IMSERC CIQTEK CW X-band Manual

CONTENTS

INTRODUCTION

The CIQTEK EPR200M X-band CW-EPR spectrometer is equipped with a compact resonator system for measuring electron resonance signals in the X-band frequency range. The system provides stable, user-friendly CW-EPR measurements for detecting paramagnetic species, including organic radicals, transition-metal ions, and material defects. The Bruker VTU 3 enables temperature-dependent EPR experiments, while the goniometer allows angle-dependent measurements for crystalline EPR studies. In addition, the xenon light source enables optically excited EPR measurements.

SAFETY

All users of IMSERC must review the general safety policies at http://imserc.northwestern.edu/about-policies.html. Plus, users should know the points below:

- Users with pacemaker are not allowed
- Emergency Exits
- Location of shower and eyewash
- No food and drink
- Dressing code

DATA MANAGEMENT

The personal data folder is created during training. The data were under the user's personal folder, which must be located under the supervisor's group folder.

EPR data on this instrument are copied on 'imsercdata.northwestern.edu' under 'data2/pcm/CQXband' within a few seconds. Please follow instructions at http://imserc.northwestern.edu/about-general-faq.html#data for details about data access.

SOFTWARE

The EPR experiment on this instrument is performed with CIQTEK X-band.

MATERIALS & METHODS

The default measurement mode of CW X-band. If user want to run an experiment with different temperature or reaction experiment, they will contact the staff.

The default working condition of INSTRUMENT-NAME is as follows:

1. Computer screen is by default deactivated. Users must start the reservation through NUCore in order to be able to turn on the computer screen.
2. Leave the acquisition software offline when user complete with the measurement.

EXPERIMENT SETUP

STEP 1. SAMPLE PREPARATION

Sample Tubes:

a) Standard EPR tube size = 4mm OD, however, sizes do vary and can be accommodated by the 4 mm tube, such as smaller size capillary tube for liquid sample.

b) EPR tubes are made out of quartz whereas NMR tubes are made out of Pyrex, which contains some iron that may or may not, depending on the sample, contribute to the EPR signal.

Tubes can be purchased by various vendors. A couple of options are,

Wilmad Glass https://sp-wilmadlabglass.com/product/4-mm-thin-wall-quartz-epr-sample-tube-250-mm-l/

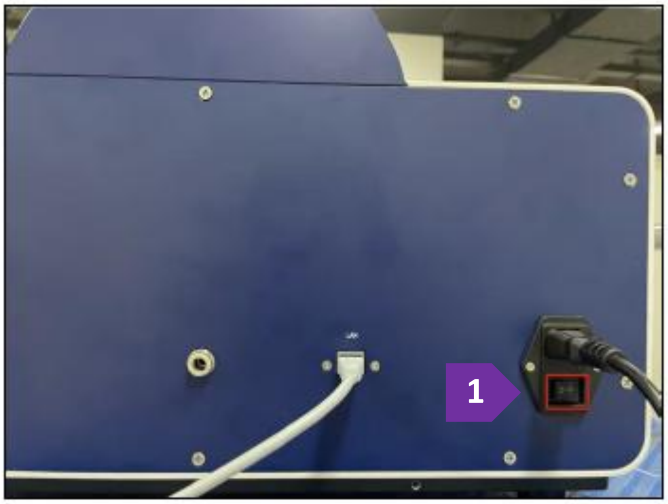
Aqueous Samples (also true for highly polar and conducting samples): The water in aqueous samples absorbs the electric part of the microwaves and begins to heat (like your microwave at home), and therefore, the sample size needs to be limited, specifically the surface area of the sample size. User can use capillary tubes to adsorb the liquid sample and wax to seal each open side. Then the capillary tubes with sample can be added into the 4 mm tube.

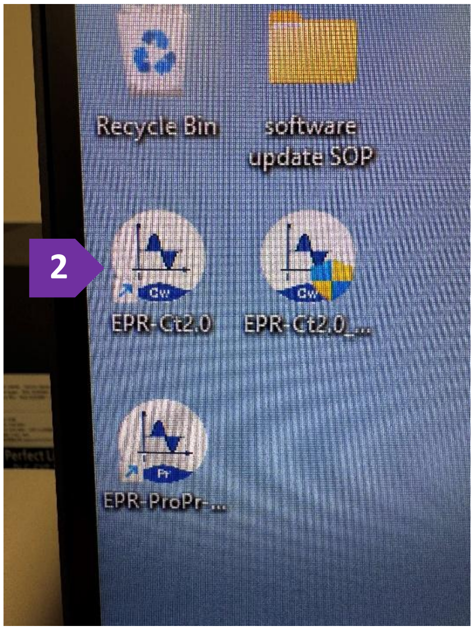
Powder samples: powder sample can be directly packed into the tube. For powder sample, 1 cm depth is enough.

STEP 2. TURN ON THE SPECTROMETER AND THE SOFTWARE

1) Turn on the following items (if not already on):

Spectrometer (if it is on, then skip), back panel of spectrometer. Allow the instrument to warm up for 30 mins before use. This will help to ensure accurate results.





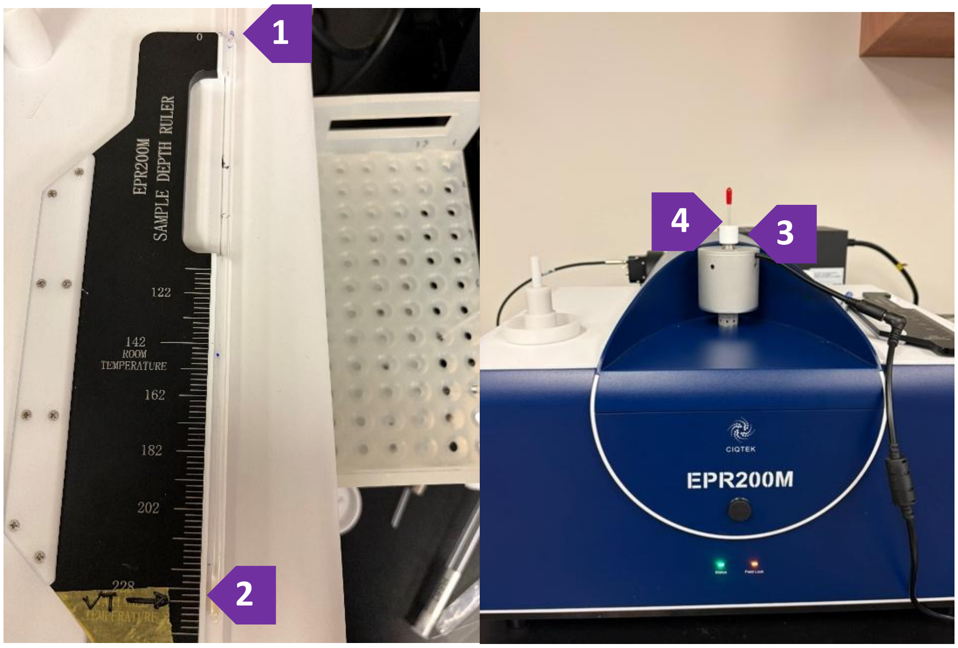
Note: 1. Power button of the spectrometer

2. "EPR-Ct2.0", CIQTEK EPR software

2) turn on the reservation on Nucore. Open the Acquisition software "EPR-Ct2.0" located on the desktop.

STEP 3. INSERT SAMPLE

1) Use the meter to measure the distance from the center of the sample. It should be around marked VT line in the rule. Then Mark the tube with black mark pen at 0 mm.



Note: 1. Mark the tube to insert the tube into the EPR instrument

2. Align the center of sample to the correct length

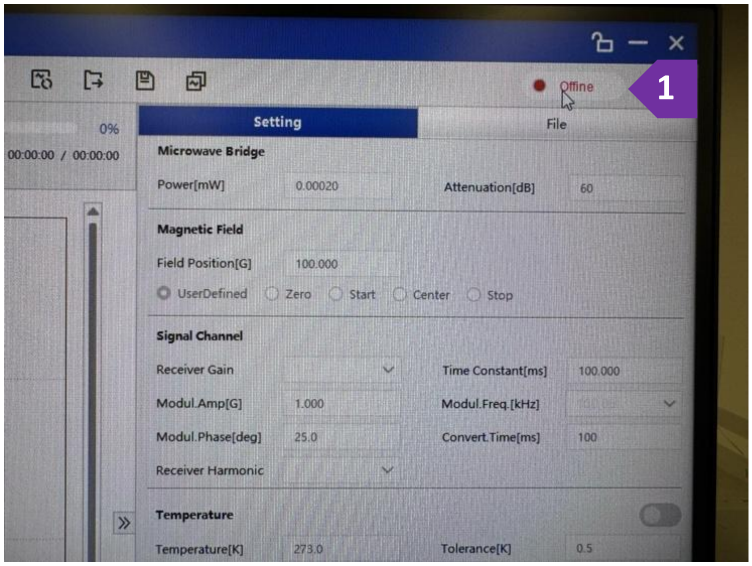
3. White nut to tighten the white sample holder

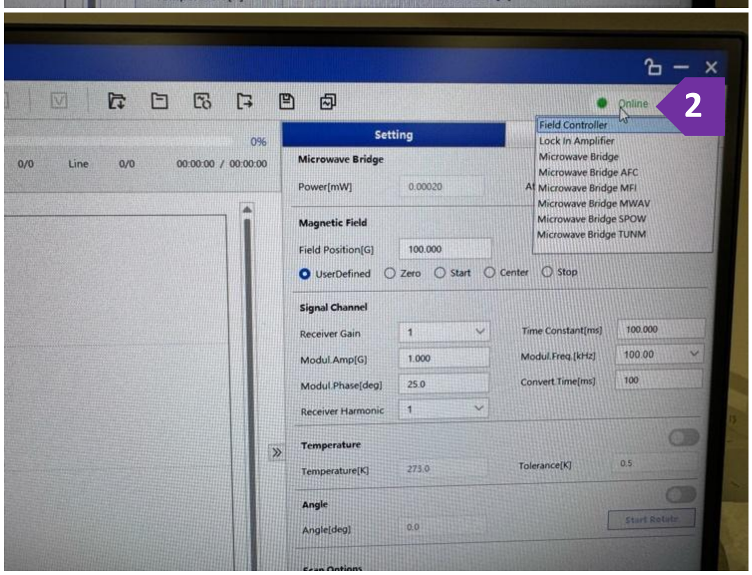
4. Align the mark in the tube with white sample holder

2) Wipe the outside of the tube with acetone or isopropanol. Losen the black screw and then Insert the tube to the white sample holder slowly. When black mark aligns with the white sample holder top, stop and tighten the black screw.

