NUCLEAR MAGNETIC RESONANCE (Continuous Wave - CW)

II. INTRODUCTION

In 1952 Felix Bloch and Edward Purcell received the Nobel Prize in physics for their discovery in 1945 of nuclear magnetic resonance. Bloch's method of observation is now widely used in many areas of science and technology. NMR is a sensitive probe of the local magnetic field in matter at the location of nuclei, and gives us information about nuclear spins and their surroundings. In the Medical field it is called Magnetic Resonance Imaging to avoid the use of the word "nuclear". This experiment has the following objectives:

(1) To observe the phenomena of nuclear magnetic resonance (NMR) of protons in H_2O and other liquids

(2) To observe the absorption and dispersion line shapes of NMR under slow passage and under non-adiabatic passage conditions, and to study their dependence on concentration of paramagnetic ions added to the liquid

(3) To measure the ratio of the magnetic moment of F^{19} to that of the proton

(4) To use the technique of lock-in detection to get improved signal-to-noise ratios in the NMR detection.

A former student commented, "The best thing that can be said about NMR is that in beginning of the experiment, a student feels overwhelmed by its complexity. As you become more familiar with it, this feeling is replaced by curiosity and eventually understanding." This is to say that while there is a great deal to learn initially about NMR, given time and a lots of effort the pieces do fall into place, and the result is an unusually rewarding laboratory experiment.

To start, you should read Liboff, Bloch's article "Nuclear Magnetism" (Jan. 1955) and Kittel's chapter "Nuclear Magnetism and Masers", pp.499-509, (both located in the NMR Reprints), and Reference 4. These are just to get you started; you should look at the other references and articles in the reprints before you write your report. Watch the NMR video before proceeding to the next section.

I. REFERENCES

1. A. Abragam, *Principles of Nuclear Magnetism*, Oxford Press, 1961. This is the definitive reference. #QC762.A23

2. F. Bloch, "Nuclear Induction", *Physical Review 60, 460*, (1946). Bloch's two-coil method is used in this experiment. #QC1. S695

3. R. Schumaker and W. A. Benjamin, *Introduction to Magnetic Resonance*, 1970. Reach Ch. 2 and Ch. 3. #QC762.S34

4. C. Kittel, *Introduction to Solid State Physics*, John Wiley 5th Ed. (1976). Read pp. 501-509 for a brief-quantitative expose of the main ideas. #QC176.K51

5. L Yuan and C. S. Wu, *Methods of Experimental Physics*, Part B, Vol. 5, Academic Press (1963), pp. 104-123 (Section 2.4.1.4). This reference discusses all the ideas necessary to do the experiment, which uses the two-coil Bloch method. #QC33.M48

6. R. Liboff, *Introduction Quantum Mechanics*, Holden Day, 1980. Sections 11.8 and 11.9 include a simple, direct derivation of NMR, along with a physical interpretation. While Liboff does not use the classical Bloch equations, he does give a good idea of what's going on. #QC174.12.L54

7. S. Walker and H. Straw, *Spectroscopy Vol. 1*, Macmillian (1962, Ch. 5. (Available in 111 Lab, not to be taken out of the laboratory). #QC451.W2 (Engineering Library)

8. NMR Reprints available from the Physics Library; *reserved under 111-LAB*

9. Watch the videos on NMR & Pulsed NMR and the video lecture series, called "Transitions" on the 111-Lab Network or get them from *the Physics Library under 111-LAB reserve.*
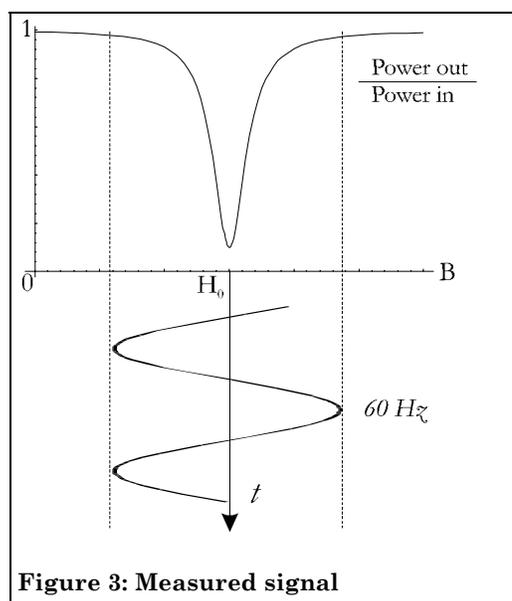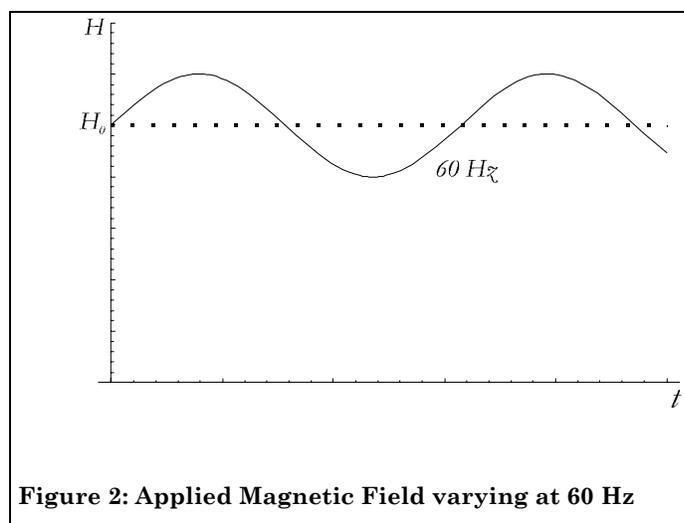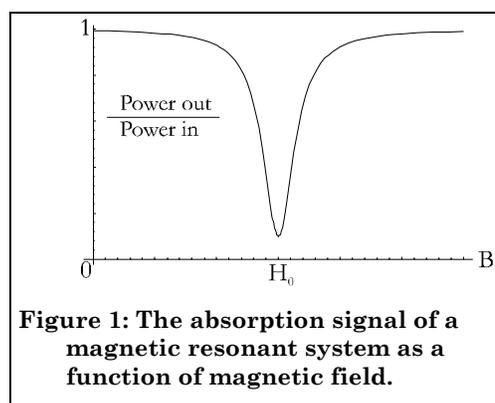
THEORY

Conceptually this experiment is quite simple, but how the data are recorded is not. It helps to know what we are going to do before we discuss what pieces of equipment we use.

Suppose we place a single nucleus between the south and north poles of the magnet. The magnetic moment of the nucleus forces the nucleus to align in such a way that the north pole of the magnet repels the north pole of the nucleus and the south pole of the magnet repels the south pole of the nucleus. This creates equal and opposite forces that form torque upon the nucleus. The nucleus begins to rotate around the vertical axis. This rotation of the nucleus is called "precession". The frequency of this precession is called the Larmor frequency. In this experiment we will place the sample of protons into the permanent magnet. This will force the protons to precess at the Larmor frequency and induce an electric field in a receiver coil that is wrapped around the sample test tube. At the same time we will apply a radio frequency to the sample. This frequency will be tuned to resonance at the precession frequency. Our goal is to observe the nuclear magnetic resonance of the protons in the sample.

A sample of protons in a magnetic field of strength H_0 has energy levels that are populated according to the Boltzmann distribution. When we send in electromagnetic radiation with photons of energy E=$h\nu_0 = \hbar\gamma H_0$, the system absorbs some of the photons and reduces the total energy in the radiation. $\nu_o = \gamma H_0 / 2\pi$ is known as the Larmor frequency, the resonance frequency of the system. The gyromagnetic ratio γ is determined from the ratio $2\pi\nu_0 / H_0$ at resonance. We are going to measure the frequency, assume the value of γ, and determine H_0. For a fixed frequency, the resonance curve looks like Figure 1.

How shall we produce this curve so that we can measure H_0 at resonance? We could set ν to a fixed value and make measurements of (power out)/(power in) for many different values of H, in small enough increments to allow an accurate determination of H_0 from a plot of the data. Of course we could also set H to a fixed value, and make measurements as ν is varied. We really don't care about the exact values of power – we need only the ratios – but we do need some way of measuring the power, which in our case is at a frequency of about 16 MHz.

Figure 1: The absorption signal of a magnetic resonant system as a function of magnetic field.

Figure 3: Measured signal

Figure 2: Applied Magnetic Field varying at 60 Hz

However, it is more satisfying and often enlightening to create a plot on an oscilloscope, so we can observe changes immediately as we adjust the equipment parameters. Let's scan H back and forth relatively slowly above and below the resonance value H_o. We will use a scan frequency of 60 Hz. The variation of H in time will look like Figure 2.

Let's put this plot together with the first one, to get Figure 3.

