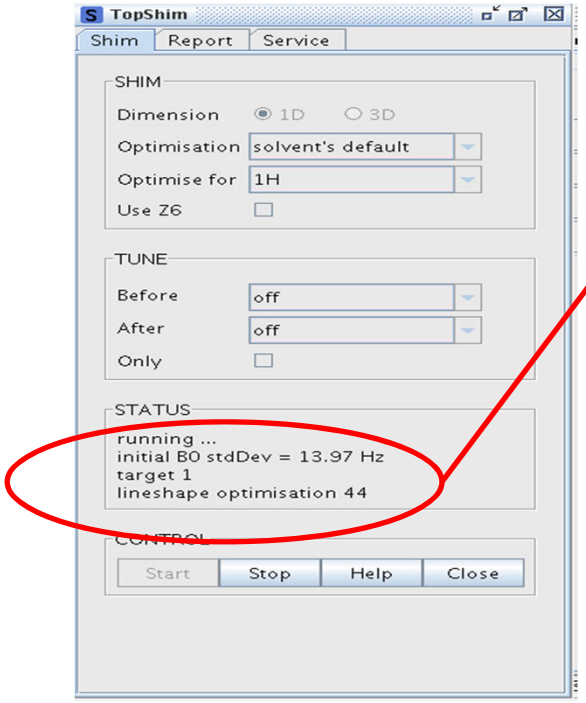
Second Echo time was too long. As a result the magnetization relaxes during the pulse sequence.

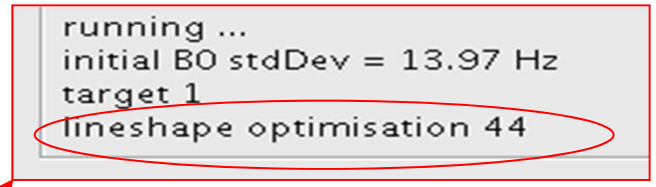
Reason:

1. The 3D homogeneity is not good (bad off-axis shim).
2. Convection.

# TopShim: Remarks during shimming

Remark: Shimming takes too much time



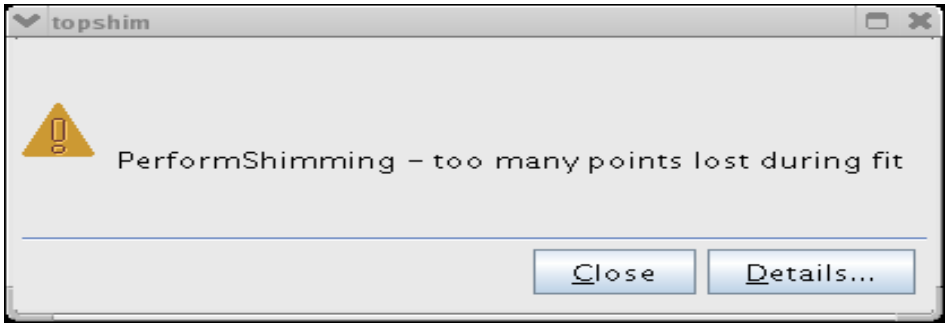




Reason and solution:

1. The 3D homogeneity is not good (bad off-axis shim).
2. Convection.

# TopShim: Remarks during shimming

Remark: Too many points lost during fit



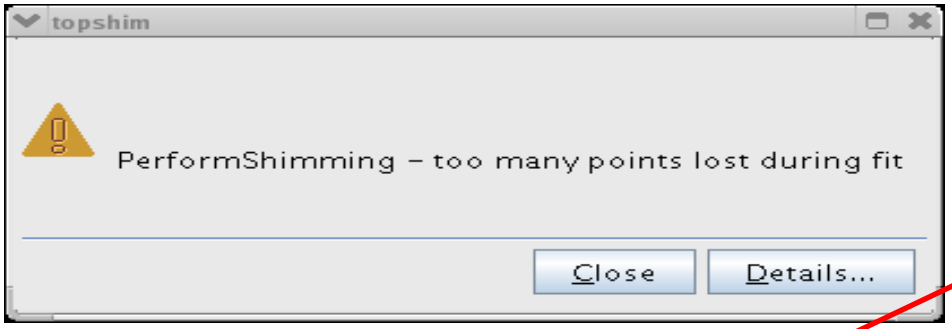

Reason and solution:

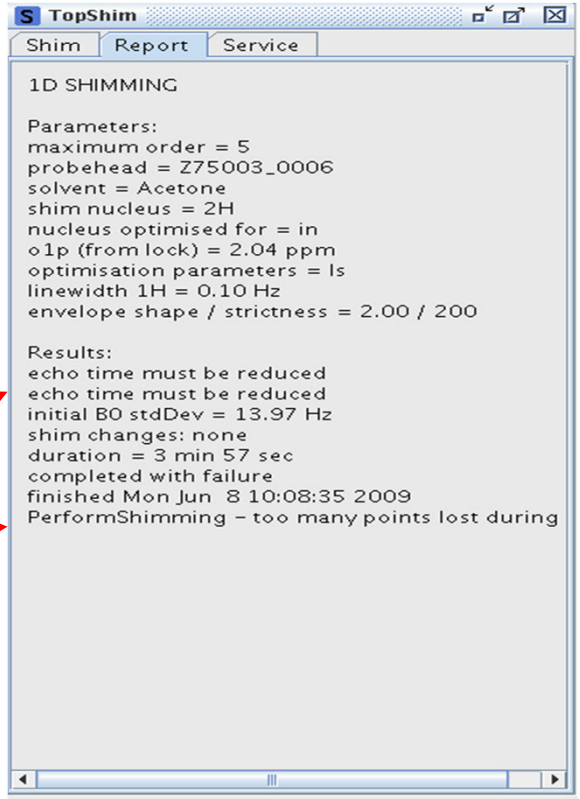
The basic homogeneity may not be sufficient.

1. Improve the homogeneity by manual or automated shimming on the lock.
2. Set very large values of high order shims to zero.

# TopShim: Remarks during shimming

Remark: Too many points lost during fit

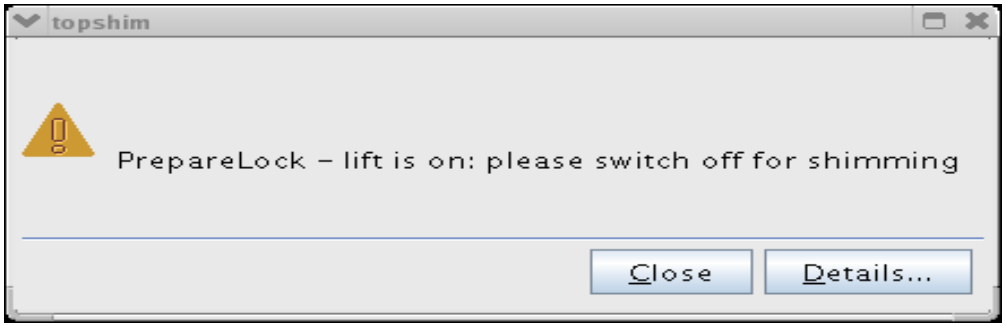



One error can cause another one

# TopShim: error message

Error message:

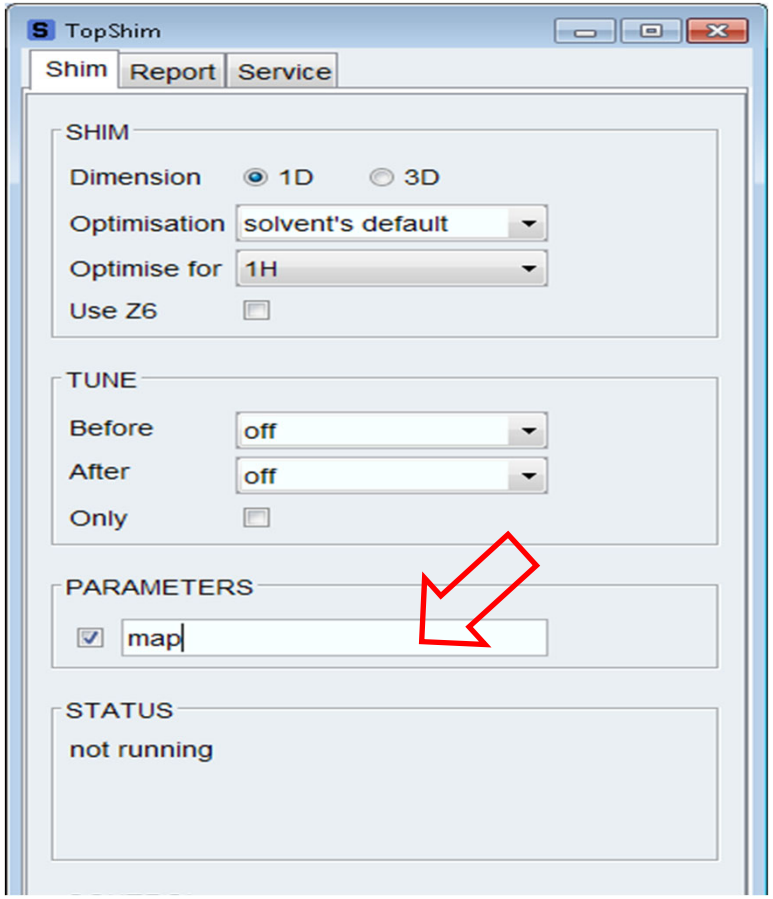



Reason and solution:

Lift is on.