STEP 4. CONNECT AND ACTIVATE SOFTWARE

1) After starting the software, hover your mouse over the Offline button located in the upper right corner of the main interface. Once you have done this, click on Offline and the instrument will automatically check the connection of each component and switch to Online



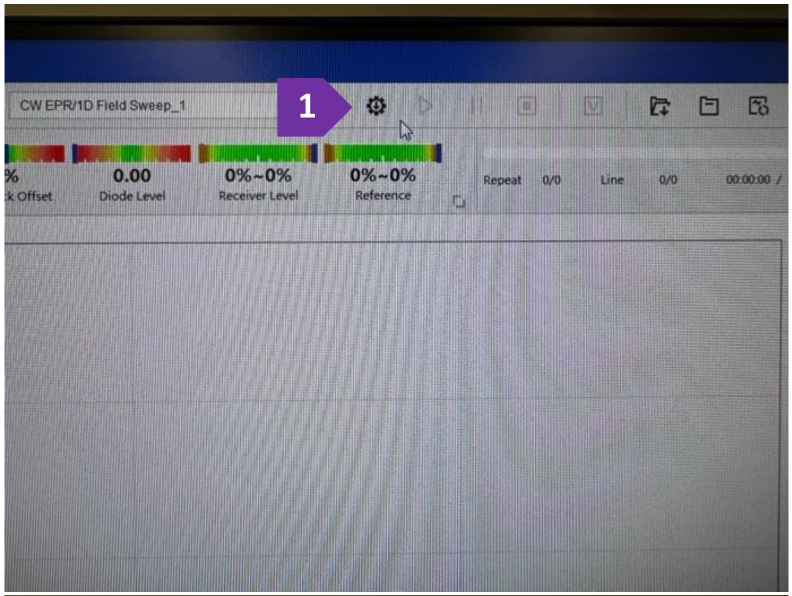


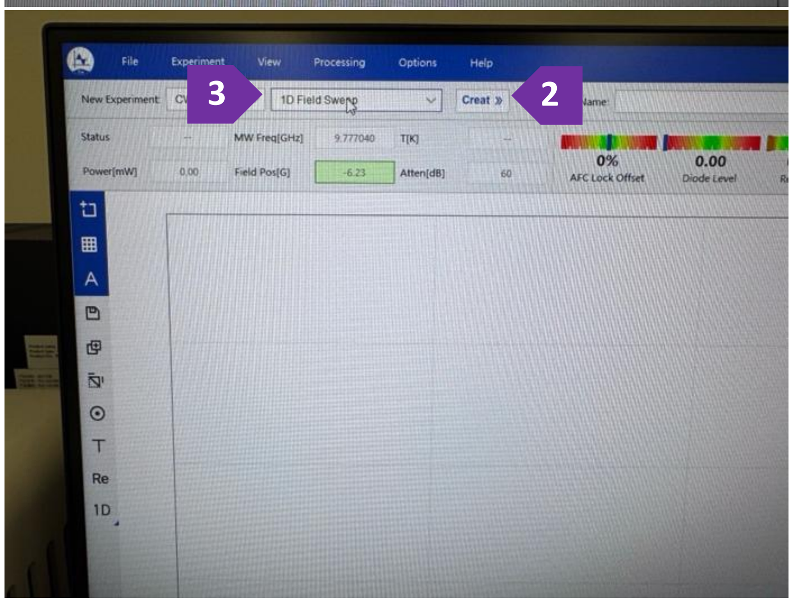
Note: 1. system is “offline”

2. system is “online”

2) Click the “Creat” to create the experiment then click the “activate” button to activate the software. After that, the “activate” button should changed to blue color.

For 1D experiment, 1D field sweep is enough.





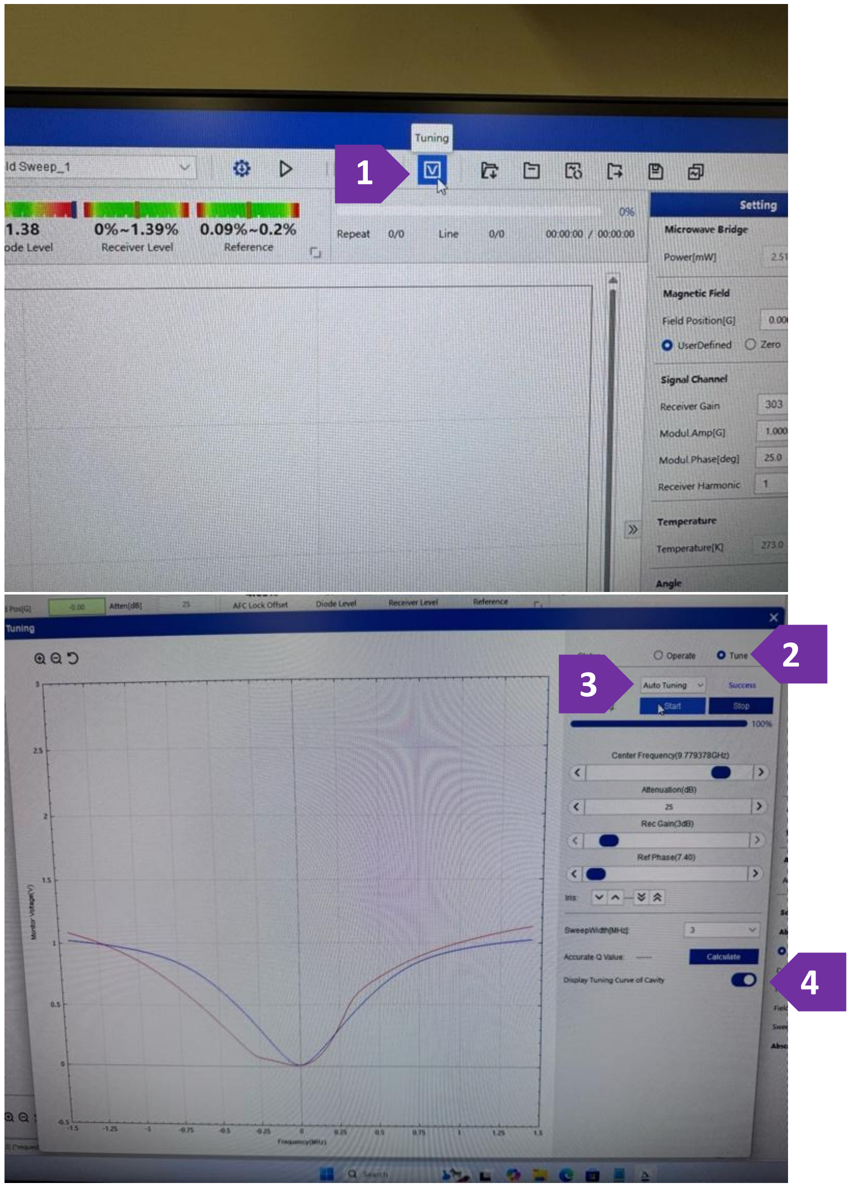
Note: 1. Activate or Deactivate button

2. “Create” button to create experiment

3. Different EPR experiments selection

STEP 5. TUNING

1) After the experiment is successfully activated, click the Tuning button in the experimental operation bar to open the Tuning window. Switch the status from operate to Tune.



Note: 1. Tuning button in the main software interface

2. Switch between "Operate" and "Tune" statue

3. Switch between "Auto tuning" and "Manually Tuning"

4. Display tunning curve

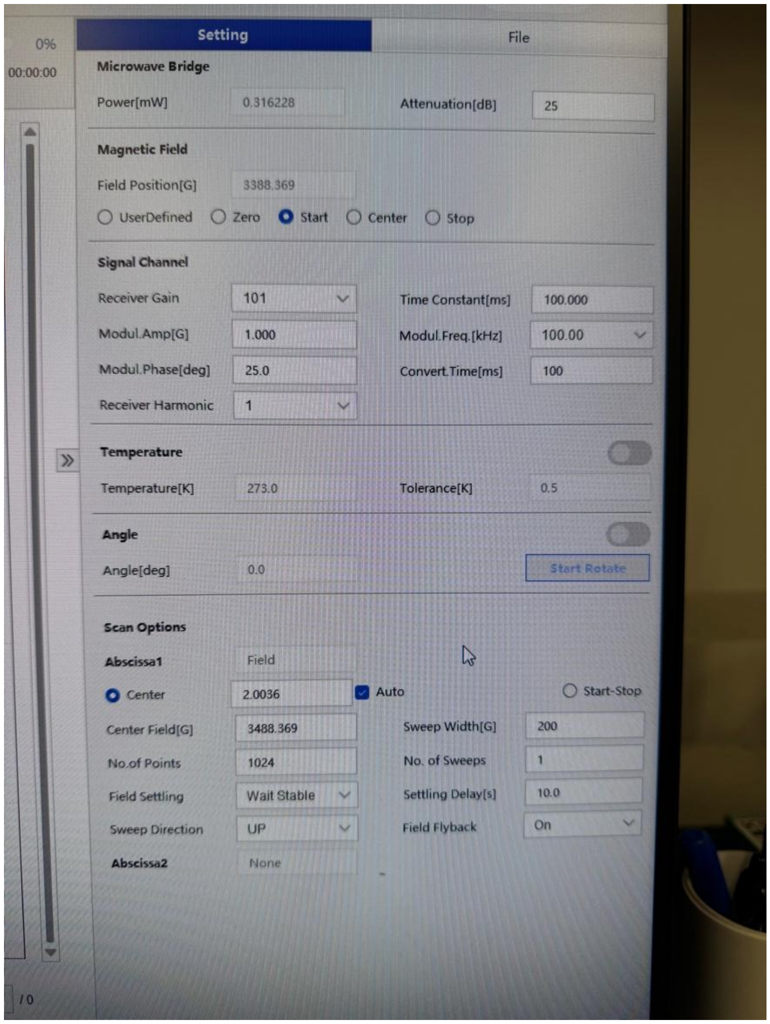
2) Turn on the "display Tuning Curve of Cavity", Adjust the attenuation to around 25 and then change the frequency to find the dip.

