Using the EPR Spectrometers

Introduction

Note there are five EPR spectrometers in the lab. These machines are different generations of Bruker spectrometers and differ mainly in that two instruments (the EMX and the EMX micro) are run through Windows, whilst the other three machines (2 × Elexsys and the W-band) are run using a UNIX operating system. The operating procedures follow identical principles, but differ slightly in practice.

At first you will practice tuning the spectrometer on an empty cavity (no sample) – the spectrometer should behave ideally under these conditions! Then you will tune the spectrometers with a range of samples, differing in their phase (solid, liquid), polarity of solvent, *etc*. The spectrometer can be decidedly non-ideal with real samples, and you may not be able to critically couple the cavity. With practice you learn which of the instructions below to ignore or adapt in order to tune the spectrometer for your samples!

REMEMBER THAT EPR IS A MAGNETIC RESONANCE TECHNIQUE! It is advisable that you remove your watch and any credit/bank cards to a safe place in the lab before switching on the magnetic field.

Switching the EPR Spectrometers On.

1. Turn heat exchanger on (internal, clean coolant)
2. Turn magnetic field on
3. Turn console on
4. Run console software "Win EPR acquisition" for EMX, "Xenon" for EMX Micro and "XEPR" for Elexsys and W-band
5. The spectrometers should now be switched on and ready to tune.
6. The spectrometer needs to be calibrated for the particular frequency and resonator that are being used. Your demonstrator will show you which file to use for your operating frequency, and how to read it in.

Tuning the EPR Spectrometers: EMX and EMX Micro

1. Open the Microwave Bridge Control Dialogue Box (using **MW Button** on EMX, **Tuning Panel button** on EMX Micro).
2. Switch the Microwave Bridge from **Standby** to **Tune**.
3. Set attenuation to **25 dB**.
4. Adjust the **microwave frequency** (using the slide bar; for large steps click and drag the square, medium steps click inside the bar and small steps use the arrows at either end) until the **dip is centred**.
5. Tune the **signal phase** (using the slide bar) until the dip is symmetrical and has a maximum depth.
6. Optimise the dip using the **Iris** controls.
7. Switch the Microwave Bridge from **Tune to Operate** and readjust the frequency using the slide bar until the AFC meter (Lock offset on Micro) is centred.
8. Increase the **attenuation** (*i.e.* decrease the microwave power) to **50 dB**.
9. Adjust the **bias** using the slide bar to **centre the diode current**.
10. To critically couple the cavity gradually decrease the attenuation down to 0 dB (increase the microwave power) and use the **iris** controls to **re-centre the diode current** if it drifts.
11. Set the attenuation to 10 dB and adjust the **signal phase** in small steps to obtain a local maximum for the diode current.
12. Verify that the cavity is critically coupled by increasing the attenuation in 10 dB steps checking that there is virtually no change in the diode current and the AFC meter (lock offset on Micro).
13. Go to power at which you want to work step by step and if the **lock** moves adjust it with the frequency.
14. With time and changes of temperature, the diode current and lock offset may drift, bring them back using the iris arrows and frequency control (do not adjust them when scanning as this may produce artefacts on the spectrum).

Tuning the EPR Spectrometers: E580 X (X/K band)

1. **Connect to spectrometer**. Go to Acquisition Connect spectrometer (the spectrometer must be switched **on**)
2. **Open Tuning Panel**
3. Switch the Microwave Bridge from **Standby** to **Tune**
4. Set attenuation to 2**0 dB**.
5. Turn **Reference Arm** off
6. Centre the dip with the **Frequency.**
7. Maximise dip by adjusting the **Iris**.
8. Adjust the **Phase** so that the bottom of the dip does not move when you switch between **Reference Arm** on and off.
9. With **Reference Arm** on, switch to **Operate** mode.
10. Set the attenuation to 40 dB and use the **bias** to adjust the diode current to 200 and the **frequency** to adjust the **lock offset** to 0.
11. Reduce the attenuation in 10 dB steps and use the **iris** to maintain a diode current of 200. Adjust the **frequency** to maintain a **lock offset** of 0.
12. At 0 dB find the local maximum of the phase.
13. Go to the power at which you want to work.