Now we will use the concept of "signal" to express the power ratio. We will plot the electric field, rather than the power, of the outgoing radiation at the frequency f_o as a function of time and call it the signal. The amplitude of this signal is a measure of the power absorption in the sample.
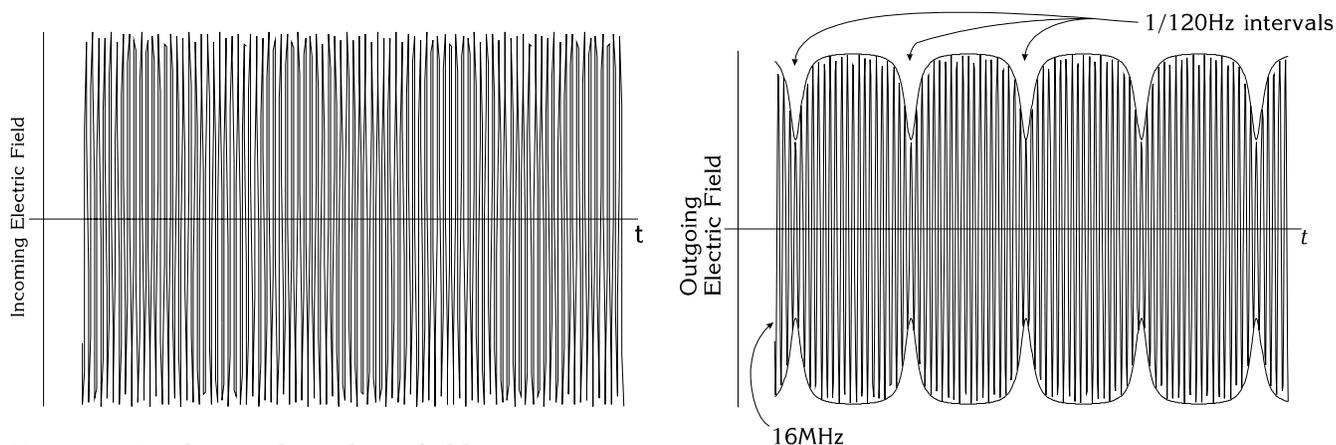

Figure 4: Incident and resultant fields.

The electric field at a frequency of 16 MHz is now modulated in amplitude at a frequency of 60 Hz. The magnitude of the amplitude when plotted in time is a measure of the resonance curve. The function of the detector is to rectify the 16 MHz signal, put it through a low pass filter to remove the 16 MHz component but leave the modulation component at 60 Hz. The signal is sent to an oscilloscope whose sweep frequency is set at 60 Hz. The display shows the amplitude of the modulation as a function of time (really a function of B), and consequently displays the desired resonance curve.

A block diagram with signals at the various stages appears on the next page.

To summarize, we take a liquid sample in a test tube and place it in a magnetic field. We apply a radio frequency magnetic field to the sample by placing it near a transmitter coil, and tune the frequency to resonance at the Larmor frequency, the precession frequency of the protons. As the protons precess, they induce an electric field in a receiver coil wrapped around the sample. The amplitude of the electric field is a maximum when the frequency of the applied RF field exactly matches the Larmor frequency. In a detector circuit we rectify the RF field, filter it to get a DC voltage proportional to the amplitude of the field, and display the voltage on an oscilloscope.

To take data, we set the frequency of the RF to the Larmor frequency for the field produced by the permanent magnet, and then sweep the magnetic field amplitude sinusoidally in time at 60 Hz, above and below the value for resonance (we say that the field is modulated sinusoidally with a frequency of 60 Hz). The detector output is a plot of the resonance curve, the amplitude of the detector signal vs. magnetic field applied to the sample, for a fixed frequency.
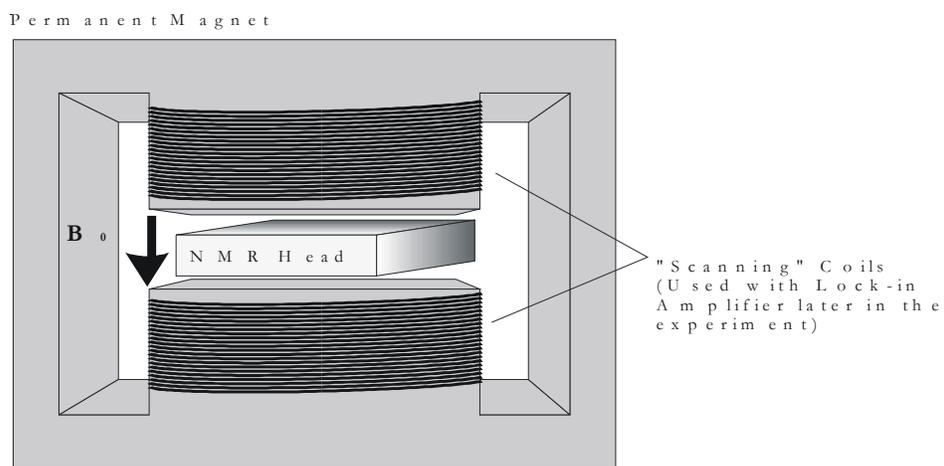
Permanent Magnet

Figure 5: Permanent Magnet; showing position of NMR head.
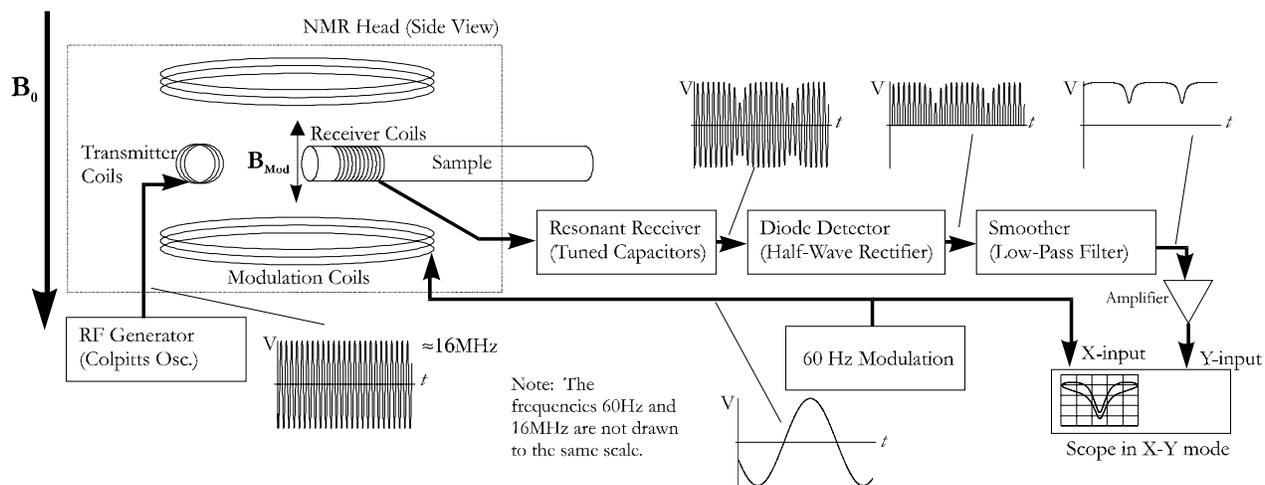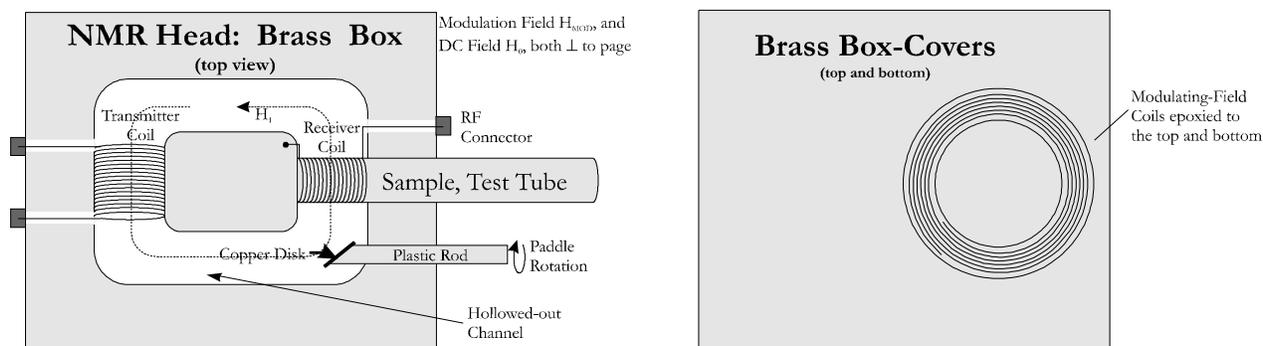

Figure 6: Block Diagram.

Figure 7: NMR Head Detail.

EQUIPMENT

A. <u>Magnet:</u> In the first part of this experiment we are using a permanent magnet. The wire coils wrapped around the poles of the permanent magnet are for the purpose of varying the field at a very low frequency and are needed in the later part of the experiment, where a lock-in amplifier is used.

B. <u>NMR Head</u>: see Figure 7. The NMR head is a brass box containing a radio frequency transmitter coil positioned perpendicularly to a receiver coil into which test tubes are inserted. The test tubes contain samples of protons in H_2O and other liquids. The head is placed between the poles of the permanent magnet. Do <u>not</u> unnecessarily remove this head from the magnet, nor disconnect its cables. Instead, you may examine the spare head on the laboratory table.

The top and bottom covers of the NMR head have 7-turn pancake coils which produce a modulation field $H_{\mathrm{mod}} \cos(2\pi f_m t)$, where f_m is 60 Hz. The amplitude H_{mod} is controlled from the modulation unit; $H_{\mathrm{mod}} \approx 1.7$ gauss/amp of modulation current.

C. <u>NMR Box</u>: This black box is permanently mounted on the magnet stand and is not to be removed or disassembled; do not remove the cables. It contains the 16.54x,xxx Mhz, tunable RF oscillator, a tunable receiver (left hand knob), diode detector (right hand knob), low-pass filter, and an amplifier for the detector output. Refer to NMR RF Box Circuit Diagram located in the CW

Appendix I.

