

The University of Texas at Austin
Electron Paramagnetic Resonance Facility



Bruker EMX+ CW-EPR Spectrometer

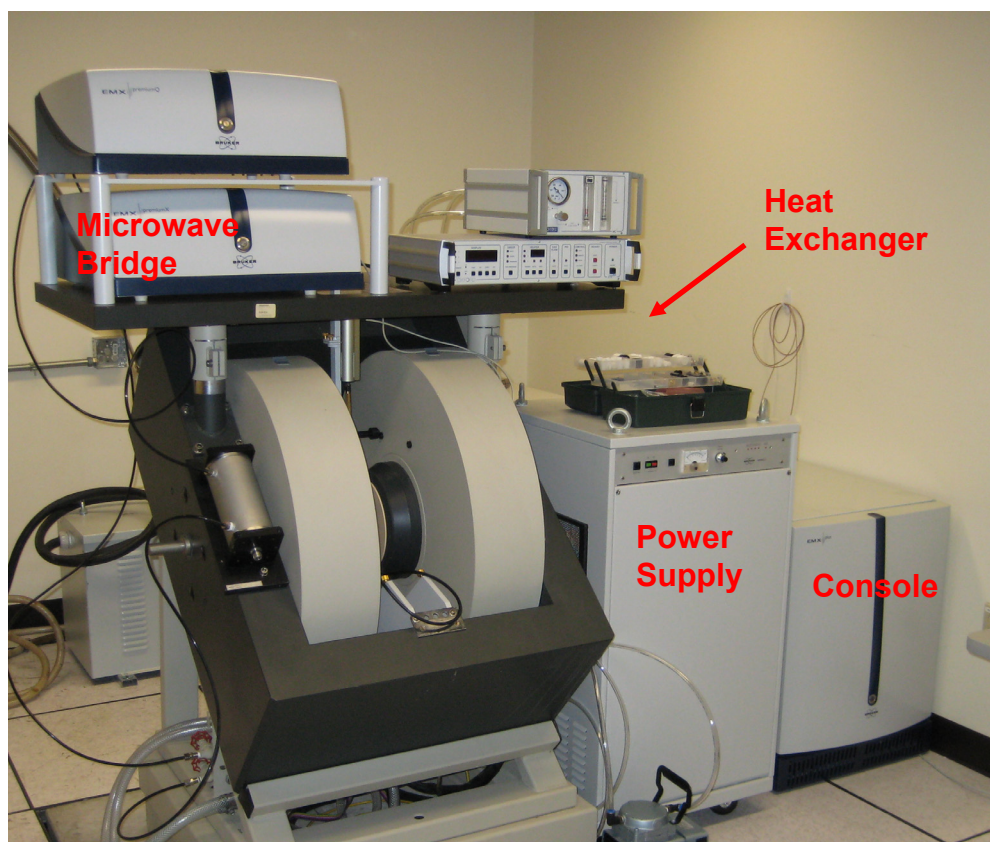
Contents:

General Notes.....	2
Turning on the Instrument	2
Collecting a Spectrum.....	3
Turning off the Instrument.....	7
Tips for Spectrum Optimization	8
Variable Temperature Unit	9
Helium Temperature Control System	12
Q-Band.....	18
ENDOR.....	21

General Notes

- Never look into the cavity or waveguide while the microwave bridge is on.
- Always change samples while in standby mode.
- Do not switch the instrument directly from standby to operate (or operate to standby). Always change to tune mode, wait for the instrument to change, then switch to standby or operate.
- When changing accessories or cavities, turn off the magnet.
- When changing cavities, always completely lower the iris screw before disconnecting the old cavity. After connecting the new cavity, raise the iris screw to approximately the midpoint before attempting to auto tune.
- If you break a sample in the cavity, do not use solvent to wash the inside of the cavity. This will dissolve some of the components of the cavity.

Turning on the instrument



2. Turn on the water source at the wall on the left side of the room. Turn valve $\frac{1}{4}$ turn.
3. Turn on heat exchanger at switch near the back wall of the room. Verify that the orange 'Tank Full' light is on.

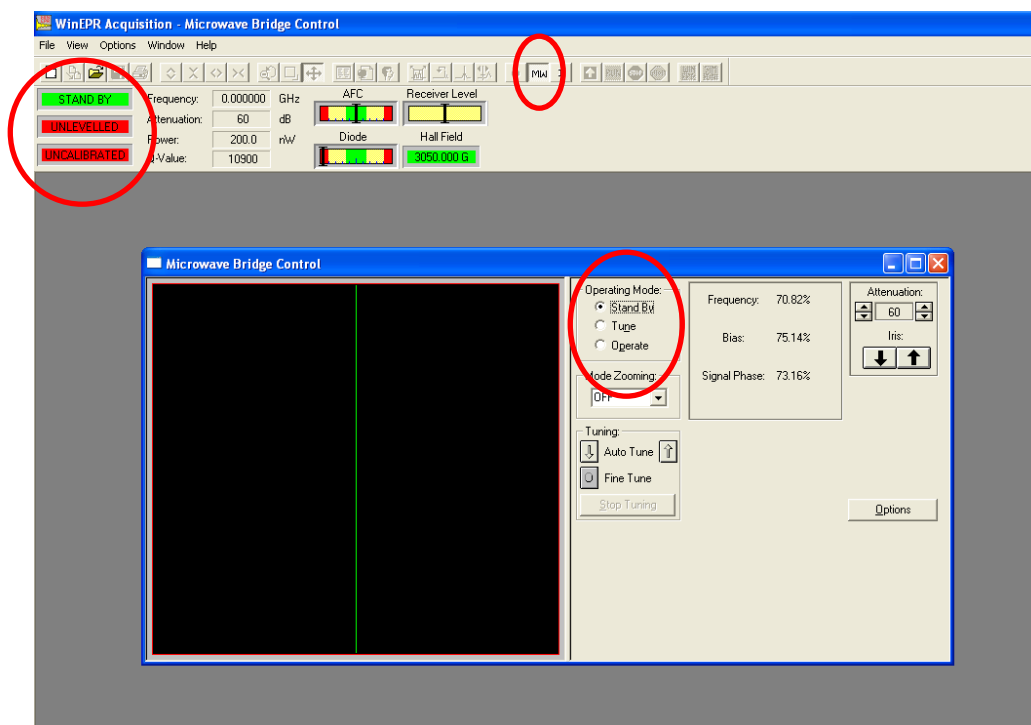
4. Turn on microwave bridge at switch on the back of the unit.
5. Turn on console by pressing blue flashing button on the front of the unit.



6. Turn on the electricity to the power supply by pressing black button, wait until all of the lights on the right side of the unit go out, and then press green button to turn on the magnet. The reading on the dial should not exceed 10 on the lower scale and none of the lights on the right side of the panel should turn back on. If either situation occurs, press the red button to turn the magnet off, wait a few seconds, then press the black button to turn the power supply off before addressing the problem.

