

April 22, 2000

### Nuclear Magnetic Resonance-P410/510 Overview

It is impossible to overestimate the importance of NMR for physics, chemistry, biology and medicine. Yet, before 1946, the nuclear spin resonance had not been observed, despite several attempts to see it.

In the P410/510 Lab you have a unique opportunity to get direct experience with NMR and a basic understanding of the physics involved. There are three experiments:

- G7:** The cw(continuous wave) experiment. Probably this is the one you should do if you have had no previous contact with NMR. It is, however, a fairly long and difficult experiment, yet worth the effort it takes. The effect of "saturation" and of small amounts of paramagnetic ions is studied in detail.
- G7a:** The spin-echo experiment. This is a special, extremely clever, technique for measuring spin-spin relaxation times in different materials. The emphasis is on the physics of spin relaxation rather than the NMR itself. This technique avoids the problem of magnet inhomogeneity, but not self diffusion. However, the diffusion effect often can be separated from  $T_2$  in the data analysis.
- G7b:** This is our most sophisticated NMR experiment.  $H^1$ ,  $F^{19}$  and  $Li^7$  resonances are studied. A computer is used to control various sequences of pulses to make  $T_2^*$  and  $T_2$  measurements (the latter is unaffected by magnet inhomogeneity and self diffusion), accurate  $T_1$  measurements (this experiment is the only one which can do this), the chemical shifts for fluorine and lithium in different chemical environments, and the Knight shift in metallic lithium. It will represent a certain investment of time to do this experiment, but the pay-off is an introduction to important techniques used in real experiments with NMR. It is recommended that you do the G7 experiment first unless you already have some NMR background.

## Experiment G-7

## Nuclear Magnetic Resonance

Read the section on "Description of the Apparatus". Read "Getting Started" and do this part. Start reading the American Journal of Physics article by Pake, which is included in these notes. Pay particular attention to understanding the formulas on page 450—where do they come from, and what is their role in this experiment.

Then proceed to the rest of the experiment.

Measure carefully:

1. The magnetic moment of the proton. ✓
2. The relative moments of  $\text{H}^1$  and  $\text{F}^{19}$ . ✓

Measure qualitatively and understand:

3. The effects of overmodulation (large  $H_0$  modulation) and saturation (large  $H_1$ — the rf) on the line shape. ✓
4. The dependence of signal level on rf power level for protons in water as a function of paramagnetic ion concentration.
5. The behavior of the proton resonance in paraffin as it passes from liquid to solid.
6. The splitting of the proton resonance in gypsum as a function of the orientation of the gypsum crystal.

Measure roughly:

7.  $T_1$  for protons in highly purified (low conductivity) water.
8.  $T_2$  for protons in water, both from line width and wiggles, as a function of paramagnetic ion concentration.

## References †

- \*1. G.E. Pake, **Fundamentals of Nuclear Magnetic Resonance Absorption, I and II**, *American Journal of Physics*, **18**, I: p.438; II: p.473 (1950). A basic reference— read this first!
- \*2. G.E. Pake, **Nuclear Magnetic Resonance**, *Solid State Physics*, vol 2, p1 (1956). A second review article by Pake, written 6 years after ref. 1. This article describes the chemical and Knight shifts, and has more detail about the relaxation mechanisms.
- \*3. F.Bloch, *Physical Review*, vol 70, p460(1946). One of the original 1946 papers on the discovery of NMR. This paper introduces the famous Bloch equations used in this experiment and everywhere NMR is discussed.
- \*4. **Relaxation Effects in Nuclear Magnetic Resonance Absorption**, N. Bloembergen, E.M. Purcell, R.V. Pound, *Physical Review*, vol 73, p679(1948) A general discussion of relaxation.
- \*5. **A Radiofrequency Spectrograph and Simple Magnetic-Field Meter** , R.V.Pound and W.D.Knight, *Physical Review* , vol 21, p 219(1950). This describes the famous “Pound oscillator”, widely used for NMR applications.
- \*6. **A Steady-State Transient Technique in Nuclear Resonance** , R.Gabillard, *Physical Review*, vol 85, p694(1952). Describes “wiggles”.

## Reference Books on NMR

- 1. A. Abragam, *Principles of Nuclear Magnetism*, Oxford Univ. Press, reprinted 1989.
- 2. C.P. Slichter, *Principles of Magnetic Resonance*, Third Edition, Springer-Verlag, 1989.
- 3. E.Fukushima and S.B.W. Roeder, *Experimental Pulse NMR, A Nuts and Bolts Approach*, Addison-Wesley Publishing Co., 1981. (The P410/510 Library has this book.)

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† “starred” references are reprinted in the back of these notes.

### Getting Started

This will tell you how to get started, and how to find the resonance for the first time.

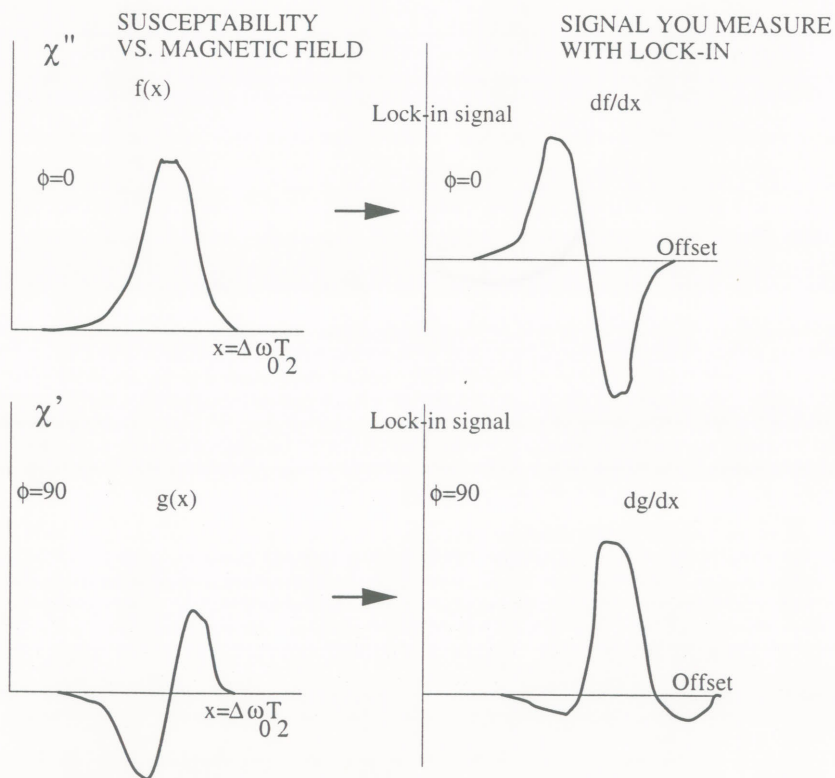
Mount the  $\text{Cu}^{++}$   $10^{20}$  ions/cc water sample inside the magnet. Check the tune of the resonant circuit by disconnecting the input of the rf amplifier and putting this signal into the Y axis of the oscilloscope. The rf signal should be less than 2 mv. If not, read the section on "Tuning the Resonator" and follow the tuning procedure to reduce the reflected signal from the resonator.