In more detail, the oscillator generates an RF signal that produces a magnetic field $H_1 \cos(2\pi f t)$ in the sample. The frequency is determined by $1/\sqrt{LC}$ where L and C are the combined inductance and capacitance of the coil in the NMR head, variable capacitors in the NMR box, and the cables connecting the two. One of the capacitors tunes the circuit to resonance at the Larmor frequency. Because the resonant circuit includes inductors in the head and in the cables, as well as capacitors in the box and the cables, touching or moving anything during measurements makes the frequency unstable and introduces lots of noise. Be gentle, and keep your hands off while taking data

The amplitude of the RF field H_1 is controlled by the DC supply voltage V_1 to the oscillator. The direction of H_1 lies in a plane perpendicular to DC field H_O of the large permanent magnet. However, the direction relative to the axis of the receiver coil can be adjusted by rotating a copper disk on a "paddle," which controls the phase of the leakage voltage into the receiver coil. Changing phase

enables us to observe either absorption or dispersion or a mixture of the two. In this lab we will observe adiabatic absorption or dispersion, and non-adiabatic absorption or dispersion modes. See Figures 7A, 7B, and 7C for examples.
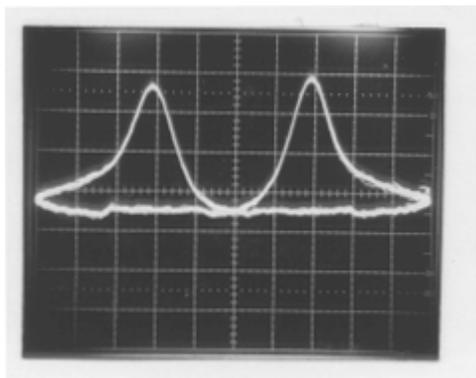

Figure 7A: Adiabatic (Slow passage) – Absorption. Protons in ~ 1.0 Molar Mn⁺⁺ in H₂O
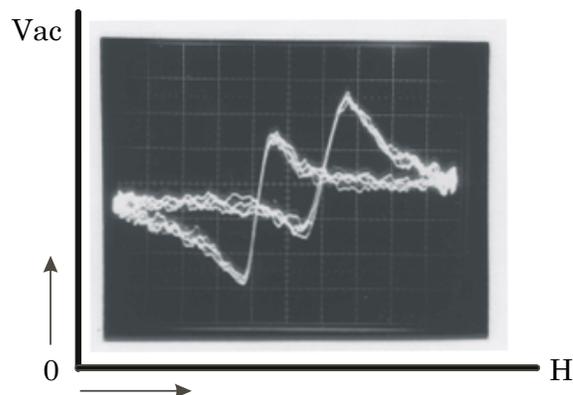

Figure 7B: Adiabatic (Slow Passage) – Dispersion. Protons in ~ 1.0 Molar Mn⁺⁺ in H₂O
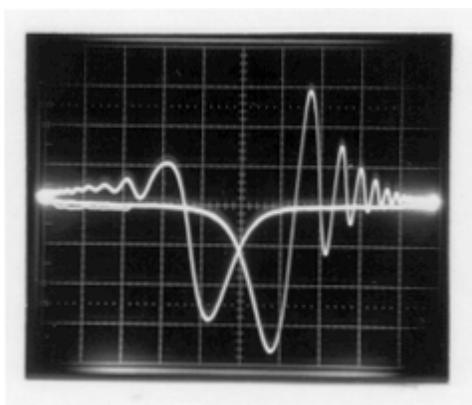

Figure 7C: Non-Adiabatic passage - Absorption
Protons in ~ 0.1 Molar Mn⁺⁺ in H₂O

D. <u>Block Diagram</u> Refer to Figure A for the NMR Block Diagram:

The NMR head is placed in the DC field $H_0 \approx 3900$ gauss of a large permanent magnet. The simplest method for observing NMR is to sweep the magnetic field through resonance at 60 Hz using H_{mod} in addition to H_0. Also, it is helpful to display the NMR signal V_{ac} on the y-axis of an oscilloscope, whose x-deflection voltage is a 60 Hz sine wave, phase shifted, available from the modulation unit.

The signal from the NMR box is amplified by the PAR 113 amplifier which is used to limit the upper and lower pass frequency (typically 1 kHz and 3 Hz), thereby rejecting unwanted frequencies and improving the visibility of the desired signal. The Fluke 1953A frequency counter reads the NMR oscillator frequency without perturbing the oscillator.

The coils wrapped around the pole pieces of the magnet were initially used to magnetize the Alnico alloy of the poles, but are no longer needed or used for this purpose. Instead, they are used in the second part of the experiment for superimposing on H_0 a small monotonically increasing field $H_2(t)$ generated by the Function Generator (a "ramp" field). The field reaches a maximum amplitude

of about 60 gauss. The ramp frequency can be as small as 0.01 Hz, thereby enabling slow, repetitive scanning in one direction through magnetic resonance. The Lock-in amplifier (see Appendix) is used for recording the derivative of the NMR signal on a chart recorder.

     E. <u>Samples</u>: To observe proton resonance, use the prepared set of samples of H_2O + $MnCl_24H_2O$ with yellow mylar tape on the top. The Mn molarity (M) ranges from M = 3.3, 1.0, 0.33, ..., to 10^{-5} moles of $MnCl_24H_2O$ per liter of solution, and gives a wide range of relaxation times. A one molar sample contains 19.7 grams of $MnCl_24H_2O$ in 100 cc of mixed solution. Other useful samples are glycerin with a small amount of $FeCl_3$, and pure H_2O. For F^{19} we are going to use Teflon rods. Samples should be tightly stopped and contain no air bubbles. Be careful not to drop or open the test tubes. Call for the staff if any solution comes out of the test tubes.

     F. <u>Digital Oscilloscope</u>: This experiment uses a Digital Storage oscilloscope in order to examine the weak resonance signals. See the included manual located in the reprints on how to use the digital storage scope. The output signal is also connected to the computer so that the data could be transferred to the computer and stored for later use. The instructions on how to transfer the data to the computer are located in the CW Appendix IV.
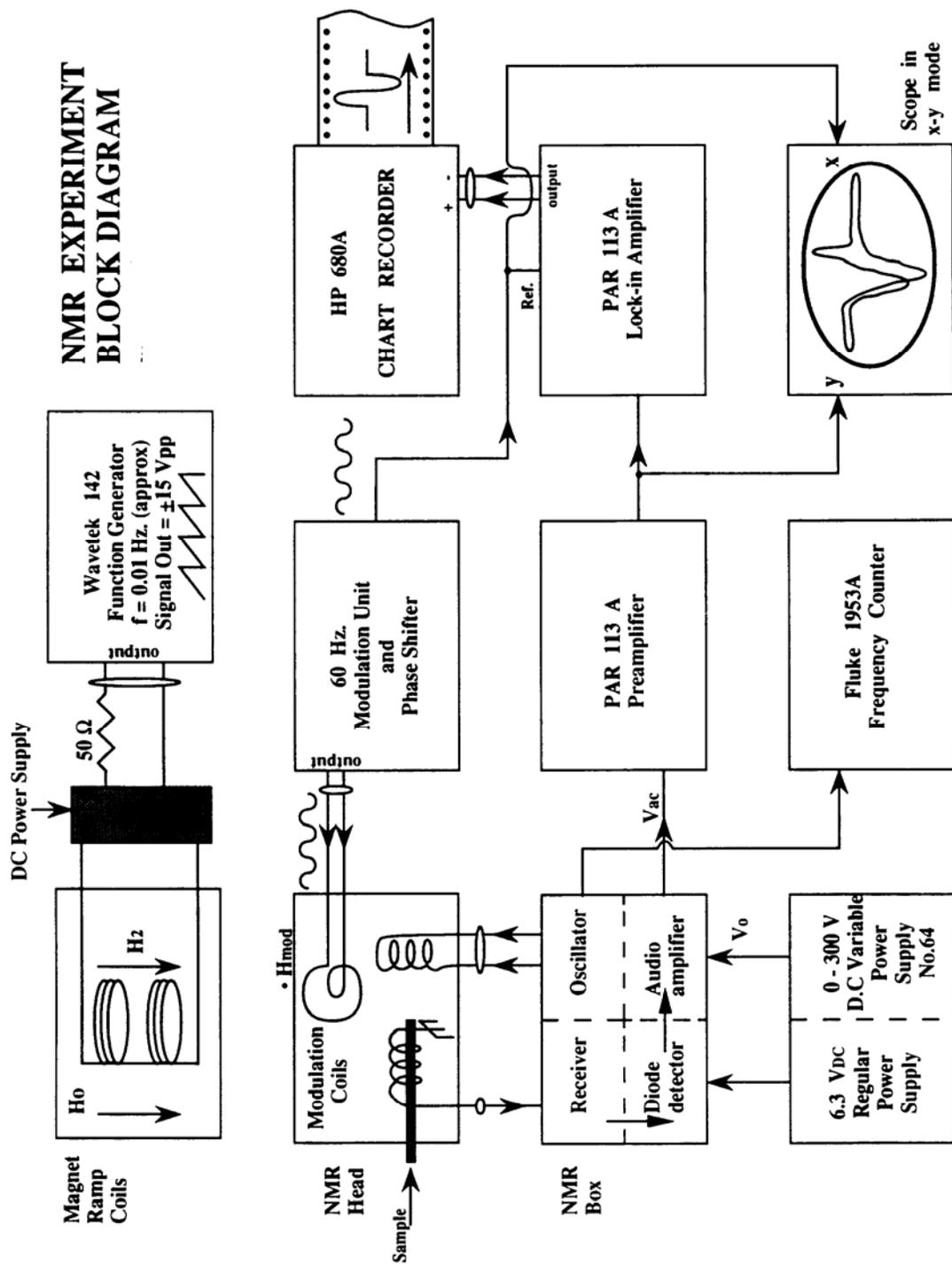
Figure A: NMR Block Diagram
Note: The Strip Chart recorder has been replaced with the computer.