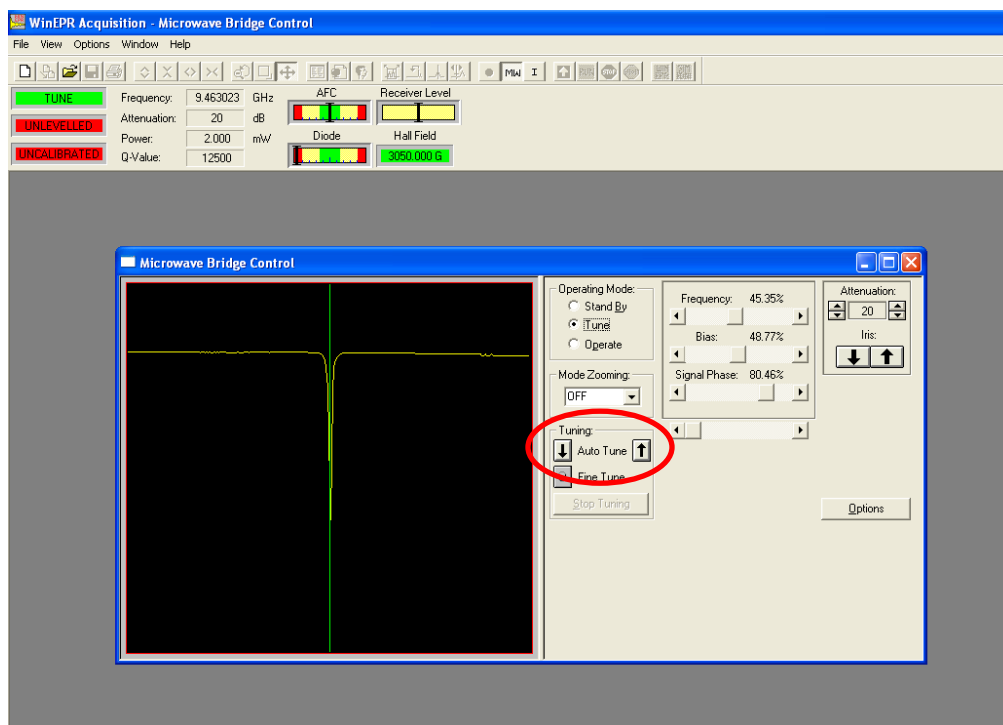
Collecting a Spectrum

1. Open **WinEPR Acquisition** program on the desktop.

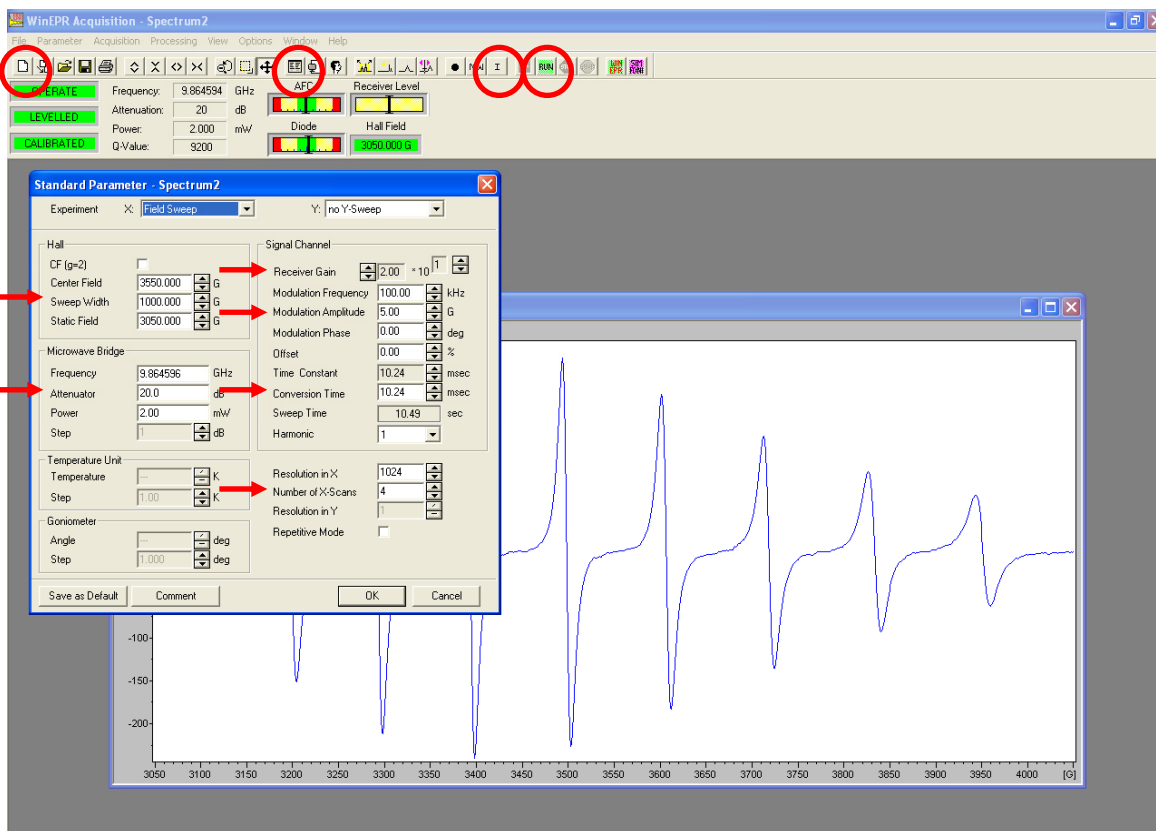





2. The *Microwave Bridge Control* window should open automatically. If it doesn't, select the **MW** button from the toolbar.

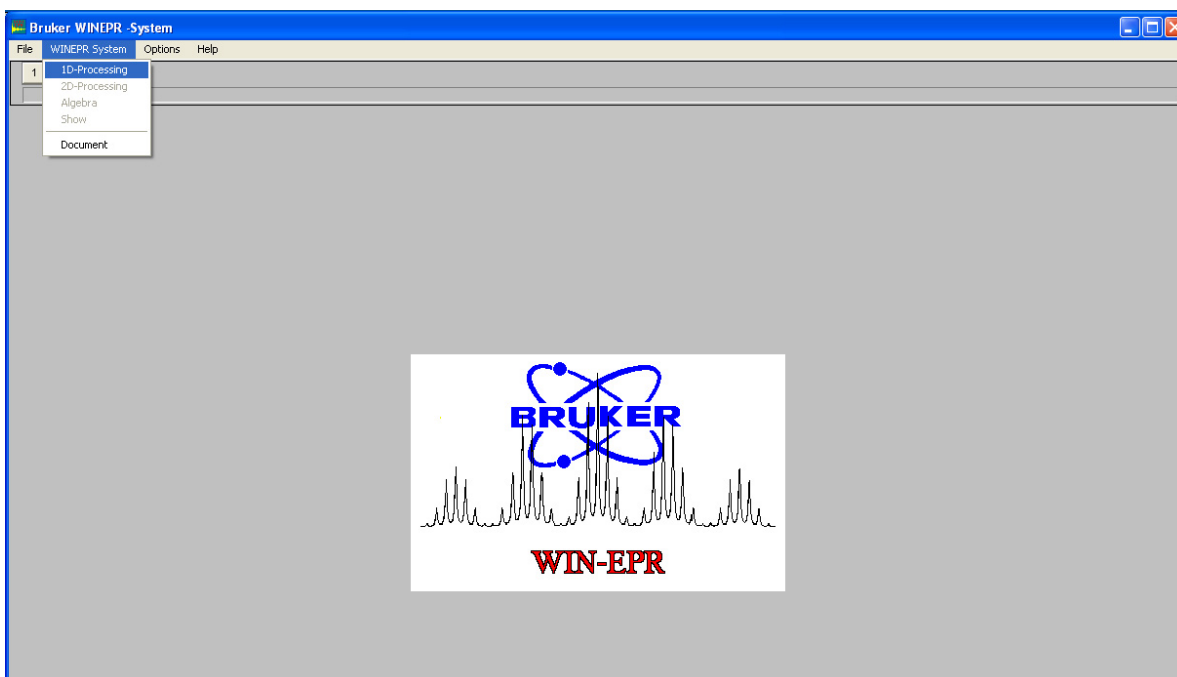
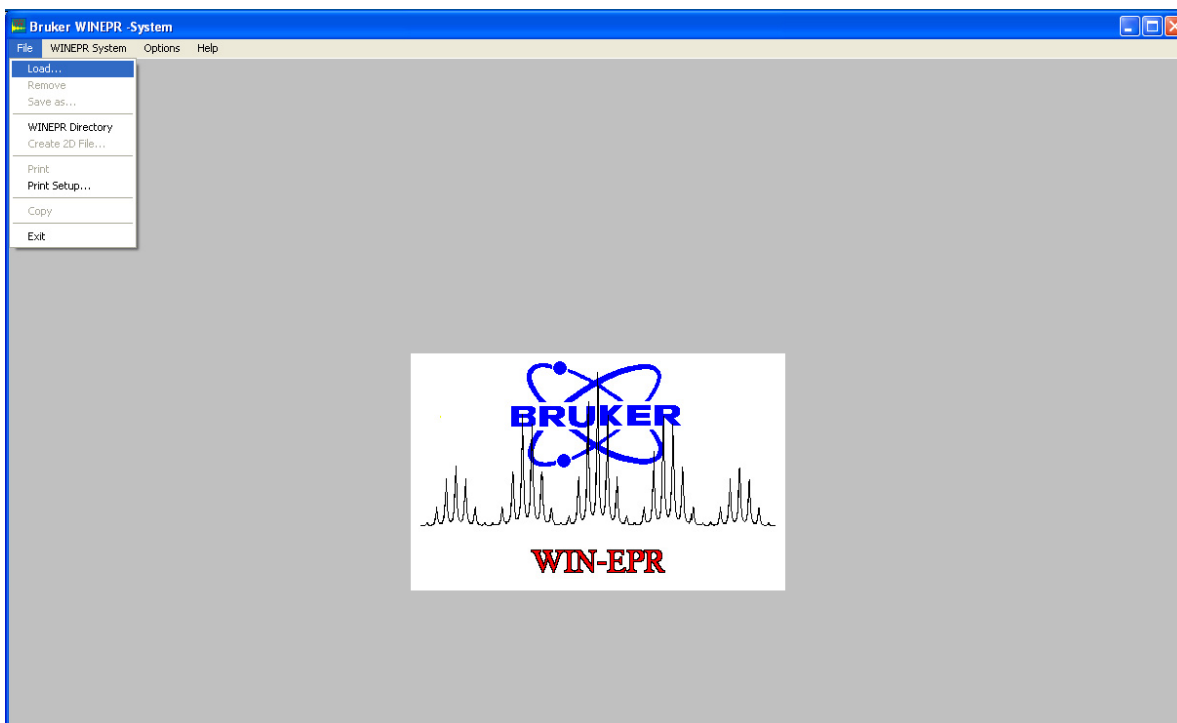
- The instrument should be in standby mode (indicated by the radial button in the microwave bridge control window and the top status bar in the top left of the main window). Insert the sample into the cavity. To insert the sample, loosen the collet nut from the top of the cavity and remove the stopper. Select the appropriate collet for your size sample tube from the tackle box on top of the power supply. The correct size collet should fit onto your sample tube with minimal effort, but not be so loose that it slips off if you let go of it. Place the chosen collet in the top of the cavity and loosely affix the collet nut. Wipe any finger prints or dust off the sample tube and insert into the cavity. Your tube should be inserted so that the volume of your sample is approximately centered above and below the black box on the front of the cavity. Tighten the collet nut to secure your sample.
- Change the instrument status to *Tune*. A horizontal yellow line with a dip should appear in the window.



