Variable Temperature Operation

AVIII 400 MHz Spectrometer

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PREFACE

Purpose of This Document

This user guide aims to familiarize you with variable temperature operations of the AVIII 400 NMR Spectrometer. The document does not cover all the basic information and details of the application.

Intended Audience

This document is intended for users of AVIII 400 NMR spectrometer who are familiar with the basic operation of the spectrometer operation. Please refer to "AVIII 400 User Guide" for the basic operations of AVIII 400 NMR spectrometer. This document is *not* intended to replace any form of official Bruker user guides or related Bruker documents.

1 Introduction

The AVIII400 NMR spectrometer is equipped with a 400 MHz Bruker BBFO probe. This instrument is suitable for analyzing the time and air sensitive samples. It is also suitable for a study of reaction kinetics of chemical reactions and for a variable temperature (VT) NMR experiment. Prior user training is required to operate the spectrometer. Additional training is available for the VT experiment. The web reservation is required to use AVIII 400 NMR spectrometer. The spectrometer is running on a Bruker TopSpin software.

1.1 Safety

Iron and other ferro magnetic objects must **NOT** be brought into the vicinity of the magnets. The strong magnetic fields may erase the information of credit card, student ID card, and other magnetic media. *No admission for persons with pacemakers and other metallic implants*.

1.2 NMR Sample Preparation

- Always use clean and dry sample tubes
- Use medium to high quality sample tubes
- Filter sample solution if particles are present
- Keep the sample volume approximately 0.5 – 0.6 mL.
- Wipe the sample tube clean before inserting into magnet
- Use a ceramic spinner for variable temperature operation
- Use a sample depth gauge to adjust position of sample spinner

1.3 NMR Probe

The AVIII 400 MHz NMR spectrometer is equipped with a BBFO probe. The BBFO probe has two radio frequency channels (^{1}H and X-nucleus) with a built-in capability of automatic tuning and match (ATM). The high frequency channel is tuned to for ^{1}H observe and decoupling. The observe channel (X) covers a frequency range from ^{109}Ag to ^{19}F. The probe temperature range is from -150 to 150 °C. The commonly used acquisition files for this probe are prefixed with "*bbfo*".

2 High Temperature Operation

The high temperature operation does not involve the change of the VT apparatus and accessories. However, it requires a change of the supply VT gas from the compressed air to the in-house nitrogen gas.

2.1 Preparation

2.1.1 Switch the Gas Supply to Nitrogen Gas:

It is highly recommended to use nitrogen gas for high temperature operation due to possible oxidization of probe electronic components occurring at high temperatures. The compressed air gas supply setup for room temperature operation is shown in Figure 1. In this setup, switch **S1** is **on**, **S2**, is **off**, and **S3** is pointing to the left (compressed air). To switch the gas supply to the nitrogen gas, first turn on **S2** by turning it 90º down, then turn **S3** 180º to the right, and finally turn off **S1**, as shown in Figure 1.

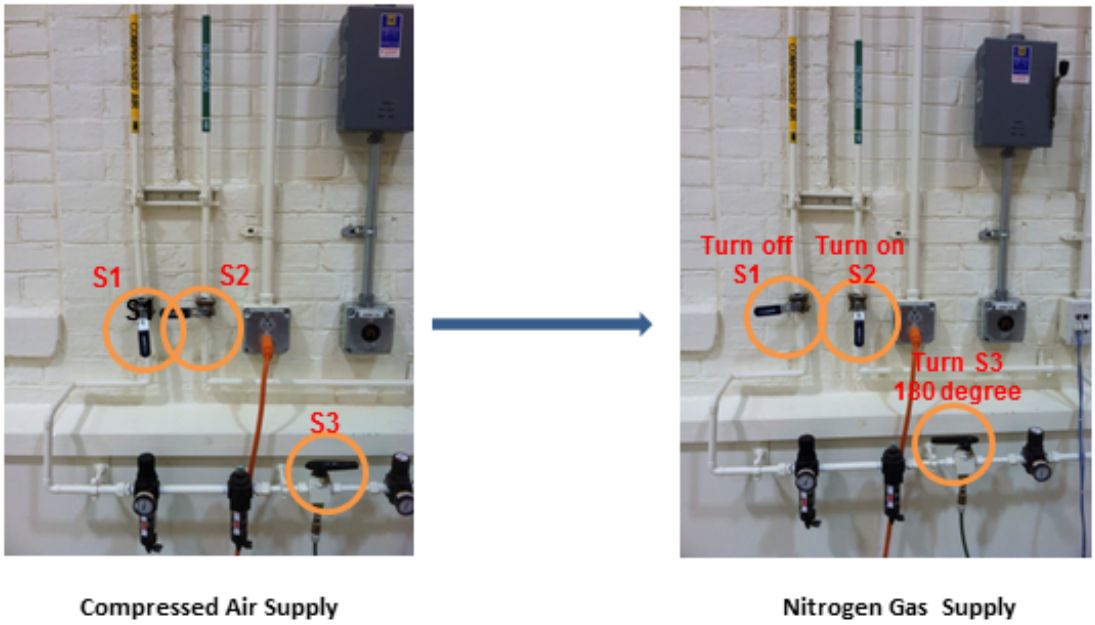

Figure 1: Switch Gas Supply from Compressed Air to Nitrogen Gas

2.1.2 Spinner

Use a *ceramic spinner* to avoid melting of regular blue spinner for the high temperature operation.

