TEACH SPIN
Instruments Designed for Teaching

Pulsed/CW NMR Spectrometer

PS2-B
INSTRUCTOR'S MANUAL

A PRODUCT OF TEACHSPIN, INC.

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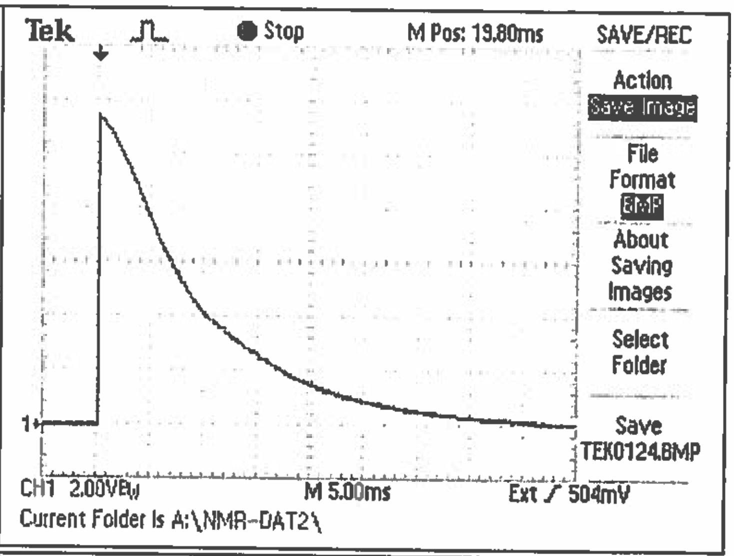
TEACH SPIN

PS2-B Pulsed/CW NMR Spectrometer Data

S/N: 199 Date:6/7/2012 120V Tested By:jfr

FID Distilled Water

Freq (MHz): 21.49060
A_len (µs): 2.68
Period (s): 4.0
Gain: .75
TC: .01
X: - 1.91
Y: + .36
Z - 0.2
Z^2: - 2.04



Current Folder Is A:\NMR-DAT2\

Spin Echo-2 Pulse
Heavy Mineral Oil

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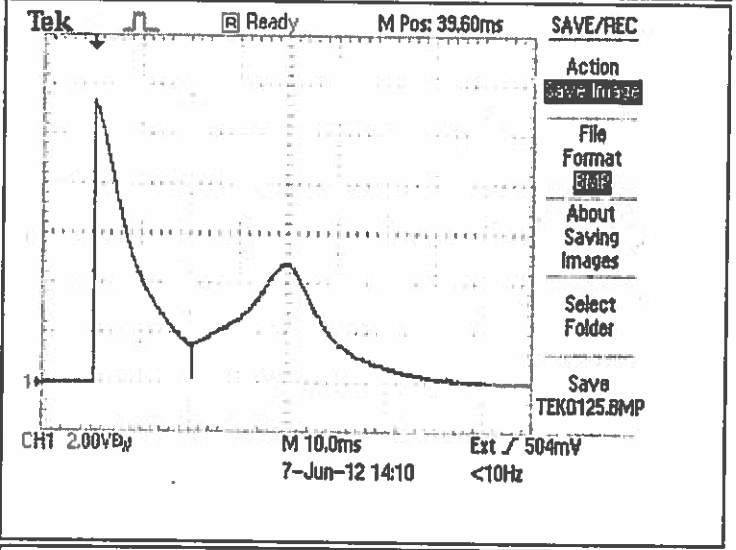
B_len (µs): 5.34
Tau (ms): 20.0
Period (s): .48



T_2 – Meiboom-Gill Seq.
Light Mineral Oil

Freq (MHz): 21.49060
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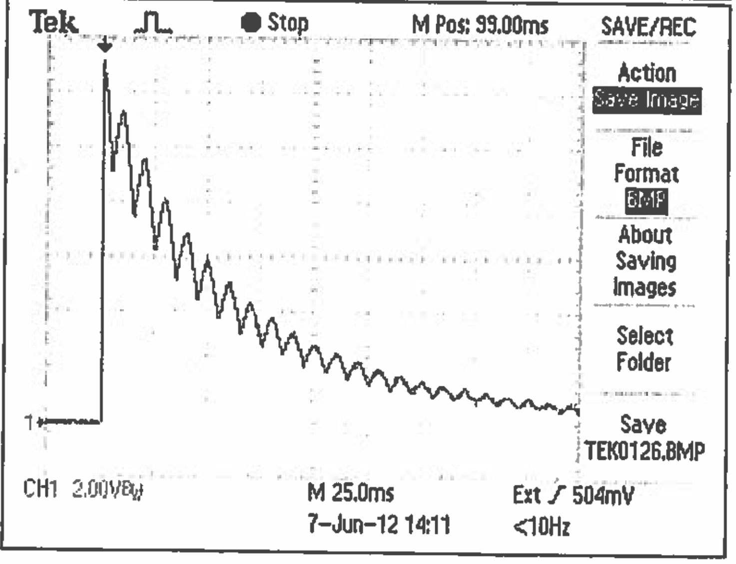
Number B: 25
Period (s): 1.0



TEACHSPIN

PS2-B Pulsed/CW NMR Spectrometer Data

S/N: 199 Date:6/7/2012 120V Tested By:jfr

FID Fluorinert FC-70

Freq (MHz):	20.21445
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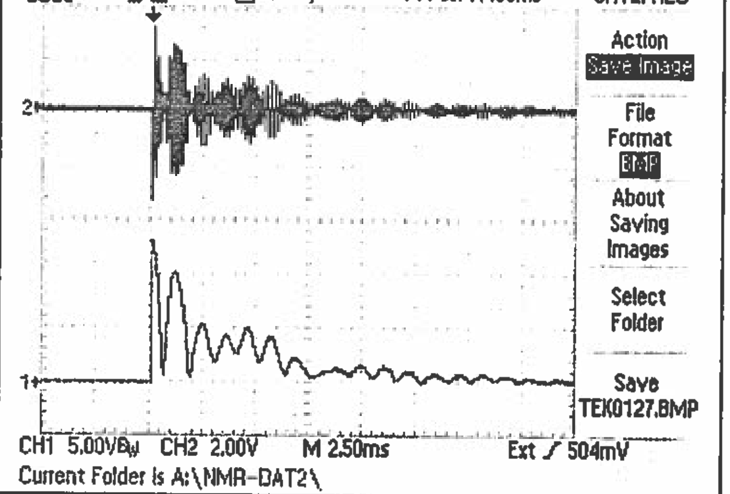
Period (s):	.6
Gain:	.75
TC:	.01



M Pos: 7.400ms

CH1 5.00VBw CH2 2.00V M 2.50ms Ext / 504mV

Current Folder is A:\NMR-DAT2\

FFT Fluorinert FC-70

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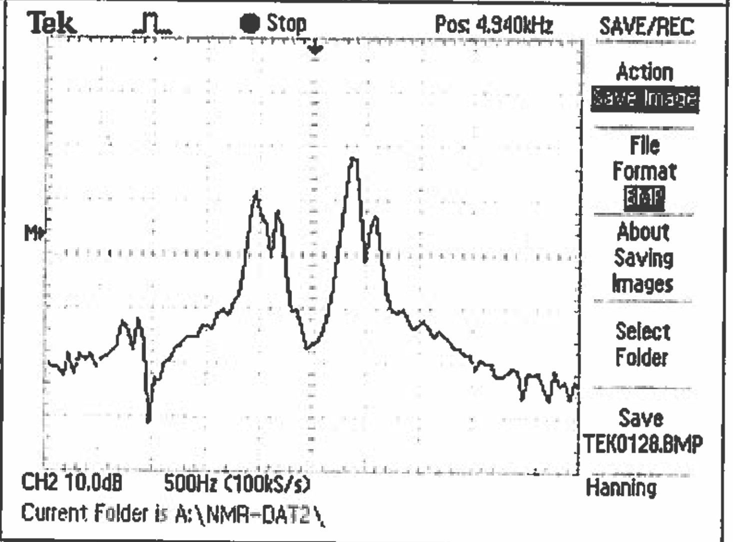
Average:	0



Pos: 4.940kHz

CH2 10.0dB 500Hz (100kS/s) Hanning

Current Folder is A:\NMR-DAT2\

CW Resonance
Fluorinert FC-70

Freq (MHz):	20.21976
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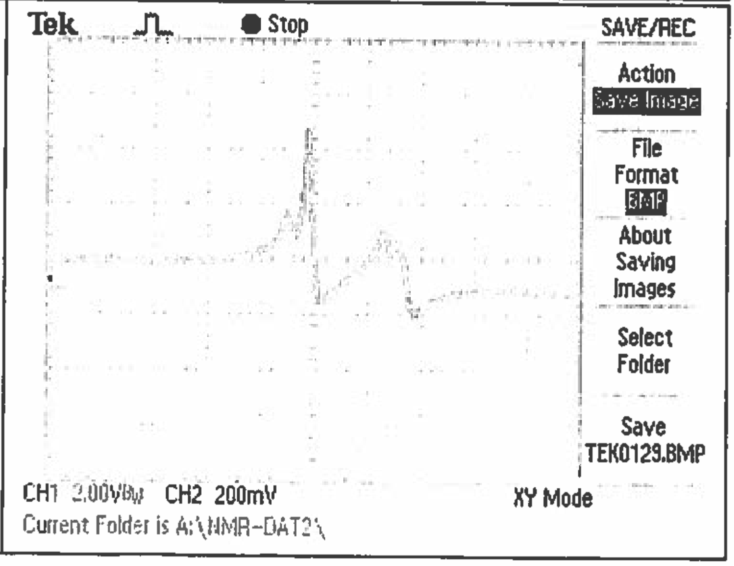
Sweep rate:	20s
TC:	3.3
Field bias:	0.0G
Gain:	.75
CW Power	-20dBm



CH1 2.00VBw CH2 200mV XY Mode

Current Folder is A:\NMR-DAT2\

TeachSpin Inc.