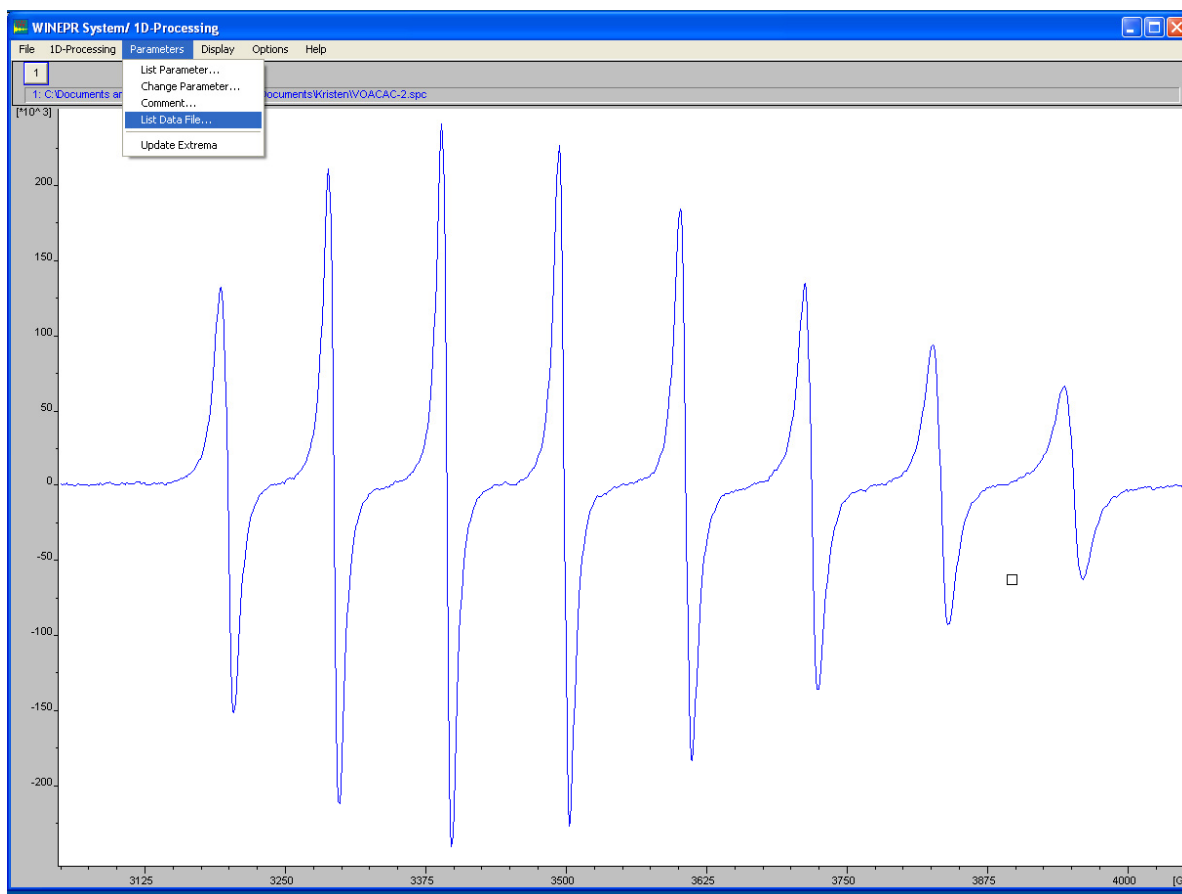
- For most samples, the auto tune function will work. Initiate auto tune by selecting either the up or down arrow surrounding Auto Tune. **Do not click on anything while it is trying to auto tune.** When the auto tune process is complete, all three status bars in the top left of the main window will turn green and the first box will read *Operate*.



6. Open a new spectrum window by selecting the  button from the toolbar or from the *File* drop down menu. Open the Instrument parameters menu by selecting the **I** button on the toolbar or from the *Parameters* drop down menu. Verify the calibration box is checked and close the parameters box. Open the *Standard Parameters* window by selecting the  button and set the parameters as necessary. Click Ok and click on the spectrum window to set it as active, then click the **Run** button from the toolbar to collect the spectrum.
7. Re-open the *Standard Parameters* window by selecting the  button. Change the parameters as necessary to optimize the spectrum. Each time you select the run command it will replace the spectrum in the current window. To avoid losing any spectrum you wish to save while optimizing, either save the spectrum or open a new experiment window and transfer the current parameters to that experiment. If you choose to open additional experiments, be careful to keep track of what parameters are being used and what parameters have been sent to the instrument.
8. When finished, save the spectrum. Each research group has a designated folder in the My Documents directory where you may save any relevant files. All data will be archived and deleted from the computer annually. Please refrain from saving any files elsewhere on the computer. Any files saved elsewhere will be deleted without warning.



9. To export the data for use in a graphing program, use the **WinEPR Processing** application. From the *File* menu, select *Load* and choose the desired spectrum from the dialog box that appears. A box with a number 1 will appear in the upper left corner. Then, from the *WinEPR System* menu, select *ID Processing*, your spectrum should appear in the main window.
10. From here it is now possible to perform any manipulations or measurements on the spectrum.



11. To export the data as a list of data points in a text file, select *List Data File* from the *Parameters* menu. A dialog box will appear with a list of all of the data points for the spectrum. The experimental parameters used to collect the spectrum **will not** be in this text file. They are, however, still contained in the original *.par file from the Acquisition program. Opening the file in the Acquisition program, will allow you to retrieve this information.

Turning off the instrument

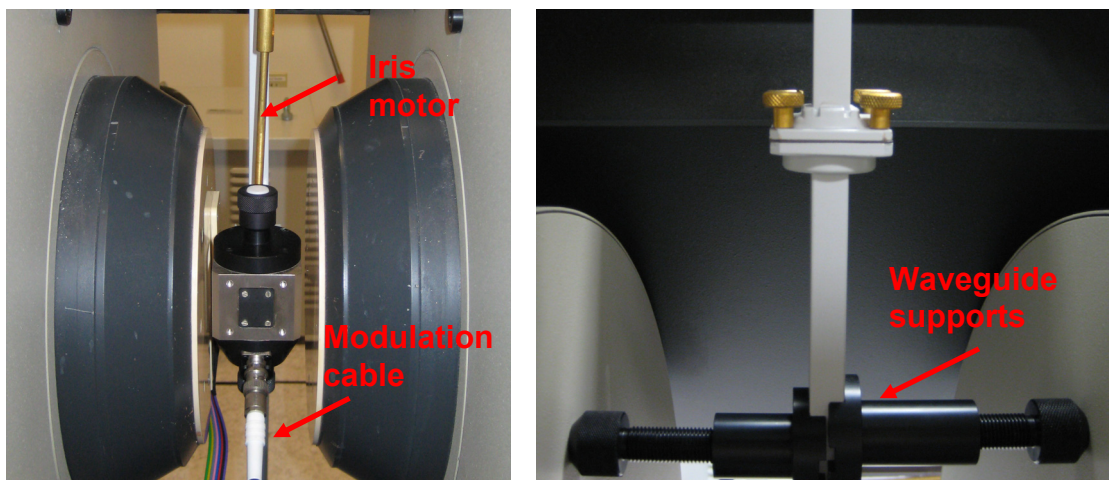
1. To turn off the instrument, follow the reverse order as turning it on. Be sure to also disconnect any accessories that you installed while using the instrument and replace the collet used to hold your sample with a stopper to prevent dust from accumulating in the cavity when the instrument is not in use.
2. Press the red button on the power supply to turn off the magnet, wait a moment, then press the black button to turn off the electricity.
3. Press the blue light on the front of the console.
4. Turn off the microwave bridge at the switch on the back of the unit.
5. Turn off the heat exchanger.
6. Turn off the water supply.

Tips for Spectrum Optimization

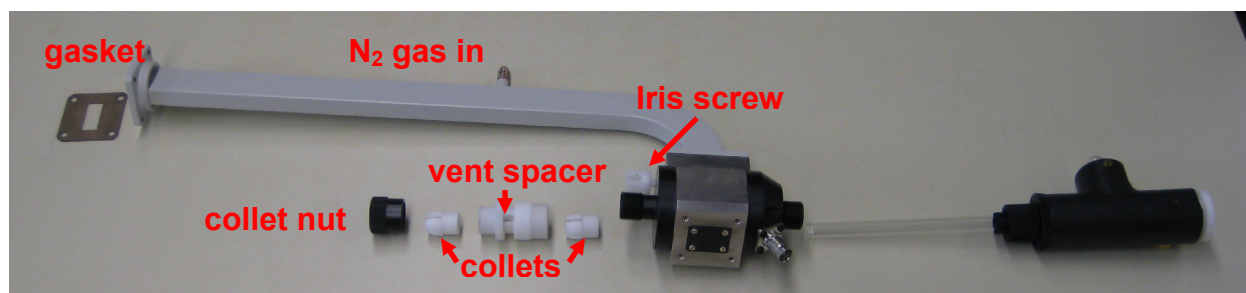
- Most X-band EPR spectra of transition metals are recorded between 4-100 K with a sample volume of about 300 μL and a concentration $10^{-3} - 10^{-5}$ M. The concentration necessary depends upon the spectral linewidth; signals with a narrow linewidth require lower concentrations than those with a broad linewidth.
- For organic radicals, a sample concentration of 10^{-7} M is typically sufficient for a strong spectrum.
- Optimizing a spectrum of an unknown sample containing a transition metal ion:
 1. Set initial values for microwave power and modulation amplitude at 20 mW and 10 G, respectively. Extend the sweep width to include a magnetic field range of about 1000 – 4000 G. This will cover the typical range of g -values for transition metal ions. The field should be scanned at a moderate time constant – approximately 5 minutes to cover the entire sweep width (time constant no greater than 0.1 s.). At these settings it is likely that you will see a strong signal although it may lack fine structure, this will be optimized later.
 2. Once a signal is observed, begin optimizing the parameters one at a time.
 - First, adjust the microwave power. The signal amplitude will increase with power as long as the rate of radiation-induced transitions is less than the rate of spin-lattice relaxation. When saturation occurs, the signal amplitude lags and the resonance line becomes distorted masking the true line shape and any fine structure.
 - Next, adjust the modulation amplitude (MA). The optimum value of MA can be determined by acquiring the spectrum at a set modulation. If the linewidth of the narrowest line in the spectrum is much greater than MA, then overmodulation effects have not occurred. However, if the linewidth approximately equals MA, distortions are likely present. Decrease the MA by approximately half and recollect the spectrum. If the linewidth is still equal to MA, then distortions are still present and it is necessary to decrease MA again until the linewidth no longer decreases with decreasing MA. In general for strong samples, the MA should be set to $1/4^{\text{th}}$ the width of the narrowest line. If the signal is very weak, setting the MA equal to the true linewidth will produce a slightly distorted but much stronger signal.
 - Finally, set the time constant and scan time. The time constant is varied to maximize the signal-to-noise ratio. Once the ideal time constant is determined, use this to determine the scan time. To record a spectrum that is not distorted, the spectrometer should take 8 – 10 times the time constant to scan the maximum-to-minimum peak of the sharpest line. Scan times significantly shorter than this will result in a distorted signal. For example, if the sharpest line has a peak-to-peak width of 1 G and the optimum time constant is 0.1 s, then the spectrometer should take 1 s to scan 1 G. If the sweep width is 1000 G, then the total scan time should be 1000 s (or 16.6 min).
 3. Finally, it may be desirable to determine the optimum temperature for collecting a spectrum. This is done simply by using the optimized parameters determined above and collecting the spectrum over a range of temperatures.