2.1.3 Room Temperature Experiment

It is highly recommended to obtain an NMR spectrum at the room temperature as a baseline spectrum before altering the sample temperature. The procedures of acquiring a routine 1D NMR spectrum has been described in "*AVIII 400 User Guide*"

2.2 High Temperature Setup

1. In the command line of the TopSpin Software Interface, type *edte* and a Temperature Control Suite window appears as shown in Figure 2. The **Temperature** Tab contains VTU State (**On** or **Off** buttons), *Sampler temperature*, *Target Temperature* with a **Set** button. It also shows the probe gas supply with adjustable Target Gas Flow

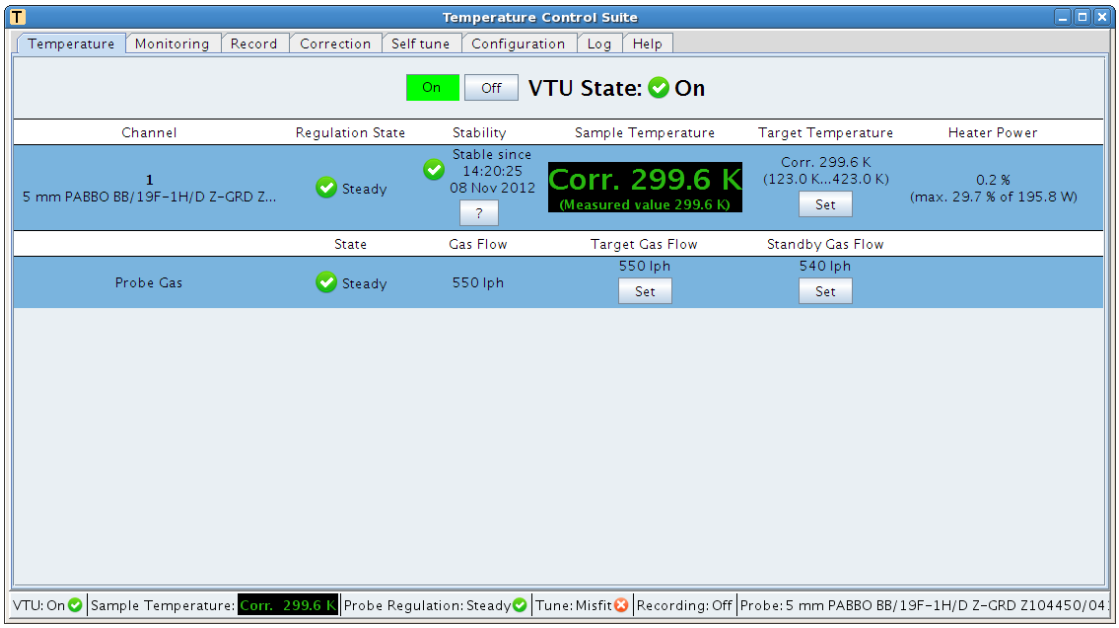

Figure 2: Temperature Control Suite

2. Make sure *Target Gas Flow* is set to 550 lph. If *Target Gas Flow* is set at a different value, click on **Set** to change *Target Gas Flow* to 550 lph.

3. Click on Correction Tab in the Temperature Control Suite (Figure 3), select an appropriate correction parameter settings according to the desired target temperature. In this example, a file named "*bbfoht_305.1-348.1*" is selected. Click on **Set** button to assure the correction temperature calibration parameter are loaded for the high temperature run.

   Note: user may also create a temperature calibration curve. An ethylene glycol sample is used for high temperature calibration. Use standard proton parameter and set rg to 1. Take a proton spectrum and measure the chemical shift difference between two peaks. Use a calibration curve or online tools to determine the actual

temperature. Please consult the NMR spectroscopist for accurate temperature calibration.

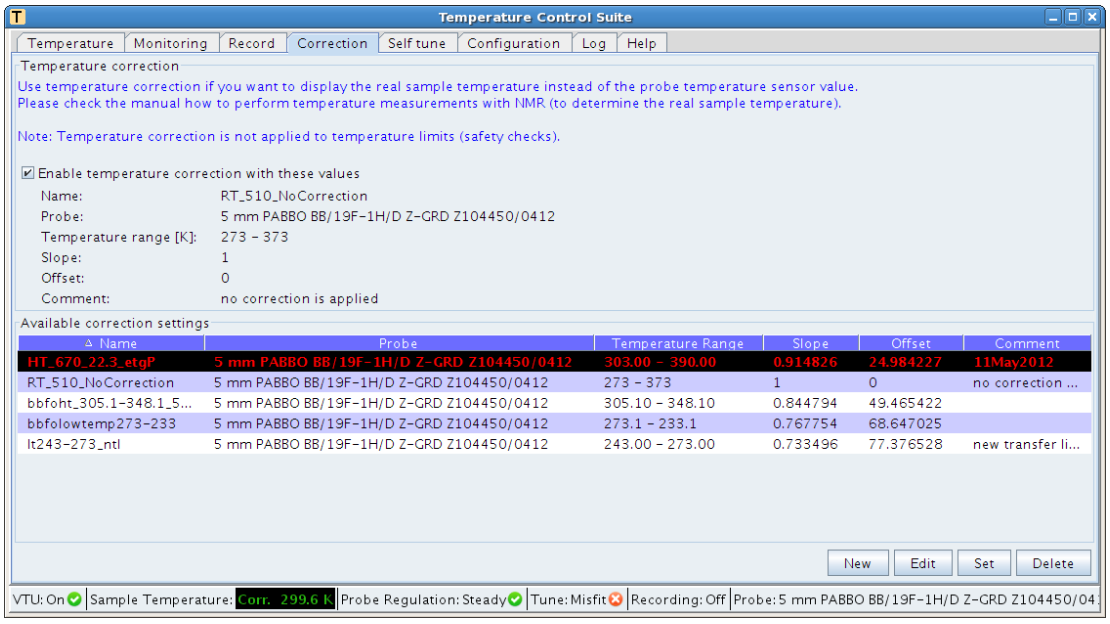

Figure 3: Select Appropriate Temperature Correction Parameter File

4. Click on **Self Tune** Tab (Figure 4), select an appropriate self-tune file. In this example, we use "*bbfo_550_313K*" as the self-tune file. Click on **Restore to Channel 1** to activate the adaptive temperature regulation.