PULSED/CW NMR SPECTROMETER

INSTRUCTOR'S MANUAL INDEX

Introduction

The Instrument

Getting Started

Experiments

Specifications

I. INTRODUCTION

A. OVERVIEW OF THE INSTRUMENT

Congratulations, you have acquired for your students the most versatile, sensitive, rugged and reliable nuclear magnetic resonance spectrometer designed specifically for instruction. The specifications of this unit rival any research grade unit in this frequency range in terms of sensitivity, stability, capabilities and state- of-the-art electronics. And yet, the unit was designed from the outset for student instruction. By that we mean that students, and not a computer, set all of the experimental parameters. Students can make many mistakes including miswiring the spectrometer and incorrectly setting any and all of the parameters without damaging the unit. For the one case where incorrect wiring might do some damage, the unit has special connectors which make those connections impossible with the cables provided.

All of the data is presented in analog form for examination on a digital storage oscilloscope or a computer. Students (and faculty) can then choose how they wish to perform data reduction or analysis. No proprietary software programs are needed to operate the unit, so no software updates are needed. TeachSpin is convinced that the "volt" will never go out of style, and that the mode of data storage and analysis is a choice best left to the individual user. Although data storage and analysis hardware and software is changing so rapidly that what is "hot" today may be obsolete tomorrow, your TeachSpin spectrometer, with its analog output signals, will be capable of taking research grade data long into the future.

Our first NMR instrument PS1-A,B is no longer available because some of its essential electronics components are no longer being manufactured. (It continues, however, to teach students pulsed NMR spectroscopy of protons at more than 170 institutions all over the world.) PS2-A is a completely redesigned spectrometer. The many differences and innovations are presented in the following list.

1. Students can study NMR signals from **two** types of nuclei, protons (hydrogen nuclei) and fluorine. Since the field of the permanent magnet is constant, this is accomplished by changing the spectrometer frequency.
2. PS2-A is both a pulsed and a continuous wave (CW) spectrometer.
3. The unit has both amplitude (envelope) and phase sensitive detection built into its receiver.
4. The RF probe head has a single coil and a 50 Ω input impedance; a matched unit.
5. The field and frequency have increased to 21 MHz proton for resonance.
6. The magnetic field is stabilized to 1 part in 2 x 10^6 over a 20 minute interval.
7. Adjustable electric shim coils that can be used to increase the magnetic field homogeneity are part of the RF sample probe system. They can also be used to create known gradients for measuring diffusion as well as for one-dimensional imaging.
8. The homogeneous high magnetic field allows direct detection of inequivalent fluorine and protons nuclei (chemical shifts) in the free induction decay signal.

9. A Lock-In detection module can detect CW signals from solids with wide lines.
10. Both magnetic field and RF frequency sweeps are built in for studying CW resonance.
11. Digital clock stability in both the RF frequency and the pulse width synthesis are integral to the design.
12. The receiver recovery time (after pulse) has been improved by a factor of five to approximately 15 μs, making signals from "soft" solids available for study.

The electronics system was designed by Dr. Norman Jarosik of the Princeton University Physics Department. Norman is a staff scientist in the "gravity Group" and the chief engineer of WMAP, the satellite that has been sensing and mapping the anisotropies in the microwave radiation left over from the Big Bang of the early universe. He also designed the PS-1 A and B whose well deserved reputation for reliability, as well as sensitivity, is known world-wide. Norman has been involved with TeachSpin from its 1992 inception.

Nuclear magnetic resonance is a large and mature field of physics. There certainly is a lot to learn and a real potential for a student to explore his or her own ideas in this area, perhaps even to find a real research project. We cannot think of a better instrument for students to pursue their own open-ended sets of experiments. But a new student should not be intimidated by the prospect of learning this vast subject. TeachSpin has outlined a manageable way to begin the study of NMR. Students can begin with straight-forward experiments that will develop their confidence and understanding and then branch out to more advanced measurements. This instrument is accessible, after all, it was designed from the moment of inception for the student. Enjoy!

B. OUTLINE OF THE PHYSICS

B.1 Brief History

In 1946, nuclear magnetic resonance (NMR) in condensed matter was discovered simultaneously by Edward Purcell at Harvard and Felix Bloch at Stanford using different instrumentation and techniques. Both groups, however, placed a sample containing magnetic nuclei in a uniform magnetic field and observed the response of those nuclei to a continuous (CW) radio frequency magnetic field as the field was tuned through resonance. This discovery opened up a new type of spectroscopy which has become one of the most important tools available to physicists, chemists, geologists, and biologists.

In 1950, Erwin Hahn, a postdoctoral fellow at the University of Illinois, again placing his sample of condensed matter in a uniform magnetic field, explored the response of the magnetic nuclei to pulse bursts of these same radio frequency (RF) magnetic fields. Hahn was interested in observing transient effects on the magnetic nuclei after the RF bursts. During these experiments, he observed a "spin echo" signal; that is, a signal from the magnetic nuclei that occurred after a two pulse sequence, at a time equal to the delay time between the two pulses. This discovery, and his brilliant analysis of the experiments, gave birth to a new technique for studying magnetic resonance. This pulse method originally had only a few practitioners, but now it is the method of choice for most laboratories. For the first twenty years after its discovery, continuous wave (CW) magnetic resonance apparatus was used in almost every research chemistry laboratory, and no commercial pulsed NMR instruments were available. However, since 1966 when Ernst and Anderson showed that high resolution NMR spectroscopy can be achieved using Fourier transforms of the transient response, and cheap fast computers made this calculation practical, pulsed NMR has become the dominant commercial instrumentation for most research applications.

Widely used in physics and chemistry to characterize materials, NMR is a microscopic method in the sense that it probes the nuclei and their immediate surroundings. Within a certain solid, for instance, there may be a variety of local magnetic fields. A magnetic measurement by a magnetometer measures an average field. NMR, on the other hand, is capable of measuring the local field at atomic nuclei. Another example would be a molecule containing a several atoms of the same element, for instance carbon, in various different configurations. The NMR signal will be different for each one of these configurations. The microscopic nature of the NMR measurement makes it extremely useful, and often unique. Of course, in order to have a signal of detectable magnitude, we need many molecules of the same configuration to occur within the sample. The nuclei investigated in this set of experiments, hydrogen (proton) and fluorine, are very abundant. and give particularly strong signals.

This technology has also found its way into medicine. MRI (magnetic resonance imaging; the word “nuclear” being removed to relieve the fears of the scientifically illiterate public) scans are revolutionizing radiology. This imaging technique seems to be completely noninvasive, produces remarkable three dimensional images, and has the potential to give physicians detailed information about the inner working of living systems. For example, preliminary work has already shown that blood flow patterns in both the brain and the heart can be studied without dangerous catheterization or the injection of radioactive isotopes. Someday, MRI scans may be able to pinpoint malignant tissue without biopsies. MRI is only in its adolescence, and we will see many more applications of this diagnostic tool in the coming years.

You have purchased a pulsed and CW NMR spectrometer designed specifically for teaching. The PS2-A is a complete spectrometer, including the magnet, magnet temperature controller, pulse generator, oscillator, pulse amplifier, sensitive receiver, linear amplitude and phase-sensitive detector, sample probe, gradient coils with dedicated current regulated supply and a CW lock-in detector. You need only supply the oscilloscope and the substances you wish to study. Now you are ready to learn the fundamentals of both CW and pulsed nuclear magnetic resonance spectroscopy.

Nuclear magnetic resonance is a vast subject. Tens of thousands of research papers and hundreds of books have been published on NMR. We will not attempt to explain or even to summarize this literature. Some of you may wish to do only a few simple experiments with the apparatus and achieve a basic conceptual understanding, while others may aim to understand the details of the density matrix formulation of relaxation processes and do some original research. The likelihood is that the majority of students will work somewhere in between these two extremes. In this section we will provide a brief theoretical introduction to many important ideas of PNMR. This will help you get started and can be referred to later. These remarks will be brief, not completely worked out from first principles, and not intended as a substitute for a careful study of the literature and published texts. An extensive annotated bibliography of important papers and books on the subject is provided at the end of this section.

B.2 Theory

Magnetic resonance is observed in systems where the magnetic constituents have **both a magnetic moment** and **an angular momentum**. Many, but not all, of the stable nuclei of ordinary matter have this property. In "classical physics" terms, magnetic nuclei act like a small spinning bar magnet. For this instrument, we will be concerned with only two nuclei, the nucleus of hydrogen, which is a single proton, and the nucleus of fluorine which contains both protons and neutrons. Both nuclei can be thought of as small spinning bar magnets with a magnetic moment μ and an angular momentum J, which are related by the vector equation:

$$\boldsymbol{\mu} = \gamma \mathbf{J} \qquad (1.1)$$

The proportionality factor γ is called the "gyromagnetic ratio" and its values are unique to each kind of nucleus in the experiment.

The nuclear angular momentum is quantized in units of $\hbar$ as:

$$\mathbf{J} = \hbar \mathbf{I} \qquad (1.2)$$

where **I** is the "spin" of the nucleus.

The magnetic energy U of the nucleus in an external magnetic field is:

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} \qquad (1.3)$$

If the magnetic field is in the z-direction, then the magnetic energy is:

$$U = -\mu_z B_o = -\gamma \hbar I_z B_o \qquad (1.4)$$

Quantum mechanics requires that the allowed values I_z, m_I, be quantized as

$$m_I = I, I-1,\ I-2,\ I-3\ldots\ -I. \qquad (1.5)$$

Both of the nuclei we are investigating, the proton (hydrogen nucleus) and the fluorine nucleus have spin one half ($I = 1/2$). Therefore, the allowed values of I_z are simply

$$m_I = \pm 1/2 \qquad (1.6)$$

This means that there are only two magnetic energy states for these nuclei when residing in a constant magnetic field B_0. These states are described in Figure 1.1.