Variable Temperature Unit

Installation:



1. From the *Microwave Bridge Control* window, verify the instrument is in standby mode (turn to tune mode first from operate, **do not go directly from operate to standby**). Move the iris motor out of the way by first lifting up the lower portion of the brass rod to disconnect it from the cavity, and then loosen the screw on the underside of the bridge table to slide the motor off to the side and retighten the screw. Disconnect coaxial cable from the front of the cavity. Loosen the waveguide supports and remove them. While holding onto the cavity, loosen the screws connecting the middle segment of the waveguide. Remove the cavity, being careful not to drop the gasket when separating the waveguide.



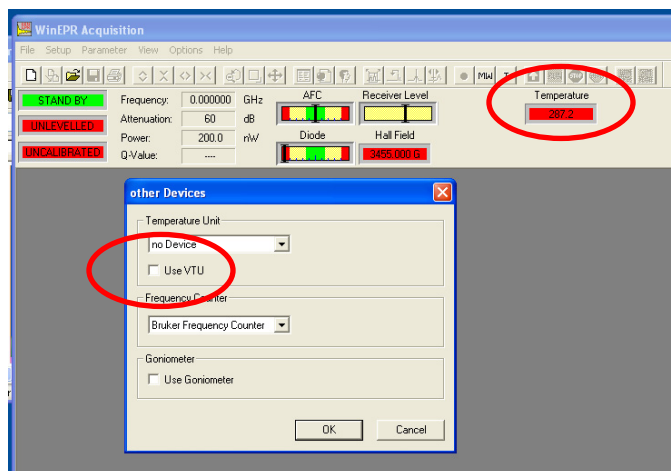
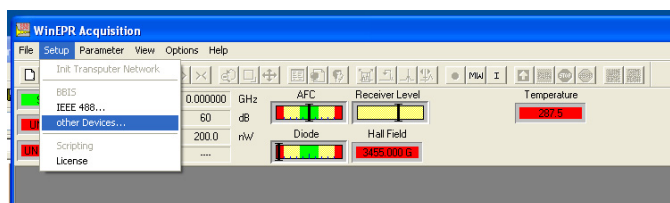
2. Disconnect the collet nuts from the top and bottom of the cavity and remove the collets from either end. Carefully insert the quartz N₂ Dewar tube from the bottom of the cavity and tighten the lower collet nut (with the opening of the Dewar tube pointing toward the back of the cavity). Add a collet to the top of the cavity to support the Dewar tube, attach the white vent spacer, and add upper collet for the sample tube and collet nut.
3. Insert the thermocouple into the bottom of the Dewar assembly and attach wire.
4. Reattach the cavity to the waveguide (with gasket). Replace waveguide supports, reconnect iris motor, and reconnect coaxial cable. When replacing waveguide supports, **position both supports before tightening them**. If you tighten one without the second in place it will put a lot of strain on the waveguide and cavity will no longer be centered in the magnet.

5. Attach N₂ gas supply to back of waveguide and start purge.

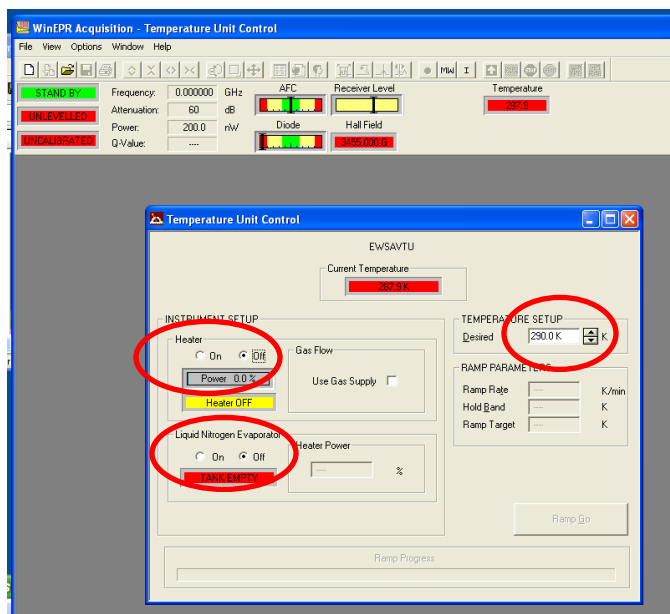
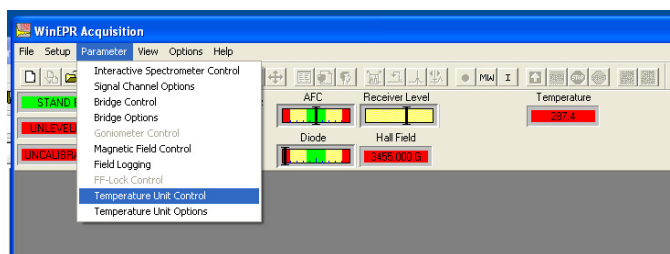
6. Grease both ends of the transfer line and connect the transfer line to the back of the Dewar tube assembly. Secure transfer line to support rod using spring. Remove the highlighted glass stopper from the evaporator unit and slowly lower evaporator into full liquid N₂ Dewar and secure with springs. Position the Dewar (with evaporator unit inserted) below the end of the transfer line and attach the transfer line using springs.



Replace stopper in evaporator unit to initiate flow of N₂ through the transfer line.



7. In the **WinEPR Acquisition** program, close all open windows. From the *Setup* menu, select *Other Devices*. (The Setup menu won't appear unless all windows are closed.) In the dialog box that opens, check the *Use VTU* box. You do not need to select anything from the drop-down menus. After you click ok, a temperature status box will appear in the main screen.



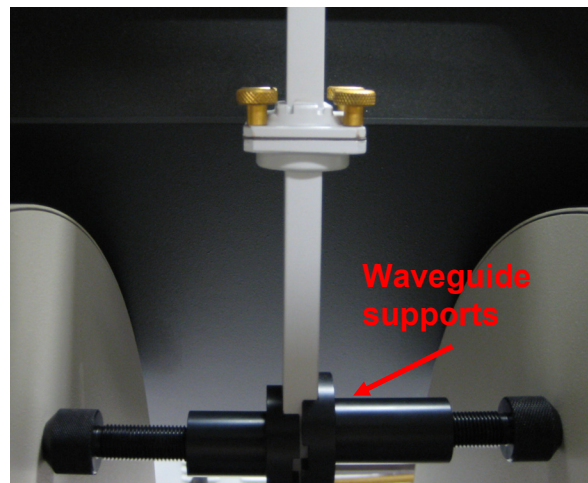
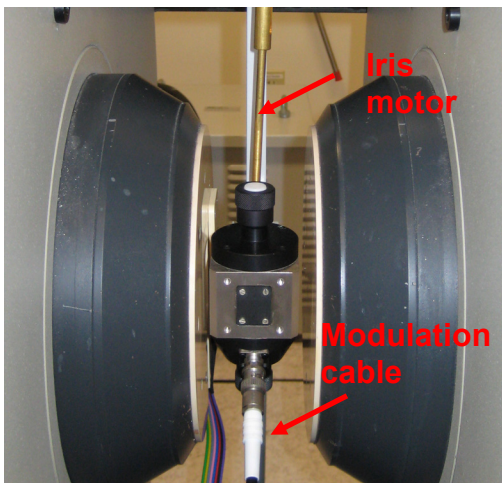
8. From the *Parameters* menu, select *Temperature Unit Control*. In the *Instrument Setup* box, turn both the heater and evaporator on. In the *Temperature Setup* box, type in the desired temperature and then click somewhere else in the window. (It is also possible to control the temperature of the cavity through the *Standard Parameters* window.) The heater power is automatically controlled by the system based upon the set temperature. Do not manually change this parameter. The temperature of the cavity will display both in this window and at the top of the main screen. When the cavity reaches the desired temperature, the boxes will turn green and you can proceed with your experiment.
9. When finished with the experiment, remove your sample from the cavity. Slowly warm the temperature of the cavity by raising the set temperature by 50 K until you reach room temperature. Once the cavity has returned to room temperature, you can discontinue the N₂ gas purge.
10. Carefully disassemble the VTU in the reverse order and return the components to their designated areas. Replace both the top and bottom collets with stoppers to prevent dust from accumulating in the cavity when not in use.
11. Shut down the instrument.

Helium Temperature Control System

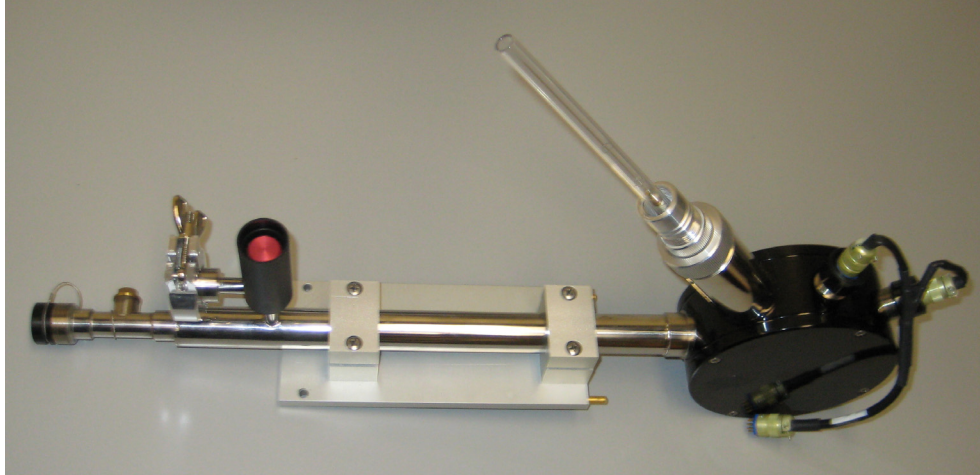
- Prior to use, both the cryostat and the helium transfer line must be under high vacuum, approximately 10^{-6} Torr. It is usually necessary to pump down on each component for 24 hours.
- The following directions are for operation using liquid helium. The system can be used with liquid nitrogen, although there are slight differences during operation.

