III. GETTING STARTED

A. SPECTROMETER SET UP – PULSE MODE

There are three major parts to this spectrometer, the “MAGNET” (with RF Sample Probe mounted inside), the “MAINFRAME” (with the Receiver, Synthesizer, Pulse Programmer, Lock-In, and built-in DC Power supply) and the PS2 CONTROLLER (with Magnet Temperature and Field Gradient electronics). These three units are interconnected. All three are powered by a single regulated DC power supply (+5 V, ±15 V) mounted inside the Mainframe case. You can see each of these components in Figure 3.1.

![Figure 3.1 The PS2-A Spectrometer: Magnet, Mainframe and PS2 Controller](image)

Begin by connecting up these three units. The gray cable from the PS2 Controller marked DC Input Power connects to the rear of the Mainframe. The blue coaxial cable, with the reverse gender BNC connector, attaches to the Receiver reverse gender panel connector marked “Sample”. The gray cable from RF Sample Probe connects to the rear panel of the PS2 Controller marked “MAGNET GRADIENT/MODULATION”. The gray cable from the lower part of the case of the magnet connects to the rear panel of the PS2 Controller marked “MAGNET TEMPERATURE”. The AC power cable connects to the universal power entry plug on the rear of the Mainframe.

The rest of the connections are to be made with the blue BNC cables on the Mainframe and into your oscilloscope. TeachSpin recommends that students begin these experiments using a digital oscilloscope. A computer will also serve as a data storage device, but we believe it is more appropriate to use an oscilloscope first and then other options can be considered, after students have become thoroughly familiar with the spectrometer.
Connections and Basic Settings for Pulse Mode

1. Connect the blue 18 inch reverse gender cable from Pulsed RF Out (Synth) to Pulsed RF In (Rec)

2. The following are connections made with 12 inch blue BNC Cables:
   - Q (PP) to Q (Synth)
   - I (PP) to I (Synth)
   - Blanking Out (PP) to Blanking in (Rec)
   - Ref Out (Synth) to Ref In (Rec)

3. The following are connections made with 36 inch blue BNC cables to a two channel digital oscilloscope:
   - Sync Out (PP) to Input Trigger
   - Env. Out (Rec) to Channel 1
   - Q Out or I Out (Rec) to Channel 2

4. Turn Off: CW Out (Synth), B Pulse (PP), MG (PP)
   - Toggle Sync to A (PP)
   - Toggle Pulse to A (PP)
   - Ref Out (Synth) –Toggle Turn On
   - Filter TC to .01 (Rec)
   - Gain to 75% (Rec)
   - Toggle Band to P (for proton) (Rec)
   - Toggle Blanking (Rec) On, Width 75% (Rec)

 **Do NOT connect to:**
   - Receiver – CW IN, RF Out
   - Synthesizer – Sweep In, CW Out
   - Pulse Programmer – Ext Start
   - Lock-In – All Connectors.

If you have made all the connections specified, you have set up the spectrometer for your first experiments. Turn it on with the power switch you will find on the rear panel of the Mainframe, at the power entry plug. The only pilot lights that should go on are the one on the PS2 Controller and the “error signal indicators”. However, all three LCD displays should light up and initially display “TeachSpin”.

B. DIGITAL SETTING OF PARAMETERS

B.1 Overview

Before you attempt an experiment, you should get used to setting the parameters of the three digital modules. Three of the modules on PS2-A’s Mainframe, the Synthesizer, the Pulse Programmer and the Lock-In/Field Sweep, are adjusted digitally with one knob in the upper right hand corner. With this control the experimenter first selects the parameter and then changes its value. The LCD screen at the top of the module displays both the name of the parameter and the value selected. It may take some practice to become proficient with this control, but in a short time students will have the muscle memory needed to adjust these units seamlessly.
There is one disadvantage to this control system. The current value of only one parameter appears on the screen at any given time. The values of the other parameters can easily be obtained by scrolling through the menu. However, only one value at a time can be viewed or changed. Of course, students can always record the values they have chosen for each of the parameters. We trust that data books may still be in fashion. We encourage writing!

B.2 DEFAULT SETTINGS

The settings which have been preprogrammed into each unit of the PS2-A Mainframe electronics are listed below. You should check these to assure that the unit is operating correctly. In each module, the parameter we have shown as underlined appears on the screen as underlined and is flashing.

<table>
<thead>
<tr>
<th>SYNTHEZER</th>
<th>PULSE PROGRAMMER</th>
<th>LOCK-IN / FIELD SWEEP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>F</strong> (flashing) –</td>
<td><strong>A</strong> (flashing)</td>
<td><strong>G</strong> (flashing) Gain: 80 V/V</td>
</tr>
<tr>
<td>Frequency: 18.00000 mHz</td>
<td>A_len: 0.02 µs</td>
<td>P Ref Phase: -180°</td>
</tr>
<tr>
<td><strong>P</strong> Refer Phase: -180°</td>
<td>B_len: 0.02 µs</td>
<td>T Time Const: 0.5 s</td>
</tr>
<tr>
<td><strong>A</strong> CW Pwr: -10 dBm</td>
<td><strong>T</strong> tau: 0.0001 s</td>
<td>M Mod Amp: off</td>
</tr>
<tr>
<td><strong>S</strong> Sweep: 0 kHz/V</td>
<td><strong>N</strong> Num_B: 0</td>
<td>H Fld off: 0.00 G</td>
</tr>
<tr>
<td></td>
<td><strong>P</strong> Period: 0.2 ms</td>
<td>S Swp Md: off</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A Swp Amp: 0.039 G</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D Swp Dur: 10 s</td>
</tr>
</tbody>
</table>

B.3 SETTING PARAMETERS

The push-to-select” knob is used in three stages.