3) Select the "Auto Tuning" in tuning type and then click the "start" button to complete auto-tuned.

4) After the auto-tuned, switch the status back to the "operate" and then close the tunning window.

STEP 6. COLLECTING A SPECTRA

Go back the main software window, click the setting panel in the right of the window.



the above picture of parameters could be used as a starting point.

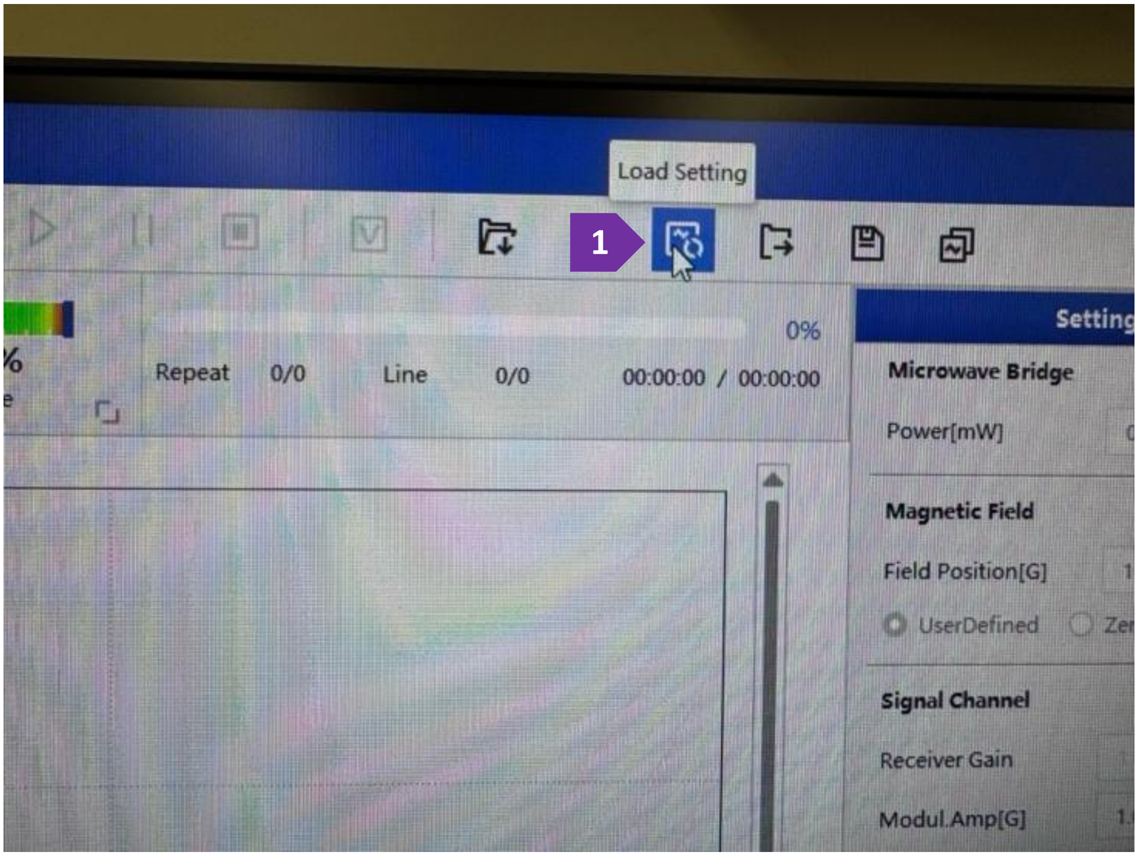
Usually, the attenuation is larger than 16 dB. The Modul Amp is between 0.5 and 3.

To find the signal, you need to change the center field and sweep width.

Please allows the setting delay to 10s for the field sweep.

When everything is set up, click the “Start” button to start the data collection. During the acquisition, all the condition monitors, such as AFC lock Offset, Diode level, Receive level and Reference should be both in the middle.

Note: If you want to use previously parameters, after creating a new experiment, please click the load button to load the previous experimental parameters.



Note: 1. Load setting from previous experiment file

STEP 6. SAVING THE DATA

As a .epr File

File => Save as… => My Computer => D disk => Data => User's name folder

** The software saves two files: one for the spectra with the parameters and one picture of the spectra.

As an ASCII file

File => Export… => Destination (notice the file type is ASCII format)

Open this file in Excel and it is delimited with tabs; format as necessary.

ENDING WORK

(1) After your experiment, bring the attenuation back to 60 dB.
(2) Change magnetic field position to 50 Gauss.
(3) Click the deactivate button, the icon should turn gray.
(4) Click the Online, switch it to offline mode.
(5) Move your sample from the spectrometer.
(6) Keep desk top clean
(7) Logout from NUcore

TROUBLESHOOTING

Please contact IMSERC staff Dr. Jinlei Cui and Dr. Chris Malliakas when you have issues.

REVISIONS

Use was made of Bruker CIQTEK CW X-band at Northwestern University, which has received support from National Science Foundation (CHE-9871268) and International Institute for Nanotechnology (IIN).

V 1.0 2025/02/16	Release of original version of IMSERC CIQTEK CW X-band V1.0

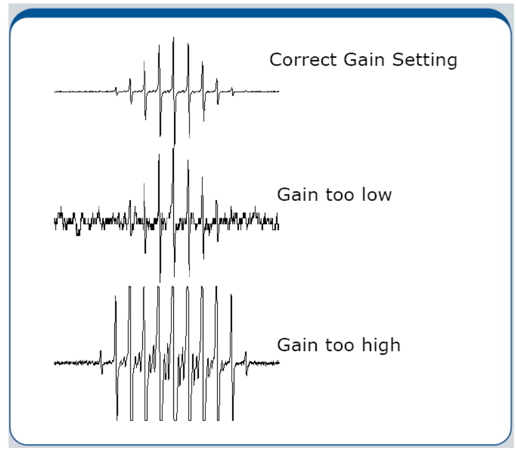
APPENDIX A: HOW TO OPTIMIZE THE PARAMETERS

1) ***Center Field and Sweep Width*** – Center field should be set at the center of your EPR signal and the sweep width should include the signal and enough baseline.

2) ***Receiver Gain*** – Depends on the strength of the EPR signal from your sample. If your signal is saturated lower the Receiver Gain.

Strong Signal = Low R.G.

Weak Signal = High R.G.



3) ***Power Level***

Perform a Power Sweep

If you need, you can do a 2D field-power experiment to find the best power set up.

4) ***Modulation Amplitude*** – Helps decrease low frequency noise (i.e. thermal fluctuations, electronic vibrations, drafts in the room, etc.)

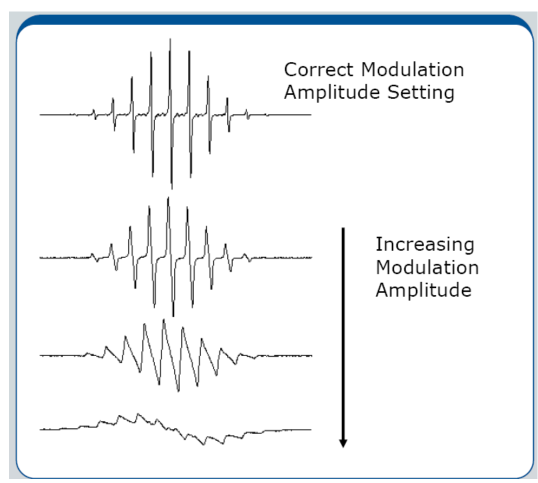
→ Compromise between sensitivity and resolution

→ If too large => Will distort/broaden signal

If too small => Disadvantage because S/N will not be as good

→ This value is sample dependent

* The more hyperfine splitting, the smaller the value should be



5) ***Time Constant*** – filters out high frequency noise (slows down the response time of the spectrometer)

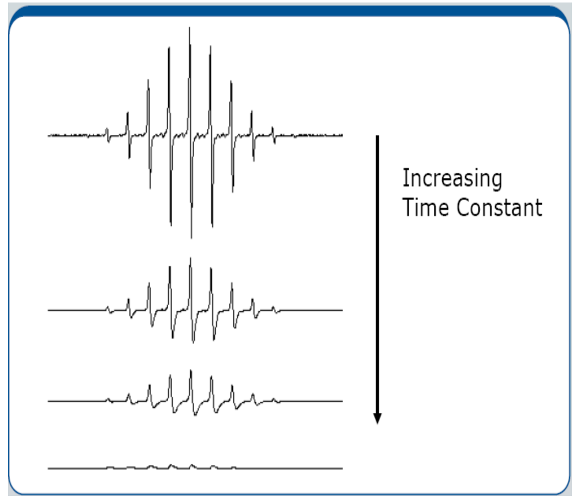
→ Set to 1/10 the time it takes to sweep through the narrowest line of interest

→ Too Low => Get a lot of noise

→ Too High => Filters out your EPR signal

**Want to increase for weak signals. If a long Time Constant is used use a slower scan rate.

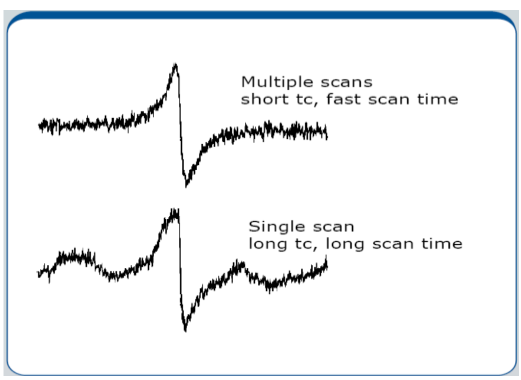
**For very narrow lines increase the Time Constant by 2 and increase the number of data points (Resolution in X).