THE EXPERIMENT: PROCEDURES

A. Getting Started:

1) HEATHKIT POWER SUPPLY. Flip the POWER switch to STANDBY and wait 1 minute; then switch to ON. Set the meter switch to the RIGHT. Set the amplitude of the RF field by adjusting the B+ OUTPUT knob to 150 volts, as read by the voltmeter.

2) H_{mod} Magnetic field modulation control panel. Flip POWER and SWEEP ON switches up. Turn the AMPLITUDE ADJUST knob to its maximum CW position to maximize the modulation of the field. This sends about 1.7 amp at 60 HZ to the modulation coils, which corresponds to about 2.9 gauss.

3) The PHASE ADJUST knob on the H_{mod} panel changes the phase of the modulation signal sent to the x-input of the scope relative to the signal sent to the modulation coils, and hence relative to the detected output signal sent to the y-input of the scope. In short, it changes the phase between the x and y signals. No need to set it at this time.

4) PRE-AMP, Model 113. Turn the unit on and test the battery by pushing the battery test switch to the + and then - positions. The green light should come on both times. Plug the AUDIO OUTPUT from the NMR box into INPUT A and make sure that the DC /GND/AC switch next to the A input is in the AC position. Also make sure that the B input switch is on GND.

Note that if you suddenly lose your original signal while you are making various adjustments - if your scope trace goes flat - you should push down on the OL REC overload recovery switch located above the output of the Pre-Amp.

Set the gain to 50, the LF ROLL-OFF to 3 Hz, and the HF ROLL-OFF TO 10K. You will probably have to adjust these later to make your signal as clean as possible without losing any of its major features.

5) Turn on the frequency counter (Fluke 1953A Counter Timer) and the oscilloscope. Put the scope in the x-y mode.

6) Now you're ready to go. Insert a glycerin sample into the NMR HEAD and find the resonance signal by doing the following. Look up in the NMR TABLE – CW Appendix II of the manual - the NMR frequency for H^1 in a 10 kilogauss field. Knowing this number and that our H_0 is about 3.9 kG, calculate the approximate NMR frequency for our set-up (around 16.54xxx). Turn the TRANS FREQ knob on the NMR BOX until the counter reads this value. Now adjust the receiver coil to resonance by adjusting the C_R control so that the receiver frequency matches that of the transmitter. Start with it at the fiducial mark.

Slowly vary the frequency around the value you calculated above. You should be able to find resonance, and your signal should look like Fig. 8. Note that the resonance condition is very sensitive to frequency, so go slowly. Once you have found it, "peak-up" your signal by readjusting CR on the NMR BOX for maximum signal. If you don't find a signal after you've fussed with everything, ask for help.

Move the NMR HEAD around gently in the magnet gap until you have maximized the number of "wiggles" and minimized the line width. This will place the head in the most uniform or homogeneous region of the magnet, and you want to keep it there. Once you have set the position for the day, don't change it. Some of your calculations depend on the field's being the same for successive measurements. Repeat this procedure each day when you first come into the lab, since other people may have changed the head position from what you have determined is the best.

7) Read over the REPORT section to be sure you take all the necessary data. Read over the information located in the CW Appendix IV how to transfer data to the computer.

TAKING DATA

A. The RF is tuned to exact resonance when f is set for reflection symmetry of the signal about the midpoint of the H_{mod} trace on the scope, for both slow passage and for non-adiabatic passage conditions. By using the glycerin sample you can find a narrow line in the homogeneous region of the magnet and measure the resonant frequency and hence (by knowing γ) the magnetic field to high precision. The use of NMR to find precise magnetic field strengths is a standard technique.

B. By recalling that $(\Delta f/f) = (\Delta H/H)$, where f is the frequency and H is the magnetic field, you can devise a method of calibrating (in gauss/div) the field axis of the oscilloscope. Then you can transfer the data to the computer of four signal modes (absorption/dispersion; slow passage/non-adiabatic passage).
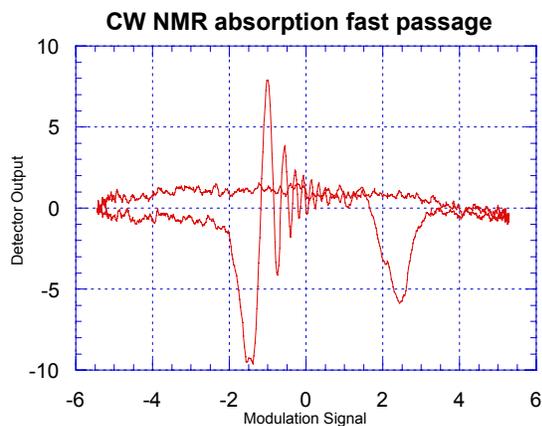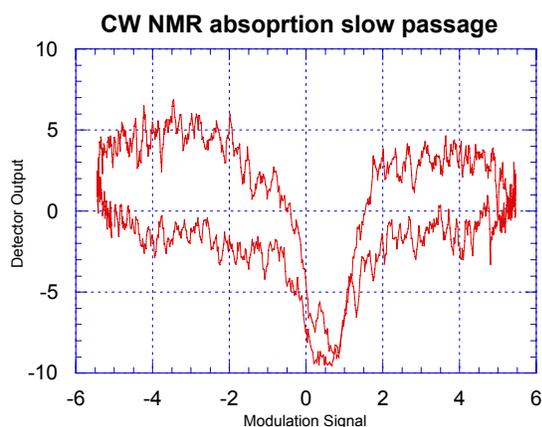

Figure 8: 0.1 Molar Mn^{++} in H$_2$O

Figure 9: 1 Molar Mn^{++} in H$_2$O
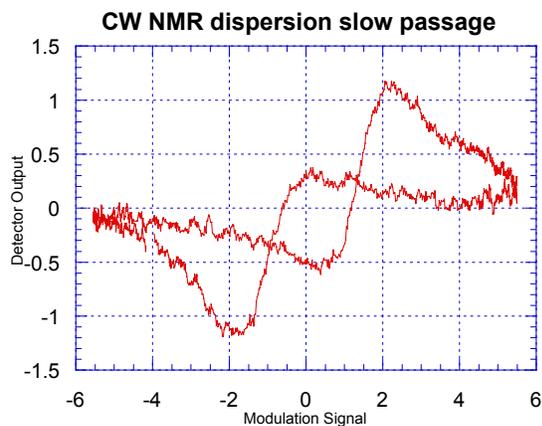

Figure 10: 1 Molar Mn^{++} in H$_2$O

C. Replace the glycerin sample with a 0.01M Mn^{++} sample; again this signal should look like Figure 8. Download this non-adiabatic rapid passage absorption mode data to the computer. (See REPORT, #3.) Now insert a more highly doped sample, 1M Mn^{++}. The paramagnetic Mn^{++} ions relax the proton spins and the signal is more nearly a slow passage absorption mode. By further rotating the paddles you should be able to get a signal like Fig. 10, approximately a slow passage dispersion mode. You may have to increase V_1 to see this.

D. For F^{19} resonance we are using a Teflon rod. Note that the F^{19} resonance is a little harder to find. Using the same procedures as for H^1, find resonance curves for F^{19}. Accurately measure the NMR frequency ratio of F^{19} to H^1. To do that, measure $f(H^1)$ and $f(F^{19})$ each a number of times under identical conditions.

E. Lock-in Amplifier Operation: For fine tuning of the NMR resonance, we can leave the frequency f and all other parameters fixed and optimized, and vary the "total-DC" magnetic field by adding a small field H_2 by Wavetek 142 generator drive of the magnet coils. The following diagrams show what this change does to the signal. See Figure 11.

Read the "Basic Introduction to Lock-in Amplifiers," attached in the CW Appendix III, and the PAR Model 128A Lock-in Amplifier Manual (copied in reprints). In this apparatus, the lock-in amplifier records the derivative $dV_{ac}(H)/dH$ of the NMR signal on a strip chart recorder as the frequency sweeps slowly through resonance by ramping H_2 with the Wavetek generator. The signal-to-noise ratio can be 100x larger than the oscilloscope resonance signals; this method is used to find and record weak signals. It also provides a convenient way to record the line width ΔH of a signal.

As usual, getting started is not trivial. First you need to have a good signal on the oscilloscope. Then turn on the magnet power supply, the lock-in, and the Wavetek. Set the Wavetek for a .03 Hz triangular scan of maximum amplitude. If you are not familiar with the Wavetek, borrow another oscilloscope and look at the output signal, and the effects of turning or switching the knobs. Check out the OFFSET control.