Tuning the EPR Spectrometers: E580 Q/S (and E580 X at L band)

Login: xuser
Password: user@xepr
Program: xepr

1. **Connect to spectrometer**. Go to Acquisition Connect spectrometer (the spectrometer must be switched **on**)
2. **Open Tuning Panel**
3. Switch the Microwave Bridge from **Standby** to **Tune**
4. Set attenuation to **30 dB**.
5. Cick **Full Scale** under **Mode Zoom**
6. Find the dip by switching the **Mode Curve Segment** between **Lower, Middle** and **Upper.**
7. Once you have found the dip, click **Zoom To Dip**
8. Using the **Iris** control adjust dip to maximum depth
9. Click **Lock Search**
10. When **Matching** and **Matching Fine** are **0** decrease the attenuation in 10 dB steps to the power you require, and adjust the **Iris** to correct the Matching Fine on the way.
11. . Click **AFC Fine Tuning**

Tuning the EPR Spectrometers: W-band

Login: xuser
Password: user@xepr
Program: xepr

1. First you need to **connect to spectrometer**. Go to Acquisition Connect spectrometer (the spectrometer must be switched **on**).
2. Enter E600 in the window and click OK.
3. Go to Microwave Bridge Tuning.
4. Switch the Microwave Bridge from **Standby** to **Tune** (with bias off).
5. Set attenuation between **16-20 dB** (by clicking the arrows **|** and **|**).
6. Adjust the **microwave frequency** (using the slide bar; for large steps click and drag the square, medium steps click inside the bar and small steps use the arrows at either end) until the **dip is centred**.
7. Switch the Microwave Bridge from **Tune to Operate** (with bias off) and readjust the frequency using the slide bar until the Lock Offset meter is centred.
8. Keeping the **diode** current at **0**, decrease the attenuation (*i.e.* increase the microwave power) step by step move the attenuation to **0 dB** adjusting with the iris coupling when necessary (if the diode moves).
9. Roughly tune the **signal phase** at **16-20 dB** by switching back to **Tune** mode then moving **bias** to centre and toggling between **bias on** and **off.** The dip should be bigger with bias on and in the same position as with the bias off, the position can be adjusted by moving the **phase** (you might also need to increase the bias).
10. Switch the Microwave Bridge from **Tune** to **Operate** (with bias on) and readjust the frequency using the slide bar until the Lock Offset meter is centred (at 0).
11. **Increase attenuation to 60 dB** and adjust **diode to 200** with bias.
12. Keeping the **diode** current at **200**, decrease the attenuation step by step to **10 dB** adjusting with the iris coupling when necessary (if the diode moves).
13. When attenuation is at **10 dB** move **Lock Offset** to **0** with frequency.
14. Fine tune the **signal phase** by moving phase in one direction until **diode** stops increasing.
15. Put to the power at which you want to work step by step and if the **lock** moves adjust it either with the knob on the bridge (W-band) or using the frequency.

May need to repeat all the steps until system is stable.

Recording a spectrum:

1. **Tune** the spectrometer **with sample** tube in place.
2. Set the **sweep width** and the **centre field** (make sure the sweep width is wide enough to record your entire spectrum and leave a baseline on either side of your signal).
3. Set the **microwave power** (in order to determine the optimal power try a few test scans; the signal should increase with the square root of the power until saturation occurs, start with a few mW and reduce as necessary).
4. Set the **receiver gain,** which controls the signal intensity (start with around 10^3 – 10^4 and increase or decrease as necessary; if the spectrum is too intense it will be chopped off at the top and/or the bottom).
5. Set the **modulation amplitude**, which is equivalent to a slit width in optical spectroscopy, *i.e.* the larger the modulation amplitude the greater the intensity of the signal, but the poorer the resolution (start with a large value, *i.e.* 10 G, until you have found the spectrum and then reduce the value until the shape of the spectrum does not change; a modulation amplitude that is too high will give a distorted spectrum).
6. Click the **Run** button to acquire a spectrum; you can enter a **comment** using the comment button (a picture of a head for EMX and EMX micro) or during saving (for the Elexsys and W-band) and then **save** your spectrum.
7. When you are finished, open the Microwave Bridge Control and **switch back to Tune before removing the sample**.