Assuming this is ok, set up:

1. The Wavetek. The sine wave amplitude should be 10 v peak/peak. This should be a  $\approx 80$  mv peak/peak signal at "COIL OUT" on the modulator panel. The MOD switch should be LEFT. The frequency should be 330 Hz.
2. The Lock-in amplifier is set to a gain of 100 mv.  $\times 4.0 = 400$  mv. The time constant is 0.3 sec. REF IN should receive one of the two signals from the HI on the Wavetek. All other pushbuttons should be OUT. Adjust the phase  $\phi$  knob to about 1 o'clock. Later, peak it up on the signal.
3. The modulator control panel:
  - ✓ a) attenuator set for 20 dB in.
  - b) offset is 5.0, gain is LEFT, Bandwidth is RIGHT, width is LEFT. The other controls affect the ramp for the XY recorder, and will be set up later.
  - c) the PHASE SHIFTER should be set on the right hand mark. This guarantees you will measure the derivative of  $\chi''$  rather than the derivative of  $\chi'$  or a mixture of the two.
- ✓ 4. Now turn on the DC current to the magnet. **FIRST:** set the variac to zero (important!). Set the coarse control to 8.13 and the fine control to 5.71. Turn on the power supply and the regulator below the power supply. Slowly raise the variac until the needle on the regulator meter is centered at 25 (there is a mark there). **DO NOT EVER let the regulator meter exceed full scale. Doing this will burn out the regulator, which must then be repaired by Nick.** The current should be 2.7 amps and the regulator meter at 25. If it is far off this mark, readjust the variac and the regulator coarse control until a) the current is 2.7 amps, b) the regulator meter is centered at 25. Both conditions must be satisfied.
5. Next slowly tune the magnet current (usually with the fine control) until you see the lock-in meter "blip" indicating you have moved quickly through the resonance. Try to do this very slowly. Once you see something, leave the regulator controls alone, and tune the offset, again slowly. If you really did pass through the resonance, you should see a strong signal. For example, I saw a signal of +46 peaking at 5.00 on the offset dial, and -55 at 4.74 on this dial. Tuning is complicated by the fact that transient

signals occur when you change the magnet current, leading you to falsely conclude you are near the resonance. Slow tuning is therefore essential. Keep the time constant at 0.3 sec for this.

6. Adjust the lock-in gain so that the signal is at most 50-70 on the meter. If you do not see a signal, or else you see one, but it does not have both positive and negative peaks, call your instructor. Do not proceed with the experiment until you have satisfactory results at this stage.
7. Now set up the XY recorder and make a trace of this signal. Dry runs with the pen up are usually the way to start, until you get it right. See the section on setting up the XY recorder before you start this.
8. By now, you should have read and understood up to page 450 in the article "Nuclear Magnetic Resonance I" by G.E. Pake. Section D. "The Bloch Formalism" is the key part, The two formulas just above formula 11.10 give  $\chi'$  and  $\chi''$  for the resonance, including the possibility of saturation. Note that you have just measured the *derivative* of the curve for  $\chi''$  at the top of Fig. 4. The reason for this will be explained later. *You have not measured the lower curve in fig. 4!* This is a very common mistake, since the curves are very similar in appearance.



9. Be sure to turn everything off before you leave the lab. Put the cap back on the recorder pen.

### Description of the Apparatus

A horizontal magnetic field ( $\vec{H}_0$ ) is produced by an iron electromagnet powered by a very highly regulated power supply (few parts per million regulation!).

A fixed frequency (10 MHz) continuous (CW) rf voltage is applied to a small coil surrounding the sample, which is inside the magnetic field. The rf magnetic field ( $\vec{H}_1$ ) is at right angles to the DC field, so can induce spin flip transitions (quantum mechanical point of view) or rotate the magnetization vector around the  $\vec{H}_1$  axis (Bloch semi-classical point of view). Both these ways of looking at it are equivalent, and are discussed in the references.

When  $H_0$  gives a Larmor frequency equaling 10 MHz, the rf can have a cumulative effect on the spins (resonance). This causes a detectable change in the sample magnetization, i.e. the magnetic susceptibility. Now the rf coil is part of a tuned LC resonant circuit which has been carefully matched to the impedance of the cable feeding the rf into the coil, so that no rf signal is reflected from the resonant circuit. Changing the susceptibility of the sample upsets this matched condition and causes some of the rf to be reflected back. The reflected rf is mixed with some of the original rf signal, and converted to a low frequency 330 Hz signal because the magnetic field  $H_0$  is being modulated at this frequency. This is detected by the lock-in amplifier. So the net result is a signal from the lock-in when  $B_0$  is tuned onto the resonance.

The  $H_0$  horizontal magnetic field has three parts: a) a DC signal, b) a very small 330 Hz modulation (when set correctly, the modulation is a small fraction of the resonance width), and c) a slow ramp to allow plotting of the resonance curve. The modulation is done by sending a time-varying current through the coil wound on the right-hand pole of the electromagnet.