The energy separation between the two states, ΔU, can be written in terms of an angular frequency or as

$$\Delta U = \hbar \omega_0 = \gamma \hbar B_0$$

or

$$\omega_0 = \gamma B_0 \qquad (1.7)$$

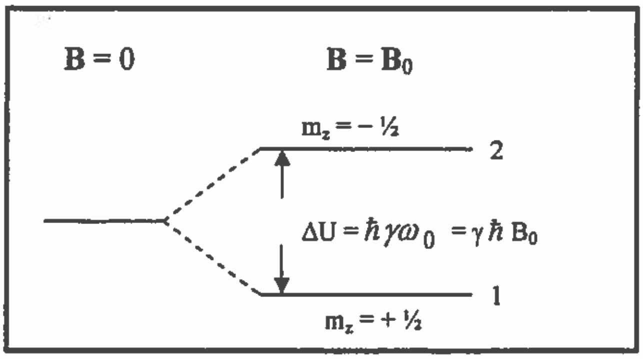


Figure 1.1 Energy State Separation in a Magnetic Field

Equation 1.7, $\omega_0 = \gamma B_0$ describes the fundamental resonance condition.

$$\begin{aligned} &\text{For the proton:} & \gamma_{proton} &= 2.675 \times 10^8 \text{ rad/sec-tesla} \\ &\text{For Fluorine:} & \gamma_{fluorine} &= 2.517 \times 10^8 \text{ rad/sec-tesla} \end{aligned} \qquad (1.8)$$

For the proton, the numerical relationship between the resonant frequency and the constant magnetic field is worth remembering:

$$f_{proton}\,(\text{MHz}) = 42.58\, B_0 \text{ tesla} \qquad (1.9)$$

If a one milliliter (ml) sample of water (containing about $7\text{x}10^{19}$ protons) is placed in a magnetic field in the z-direction, a nuclear magnetization in the z-direction eventually becomes established. This nuclear magnetization occurs because of unequal population of the two possible quantum states. If N_1 and N_2 are the number of spins per unit volume in the respective states, then the population ratio (N_2 / N_1), in thermal equilibrium, is given by the Boltzmann factor as:

$$\frac{N_2}{N_1} = e^{\frac{\Delta U}{kT}} = e^{\frac{\hbar\omega_0}{kT}} \qquad (1.10)$$

and the magnetization is

$$M_Z = (N_1 - N_2)\,\mu \qquad (1.11)$$

The thermal equilibrium magnetization per unit volume for N magnetic moments is

$$M_0 = N\mu \tanh\left(\frac{\mu B}{kT}\right) \approx N\frac{\mu^2 B}{kT} \qquad (1.12)$$

where $N = N_1 + N_2$

This magnetization does ***not*** appear instantaneously when the sample is placed in the magnetic field. It takes a finite time for the magnetization to build up to its equilibrium value along the direction of the magnetic field (which we define as the z-axis). For most systems, the z-component of the magnetization is observed to grow exponentially as depicted in Figure 1.2. The differential equation that describes such a process assumes that the rate of approach to equilibrium is proportional to the difference between the equilibrium value M_0 and the instantaneous value M_z(t):

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z}{T_1} \qquad (1.13)$$

where T_1 is called the spin-lattice relaxation time.

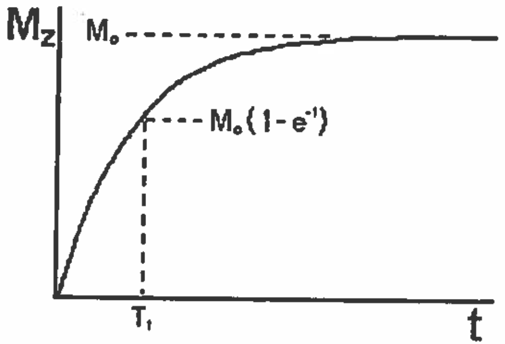


Figure 1.2 Magnetization vs. time for a sample placed in a magnetic field

If the unmagnetized sample is placed in a magnetic field, so that at t = 0, $M_z = 0$, then direct integration of equation 1.13, with these initial conditions, gives:

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}}) \qquad (1.14)$$

The rate at which the magnetization approaches its thermal equilibrium value is characteristic of the particular sample. Typical values range from microseconds to seconds. What makes one material take 10 microseconds to reach equilibrium while another material (also with protons as the nuclear magnets) takes 3 seconds? Obviously, some processes in the material make the protons "relax" towards equilibrium at different rates. The study of these processes is one of the major topics in magnetic resonance.

Although we will not attempt to discuss these processes in detail, a few ideas are worth noting. In thermal equilibrium, more protons are in the lower energy state than the upper. When the unmagnetized sample was first put in the magnet, the protons occupied the two states equally that is ($N_1 = N_2$). During the magnetization process energy must flow ***from*** the nuclei ***to*** the surroundings, since the magnetic energy from the spins is reduced. The surroundings which absorb this energy are referred to as "the lattice", even for liquids or gases. Thus, the name "spin-lattice" relaxation time for the characteristic time of this energy flow.

However, there is more than energy flow that occurs in this process of magnetization. Each proton has angular momentum (as well as a magnetic moment) and the angular momentum must also be transferred from the spins to the surroundings during magnetization. In quantum mechanical terms, the "lattice" must have angular momentum states available when a spin goes from $m_I = -1/2$ to $m_I = +1/2$. In classical physics terms, the spins must experience a torque capable of changing their angular momentum. The existence of such states is usually the critical determining factor in explaining the enormous differences in T_1 for various materials. Pulsed NMR is ideally suited for making precise measurements of this important relaxation time. The pulse technique gives a direct and unambiguous measurement, where as CW spectrometers require a difficult, indirect, and imprecise technique to measure the same quantity.

What about magnetization in the x-y plane? In thermal equilibrium the only **net** magnetization of the sample is M_z, the magnetization along the external constant magnetic field. This can be understood from a simple classical model of the system. Think of placing a collection of tiny current loops in a magnetic field. The torque τ on the loop is $\mu \times B$ and that torque causes the angular momentum of the loop to change, as given by:

$$\tau = \frac{d\mathbf{J}}{dt} \quad \text{or} \quad \boldsymbol{\mu} \times \mathbf{B} = \frac{d\mathbf{J}}{dt} \qquad (1.15)$$

For our nuclei, equation 1.15 becomes:

$$\boldsymbol{\mu} \times \mathbf{B} = \frac{1}{\gamma}\frac{d\boldsymbol{\mu}}{dt} \qquad (1.16)$$

Equation 1.16 is the classical equation describing the time variation of the magnetic moment of the proton in a magnetic field. It can be shown from equation 1.16 that the magnetic moment will execute precessional motion, depicted in 1.3. The precessional frequency $\omega_0 = \gamma B_0$, is just the resonant frequency in equation 1.7.

If we add up all the magnetization for the 10^{20} nuclei in our sample in thermal equilibrium, the μ_z components sum to M_z, but the x and y components of the individual magnetic moments add to zero.

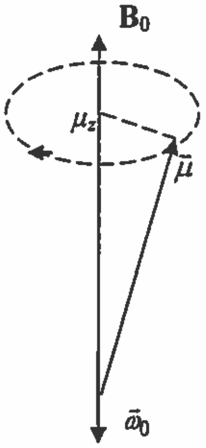


Figure 1.3

For the x-components of every nucleus to add up to some M_x, there must be a definite phase relationship among all the precessing spins. For example, we might start the precessional motion with the x-component of the spins lined up along the x-axis. But that is not the case for a sample simply placed in a magnet. In thermal equilibrium, the spin components in the x-y plane are oriented randomly. Thus, in thermal equilibrium there is no transverse (x or y) component of the net magnetization of the sample. As we shall soon see, however, there is a way to ***create*** such a transverse magnetization using radio frequency pulsed magnetic fields. The idea is to quickly rotate the thermal equilibrium magnetization M_z into the x-y plane and thus create a temporary M_x and M_y. Let's see how this is done.

Equation 1.16 can be generalized to describe the classical motion of the net magnetization of the entire sample. It then becomes

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \quad . \qquad (1.17)$$

where **B** is any magnetic field, including time dependent rotating fields.

Suppose we apply not only a constant magnetic field $\mathbf{B}_0\hat{k}$, but a rotating (circularly polarized) magnetic field of angular frequency ω the x-y plane so the **total** field is written as †

$$\mathbf{B(t)} = B_1 \cos\omega t\hat{i} + B_1 \sin\omega t\hat{j} + B_0\hat{k} \qquad (1.18)$$

The analysis of the magnetization in this complicated time dependent magnetic field can best be carried out in a non-inertial rotating coordinate system. The coordinate system of choice is rotating at the same angular frequency as the rotating magnetic field with its axis in the direction of the static magnetic field. In this ***rotating coordinate system***, the rotating magnetic field appears to be stationary and aligned along the x* axis (Figure 1.4). However, from the point of view of the rotating coordinate system, B_0 and B_1 are not the only magnetic fields. An **effective field** along the z* direction, of $-\frac{\omega}{\gamma}\hat{k}*$ must also be included.

Let's justify this new effective magnetic field with the following physical argument.

Equations 1.16 and 1.17 predict the precessional motion of a magnetization in a constant magnetic field $B_o\hat{k}$. Suppose one observes this precessional motion from a rotating coordinate system which rotates **at the precessional frequency.** In this frame of reference the magnetization appears stationary, in some fixed position. The only way a magnetization can remain fixed in space is if there is no torque on it. If the magnetic field is zero in the reference frame, then the torque on **M** is always zero no matter what direction **M** is oriented. The magnetic field is zero (in the rotating frame) if we add the effective field $-\frac{\omega}{\gamma}\hat{k}*$ which is equal to $B_o\hat{k}*$

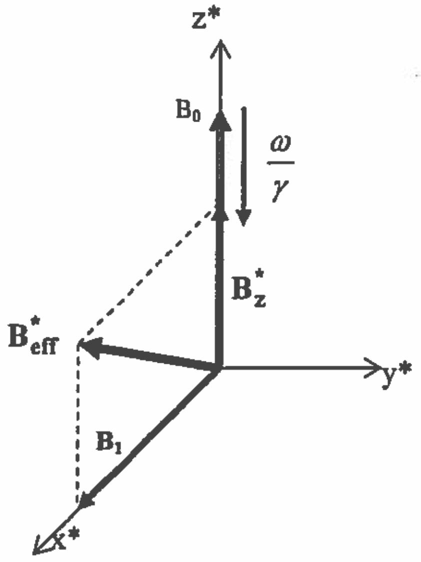


Figure 1.4

Transforming the magnetic field expression in equation (1.18) into such a rotating coordinate system, the total magnet field in the rotating frame B* is

$$\mathbf{B}^*_{\mathrm{eff}} = B_1\hat{i}* + (B_0 - \frac{\omega}{\gamma})\hat{k} \qquad (1.19)$$

Figure 1.4 is a representation of Equation 1.19. The classical equation of motion of the magnetization as observed in the rotating frame is then

$$\left.\frac{d\mathbf{M}}{dt}\right|_{rot} = \gamma\mathbf{M}\times\mathbf{B}^*_{\mathrm{eff}} \qquad (1.20)$$

which shows that **M** will precess about B^*_{eff} in the rotating frame.