   Note: a self-tune file contains PID parameters pre-stored to regulate sample temperature to a selected target temperature. One can generate a self-tune file by click *on **Start** button in the Start Self Tune column after sample temperature is reached to the target temperature. It takes 3 to 5 minutes for self-tuning.*

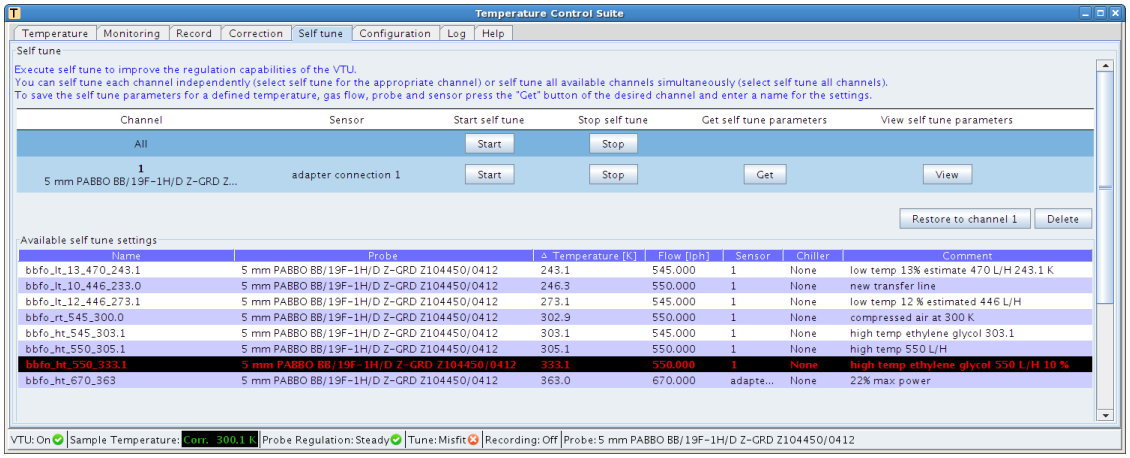

Figure 4: Selection of Appropriate Self Tune File

5. After *Correction and Self-Tune* file are selected, click on **Temperature** Tab (Figure 2), in *Target Temperature* column, click **Set** to set a sample temperature Kelvin as shown in Figure 5. In this example, the target temperature is changed from 300.1 K to 320 K. Click on **OK** to set the sample target temperature.

Figure 5: Change Target Temperature

6. Now click on **Monitoring** Tab and check the boxes in front of *Current Temperature and Target Temperature* as circled in Figure 6. The current temperature slowly approaches to the target temperature as shown in the following figure.

   Note: depending on selected target temperature, it may take a few minutes or longer to for the current temperature to reach the target temperate.