Figure 11: Lock-in amplifier signals
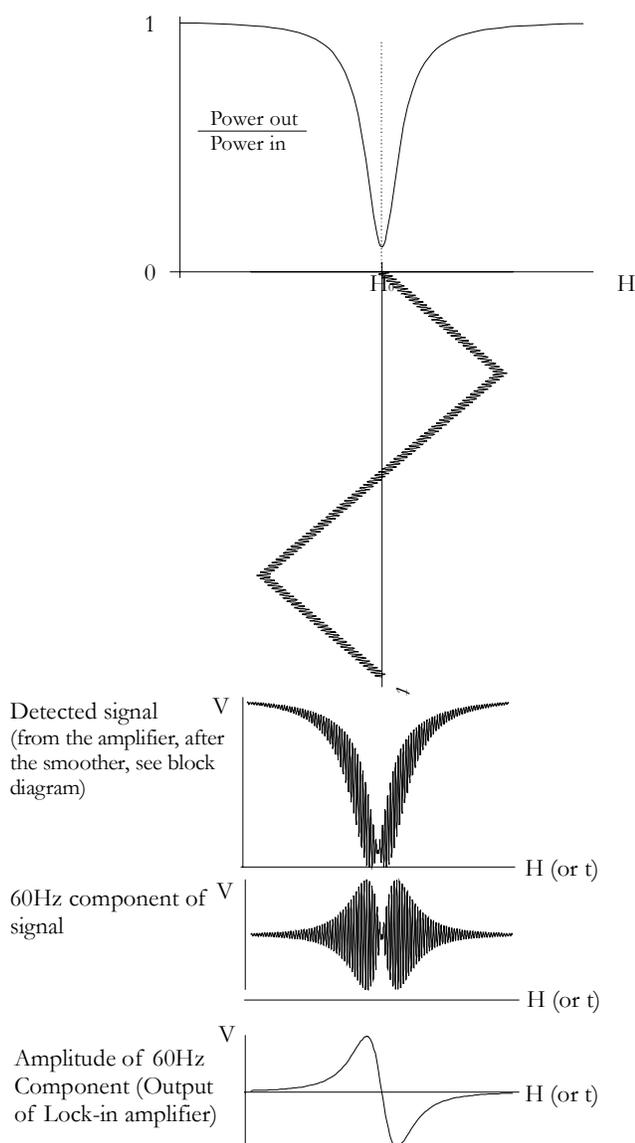
You want to sweep the field as shown in Figure 11. Unfortunately, the magnet power supply cannot supply a negative current, so the sweep starts at the resonance field Ho. Consequently, the sweep is not symmetrical, and half the resonance curve is lost. Therefore you must change the RF to a higher value to put the resonance at the center of the triangular sweep. This means you must put

the resonance curve on the scope at one end rather than in the center, at a larger frequency than used in the previous part of the experiment. How much? Experiment to find out.

Connect the output of the pre-amplifier to the A-input of the lock-in amplifier. Set the lock-in controls as follows: Phase - 0; Mode - FUND; zero offset, switch off; Time Constant - 1; DC Prefilter - 1sec. Connect phase input (ref) to the phase adjust on the H_{mod} panel. Connect output of the lock-in to the Y-input of the Computer Interface Unit.

Now how do you start? Turn the amplitude of Hmod way down, almost to zero. Refer to the diagrams above. For the first part of the experiment, Hmod was large; for this part it must be small. But of course once you get things working, try twisting all the knobs to peak up the signal. You should see the resonance curve sweeping across the face of the scope, and off the end. A few seconds later it should return and sweep across and off the other end. The needle on the lock-in should go right and left. The voltage on the magnet power supply should go from zero up and back again. If you are monitoring the Wavetek output on another oscilloscope, the horizontal line should go up and down from zero. When it is halfway up, the resonance curve should be in the center of the scope.

Using H_2O samples of molarity 3, 1, 0.3, 0.1, 0.03 molar Mn^{++}, adjust the mode to absorption and set Hmod small, ~1/8 the line width; this takes the derivative (see Ref. 2, p. 51). Adjust the lock-in amplifier and record the derivative on the HP 680A strip chart recorder.

Figure 12 shows a typical result for a 1 Molar sample. The two sharp glitches occur at the ramp voltage rapid reset. Chart speed = 5 cm/minute; Wavetek: q15V at 0.01 Hz; lock-in time contact = 0.3 sec; sensitivity = 25 mV on channel A input; DC pre-filter = 100 ms; input filters: hi-pass = 50 Hz, lo-pass = 0.1 kHz; mode = fund f; lock-in reference phase adjusted to give maximum peak-to-peak signal on lock-in meter; output zero offset adjusted to center trace on paper. By scanning more slowly, one can get a good measure of the line width H between the peaks. To measure the signal-to-noise ratio (S/N), one can increase the input gain by, say, 10x or more to record the RMS noise off resonance.

For the NMR paddle set to dispersion mode and a 0.33 Molar sample, the lock-in signal is shown in Fig. 13 under very similar conditions to Fig. 12.
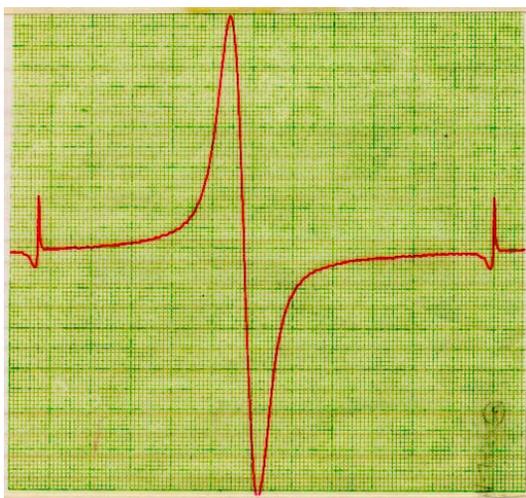

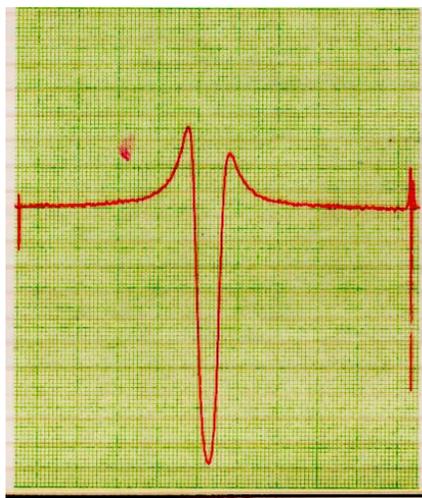**Figure 12: Protons in Mn⁺⁺ in H₂O Absorption Mode. Output from Lock-In**

Figure 13: ~0.3 Molar Mn⁺⁺ in H₂O Dispersion Mode. Output from Lock-In

REPORT

Include the following data, analysis, and calculations.

1.a. The Bloch Equations are the key to understanding this experiment:

$$\frac{d}{dt} M_x = \gamma(\vec{M} \times \vec{H})_x - \frac{M_x}{T_2} \tag{a}$$

$$\frac{d}{dt} M_y = \gamma(\vec{M} \times \vec{H})_y - \frac{M_y}{T_2} \tag{b}$$

$$\frac{d}{dt} M_z = \gamma(\vec{M} \times \vec{H})_z + \frac{(M_0 - M_z)}{T_1} \tag{c}$$

What is **M**? Is **H** a magnetic field inherent in your sample, or is it an applied field? Derive equations (a) to (c) for the case of no damping (none of the T_1 or T_2 terms). Hint: consider the classical torque equation **N** = d**L**/dt.

The equations you derived are applicable to a set of identical magnetic moments (spins), i.e., all the spins see the same magnetic field. The damping terms in (a) to (c) are added to take the different environment of each spin into account.

1.b.   In equations (a) and (b), T_2 is often called a *dephasing time,* the time required for $(\mathbf{M})_{x,y}$ to decay to zero after the resonance condition is removed. What is getting out of phase? How can this arise from inhomogeneities in **H**?

1.c. T_1 is the relaxation time for the z-component of **M** to come to an equilibrium value M_O when the resonance condition (applied RF) is removed. (You can see this by setting **H** to zero in (c).) What determines this equilibrium value, and what is it? [Hint: look at the classical Boltzmann distribution.]

1.d.   What (very general) physical factor of your sample accounts for the magnitude of T_1? [Hint: M_O is a thermal equilibrium magnetization.] More specifically, how might the addition of *paramagnetic* ions Mn^{++} affect T_1 (qualitatively)?

2.   Measure the magnetic field H_O of the magnet as precisely as you can in Gauss (average value and standard deviation). Are paramagnetic corrections significant? Measure H_O on several different days: does it vary? Why?

3.   Include best computer plot with calibrated H axes for proton signals in glycerin, showing the "best wiggles." Estimate the magnetic field inhomogeneity from the damping rate of the wiggles [see Ref. 1, pp. 84-86; and Ref. 2, p. 53; and problem 2-7, p. 57].

4.   Computer plots with calibrated H axes for absorption and for dispersion NMR signals in H_2O under slow passage and under non-adiabatic passage.

5.   Measure as precisely as you can the ratio of the magnetic moment of F^{19} to H^1, with standard deviation. Show best scope photo of F^{19} resonance.

6.   Record and show sequence of absorption lock-in trace from chart recorder for protons for M = 3, 1, 0.3, 0.1, 0.03 Molar Mn^{++}. Measure line width *H in Gauss and plot *H vs. Molarity; explain this graph; what is the residual line width (in Gauss) due to field non-uniformity?

8. From your best lock-in data for resonance in 1 Molar Mn^{++} in H_2O, compute the expected S/N ratio for the deuteron resonance in a 1 Molar Mn^{++} in D_2O sample under two different assumptions:

        i) The field H_O is kept at 3900 G and the oscillator frequency is adjusted to $f(H^2)$.

        ii) The oscillator frequency is kept at 16.5 MHz and the DC field is adjusted for resonance.