1. Rotate the knob to display the desired parameter.
2. Push the knob into the panel and hold for a second or two until a beep indicates that the parameter has been selected.
3. Now you can change the value of the selected parameter by rotating the knob until your chosen value is displayed.

This process might best be explained by an example. Consider the synthesizer. If the Mainframe power has just been turned on, the capital letter F is both underlined and flashing and the number 18.00000 mHz appears on the screen. There are four functions that can be selected and varied by this control. They are:

F: the Frequency of the internal synthesizer
P: the relative Phase of the reference signal being routed to the receiver module
A: the Amplitude of the continuous wave (CW) rf output signal used when the spectrometer is configured for CW NMR detection.
S: the Sweep of the NMR rf frequency which is also used in CW NMR detection.
†: the arrow is not a parameter. It is actually part of the menu and is used to return the control knob to the choices on the upper line of the menu.
Suppose you wish to set the synthesizer frequency to 21.350 mHz, the Larmor precession frequency for your particular unit, which was marked on the serial number label. How do you do this? Since the letter F is flashing, the default program has already selected Frequency for you. If you simply turn the knob, you will see the selected parameter change to P (phase), A (CW power), S (sweep).

To activate the parameter you wish to set, in this case frequency, start with the F flashing and then push the knob into the panel and hold it in until you hear the beep. The flashing will stop, but the F will still be underlined. Another underline will then appear at the 0.1 mHz decade on the display. Turning the knob will now change the frequency by 0.10 mHz per “click”.

The coarse control of the frequency control has been activated and turning the knob can get us to 21.3 mHz, but that is not the value we want. Pushing in the knob and again waiting for the beep will move the underline to the .001 mHz position. Now, turning the knob will change the frequency in these smaller, 1 kHz steps. Another push and the underline will translate to .001 mHz or 10 Hz, the smallest frequency steps possible with the synthesizer.

By a combination of pushing and rotating, the entire menu of variables in each module can be accessed and the desired values assigned. Two things are important to remember. First, the chosen value of the parameter will only be set when the knob has been pushed in long enough for the “beep” to sound. This delay was installed to prevent accidental pushes, during rotations, from causing changes. Second, you must remember that the value of only ONE parameter at a time can be displayed. It might be wise to check all the parameters before beginning an experiment. Be sure to record these values!

An example: Perhaps you have “inherited” the spectrometer from your classmate who left the power on to the Mainframe. Supposing she was using it in the CW mode, with the frequency sweep option running. If you now attempt a pulsed experiment, without turning off the frequency sweep option, you will observe some bizarre signals. You might then incorrectly conclude that the spectrometer needs repair!

Even in a simple single 90° pulse experiment, where one is only observing the free precession decay (FID) of the proton spins, previously programmed parameters can cause serious problems. Suppose the period P (the time between repeated 90° pulses) is short compared to the spin-lattice relaxation time T1. In such a case, the spins are not give sufficient time to return to thermal equilibrium magnetization before the 90° pulse of the RF occurs. Thus, the signal will be reduced in amplitude, possibly so much that it is not observable. There is nothing wrong with the spectrometer; it has just been set up incorrectly.

**ITALIC**

IT IS ESSENTIAL THAT ALL THE PARAMETERS HAVE BEEN INTERROGATED AND RECORDED BEFORE EMBARKING ON AN EXPERIMENT.
C. SINGLE PULSE EXPERIMENTS

C.1 Set Up

All of the experiments described in this section can be done with a single A pulse that is repeated with a period P. The first thing to do is to select a sample with a high density of protons. Mineral oil is a good choice. Two types are supplied with the unit. It is essential that the correct volume of sample be used for all experiments. Large errors are introduced into the measurements if too much sample is placed in the vials. The explanation for this systematic error is as follows:

The RF coil which surrounds the sample is a solenoid approximately 12 mm long. The RF field from such a solenoid is only reasonable uniform over about half of its overall length. Therefore, if the sample only fills about 5 mm of the tube and is placed so that those 5 mm are in the center of the solenoid, all the spins in the sample will experience nearly the same magnitude of the RF magnetic field during the pulse burst. Thus, all of the spins will be “rotated” (tipped) the same amount. Figure 3.2 shows the correct volume and placement of a sample. Note that the O-Ring stop is located 39 mm from the center of the sample. This places the sample both at the center of the RF solenoid and at the center of the gradient and modulation coils.

Before you place the sample into the RF probe and search for your first NMR signal, you must tune the RF probe to the Larmor precession frequency of the proton in the ambient magnetic field. Since the spectrometer has no “pickoff points” in which you can examine the RF currents through the solenoid, TeachSpin has provided you with a “pickup probe” which can be inserted into the sample chamber to measure the RF fields DURING THE PULSE.

If the RF solenoid is tuned to resonance at the spectrometer’s synthesized frequency (by the two tuning capacitors in the RF Sample Probe), then the RF magnetic field will also be at a maximum in the coil. The inserted pickup probe’s voltage will also be a maximum when the sample solenoid is tuned to resonance.

Since the single solenoid coil in the RF Sample Probe serves as both a transmitter (to tip the spins) and a receiver (to produce an emf from the free precession of the magnetization), it is essential that it be tuned (or very nearly tuned) when searching for a signal. The unit is shipped from the factory tuned for a proton resonance, but, if this is your first attempt at PNMR with this unit, it is anybody’s guess how the last user has left the tuning capacitors on the RF Sample Probe.
Place the coil end of RF pickup probe in the center of the sample solenoid. Secure it in place. Attach the BNC connector to Channel 1 of your oscilloscope. (The oscilloscope should have a bandwidth of at least 30 mHz.)