Installation (X-band):

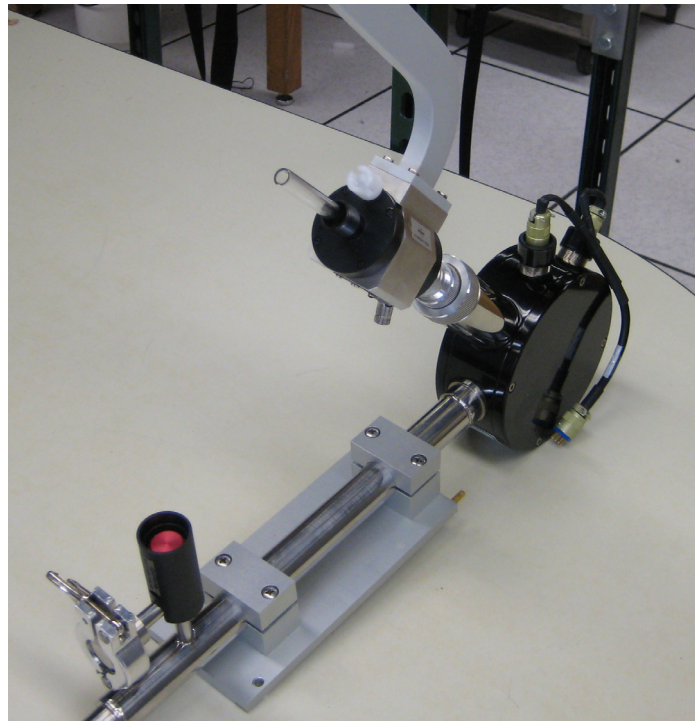
Connecting the cryostat



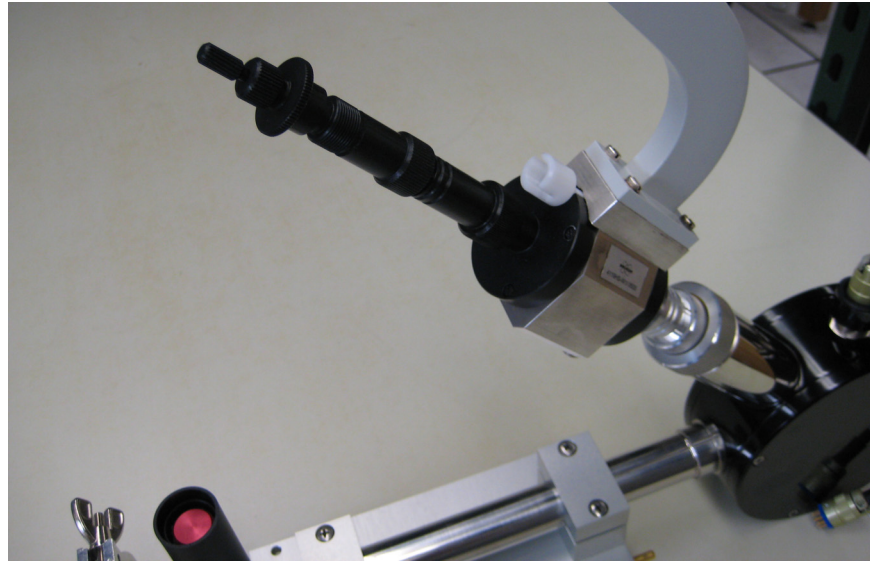
1. From the *Microwave Bridge Control* window, verify the instrument is in standby mode (turn to tune mode first from operate, **do not go directly from operate to standby**) and that the magnet is off. Move the iris motor out of the way by first lifting up the lower portion of the brass rod to disconnect it from the cavity, and then loosen the screw on the underside of the bridge table to slide the motor off to the side and retighten the screw. Disconnect coaxial cable from the front of the cavity. Loosen the waveguide supports and remove them. While holding onto the cavity, loosen the screws connecting the middle segment of the waveguide. Remove the cavity, being careful not to drop the gasket when separating the waveguide.



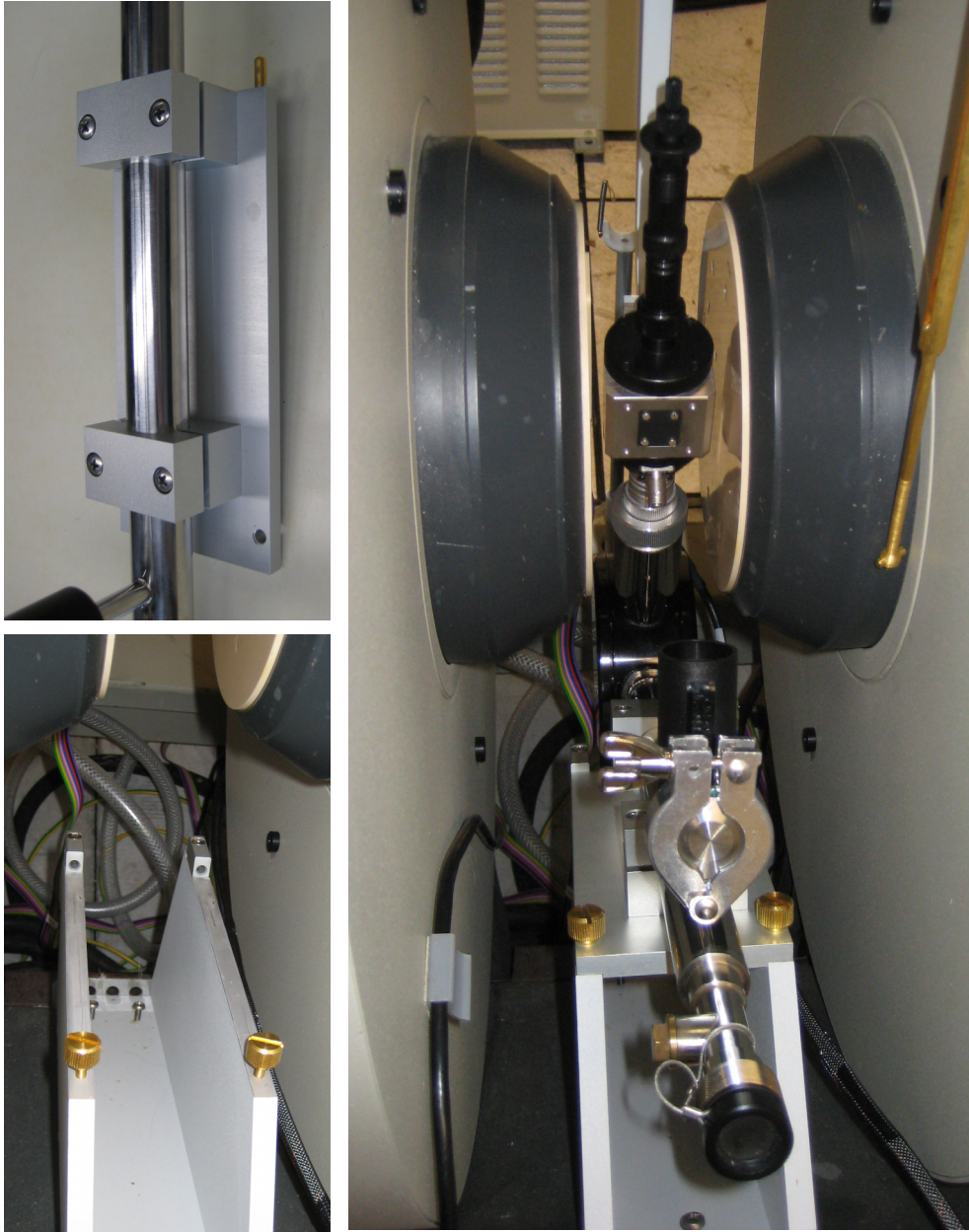
2. Remove both the top and bottom collet nuts from the high sensitivity cavity. Obtain the X-band cryostat from the bottom shelf of the bookcase. **Do not lift or hold the cryostat by the black protective cover.** Set the cryostat on the table so that the black protective cover is pointing up. Unscrew the cover and carefully slide straight off. **Do not loosen or move the lower silver connection below the protective cover.** This is the height adjustment for the cryostat. Changing this can cause damage to the waveguide or bridge interface when tightening down the connections on installation.



3. Slide the cavity onto the Dewar tube, and tighten the first silver connection.

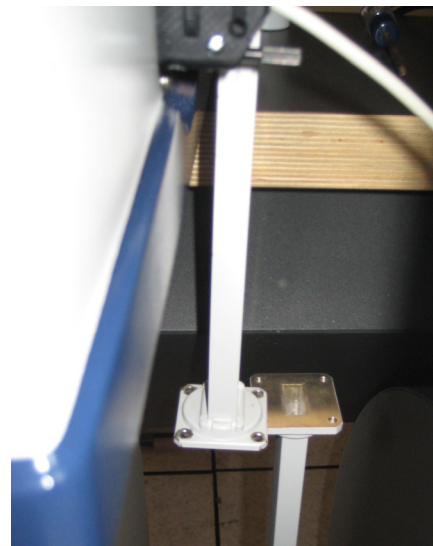


4. In the tackle box on the top of the power supply, there is a black, 2-piece cavity adapter. Unscrew the adapter at the middle joint and remove the o-ring. Slide the lower cavity adapter onto the Dewar tube and tighten to the top of the cavity. Place the o-ring on the Dewar tube and attach the top cavity adapter. To the top of the cavity adapter, attach the 'top-hat' sample holder.
5. Loosen the screws connecting the waveguide to the microwave bridge (but do not disconnect) and move the bridge so that the waveguide hangs to the back left side of the opening in the table. Remove the brass screws from the silver mounting plate on the front center of the magnet.



6. Position the cryostat into the magnet by first inserting the waveguide then slide the silver mounting plate into place. Tighten the screws on the mounting plate.

7. Reposition the microwave bridge by carefully sliding it back into place. The height adjustment (lower silver connection on the cryostat) is set so that the waveguide will fit exactly. This makes it difficult to reposition the bridge and insert the gasket. Once everything is aligned, tighten the brass screws connecting the two segments of the waveguide as well as the screws connecting the waveguide to the bridge. Replace waveguide supports, reconnect iris motor, and reconnect coaxial cable.
8. Connect electrical connection to the back of the cryostat. The cables are hanging off the back of the bridge table. Be sure to select the cable for the X-band cryostat.