6.) ***Conversion Time*** – The amount of time the AC to DC converter spends at each point.

→ Rule of Thumb: Set = to the Time Constant

7.) ***Number of sweep (i.e. Signal Averaging):*** The baseline quality of your spectrum is improved by accumulating several short scans rather than taking one long scan.



Using appropriate experimental parameters is critical for obtaining a high-quality EPR spectrum.

Here are some tips for optimizing EPR signal.

(1) Modulation amplitude

Usually, when modulation amplitude is smaller than the linewidth of sample signal, the SNR increases with increasing modulation amplitude. The caveat is that the signal may broaden as the modulation amplitude becomes larger, leading to distortion in spectrum. For spectra with narrow peaks, smaller modulation amplitude leads higher resolution of individual peaks. To obtain maximized signal strength without distortion, the modulation amplitude should be smaller than 1/3 of the sample linewidth.

(2) Modulation frequency

To minimize the noise from microwave bridge around 1/f, most X-band EPR experiment choose to work with 100 kHz modulation amplitude. For samples with a relaxation time larger than 10 μs (1/100 kHz), high frequency may induce additional artifacts such as broadening. In practice, using 100 kHz is appropriate for samples with 35 mG linewidth; however, for sample with extremely narrow linewidth, a slower frequency is commended to avoid signal distortion.

(3) Time constant

Time constant is a parameter for adjusting the sampling window on the lock-in amplifier. If choosing properly, time constant can be used as a filter to remove noise. A small time constant leads to higher resolution but also more noise. A larger time constant results in less noise. If time constant is too large and the scan time is too short, signal may be lost, leading to distortion in spectrum. Usually, time constant is chosen to be smaller than 1/10 of the narrowest peak in a spectrum.

(4) Sampling time and points

The equation for computing acquisition time is:

Acquisition time = number of points × time constant × number of scans

Increasing the number of scans enhances higher signal-to-noise ratio. Using more points and longer scan time increases the resolution of spectra.

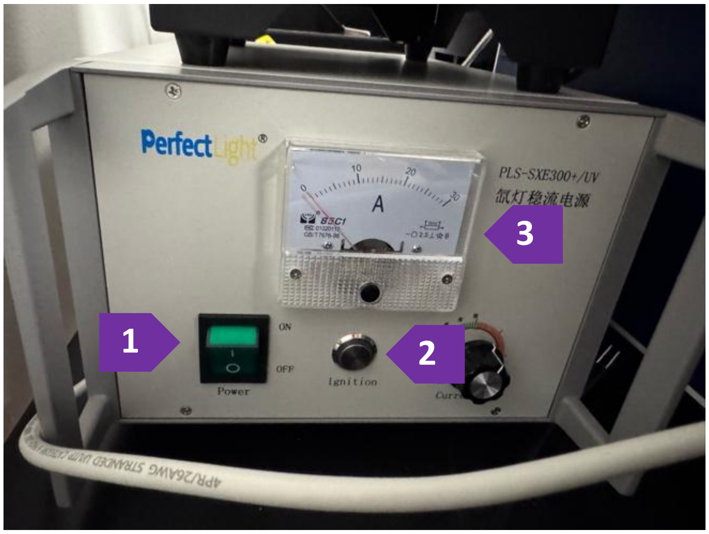
(5) Microwave power

The intensity of EPR signal is proportional to the square root of power of microwave ($\sqrt{P}$). However, excessive microwave leads to saturation of EPR signal, and the relation between signal intensity and microwave power is no longer linear. A 2D Field-Power Sweep experiment may be useful for choosing the optimal microwave power.

APPENDIX B: LIGHT SOURCE OPERATION

To start the light source, please take the following steps:

1) Turn on the power supply.
2) Press the ignition button for 3 -5 seconds. The light will be on, and then immediately release the ignition button. The current will be around 15A. The current should be in the range between 13-20A.

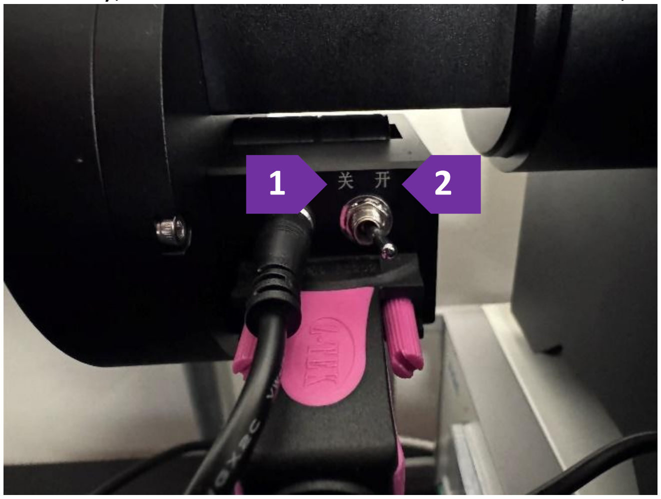


Note: 1. Power button

2. Ignition button

3. current gauge

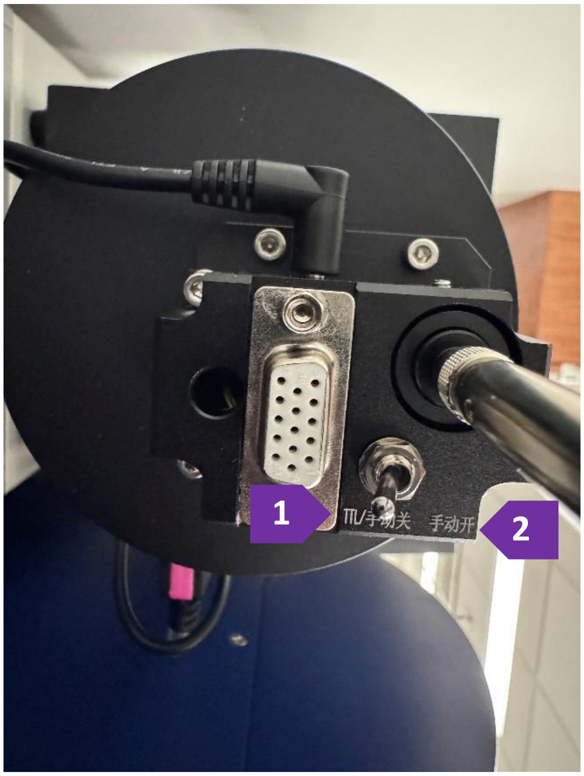
3) Currently, there is no filter in the filter wheel switch, so just turn it on.



Note: 1. Power button status “Off”

2. Power button status “On”

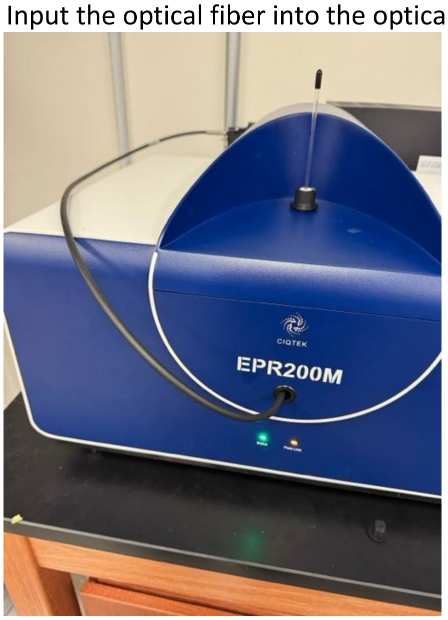
4) Turn on the electronic shutter module manually. You should find a white light from the end of the optical fiber.



Note: 1. status “Close”

2. status “Open”

5) Input the optical fiber into the optical window of spectrometer.



Note: optical filter can be installed in the filter wheel switch. To switch different filter, please open the spectrometer configuration, and then open the optical filters. You need to chose the correct position for the installed or wanted filter.

To shut down the light source, please take the following steps.

(1) Turn off the electronic shutter module manually.
(2) Turn off the power supply.

Precautions:

(1) Do not move the light source while it is operating
(2) Do not look directly at the light output port.
(3) The light source operating current range is 13 A to 20 A. Do not exceed this range.
(4) Wear UV protection glasses when using Xenon lamps.
(5) Do not look directly at the fiber optic output to avoid eye injury.

APPENDIX C: DIFFERENT TYPE OF EPR EXPERIMENT

Note: The CIQTEK EPR can do more types of EPR experiment. Please refer to the following possible experiments by CIQTEK manual.

5.Supported Experiments

5.1 1D Field Sweep

A simple 1D field sweep is the most widely practiced EPR experiment. The data is collected by recording the EPR signal at different external magnetic field.

Experimental parameters

A general starting protocol for creating an experiment is described in **Chapter 3**. Once the experiment is created and activated, set the experimental parameters in the parameter panel. Some typical values are given in **Fig. 5.1**.

Fig 5.1 Parameter setting.

The parameter panel includes: Microwave Bridge, Magnetic Field, Signal Scan, Temperature, Angle and Scan Options.

Microwave Bridge:

Power [mW]: the power of microwave. The microwave power is can be adjusted by attenuation input.

Attenuation [dB]: the attenuation is an indicator of microwave power, where

CIQTEK

higher attenuation corresponds to lower microwave power. EPR200M has an attenuation range of 0-60 dB.