1. Set the synthesizer frequency to the frequency marked on the unit’s labels. (Labels are on both the magnet and the Mainframe.)
2. Set A_len to 2.5 μ (or longer)
   Set P to 100 ms
   Leave all other settings as they have been set
3. Set the parameters on the Oscilloscope
   Trigger: Ext, Normal, Rising, > 0.1 Volt, positive slope
   Sweep: 2 μs/division
   Channel 1: 5 V/div, DC, Full bandwidth

With this time scale on your ‘scope, you are observing the RF field inside the solenoid DURING THE PULSE. This is not a magnetic resonance signal. If the RF Sample Probe is properly tuned, you should observe an RF burst of about 40 volts peak-to-peak lasting about 3 μseconds. Try adjusting the two capacitors on the tuning side. The tuning side is the side near the gray cable (the left side) coming out of the RF Sample Probe. The capacitor nearest the sample hole is a piston capacitor (1 – 30 pf fine tuning) and the one farthest from the hole is the compression capacitor (25 – 150 pf coarse tuning). Changing these capacitors should have a dramatic effect on the amplitude of the pickup signal. Adjust for maximum amplitude. If you cannot achieve about 40 V peak-to-peak voltage, something is wrong. Stop here and investigate the problem.

C.2 Free Induction Decays, FID (Free Precession); Protons

You are now ready to do your first magnetic resonance experiment with the PS2-A. Start with one of the mineral oil samples. Since you now wish to observe the precessing magnetization (collection of spins) AFTER THE RF PULSE HAS BEEN TURNED OFF, you need to change the time scale on the oscilloscope. The RF burst that tips the magnetization from its thermal equilibrium orientation along the z-axis (the direction of the DC magnetic field) to create some transient component along the x-y plane, does so on a time scale of microseconds (10^{-6} s). But this x-y magnetization precesses in the x-y plane for times of the order of milliseconds (10^{-3} s). Thus, the sweep times on the oscilloscope should be adjusted to 0.5 – 1.0 ms/div. Channel 1 of the ‘scope should be connected Env Out from the receiver.

The second input on the oscilloscope should be connected to either the I or the Q output from the receiver. Remember (see Ch. 2, Sec. A.1) that the I and Q outputs are the product of the signal from the precessing spins multiplied by the reference signal from the oscillator. The equation is:

$$\sin(\omega_{\text{ref}} t) \cdot \sin(\omega_{\text{spins}} t) = \frac{1}{2} \cos(\omega_{\text{ref}} - \omega_{\text{spins}}) t - \frac{1}{2} \cos(\omega_{\text{ref}} + \omega_{\text{spins}}) t$$

Since the term $\omega_{\text{ref}} + \omega_{\text{spins}}$ is filtered out (it is approximately 40 MHz), it is the difference signal that is presented at the output. We call this the “beat” signal. It is essential that the beat frequency be at, or near, zero so that the oscillator has the same frequency as the precession frequency of the spins being examined.

Set all four potentiometers on the PS2 Controller – field gradients X, Y, Z, Z^2, to zero. Place your mineral oil sample in the RF Sample Probe and look for an FID signal. You should see one on the oscilloscope. Now there are many parameters to play with. Study their effects on the FID signal. You should do just that – play with them – vary them – record your results. You should try to explain everything you observe. If you cannot, talk with your instructor.
Some of the parameters to vary are listed below.

<table>
<thead>
<tr>
<th>1. Gain</th>
<th>8. Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Filter TC</td>
<td>9. Magnetic Field Gradients</td>
</tr>
<tr>
<td>3. A_len (Pulse length)</td>
<td>10. Close the Temperature Control Loop</td>
</tr>
<tr>
<td>4. P period</td>
<td>11. Sample Placement in Solenoid</td>
</tr>
<tr>
<td>5. Tuning capacitors (RF Sample Probe)</td>
<td>12. Take the Fast Fourier Transform of the signal from either I or Q output from receiver – tune off resonance</td>
</tr>
<tr>
<td>6. Matching Capacitors</td>
<td></td>
</tr>
<tr>
<td>7. Frequency</td>
<td></td>
</tr>
</tbody>
</table>

The following is a list of things to do and questions you should be able to answer based on your experimentation with these single pulse measurements.

1. How do you know if you have a 90, 180, 270 or 360 degree “pulse”?
2. Calculate the approximate average $B_1$ field during the pulse.
3. Describe the differences in the signals from I, Q, Env Outputs.
4. How would you measure the field stability of the magnet?
5. Plot the magnetic field as a function of time after you close the temperature control loop.
6. What is the effect of the filter time constant on the signal?
7. Using a single 90 degree pulse, plot the maximum signal amplitude as a function of the period (repetition time). Explain your data.
8. How do you determine that the spectrometer is “on resonance” – namely that the free precession frequency is the same as that of the spectrometer’s synthesizer?
9. Is there a signal when the spectrometer is off resonance? Explain. Suppose you tune it “way” off resonance? Is there a signal then? Keeping the A_len constant, tune the spectrometer’s frequency away from resonance and explain what you observe. (Note: you should adjust the tuning capacitor in the RF Sample Probe for the maximum signal amplitude as you change the frequency.) A careful examination of effective fields in the rotating coordinate system will greatly help you understand your data.
10. Adjust the magnetic field gradient coils several times. Figure 3.4 shows our data from the Env. Output. Can you achieve this long – or maybe longer decay times?
11. Place some distilled water in a vial and repeat some of these measurements. What is the decay time? How does the signal depend on the period, on pulse length (A_len, etc.)? Explain what you observe. Which properties are the same and which are different between water and mineral oil?

