VT experiments on Bruker NMR spectrometer

by Monika Ivancic, written on 9-3-2015 (hot) and 10-20-2016 (cold)

Performing VT (Variable Temperature) experiments on the NMR spectrometer is not a simple task. **Special care must be taken and instructions specifically followed, to avoid damage to the equipment!!!** Please be careful, use proper protection and allow ample time for the instrument to reach desired temperature. You will also need ample time (**at least 20 min**) for the instrument to get back to room temperature and equilibrate. It is YOUR responsibility to ensure that this be accomplished BEFORE the next user is signed up on the calendar.

For high temperature experiments: (written on 9-3-2015, updated 10-21-2016)

If you are planning to go up to only 60^0C, you do not need to switch to N_2 gas, you may go ahead and skip step 1., and proceed to 2.. If you need a temperature of 65^0C or higher, you **MUST switch to N_2 gas** for feeding the instrument (see 1.).

Insert the sample: The 'regular' blue POM spinner is OK to use up to 80°C. If you're going above 80°C, use the white ceramic spinner. (blue spinner < 80^0C; white spinner > 80°C to150°C)

1. Switch the instrument's air supply from dry air to N_2 gas:

a) in TopSpin, type 'edte' to open the temperature control monitor. Turn off VT control (VTU state at top).

b) Make sure that the black N_2 tubing has been placed behind console and is attached to the N_2 gas cylinder. Hook this line up at the quick release behind the console (UPS side).

c) Open up the N_2 gas cylinder at the main valve and open side valve to ensure gas is flowing to the instrument. Adjust the pressure to 80psi (instrument requirement).

d) Check pressure gauge inside right side of console to make sure it points to the green arrow. If not, make adjustments to the pressure on the N_2 gas cylinder.

e) Once you know that gas is flowing thru the instrument, turn VT control back on (in 'edte') with the set point being 25°C (under the 'configuration' tab, change to Celsius).

2. Start increasing the temperature:

a) Increment temperature in steps of about 20°C. You may follow the temperature increase by going to the 'monitoring' tab in the 'edte' GUI, and click on the 'set temp' and the 'current temp' options (and anything else you may want to monitor as the temp increases).

b) You may need to adjust "VT gas" (Target gas flow), depending on the desired temperature. Bruker recommends **535 lph between 0°C and 80°C**, then 450 lph between 90°C and 120°C, and 350 lph between 120°C and 150°C.

b) Once you reach the desired temperature, wait about 10 min for your sample to equilibrate (if your sample is already in the magnet).

c) If your sample is not already in the magnet, you may insert your sample after the desired temp has been reached, keeping in mind that the extra air flow will likely decrease the temp at the sample area. Also be considerate of using N_2 gas, please have the lift air on for as short a time as possible !

d) After waiting about 10 min for your sample to equilibrate, you need to re-tune and re-shim the sample ('atma' and 'topshim') prior to acquiring data. Make sure to create a new dataset ('edc' or 'new') prior to acquiring data at this new temperature!

3. A note about sample temperature:

The temperature of your sample will be slightly different from the set temperature, because the thermocouple is 1-2 cm below where the sample sits. IF you need to know the exact sample temperature, you will need to run a "temperature standard" first. Use 'ethylene glycol' when going hot.

4. A note about shim temperature:

The shim coils MUST NOT go above 60ºC or 333K – the shim temperature is shown on the 'status bar' at the bottom of the TopSpin software display (if not, go to -> Preferences, under 'status bar', make sure shim temp is checked; you will need to exit and re-enter TopSpin for changes to take effect). If the shim temp starts approaching that value, you need to turn on the 'shim cooling gas' located at the back of the console (UPS side).

5. Cooling down the sample:

a) slowly decrease the temperature, in steps of about 20ºC. Ensure that temp isn't changing by more than 10ºC/min.

b) You may want to increase "VT gas" (Target gas flow), here. Bruker recommends 535 lph between 0ºC and 80ºC, but you may go to a higher gas flow if you find that helps with decreasing temperature.

