DCIF Low-Temperature EPR Spectroscopy Manual

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Introduction

This manual briefly describes how to set-up the DCIF Electron Paramagnetic Resonance (EPR) spectrometer for low-temperature EPR experimental acquisitions, how to control the temperature (T), how to change samples and how to measure spectra. If you wish to learn more about the ESR900 cryostat (e.g. how to clean it, yeah right) read the Operators Manual. The DCIF requires that all new users of the EPR instrument (either room temperature or low-temperature experiments) to attend an introductory course. Once you've been trained, EPR time can be reserved on-line through the workstation cruella. You are required to provide your own liquid helium. The amount of helium used depends on the temperature. The following tares can be used as a guideline:

Experiments at 5K require ~1.5 litres/hour
Experiments at 10K require ~1 litre/hour
Experiments >20K require ~0.5 litre/hour

Note that these rates are just a guide. *Your* usage will vary! Initial cooling of the cryostat uses about 2 litres, and additionally ~ 0.5-1 litres of helium are lost per day when the Helium dewar is not being used due to boil-off. A 30 litre dewar will typically last for approximately 2-3 days of measurements. Try to plan your experiments ahead and/or combine your measurements with other people so that measurement can be run on consecutive days. This ensures efficient usage of helium and keeps the setup time for the instrument to a minimum.

Assembly of the liquid-helium EPR cryostat

Figure 1 below shows a schematic cartoon of the set-up required for low-temperature measurements. It is important to remember that these assemblies are extremely fragile (particularly the cryostat and transfer line) and extremely expensive (>$20,000.00). Please exercise caution and good judgment when using this equipment. The main parts are the EPR cavity (1), the ESR900 cryostat (2), a helium transfer line (GFS350) with automatic needle valve (3), the dewar with liquid helium (4), a GF3 He-pump with flow meter (5) and the Oxford temperature controller ITC-503 (shown as ITC-4). Figure 2 illustrates the cryostat and cavity assembled in place between the magnets of the EPR.

Figure 1. Schematic sketch of the set-up needed for low-temperature EPR.

Please be aware that the Chemistry Department has three (3) cryostat / He transfer line assemblies. Each of these assemblies has it's own temperature calibration file stored in memory of the ITC-503. They are configured as follows:

- Sensor #1: DCIF cryostat
- Sensor #2 Stubbe group cryostat

- Sensor #3 Lippard group cryostat

and are clearly marked on the back of the ITC-503. It is important to note that the cryostat and He transfer line work together as a matched set. Do not mix and match these assemblies nor attempt to use the wrong sensor channel.

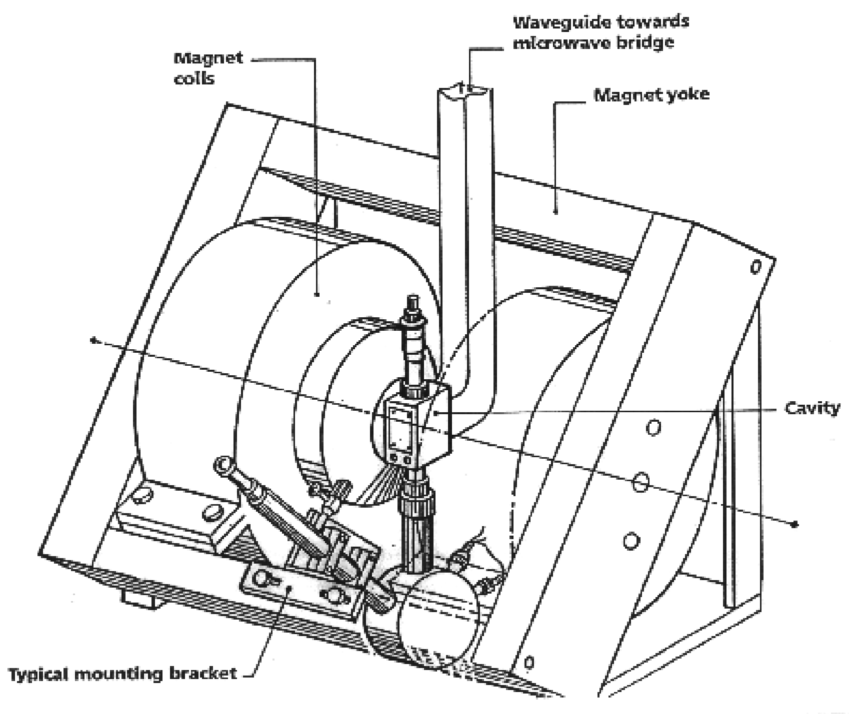

Figure 2. Assembly of the cryostat / cavity in between the two magnet poles of the EPR