![Figure 3.4 FID of Heavy Mineral Oil](image-url)
C.3 The 180° Pulse

The experimental criterion for obtaining a 180° pulse, that is an RF burst that rotates the thermal equilibrium magnetization from the + z to – z axis, is a pulse approximately twice as long as a 90° pulse, yet one that leaves no FID signal after it. Why no signal? Well, if this pulse has rotated the magnetization exactly 180°, it has left no component of $M_0$ in the x-y plane. No x-y magnetization, no FID signal!

You may, however, have tried to obtain a 180° pulse and found a small signal after the pulse that you cannot eliminate by making the pulse time longer or shorter or even by changing the frequency. What is the problem?

To explain the effect, one must carefully examine what is happening during the RF pulse. When the signal for the pulse comes from the pulse programmer, the RF power is connected to the sample coil. An RF oscillating current rapidly builds up in the coil at the synthesizer frequency. It takes time, (~ 0.2 $\mu$s) to build up the current, since it is a tuned circuit. Then, the signal comes from the pulse programmer to turn off the current, to “open the switch” and end the pulse. The solenoid is disconnected from the synthesizer. But again, because the coil is part of a series resonant circuit, the current takes a finite time to die out. This is called “ring-down”.

Now, suppose that the resonant circuit of the sample coil was tuned to a frequency slightly different from the frequency of the synthesizer. When the coil is disconnected from the synthesizer, the RF oscillating current will decay to zero at this different frequency. Thus the spins have been subjected to two different frequencies during the entire burst of RF oscillating fields.

You should be able to show, with diagrams and by considering the effective field in the rotating frame, that one cannot obtain a true 180° pulse under this condition. One will always observe a FID signal after a pulse with two frequencies.

Luckily, you can easily eliminate the problem:

1. Tune the spectrometer to resonance and obtain the best 180° pulse possible by varying the pulse width.
2. Adjust the fine tuning capacitor in the RF Sample Probe a small amount. (Remember which way you changed it!)
3. Change the pulse width and see if the “tail” of the FID after the 180° pulse is smaller or larger. If it is smaller, continue to adjust the fine tuning the same direction. If larger, reverse your tuning direction.
4. Keep changing the pulse width and the tuning capacitor until you achieve a null after the 180° pulse.
5. Note, when you change the tuning capacitor, you are affecting three parameters of the spectrometer. They are:
   a) The amplitude of the RF magnetic field during the pulse.
   b) The “ring-down” frequency of the RF pulse.
   c) The amplitude of the FID signal (because the effective gain of the receiver changes).
6. How do you know if you have correctly tuned the RF Sample Probe? If it is correctly tuned for pulsed signals, the following criteria should be met:
   a) After a 180° pulse, there should be no (or very small) FID signal. You should achieve nearly perfect magnetization inversion.
   b) The 180° pulse width should be approximately twice as long as the 90° pulse, that is a 90° is 2.5 μs, a 180° is 5μs.
   c) The amplitude of the FID signal following a 90° pulse on a mineral oil sample should be comparable to the data taken at the factory and posted in this manual.

7. If the above criteria are not met, you may have tuned the system to some peculiar configuration that is incorrect. So start again.
   a) First: make sure your synthesizer frequency is actually at the Larmor procession frequency of the spins. As we pointed out before, this is done by creating a zero beat signal on either the Q or I phase detector. Look out for aliasing effects on your digital oscilloscope. They can badly mislead you.
   b) Second: set the A pulse width (A_len) to 1μs, a pulse width that can, at best, produce about a 40° rotation of the magnetization. Set P to at least 0.3 seconds for a mineral oil sample. (For other samples, make sure P is at least three times the spin-lattice relaxation time.)
   c) Now adjust the tuning capacitor to maximize the signal. Note: If the signal increases, it may be due to all three effects listed in item 5 above. As long as you have correctly set the synthesizer frequency to the Larmor frequency of the spins, any increase in the FID signal amplitude will bring the probe closer to the correct setting.
   d) Change the pulse length to achieve a 180° pulse. Adjust the fine tuning capacitor to achieve a perfect 180° pulse as described in item 6 above.

What you are doing is simply tuning the series resonance circuit of the sample solenoid to the exact frequency of the synthesizer. When that has been accomplished, the spins only experience one frequency during the entire pulse burst. You should be able to achieve a near perfect result.

This is the best way to tune the spectrometer for all pulsed experiments. It assures that only one frequency is imposed on the spin system during the pulses. This “two frequency” effect cannot be observed from a 90° pulse, so it is best to tune the spectrometer with a 180° pulse before doing any experiments.
C.4 Free Precession; Fluorine

C.4.a Overview

The spectrometer comes with several fluorine liquids that should now be studied. In this spectrometer, the magnetic field is kept constant and it is the RF frequency that is changed to observe the fluorine NMR signals. It is necessary to retune the spectrometer to detect the fluorine free precession signals. But, before you do that, it important to adjust the magnetic field gradient coils so that the field at the sample has its maximum homogeneity. This can best be accomplished with the protons in the water sample.

The data shown in Figure 3.5 shows a decay time of about 25 ms due to the field inhomogeneities over the sample. (At this time, you will have to accept our word for that causality. You will soon see decay times that are due to the sample.) You should be able to adjust your spectrometer to have at least 5 ms decay times.

The adjustment of the field gradients should be done with the temperature control loop closed and the magnetic field stabilized. This will prevent the field and the field gradients from drifting during the upcoming measurements of fluorine signals. A fluorine nucleus has a smaller magnetic moment than the proton so that, in the same magnetic field, the resonance frequency of the fluorine will be lower than that of the proton by about 6%.