Magnetic Field:

Field Position [G]: The static magnetic field position. Four positions are available: the zero field (0 Gauss), and three other options, which are the **Start**, **Center,** and **Stop** values set in **Scan Options** below.

Signal Scan:

Receiver Gain: The receiver gain determines the signal (and noise) strength at the receiver end.

Time Constant [ms]: Time constant functions as a filter to remove noise.

Modul. Amp. [G]: Modulation amplitude. The modulation amplitude is affected by probe and modulation frequency. The operational range on EPR200M is 0-10 Gauss.

Modul. Freq. [kHz]: Modulation frequency. The range of modulation frequency is 10~100 kHz.

Modul. Phase [deg]: Modulation phase. The modulation phase must be adjusted based on Modulation Frequency, Receiver Harmonic, etc. The software will choose the optimal modulation phase for given Modul. Amp. And Modul. Freq. In CW experiment, the signal should be optimized so that the majority is aligned with the real axis (Re) and minimum signal falls on the imaginary axis (Im). If not, adjust this parameter to further optimize the phase.

Convert. Time [ms]: Conversion time. Conversion time is the time duration to step between two neighboring magnetic field values. Adjust this parameter to control the sweep rate during an experiment.

Receiver Harmonic: The lineshape of the acquired spectrum. Currently, the software supports the first- and second-derivative lineshapes.

Temperature:

Switch: Connect the temperature controller to bridge control

Temperature [K]: Experimental target temperature.

Tolerance [K]: Determines the range of temperature. Once tolerance is switched on, no experiment will proceed if the temperature is out of range.

Angle:

Switch: Connect the goniometer to bridge control

Angle [deg]: Set the angle of sample. To rotate the sample, give an input then click the Start Rotate button.

Scan Options:

Abscissa1: Magnetic Field

Center: Using the Center field and Sweep Width to determine the range of sweep. If choosing Auto, the software will calculate the center field based on the given g-value (default g = 2.00).

Start-Stop: Using the Start and Stop magnetic field value to determine the range of sweep.

No. of Points: Number of magnetic field points。

No. of Sweeps: Number of scans collected。

Field Settling: Field stabilizing mode. In Wait Stable mode, the readout must be same as the expected field values before start sweeping. In Given Delay mode, sweeping starts right after the Settling Delays.

Sweep Direction: The direction of magnetic field sweep. Up: starting from low field to high field. Down: starting from high field to low field.

Field Flyback: If turned on, the magnetic field will return to initial value.

Using appropriate experimental parameters is critical for obtaining a high-quality EPR spectrum. Here are some tips for optimizing EPR signal.

(1) Modulation amplitude

Usually, when modulation amplitude is smaller than the linewidth of sample signal, the SNR increases with increasing modulation amplitude. The caveat is that the signal may broaden as the modulation amplitude becomes larger, leading to distortion in spectrum. For spectra with narrow peaks, smaller modulation amplitude leads higher resolution of individual peaks. To obtain maximized signal strength without distortion, the modulation amplitude should be smaller than 1/3 of the sample linewidth.

(2) Modulation frequency

To minimize the noise from microwave bridge around 1/f, most X-band EPR experiment choose to work with 100 kHz modulation amplitude. For samples with relaxation time larger than 10 μs (1/100 kHz), high frequency may induce additional artifacts such as broadening. In practice, using 100 kHz is appropriate for sample with 35 mG linewidth; however, for sample with extremely narrow linewidth, a slower frequency is commended to avoid signal distortion.

(3) Time constant

Time constant is a parameter for adjusting the sampling window on the lock-in amplifier. If choosing properly, time constant can be used as a filter to remove noise. A small time constant leads to higher resolution but also more noise. A larger time constant results in less noise. If time constant is too large and the scan time is too short, signal may be lost, leading to distortion in spectrum. Usually, time constant is chosen to be smaller than 1/10 of the narrowest peak in a spectrum.

(4) Sampling time and points

The equation for computing acquisition time is:

Acquisition time = number of points × time constant × number of scans

Increasing the number of scans enhances higher signal-to-noise ratio. Using more points and longer scan time increasing the resolution of spectra.

(5) Microwave power

The intensity of EPR signal is proportional to the square root of power of microwave ($\sqrt{P}$). However, excessive microwave leads to saturation of EPR signal, and the relation between signal intensity and microwave power is no longer linear. A 2D Field-Power Sweep experiment may be useful for choosing the optimal microwave power.

Procedure

See **Chapter 3**

5.2 1D Time Sweep

1D Time Sweep is a 1D time scan experiment. In 1D Time Sweep, the signal intensity at a single locked magnetic field is monitored over time.

Applications

This experiment is designed for monitoring transient EPR signal with extremely short lifetime.

Experimental parameter setup

Most of the parameters are setup in the same way as described in **Section 5.1**. The following section is focused on the setup of time resolution.

Resolution [ms]: The resolution of time step. In a 1D time sweep, this is set to the same value as Convert. Time.

No. of Points: Number of time points in an experiment.

No. of Sweeps: Number of scans.

Fig 5.2 1D Time Sweep parameter setup.

Procedure

Determining the field value to be monitored. Measuring a 1D Field Sweep for sample is helpful. For 1D Field Sweep experiment, see **Section 5.1**.

(1). Click on New Experiment the choose CW EPR-1D Time Sweep. Click Create to finish.

(2). In Magnetic Field panel, set Field Position. This is the field value to be monitored.

Fig 5.3. Setting up static field for 1D Time Sweep.

(3). Setting parameters. Most parameters are similar to the settings in a 1D Field Sweep. The parameters in Scan Options panel require some prior knowledge regarding the time scale or kinetics of the measured sample.

(4). Press Start.

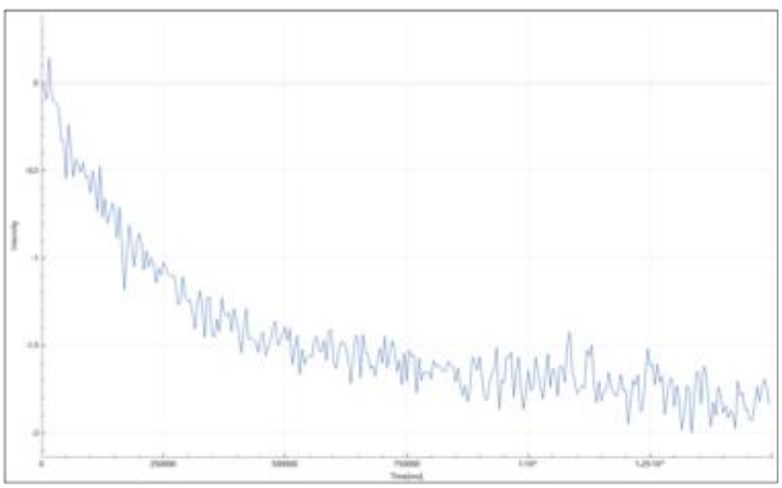


Fig 5.4 Experimental results from a 1D Time Sweep experiment of a transient radical.

(4). Save the experimental data.

(5). Data fitting. The experimental results can be fitted using an exponential decay curve to

58

obtain the half-life of the spin species. A fitting example is given in **Fig 5.5**.

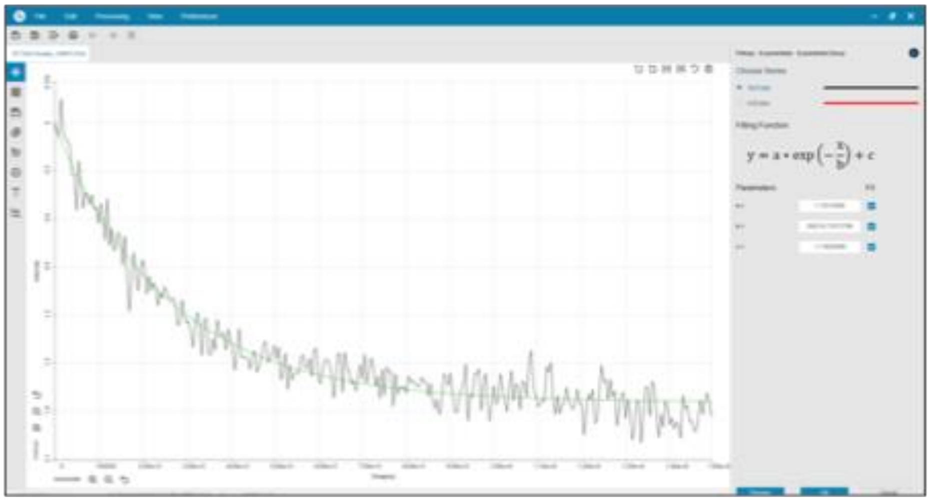


Fig 5.5 Fitting the lifetime of a 1D Time Sweep data.

◆ **Caution**

(1) In 1D time sweep, the users should have prior information of the EPR spectrum of the sample for choosing a specific value to be monitored. If optical irradiation, heat, or any additional chemical is needed to produce a decaying EPR signal *in-situ*, it is recommended to obtain a 1D Field Sweep before these conditions. For samples with increasing EPR signal, a 1D Field Sweep is recommended after the 1D Time Sweep to determine the end-point signal intensity. For transient species, spin trap techniques may increase the observation window.

(2) In a 1D Time Sweep, the time constant can be increased to minimize noise. However, an inappropriate time constant may also cause additional artifacts in data.

(3) For samples with strong signal, adjust gain before starting 1D Field Sweep.

(4) When the spectrum is narrow, the peaks may shift due to inhomogeneity; therefore, 2D experimental could be another option.

(5) Before starting experiment, make sure the static field is set to the appropriate value.

(6) To optimize the accuracy of experimental data, turn on the spectrometer and set the static field to a non-zero value for an hour to equilibrate the electronics in the instrument.