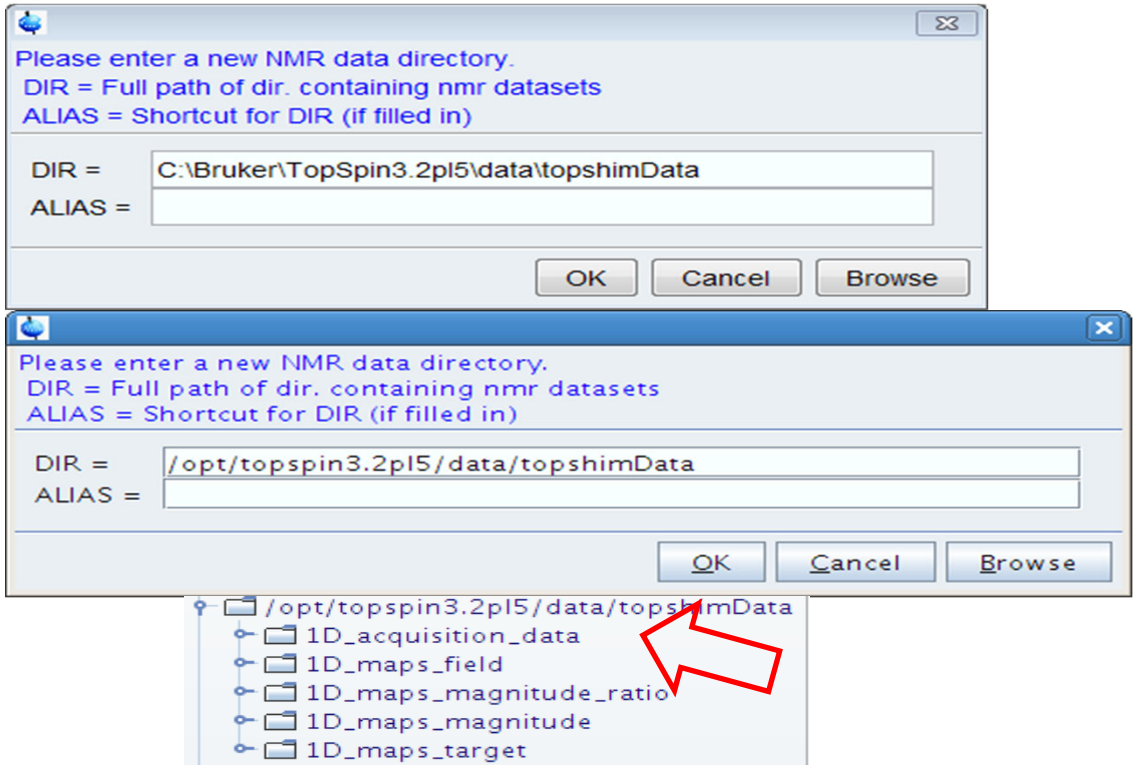
Sample is not locked.

# TopShim:



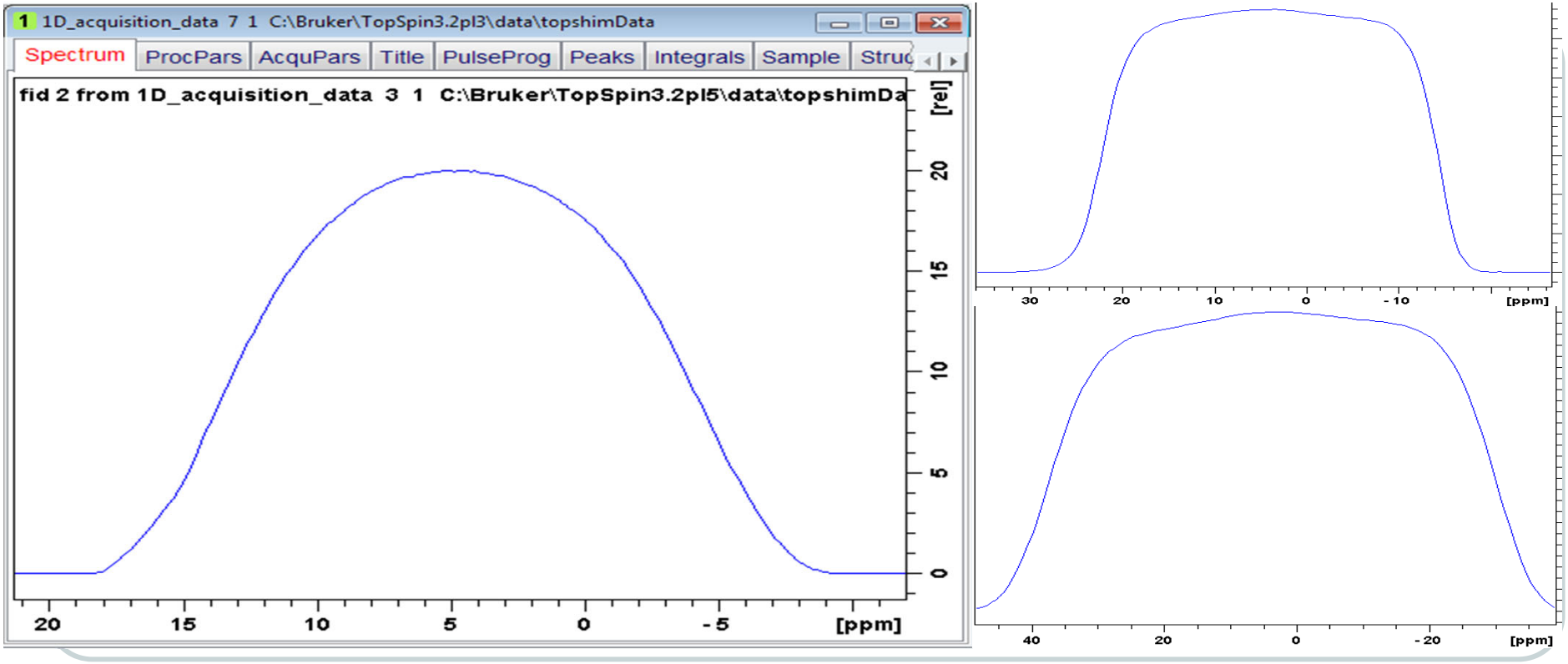

- Use e.g. Sucrose in H2O/D2O
- Start TopShim with the option “map“
- A Shim optimization will not be executed
- The current state will be documented with a Z-gradient profile.