#### MODULATION OF $H_0$

<u>TYPE</u>	<u>SOURCE</u>	<u>MAGNITUDE(GAUSS)</u>
DC FIELD	POWER SUPPLY	~2500 GAUSS
330 HZ	WAVETEK+ MODULATION PANEL	~1-2 GAUSS (OR LESS)
SLOW RAMP	MODULATION PANEL	~2-10 GAUSS

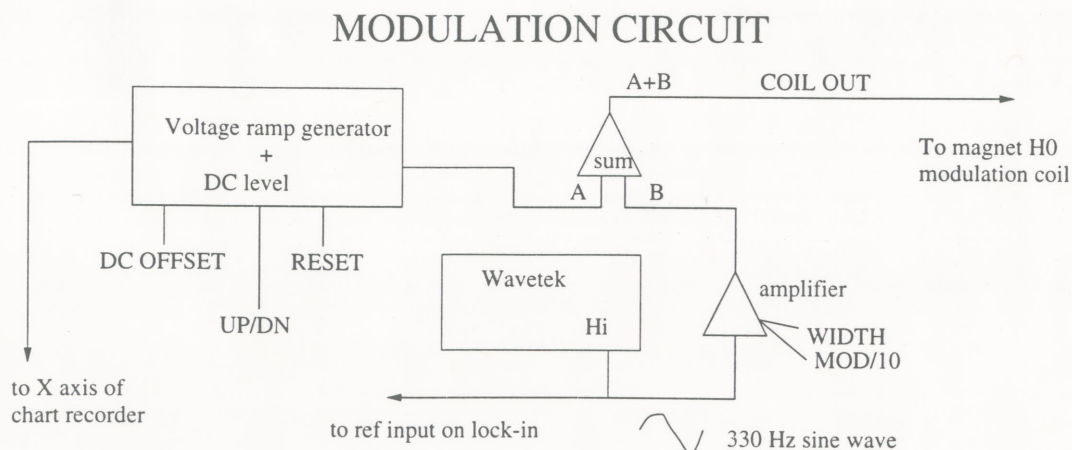
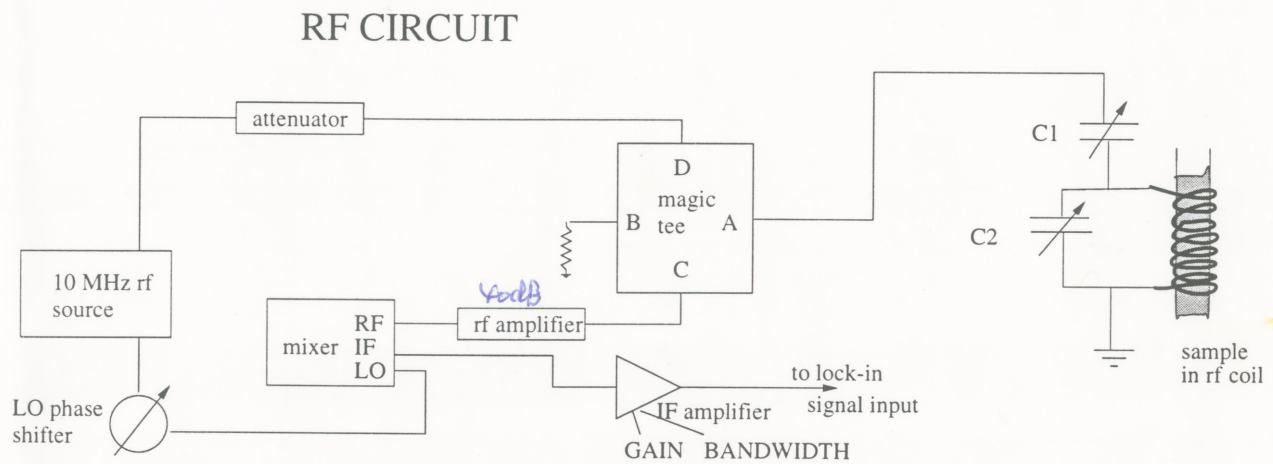
$$\text{---} + \text{~~~~} + \text{---} = H_0(t)$$

“overmodulation of  $H_0$ ” refers to making the 330 Hz modulation large compared to the resonance width, thus distorting the resonance line shape.

## How the NMR Detector Works

Near to the resonance, the nuclear spins give a small change in the susceptibility, changing the inductance of the rf coil by a small amount. This mismatches the tuned circuit, resulting in a reflected signal. This rf signal is very small, but it is modulated by the 330 Hz signal across the magnet coil which originates from the Wavetek. In order to detect this reflected rf signal, it passes through a magic tee (see below), is amplified about 40 dB and goes into the mixer, where it is combined with the local oscillator (unmodulated) signal. The "IF" output of the mixer is now a signal at the 330 Hz frequency. It is amplified by the IF amplifier which has a bandwidth and gain controllable by switches on the control panel. The IF amplifier output goes to the lock-in signal input.

The circuit can be divided into an rf part and a modulation part. These are shown in the diagram below.



The magic tee works as follows: consider a matrix with the rows (inputs) labelled by "A", "B", etc. and the columns (outputs) labelled in the same way. Then the operation of the magic tee can be represented by a 4 x 4 matrix:

$$\frac{1}{\sqrt{2}} \begin{pmatrix} A & B & C & D \\ 0 & 0 & 1 & 1 \\ 0 & 0 & -1 & 1 \\ 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix}$$

Which means, for example, a signal entering at C appears with magnitude  $\frac{1}{\sqrt{2}}$  at A and the same magnitude, but inverted at B. This means that  $\frac{1}{2}$  the power input to C appears at A and  $\frac{1}{2}$  at B. In our case, the terminal B is terminated with a  $50\Omega$  resistor, so there is no reflection. Terminal C contains only the reflected signal entering A and not the rf from the attenuator, half of which goes to the rf coil and half of which is absorbed in the termination at B.