Connecting the transfer line

1. Connect electrical connection from the main unit to transfer line. *The cable just plugs in—do not turn. Connect the clear plastic tubing from the small vacuum pump to the transfer line. Turn on the temperature controller.
2. Verify that the sample tube is sealed with the top-hat plug.
3. Set the ‘set temperature’ of the temperature by holding down the *set* button and using the *raise/lower* button to set the temperature to 4.2 K.
4. Place the thermocouple reference junction into liquid nitrogen. The temperature controller should now read room temperature.
5. Set gas flow to 100% on the temperature controller and wait for the needle valve in the transfer line to close. This should take less than 3 minutes.
6. Remove the protective cover from the cryostat end of the transfer line.
7. Open the needle valve on the gas-flow control box fully by turning it counterclockwise. Turn on the vacuum pump.
8. Attach the gas vent valve with soccer ball bladder to the top of the liquid helium Dewar. **Verify that the vent valve is open.** Slowly lower the transfer line into the tank. Adding the transfer line too quickly can cause excessive bleed-off of gas.
9. As soon as the transfer line is lowered into the gas, insert the other end into the side arm of the cryostat until the knurled nut just touches the thread on the arm—do

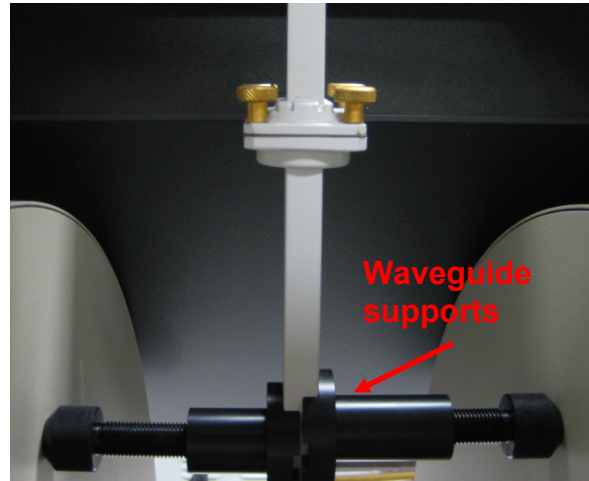
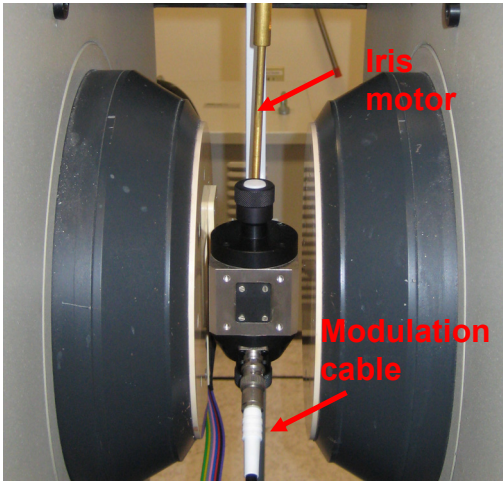


not connect yet. Watch the flow gauge, after a few minutes when the transfer line cools down the flow should drop to about 1.5 L/hr. Once the flow is 1.5 L/hr, tighten the connection of the transfer line to the cryostat. If this flow rate isn't reached after 20 minutes, the transfer tube may be blocked or the needle valve may not be opening correctly.

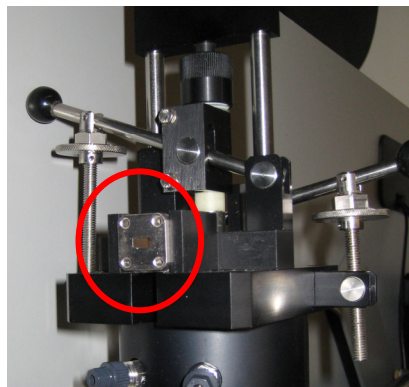
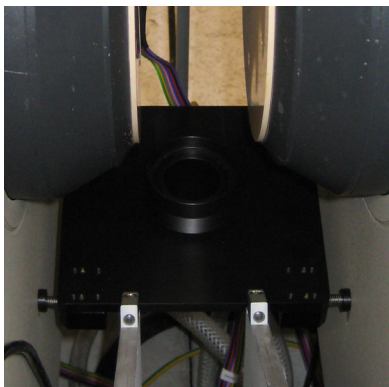
10. When you connect the transfer line to the cryostat, the flow will drop. After about 10 minutes, the flow should increase back to 1.5 L/hr again. If not, there may be a blockage in the cryostat.
11. The cryostat cool down time to reach 4.2 K is typically between 40 and 60 minutes.

Q-Band

Installation:

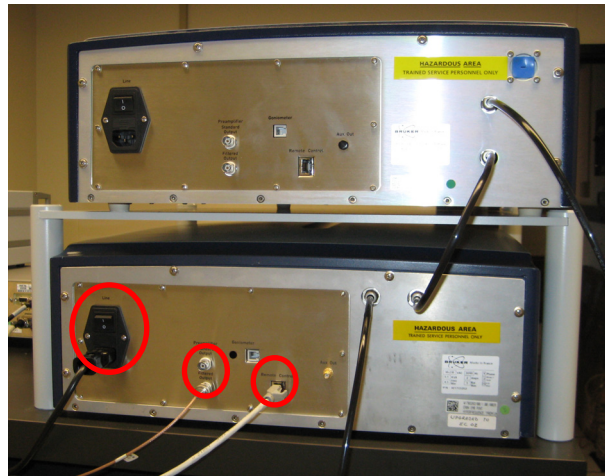


1. From the *Microwave Bridge Control* window, verify the instrument is in standby mode (turn to tune mode first from operate, **do not go directly from operate to standby**). Move the iris motor out of the way by first lifting up the lower portion of the brass rod to disconnect it from the cavity, and then loosen the screw on the underside of the bridge table to slide the motor off to the side and retighten the screw. Disconnect coaxial cable from the front of the cavity. Loosen the waveguide supports and remove them. While holding onto the cavity, loosen the screws connecting the middle segment of the waveguide. Remove the cavity, being careful not to drop the gasket when separating the waveguide. Place plastic covers over both ends of the waveguide (stored in lower part of tackle box on top of power supply).
2. Disconnect the waveguide from the bridge and cover port with plastic cover. Return cavity and waveguide segment to the storage case.



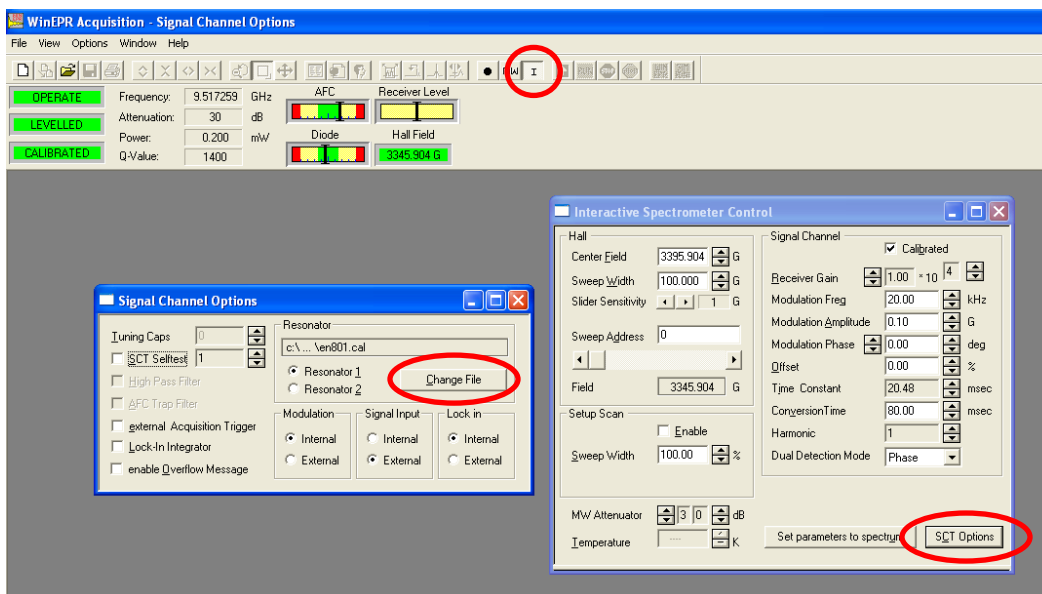
3. Install support stand near bottom of the cavity at black pegs. Always tighten/loosen screws on right side of support stands when moving in and out of the magnet.

- Remove cavity from case and install into cryostat. Attach the small bent portion of the waveguide to the back of the cavity using the four brass screws. Remember to include the Mylar gasket in the connection. Do not completely tighten the screws.
- Install cavity into magnet. Attach waveguide to Q-band microwave bridge using silver screws. Connect modulation cable to the front of the cavity using the connection on the right.
- At the back of the bridge, transfer power (Line), Ethernet (Remote Control), and cable (Preamplifier, filtered output) cables from the X-band bridge (lower) to Q-band bridge (upper).



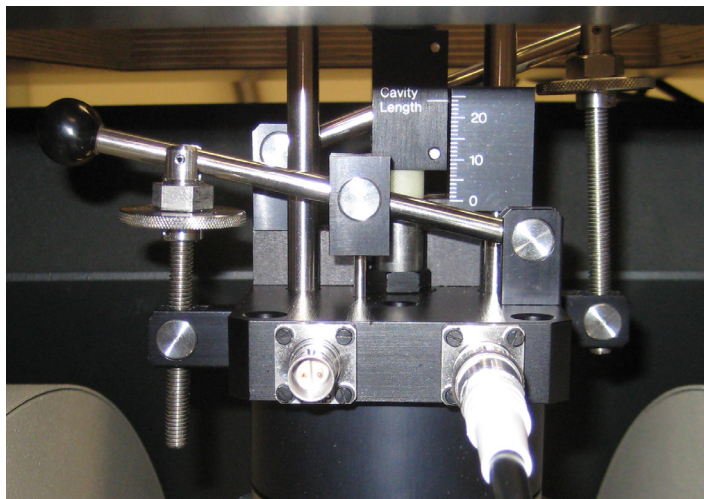
Inserting a Sample:

- Select the correct size sample holder from the storage case. Screw the sample holder onto the end of the sample rod. Insert sample so only 50 mm of the sample tube is visible.
- On the cavity, loosen the knob securing the plug and remove.
- Open the **WinEPR Acquisition** program.