# TopShim



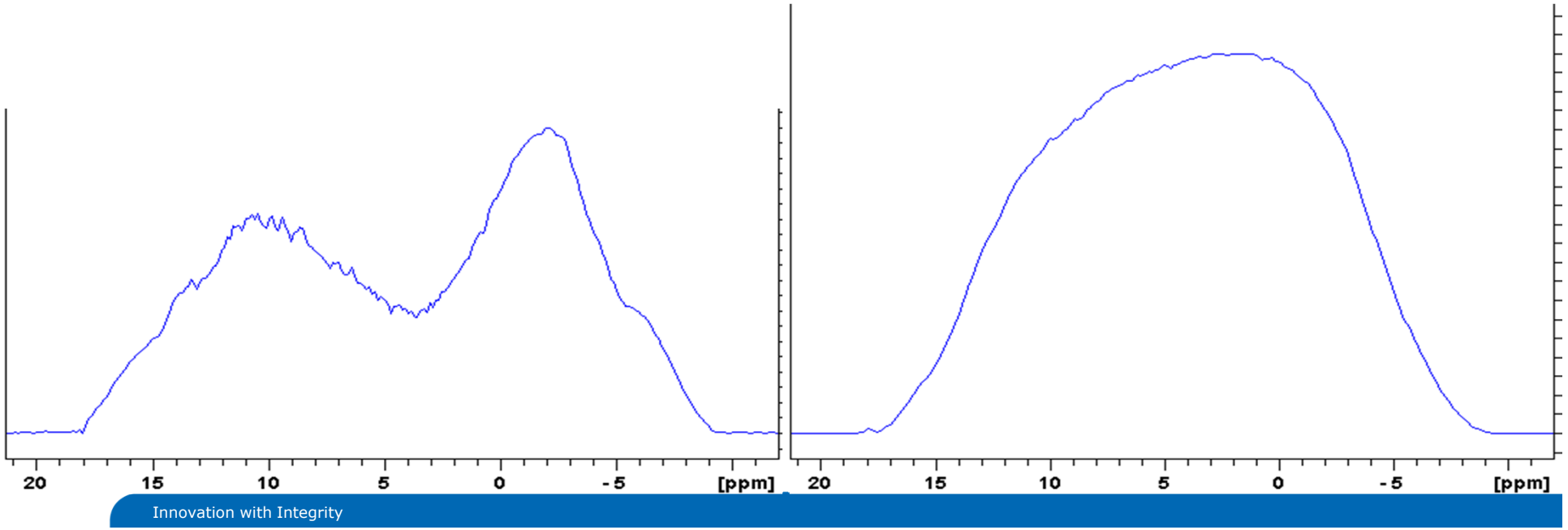

- The results will be stored in the folder: topshimData
- This folder is a sub folder of TopSpin
- Please Note: These data will be removed with the next TopShim run !!
- Send us this dataset directory for investigation

# TopShim – good Z-gradient profile



# TopShim – critical Z-gradient profile

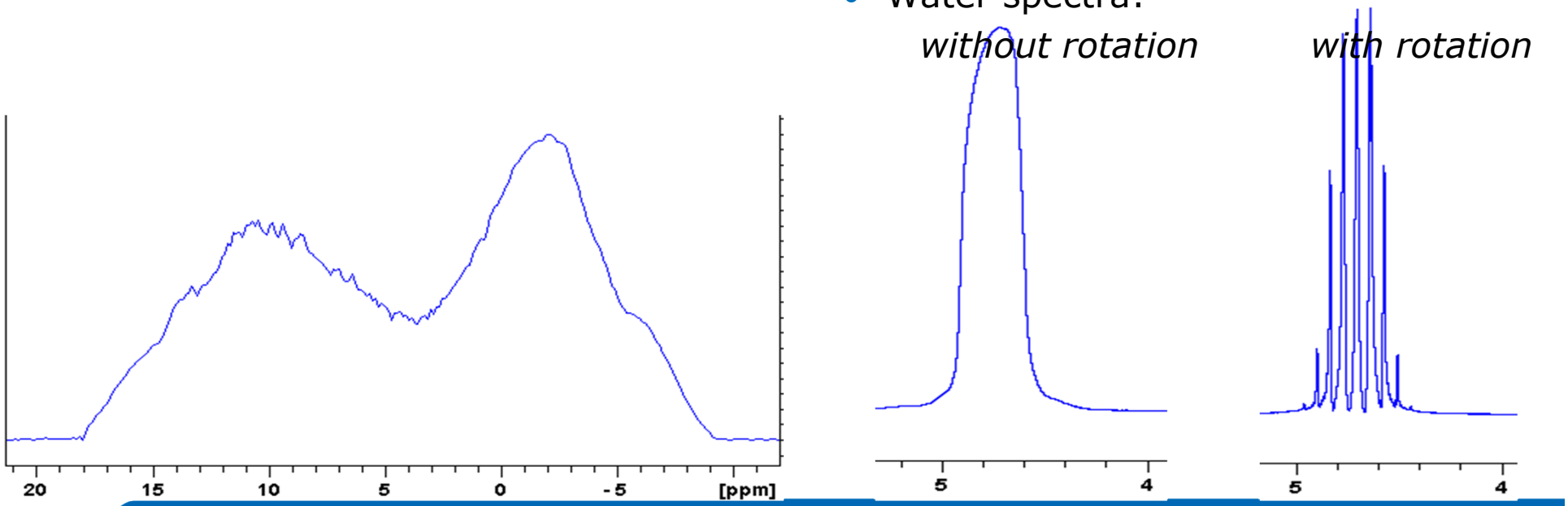
- no hardware defect!
- Off-Axis Shims are really bad !



# TopShim – critical Z-gradient profile

- no hardware defect!
- Off-Axis Shims are really bad
- Water spectra:

*without rotation* *with rotation*



# TopShim – critical Z-gradient profile

- no hardware defect!
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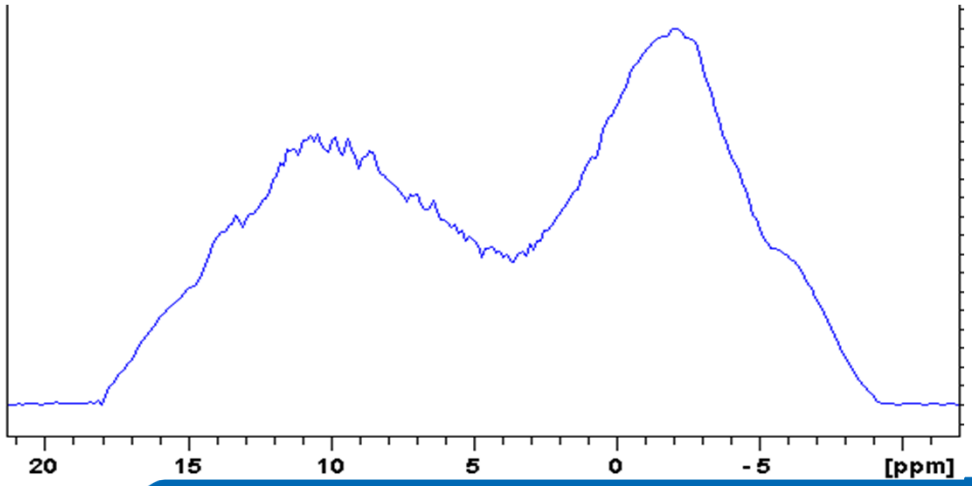
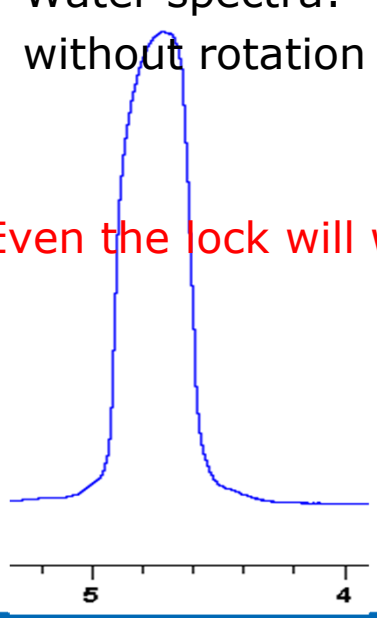
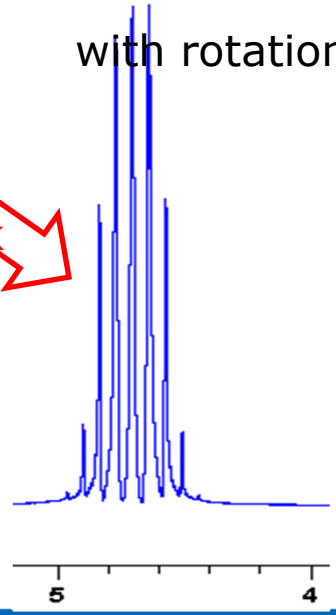
- Water spectra:
- without rotation with rotation