### Tuning $C_1$ and $C_2$

It is absolutely critical to match the resonant circuit with the sample in place so that the reflection off the nuclear resonance is less than a few millivolts. This must be retuned each time the sample is changed. Water and freon call for very different settings, for example.

The reason this is critical is that otherwise the rf signal will saturate the 40 dB gain rf amplifier and it will be impossible to observe the nuclear resonance.

One of the capacitors ( $C_2$ ) is in parallel with the coil around the sample, the other one ( $C_1$ ) is in series with the signal cable connected to this parallel resonant circuit (see diagram).

Physically, the two capacitors are made of concentric cylinders one of which is moved into the other to increase the capacitance when you turn the little screw at the bottom of the sample holder, just below where the signal cable enters.  $C_1$  is the one on the right,  $C_2$  is the one on the left.

What you are doing by adjusting the two capacitors is a) tuning the resonant frequency to be exactly 10 MHz, b) tuning the impedance seen by the signal to this resonant circuit to be 50 ohms so that it is matched and no reflection occurs. In other words, you are adjusting the complex impedance at this particular rf frequency to have a real value of 50 ohms and an imaginary value of zero.

It is a "two-dimensional" tune. If you do not do it systematically, it can lead to infinite frustration and prevent doing the measurement of the nuclear resonance.

Here is a procedure which we found to be reasonably efficient.

1. Set up the oscilloscope so that the X axis is driven by the rf input to the attenuator. You should see a horizontal line a few cm wide on the scope. The trigger should be set to "X-Y" and "video". This means that the sweep is driven by the rf and not internally. Disconnect the input to the rf amplifier and put it into the Y axis input of the scope. Set the Y scale to 10 mv/cm. You should see an ellipse, which in some cases is a tilted line.
2. Begin by backing both capacitor screws ccw until they are stopped. Then, with a water sample in place, turn  $C_2$  (left side) cw just under 14.5 turns. Then turn  $C_1$  cw just under 9 turns. Set the left screw to 2 o'clock, and the right screw to 1 o'clock. Try turning the two adjustment screws back and forth about  $\frac{1}{2}$  turn. The scope should show that you are sensitive to these motions, which means that you are not very far off the right settings. If there is little visible change when you do this, it means that the capacitor is far from the correct setting. You have to make larger adjustments on each one independently until you do find a region sensitive to  $\frac{1}{2}$  turn changes on either one.
3. Now begin the search for the match condition. With either capacitor, adjust until you see a tilted line  $\leq 4$  cm high on the 10 mv scale. Turn  $C_2$  cw (clockwise) until you see a upright ellipse. Then turn  $C_1$  ccw (counter-clockwise) until you see the line again. Continue this procedure, alternating between

the two sides and observing the height of the line. It should gradually be getting smaller in height. (If it is instead getting larger, you have gone too far— back off  $C_2$  ccw and start again). Gradually, the height of the line decreases, and you find you are making smaller and smaller adjustments— the line to ellipse transition is getting increasingly sensitive. Switch when appropriate to lower scales until you have reached the 2 millivolt/cm scale on the Y axis. Tweak each capacitor in turn (they are usually turned in opposite directions) until you have achieved a *horizontal line* less than, say, 0.2 cm high on the 2 millivolt scale. Then you are finished, at least for this sample.

In the final stages of the tuning procedure, the magnet should be on. Recheck the tuning after things have warmed up a bit— it has a tendency to drift.

### Wavetek Settings

These can be set once and for all. Set the *frequency* to 0.33 times 1K (Hz) to get 330 Hz. Set the *sweep width* to OFF, the *DC offset* to OFF, the *waveform* (rightknob) to a SINE WAVE and the *amplitude* to about 10 volts peak to peak. The latter is not too critical.

The output of the Wavetek goes to two places: “MOD IN” on the modulator, and to the “REFERENCE IN” on the lock-in amplifier.

### XY Recorder

Install the pen so that the rim is BELOW the prongs which grab it on the moving part of the recorder. Otherwise it will not write. Ask the instructor to show you if this is not clear. You have to remove the pen cap before installing it. Tape a piece of paper in place before installing the pen. This should be done with the recorder on STANDBY.

The X ramp goes from 0 volts to  $\pm 10.4$  volts. The sign is determined by the choice of “UP” (+) or “DOWN” (-) on the modulator front panel. Setting this same switch to the center position stops the ramp wherever it happens to be, which is useful for setting up the XY recorder.

The X axis has a maximum travel of about 15 cm. The settings work are 2 v/cm (var), with the offset adjusted to keep the whole trace centered on the paper.

For the Y axis, it depends but it is usually good to set the offset so that zero signal from the lock-in is in the center. With the peak lock-in signal about 60 on the lock-in meter, 1 v/cm (var), with the variable gain set so the signal was just on scale to the right worked. This way, you can record both positive and negative signals.

The “RATE” switch on the modulator panel controls the ramp rate. Setting it to the LEFT position gives the slowest ramp, which is the one recommended. For tests you might want to use the RIGHT or CENTER positions.

To setup the data, run the ramp up and stop it at about 5 volts so that the recorder is in the center of its travel. Then use the OFFSET potentiometer to move the signal into the center of the paper.

ALL THIS SHOULD BE DONE WHEN THE PEN IS UP, but the recorder is in "M" position, not "STANDBY". This means that the pen will move, but not write anything. When you are ready to record the data, flip the RESET switch on the modulator to the RIGHT, and the UP/DN switch to UP. The pen should move to the bottom of the page. Then put the pen DOWN and flip the RESET switch to the LEFT to start the ramp. RATE should be LEFT. This will trace out your curve, which if you have been careful about the gain will not go off scale anywhere. When the curve is finished, put the pen UP before setting RESET to the RIGHT.

*When you are finished taking data with the pen recorder, it is VERY IMPORTANT that you remove the pen, and put the cap on. Otherwise, the pen will dry out and not be available to the next user, causing a considerable delay and inconvenience.*

### Lock-in Settings

Be sure that you understand how a lock-in amplifier works. Ask your instructor to explain it to you or give you something to read if you don't understand.