Day before the measurement:

The cryostat / cavity assembly should be prepared and readied for experiments. Disconnect the coax cable from the front of the cavity and the brass spinner that drives the white iris-screw. There is a small teflon® lock nut that must be loosened prior to removal. Next, remove the black/white waveguide stabilizers and remove the cavity from the bridge by removing the 4 screws with which the waveguide is attached to the microwave source. Remove the white caps from the top and bottom of the cavity by unscrewing the black lock-rings. Be very careful not to let any dust or moisture get into the cavity, as cavities cost $15,000-$20,000, and are very difficult / time consuming to clean.

Unscrew the black upper positioning assembly and the brass spacer from the cryostat. See picture below. Carefully slide the cavity over the quartz tube in the cryostat and screw the cavity on the cryostat until you feel some resistance, don't over-tighten it.

Please exercise extreme caution when installing or removing the cavity from the cryostat. The quartz tube / assembly is under vacuum and very fragile. Damage to this assembly will lead to a substantial down time!

Make sure that the cavity and waveguide are in the correct orientation. Screw the upper black cover back on to the cavity. Make sure that all the o-rings are in place. Place the cryostat /cavity assembly back between the magnets. Secure the cryostat with the two large brass thumbscrews onto the cryostat-support and connect the waveguide to the Microwave Bridge. Do not forget to put the rubber gasket back in the proper orientation. Reconnect the coax cable to the cavity and the brass spinner into the white iris screw. Finish by reinstalling the teflon® lock nut.

Evacuate the cryostat overnight using the DCIF pumping station. Attach the pumping station to the black-red valve on the cryostat. Put the valve on the pump in position 1, start the main power, and evacuate the line to ~10^{-3} Torr. Next, open the valve on the cryostat and pump the cryostat to a pressure of ~10^{-3} at sensor 2. This should be pumped for several hours at ~10^{-3} Torr. The following morning the cryostat will be ready for use.

Day of the measurement:

First, close the black-red valve on the cryostat, turn the yellow knob on the rough pump to the '0' position, and shut down the pumping station. Turn off the main power and remove the connection between the cryostat and the pumping station.

Prior to cooling, the cryostat must be purged with nitrogen gas. This nitrogen purge will remove any excess water and prevent condensation during the cryostat cool-down. Attach the Tygon® to the top of the cryostat assembly and start purging nitrogen (slowly) through the waveguide/cavity. When purging the cryostat assembly, carefully listen for a "gurgling" sound. A "gurgling" sound would indicate water in the helium transfer coils. Continue to purge the cryostat until the "gurgling" disappears. Fill the dewar at the back of the EPR magnet with liquid nitrogen and put the thermocouple of the cryostat (the blue plastic line) into the liquid nitrogen. The liquid nitrogen serves as a reference temperature for the thermocouple that measures the temperature of the He-flow just below the EPR tube. Note that this step is not required if your are using the DCIF cryostat as this unit has a Cernox sensor and does not require an external reference. Connect the arrow-shaped 10–pin cable from the cryostat to the back of the ITC-503 temperature controller. Again, the controller is configured as follows:

- Sensor #1: DCIF cryostat
- Sensor #2 Stubbe group cryostat
- Sensor #3 Lippard group cryostat

The assembly of the He-transfer line **requires two persons**, as excessive bending of the transfer line will cause permanent damage. The transfer line does not need to be pumped before every usage, once every 1-2 months is sufficient. Slide the brass knob and o-ring over the leg of the He-transfer line to a position ~1-2 feet from the bottom of the leg. Connect the ITC-503 T-controller to the motor transfer (the dark blue device labeled "Oxford Instruments") on the He- line that drives the needle valve. Switch on the ITC-503 T-controller, it should read about 295 K on channel 1 (or whichever channel you are using). Wait for the gas flow to initialize (the Gas Flow light will at this point stop flashing). On the PC, open the program Oxford Bench. Open ITC-503 and connect to ITC. By default, the needle valve is closed when the T-controller is switched on. Open the needle valve to 50%. You can check whether the needle valve responds by feeling its vibration. Wait for the vibrations to stop. Opening the needle valve from closed to 50% open takes 1-2 minutes. Unscrew the protective steel cover from the end of the "arm" of the He-transfer-line. Make sure that the safety valve on the He-dewar is open (so that build-up pressure can escape).