Important constants to note are:

| Proton’s NMR Frequency:        | 42.576 mHz/T |
| Fluoirne’s NMR Frequency:      | 40.044 mHz/T |
| \[ f_{\text{fluorine}}/f_{\text{proton}} = 0.9408 \] |

C.4.b Fluorine Liquid FID

The following is a set of directions and questions to guide your exploration of the fluorine free induction decay signal.

1. Calculate the new resonant frequency for fluorine and set the frequency of the synthesizer to this new LOWER frequency.
2. Place the RF pickup probe in the sample chamber. Adjust the tuning capacitors in the RF Sample Probe for maximum signal. This should produce an approximately 40 volt peak-to-peak RF burst during the pulse.
3. Switch the BAND toggle on the receiver to f.
4. Start with the clear liquid sample labeled FC-770. Place a few drops in a sample vial. Place a black rubber stopper on it with an O-ring collar.
5. Adjust the A_len to produce a 180° pulse.
6. Tune the RF probe to achieve a near perfect 180° pulse (no “tail”).
7. Adjust A_len to produce a 90° pulse.
8. Study the FID signal amplitude as a function of the period P. Vary P over a wide range and plot your data. Describe the ways this plot differs from what you found for the water and mineral oil samples.

C.5 Fast Fourier Transform

The FID signal from FC-770 looks very different from the mineral oil or water sample. The decay time is shorter and clearly not exponential. The explanation of this signal starts by considering the possibility that there is more than one “kind” of fluorine atoms in this liquid. By “kind,” we do not mean different isotopes of fluorine. All of our nuclei are F\(^{19}\). We mean that in this complex liquid, fluorine atoms may be located in different parts of the molecule with different local surroundings. These different local surroundings create different local magnetic fields. Since it is the total field at the nucleus that determines the nuclear precession frequency, different nuclear sites produce different precession frequencies. This very important property is essential for chemical and biological analysis of various samples. It has a name. It is call the Chemical Shift.

To analyze how many different fluorine sites there are in FC-770, we will look at the fast Fourier transform (FFT) of the FID signal from the phase sensitive detectors. To do this, it is essential that the spectrometer’s frequency be off resonance so that the FID signal from Q looks like Figure 3.5. The FFT of this signal is shown in Figure 3.6.

![Figure 3.5 FID of FC-770](image1)

![Figure 3.6 FFT of FC-770](image2)

Clearly Figure 3.6 shows that there are three distinct peaks indicating at least 3 inequivalent fluorine sites. One peak, however, may actually be two peaks that are very close together. There may also be a fifth peak at a much smaller intensity. Chemists, especially organic chemists, use this technique to identify certain atomic clusters in molecules.

One can examine these spectra for different repetition periods P. What does this tell you?

Why didn’t we see chemical shifts in mineral oil? It turns out that fluorine atoms typically have much larger chemical shifts than protons. Proton chemical shifts can be observed in some liquids...
by carefully adjusting the gradient coils for optimum field homogeneity and using a substance where these shifts are large. We have observed proton chemical shifts in ethyl alcohol and toluene, and many other substances can be used. But all of the principles of studying “chemical shifts” can be learned with your PS2-A using fluorine liquids. That’s why we have provided you with several safe fluorine liquids to study.

C.6 Fluorine Solids FID

What differences can be observed between solids and liquids? Teflon is a common solid worth studying with these simple one pulse experiments. How does the Teflon compare with the fluorine liquids? You may not know that there are several kinds of Teflon – some made from recycled material and some “virgin”. You might want to see if they exhibit any different NMR properties.

D. TWO PULSE EXPERIMENTS

Next we will consider experiments that have two pulses, A and B, which are separated in time. Here, a single pulse sequence consists of two bursts of RF magnetic field (whose length you can choose with A_len and B_len) separated by a variable time, \( \tau \). Thus, there are four parameters to program into the pulse programmer: A length, B length, \( \tau \) (the time between A and B), and P, the repetition time of the entire A, B cycle.

D.1 Spin-Lattice Relaxation Time, \( T_1 \)

D.1.a Overview

In the introduction section, we discussed the time it takes for the z-component of the magnetization to grow to its thermal equilibrium value. Equation 1.14 models the situation where the sample starts from zero magnetization \( M_z(0) = 0 \) and grows to \( M(\infty) = M_0 \), its thermal equilibrium magnetization value. \( T_1 \) is a very important physical parameter since it tells us about the mechanism of the spins interacting with their environment. There are materials that have \( T_1 \) values as short as microseconds and some that have \( T_1 \) values as long as several seconds. Let’s examine some experimental ways of measuring it.

Actually, you have already made some crude estimates of \( T_1 \). You should have observed a decrease in the FID signal strength for decreasing repetition time P in the single pulse experiments. Sometimes, that decrease is not observed until \( P \sim 50 \text{ ms} \) and for other samples, the decrease was noticeable for \( P \sim 1 \text{ second} \). The explanation for this, as you may have realized, is that too rapid a repetition time does not give sufficient time for the spins to return to their thermal equilibrium value before the 90° pulse. This condition is often referred to as saturation. By looking at these plots of signal vs. \( P \), one can make a reasonable assessment as to the spin-lattice relaxation time.

D.1.b Measuring \( T_1 \)

But let’s do better than this estimate. A good sample to start with is mineral oil. The best place to begin is with the differential equation that governs the process of the spins returning to their thermal equilibrium value (1.13).
\[ \frac{dM_z(t)}{dt} = \frac{M_0 - M_z(t)}{T_1} \] (1.13)

Now, however, we will consider a new set of initial conditions. The first pulse, A, will be a 180° pulse, which takes \( M_0 \) (in the +z direction) and rotates it 180° so that it is now in the –z direction. The magnetization will then return to \( M_0 \) in the +z direction with a time constant of \( T_1 \). From the differential equation we can see that the rate of return is proportional to the difference between the instantaneous value of \( M_z(t) \) and the thermal equilibrium value \( M_0 \). Since the initial conditions are not the same as those described in Chapter 1, equation 1.14 will not be valid. It is the job of the student to derive and plot the mathematical equation that describes the way the magnetization returns to equilibrium after an initial 180° pulse.