- In the *Interactive Spectrometer Control* dialog box, select *SCT Options*. Load the calibration file for the Q-band cavity (qtw.cal) and close the box. Verify that the *Calibrated* box is checked and close the window.

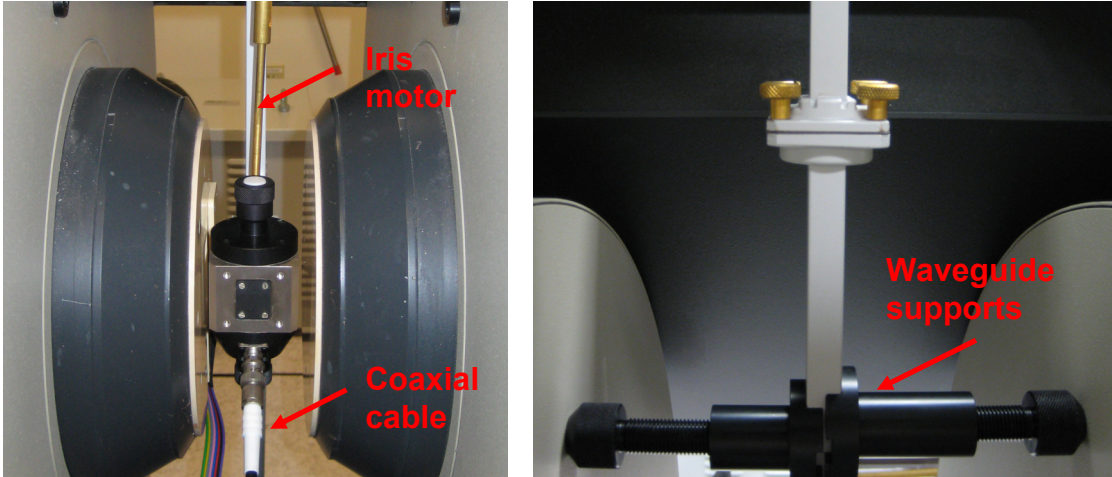
5. In the *Microwave Bridge Control* window, manually tune the cavity. First set the microwave frequency to approximately center of the microwave frequency band. Adjust the empty cavity length to find the mode curve. The cavity length should be about 24 mm.



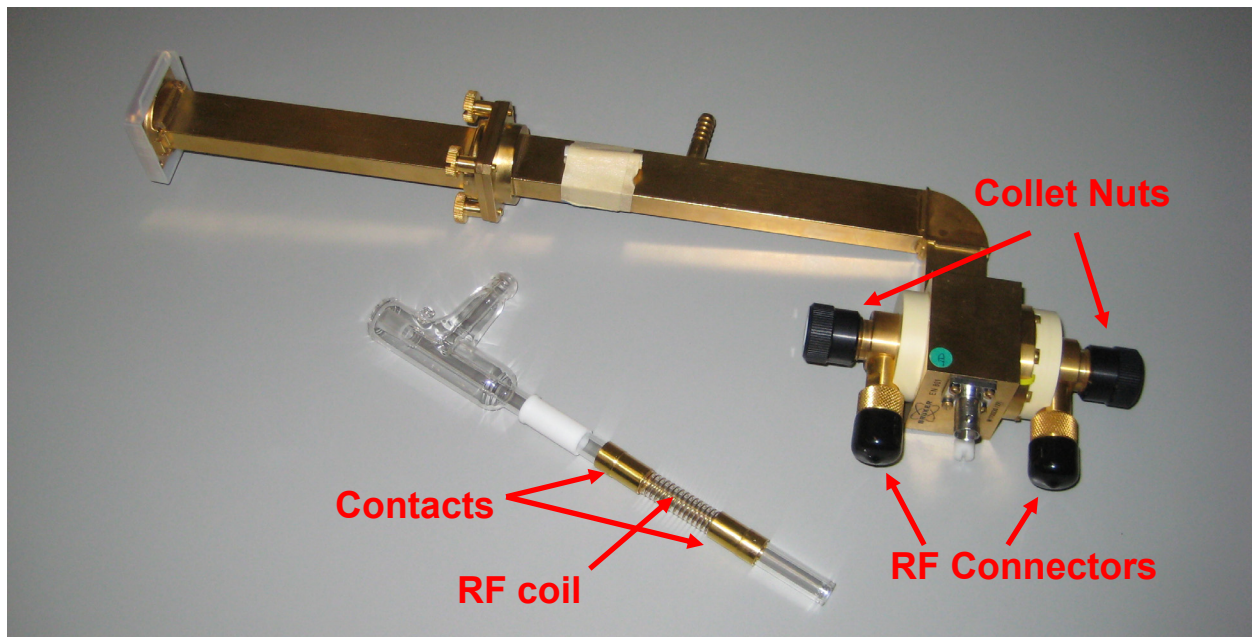
6. While still in tune mode, insert the sample into the cavity. Insert the sample rod as far as it will go (the sample will get pushed further into the sample rod when it hits the bottom of the cavity). Notice where the colored lines on the sample rod indicate sample position. If you have a solution or solid sample that occupies the entire sample tube, this will be the final position of your sample in the cavity. If you have a point sample/single crystal, you will need to move the sample to 6 mm above the bottom of the cavity, so insert the sample rod as far as it will go then using the colored lines as a guide, move the sample back 6 mm. Remember this position!
7. Raise the sample rod so that the sample is back out of the cavity. In the *Microwave Bridge Control* window, you should be able to see the mode curve you centered previously. Insert the sample slowly (to the predetermined position) and simultaneously adjust the cavity length to keep the mode curve centered in the display.
8. Switch to the *Operate* mode of the microwave bridge and continue with the fine adjustment as usual, using the iris screw on the left side of the cavity for adjustments. **Autotune is not possible with this cavity.**

ENDOR

Installation:

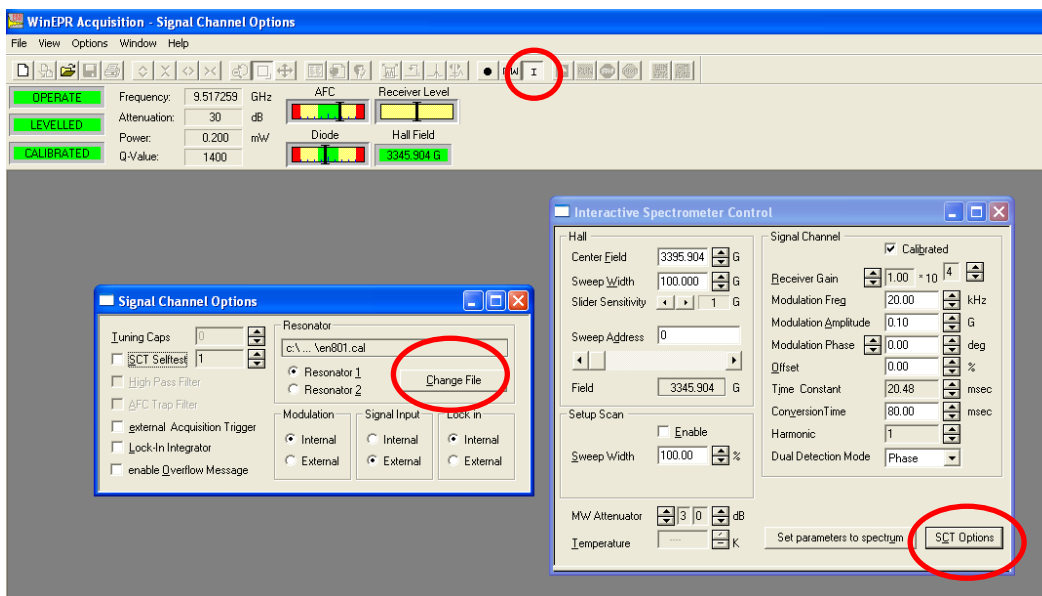
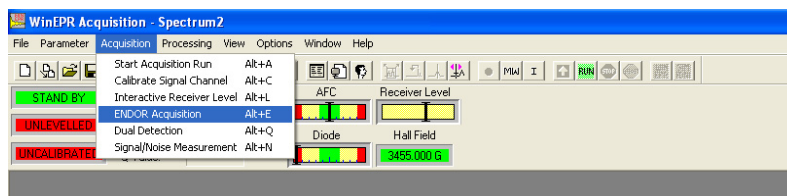


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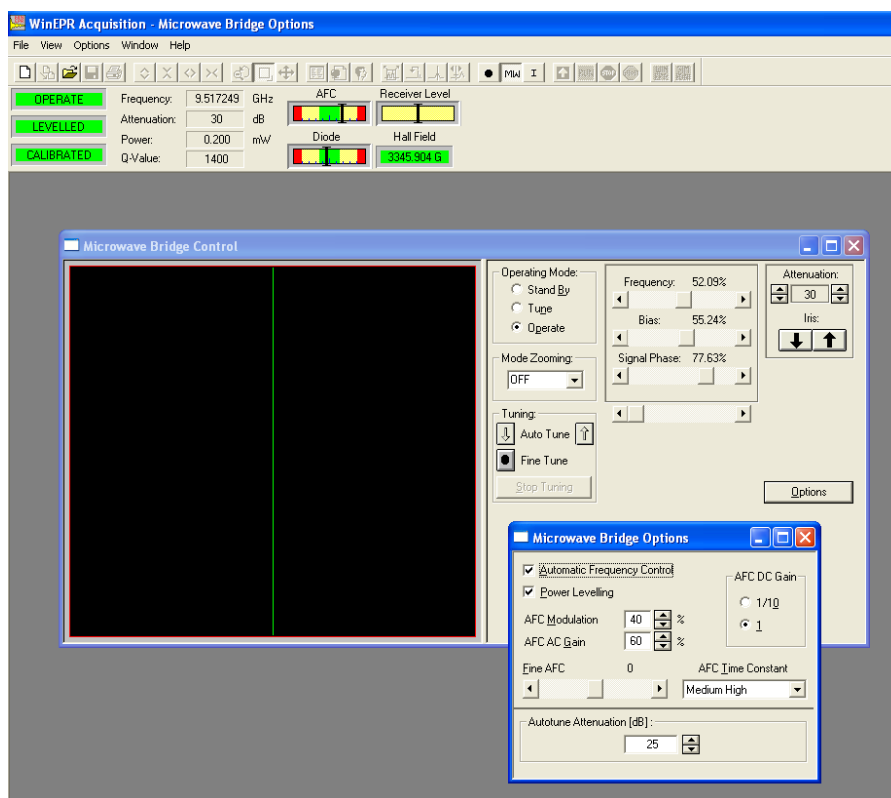