A good place to start is with the gain on the 100 mv scale, and the multiplication set to 4.0. The time constant can be set to 0.3 sec. The output zero offset should be set so that zero input signal reads zero on the meter. All pushbuttons should be out.

Adjust the phase on the lock-in to maximize the signal after you find the resonance.

### Hints For Doing the Experiment †

1. The magnetic moment is measured by measuring the magnetic field using a Hall probe (ask Nick to give you one). 2.5 on the 10K scale is 2500 gauss, for example. Don't forget to check the zero and the calibration. The earth's field is about 0.8 gauss. The rf frequency can be measured with the frequency meter. Use this information to calculate the proton magnetic moment in nuclear magnetons:  $\frac{e\hbar}{2M_{\text{proton}}c}$ .
2. I suggest that you postpone the measurement of the  $\mathbf{F}^{19}$  nuclear magnetic moment until the end, since substantial retuning of  $C_1$  and  $C_2$  is needed due to the difference in dielectric constants between water and freon.
3. The effect of overmodulation (large 330 Hz modulation of  $H_0$ ) can be checked by using the MOD switch first in the x1 position (LEFT) and then in the MOD/10 position (RIGHT). If the 330 Hz signal is too large, you will see higher harmonics of 330 Hz. This can be checked by using the 2F button on the lock-in. Overmodulation means that the curve you trace out will no longer be a derivative of the

† The numbers refer to numbers of the items on page 2.

susceptibility, but will contain higher derivatives and be therefore distorted. An even more direct test is to see if the signal is proportional to the amplitude  $a$  of the modulation. If it is, it will drop by a factor of 10 if  $a$  decreases by that factor. Nonlinear terms:  $a^2$  etc. mean higher harmonics are present. With the settings recommended and the  $10^{20}$  ions/cc  $\text{Cu}^{++}$  sample, this was not too important. A small amount of harmonics were present, but the x1 setting was nearly proportional— 10 times— the MOD/10 setting. This was not checked for other samples, so be careful to check this. The effect of saturation is found by changing the rf attenuator to find the signal level with the maximum signal. For the  $10^{20}$   $\text{Cu}^{++}$  ions/cc sample, this was found to be 20 dB, which is an  $H_1$  a factor of 100 lower than 0 dB setting of the attenuator. From this, plus some other experimental numbers, it is possible to derive the product  $T_1 T_2$ . See the more detailed remarks on overmodulation and saturation which follow this section.

- 4.+8. The relaxation rate  $\frac{1}{T_2}$  for spin-spin relaxation is proportional to the concentration of paramagnetic ions because the magnetic moment of the unpaired electrons is  $\approx 1000$  times the nuclear magnetic moment. So the effect of even a few paramagnetic ions on creating local magnetic fields can be very large. You should plot  $\frac{1}{T_2}$  vs. concentration on a log-log scale. If the rate increases linearly with ion concentration, it will appear as a straight line with a slope of 1. However, at very low concentrations, the line width (proportional to  $\frac{1}{T_2}$ ) primarily gives a measure of the magnetic field inhomogeneity, not  $\frac{1}{T_2}$ , so you should see the line become a constant. The G7a experiment uses the spin-echo method to get around the experimental problem of an inhomogeneous magnet.

The situation is less clear for the relaxation time  $T_1$ . You should also study this vs. ion concentration. This kind of relaxation represents an exchange of energy between the proton spin and its environment. The saturation field measurement gives  $T_1 T_2$ . You can also make a log-log plot for this quantity vs. ion concentration.

5. What do you expect? The greater mobility of the protons in the parafin has a big effect on the  $T_2$  you measure. Try to explain your results qualitatively.
6. Gypsum is  $\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . The protons in the water of hydration occupy two different chemical environments, hence there is a small relative shift in the resonance between them. Try to determine this splitting (in gauss). This kind of shift is very important in organic chemistry, where it has been used to determine the structure of many organic compounds. Why does the splitting of the resonance depend on the orientation of the crystal?
7. It takes great care to get  $T_1$  in pure water. Compare your answer to the experimental value of 2.3 seconds. Try ordinary distilled water too.

Highly purified water must be used, because even distilled water contains a minute amount of paramagnetic impurities, which, if present, completely dominate  $T_1$  and  $T_2$ . It is hard to find water which

is sufficiently pure to allow measurement of the intrinsic relaxation times. Before filling a sample tube with low conductivity water (ask the instructor if you can't find it), wash the tube very thoroughly with the water.

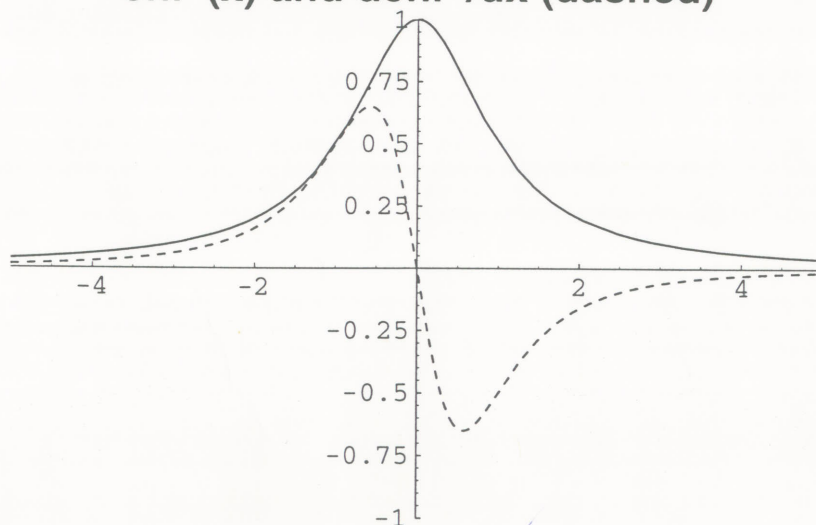
### Effect Of Overmodulation

Install the  $10^{20}$   $\text{Cu}^{++}$  ions/ $\text{cm}^3$  for the overmodulation and saturation studies. Later, you can try other samples.