6. Achieving RT and ejecting sample:

a) Once you've reached 25ºC, you may eject the sample (or you may eject it sooner, but ensure that you are present at the spectrometer until the normal temperature is reached)

b) The temperature should be stabilized at 25ºC (green) and "VT gas" (Target and Standby gas flow are BOTH at 535 lph). The spectrometer is ready for the next user!

Low temperature experiments

(by Monika Ivancic, October 20th, 2016)

There is no chiller on the Bruker NMR spectrometer, so if you absolutely must use the Bruker to go cold, you will need to use the small LN2 dewar with the LN2 Exchanger for any temperature below ambient. The Varian NMR does have a chiller, so if you need temps between 0^0C and 25^0C, and ^{1}H spectra will do, please use the Varian for this purpose.

To prepare for this experiment:

a) Make sure that you start with the LN2 dewar being at least half full! (Use the magnet LN2 supply or the department LN2 supply in the loading dock.)

b) Make sure to start with a new N_2 gas cylinder. It would be great to have a different source of N_2 gas (such as blowoff from a high pressure LN2 dewar), but the departmental needs aren't great enough to justify the expenses associated with this. Also, the N_2 gas needs to be at 80psi entering the instrument.

Insert the sample: The 'regular' blue POM spinner is OK to use down to 0ºC. If you're going below 0ºC, use the white ceramic spinner. (blue spinner > 0^0C; white spinner < 0ºC to -150ºC)

Acquire a room temperature spectrum! It is always good to have a reference point to know your sample is pure and ready to be brought to a low temperature.

1. Switch the instrument's air supply from dry air to N_2 gas:

a) in TopSpin, type 'edte' to open the temperature control monitor. Turn off VT control (VTU state at top).

b) Make sure that the black N_2 tubing has been placed behind console and is attached to the N_2 gas cylinder. Hook this line up at the quick release behind the console (UPS side).

c) Open up the N_2 gas cylinder at the main valve and open side valve to ensure gas is flowing to the instrument. Adjust the pressure to 80psi (instrument requirement).

d) Check pressure gauge inside right side of console to make sure it points to the green arrow. If not, make adjustments to the pressure on the N_2 gas cylinder.

e) Once you know that gas is flowing thru the instrument, turn VT control back on (in 'edte') with the set point being 25ºC (under the 'configuration' tab, change to Celsius).

2. Insert the LN2 exchanger into the LN2 dewar:

a) First make sure the dewar is at about the appropriate distance from the magnet. The LN2 exchanger line needs to come directly to the probe without being stretched or bent. Small adjustments can be made after attaching the LN2 exchanger transfer line to the probe (see d)).

b) turn off temp control in 'edte'

c) disconnect the air line (which now has N_2 gas flowing thru it) from probe and connect the LN2 exchanger transfer line to the probe by placing it onto the ball seal and using the clamp pin to hold it there securely (screw the clamp pin, so it stays in place).

d) at this point you can adjust the positioning of the LN2 dewar, such that the LN2 exchanger transfer line is not bent

e) connect the N_2 gas supply that you disconnected from the probe and connect it to the ball seal on top of the LN2 dewar (at the other end of the LN2 exchanger transfer line). Note that this N_2 gas flows thru the LN2 dewar where it gets super cold before entering the probe.

f) don't forget to connect the 'regulation heater' to the VTA that sits on the floor (TC – LN2); line up the notch, press together and then screw on slightly.

3. Start cooling down the probe:

a) in 'edte' turn temp control back on; can set to a low temperature like 0^0C

b) the LN2 Exchanger connection/air flow should appear as a separate channel, below the probe channel; if it doesn't you forgot to do step 4f), however you can't make any adjustments here

c) turn VT gas (gas flow) up; Bruker recommends a setting of 1300lph, but on 10-18-2016 we found out that this is way too high, the probe won't stabilize at 0^0C, but will continue to drop in temperature quickly (a gas flow of 300lph worked for stabilizing probe at 0^0C).