Once the equation has been determined, an interesting problem arises. How do you determine the instantaneous value of \( M_z(t) \)? Remember, the spectrometer never directly detects \( M_z \). All of the spectrometer’s NMR signals come from precessing magnetization in the x-y plane. This x-y precessing magnetization induces an emf in the sample coil. The “trick” is to follow the initial 180° pulse with a 90° pulse to interrogate the z-magnetization. This second pulse rotates the z-magnetization 90° into the x-y plane. The initial amplitude of the FID after the 90° pulse is proportional to the \( M_z \) magnetization just before the pulse. This two-pulse sequence is then repeated with different times, \( \tau \), between the A and B pulses. Note that for \( \tau \gg T_1 \), the initial amplitude of the FID should be proportional to \( M_0 \).

Using this two pulse sequence, measure the \( T_1 \) of your mineral oil sample. Do this in two ways.

1. There is a time, \( \tau_0 \) such that the amplitude of the FID signal is zero. This zero-crossing time can be used to make a better estimate of \( T_1 \). Derive the expression for extracting \( T_1 \) from this time measurement.

2. Plot your data in any way you can support and extract \( T_1 \) from this plot. Estimate your systematic errors. Note: Having an accurate value of \( M_0 \) (or a signal proportional to \( M_0 \)) is very important. Suppose, for example, that there is a 10% error in the measurement of \( M_0 \). How will that effect the measurement of \( T_1 \)? Think of some clever ways to determine \( M_0 \) accurately.

Warning: All of the Bloch equations describing the spin systems start on the premise that the spin system is in thermal equilibrium before the first pulse is applied. Since these pulse sequences are applied every P seconds, it is essential that the spins be given adequate time after the last pulse in the sequence to recover to thermal equilibrium. How much time needed? At least 3 \( T_1 \), or better yet, 10 \( T_1 \) for accurate measurements. It is crucial to make a good estimate of \( T_1 \) before you attempt an accurate experiment of any magnetic resonance parameter.

D.2 Spin-Spin Relaxation Time, \( T_2 \)

D.2.a Overview

The spin-spin relaxation time, \( T_2 \), is the time constant characteristic of the decay of the transverse magnetization of the system. Since the transverse magnetization does not exist in thermal equilibrium, a 90° pulse is needed to create it. The decay of the free induction signal following this
pulse would give us $T_2$ if the sample was in a perfectly uniform magnetic field. As good as the PS2-A magnet is, it is not perfect. If the sample’s $T_2$ is longer than a few milliseconds, a spin-echo experiment is needed to extract the real $T_2$. For $T_2 < 0.5$ ms, the free induction decay time constant is a good estimate of the real $T_2$ if the field gradients have been adjusted for maximum homogeneity over the sample.

D.2.b Two Pulse-Spin Echo

We have already discussed the way a 180° pulse following a 90° pulse reverses the x-y magnetization and causes a rephasing of the spins at a later time. (See Chapter I, Section B) This rephasing of the spins gives rise to a spin-echo signal that can be used to measure the “real” $T_2$. The pulse sequence is:

$$90° - τ - 180° - τ - \text{echo maximum (total time, } 2τ)$$

A plot of the echo amplitude as a function of the delay time $2τ$ will give the spin-spin relaxation time $T_2$. The echo amplitude decays because of stochastic processes among the spins, not because of inhomogeneity in the magnetic field. The decrease in the echo amplitude is our window into the “real” processes.

![Figure 3.7](image)

D.2.c Multiple Pulse – Multiple Spin Echo Sequences

D.2.c.1 Carr-Purcell

The two pulse system will give accurate results for liquids when the self diffusion times of the spin through the magnetic field gradients is slow compared to $T_2$. This is not often the case for common liquids in this magnet. Carr and Purcell devised a multiple pulse sequence which reduces the effect of diffusion on the measurement of $T_2$. In the multiple pulse sequence, a series of 180° pulses spaced a time $τ$ apart is applied as:

$$90° - τ - 180° - 2τ - 180° - 2τ - 180° - 2τ - etc.$$  

This creates a series of echoes equally spaced between the 180° pulses. The exponential decay of the maximum height of the echo envelope can be used to calculate the spin-spin relaxation time. The time interval, $2τ$, between the 180° pulses should be short compared to the time of self diffusion of the spins through the field gradients. If that is the case, this sequence significantly reduces the effects of diffusion on the measurement of $T_2$. 
D.2.c.2 Meiboom-Gill

There is a serious practical problem with the Carr-Purcell pulse sequence. In any real experiment with real apparatus, it is not possible to adjust the pulse width and the frequency to produce an exact 180° pulse. If, for example, the spectrometer was producing 182° pulses, by the time the 20th pulse was turned on, the spectrometer would have accumulated a rotational error of 60°, a sizeable error. This error can be shown to affect the measurement of $T_2$. It gives values that are too small.

Meiboom and Gill devised a clever way to reduce this accumulated rotation error. Their pulse sequence provides a phase shift of 90° between the 90° and the 180° pulses which prevents the accumulated error to the first order. The M-G pulse train gives more accurate measurements of $T_2$. All of your final data on $T_2$ should be made with the Meiboom-Gill phase shift on. The only reason it is not permanently built into the instrument is to allow you to see the difference in the echo train with and without this phase shift.