Assume that you have set the rf phase control on the modulation control panel (just above the attenuator) so that you are seeing a lockin signal vs. ramp voltage which looks something like the dashed curve in the figure below. You are now observing the imaginary or dissipative part of the susceptibility  $\chi$ , which is called  $\chi''$ . The reason why the curve looks like the dashed curve rather than the solid curve is that the lockin measures the *derivative* of the signal, rather than the signal itself. This is because the lockin takes the product of the reference signal,  $\cos(\omega_0 t)$  and the reflected and mixed rf signal, then integrating this product over whatever time constant you have chosen. This is a time which is many periods long. If the output of the mixer is  $f[x]$  without the modulation of  $H_0$ , it will be  $f[x + a \cos(\omega_0 t)]$  if  $H_0$  is modulated with an amplitude  $a$  (in dimensionless units). The lockin signal is then given by the formula below:

(Define  $x \equiv T_2^*(\omega_0 - \omega)$  and divide  $\chi$  by  $\frac{1}{2}\omega_0 T_2^* \chi_0$ . See the article I by Pake in AJP, page 450, formulas 12.02 and 12.03.)

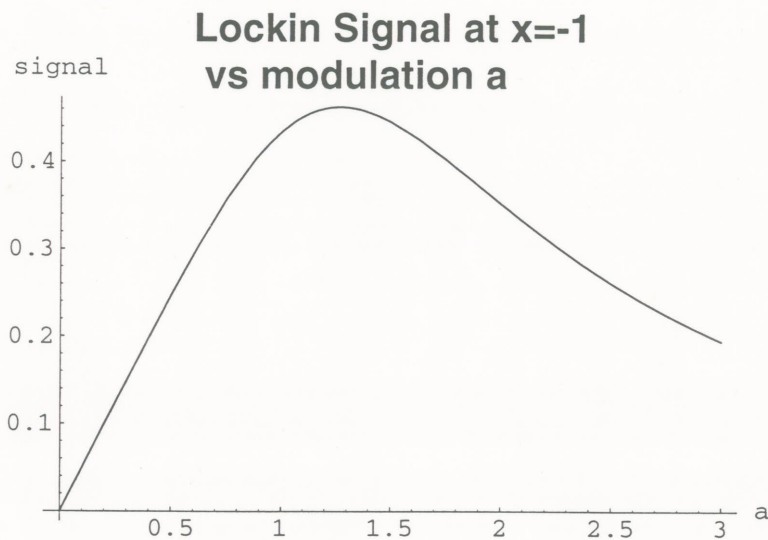
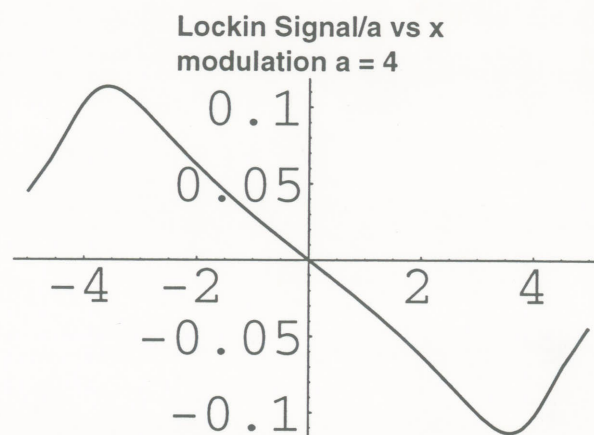
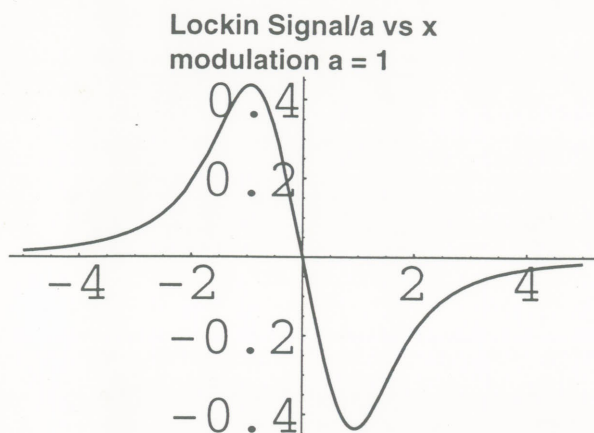
### $\chi''(x)$ and $d\chi''/dx$ (dashed)



$$\int_0^{2\pi} \cos(\omega_0 t) f[x + a \cos(\omega_0 t)] dt \approx a\pi \frac{df[x]}{dx}$$

*Handwritten notes:  $\omega_{mod}$  (red),  $\omega_{modulation}$  (blue),  $\omega_{mod}$  (blue)*

This is only true if the modulation amplitude  $a$  is small enough so that we can keep only the first term in a Taylor series expansion in  $a$  of  $f[x + a \cos(\omega_0 t)]$ . What happens as you increase the modulation  $a$ ?



The modulation is linear in  $a$  up to just under  $a = 1$ . For overmodulation, say  $a = 3$ , the resonance curve is distorted and reduced in magnitude. The graph above shows that, at  $x = -1$ , the maximum signal occurs for  $a \approx 1.3$ . So this suggests a simple way to see experimentally when the modulation is too large. Increase the modulation by using the amplitude control on the Wavetek (after setting to MOD x 1 on the control panel). If you are set at  $x = \pm 1$  (the maximum signal for small modulation— use MOD x 1/10 to find this with the ramp off, of course, you can quickly find the maximum signal. Check the linearity of the signal with the Wavetek amplitude for amplitudes smaller than this. Work in the region where the signal is linear in the amplitude.