5.3 2D Field-Power Sweep

2D field-Power Sweep is an experiment for sweeping the sample response to microwave of different power. In a non-saturating regime, EPR signal is proportional to the square root of microwave power (√P). When the microwave power is too strong, the transition frequency is larger than $1/T_1$ of the spins. If is referred to as saturation. In a saturating regime, EPR signal intensity does not increase linearly with microwave power. The data set obtained from a 2D Field-Power Sweep can also be used for measuring the T_1 of the spins. For signal with homogeneous broadening, the linewidth increases with microwave power, the T_2 relaxation time can be obtained by monitoring the change of linewidth under different microwave power.

The theory stems from the classical Bloch equation, and the relation between the max-to-min intensity of signal peak and microwave power is described by:

$$I_{\mathrm{pp}}(P) = I_0 \frac{\sqrt{P}}{(1 + P/P_{1/2})^{b/2}}$$

where I_{pp} is the signal intensity, I_0 is a proportional constant, P is the microwave power, and $P_{1/2}$ is the power at half saturation (s), and b is the inhomogeneous broadening. Saturation is calculated by equation:

$$s = \frac{1}{1 + \gamma^2 {B_1}^2 T_1 T_2}$$

where γ is the gyromagnetic ratio ($\gamma = -1.7609 * 10^{-2}\mathrm{ns}^{-1}\mathrm{Gauss}^{-1}$ at $g = 2$), and B_1 is the amplitude of the orthogonal field from the microwave irradiation. B_1 is can be calculated by equation $B_1 = \alpha\sqrt{\mathrm{P}}$, where α is a power constant and is relevant to probe quality. At half saturation ($s = 1/2$), $T_1 = \frac{1}{\gamma^2 {B_1}^2 T_2}$.

From the integrated form of Bloch equation, the relation between signal linewidth (W_{pp}) and T_2 is described by equation

$$W_{\mathrm{pp}} = \frac{2}{\sqrt{3}\gamma T_2 s^{1/2}}$$

- **Caution**

The Q-factor of each resonator may vary; an alternative method to obtain conversion factor is to measure the T_1 and T_2 of a sample then calculate the value using equation: $\alpha = \sqrt{\frac{1}{\gamma^2 P_{1/2} T_1 T_2}}$.

The 2D Field-Power Sweep can be used as an optimization experiment for collecting a

60

reliable 1D Field Sweep to ensure that signal is not saturated or distorted by strong microwave irradiation.

Reference: Mailer, C., T. Sarna, H.M. Swartz, J.S. Hyde. *J. Magn. Res.*: 25, 205, 1977.

Application

(1) The intensity of EPR signal does not always increases linearly with microwave power. Too much power leads to saturation and eventually loss of both signal intensity and resolution. For a sample with unknown features, the first EPR experiment should be a 2D Field-Power Sweep for optimizing the microwave power.

(2) Saturation behavior is related to relaxation behavior, and both T_1 and T_2 are informative of the environment around the spin center.

Fig. 5.6 2D Field-Power Sweep Experimental Parameter setup.

Experimental parameters

Abscissa1: Magnetic Field.

For setting up parameters related to normal field sweep, use Section 5.1 as reference.

Abscissa2: Microvave Power.

61

Start Atten. [dB]: the starting attenuation value.

Step [dB]: attenuation step size.

No. of points: number of attenuations.

Settling Time [s]: the time delay between two sweeps.

Procedure

(1). Use the instructions in Section 5.1 as a reference to setup center field, sweep width, receiver gain, time constants etc. The receiver gain may saturate at high microwave power and therefore should be adjusted.

(2). Click New Experiment then create a CW EPR-2D Field-Power Sweep. Click Create button to finish.

(3). Setting Parameter. Most of the experimental parameters can be set up referring to the 1D Field Sweep experiment. The parameter settings in Abscissa2 should be adjusted according to the sample characteristic.

(4). Click Start to start acquisition.

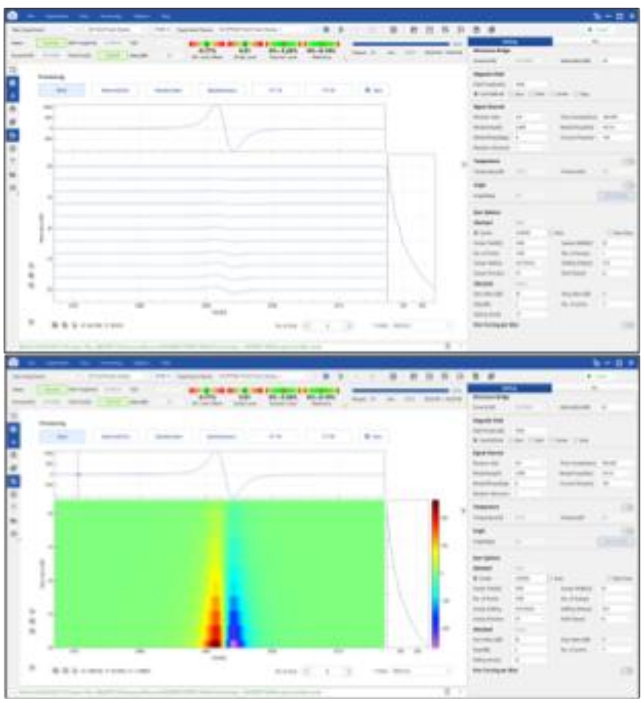


Fig 5.7 The 2D Field-Power Sweep of a DPPH sample.

(5). Save data.

Data processing

Under linear regime, EPR signal intensity increases linearly with the square root of microwave power. Under high power, the transition rate may be faster than the spin-lattice relaxation $1/T_1$, the signal enhancement is no longer linear.

The 2D data set can be processed using P-half fitting method, which is described by the software manual.

◆ **Caution**

The microwave field strength and Q value vary in different resonators. If precise calculation is needed, contact engineers of CIQTEK for calibration parameters.

5.4 2D Field-Delay Sweep

2D Field-Delay Sweep is a program which acquires a spectrum after a given delay time for studying the change of EPR signal over time.

Application

For samples with two or more paramagnetic species, using 2D Field-Delay Sweep is more appropriate.

Experimental parameters

Abscissa 1: Magnetic Field. For setting up parameters related to normal field sweep, use Section 5.1 as reference.

Abscissa2: Time.

Delay[s]: delay time. The delay between each field sweep.

No. of Points: the number of field sweep needs to be acquired.

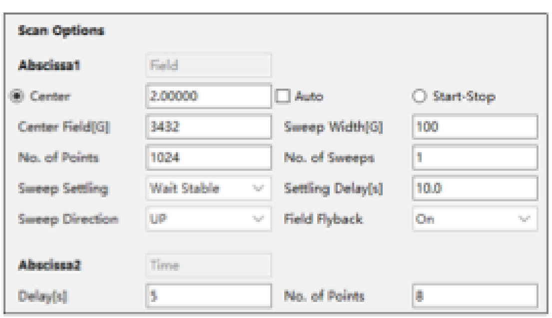


Fig 5.8 2D Field-Delay Sweep experimental parameter setup.

Procedure

(1). Click New Experiment then CW EPR-2D Field-Delay Sweep experiment. Click Create to finish.

(2). Parameter setup. Most of the parameters are similar to 1D Field Sweep.

(3). Click Start to start experiment.

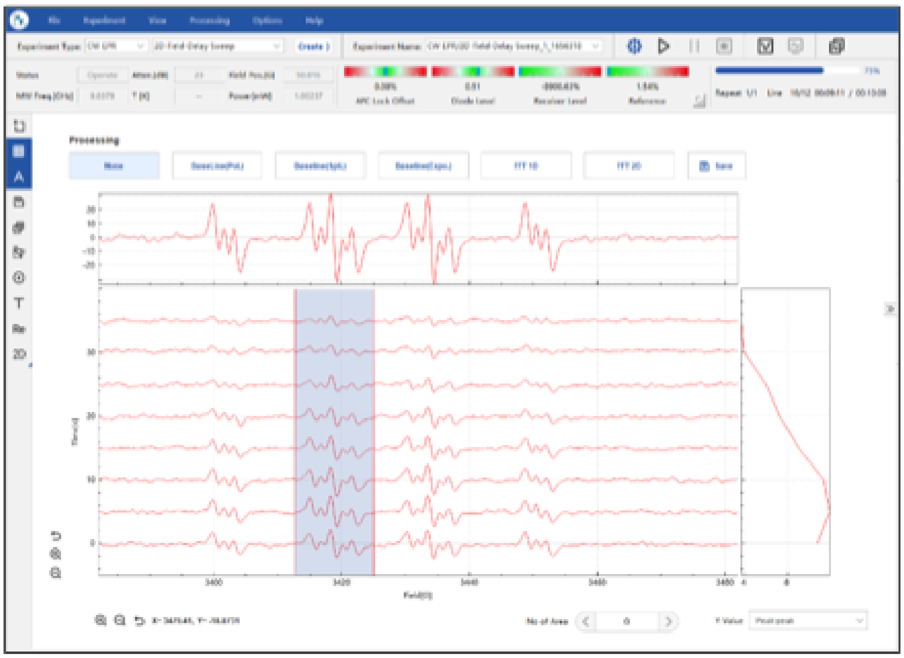


Fig 5.9 The 2D Field-Delay Sweep of DMPO-NH_2 radical.

(4). Save data.

◆ **Caution**

(1). When the kinetics of reacting species is faster than sweep time, using 1D Time Sweep is more appropriate. For species with more than one EPR signals at different magnetic field values, performing 1D Time Sweep at several field is or using 2D Time-Field Sweep is more appropriate.

(2). When the sweep field is wide enough, and the center field is at g -value of the paramagnetic species, the user may start 2D Field-Delay Sweep without using a 1D Field Sweep. When producing a stable radical, a 1D Field Sweep can be used for optimizing experimental setup.