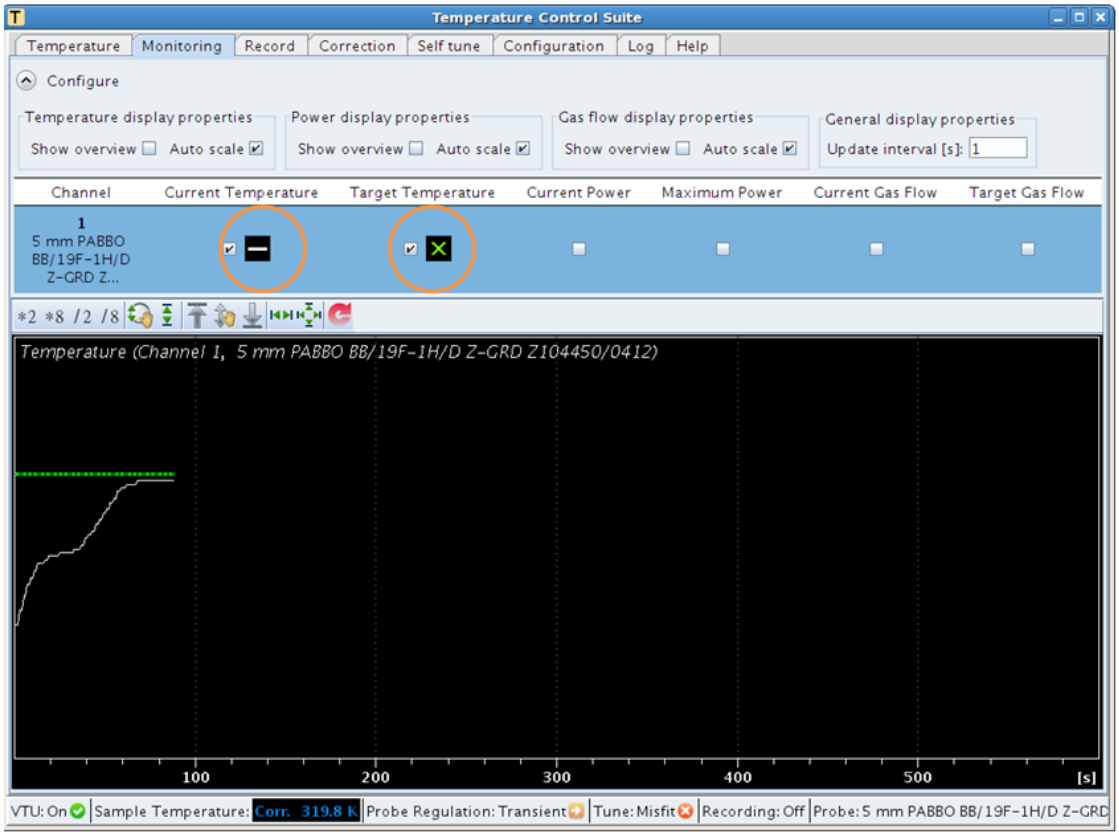

Figure 6: Monitoring Current and Target Temperatures

7. Once the target temperature is achieved, go back to **Temperature** Tab, wait until the digits in the Sample Temperature field turning into green and the temperature stability is checked as circled in Figure 7.

   Note: the Sample Temperature indicator is color coded. When the sample temperature is regulated, it turns into green. It shows blue and red with respect to the cases when the sample temperature is lower than and higher than the target temperatures.

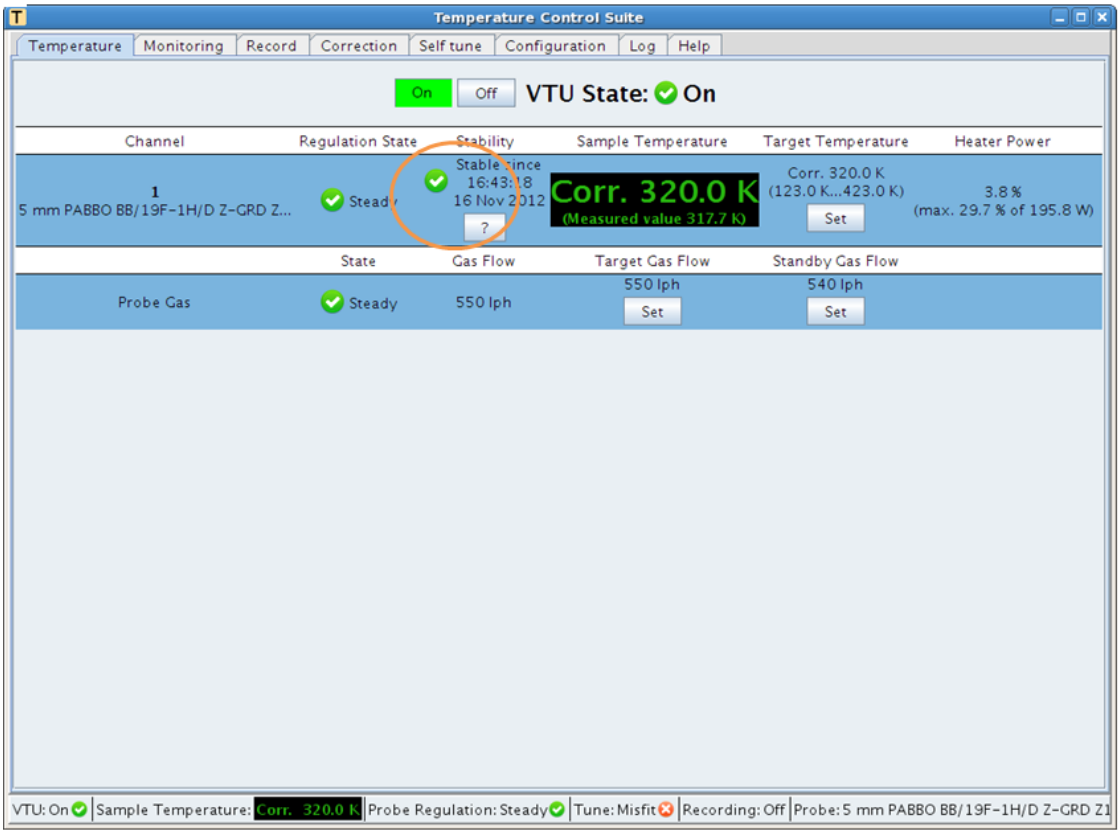

Figure 7: Target High Temperature Achieved

8. When sample temperature changes, the lock signal may fluctuate. Before acquiring NMR data, the shimming settings should be readjusted by typing *topshim* in the command line. Start NMR data acquisition after the auto-shimming.

2.3 Finish Up

When the high temperature measurements have completed, follow these steps to finish up:

1. After the high-temperature measurement has completed, in **Correction** Tab of the Temperature Control Suite (see Figure 3), first select the correction file of "*RT_510_NoCorrection*" and then click on **Set** to load the correction parameters.

2. Click on **Self Tune** Tab of the Temperature Control Suite, select the self-tune setting file of "*bbfo_rt_545_300.0*" (see Figure 4), then click on **Restore to Channel 1** button to load the self-tune parameters.

3. In **Temperature** Tab of the Temperature Control Suite, set *Target Sample Temperature* to 300 K as described in step 5. Wait until the target sample temperature reduces to 300 K.

   Note: if the target sample temperature is higher than 320 K, make sure the target sample temperature is reduced in steps (preferably 15 to 20 K each step) to avoid extreme thermal stress in probe components.

4. When the target sample temperature reaches to 300 K, eject NME sample by type "*ej*" in the command line of the TopSpin NMR software interface.

5. Switch the gas supply from nitrogen gas to compressed air. To do so, refer to Figure 1 and the procedure described in section 2.1.1, first turn the switch **S1** on, then turn the switch **S3** by 180º such that it is pointing to the left. Finally turn off **S2**.