8.   Under condition 2. above, compute the S/N ratio expected for O^{17} NMR resonance in naturally abundant water; compare to Ref. 4, Fig. 4.
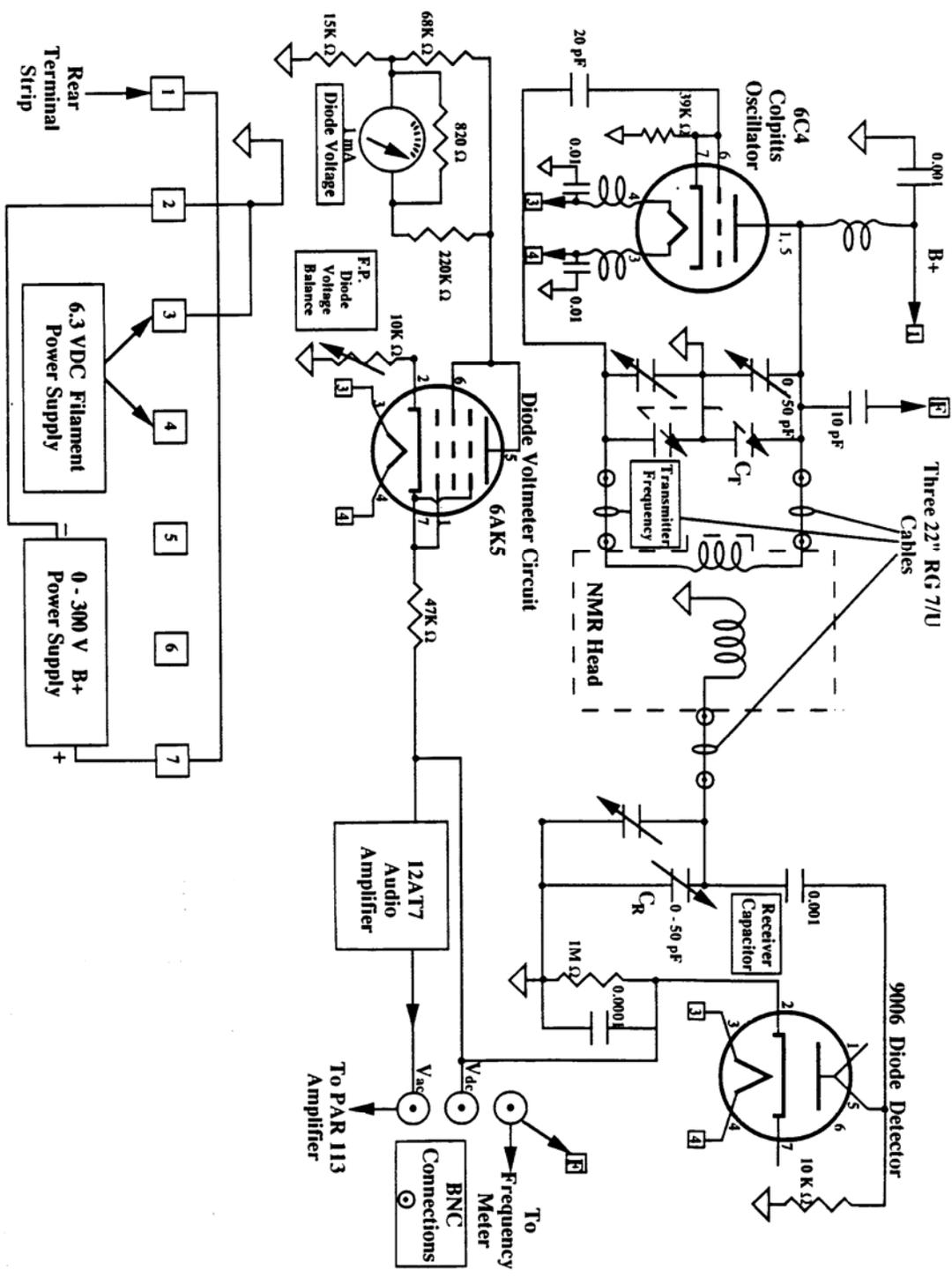
CW Appendix I: NMR RF Black Box Circuit Diagram

ISOTOPE (*indicates radioactive)	n-m-r FREQUENCY in mc. for a 10 Kilogauss field	NATURAL ABUNDANCE %	RELATIVE SENSITIVITY for equal number of nuclei at constant field	at constant frequency	MAGNETIC MOMENT μ in multiples of the nuclear magneton (eh/4πMc)	SPIN I in multiples of $\frac{h}{2\pi}$	ELECTRIC QUADRUPOLE MOMENT Q in multiples of e x 10^{-24} cm²
n^1*	29.17	—	0.322	0.685	−1.9135	1/2	—
H^1	42.57	99.9844	1.000	1.000	2.79245	1/2	—
H^2	6.535	1.56×10^{-2}	9.64×10^{-3}	0.409	0.85732	1	2.77×10^{-3}
H^3*	45.41	—	1.21	1.07	2.9785	1/2	—
He^3	32.44	1.3×10^{-4}	0.443	0.762	−2.128	1/2	—
Li^6	6.267	7.43	8.51×10^{-3}	0.392	0.8221	1	4.6×10^{-4}
Li^7	16.55	92.57	0.294	1.94	3.257	3/2	$\sim 2 \times 10^{-2}$
Be^9	5.987	100.	1.39×10^{-2}	0.703	−1.178	3/2	2×10^{-2}
B^{10}	4.576	18.83	1.99×10^{-2}	1.72	1.801	3	6×10^{-2}
B^{11}	13.67	81.17	0.165	1.60	2.689	3/2	3×10^{-2}
C^{13}	10.71	1.108	1.59×10^{-2}	0.251	0.7023	1/2	—
N^{14}	3.077	99.635	1.01×10^{-3}	0.193	0.4037	1	2×10^{-2}
N^{15}	4.316	0.365	1.04×10^{-3}	0.101	−0.2831	1/2	-26×10^{-3}
O^{17}	5.772	3.7×10^{-2}	2.91×10^{-2}	1.58	−1.893	5/2	-5×10^{-3}
F^{19}	40.07	100.	0.834	0.941	2.628	1/2	—
Na^{21}	—	0.257	—	—	—	⩾3/2	—
Na^{22}*	4.434	—	1.81×10^{-2}	1.67	1.745	3	—
Na^{23}	11.262	100.	9.27×10^{-2}	1.32	2.217	3/2	<0
Mg^{25}	2.606	10.05	2.68×10^{-2}	0.714	−0.8547	5/2	—
Al^{27}	11.10	100.	0.207	3.04	3.641	5/2	0.149
Si^{29}	8.460	4.70	7.85×10^{-2}	0.199	−0.5549	1/2?	—
P^{31}	17.24	100.	6.64×10^{-2}	0.405	1.131	1/2	—
S^{33}	3.267	0.74	2.26×10^{-3}	0.384	0.6429	3/2	-8×10^{-2}
S^{35}*	—	—	—	—	—	—	6×10^{-2}
Cl^{35}	4.173	75.4	4.71×10^{-3}	0.490	0.8210	3/2	-7.97×10^{-2}
Cl^{36}*	—	—	—	—	—	—	-1.68×10^{-2}
Cl^{37}	3.474	24.6	2.72×10^{-3}	0.408	0.6835	3/2	-6.21×10^{-2}
K^{39}	1.987	93.08	5.08×10^{-4}	0.233	0.3910	3/2	-3×10^{-2}
K^{40}*	2.470	1.19×10^{-2}	5.21×10^{-3}	1.55	−1.296	4	—
K^{41}	1.092	6.91	8.43×10^{-5}	0.128	0.2148	3/2	-2×10^{-2}
Ca^{43}	—	0.13	—	—	—	—	—
Sc^{45}	10.34	100.	0.301	5.10	4.749	7/2	—
Ti^{47}	2.400	7.75	2.10×10^{-3}	0.659	−0.7873	5/2	—
Ti^{49}	2.401	5.51	3.76×10^{-3}	1.19	−1.102	7/2	—

CW Appendix II: NMR Frequency Table

CW Appendix III

Part of Lock-In Manual model SRS 830

Lock-in amplifiers are used to detect and measure very small AC signals - all the way down to a few nanovolts! Accurate measurements may be made even when the small signal is obscured by noise sources many thousands of times larger.

Lock-in amplifiers use a technique known as phase-sensitive detection to single out the component of the signal at a specific reference frequency AND phase. Noise signals at frequencies other than the reference frequency are rejected and do not affect the measurement.

Why use a lock-in?

Let's consider an example. Suppose the signal is a 10 nV sine wave at 10 kHz. Clearly some amplification is required. A good low noise amplifier will have about 5 nV/⊕Hz of input noise. If the amplifier bandwidth is 100 kHz and the gain is 1000, then we can expect our output to be 10 ③V of signal (10 nV x 1000) and 1.6 mV of broadband noise (5nV/⊕Hz x ⊕100 kHz x 1000). We won't have much luck measuring the output signal unless we single out the frequency of interest.

If we follow the amplifier with a band pass filter with a Q=100 (a VERY good filter) centered at 10 kHz, any signal in a 100 Hz bandwidth will be detected (10 kHz/Q). The noise in the filter pass band will be 50 ③V (5 nV/⊕Hz x ⊕100 Hz x 1000) and the signal will still be 10 ③V. The output noise is much greater than the signal and an accurate measurement can not be made. Further gain will not help the signal to noise problem.

Now try following the amplifier with a phase sensitive detector (PSD). The PSD can detect the signal at 10 kHz with a bandwidth as narrow as 0.01 Hz! In this case, the noise in the detection bandwidth will be only 0.5 ③V (5 nV/⊕Hz x ⊕.01 Hz x 1000) while the signal is still 10 ③V. The signal to noise ratio is now 20 and an accurate measurement of the signal is possible.
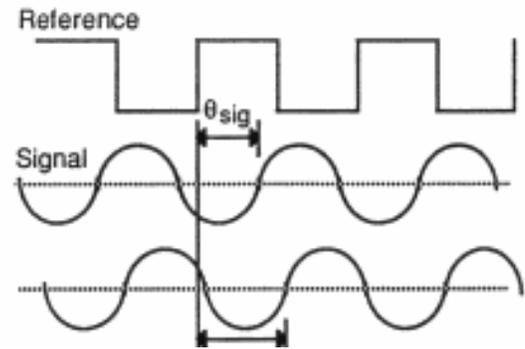
What is phase-sensitive detection?