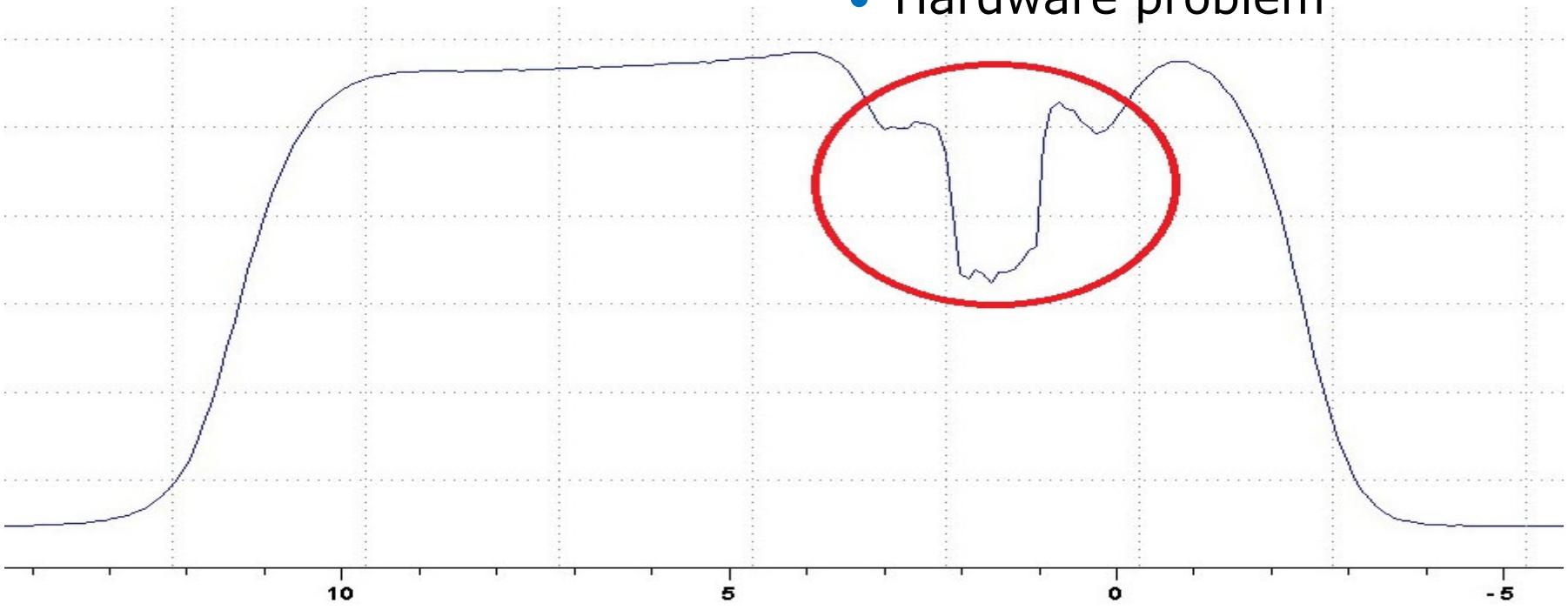

Even the lock will work



# TopShim – critical Z-gradient profile

- Hardware problem



# TopShim – critical Z-gradient profile

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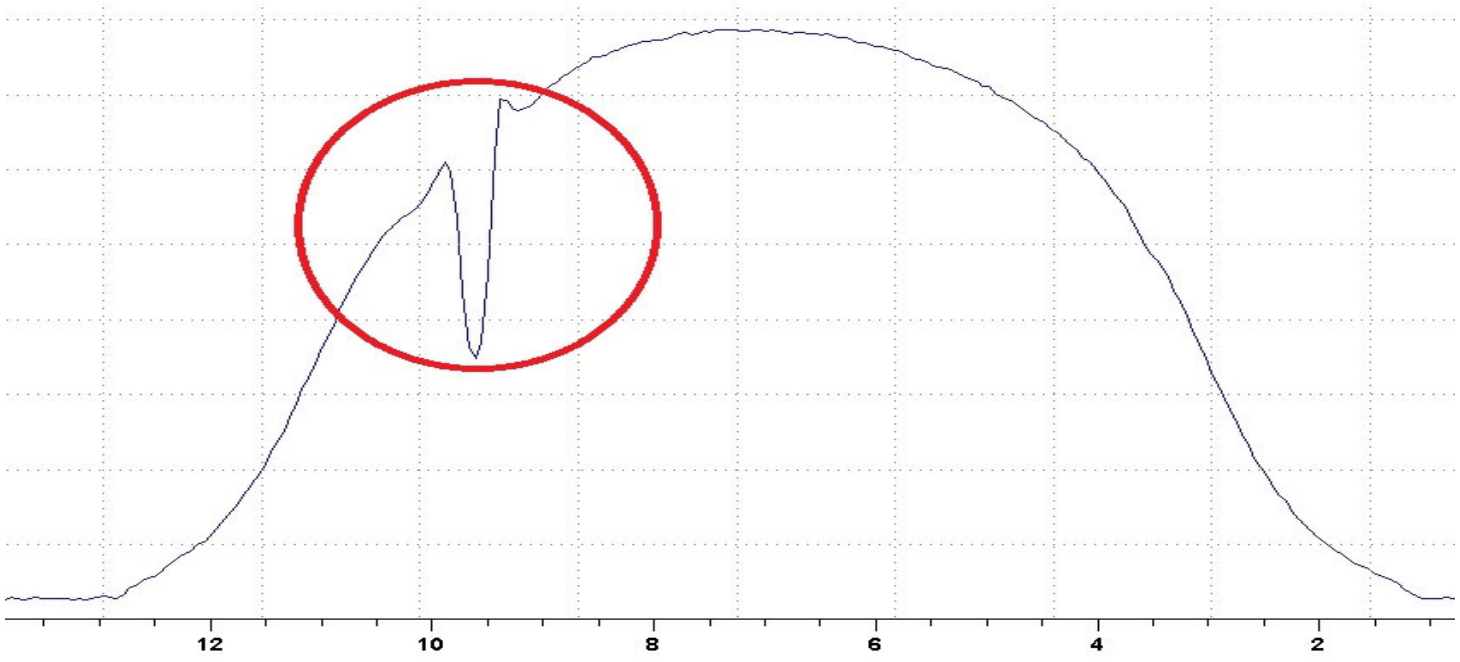
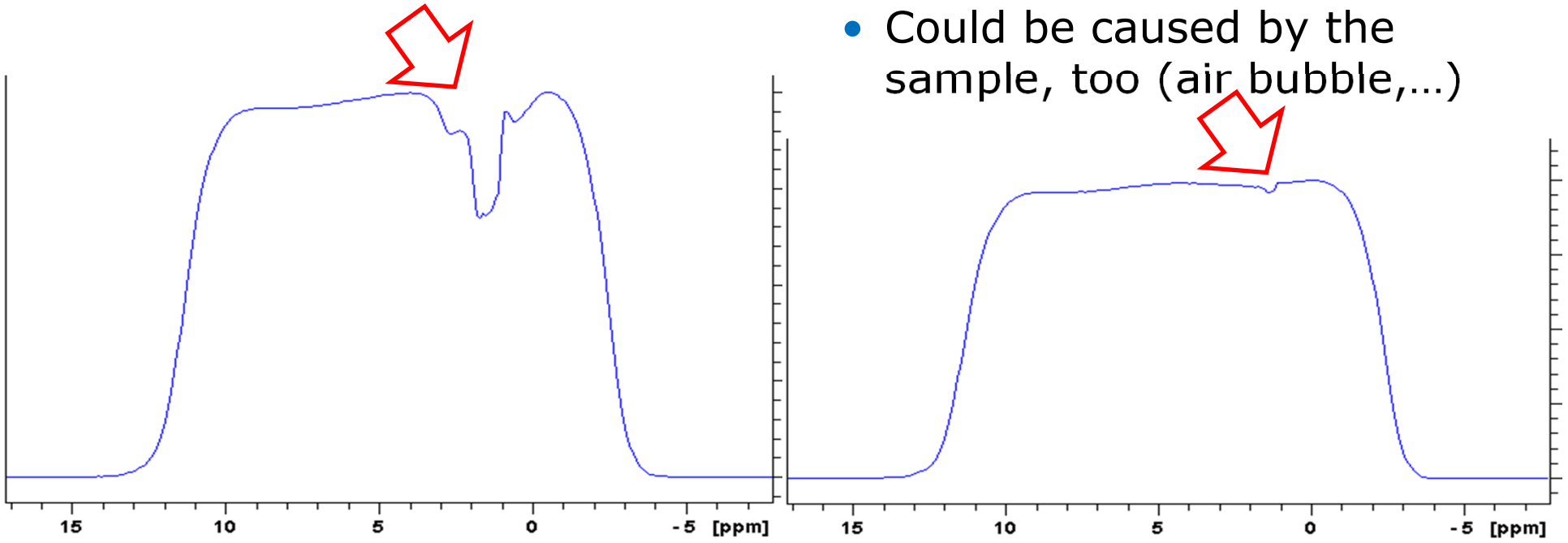