[†] What is actually applied is an oscillating field $2B_1\cos\omega t\hat{i}$. But that can be decomposed into two counter rotating fields $B_1(\cos\omega t\hat{i} + \sin\omega t\hat{j}) + B_1(\cos\omega t\hat{i} - \sin\omega t\hat{j})$. One of the counter rotating fields can be shown to have no practical affects on the spin system and can be ignored in this analysis.

Suppose now, we create a rotating magnetic field at a frequency ω_0 as such that

$$\frac{\omega}{\gamma} = B_0 \quad \text{or} \quad \omega = \gamma B_0 = \omega_0 \tag{1.21}$$

In that case, $\mathbf{B}^*_{\text{eff}} = B_1\hat{i}^*$, a constant magnetic field in the x* direction (Figure 1.5). Then, the magnetization M_z begins to precess about this magnetic field at a rate $\Omega = \gamma B_1$, (in the rotating frame). If we **turn off** the B_1 field at the instant the magnetization reaches the x-y plane, we will have created a transient (non-thermal equilibrium) situation where there is a net magnetization in the x-y plane. If this rotating field is applied for twice the time the transient magnetization will be - M_z and if it is left on four times as long the magnetization will be back where it started, with M_2 along the z* axis. These are called:

90° or π/2 pulse → $M_z \rightarrow M_y$
180° or π pulse → $M_z \rightarrow -M_z$
360° or 2π pulse → $M_z \rightarrow M_z$

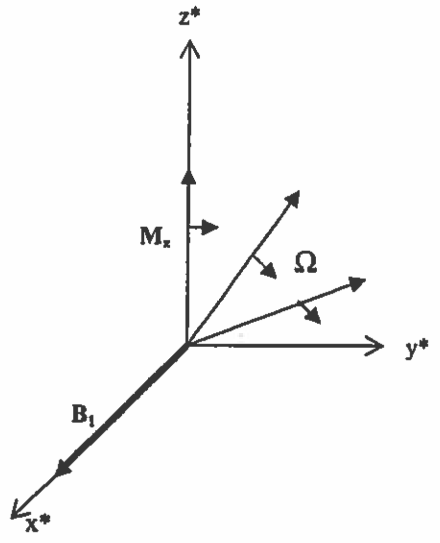


Figure 1.5

In the laboratory (or rest) frame, where the experiment is actually carried out, the magnetization not only precesses about B_1, but rotates about $\hat{k}$ during the pulse. **It is not possible, however, to observe the magnetization during the pulse.** Pulsed NMR signals are observed AFTER the transmitter pulse is over? But, what is there to observe AFTER the transmitter pulse is over? The spectrometer detects the **net magnetization precessing about the constant magnetic field $B_0\hat{k}$ in the x-y plane. Nothing Else!**

Suppose a 90° (π/2) pulse is imposed on a sample in **thermal equilibrium.** The net equilibrium magnetization will be rotated into the x-y plane where, after the pulse, it will precess about $B_0\hat{k}$. But the x-y magnetization will not last forever. For most systems, this magnetization decays exponentially as shown in Figure 1.6. The differential equations which describe the decay **in the rotating coordinate system are:**

$$\frac{dM_{x^*}}{dt} = -\frac{M_{x^*}}{T_2} \quad \text{and} \quad \frac{dM_{y^*}}{dt} = -\frac{M_{y^*}}{T_2} \tag{1.22}$$

whose solutions are,

$$M_{x^*} = M_0 e^{-\frac{t}{T_2}} \quad \text{and} \quad M_{y^*} = M_0 e^{-\frac{t}{T_2}} \tag{1.23}$$

where the characteristic decay time T_2 is called the **Spin-Spin Relaxation Time.**

One simple way to understand this relaxation process, from the classical perspective, is to recall that each nucleus is itself a magnet and produces a magnetic field at its neighbors. Therefore, for a given distribution of nuclei, there must also be a distribution of ***local*** fields at the various nucleus sites. Thus, the nuclei precess about $B_0\hat{k}$ with a distribution of frequencies, not a single frequency ω_0.

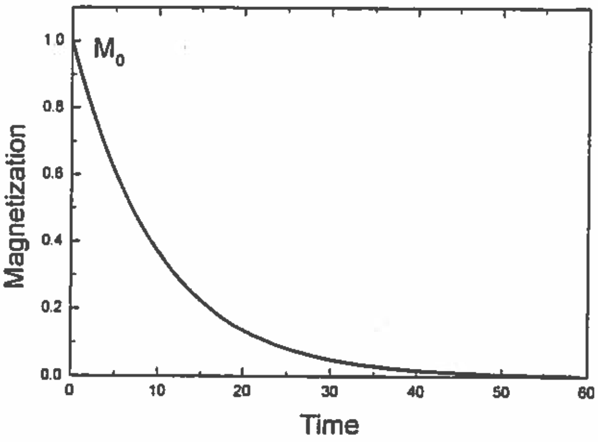


Figure 1.6

Even if all the nuclei begin in phase (after the 90° pulse), they will soon get out of phase and the net x-y magnetization will eventually go to zero. A measurement of T_2, the decay constant of the x-y magnetization, gives information about the distribution of local fields at the nuclear sites.

From this analysis, it would appear that the spin-spin relaxation time T_2 can be determined by simply plotting the decay of M_x(or M_y) after a 90° pulse. This signal is called the free ***precession or free induction decay*** (FID). If the field of the magnet were perfectly uniform over the entire sample volume, then the time constant associated with the free induction decay would, in fact, be T_2. But, in most cases, it is the nonuniformity of the magnet's field over the sample that is responsible for the observed decay constant of the FID. At its center, the PS2-A's magnet has sufficient uniformity to produce at least a .3 millisecond decay time. Using the electric shim coils (See Section II.F), students can improve the homogeneity so that decay time due to the magnet (called T_2^* in the jargon) is as long as 5 milliseconds, and, possibly, longer. Thus, for a sample whose $T_2 < 5$ ms, the free induction decay constant is also the T_2 of the sample. But what if T_2 is actually 5 msec or longer? The observed decay will still be about 5 ms. Here is where the genius of Erwin Hahn's discovery of the spin echo plays its crucial role.

Before the invention of pulsed NMR, the only ways to measure the real T_2 were to improve the magnet's homogeneity and to make the sample smaller. But, PNMR changed this.

Suppose we use a two pulse sequence, the first one 90° and the second one, turned on a time τ later, a 180° pulse. What happens? Figure 1.7 shows the pulse sequence and Figure 1.8 shows the progression of the magnetization in the rotating frame.