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3 Low Temperature Operation

The low temperature operation involves installing VT apparatus and accessories, including filling the liquid nitrogen dewar, installing the nitrogen gas transfer line, and setting up target sample temperature.

3.1 Preparation

3.1.1 Liquid Nitrogen Dewar

The source of the NMR probe cooling is from the controlled evaporation of liquid nitrogen. So the first step is to fill a 25-L liquid nitrogen (LN2) dewar (Figure 8) with liquid nitrogen using a filling station in the Cylinder Storage Room (073 BRL). Place the LN2 dewar on the labeled spot near the magnet.

Note: Safety glass and face shield are required to fill liquid nitrogen.

Figure 8: Liquid Nitrogen Dewar on Labeled Spot Near the Magnet

3.1.2 Switch Gas Supply to Nitrogen Gas

It is highly recommended to use the nitrogen gas for low the temperature operation due to possible moisture condensation even iced-up inside of the probe occurring at the low temperatures. The compressed air gas supply setup is shown in Figure 9, in which **S1** is at **on** position, **S2**, is at **off** position, and **S3** is pointing to the **left**. To switch the gas supply to the nitrogen gas, first turn on **S2**, then turning **S3** to the right, and finally turn off **S1**, as shown in Figure 9.

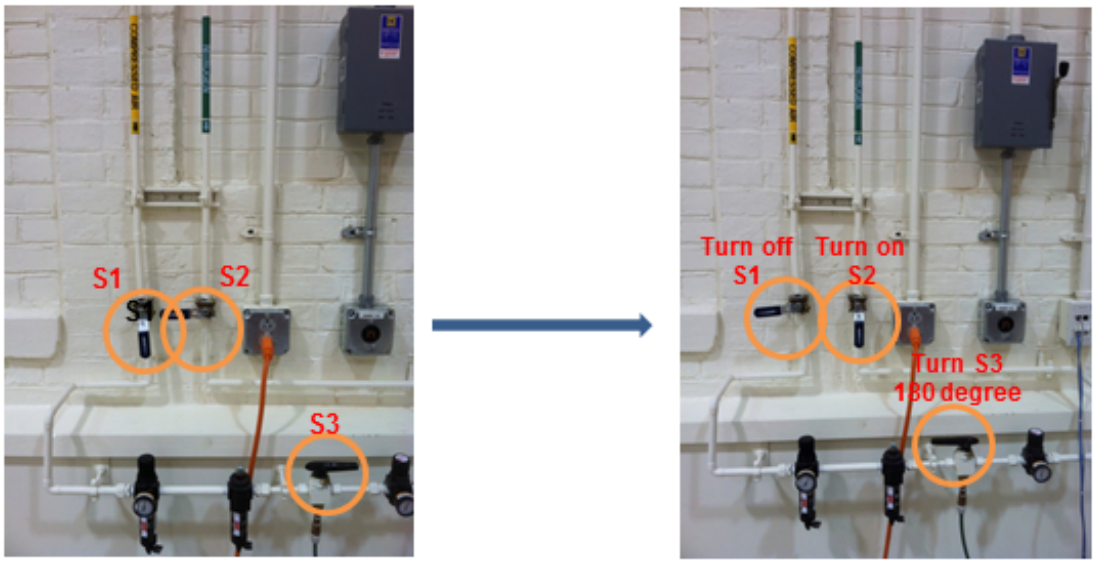

Figure 9: Switch Gas Supply from Compressed Air to Nitrogen Gas

3.1.3 Use Ceramic Spinner

Use a ceramic spinner to avoid possible damage of the regular blue spinner for the low temperature operation.

3.1.4 Room Temperature Experiment

It is highly recommended to get an NMR spectrum at room temperature as a baseline spectrum before changing sample temperature. The procedures of acquiring a routine 1D NMR spectrum have been described in "*AVIII 400 User Guide*"

3.2 Low Temperature Apparatus

To connect the LN2 transfer line, follow these steps:

1. In the command line of TopSpin software interface, type "*edte*" to start the Temperature Control Suite. Click on **Off** button to turn off the Variable Temperature Unit (VTU) as shown in Figure 10. In this way, the probe heater is turned off.

   Note: it is important to turn off the VTU before connecting the LN2 transfer line to the probe to prevent the overheating of the NMR probe.