Again, it is important to stress here that it ***requires 2 people*** to properly, and safely, handle the transfer line. Excessive bending and /or torque will permanently damage the transfer line! These transfer lines are very delicate and very expensive. Please exercise caution.

Cautiously open the top-valve of the He-dewar and insert about 2 feet of the He-transfer-line leg into the dewar. Be wary of the initial He plume when opening the dewar to atmosphere. **Always remember to wear safety-goggles and gloves!** Tighten the brass ferrule onto the dewar. Test whether there is He flowing through the He-transfer line by immersing the tip into ethanol and watch the bubbles. Slowly lower the leg further down into the dewar. Remove the black cap of the cryostat and move the arm of the He-transfer line into the cryostat. You may need to **gently** wiggle it a little to find the hole that allows you to move the arm all the way down into the cryostat. **Do not force it!** It will bend. Initially, connect the arm to the cryostat loosely. Next, attach the He-transfer line to the He-flow meter/pump using the white tubing and start the pump. If the flow gauge (the ball on the right hand side of the pump) doesn't 'bounce' right away you've got an ice block. If this is the case you'll need to remove the transfer line and warm everything back up to room temperature and the start over.

Slowly lower the He-transfer line all the way down into the He-dewar and tighten the brass ferrule. The helium flow will increase after a few minutes from 0.5 L to 2.5 L/hour. You can then tighten the knob that connects the He-transfer line to the cryostat. This will result in a drop in He-flow. After a few minutes the temperature will start to go down. Cooling down from room temperature to 4 K typically takes between 20 and 45 minutes. To minimize He waste, it is best to decrease the needle valve to ~30%. Once the temperature starts to drop, close the He flow even further (i.e. the smallest flow necessary) once the temperature has reached 4 K.

Temperature control

Start by adjusting the flow manually so that a temperature is reached which is ~ 25% below that of the desired temperature (i.e., 4 K for 5 K, 8 K for 10 K, etc.). At temperatures below 5 K, the temperature is controlled by the He-flow only in the manual mode (i.e. no heater). Adjust the P, I, and D according to Table 1.

	DCIF Cryostat			Stubbe Cryostat			Lippard Cryostat		
Temp (K)	**P**	**I**	**D**	**P**	**I**	**D**	**P**	**I**	**D**
4-15							6.0	1.0	0
15-30	22.52	1.0	0				5.0	1.0	0
30-60							4.0	1.0	0
60-115	12.31	1.9	0				3.0	2.5	0.5
115-225							3.0	2.5	0.5

Table 1: Settings for P (proportional bandwidth), I (integration time), and D (derivative action time) for best T-control in different T-ranges.

Put in the desired temperature and switch from manual to automatic temperature control. The heater output and flow are now automatically adjusted to reach the desired temperature. Let the sample equilibrate a few minutes after the desired temperature is reached before taking spectra. When changing a sample, make sure to switch the temperature controller to manual and manually set the heater output to 0V before changing a sample. If this is not done, the temperature will rapidly jump to a higher temperature wasting both He and time, as it will take a long time to cool the sample back down. Also, don't forget to put the Microwave Bridge in stand-by mode.

The different parameters such as T, heater output, gas flow can be continously recorded using the XY-plot feature. To do this, use the pull down menus go to windows > xyplot > define x and y signals. This can be used to make sure that the temperature remains constant during lengthy measurements.

Changing a sample

First verify that the Microwave Bridge is in the stand-by mode and that the temperature control is on manual with no heater-output. Clean the tube from ice by rubbing it repeatedly with a Kimwipes® or a paper towel. Slide the black sample stabilizing cap and o-ring over the EPR tube. Switch the pump off and wait until atmospheric pressure is reached (watch for the He-flow meter to jump). Remove the cap from the top of the cryostat (or remove the previous sample) and gently put the new tube / cap assembly into the cryostat. Start the pump immediately after securing the black cap. Lower the EPR tube all the way down into the cavity and cap the tube with a rubber stopper to prevent O_2 and water from condensing on the sample. Keep the time that the cavity is open to the air as short as possible, either by closing it with a finger or having the sample already prepared, before swapping samples. This minimizes the build-up of ice inside the cryostat and obstruction of the He-flow. It sometimes happens that the temperature does not decrease after replacing the sample. Most of the time the bottom of the EPR tube is then frozen to the cryostat and the He-flow is blocked. Do not try the remove the EPR tube with force, as it will break. Instead increase the temperature to ~60-110 K. Once the sample tube is loose, gently slide the tube a little higher and quickly decrease the temperature with a nice flow of He. This procedure often cleans out any blockage.