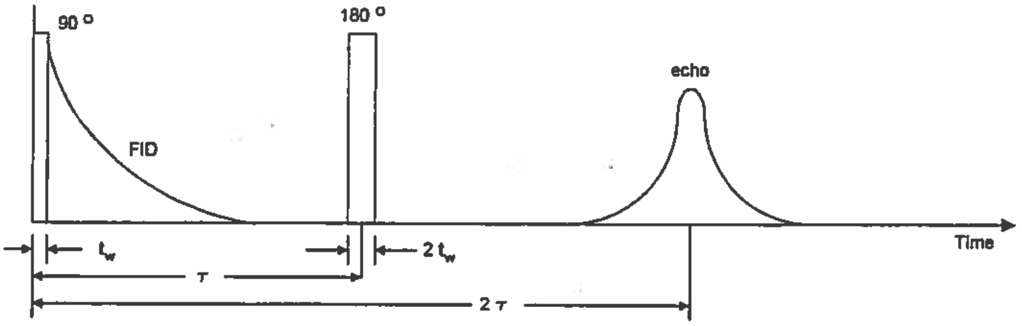


Figure 1.7: A 90° - 180° Pulse Sequence

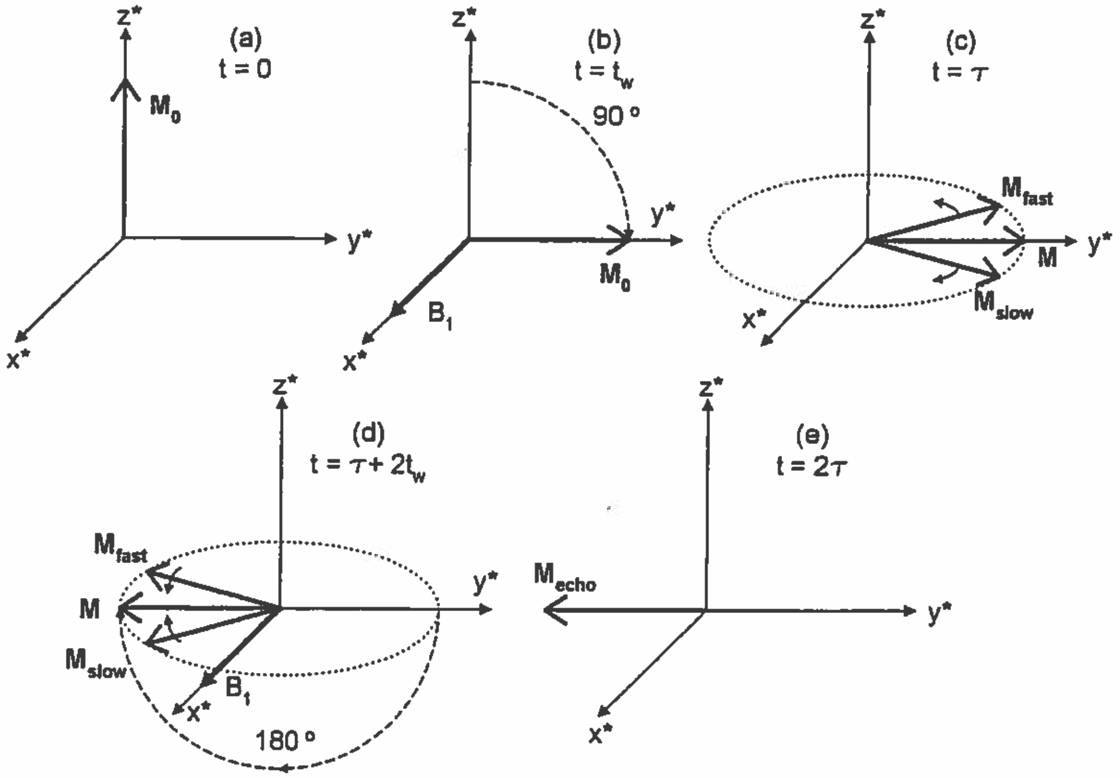


Figure 1.8: Progression of the Magnetization in the Rotating Frame
a) Thermal equilibrium magnetization M_0 along the z axis before the rf pulse.
b) M_0 rotated to the y-axis after the 90° pulse.
c) The magnetization in the x-y plane is decreasing because some of the spins Δm_{fast} are in a higher field, and other spins Δm_{slow} are in a lower field static field.
d) The spins are rotated 180° (visualize flipping the entire x-y plane like a pancake on the griddle) by the pulsed if magnetic field.
e) The rephasing the three magnetization "bundles" to form an *echo* at t = 2t.

Study the diagrams in Figures 1.7 and 1.8 carefully. The 180° pulse allows the x-y magnetization to rephase to the value it would have had with a perfect magnet.

The echo process is analogous to an egalitarian and PC foot race for a kindergarten class, a race that makes all the children in the class winners, no matter how fast they can run. What if the race had the following rules? All the children are to line up at the starting line. At the first whistle, they are to run as fast as they can down the field. At the second whistle, they are to turn around and run back toward the starting line. First person back wins!! Of course, it is a tie, except for the ones who "interfere" with one another or fall down. As the children run away, the field spreads out with the fastest ones getting farther and farther ahead. At some point there is no semblance of order. On the trip back, as the faster ones overtake the slow pokes, who are now in the lead, the group comes together again "rephasing" as they pass the start line.

In Pulsed NMR, the 180° pulse is like that whistle. The spins in areas of larger field get out of phase by $+\Delta\theta$ in a time τ. After the 180° pulse, they continue to precess faster than M while the slower precessing spins do just the opposite. At 2τ all the spins return to the in-phase condition and then again dephase.

Yet some loss of $M_{x,y}$ magnetization has occurred and the maximum height of the echo is not the same as the maximum height of the FID. This loss of transverse magnetization occurs because of stochastic fluctuation in the local fields at the nuclear sites which is not rephasable by the 180° pulse. These are the real T_2 processes that we are interested in measuring. To find the "real" T_2, we use a series of $90° > \tau > 180°$ pulse experiments, varying τ, and then plotting the echo height as a function of time between the FID and the echo.

The transverse magnetization as measured by the maximum echo height is written as:

$$M_{xy}(2\tau) = M_0 e^{-\frac{2\tau}{T_2}} \tag{1.24}$$

That's enough theory for now. **Let's summarize:**

1. Magnetic resonance is observed in systems whose constituent particles have **both** a magnetic moment and angular momentum.
2. The resonant frequency of the system depends on the applied magnetic field in accordance with the relationship $\omega_0 = \gamma B_0$ where

$$\gamma_{\text{proton}} = 2.675 \times 10^8 \text{ radian/sec-tesla}$$

or

$f_{\text{proton}} =$ 42.58 MHz/tesla (for protons)

$f_{\text{fluorine}} =$ 40.055 MHz/tesla (for fluorine)

3. The thermal equilibrium magnetization is parallel to the applied magnetic field, and approaches equilibrium following an exponential rise characterized by the constant T_1 the spin-lattice relaxation time.

4. Classically, the magnetization (which is the vector sum of the individual magnetic moments of the nuclei) obeys the differential equation

$$\frac{d\mathbf{M}}{\mathrm{dt}} = \gamma(\mathbf{M} \times \mathbf{B})$$

where **B** may be a time dependent field.

5. Pulsed NMR employs a rotating radio frequency magnetic field described by

$$\mathbf{B}(t) = B_1 \cos\omega t\hat{i} + B_1 \sin\omega t\hat{j} + B_0\hat{k}$$

6. The easiest way to analyze the motion of the magnetization during and after the rf pulsed magnetic field is to transform into a rotating coordinate system. If the system is rotating at an angular frequency ω along the direction of the magnetic field, a fictitious magnetic field must be added to the real fields such that the total effective magnetic field in the rotating frame is:

$$\mathbf{B}^*_{\mathbf{eff}} = B_1\hat{i}* + (B_0 - \frac{\omega}{k})\hat{k}*$$

7. On resonance $\omega = \omega_0 = \gamma B_0$ and $\mathbf{B}^*_{\mathbf{eff}} = B_1\hat{i}*$. In the rotating frame, during the pulse, the spins precess around $\mathbf{B}^*_{\mathbf{1}}$.

8. A 90° pulse is one where the pulse is left on just long enough (t_w) for the equilibrium magnetization M_0 to rotate to the x-y plane. That is;

$$\omega_1 t_w = \pi/2 \text{ radians} \quad \text{or} \quad t_w = \frac{\pi}{2\omega_1}$$

But

$$\omega_1 = \gamma B_1$$

(since, on resonance, B_1 is the only field in the rotating frame.)

So,

$$t_w(90^\circ) = \frac{\pi}{2\gamma B_1} \quad \text{duration of the 90° pulse} \qquad (1.25)$$

9. T_2 - the spin-spin relaxation time - is the characteristic decay time for the nuclear magnetization in the x-y (or transverse) plane.

10. The spin-echo experiments allow the measurement of T_2 in the presence of a nonuniform static magnetic field. For those cases where the free induction decay time constant, (sometimes written T_2*) is shorter than the real T_2, the decay of the echo envelope's maximum heights for various times τ, gives the real T_2.

C. REFERENCES

The following is a rather long list, and you certainly will not have the time all of them. In fact, you may only have time to read a rather small percentage of what is listed. But, you must take the time to read some of them so you have a basic understanding of magnetic resonance spectroscopy.

C.1 Books

C.P. Slichter: "Principles of Magnetic Resonance" Springer Series in Solid-State Sciences 1 Third Edition (1990) Springer-Verlag
A complete text with problems, clear explanations, appropriate for advanced undergraduate or graduate level students. **Any serious student of magnetic resonance should own it.** Everyone should read at least some of it. This reference contains a nearly complete bibliography of the important papers published in both NR and ESR spectroscopy. Consult this text for references to particular subjects.

T.C. Farrar, E.D. Becker: "Pulsed And Fourier Transform NMR", Academic Press 1971
A good introduction, with simplified mathematics, to the subject. Gives students a physical feel for the basic ideas of PNMR.

G. E. Pake and T. L. Estle: "The Physical Principles of Electron Paramagnetic Resonance", Benjamin-Cummings, Menlo Park CA (1978)
Don't let the title ESR scare you away from using this excellent text. It has clear discussions of important ideas of magnetic resonance, such as the rotating coordinate systems etc.

R. T. Schumacher: "Introduction to Magnetic Resonance", Benjamin-Cummings, Menlo Park CA 1970.

N. Bloembergen: "Nuclear. Magnetic Relaxation", W.A. Benjamin, New York 1961
This is Bloembergen's Ph.D. thesis, reprinted, but it is like no other thesis you will ever read. Describes some of the classic ideas of magnetic resonance, still very worth reading, you will see why he is a Nobel Laureate.

A. Abragam: "Principles of Nuclear Magnetism", Clarendon, Oxford 1961
This text is in a class by itself, but not easy for the beginner. Abragam has his own way of describing NMR. Important, but clearly for advanced students.

E. R. Andrew, "Nuclear Magnetic Resonance &' Cambridge University Press, New York, 1956
A good general discussion of theory, experimental methods, and applications of NMR.

C. Kittel "Introduction to Solid State Physics" 5th edition, Wiley, New York 1976 in Chapter 16.
A reasonable place to begin the subject of magnetic resonance, very brief, not fully worked out, but a good first overview;

D. M. S. Bagguley editor: "Pulsed Magnetic Resonance: NMR, ESR, and Optics, a Recognition of E.. L. Hahn, Clarendon Press, Oxford *1992.*
A wonderful collection of historical reminisces and modem research applications of pulsed magnetic resonance. Useful for advanced students.

C.2 Papers

E. L. Hahn: "Spin echoes" Phys. Rev 80, 580-594 (1950)
The first report oil PNMR and still a wonderful explanation, worth reading.

H. Y. Carr, E. M. Purcell: Effects of diffusion on free precession in nuclear magnetic resonance experiments. Phys Rev 94, 630-638 (1954)
Anything Ed Purcell signs his name to is worth reading! This certainly is one such example. A must for PNMR.

N. Bloembergen, E. M. Purcell, and R. B. Pound: "Relaxation effects in Nuclear Magnetic Resonance absorption," Phys. Rev. 73, 679-712 (1948)
A classic paper describing basic relaxation processes in NMR.

S. Meiboom, D. Gill: Rev of Sci Instruments 29, 6881 (1958)
The description of the phase shift technique that opened up multiple pulse techniques to measuring very long T_2's in liquids.

K. Symon, "Mechanics" 3d ed. Addison-Wesley, Reading, MA (1971)
A good place to learn about rotating coordinate systems, if you don't already understand them.

R. G. Beaver, E. L. Hahn, Scientific American 6, 251 (1984)
A discussion of the echo phenomenon and mechanical memory.

II. THE INSTRUMENT

A. RECEIVER MODULE

A.1 Overview

The basic function of the receiver module is to amplify the small voltage induced in the sample coil by the precessing nuclear spin polarization to a large enough amplitude where it can be easily displayed on an oscilloscope. After passing through the input coupling circuitry, the signal from the sample coil is amplified by a fixed gain low noise amplifier (LNA) with approximately 20 dB of gain and noise figure of approximately 2.5 dB.