Lock-in measurements require a frequency reference. Typically an experiment is excited at a fixed frequency (from an oscillator or function generator) and the lock-in detects the response from the

experiment at the reference frequency. In the diagram below, the reference signal is a square wave at frequency ω_r. This might be the sync output from a function generator. If the sine output from the function generator is used to excite the experiment, the response might be the signal waveform shown below. The signal is

V_{sig} $\sin(\omega_r$ t + $\theta_{sig})$ where V_{sjg} is the signal amplitude.

The SR830 generates its own sine wave, shown as the lock-in reference below. The lock-in reference is $V_L \sin(\omega_L t + \theta_{ref})$.

The SR830 amplifies the signal and then multiplies it by the lock-in reference using a phase-sensitive detector or multiplier. The output of the PSD is simply the product of two sine waves.

$V_{psd} = V_{sig} V_L \sin (\omega_r t + \theta_{sig}) \sin(\omega_L t + \theta_{ref})$

$=1/2 V_{sig} V_L \cos ([\omega_r - \omega_L] t + \theta_{sig} - \theta_{ref}) - 1/2 V_{sig} V_L \cos ([\omega_r + \omega_L] t + \theta_{sig} + \theta_{ref})$

The PSD output is two AC signals, one at the difference frequency ($\omega_r - \omega_L$) and the other at the sum frequency ($\omega_r + \omega_L$).

If the PSD output is passed through a low pass filter, the AC signals are removed. What will be left? In the general case, nothing. However, if ω_r equals ω_L, the difference frequency component will be a DC signal. In this case, the filtered PSD output will be

$V_{psd} =$ $1/2 V_{sig} V_L \cos(\theta_{sig} - \theta_{ref})$

This is a very nice signal - it is a DC signal proportional to the signal amplitude.

Narrow band detection

Now suppose the input is made up of signal plus noise. The PSD and low pass filter only detect signals whose frequencies are very close to the lock-in reference frequency. Noise signals at frequencies far from the reference are attenuated at the PSD output by the low pass filter (neither $\omega_{noise}-\omega_{ref}$ nor $\omega_{noise}+\omega_{ref}$ are close to DC). Noise at frequencies very close to the reference frequency will result in very low frequency AC outputs from the PSD ($|\omega_{noise} + \omega_{ref}|$ is small). Their attenuation depends upon the low pass filter bandwidth and roll-off. A narrower bandwidth will remove noise sources very close to the reference frequency, a wider bandwidth allows these signals to pass. The low pass filter bandwidth determines the bandwidth of detection. Only the signal at the reference frequency will result in a true DC output and be unaffected by the low pass filter. This is the signal we want to measure.

Where does the lock-in reference come from?

We need to make the lock-in reference the same as the signal frequency, i.e. $\omega_r = \omega_L$. Not only do the frequencies have to be the same, the phase between the signals can not change with time, otherwise $\cos(\theta_{sig} - \theta_{ref})$ will change and V_{psd} will not be a DC signal. In other words, the lock-in reference needs to be phase-locked to the signal reference.

Lock-in amplifiers use a phase-locked-loop (PLL) to generate the reference signal. An external reference signal (in this case, the reference square wave) is provided to the lock-in. The PLL in the lock-in locks the internal reference oscillator to this external reference, resulting in a reference sine wave at ω_r,, with a fixed phase shift of θ_{ref}. Since the PLL actively tracks the external reference, changes in the external reference frequency do not affect the measurement.

All lock-in measurements require a reference signal.

In this case, the reference is provided by the excitation source (the function generator). This is called an external reference source. In many situations, the SR830's internal oscillator may be used instead. The internal oscillator is just like a function generator (with variable sine output and a TTL sync) which is always phase-locked to the reference oscillator.

Magnitude and phase

Remember that the PSD output is proportional to $V_{sig} \cos\theta$ where $\theta = (\theta_{sig} - \theta_{ref})$. θ is the phase difference between the signal and the lock-in reference oscillator. By adjusting θ_{ref} we can make θ equal to zero, in which case we can measure $V_{sig} (\cos\theta=1)$. Conversely, if θ is 90°, there will be no output at all. A lock-in with a single PSD is called a single-phase lock-in and its output is $V_{sig} \cos\theta$.

This phase dependency can be eliminated by adding a second PSD. If the second PSD multiplies the signal with the reference oscillator shifted by 90°, i.e. $V_L \sin((\omega_L t + \theta_{ref} + 90°)$, its low pass filtered output will be

$$V_{psd2} = 1/2\ V_{sig}V_L \sin(\theta_{sig} - \theta_{ref})$$

$$V_{psd2} \sim V_{sig} \sin\theta$$

Now we have two outputs, one proportional to $\cos\theta$ and the other proportional to $\sin\theta$. If we call the first output X and the second Y,

$$X = V_{sig} \cos\theta \qquad\qquad Y = V_{sig} \sin\theta$$

these two quantities represent the signal as a vector relative to the lock-in reference oscillator. X is called the 'in-phase' component and Y the 'quadrature' component. This is because when $\theta=0$, X measures the signal while Y is zero.

By computing the magnitude (R) of the signal vector, the phase dependency is removed.

$$R = (X^2 + y^2)^{1/2} = V_{sig}$$

R measures the signal amplitude and does not depend upon the phase between the signal and Lock-in reference.

A dual-phase lock-in, such as the SR830, has two PSD's, with reference oscillators 90° apart, and can measure X, Y and R directly. In addition, the phase ϕ between the signal and lock-in reference, can be measured according to

$$\phi = \tan^{-1}(Y/X)$$

WHAT DOES A LOCK-IN MEASURE?

So what exactly does the SR830 measure? Fourier's theorem basically states that any input signal can be represented as the sum of many, many sine waves of differing amplitudes, frequencies and phases. This is generally considered as representing the signal in the "frequency domain". Normal oscilloscopes display the signal in the "time domain". Except in the case of clean sine waves, the time domain representation does not convey very much information about the various frequencies which make up the signal.

What does the SR830 measure?

The SR830 multiplies the signal by a pure sine wave at the reference frequency. All components of the input signal are multiplied by the reference simultaneously. Mathematically speaking, sine waves of differing frequencies are orthogonal, i.e. the average of the product of two sine waves is zero unless the frequencies are EXACTLY the same. In the SR830, the product of this multiplication yields a DC output signal proportional to the component of the signal whose frequency is exactly locked to the reference frequency. The low pass filter which follows the multiplier provides the averaging which removes the products of the reference with components at all other frequencies.

The SR830, because it multiplies the signal with a pure sine wave, measures the single Fourier (sine) component of the signal at the reference frequency. Let's take a look at an example. Suppose the input signal is a simple square wave at frequency 'f'. The square wave is actually composed of many sine waves at multiples of 'f' with carefully related amplitudes and phases. A 2V pk-pk square wave can be expressed as

$S(t) = 1.273\sin(\omega t) + 0.4244\sin(3\omega t) + 0.2546\sin(5\omega t) + ...$

where $\omega = 2\pi f$. The SR830, locked to 'f' will single out the first component. The measured signal will be $1.273\sin(\omega t)$, not the 2V pk-pk that you'd measure on a scope.

In the general case, the input consists of signal plus noise. Noise is represented as varying signals at all frequencies. The ideal lock-in only responds to noise at the reference frequency. Noise at other frequencies is removed by the low pass filter following the multiplier. This "bandwidth narrowing. is the primary advantage that a lock-in amplifier provides. Only inputs at frequencies at the reference frequency result in an output.

RMS or Peak?

Lock-in amplifiers as a general rule display the input signal in Volts RMS. When the SR830 displays a magnitude of 1V (rms), the component of the input signal at the reference frequency is a sine wave with an amplitude of 1 Vrms or 2.8 V pk-pk.

Thus, in the previous example with a 2 V pk-pk square wave input, the SR830 would detect the first sine component, $1.273\sin(\omega t)$. The measured and displayed magnitude would be 0.90 V (rms) $(1/\sqrt{2} \times 1.273)$.

Degrees or Radians?

In this discussion, frequencies have been referred to as 1 (Hz) and ω ($2\pi f$ radians/sec). This is because people measure frequencies in cycles per second and math works best in radians. For purposes of measurement, frequencies as measured in a lock-in amplifier are in Hz. The equations used to explain the actual calculations are sometimes written using ω to simplify the expressions.

Phase is always reported in degrees. Once again, this is more by custom than by choice. Equations written as $\sin(\omega t + \theta)$ are written as if θ is in radians mostly for simplicity. Lock-in amplifiers always manipulate and measure phase in degrees.