5.5 2D Field-Modul. Amp. Sweep

2D Field-Modul.Amp. Sweep is a program for collecting a spectrum at each different modulation amplitude. This experiment can be used as an experiment for optimizing modulation amplitude for collecting a 1D Field Sweep. The choice of modulation amplitude affects the line shape and intensity of EPR signal. Using large modulation amplitude increases signal intensity; however, if the amplitude is too large compared to the signal linewidth, the peak is broadened and may have reduced intensity. In general, if the sensitivity is not a limiting factor in data collection, using smaller modulation field increases signal resolution.

The modulation field can also be calibrated using this experiment. The calibration file for each resonator is provided by our engineers.

Application

2D Field-Modul.Amp. Sweep can be used for optimizing the modulation amplitude.

Experimental parameters

Abscissa1： Magnetic Field. Use **Section 5.1** as a reference for choosing experimental parameters.

Abscissa2： Modul. Amp.

Start Value [G]： The starting value of the modulation amplitude.

Step [G]: Step size of modulation amplitude.

No. of Points: Number of steps.

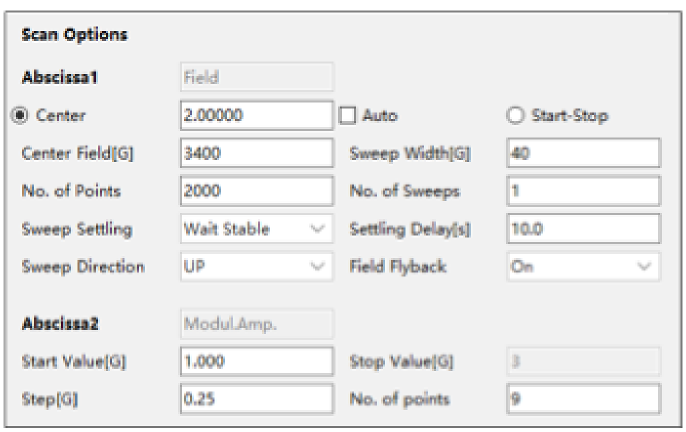


Fig 5.10 2D Field-Modul.Amp. Sweep Experimental Parameter setup.

65

Procedure

(1). Use the instructions in **Section 5.1** as a reference to setup center field, sweep width, receiver gain, time constants etc.

(2). Click New Experiment then create a CW EPR-2D Field-Modul.Amp. Click Create button to finish.

(3). For more scan options, use **Section 5.1** as reference.

(4). Click Start to start acquisition.

(5). Save data.

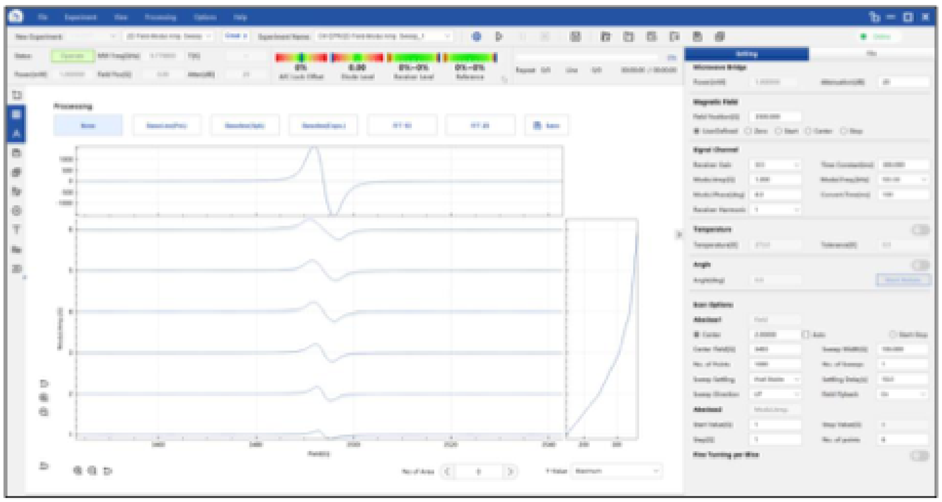


Fig 5.11 A 2D Field-Modul.Amp. Sweep data set from DPPH radical.

5.6 2D Field-Temperature Sweep

Temperature plays a critical role in acquiring a good spectrum. This program allows users to obtain information regarding the thermodynamics and kinetics of a system by collecting spectra at a range of temperatures. In this experiment, uses should be aware that If the signal is sensitive to temperature, it is best to adjust receiver gain to avoid saturation at all temperatures.

The experimental temperature is controlled by a temperature controller. The temperature controller uses the PID feedback loop and therefore cannot reach the target temperature immediately. To guarantee that each spectrum is acquired at the exact temperature, set appropriate tolerance and time delay between each temperature point. When the temperature is stabilized within the given range, the program acquires a spectrum and start changing temperature again. Using a large tolerance can reduce the total acquisition time. While the temperature is stabilizing, maintain good gas flow and heat exchange in the cavity.

Application

This program is useful for temperature-sensitive species.

Experimental parameter setup

Abscissa1： Magnetic Field. Use **Section 5.1** as a reference for choosing experimental parameters.

Abscissa2： Temperature

Start Temp.[K]： The starting temperature.

Step [K]: temperature step size.

No. of Points: number of steps.

Setting Time [s]: the time delay between two sweeps.

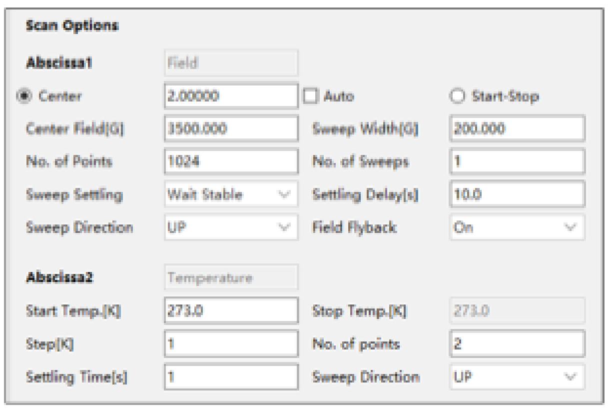


Fig 5.12 2D Field-Temperature Sweep Experimental Parameter setup.

Procedure

(1). Use the instructions in **Section 5.1** as a reference to setup center field, sweep width, receiver gain, time constants etc.

(2). Click New Experiment then create a CW EPR-2D Field-Temperature Sweep.

(3). For more scan options, use Section 5.1as reference.

(4). Click Start to start acquisition.

(5). Save data.

5.7 2D Field-Angle Sweep

In single-crystal samples, peak position shifts with changing angle between the crystal axis and the magnetic field. Users can simulate several spectra collected at different angles to analyze the symmetry and anisotropy of the paramagnetic species in crystal.

2D Field-Angle Sweep is an automated rotation experiment. The program rotates a goniometer mounted on top of the EPR probe across a range of angles and collects a spectrum at each different position.

Application

2D Field-Angle Sweep can be used for samples with resolved anisotropy, mostly single crystal, such as diamond. The shift in peak position is usually periodic.

Experimental parameter setup

Abscissa1: Field.

For setting field sweep parameters, use the procedure in **Section 5.1.** This section is focused on setting the parameters for rotation.

Abscissa2: Angle

Start Angle [deg]: This is the angle of the first sweep.

Step [deg]: The step size of rotating angle.

No. of Points: The number of angles/sweeps.

Fig 5.13 2D Field-Angle Sweep parameter setup

Procedure

(1). Use the instructions in Section 5.1 as a reference to setup center field, sweep width, receiver gain, time constants and etc.

(2). Click New Experiment then create a CW EPR-2D Field- Angle Sweep. Click Create button to finish.

(3). For more scan options, use **Section 5.1** as reference.

(4). Click Start to start acquisition.

(5). Save Data.

Fig. 5.14 A 2D Time-Field Sweep data set of a single-crystal.

5.8 2D Time-Field Sweep Experiment

2D Time-Field is an automated experiment that acquire a time sweep at different field. This experiment is used for measuring the change in spectrum over time at a range of field values.

Application

This program can be used for monitoring the fast kinetics of multi-spin systems.

Experimental parameter

Abscissa1: Time

Resolution [ms]: the resolution of time step.

No. of Points: Number of time points in an experiment.

No. of Sweeps: Number of scans.

Abscissa2: Magnetic Field

Start Field [G]: the first static field to be monitored.

Stop Field [G]: the last static field to be monitored.

No. of Points: the number of static fields.

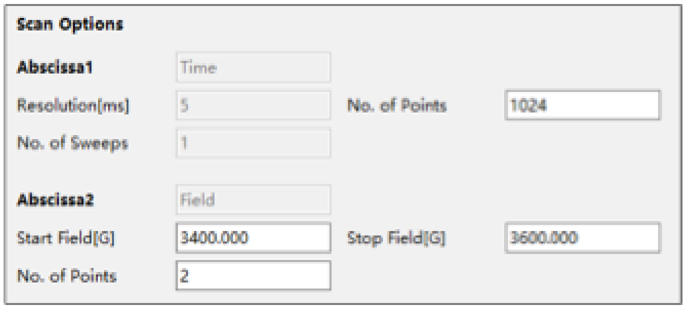


Fig 5.15 2D Time-Field Sweep experimental parameter setup.

Procedure

(1). Click New Experiment then create a CW EPR-2D Time-Field Sweep. Click Create button to finish.

(2). For more Scan Options, use Section 5.2 as reference.

(3). Click Start to start acquisition.

(4). Save data.

◆ **Caution**

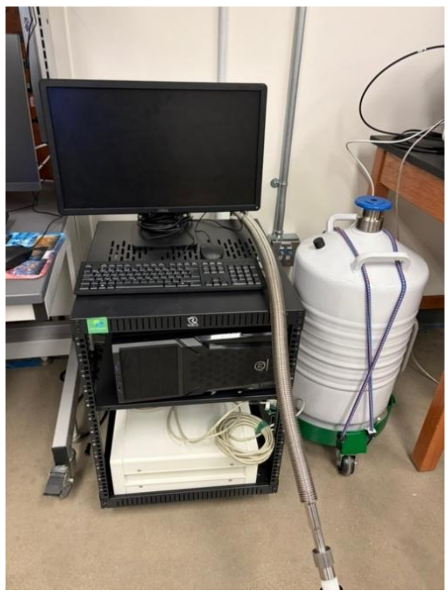
Using 2D Time-Field Sweep for reversible reaction is highly recommended. Such reactions are usually triggered by an external source, such as optical signal etc.