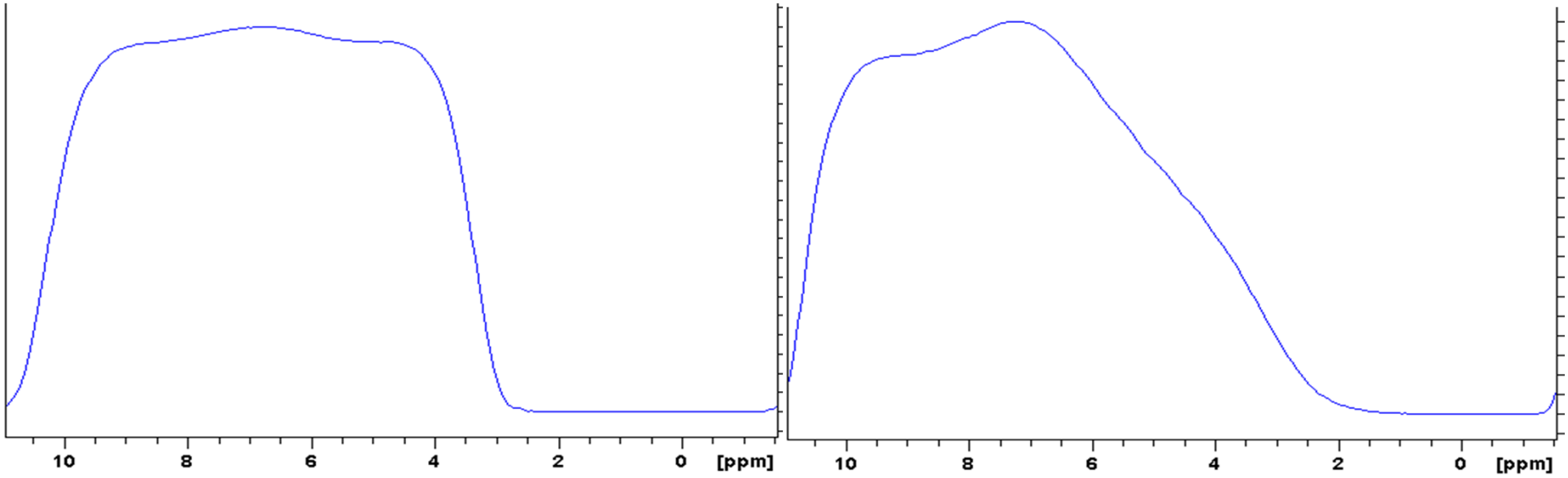
# TopShim – critical Z-gradient profile

- Hardware problem
- Could be caused by the sample, too (air bubble,…)



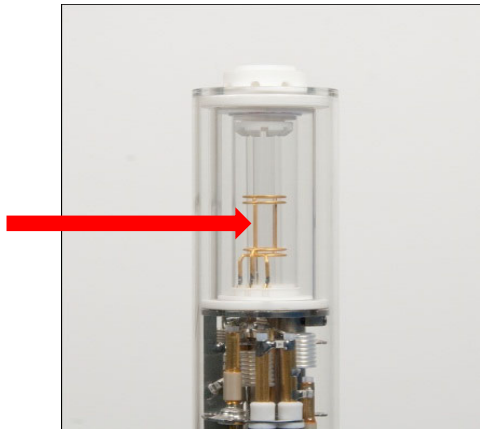
# TopShim – critical Z-gradient profile

- Hardware problem
- Please contact Bruker!

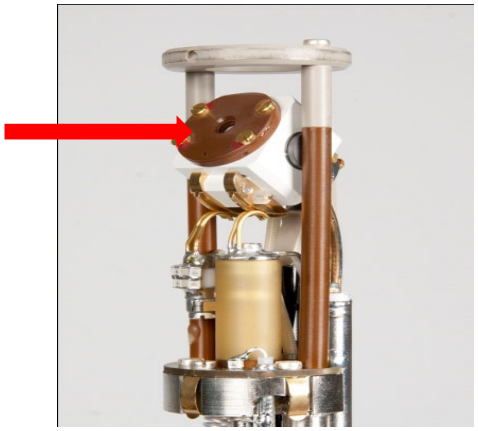


# NMR Thermometer

High Resolution



HR-MAS



**Heating of the sample by RF ~2K**

**0 – 12 Hz shifts**

$H_2O$: ~ 0.01ppm / K
@600MHz = 6Hz / K

**Heating of the sample by MAS up to 30K**

# NMR Thermometer

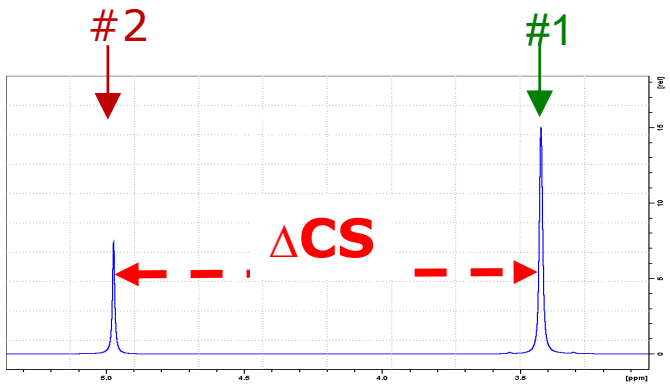
- **Measuring**
- **Regulation of the temperature in the sample**
- **Monitoring**

**Method of measurement is known:**

**Measure the temperature dependent Chemical Shift**

**Regulation**

# NMR Thermometer




Solvent with at least two $^{2}H$ lines with different temperature dependent behavior of the CS.

**Measure ΔCS**

L-TRX (2G DigiLock) transmits and detects two frequencies simultaneously.

#1 is fixed = **Lock**
Defined CS of the Lock-Peak:. Field is regulated, so that the Peak is on Resonance.

#2 is variable = **Temperature**
CS of the second Peak. Frequency is regulated, so that the Peak is on Resonance.

# NMR Thermometer - Advantages

The advantages are analogue to the solvent as Lock-substance

Solvent has exact the temperature of the sample

Solvent is spectroscopically independent of the sample

No additional spectra have to be recorded

Update of the temperature with high rate (as Lock, about 6600/s)

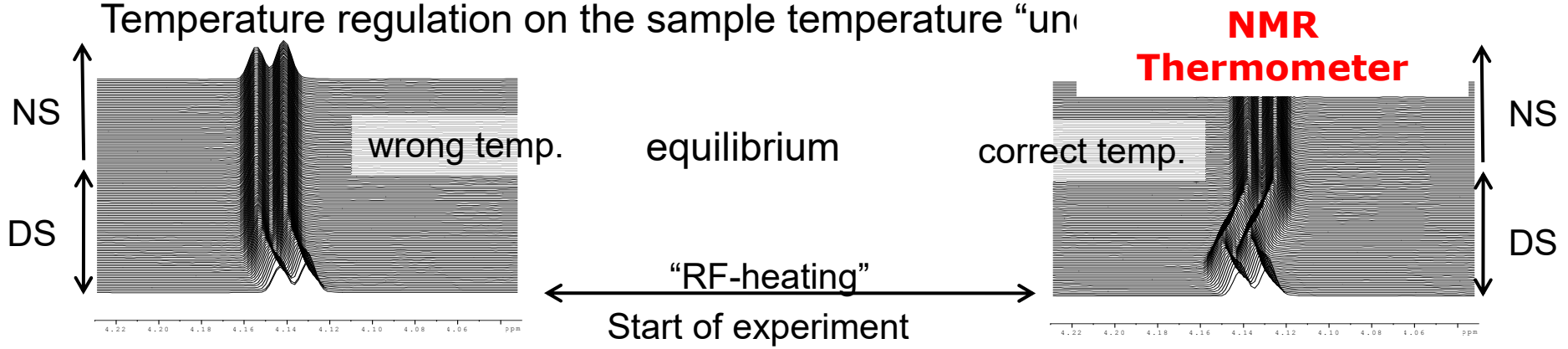
Fast and easy data transfer between BSMS and SmartVT unit because of integrated infrastructure. L-TRX ELCB BSVT