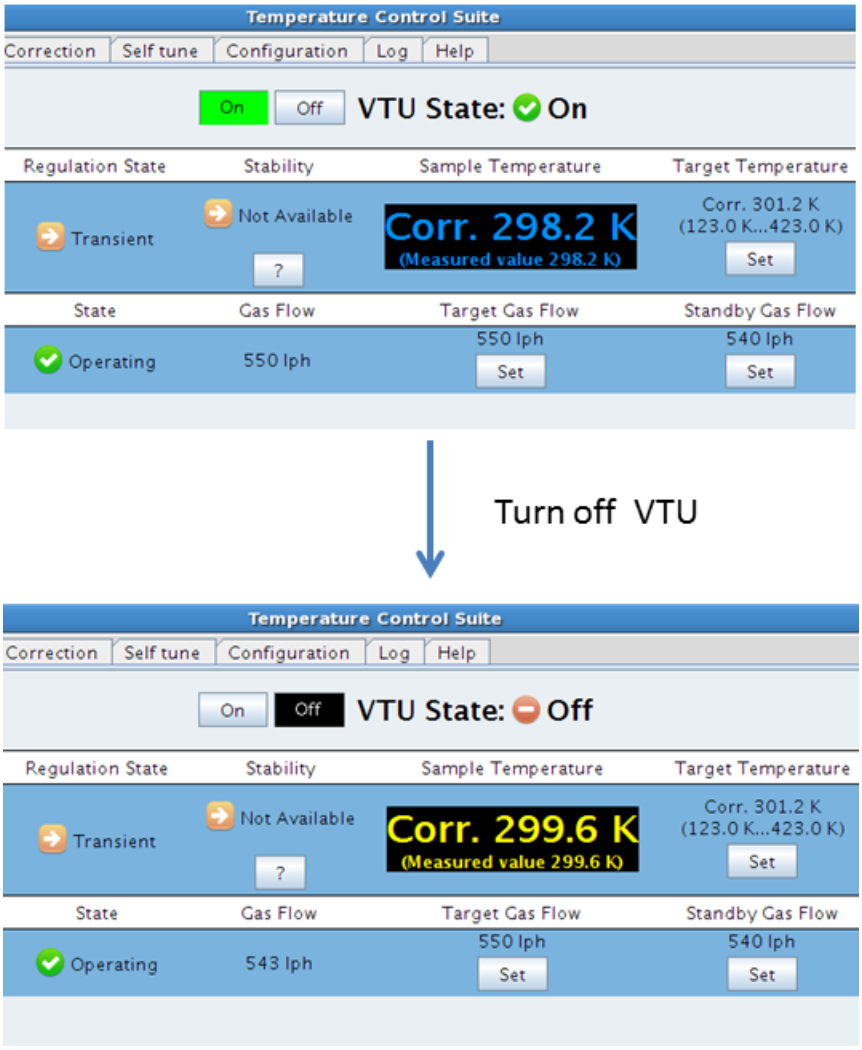

Figure 10: Turn Off the Variable Temperature Unit

2. Disconnect the black VT gas hose from the probe and remove the VT adaptor as shown in Figure 11.

Figure 11: Remove the VT Gas Hose and the VT Adaptor from Probe

3. Make sure the o-rang is on the heater end of the nitrogen transfer line and remove green pressure relief cap on the transfer line (Figure 12)

Figure 12: The o-ring and Pressure Relief Cap

4. Insert the heater of the nitrogen gas transfer line into the LN2 dewar **SLOWLY** as shown in Figure 13. *Note: Safety glass is required in this operation.*

Figure 13: Insertion of N2 Transfer Line into LN2 Dewar

5. After the transfer line is in the dewar, use a clamp to seal the heater on the top of dewar. *Note: the clamp must be screwed down tightly using a butterfly nut. Otherwise it will take much longer time to cool the probe down.* After all pressure is released from the pressure relief port, screw down the green cap. These procedures are demonstrated in Figure 14.

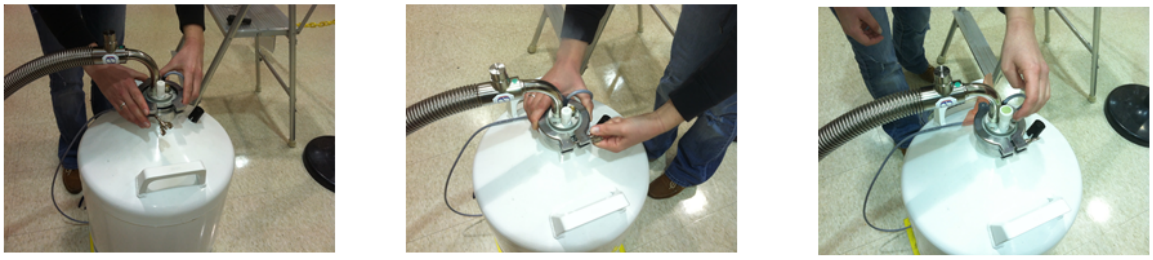

Figure 14: Screw down the Seal Clamp and the Green Cap

6. Attach the transfer line **SLOWLY** into the probe. Keep the transfer line horizontal when inserting the transfer line into the probe. The transfer line should be inserted into the probe without any resistance if the position of the dewar and transfer line is correct. (see Figure 15). Once the transfer line is in place, screw down the cap screw to seal the transfer line to the probe. (see Figure 15)

   Note: never exert force to push the transfer line into the probe. Ask for help if needed.

Figure 15: Insertion of the Transfer Line into the Probe

7. Connect the transfer line cable to the LN2 box near the base of the magnet as shown in Figure 16.

Figure 16: Connecting Transfer Line Cable to the LN2 Box

8. At this point, the Temperature Control Suite shows the **Chiller N2 Evaporator** added to the channel 2 as shown in the Temperature Control Suite (Figure 17).

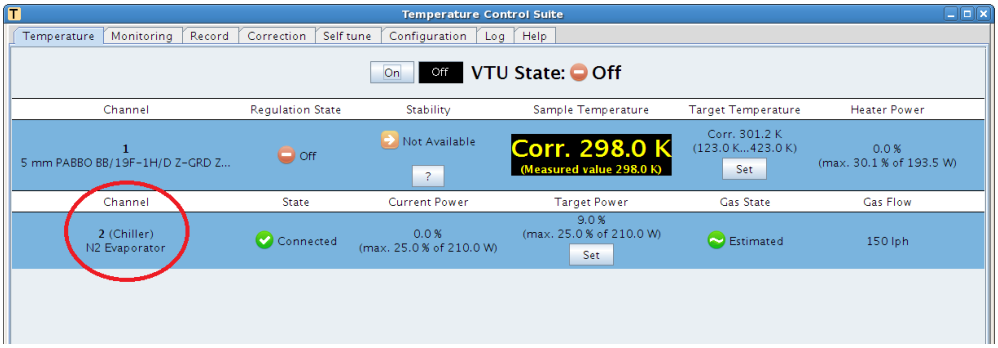

Figure 17: N2 Evaporator Added as a New Apparatus

3.3 Low Temperature Setup

To set up NMR sample at low temperature, follow these steps:

1. Click on Correction Tab of the Temperature Control Suite, select a correction file that suitable to the target temperature. In this example, a file "*bbfolowtempertaure280-300*" is selected (Figure 18). Click on **Set** button to continue.