Figure 3.8 Meiboom-Gill Sequence

Figure 3.9 Carr-Purcell Sequence

D.2.c.3 Self Diffusion

Carr and Purcell showed that self diffusion leads to the decay of the echo amplitude. For the case where the field gradient, $\partial B/\partial z$, is in the z-direction, the magnitude of the echo gradient as a function of delay time $\tau$ is given by the expression:

$$M(\tau) = M_0 e^{-\gamma^2 \left( \frac{\partial B}{\partial z} \right) \frac{D \tau^3}{12}}$$

(3.1)

If the sample is placed in a known field gradient, it is possible to use this pulse sequence to measure $D$, the diffusion constant. This is an advanced experiment to be attempted only after mastering the basic measurements of $T_1$ and $T_2$. 

III - 15
E. CONTINUOUS WAVE (CW) EXPERIMENTS

E.1 Overview

Historically, NMR experiments were all done using some variation of what is called CW experiments. They are rarely carried out today, but it is worth a student’s time to carry out a few CW experiments and to understand how to analyze the data they produce. All of these experiments use a continuous, rather than pulsed, radio frequency field which is imposed on a sample inside a coil or cavity. In some experiments the RF frequency is swept, but in the experiment we will consider, both the RF frequency and its amplitude remain constant. It is the magnetic field that is varied through the resonance condition. Consider the experimental set up shown in Figure 3.10.

![Figure 3.10 Schematic of Configuration for CW Experiments](image)

Both the A and B pulses have been turned off and the CW OUT on the synthesizer is connected to the CW In on the receiver. The CW toggle is turned on. Remove the BNC cable from the Pulsed Power In connector. Now the spectrometer can be represented by the schematic shown in Figure 3.10. Here, the RF power is directed to the sample coil via the 20 db directional coupler. Most of the power goes to the 50 \( \Omega \) termination, but one hundredth of the power travels down the 50 \( \Omega \) cable towards the RF probe. That power excites the solenoid surrounding the sample.

Now, suppose you are clever enough to adjust the capacitors in the RF Sample Probe such that the impedance at the input of the probe is exactly 50 \( \Omega \), pure resistance. You have succeeded in exactly matching the input impedance of the probe to the cable’s characteristic impedance. For such a case, there is no reflected signal from the probe and thus no signal that travels from the probe down to the Low Noise Amplifier (LNA). The output of the LNA is then only noise.

But this 50 \( \Omega \) match was accomplished with a sample in the RF solenoid. The sample has a small, but very important effect on the inductance and the dissipation of this solenoid. The nuclear spins affect the inductance since they are magnetic and the spins’ coupling to their local surroundings affects the dissipation in the coil. It is these small effects that are used to detect magnetic resonance.

Suppose the sample is now subjected to a DC magnetic field whose magnitude is slowly changed with time. If the magnetic field is swept through the so called “resonance condition” where \( B_0 = \omega / \gamma \) (\( \omega \) = angular frequency of the RF field), then both the inductance and the dissipation of the solenoid change. This change causes changes in the impedance match at the input to the RF probe. The probe is no longer matched. That means a reflection occurs at the input, sending a signal down the cable to the LNA. This signal is then amplified, phase and amplitude detected and ultimately recorded.
This description is rather brief. It is advisable for a student to look up some references to obtain a more complete description which includes a mathematical analysis of CW resonance experiments.

### E.2 Probe Matching, Theory

How is it possible to match the RF Sample Probe to 50 Ω (resistant impedance) when the only components inside the RF Sample Probe are capacitors and an inductor? The inductor’s resistance is much smaller than 50 Ω. Here is an explanation.

Consider a simple series resonant RCL circuit with component values R, C, and L. The impedance of the series combination of these three elements, Z_S, is simply the sum of their individual impedances,

\[ Z_S = Z_R + Z_C + Z_L \]  \hspace{1cm} (3.2)

For each element, the impedance is simply the sum of the real (resistive) part R and the reactive (imaginary) part X, \( X = R + X \). For each component these are:

\[ X_R = R \]  \hspace{1cm} (3.3)

\[ X_C = \frac{-i}{\omega C} \]  \hspace{1cm} (3.4)

\[ X_L = i\omega L \]  \hspace{1cm} (3.5)

We can write \( Z_S \) in terms of resistance and reactances as:

\[ Z_S = R + X_C + X_L = R + X_S \]  \hspace{1cm} (3.6)

where we have defined \( X_S = X_C + X_L \) as the sum of the reactance of the sample coil and its series tuning capacitor.

Since the last element in the circuit (the matching capacitor) is going to be added in parallel with the series combination of the above three elements, we want to convert the value of \( Z_S \) into an admittance, \( Y_S = 1/Z_S \). (Admittance is the complex equivalent of a conductance, so for parallel combination you simply add admittances.)

\[ Y_S = \frac{1}{Z_S} = \frac{1}{R + X_S} \]  \hspace{1cm} (3.7)

The admittance may be expressed as a sum of its real part, the conductance, \( G_S \) and its imaginary part, the susceptance, \( B_S \).

\[ Y_S = G_S + B_S = \frac{1}{R + X_S} = \frac{R - X_S}{R^2 - X_S^2} \]  \hspace{1cm} (3.8)

We can make the identifications \( G_S = \frac{R}{R^2 - X_S^2} \) and \( B_S = \frac{-X_S}{R^2 - X_S^2} \).