# NMR Thermometer

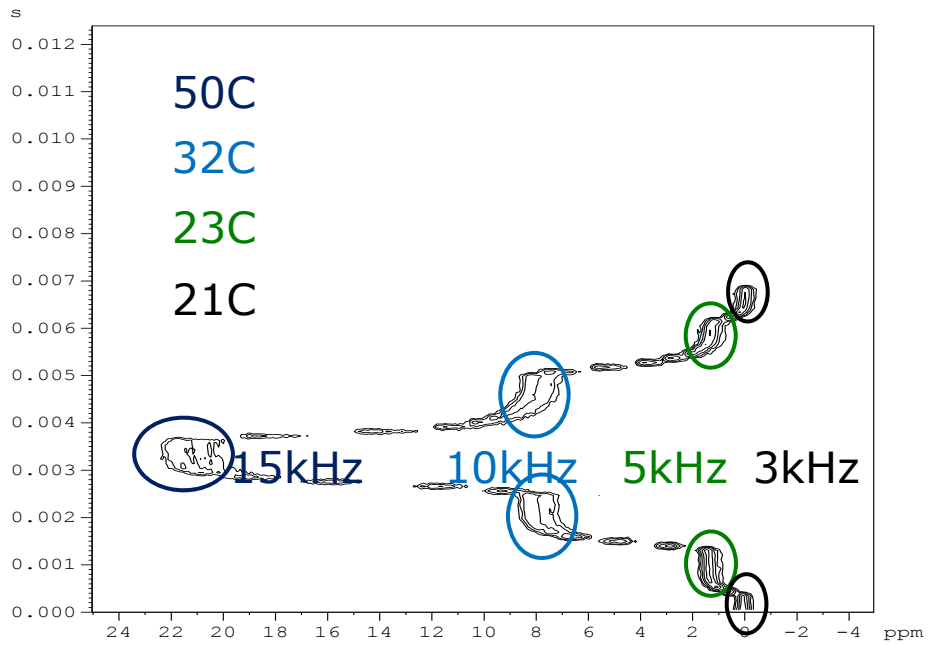
"Correct" temperature (if calibrated correctly).

Identical temperature on different probes and spectrometers.

Temperature regulation on the sample temperature "un

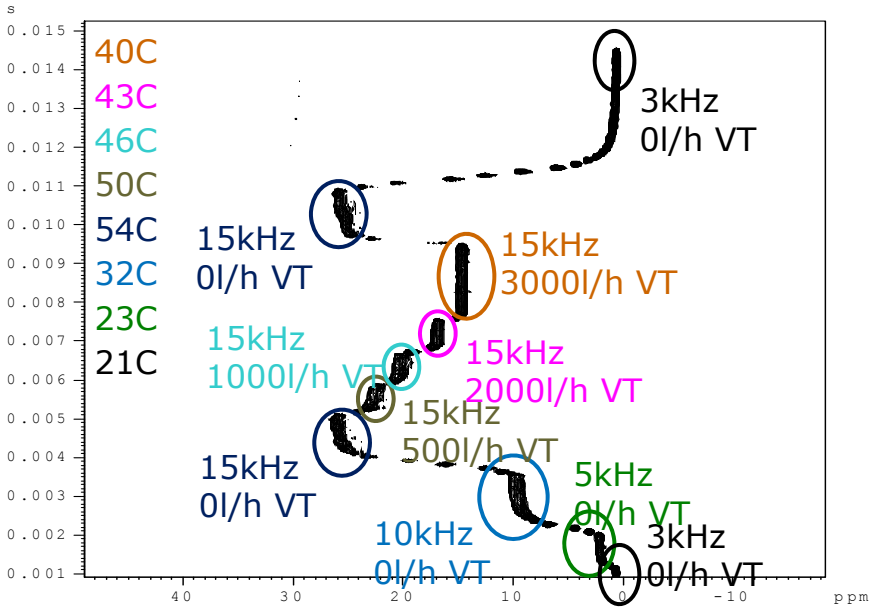


# Influence of Magic Angle Spinning on the Temperature



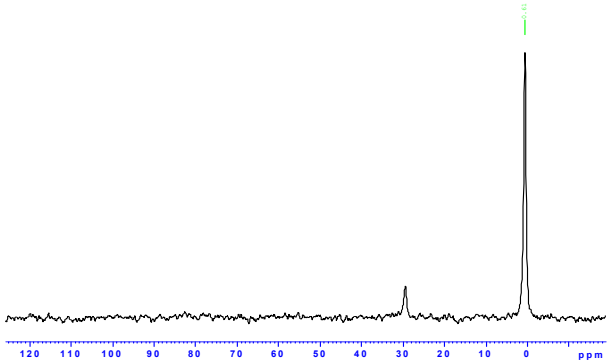

- Center packed sample (4mm, ZrO powder)
- 21C at 3kHz (room temperature, referencing)
- Lead nitrate for temperature calibration, 0.753ppm/K
- Spin rate was changed within running experiment
- Maximum temperature difference about 30K above RT

# Influence of Magic Angle Spinning and VT Gas on the Temperature

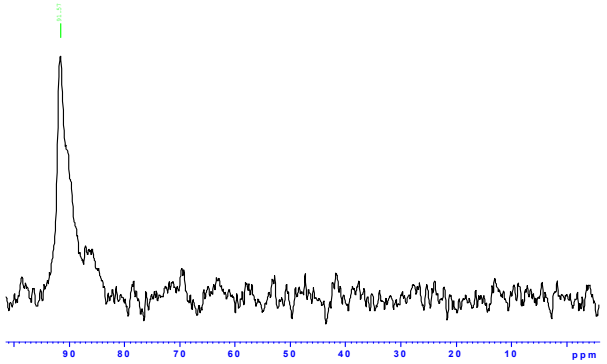



- Center packed sample (4mm, ZrO powder)
- 21C at 3kHz (room temperature, referencing)
- Lead nitrate for temperature calibration, 0.753ppm/K
- Spin rate was changed within running experiment and VT gas flow was adjusted
- Maximum temperature difference about 34K above RT