APPENDIX D: VARIABLE TEMPERATURE EXPERIMENT

Note: The CIQTEK EPR can do more types of EPR experiment. Please refer to the following possible experiments by CIQTEK manual.

If you need use VTU 3 for variable temperature, please contact Dr. Jinlei Cui for additional training.

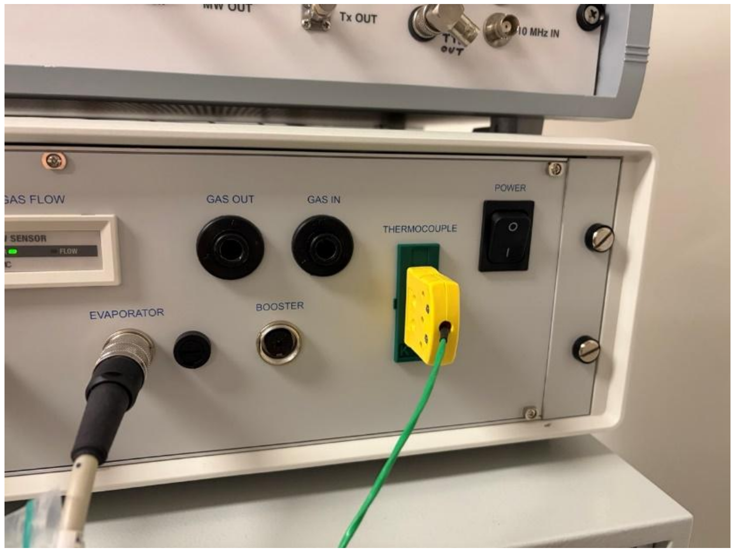
Low temperature is necessary for EPR to enlengthen the spin-lattice relaxation time of electron, enhance the signal intensity and freeze the dynamics of electron. Currently, the VTU 3 is connected with the loop resonator, which includes controller, finger-dewar and LN_2 tank. It enables the experiment temperature from 100k to 300k. To do the VTU experiment, please do the following steps.



Portable VTU Station

(1) fill the LN2 tank in the cryogen dock station

(2) turn on the VTU controller and turn on the computer. if the LN2 tank is empty, it will show multi errors. The errors will disappear when LN2 is refilled.

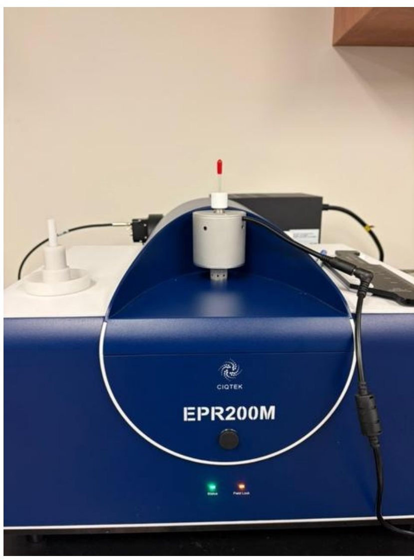


(3) slowly re-cap the LN2 tank with the transfer-line. The LN2 will boil off quickly in the beginning. (do not forget the o-ring)

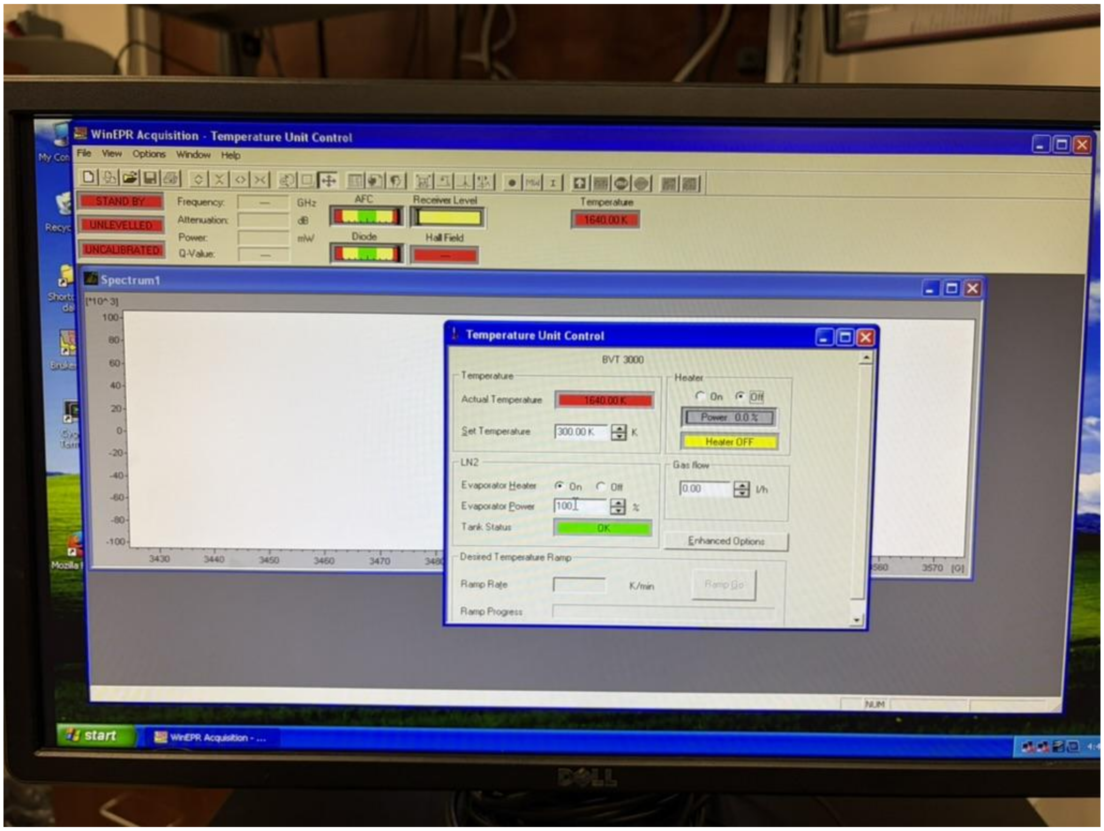
(4) connect the figure dewar with LN2 tank transfer line.

(5) Connect the heater line and thermal couple line. (the cable are connected to lakeshore thermal controller)

(6) Connect the power cable for the top heater adapter. (supply by the voltage transformer)



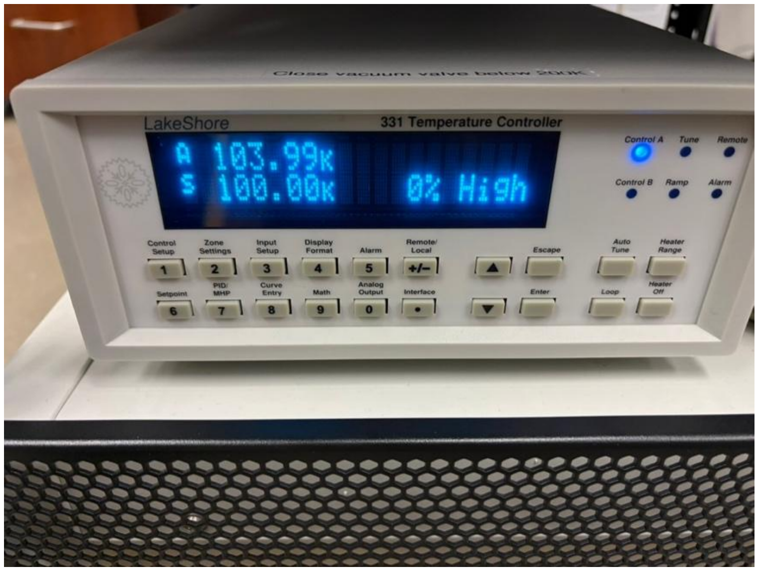
(7) Open the software "Bruker EMX", in the "file" tab, click the "new experiment". Then open "Temperature control unit" in the "view" tab. (ignore the errors).



(7) Click “on” in the evaporator “heater”, input “100” in the evaporator power.

(9) The temperature in the software is not correct. Instead, we use a lakeshore thermal controller to monitor and set the temperature. So, ***do not*** turn on the heater in the EPR software window.

(10) Turn on the lakeshore thermal controller (power button is in the back). In the thermal controller, click the setpoint, input the set temperature number and then click “enter”. Then click the “heater range”, use “up” and “down” arrow to chose “high” for heater range, then click”enter”.



For the different temperature, the following table could be used a good reference for setting up.

Set-point (k)	**Evaporator power**	**Power of heater in Lakeshore**	**Heater Range in Lakeshore**
100	100%	2%	High
125	40%	39%	High
150	20%	34%	High
175	10%	23%	High
200	10%	34%	High
250	10%	52%	High
275	5%	41%	High

(12) When the temperature is stable, tuning the resonator for your exp.

(13) when VT experiment is done, set the LN2 evaporator heater power to 25, then slowly increase the temperature to 295k by 50k one step, wait until the resonator is totally warm (usually 15 mins).

(14) Change the LN2 evaporator heater power to 0, change the LN2 evaporator heater to off.

(15) click the “heater off” in the lakeshore thermal controller, turn off the lakeshore thermal controller.

(16) disconnect the power for the heater adapter on the top of instrument

(16) close the variable temperature unit.

(17) disconnect the “heater” and “thermal couple” cable.

(18) disconnect the LN2 transfer from finger dewar

(19) disconnect and remove the transfer line from LN2 tank

(20) turn off all the instruments and relocated them to original location.