We want to match to a 50 Ω load which has an admittance \((1/50 \Omega + 0i)\), so we want to choose \( X \) so that \( G_S = 0.02 \ S \).
Consider the form of $G_S$, recalling that $X$ is imaginary, so that $X^2$ is negative. $G_S$ is a Lorentzian with a peak value of $1/R$ when $X = 0$. This makes sense because, on resonance, the reactive component vanishes and we simply have the conductance of the series resistor, which models the loss in the resonant circuit. Values of $R$ are on the order of 0.5 $\Omega$ which makes the peak of $G_S$ about $2S$. To match to 50 $\Omega$ we need a conductance of about 0.02 $S$, so we de-tune the resonant circuit, increasing the value of $-X^2$ (which is positive) until $G_S = 0.02$ $S$. We can achieve this by detuning the resonant circuit either above or below the operating frequency, $\omega$.

Now that we have the real part of the admittance matched, consider the form of the imaginary part, the susceptance.

$$B_S = -\frac{X_S}{R^2 - X_S^2} = \frac{i(1/\omega C - \omega L)}{R^2 - X_S^2}$$

(3.9)

$B_S$ is imaginary and looks roughly like the derivative of a Lorentzian. At frequencies below resonance, its imaginary component is positive, and at frequencies above resonance, its imaginary part is negative. We choose to detune the circuit so that we are operating at frequencies above the natural resonance, so that $B_S$ is negative. We then simply add a matching capacitor in parallel which has a positive susceptance of $B_S = i\omega C_m$ to cancel the negative susceptance of the detuned series resonant combination. ($B_m$ is simply the reciprocal of the capacitive reactance of the matching capacitor, $X_C = -i/\omega C_m$).

### E.3 Observing a CW Resonance

In several ways, CW resonance experiments are more difficult (and produce less accessible data) than pulsed experiments. We will take you through the details of the CW experiment using an FC-43 fluorine liquid sample.

Begin by adjusting the magnetic field gradients for optimum field homogeneity using a proton sample (water). Now retune the spectrometer to observe a fluorine FID signal. The FID signal from FC-43 and its FFT are shown in Figure 3.10 and Figure 3.11.

![Figure 3.11 FID FC-43](image)

![Figure 3.12 FFT FC-43](image)
It is clear from the FFT that FC-43 has at least two inequivalent fluorine sites separated by 1 kHz (0.8 div x 1.25 kHz/div). Performing a CW scan of this sample, we would expect to observe two resonances separated by 1 kHz in frequency “space” or by 0.25 gauss in magnetic field “space”.

However, before we can observe the CW resonance, the capacitors in the RF must be adjusted for a very good impedance match. This may take some time, especially the first time. How does one know that the coil is almost exactly impedance matched? There is a straight forward procedure which is outlined below:

1. Set up your oscilloscope for the x-y display and adjust the offset controls so that the single spot is at the center for all gain settings with the DC coupling and the INPUT grounded.

2. Now connect the output from I and Q to inputs 1 and 2 on the ‘scope. (It does not matter which output goes to which input – but the scope must be DC coupled.)

3. On the synthesizer module, go on the menu to A and adjust for minimum output, namely -65 dbm (65 db below one milliwatt). The synthesizer frequency should have been set at the resonant frequency needed to observe the FID signal on the FC-43 fluorine sample.

4. Increase the CW power level and observe the spot on the x-y display on the ‘scope. (Set the gains on x and y to 100 mV/div.) The spot will move away from center indicating a reflected signal from the probe. Use a receiver time constant of 3.3 ms to filter the signal.

5. Adjust both the tuning capacitor and the matching capacitor to return the spot to the center.

6. Increase the rf power and repeat the tuning. Do NOT saturate the amplifiers (this changes their input impedance) with too much power. Keep the power low enough to adjust the spot back to the match condition. This will take some practice. If you initially change the tuning capacitor in the wrong direction, you will not be able to achieve a match condition. (See E.2) When you are near match, the match becomes quite sensitive to changes in the matching capacitor. Final adjustments must be made with the matching plunger fine control capacitor.

7. Now you are ready to search for a CW resonant signal. You need to sweep the magnetic field over a large enough range so that you can observe the entire signal and slow enough so that you allow all the low-pass filters in the system to remain in quasi static equilibrium. The magnetic field sweep is done through the Lock-In module. The Swp IO connector provides a voltage out proportional to the field sweep. Parameters you can vary are:

   1. RF Power
   2. RF Phase
   3. Sweep Amplitude
   4. Sweep Time
   5. RC Time Constant
   6. I,Q, Env Detector

8. Compare your FFT, FID and CW signals. Are they compatible? Why are CW resonant experiments almost obsolete? How can you extract $T_1$ and $T_2$ from the CW data? Was the CW “splitting” predictable. Does one method give better signal-to-noise than the other? Explain.
Figure 3.13 shows our data for FC-43 under the following conditions:

- RF Power: 10 dBm
- TC: 3.3 ms
- Phase: 100°
- Sweep Amplitude: 0.625 gauss for 5 div on scope (half scale)
- Oscilloscope: 200 mV/div, TC 3.3 ms, x-y display,
  x-axis connected to Swp I/O (Lock-In), y-axis to Q out (Rec)
- Temperature Control Loop Closed

Note: I have “cheated” you a little here. We added an RC low-pass filter, with 10 k and 10 μf; RC ~ 0.1 seconds, between the Q out and the oscilloscope. This greatly reduced the 60 Hz pickup that we experienced taking this data. You may want to add such a simple filter to your apparatus. But, be careful to take it into account when you set your sweep rates. This pickup can be greatly reduced by keeping the magnet far away from any 60 Hz magnetic fields. These fields are strong near the transformer of the power supply inside the Mainframe. Keep the magnet as far away from the Mainframe as possible. Also, keep it away from the AC power lines in our lab.