# Temperature Calibration

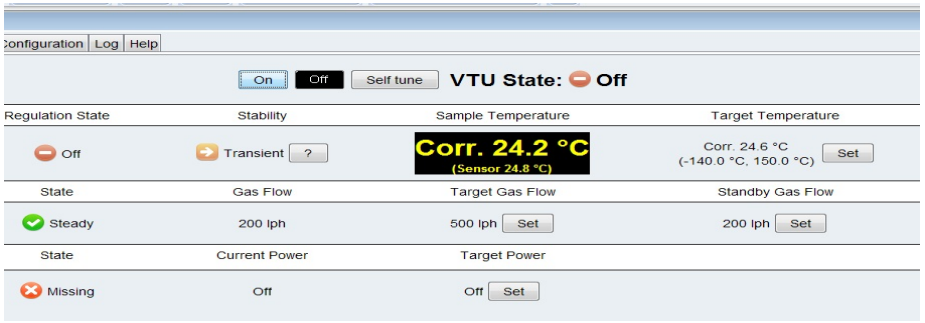



Tset=294K: 0.61ppm = 20.3C

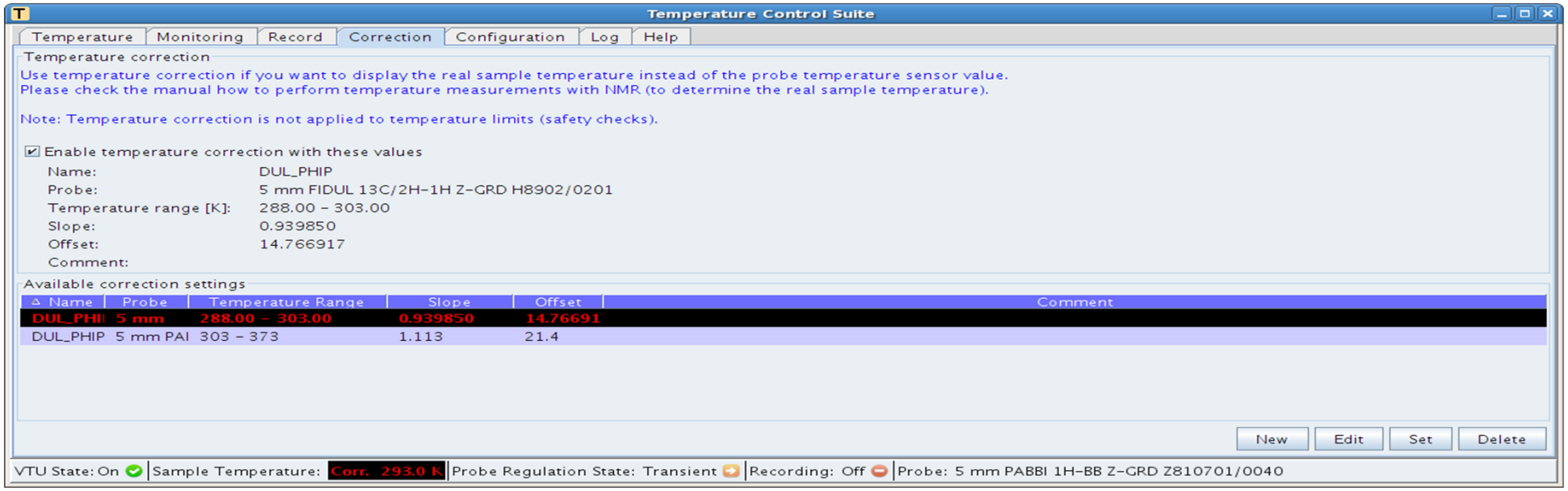



Tset=413K: 91.55ppm =141.8C

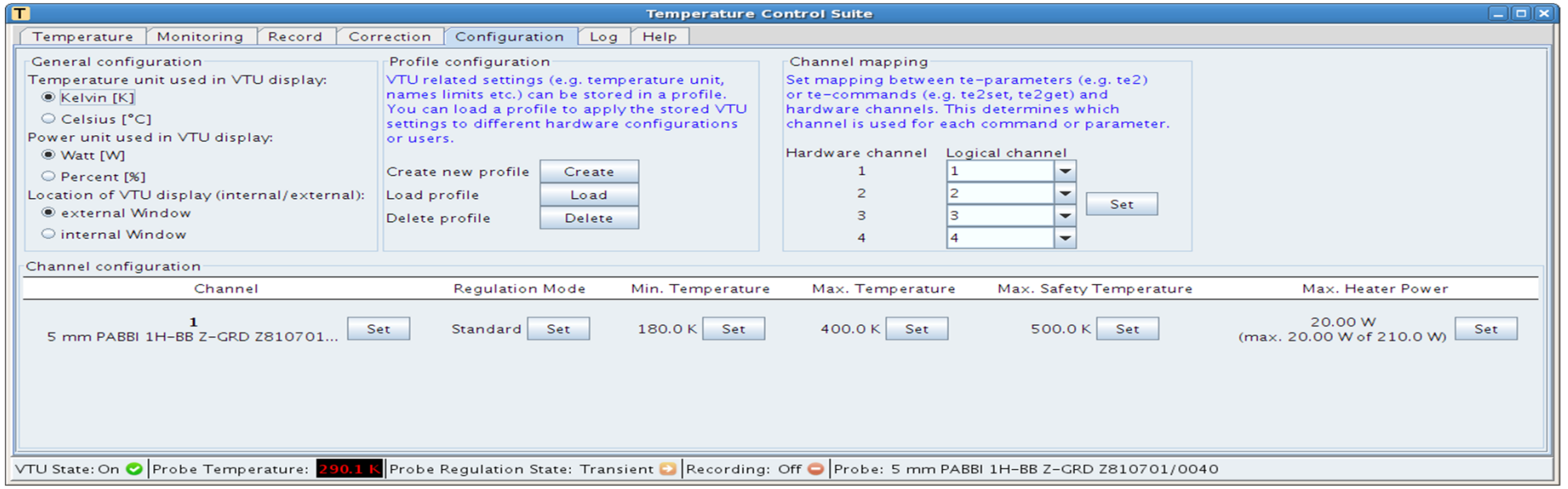
- Calibration with 2 or more temperatures
- Calibration curve is calculated either
  by EXCEL/ORIGIN or TS
  Slope:0.979424 / offset: 6.734979
- After activation EDTE shows both values



# Temperature Calibration – edte



# Temperature profiles – edte




User can store probe profiles. This way, it is easy to handle different settings.

# BSMS shim cooling and probe flush

Experiments at very high or very low temperatures need some care.

- The probe electronics should be protected from excessive heat or icing.
  - This can be done by using flush gas (on newer probes)

- The shim system and the O-rings of the magnet (vacuum sealing) must be protected from excessive temperature.
  - This can be done by using shim flush gas. A special adapter (clamp ring) is necessary for the Shim Upper Part.

# Conclusion - Solids NMR


- Calibrate your probe
- Choose carefully the flow/hardware conditions
- Use center packed samples whenever possible
- Higher flow rates can improve the overall performance
- The probe/shim needs time for thermal equilibrium (30min to 1h)
- The most versatile cap is the ZrO cap
- Keep an eye at the magnet’s shim temperature

# Conclusion - Solution NMR

- Run “self tune” with your probe (different temperature ranges >30-50K may require different PID parameters).
- Choose carefully the flow to optimize temperature gradients (higher flow typically reduces gradient but be careful not to “lift” the sample).
- If absolute temperature is of interest, calibrate the probe with a thermal standard (depends on flow rate) and set the correction in edte accordingly.
- The probe/sample needs time for thermal equilibrium (>5min).
- Choose the best hardware option get cold gas.
- Keep an eye at the magnet’s shim temperature.

# The Importance of Air!

- Are you sure what kind of gas you get out of your supply? Air or clean $N_2$?
- Does it make a difference?
- How about quality of the supplied air?

Air or $N_2$:

The answer is important, because your probe is most likely optimized for one or the other. Most new RT-PH (Room Temperature Probes) will only work nicely if used with $N_2$ -> shimming will be difficult if used with air!

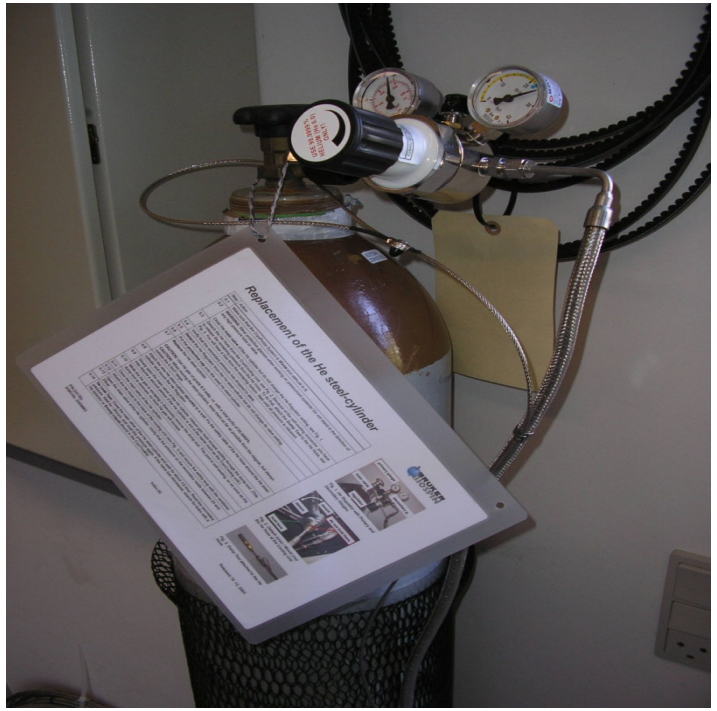
All RT HR-PH >400 MHz + all RT small volume PH:s (1mm/1.7mm)

# The Importance of Air!




Cryoprobe platforms

- Only use grade 6 helium quality (99.9999 % He)!
- Make sure the regulator is not manipulated: 24-25 bar
- Follow the instructions when replacing bottle
- In case of Shimming problems: try to increase the airflow. Watch wobble curve and lock !!