How do we convert from dimensionless variables to physical variables? By the definition of  $\gamma$ , we have  $\gamma B_0 = \omega_0$ . For protons,  $\gamma = 2.675 \times 10^4 \text{ rad sec}^{-1} \text{ gauss}^{-1}$ . It is not difficult to see that the dimensionless modulation amplitude is given by

$$a = \Delta B_0 \gamma T_2^*$$

$\Delta B_0$  is the amplitude of the 330 Hz modulation of  $B_0$ . For example,  $a = 1$  corresponds to  $\Delta B_0 = .037$  gauss if  $T_2^* = 1$  millisecond. This small field is difficult to measure with the AC Hall probe, but one could scale by the measured amplitude (easily measured) of the Wavetek from larger amplitudes. Turning this around, this could give a possible means of determining  $T_2^*$  if one can measure both  $\Delta B_0$  and  $a$  (from the signal vs a curve). It might be worth a try, especially for the  $10^{21}$   $\text{Cu}^{++}$  sample and maybe the  $10^{20}$ .

**At least be sure  $a \leq 1$ , so you are not overmodulating the resonance signal.** How do you avoid overmodulation for the  $10^{19}$  sample? The  $10^{21}$ ?

### Effect Of Saturation †

The next thing you have to study is how the magnitude of the rf signal  $H_1$  affects the resonance curve. Once again, the relevant formulas are on page 450 of the Pake article in AJP. Physically, if the rf signal is too large, the polarization is reduced because so many spin systems are being pumped out of the lower state into the upper state. This has two practical effects: a) it reduces the signal (there would be zero signal if the populations of upper and lower states were equal), b) it broadens the resonance curve, which means that (see below), when you measure  $T_2^*$  from the resonance width, you are really measuring

$$T_{2, effective}^* = T_2^* \sqrt{1 + \gamma^2 H_1^2 T_1 T_2^*}$$

When  $H_1$  is very large, this is called saturation. There is a maximum observable signal, corresponding to  $\gamma^2 H_1^2 T_1 T_2^* \approx 1$ . As Pake says on page 451, the "nuclear spin system ... is soaking up radiofrequency energy to such an extent that the relaxation processes are unable to keep it at the lattice temperature". It is as if the spin system is heated by the rf to a much higher temperature than the ambient temperature of the lattice.

On the plus side, if you measure the signal amplitude vs. attenuator setting, you will find a value for the attenuator for which there is a maximum in the signal. Increasing  $H_1$  actually *lowers* the signal above the value for which it is a maximum. Assuming you can measure  $H_1$  (see below) and already know  $T_2^*$ , you can estimate  $T_1$ . In fact, this is about the only way you can get  $T_1$  in a cw experiment like this one.

One of the first things you should do, is take curves of the signal (on the maximum—just read the lockin meter) vs. attenuator from 40 dB to 0 dB. This will be different for different samples, so you should take it for every new sample before you record the resonance curve on the chart recorder. It is surprising how little the signal varies over this very wide dynamic range in  $H_1$ , which is a factor of  $10^4$  in the magnitude of  $H_1$ . But in each case, there is a rather specific attenuator setting which gives a maximum signal. You can usually determine this to within  $\pm 2$  dB or better.

**When determining  $T_2^*$  from the width of the resonance curve, be sure that you are working far below this signal maximum point, i.e. add more attenuator.**

To see the theoretical consequence of saturation, define \*

$$s \equiv \gamma H_1 \sqrt{T_1 T_2^*}$$

The complex susceptibility (see the formulas between 11.09 and 11.10 in Pake, page 450) is:

$$\chi = \frac{1}{2} \chi_0 \omega_0 \tau_2^* \frac{1}{1 + s^2 + ix} \quad i \equiv \sqrt{-1}$$

† See the discussion in Pake II, page 477ff

\* Formula numbers refer to Pake I and II



$x$  is defined as above. The imaginary (dissipative) part of  $\chi$  is

$$\chi''(x) = \frac{1}{1+x^2+s^2}$$

The actual resonance curve measured from the lockin is the derivative  $\frac{d(H_1 \chi'')}{dx}$ :

$$D(s) \equiv s \frac{d\chi''}{dx} \Big|_{max} = s \frac{-2x}{(1+x^2+s^2)} \Big|_{max}$$

See formula 16.02, Pake II, page 477. Recall that  $|V_0| \sim H_1 \sim s$ . (The factor of  $H_1$ , or in dimensionless units  $s$  comes from the reflection being proportional to the rf voltage times  $\chi''$ .) At the maximum, the second derivative must be zero. It is straightforward to show that this occurs at

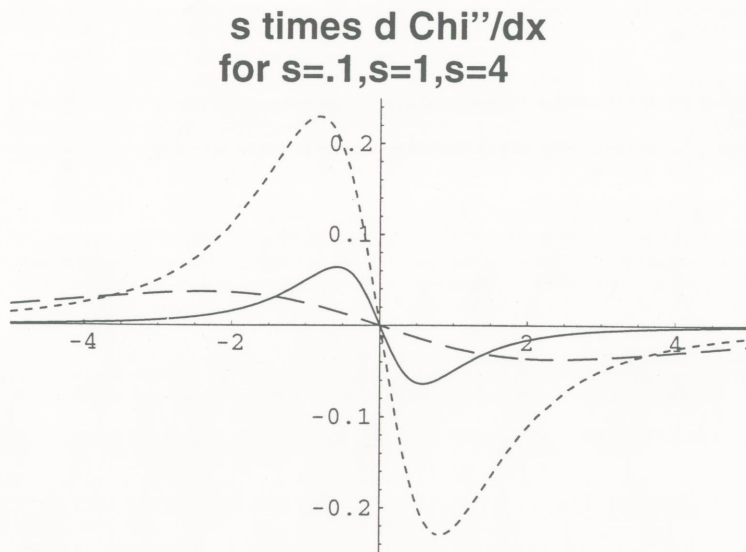
$$x_m = -\sqrt{\frac{1+s^2}{3}}$$

The last formula shows why the peak "moves out" when  $s \gg 1$ . The value of the derivative of  $s\chi''$  for  $x = x_m$  is

$$\frac{d\chi''}{dx} \Big|_{x=x_m} = \frac{1}{8} \left( \frac{3s}{1+s^2} \right)^{\frac{3}{2}} \equiv D_{max \ x}(s)$$

This is approximately what you observe when you take the attenuator curve (stay on the maximum signal by retuning  $x$ , i.e.  $H_0$  if necessary).