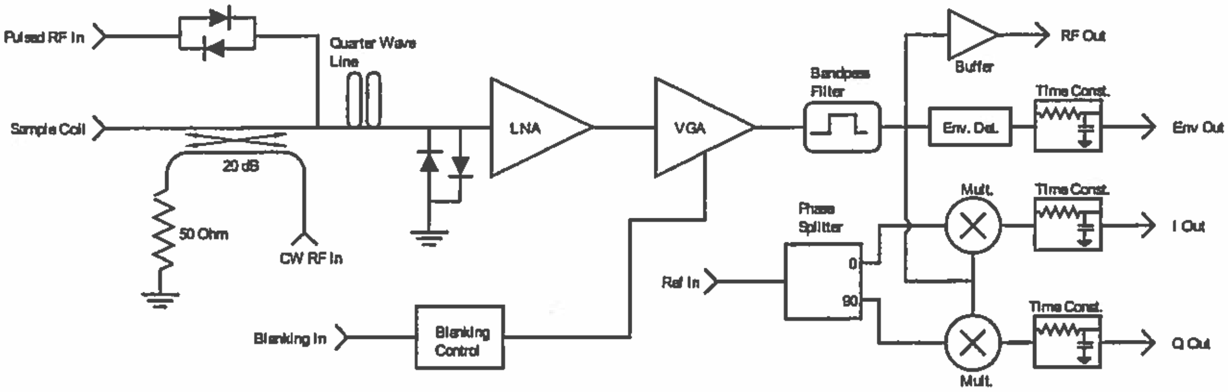


Figure 2.1

The output of the low noise amplifier is fed into a variable gain amplifier. The gain of this amplifier can be varied from 0 to 80 dB using the **Gain** control. Both of these two amplification stages are designed to have a wide enough bandwidth so that they can amplify the signals from both protons and fluorine nuclei, and have fast recovery times for pulsed NMR experiments. The output of the variable gain stage is then filtered by a narrow band filter to eliminate out-of-band noise. The center frequency of the narrow band filter can be switched between two values, corresponding to the proton and fluorine resonant frequencies, using the **Band** switch marked p and f (for proton and fluorine). A buffered version of the filter output is available at the **RF Out** connector.

The output of the filter is also sent to the inputs of the envelope detector and the phase sensitive detectors. The envelope detector tracks the amplitude of the input RF voltage and drives the **Env. Out** connector on the receiver module. The **I Out** signal from the phase sensitive detector is the product of the **Ref In** signal and the filter output, while the **Q Out** signal is a product of the **Ref In** signal shifted 90° and the filter output. By adjusting the phase of the **RF Out** signal from the Synthesizer module, you can make these signals correspond to the in-phase and quadrature components of the NMR signal. The outputs of all three detectors (**I Out, Env. Out,** and **Q Out)** are filtered by single pole RC filters (6dB/octave) as determined by the setting of the **TC** control on the receiver module panel.

The input section of the receiver module is designed for use in both continuous wave (CW) and pulsed experiments. It functions slightly differently in these two applications, so they are described separately. To start with we assume that the receiver coil is tuned so that it matches the 50 Ohm impedance of the coaxial cable connecting the sample coil to the **Sample Coil** connector on the receiver module. Chapter III, Sections C.1 and C.3 describe how the sample probe is tuned to satisfy this requirement.

A.2 Pulsed Mode Operation

In pulsed mode operation, the pulsed RF output of the synthesizer module must be coupled to the sample coil to produce the B_1 field that rotates the direction of the nuclear spin polarization. During the RF pulse, the input of the receiver must not interfere with the application of the RF pulse to the sample coil. Once the RF pulse is complete, the input of the receiver must be coupled to the sample coil so that is can amplify the induced RF signal, without interference from the Pulsed RF output of the synthesizer. Essentially, the sample coil should be connected to the synthesizer's Pulsed RF output and disconnected from the receiver during RF pulses. Between RF pulses, the opposite should be true; the sample coil should be connected to the receiver input and disconnected from the synthesizer's Pulsed RF output. See Figure 2. This entire changeover must take place in microseconds, so that signals with short T_2 may be observed. This bit of magic is performed using non-linear devices called diodes and resonant transmission lines.

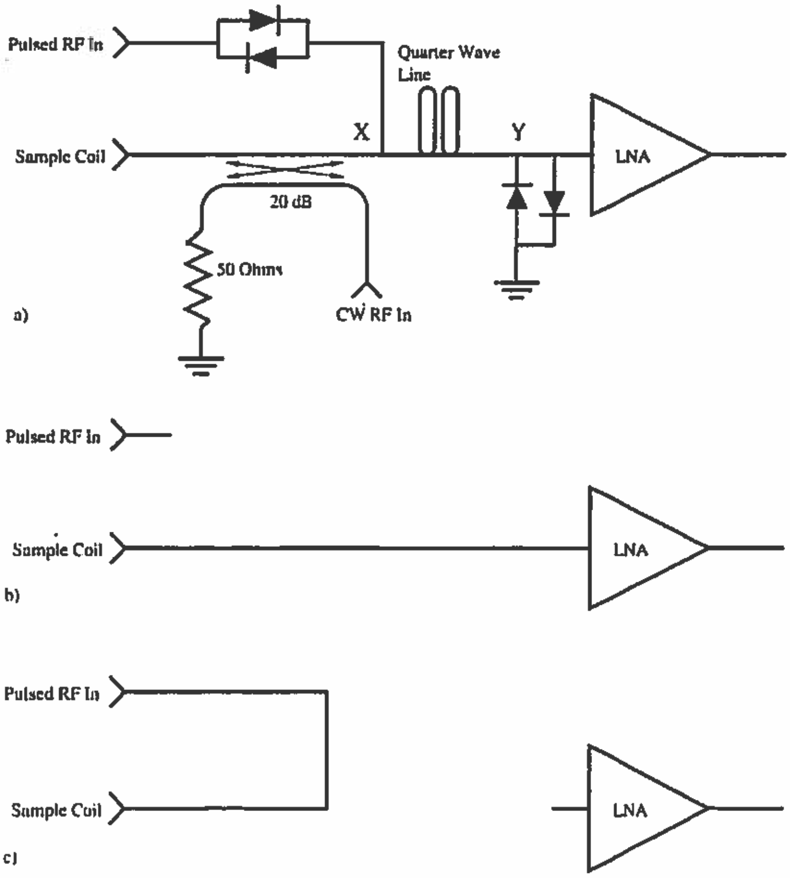
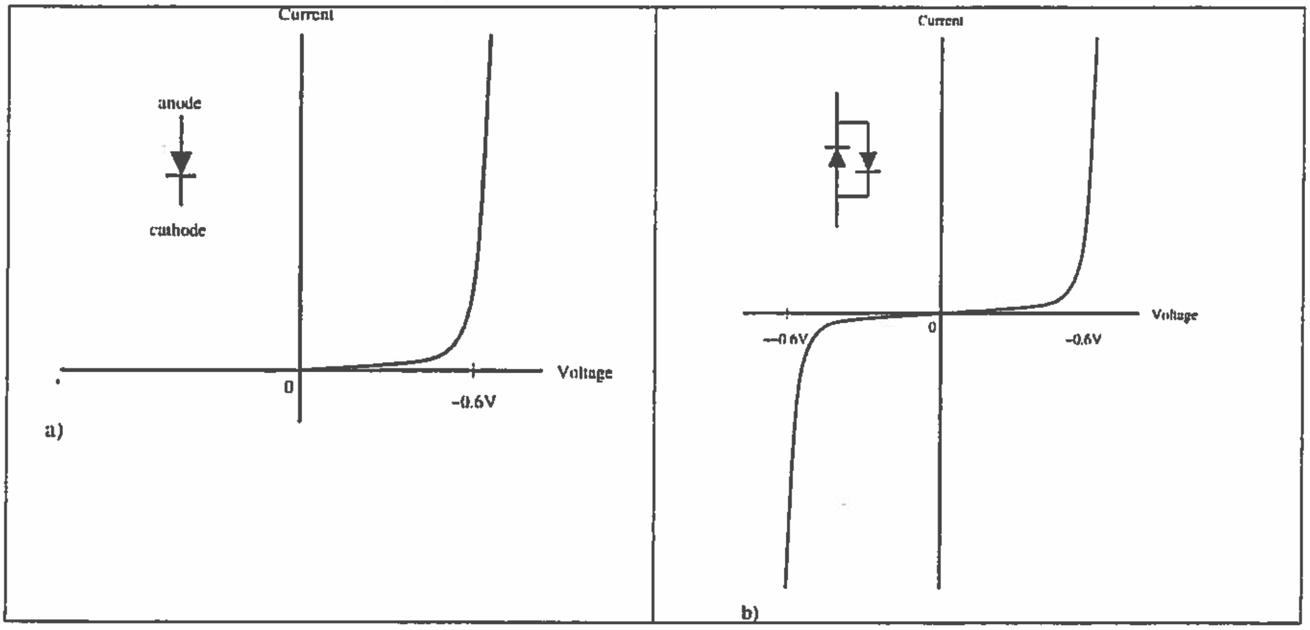


Figure 2.2 (a) PS2 input section circuit. (b) Receiver input section operation, RF pulse off. (c) Receiver input section, RF operation pulse on.

A.2a Diodes in a Nutshell

For those of you unfamiliar with diodes, a diode is a two terminal device which has very non-linear current - voltage (I-V) characteristics. The diodes used in the receiver module are silicon p-n junctions, and have I-V characteristics as shown in Figure 2.3a.