# The Importance of Air!

<u>What is the pressure? Is it stable?</u>

Magnets on air posts will move up/down!
Sample changer may fail.

Solution: Connect a buffer tank, possibly along with a higher capacity compressor.

<u>What is the dew point?</u>

Bruker recommends a dew point <-40C. Install an efficient and silent dryer!

Condensation! Corrosion! Ice build-up!

# The Importance of Air!

<u>What flow can you use without pressure drop?</u>

MAS and automation will need a larger flow (>100l/minute). Measurement may be necessary upon installation of new accessories.

<u>How clean is the air? Amount and size of particles?</u>

Clogging of MAS-PH and MAS-drive. Think about installing an oil separators and/or a filter at the outlet! The extra cost is small compared to the repair costs of a probe!

# The Importance of Air!

What temperature has the incoming air?

If you're using air directly for the VTU (no pre-cooling), you may see stability problems.

Solution: Install a pre-cooler or a large buffer tank.

If you're uncertain or have questions, please contact your Bruker Service team.

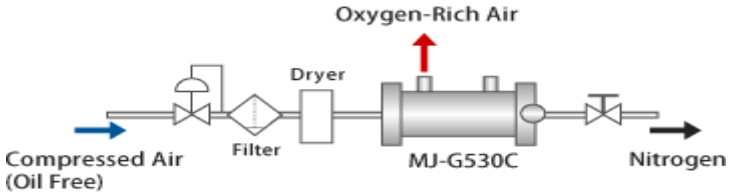
# The Importance of Air!

<u>What if I only have compressed air and need $N_2$ for a new system or PH?</u>

Solution : $N_2$-Separator.

The separator is using a membrane (passive, and only built for low flow applications)

Separate benefit: dew point will be reduced!



# High/low temperature experiments

<u>What are “extreme temperatures”?</u>

No strict definition, but outside [0-60] C would make sense ☺

<u>But my probe specs say [-150- +150] C?</u>

Yes, but it takes more than a PH to make a system.

<u>Does this mean that I should not exceed [0-60] C?</u>

Not necessarily, but if you do, take extra precaution and supervise the system during the experiment.

# High/low temperature experiments


Why are there restrictions?

1. The PH itself has limitations (material & design).
2. The shim system has a very well defined upper limit: +80C. Condensation of water could also damage it at temperatures below +4C.
3. The magnet will be in danger if parts of it are frozen - the vacuum will be softened and the insulation capacity decreased. Higher boil off, in the worst case sudden loss of cryogens and a quench, may occur.
4. The spinners have a limited temperature range (plastic ones about +60C, ceramic ones should be used at higher temperatures).

# High/low temperature experiments


<u>There are soft solutions:</u>

1. If you need to run long time experiments at high temperatures or low temperatures, you can think about special probes (ET/LTB).
2. Supervise the shim tube temperature using “coiltemp” (an AU program in Topspin) and make sure it stays (well) below +80C. Future versions of Topspin will have a protection in the software.
3. Inspect the top and bottom magnet flanges and upper part for signs of freezing. This should be done continuously during the experiment at least some time after an equilibrium state.
4. And remember the ceramic spinner …

# High/low temperature experiments


There are more/hardware solutions:

1. From 2nd half of 2008 on (in some cases earlier) most RT-PH are equipped with a built-in frame cooling that will flush the interior parts using a constant flow of air/$N_2$

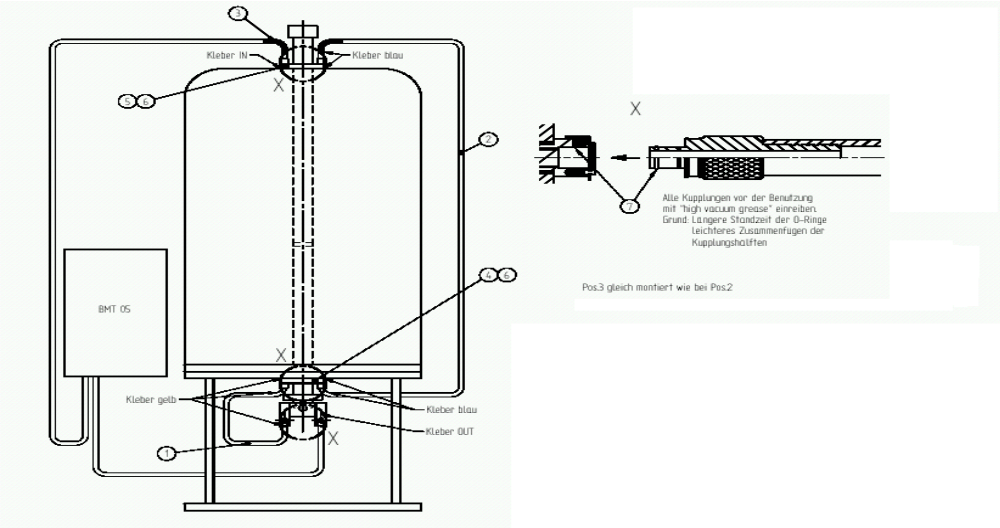
2. Upgrade with the cooling ring set that will flush the space between shim tube and RT-bore (the visible inner tube of the magnet) using air or $N_2$

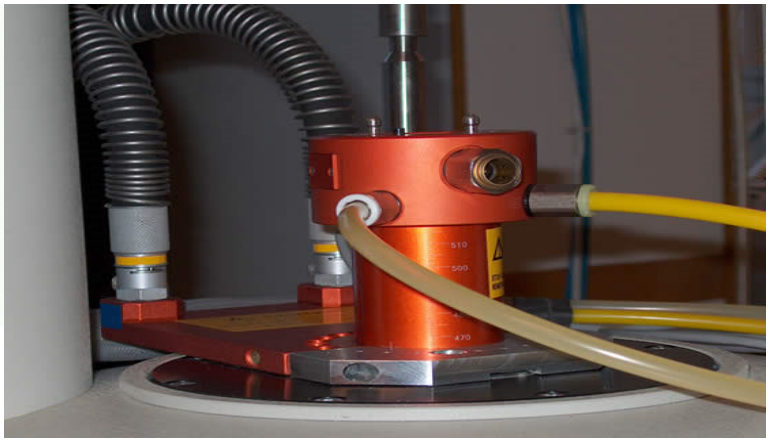
   Two version are available: one to retrofit systems delivered before 2nd half of 2008 (the shim tube needs to be taken out of the magnet), one for new systems already prepared for cooling rings (only some pieces are added, no need to remove the shim tube)

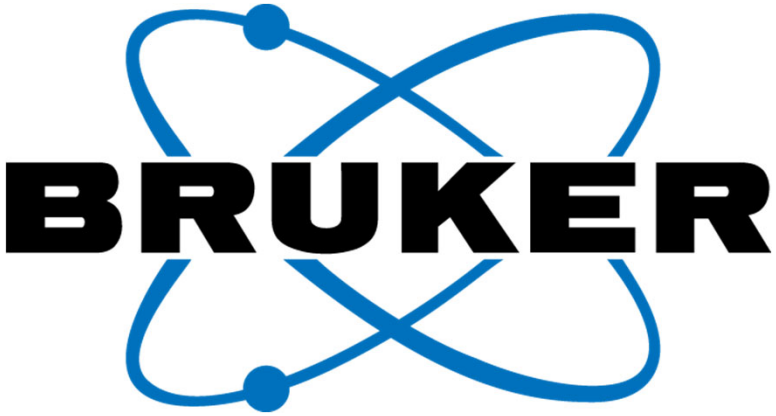
# High/low temperature experiments

There are more/hardware solutions:

3. Upgrade with water heated system that will keep the upper/lower flanges at a constant (warm) temperature






Innovation with Integrity