   Note: user may also create a temperature calibration curve. A methanol sample is used for low temperature calibration. Use standard proton parameter and set rg to 1. Take a proton spectrum and measure the chemical shift difference between two peaks. Use a calibration curve or online tools to determine the actual temperature. Please consult the NMR spectroscopist for accurate temperature calibration.

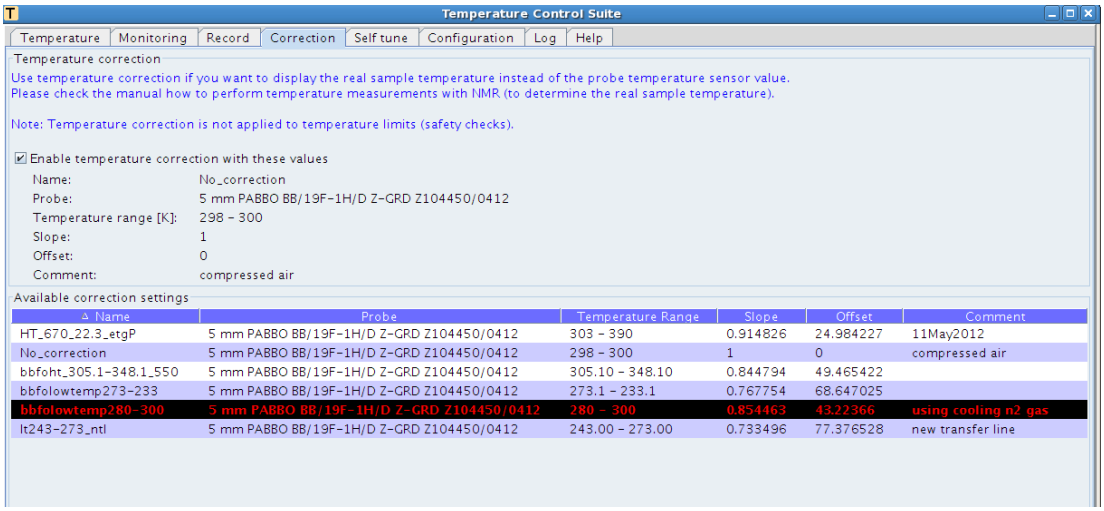

Figure 18: Selection of Correction Parameter Settings

2. Click on **Self Tune** Tab of the Temperature Control Suite, select an appropriate self-tune parameter Settings. In this example, the file "*bbfo_lt_10_446_230*" is selected as shown in Figure 19. Click on **Restore to Channel 1** to load the parameters.

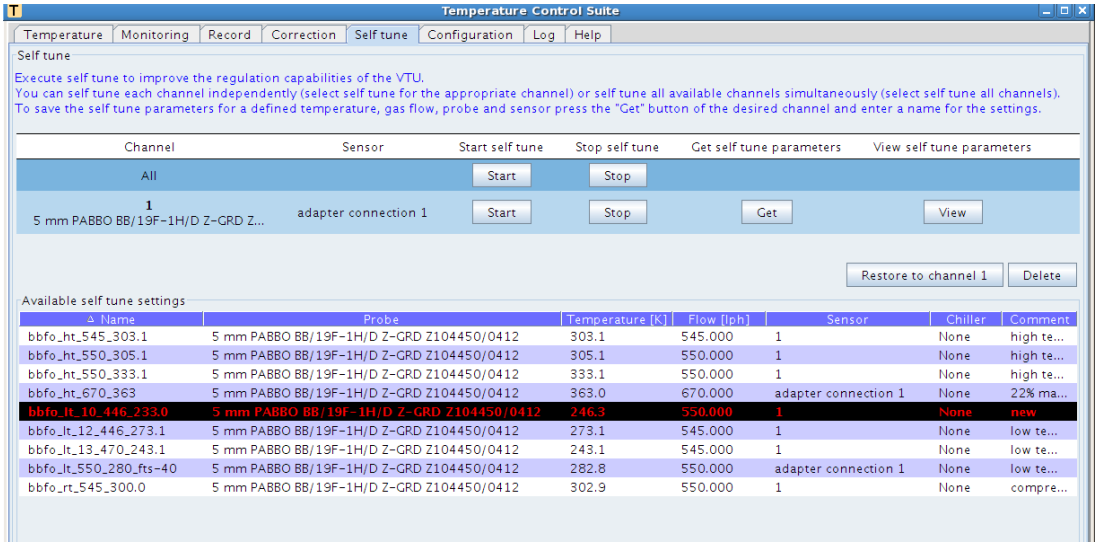

Figure 19: Selection of Low Temperature Self Tune Parameter Settings

3. In **Temperature** Tab and in *Target Temperature* column, click **Set** to set a sample temperature in Kelvin as shown in Figure 20. In this example, the target temperature is changed from 301.2 K to 238 K. Click on **OK** to finishing setting the sample target temperature.