Some basics of acquiring EPR spectra

Study the literature to gain some insight into some of the specific properties of the EPR signal for the system you are studying. Some of the more important variables / parameters to consider are the temperature, the RF power, and the modulation amplitude. You should also try to get an idea of where your signal should appear as this will save you having to run a huge time consuming survey scan.

Start the EPR acquisition program (the Acquisit icon on the desktop). Open the microwave bridge control dialog. Adjust the power to between 25-30 dB and start the tuning procedure. Go to tune-mode. Adjust the frequency manually to ~9.3-9.4 GHz, the signal dip should now appear in the center of the screen. Hit automatic tuning, this should complete in about 3 minutes. After this is done, fine-tune to get both the frequency and the diode meters in the center of the green areas. When you change the power you may have to fine-tune again. Experience has shown that it is best not to change the power by more than 20 dB, before fine-tuning again. Once the instrument is tuned properly, open the experimental parameters options dialog to adjust the spectral parameters. It is recommended you first take a survey scan spectrum over the full width of the magnetic field (center field 3100 gauss, sweep width 6000 gauss) to make sure that you don't miss any spectral features. Unless you've previously characterized your samples and know the power dependence of the signal, it is wise to start with a power of ~2 mW (20 dB). Increase the power in steps of 6 dB, and decrease the gain by a factor of two. If the signal was unsaturated at 20 dB (and thus also unsaturated at 26 dB), the signal intensity should remain constant. If it increases, the signal was saturated at 20 dB, and you should try 32 dB, and so on. To get the best signal/noise, use the highest possible power (lowest attenuation number in dB) that does not saturate your signal. Measuring the sample under non-saturating conditions is especially important for quantitative measurements. The signal/noise can also be improved either by increasing the conversion time (this in turn increases the scan-time) or by increasing the number of scans (signal averaging). The signal/noise also depends on the modulation amplitude, the higher the amplitude the better the signal-to-noise. However, one should be careful not to over-modulate. This happens when the line width of the signal is < 10 x modulation amplitude. The results are excessive line broadening and spectral distortions. It is recommended to start with a modulation amplitude of ~10 gauss for most transition-metal spectra and ~1 to 2 gauss for radical type species.

Shutdown and disassembly of the liquid-helium EPR cryostat

Remove your sample tube from the cryostat and close the top of the cryostat with the black cap. Switch on the He-pump and let He flow for at *least* 5 minutes. Switch off the He-pump and let the pressure reach atmospheric pressure. Close the needle valve fully (0%). Loosen the connection that links the He-transfer line to the cryostat slightly. The temperature within the cryostat will increase to room temperature in about 60 minutes. Close the program Oxford Bench, and switch off the power for the ITC-503 temperature controller. If you want to continue the next day and nobody else needs the EPR in between, **provided you have the instrument reserved**, you can leave the He-transfer-line and the cryostat assembled in this state. The next day, you can simply open the needle valve and start the He-pump to cool down the cryostat again. If not, wait until the temperature in the cryostat has almost reached room temperature. Switch off the nitrogen purge. Disconnect the cable between the ITC-503 and the needle-valve motor. Unscrew the "arm" of the He-transfer line from the cryostat and slide it out. Close this end of the cryostat with the black cap to prevent dust/water from entering. Unscrew the brass ferrule that connects the leg with the He-dewar and quickly remove the He-transfer line leg from the dewar. Close the upper valve of the He-dewar to prevent condensation of water/oxygen/nitrogen. Place the He-transfer line back on the 3 hooks on the wall, and cover the tip of the arm with the steel protective cover. Remove the cryostat / cavity assembly from the EPR machine and disassemble. Reinstall the cavity back into the EPR including the teflon® plugs to prevent dirt and dust from entering the cavity. Place the brass and black plastic protective covers back on the cryostat. If you are using the DCIF cryostat please return it to a staff member.

Conversion of EPR spectra into ASCII files

Open the desired data set with the WinEPR program. If you wish, ask a DCIF staff member for a copy of the programs WinEPR and SimFonia. This will allow you to process your data sets on your pc. Using the pull down menus, select File > Load. Select the WinEPR Button and go to 1D processing. Double-click on the spectrum you want to convert. Under the Parameters menu, choose List Data File. Save the data file as txt file.

Remember

Don't: - Saturate the sample

- Over-modulate

- Measure at too low or too high T

Changing samples:

- Switch to manual and switch off heater

- Put microwave bridge in stand-by

- Let the pressure in the cryostat reach atmospheric pressure before opening

- **Don't forget to switch He-pump back on after changing samples**