Switching off:

1. Open the Microwave Bridge Control and switch the microwave bridge to **Stand By** and close the Microwave Bridge Control.
2. Carefully **remove the sample** from the microwave cavity.
3. Insert an upper **collet blank plug**.
4. **Exit** the acquisition program.
5. Turn off the **magnet power supply**.
6. Turn off the **console**.
7. Turn off **heat exchanger**.
8. Record your EPR samples in the **logbook**.

Common Problems:

1. No Cavity Dip

- Cavity could be under- or over-coupled. Check the microwave frequency where you would normally expect the cavity to resonate and then adjust the iris screw for better coupling. This can occur when working with lossy samples such as aqueous solutions in flat cells or capillaries.
- Increase the microwave power. If you are using insufficient microwave power the cavity dip is difficult to observe.

2. Unable to Critically Couple the Cavity

- Adjust the sample position. If too much of a lossy (*i.e.* microwave absorbing; high dielectric loss) sample is in the absorption region you will not be able to critically couple the cavity. Move the sample up or down until you can critically couple the cavity.
- Use a smaller sample *e.g.* use a flat cell or a smaller tube, *e.g.* a Q-band tube can be used at X-band if you have a lossy sample. (Note: the size of an EPR tube is dictated by the microwave frequency and at X-band a tube with 3-4 mm i.d. is usually used; at higher frequencies smaller tubes are used (*e.g.* 1 mm i.d. at Q-band) and at lower frequencies (*e.g.* S-band) bigger tubes can be used, although the design of our resonator restricts us to X-band sized tubes).
- Microwave reference phase. The proper reference phase is important to achieve critical coupling. Follow the above procedure above to retune the cavity properly.
- Condensation in the cryostat. Liquid water is a huge microwave absorber. If you are running a low temperature experiment, make sure that you have purged the cavity with dry nitrogen to minimize water-induced losses.

3. Hints for Finding EPR Signals

- Scan over the correct magnetic field range. If you look at the wrong magnetic field values, you will miss your signals. This mistake occurs quite often when using a cryostat in the EPR cavity. Consult literature references to determine approximate g-values for the species in your sample. You can then choose the appropriate magnetic field for your sample. Most organic radicals will have a g-value of approximately 2. This corresponds to a field for resonance of approximately 3480 Gauss at a microwave frequency of 9.8 GHz. Metal ions can have large departures from $g = 2$ as well as large zero-field splittings, making it difficult to guess where the resonance might occur. Performing wide scans maximizes the probability of finding the EPR signal.
- Optimise the sensitivity. You may have a very weak signal. Follow some of the following suggestions.
- Optimise the receiver gain. You need to have sufficient receiver gain in order to get a good signal to noise ratio. Clipped signals in a spectrum are indicative of an overload in the signal channel.
- Optimise the time constant. The time constant filters out noise; however, if an excessive time constant is chosen, the signal distorts and diminishes.

- Optimise the field modulation amplitude. Excessive field modulation broadens the EPR lines and does not contribute to a bigger signal. An optimal field modulation amplitude for maximum sensitivity is approximately $\sqrt{3}\times$ line width of the EPR signal, *i.e.* the linewidth of the narrowest line in the spectrum.
- Optimise the microwave power level. The EPR signal intensity grows as the square root of the microwave power in the absence of saturation effects. When saturation sets in, the signals broaden and become weaker. Several microwave power levels should be tried to find the optimal microwave power.