Figures 2.3 (a) Single diode characteristics (b) Back-to-back diode characteristics

The current through the diode *I*, may be roughly described as an exponential function of the voltage applied between the diode's two leads, V

$$I = I_0 e^{\frac{V}{V_0}} \tag{2-1}$$

where V_0 is about 0.6 V, I_0 is a positive constant, and we take V as positive when the diode's anode is more positive that the cathode. For applied voltages much smaller that V_0 very little current flows, so the diode can be treated as a high impedance, or open circuit. (Actually, the diode has a small amount of capacitance, so a slightly more accurate model would be that of a small capacitor.) Conversely, when applied voltages are large compared to V_0, very large currents flow, so the diode can be modeled as a low impedance, or short circuit. The above discussion works when $V > 0$ (positive voltages). Note that very little current flows for any value of $V < 0$. The RF signals we are dealing with, however, are both positive and negative, so rather than using single diodes, they are used in 'back-to-back' pairs, as shown in Figure 2.3b. In this configuration, when $|V| << V_0$ the pair of diodes may be treated as an open circuit, and when $|V| > V_0$ they can be treated as a short circuit.

A.2b Operation Pulsed Mode - Between Pulses

The operation of the input section of the receiver between pulses can now be understood. (See Figure 2.2a.) For this discussion we can ignore the presence of the directional coupler in the circuit. Between pulses, no signal is coming from the pulsed RF output of the synthesizer (by definition!), and the induced voltages in the sample coil produced by the precessing nuclear spin magnetization is very small (typically 10's of μV) compared to V_0. In this case both back-to-back diode pairs act like open circuits, so the pulsed RF output of the synthesizer module is effectively disconnected from the sample coil, and the sample coil is connected to the receiver input amplifier through the $\lambda/4$ length of coaxial cable in the receiver module. (See Figure 2.2b) The back-to-back diodes across the input of the receiver module have no effect on the very small signal entering the input of the receiver.

A.2c Operation Pulsed Mode - During RF pulses

During an RF pulse the pulsed RF output of the synthesizer module swings about ± 25 V. The diodes connecting the pulsed RF output of the synthesizer to the sample coils may therefore be treated as short circuits (low impedance), so they directly connect the pulsed RF output to the sample coil as desired. (See Figure 2.2a) But wait… there seems to be a problem… the back-to-back diodes across the input of the low noise amplifier also seem to have a large voltage applied to them, and therefore can also be treated as short circuits. If these are in a low impedance state they would appear to be shorting the RF applied to the sample coil to ground through the $\lambda/4$ coaxial line. In the low impedance state, the impedance of the diodes is much less than the 50Ω characteristic impedance of the $\lambda/4$ line, so there is wave reflected from this end of the $\lambda/4$ line 180° out of phase with the was incident on the diodes. This reflected wave sets up a standing wave on the $\lambda/4$ cable, with a node at the input to the low noise amplifier (point Y), and an antinode at the opposite end of the $\lambda/4$ line (point X). Nodes in the voltage standing wave correspond to low impedance points, while antinodes correspond to high impedance points. Since the end of the $\lambda/4$ cable where the RF pulse is being coupled (point X) from the synthesizer is an antinode, this point is a high impedance, and may there for be treated as an open circuit! So the back-to-back diodes at the LNA inputs are not shorting the RF pulse to ground, since the $\lambda/4$ length of cable transforms the low impedance at its one end to a high impedance at the other end. The RF pulse from the synthesizer is therefore applied to the sample coil (See Figure 2.2c.) as desired.

A.2d Operation Pulsed Mode - Blanking

Even with the back-to-back diodes and $\lambda/4$ cable, the voltage at the input of the LNA during an RF pulse is many orders of magnitude larger than the voltage induced in the sample coil by the precessing nuclear spin polarization. In order to insure a rapid recovery after the RF pulse ends, *blanking* has been incorporated into the receiver. The **Pulse Programmer** outputs a blanking signal which starts about 10 ns before the RF pulse begins and ends when the RF pulse is complete. The receiver uses this signal to reduce the gain of its RF amplifiers during the RF pulse to prevent the amplifiers from overloading, and to prevent the capacitors in the outputs of the detectors from being charged. The blanking circuitry has the ability to extend the blanking period past the end of the RF through use of the **Blanking Duration** control. This allows for optimizing the blanking interval to compensate for different sample coil tunings.

A.3 CW Mode Operation

The key to understanding the input section of the receiver operating in the CW mode is to understand the operation of the directional coupler. When operating in CW mode the RF signals applied to the input of the receiver module are always small enough that the back-to-back diode pairs can always be treated as in the high impedance state.

A.3a Directional Couplers in a Nutshell

A directional coupler is a 4 port device that directs signals between its various ports depending on the direction of power flow. Figure 2.4a shows the symbol for a 20 dB directional coupler.

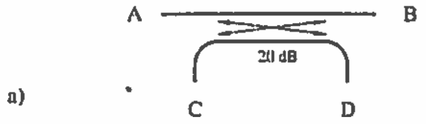


Figure 2.4a Symbol for a 20 dB directional coupler

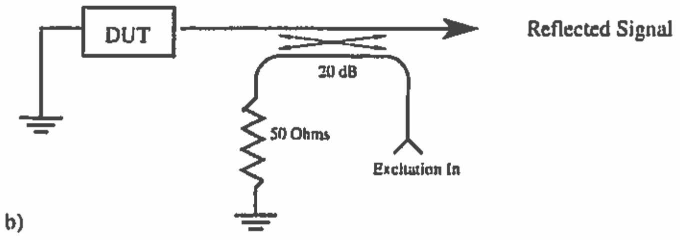


Figure 2.4b Simple reflectometer made from a directional coupler

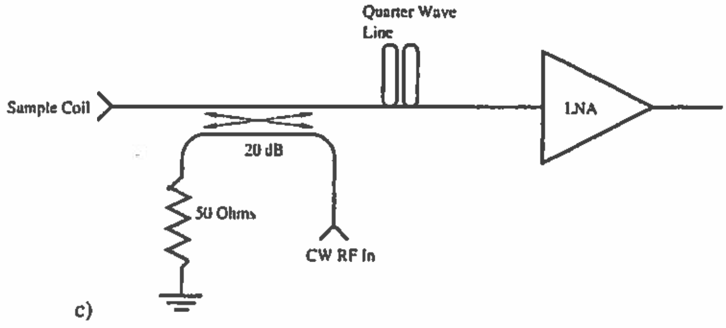


Figure 2.4c Receiver input section operating as a reflectometer

(We will assume and ideal lossless coupler for this discussion.) Directional couplers are designed for specific cable impedances, in the case of the PS2 system the reference impedance is 50 Ω. The 20 dB refers to the magnitude of the *power* coupling between the main and coupled ports. If we connect a signal source to port A of the coupler, 99% of the power will emerge from port B, 1% from port D and none from port C, the *isolated* port. Alternately, if we connect the signal source to port B, 99% of the power will emerge from port A, 1% from port C and port D will be isolated. If the signal is input to port C, 99% of the power is directed to port D and 1% to port B and port A is isolated. Finally, port C receives 99% of the power input to port D while port A gets 1% and port B is isolated.

Directional couplers are completely passive devices (they take no power to operate), and at radio frequencies are usually made from transformers. At first you may be a bit surprised by their operation, which may seem a bit like magic, but you shouldn't be. A partially silvered mirror placed diagonally in a light beam does the same thing! A word of caution - there are definite phase relationships present between the various signals described above - the amplitudes of the various waves must be summed with the appropriate phase factors when signal are input to multiple ports simultaneously. Finally, when you see a directional coupler drawn with only 1 directional port (as on the from panel of the PS2 receiver) this simply means that the unused port is terminated with a load of the characteristic impedance for which the coupler was designed.

A.3b CW Mode Reflectance Bridge

It is easy to see how to construct a reflectance bridge using the simple characteristics described above. (See Figure 2.4c.) The component to be measured is connected to port A of the directional coupler, and the output signal is monitored at port B. An excitation signal is applied to port D of the coupler and port C is terminated with a 50 Ω load. (This is the unused port which is not shown on the front of the PS2 receiver module). 99% of the excitation power emerges from port C and 1% from port A. Since port C is terminated at its characteristic impedance, all the power emerging from port C is absorbed, and none is reflected back into port C. The 1% of the excitation power emerging from port A travels to the sample to be measured. If the complex impedance of the component being measured (commonly referred to as the device under test, or DUT) is Z, the *amplitude* reflection coefficient will be

$$\frac{Z-Z_0}{Z+Z_0} \tag{2.1}$$

with a corresponding power reflection coefficient of

$$\left|\frac{Z-Z_0}{Z+Z_0}\right|^2 \tag{2.2}$$

Any reflected wave from the component being measured enters port A, and 99% of this power emerges from port B. This is the only power emerging form port B. (Port C is the only other port which couples to port B and, as previously described, no power is incident on this port since it is terminated with 50 Ω .) Therefore, by monitoring the amplitude and phase of the signal emerging from port B the reflection coefficient of the component connected to port A may be measured.

In the PS2 receiver module, port A is connected to the **Sample Coil** connector, port B to the input of the LNA through the λ/4 cable, and port D to the **CW In** connector. (See Figure 2.1 and 2.4c) For operation as a reflectometer the CW output of the synthesizer module is connected to the CW input of the receiver module to provide the RF excitation, and the sample coil is connected to the **Sample Coil** connector of the receiver module. The receivers RF output therefore is an amplified version of the signal reflected from the sample coil. **It is best practice to remove the reverse gender BNC cable from the Pulsed RF input when operating in CW mode.**

The phase sensitive detector can be used to display the phase and amplitude of the signal reflected from the sample coil. To do this the **Ref. Out** of the synthesizer module is connected to the **Ref. In** connector of the receiver module providing a phase reference signal. The in-phase and quadrature outputs then represent the two orthogonal phases of the signal reflected form the sample coil. A good way to display these signals is to place your oscilloscope in X-Y mode with equal sensitivity settings (about 1V/div) for both the X and Y axis. Set the beam to be centered in the screen when the X and Y inputs are at zero volts. The vector from the center of the screen to the displayed beam position then represents the amplitude (distance from the screen center) and phase (angle from the screen center) of the reflected signal.