Figure 20: Set a Target Low Temperature

4. Now click on **ON** button in the top row of the **Temperature** Tab to turn on the VTU (Figure 21). The heater of the transfer line will be turned on in the liquid nitrogen dewar so that the cold nitrogen gas is introduced into the probe. The probe heater is also turned on to regulate the sample temperature if the sample temperature is lower than the target sample temperature.

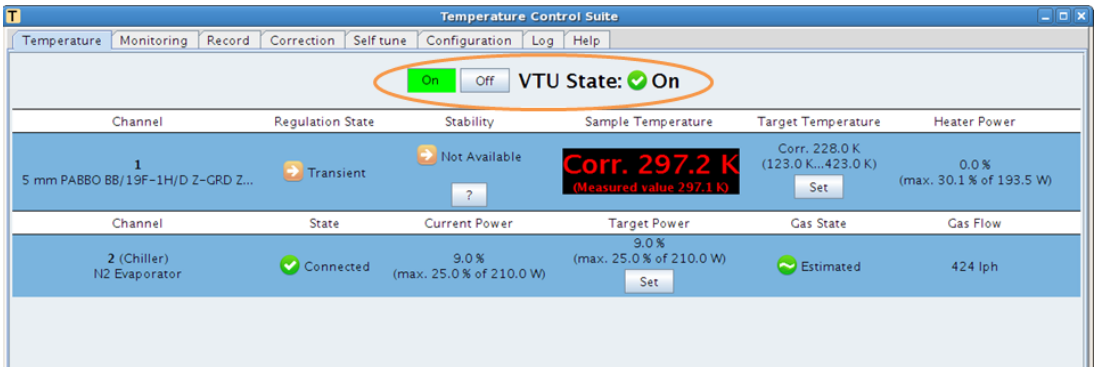

Figure 21: Turn ON the VTU

5. Now click on **Monitoring** Tab and check the boxes of *Current Temperature* and *Target Temperature* as shown in Figure 22. The current sample temperature slowly approaches to the target temperature.

   Note: it depends on the set target temperature, it may take 15 to 20 minutes or longer to reach the target temperate.

Figure 22: Sample Temperature Monitor

6. When the sample temperature reaches to the target temperature (indicated with a check marker of the Regulation State, show in Figure 23, do an automatic shimming by type *topshim* in the command line.

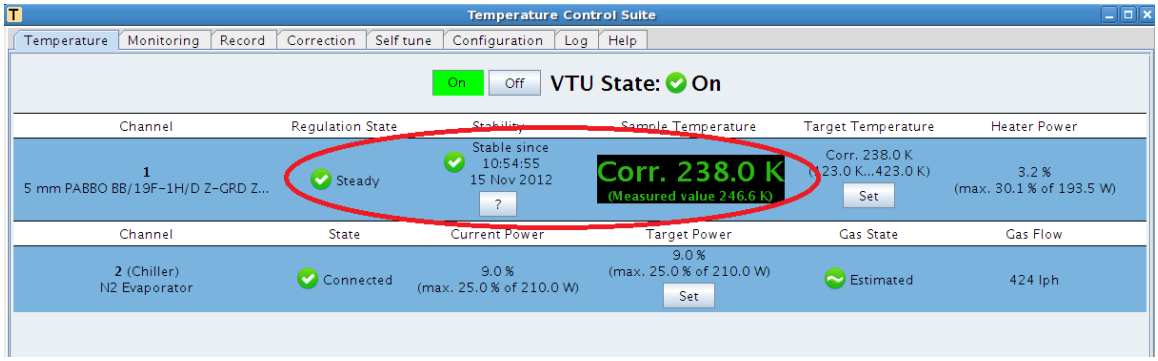

Figure 23: Target Low Temperature Achieved

Note: the Sample Temperature indicator is color coded. When the sample temperature is regulated, it turns into green. It shows blue and red with respect to the cases when the sample temperature is lower than and higher than the target temperatures.

7. After the auto-shimming, start an NMR data acquisition as described in *AVIII 400 User Guide*.

3.4 Finish Up

When the low temperature measurements have completed, follow these steps to finish up.

1. Eject the NMR sample from the probe by type "*ej*" in the command line of TopSpin software interface.

2. In **Correction** Tab of the Temperature Control Suite (see Figure 18), first select the correction file of "*RT_510_NoCorrection*" and then click on **Set** to load the parameters.

3. Click on **Self Tune** Tab of the Temperature Control Suite, select the self-tune setting file of "*bbfo_rt_545_300.0*" (see Figure 19), then click on **Restore to Channel 1** button to load the self-tune parameter for room temperature operation.

4. In **Temperature** Tab of the Temperature Control Suite, set the sample target temperature to 300 K (refer to Figure 20 and step 3 on page 18. Wait until the target temperature research to 300 K.

   Note: if the target sample temperature is lower than 280 K, make sure the target sample temperature is increased in steps (preferably 15 to 20 K for each step) to avoid the extreme thermal stress to probe components

5. When the temperature reaches to 300 K, click on **Off** button in the Temperature Tab of the Temperature Control Suite to turn of the VTU.

6. Disconnect the nitrogen gas transfer line cable from the LN2 box.

7. Detach the nitrogen transfer line from the probe.

8. Attach the VT adaptor to the probe.

9. Connect the black VT air hose quickly.

10. Click on **ON** button in the Temperature Tab of the Temperature Control Suite to turn on the VTU. Wait until the target temperature reaches and stabilizes at 300 K.

11. Switch the gas supply from the nitrogen gas to the compressed air. To do so, refer to Figure 9 and the section 3.1.2. First turn on **S1**, then turn the switch **S3** by 180º such that it is pointing to the left. Finally turn off **S2**.