The Functional SR830

The functional block diagram of the SR830 DSP Lock-In Amplifier is shown below. The functions in the gray area are handled by the digital signal processor (DSP). The DSP aspects of the SR830 are covered in the SR830 manual. They are described as they come up in each functional block description. (See Section three (3) in the SR 830 Manual)

SR830 FUNCTIONAL BLOCK DIAGRAM
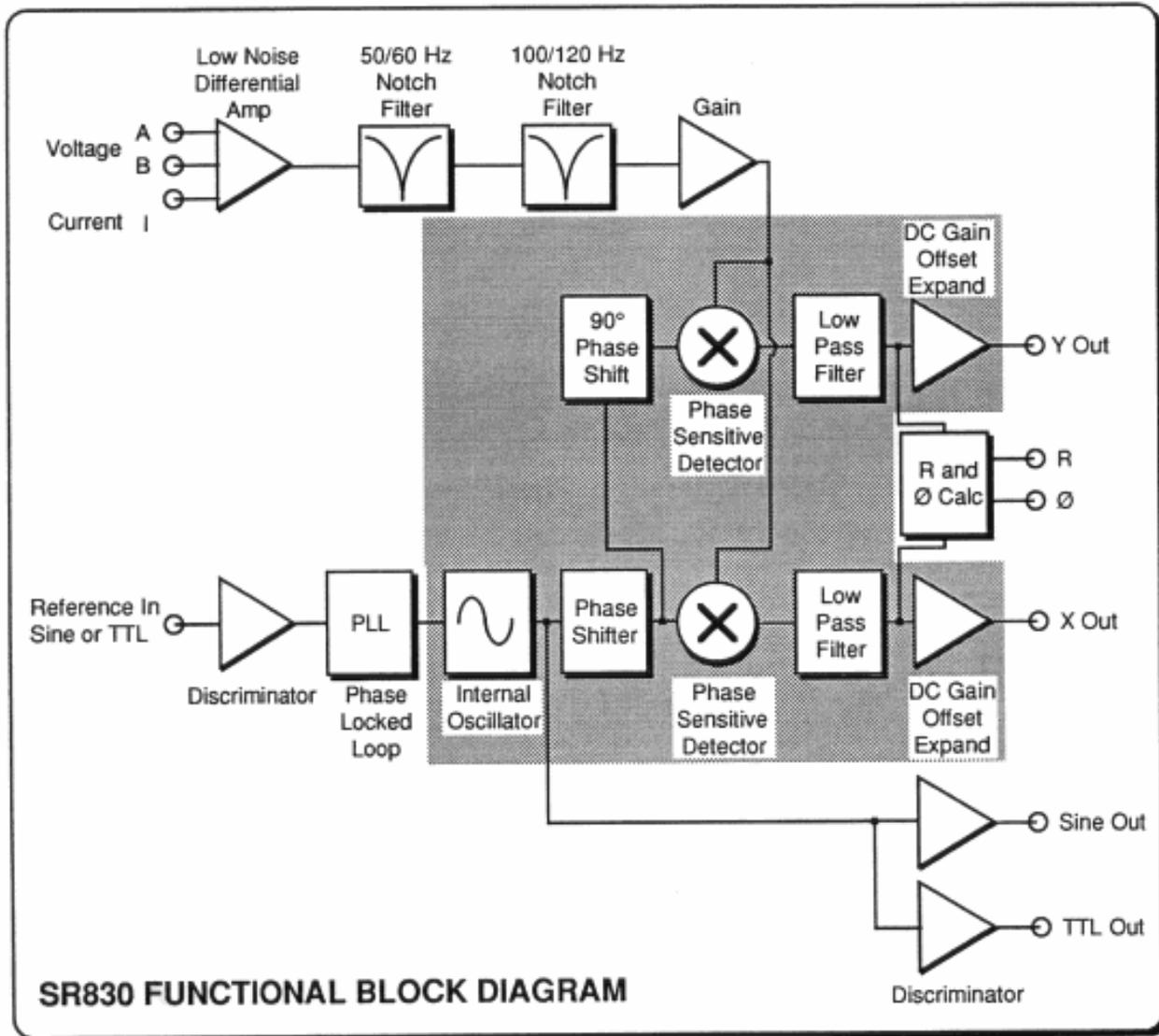
CW Appendix IV

# *How to transfer data from the scope to the computer.*

Setup:

First we need to make a connection between the computer and the oscilloscope. To do that, locate the aluminum box labeled **Computer Interface Unit**. Connect the *X input* with the knob on the **Hmod** corresponding to the sign "*to oscilloscope*". Connect the *Y input* with the output of **PRE-AMP**. Don't forget to turn on the *Computer Interface Unit.*
Now we are ready to use the computer to transfer the data.

NMR Scope Program

The program we are going to use to transfer the data is called **NMR Scope**. To get familiar with the program you might want to follow the following simple exercise.
On the desktop you will find an icon **NMR Scope**. Double click on that icon to open up the program. You will see the following window:
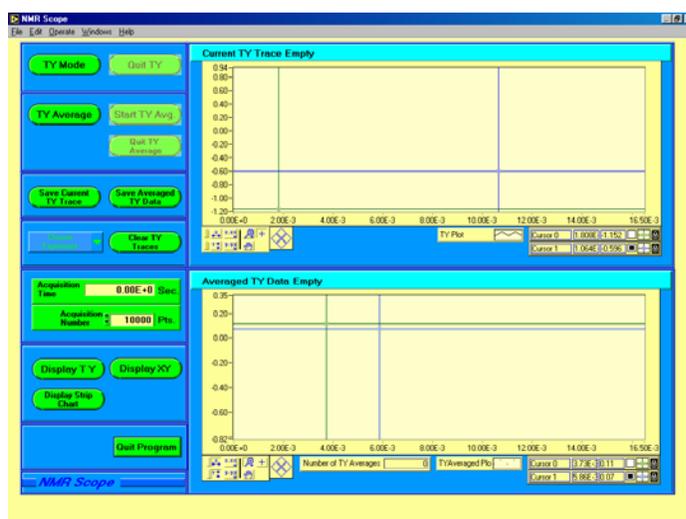

1. First select the type of experiment you are doing. There are two options: *Pulsed NMR Rising Edge Triggering* and *CW NMR Falling Edge Triggering.*

2. At the bottom left corner you will see three buttons: **Display TY**, **Display XY**, and **Display Strip Chart**. The latter one will be used later in the experiment. For now, press either **Display TY** or **Display XY** button.

3. To see the signal press the **TY Mode** or the **XY Mode**, depending on the previous choice you have made. You should now see a signal in the upper right chart. This is what it might look like:

TY Mode   XY Mode
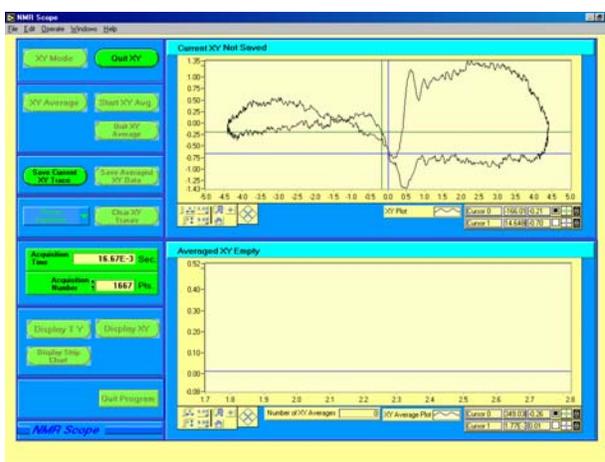
4. To stop the signal, press **Quit TY**, or **Quit XY** signal accordingly.
5. To save the data, press **Save Current TY/XY Traces**. Save the data as a .dat file format.
6. To clear the graph, press **Clear TY/XY Traces**.

Note: you can actually copy the graph and print it separately. Right click anywhere on the graph and press Copy Data. This temporary stores the image on the computer and you can paste it in most programs such as word or excel.

Averaging the Data:

We can also "average out" the signal to get a smother line. The program takes multiple samples over time and takes the average. You can average the data in wither mode: TY or XY. After choosing the mode, you might want to go over the following steps:

1. Press **TY/XY Average**. The window comes up asking if you want to "AutoSave the data." If you wish to do so, press yes and it will prompt you to save it. Otherwise, press no. In either case, you will get a window, asking to "Chose Acquisition Points." Just press ok. In the middle to the left of the program window you can set either the acquisition time or acquisition points. By default they are set to maximum.

2. Now, press **Start TY/XY Average**. The top right graph is the same as one before. The bottom right graph is the average graph. You might see similar graphs to the ones bellow:

TY Mode   XY Mode

3. To stop the signal, press **Quit TY/XY Average**.
4. To save the data press **Save Averaged TY/XY Data**.
5. To clear the graphs press **Clear TY/XY Traces**.

Strip Chart Recording Function (used in the later part of the NMR experiment)

Instead of using the actual Strip Chart Recorder, we can use the NMR Scope program to accomplish the same results. Once all the equipment has been set up properly, the use of the program is simple.

1. Set up the equipment as instructed in the section "Taking Data," part E.
2. Open the **NMR Scope** program.
3. Press the button **Display Strip Chart**. You will see that you are only given one graph space in the top right corner.
4. To start taking the data, press **Start Chart**. You will see something similar to the following graph:
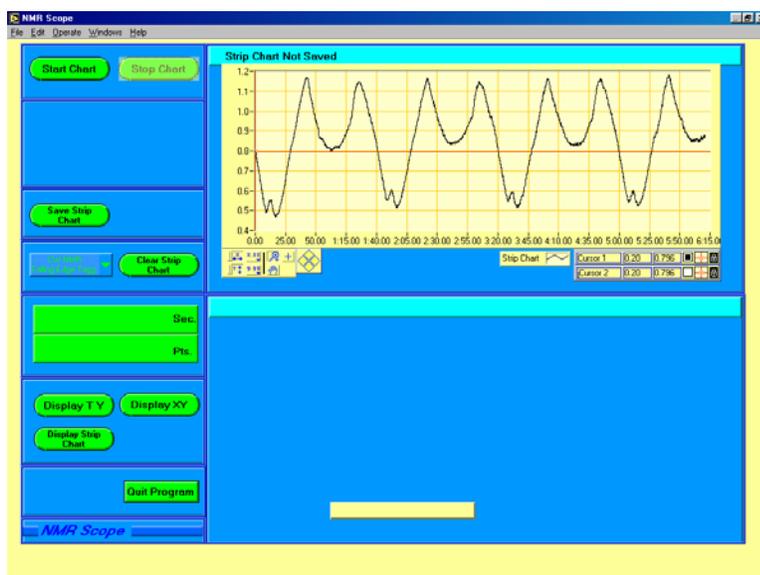
5. To stop the signal press **Stop Chart**
6. To save the data press **Save Strip Chart**
7. To clear the data press **Clear Strip Chart**

This concludes the overview of the program. If you have any more questions, you can ask one of the staff members for help.