Note: Not sure why the gas flow had to be turned that low, at higher gas flow (say 500lph) the heater power would stay at 2.5%, and the temp would stay at -1.4^{0}C, not go higher to the set point of 0^0C. Even a gas flow of 400lph caused the temperature to not stabilize at 0^0C, but was lower than this.

d) since temperature was having a hard time stabilizing at 0^0C, decided to do "self tune", which takes about 10 min. Self tune did 'correct' the instability in being able to hold temp, and we waited 10 min for self tune to complete its process. After this temp was stable and we stored these parameters (probe temp of 0^0C and VT gas at 300lph)

e) next set point is at -10^{0}C, left VT gas at 300lph and temp reached about 5 min later

f) next set point is at -20^{0}C, at first didn't increase VT gas, so temp stalled at -13.8… Had to increase VT gas to 400lph to reach a temperature of -20^{0}C; got warning about self tuning settings being off.

g) next set point is -40^{0}C and found that had to increase VT gas to 600lph to get to set temperature.

h) final set point is -80^{0}C and had to up VT gas to 1100lph to get to that temp. A new self-tune might help here! (we did not have time for this on 10-20-2016)

4. Warming up the probe:

a) can warm up the probe fairly quickly, but not faster than 10^{0}C per minute!

b) I found that one needs to decrease VT gas (Target Gas Flow) for the temperatures to go up, so reverse the instructions and now decrease gas flow when increasing temperature

c) get the temperature to approximately ambient, around 20^0 C.

5. Disconnecting LN2 Exchanger transfer line from probe

a) in 'edte' turn off temp control (this will likely cause the temperature to shoot down, since cold N2 is still flowing thru the probe)

b) unclip the transfer line from the probe (can let it hang here)

c) unclip the N_2 gas line from the ball seal at the other end of the transfer line, and connect it to the probe, seating it appropriately and using the clip for it to match up to the ball seal properly.

d) disconnect the 'regulation heater' from the LN2 VTA, then take the transfer line out of the LN2 dewar and hang it in its place on the West wall

e) in 'edte' turn on the temp control and set the temp to 25^{0}C and the Target and Standby gas flow both to 535lph (as per Bruker instructions)

6. Switching back the instruments air supply (from N_2 gas to dry air):

a) close the N_2 gas cylinder using the main valve at the top of the cylinder

b) using the quick release at the back of the console (UPS side of console) disconnect the N_2 gas line and re-connect the dry air supply line/hose

c) open the dry air supply to the Bruker spectrometer (if you closed it in the first place)

d) make sure that the dry air pressure feeding the console is sufficient, by checking the gauge at the bottom right inside the front of the console. The pressure reading should point to the green arrow, or be slightly above that.

e) in 'edte' check that temperature regulations stayed on, if not, turn it back on and ensure the set point is at 25^{0}C.

Temperature calibrations: (by Monika Ivancic, October 31st, 2016)

The temperature of the sample is always different from the reading that we get at the bottom of the TopSpin software. The thermocouple sits below the sample and air flows between the two. The further you get in temperature from ambient, the larger the difference will be between sample temperature and measured thermocouple temperature. Thus, it may be necessary to calibrate the true temperature of the sample.

There are two temperature calibration standards:

a) the methanol sample, for temp ranges from -93^{0}C to about ambient

b) the ethylene glycol sample, for temp ranges from ambient to about 100^{0}C

Both samples do not have much solvent, so center the sample about the middle of the detect region. The reason for this is so that the sample equilibrates to the set temperature fairly quickly. Also locking and shimming is not required! (so acquire unlocked)

After inserting the sample and waiting for the sample to equilibrate to temperature, acquire 1 ^{1}H scan, then efp; apk and use the

'**calctemp**' command.

Then in the GUI enter which solvent you're using. The macro should spit out the temperature of your standard, based on the Hz separation between the two peaks.

Bruker recommendations for different VT ranges:

Sample T (^{0}C)	-150 to -80	-80 to 0	0 to 80	80 to 120	120 to 150
VT gas (l/h)	1800 to 1200	1200 to 670	670 to 535	535 to 400	400 to 300
recommended VT gas (l/h)	1200	1000	535	450	350
shim gas (l/min)	20	20	0	0 to 20	20 to 60
flush gas (l/min)	5 to 10	5	0	5	5
Spinner	ceramics	ceramics	blue POM	Kel-F	ceramics