The figure below shows the lockin signal for three resonance curves:  $s=0.1, s=1$ , and  $s=4$ ; The solid line is  $s=0.1$ , the dashed line  $s=1$ , and the long dashed line  $s=4$ . This clearly shows that increasing the rf  $H_1$ , which is proportional to  $s$ , yields a maximum signal near to  $s = 1$ .



This resonance curve peak has a maximum value, now varying  $s$  ( $H_1$ ):

$$s = s_m = \frac{1}{\sqrt{2}}$$

$$D_{max\ x, max\ s} = D_{max\ x}(s_m) = \frac{1}{4}$$

To see if your attenuator curve has the right dependence on  $H_1$ , define

$$\alpha \equiv \left( \frac{H_1}{H_{10}} \right)^2$$

$\alpha$  is a ratio, so is determined solely by the attenuator setting.  $H_{10}$  is  $H_1$  with the attenuator set to 0 dB—the maximum possible rf field. If you now plot

$$\frac{\alpha^{\frac{1}{3}}}{D_{max\ x}(s)^{\frac{2}{3}}} \sim 1 + s^2 = 1 + \gamma^2 H_{10}^2 \alpha T_1 T_2^*$$

you should get a straight line if the abscissa is  $\alpha$ . The slope of this line gives you  $\gamma^2 H_{10}^2 T_1 T_2^*$ . This graphical method is probably more accurate than just measuring the attenuator setting for which  $D = D_{max\ x, max\ s}$ . The final step, either way you do it, is to determine  $H_{10}$  in gauss.

#### Measuring $H_{10}$

To get  $T_1$  from your data, you need to know  $H_{10}$  the maximum rf field with zero attenuation. How do you find this? Unfortunately, it is only possible to make a rough estimate. Of course, if you have a sample for which  $T_1$  and  $T_2^*$  are known accurately, you can turn the procedure around and find  $H_1$  for at least one attenuator setting, then scale it for other samples. In the G7b experiment,  $T_1$  and  $T_2^*$  can be found, so a sample borrowed from this experiment could accomplish this. But there is a technical difficulty: the sample tubes are of different sizes. Still, it might work.

As an alternative procedure, here is another way to go. Set the rf attenuation to zero, and measure the peak to peak voltage of the rf with the scope. Be sure to terminate the scope input with 50 ohms using a tee (otherwise the reflected signal doubles the voltage).

Since you have carefully tuned  $C_1$  and  $C_2$  so there is zero reflection, the little resonant circuit consisting of the coil around the sample and the capacitors “looks” like 50 ohms. This is the impedance  $Z_0$ . We know that, if the peak amplitude of the rf is  $V_{rf}^{pk}$  as measured on the scope, the power delivered to the coil+sample+capacitors must be

$$P = \frac{(V_{rf}^{pk})^2}{2Z_0}$$

In a resonant circuit with quality factor  $Q$  and frequency  $\omega_0$ , the power is related to the stored energy  $U$  by the formula

$$P = \frac{\omega_0}{Q} U$$

We think  $Q=75$  for the circuit here. Suppose  $V_{rf}^{pk} = 0.2$  volt.  $\omega_0 = 2\pi \cdot 10^7$  Hz. Putting it all together, the stored energy must then be

$$U = 0.48 \text{ nanojoules} = 4.8 \times 10^{-10} \text{ joules}$$

Now, in a magnetic field, the stored energy is

$$U_{mag} = \frac{\mu_0}{4} \int H_1^2 dV$$

(One factor of 2 comes from the expression for magnetic energy, another from defining  $H_{10}$  as the *peak* magnetic field, not the rms.) Assume the field is constant over a volume of about  $1 \text{ cm}^3 = 10^{-6} \text{ m}^3$ . Then

$$\frac{1}{2}U = U_{mag} = \frac{\mu_0}{4} 10^{-6} H_{10}^2$$

Solving this with  $\mu_0 = 4\pi 10^{-7}$ , gives  $H_{10} = 27.6$  amps/meter, or converting to gauss,  $B_{10}(\text{gauss}) = 10^4 \mu_0 H_{10} = 0.35$  gauss.

If you know a better way to estimate  $H_{10}$ , feel free to tell us!

### Determining $T_2^*$

We now assume that you are not overmodulated, and also not saturated. Furthermore, you have adjusted the rf phase to get the derivative of the absorption curve  $\chi''$ , a nice antisymmetrical curve with equal positive and negative peaks.

The last step is to measure  $T_2^*$  from the distance between negative and positive peaks on the resonance curve for  $\frac{d\chi''}{dx}$ . From the formulas we have already given above, this distance in x is  $\Delta x = \frac{2}{\sqrt{3}} = \gamma \Delta H_0 T_2^*$ . Here's how to measure  $\Delta H_0$ : turn off the magnet. With the Hall probe carefully aligned you should see a remnant field of about 65 gauss (notice how we carelessly confuse H and B, using the cgs units of gauss for both. Never mind!) Now adjust the ramp between 0 volts on one side and 10 volts on the other, measuring the field both times. The difference gives you the full excursion in  $H_0$  when you ramp the field. It should be on the order of 6 gauss, approximately. Using this for the full width of your plot, find the width between positive and negative peaks in gauss. This is  $\Delta H_0$ . To find  $T_2^*$ , use the formula above:

$$T_2^* = \frac{2}{\sqrt{3}} \frac{1}{\gamma \Delta H_0}$$

It is  $T_2^*$ , which includes the effect of magnet inhomogeneities. Pake assumed a perfectly homogeneous magnet, which is why he only refers to the spin-spin relaxation  $T_2$  instead of  $T_2^*$ .  $T_2^*$  is what you measure, which is why the samples with low concentrations of copper ions tend to give similar values (but not for  $T_1$ , so the saturation properties are different). Above  $10^{20}$  ions/cc, you find the spin-spin relaxation dominating over inhomogeneity effects.