2. Remove ENDOR cavity from its case on the bookshelf. Remove both the upper and lower RF connectors (under the black protective covers).
3. Obtain the ENDOR liquid N₂ Dewar tube from the storage box. Disassemble the mounting hardware for the VTU Dewar tube. Clean the brass connections above and below the coil with a Kimwipe and methanol, being careful not to touch the contacts after cleaning. Reassemble the mounting hardware using Dewar tube with the rf coil. Insert the Dewar tube and assemble the cavity as you would when using the VTU accessory. *You will be unable to insert the Dewar tube if you have not removed the RF connectors from the front of the cavity. Once the Dewar tube is installed, verify the brass contacts are aligned with the RF connectors, clean the RF connectors, clean the RF connectors and reattach them to the front of the cavity and remove black covers.
4. Install the ENDOR cavity. It will be necessary to slide the microwave bridge to the side in order to center the cavity in the magnet. Attach waveguide supports and connect coaxial cable. The iris motor **will not** connect to the ENDOR cavity.
5. Position the barstool just in front of the magnet. Remove the RF Amplifier (heavy) from the bookshelf and set on the barstool. Plug the unit into the outlet near the front of the console but do not turn the unit on yet. Connect the RF amplifier to the bottom connector on the cavity (using the cables from the shelf where the RF Amplifier is stored) and connect the top of the cavity to the bottom of the 50 ohm load attached to the left side of the magnet.
6. If desired, connect VTU accessory to cavity to perform low temperature experiments.

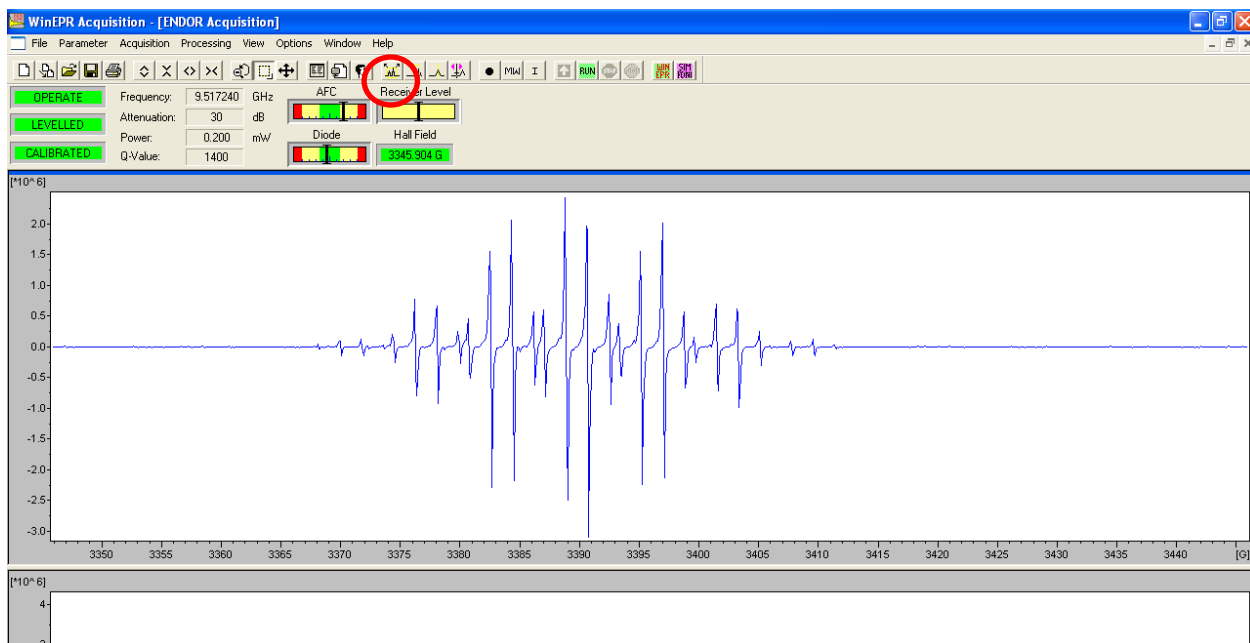
Collecting a Spectrum:



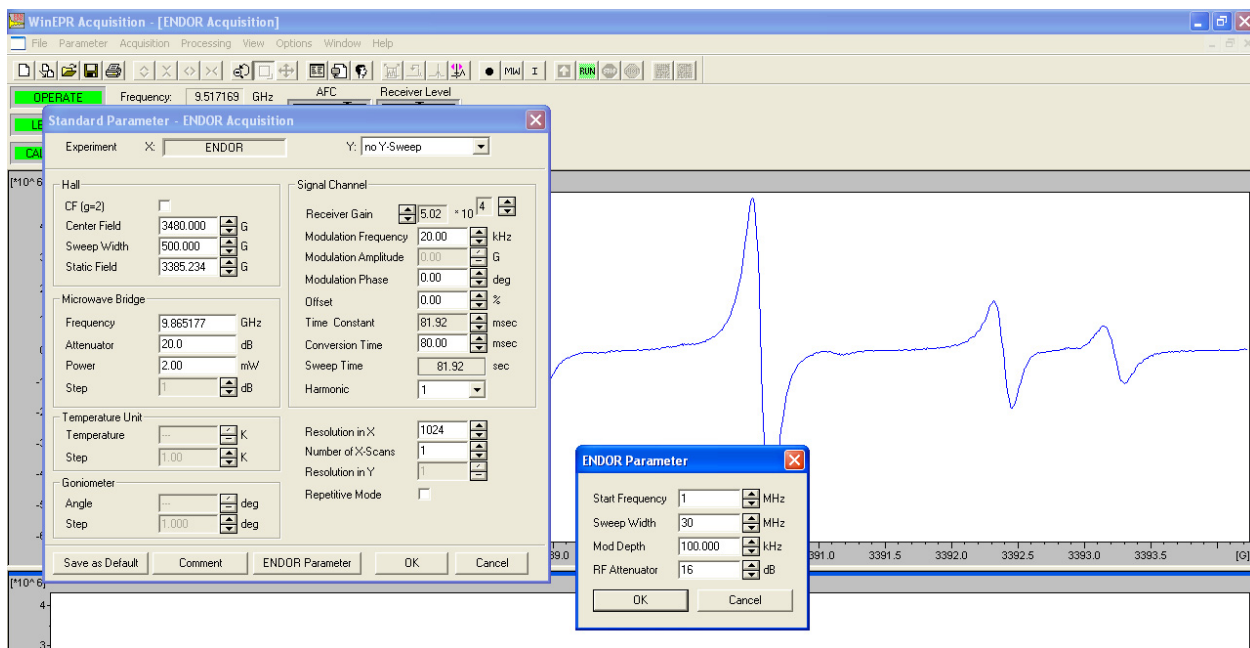
1. In the acquisition program, open a new spectrum. From the *Acquisition* menu, select **ENDOR Acquisition**. The spectrum window should now change to have an upper window to display the EPR spectrum and a lower window to display the ENDOR spectrum. Open the *Interactive Spectrometer Control* dialog box and select *SCT Options*. In the Resonator box, select *Change File*. Select **en801.cal** as the calibration file for the ENDOR cavity and close the SCT Options box.
2. From the *Parameter* menu, select *Options* to open the *Experimental Options* dialog box. Verify that the *MW Fine Tune before measurement* box is unchecked.



3. From the *Microwave Bridge Control* dialog box, select *Options*. In the *Microwave Bridge Options* dialog box that appears, make the following changes:
 - a. AFC DC Gain – 1
 - b. AFC Modulation – 40%
 - c. AFC AC Gain – 60%
 - d. AFC Time Constant – Medium High
4. Insert sample into cavity. Due to the configuration of the cavity, autotune is not available. Manually tune the cavity, using the blue aluminum rod (in the cavity storage case) to adjust the iris screw when tuning.
5. Verify that the top of the new spectrum window is selected and collect an EPR spectrum changing necessary parameters for spectrum optimization.



- Using the *Center Field and Sweep Width* tool, zoom in on the desired portion of the spectrum and recollect the spectrum.



- Click on the lower portion of the spectrum window to activate the ENDOR experiment. Open the *Standard Parameters* dialog box and enter the parameters for the ENDOR experiment. Turn on the RF amplifier at the switch on the back of the unit and verify on the front of the instrument that it is not in Standby mode. Begin collecting the ENDOR spectrum and stop. The goal is to start the RF amplifier to allow the resonator to warm up.
- Be sure that the ENDOR portion of the spectrum window is selected and use the *Interactive Receiver Control* tool and set it to the center of the sweep and right click. Wait ten minutes.

9. Change the active window to the top portion and reacquire the EPR spectrum.
10. Using the *Static Field* tool, set the magnetic field to the zero-crossing point of the desired EPR line. Right click to set field.
11. Change the active window back to the lower portion and acquire the ENDOR spectrum.
12. When the experiment is complete, remove the ENDOR cavity from the instrument and change the acquisition parameters back for use with the high sensitivity cavity.