There is an unknown phase constant (rotation about the center of the screen) arising from propagation delays from both the cable connecting the sample coil to the receiver and the amplifiers and filters in the receiver module. Both the gain and phase of the reflectometer may be calibrated by replacing the sample coil with a component with a known reflection. The simplest component to use is a resistor with a value slightly different from the nominal 50 Ω impedance of the coaxial cables. The amplitude and phase of the reflected signal may be calculated using equation 2.1. By varying the phase of the **Ref. Out** signal from the synthesizer module (using the **Phase** menu item) you can rotate the display of the reflected signal on the oscilloscope so that the real component lies along the X-axis. A word of caution -- The reflectometer in the PS2 receiver will only operate accurately when the reflection coefficient of the component connected to the Sample Coil connector is relatively small. This limitation arises from the fact the the input of the LNA is not well matched to 50 Ω, so that a standing wave can be set up between the LNA input and the device being measured.

The standing wave is small and has little effect on the measurement when the reflection coefficient of the item being measured is small, but will result in significant errors when the reflection coefficient is large, such as when a short circuit or open ended cable are present. The reason is that the input of the LNA amplifier is not matched to 50 Ω arises from the matching requirements needed to achieve low noise operation. In general the impedance matching requirements needed to achieve low noise operation are different from those needed to achieve a low reflectivity input match to the amplifier.

B. 21 MHz SYNTHESIZER

B.1 Overview

The synthesizer module is the source of the radio frequency (RF) signals used in the spectrometer. It is a modern, digitally synthesized, high stability, signal source with a wide frequency range. This unit can produce RF signals from below 1 MHz to over 30 MHz, but that is a much larger range than is needed for the operation of the NMR spectrometer. The proton and fluorine precession frequencies are only 6% different, but the field of the permanent magnet varies from unit-to-unit by several percent and will also drift with ambient temperature. Your unit has the proton's precession frequency in your magnet, at ambient room temperature, marked on the serial label. The marked frequency is a good place to start your "tuning up" of the spectrometer.

The unit has six (6) BNC connectors, three inputs and three outputs. The function of each of these connectors is described below.

1. REF Out: This refers to "reference" output signal that is connected to the **REF. In** on the receiver module. It provides a continuous wave, sinusoidal signal (CW) to the phase sensitive detectors in the receiver. The phase of this signal, relative to the phase of the

Pulsed RF Out signal can be adjusted, quasi-continuously (in one degree steps) by the selector knob using P in the menu. This signal can be switched off by the toggle above the BNC connector

2. CW Out: This is a continuous wave sinusoidal signal that is used for CW resonance detection. This signal is fed into the RF probe via the directional coupler inside the receiver module. Its amplitude can be adjusted in this module when the menu is set on A. The power is measured in dBm and can be varied in one dB steps. **This output must be connected to the CW In on the Receiver but the *BNC cable must be removed when operating in the pulse mode.*** The CW output can be turned off by the toggle above the connector.
3. Pulsed RF Out: This is the high power pulsed RF signal that is sent to the coil surrounding the sample via the receiver module. This is a reverse "gender" BNC connector which requires the reverse gender BNC cable to connect it to the RF Pulse In on the receiver module. The cables have "female" BNC connectors, and the BNC panel connectors are male. It is essential that the correct BNC cable is used. The usual BNC male cable connector will not work and should not be forced on.
4. Pulse In, I and Q: These are both inputs connected to the respective I and Q Pulse Out on the Pulse Programmer module. They receive the timing pulses that shape the RF output power used to "tip" the nuclear spins.
5. Sweep In.: This may be used to sweep the RF frequency with an external analog voltage. It may be used in observing CW NMR resonance. It should not be connected in pulse mode operation.

B.2 Specifications

Frequency: 1 – 30 MHz
Frequency Stability: ± 50 ppm
Frequency Increments: steps of 100 KHz, 1 KHz, 10 Hz
Phase: -180° to +180° in one degree steps
CW Amplitude: -10 dBm to -65 dBm in 1 dB steps
Sweep: 0, 1, 2, 5, 10, 20, KHz/Volt

C. PULSE PROGRAMMER

C.1 Overview

As its title implies, this is the module that produces timed pulse sequences used in the various pulsed NMR experiments. This unit sets the pulse lengths for what are called the A and B pulses. In pulse mode, this unit cannot change the amplitude of the RF pulse, we must adjust the **pulse length** to achieve a 90° of 180° rotation of the magnetization – the so-called "ninety or one hundred eighty degree" pulse.

There is only one A pulse in any pulse sequence. There can be as few as zero and as many as 100 B pulses. The number of B pulses appears on the menu as N, Num_B:. The length of the A pulse appears on the menu as A; A_Len: and the length of the B pulse as A B_len:. Both pulse lengths can be varied from 0.02 µs to 20.02 µs. Appearing on the menu as tau:, the time, τ, between the A and B pulse can be varied from 0.0001 s to 9.999 s. The repetition time, written on the menu as P, Period: is the time delay between repeats of the **entire pulse sequence**, meaning the complete pattern of the single A pulse and the chosen number of B pulses. The repetition time can range from 0.2 milliseconds to as long as 100 seconds. If a longer repetition time is required, the Man Start button can be used as a manual start of the pulse sequence. Set the menu to Period: manual to use this feature.

The module provides a short (~ 1 µs) trigger pulse to trigger a 'scope or a computer on either the A or the B pulse. The choice of pulse is made with the toggle marked Sync. Toggle switches are provided on both the A and B pulses to allow either pulse to be turned off as desired. The toggle marked MG is used to disable the Meibohm-Gill 90° phase shift between the A and B pulse in a pulse train that measures T_2 with multiple B pulses. The Blanking Out pulse is a pulse slightly longer than A and B which disables the receiver during the pulse and thus prevents internal capacitors from charging during the RF pulse. This facilitates a faster recovery of the receiver.

Finally, the Ext Start-input requires a TTL pulse which will start a pulse string of the one A pulse and the programmed number of B pulses instead of the internal repetition cycle. Thus, the pulse sequence can be synchronized with any data collecting instrument that the user chooses.

C.2 Specifications

1. A – A Pulse(one only) A_len: 0.02 – 20.02 µs
2. B – B Pulse (0-100_ B_len: 0.02 – 20.02 µs
3. τ tau: 0.0001 – 9.999 seconds
4. N Num_B 0 – 100
5. P Period: 0.2 ms to 100 s
6. External Start TTL Pulse 4 volts 1 µs
7. Manual Start Button
8. Sync on either A or B pulse
9. Sync Out – 0.5 µs TTL Pulse

D. LOCK-IN, SWEEP MODULE

D.1 Overview

The lock-in sweep module is used for continuous wave (CW) experiments. It is comprised of a two channel lock-in amplifier and a sweep ramp generator with a current output amplifier. Depending on the operating mode, one or both of these components may be in use simultaneously. The following sections describe the operation of this module.

D.2 The Lock-In Amplifier

The lock-in amplifier contains an internal reference oscillator operating at a fixed frequency of 20 Hz, and two identical signal channels. During normal operation, the reference oscillator is coupled to the input of the current output amplifier to provide magnetic field modulation, and is simultaneously used to demodulate the signals applied to the lock-in inputs. The output of the demodulator is filtered by a simple RC time constant, and the resultant signal is output as both an analog voltage at the front panel connectors, and a digitized value via a Universal Serial Bus (USB) output port. Both lock-in channels operate with the same signal gain, demodulation phase and time constant settings, each of which can be adjusted by the user.

D.3 Lock-In Related Menu Items

D.3a G – Gain

The gain of the lock-in amplifier can be varied from 80 V/V$_{rms}$ to 2560 V/V$_{rms}$ in factors of 2 by selecting the **G** menu item. The gain settings are calibrated in terms of rms input voltages, so an input signal of 0.0125 V$_{rms}$ with a lock-in gain setting of 80 V/V$_{rms}$ will produce a 1 volt output when the relative phase between the input signal and the lock-in reference phase is zero. If the input signal is too large for the gain setting, causing an overload condition, the **Input Overload** indicator on the front panel will illuminate. When this occurs, either the lock-in amplifier gain, or the amplitude of the input signal must be reduced to insure proper lock-in amplifier operation.

D.3b P – Phase

The phase of the lock-in demodulation is varied through use of the **P** menu item. Both lock-in channels operate with the same demodulation phase, which may be varied in 1°steps. While adjusting the phase, the upper line of the module's display switches to display the output voltages of the two lock-in amplifier outputs. Once the phase has been set to the desired value, pressing the Master Selector knob will return the cursor to the upper display line and the item menu will be displayed.

D.3c T - Time Constant

The output of the lock-in amplifier is filtered by a single RC time constant (6 dB/octave). The value of the time constant can be varied from 0.5 - 10.0 seconds using the **T** menu item. The value of the time constant also determines the rate at which the digitized outputs of the lock-in amplifier are output to the USB port for sweep modes **Off, Automatic, Triggered, Manual,** and **External.** In these modes the lock-in output signals are sampled and transmitted over the USB port twice per time constant period.

D.3c M - Modulation

The amplitude of the magnetic field modulation is set using the **M** menu item. It can be disabled, or varied from 0.03125 to 4.0 mA rms in factors of 2. While the modulation level is being adjusted, the upper line of the display will switch to display the output voltages of the two lock-in amplifier outputs. Once the modulation level has been set to the desired value, pressing the Master Selector knob will return the cursor to the upper display line and the item menu will be displayed.

D.4 Sweep Related Menu Items

D.4a H - Field Offset

The **H** menu item is used to add a constant magnetic field offset to the sample in the probe head. This current can be varied from -250 mA to + 250 mA in 1 mA steps. The setting out the field offset is *not* reflected in the **Sweep I/O** output signal, so it can be used to center the observed signal within the magnet fields sweep range. While the field offset is being adjusted, the upper line of the display will switch to display the lock-in output signals. Once the field offset has been adjusted to the desired value, pressing the Master Selector knob will return the cursor to the upper display line and the item menu will be displayed.

D.4b S - Sweep Mode

- OFF - Sweep generation is disabled. Only current corresponding to a field offset and modulation settings are applied sweep/modulation coils.
- Auto - In **Auto** mode the field sweep run continuously. The sweep extends from $-I_{\max}$ to $+I_{\max,}$ where is the value selected in the **Sweep Amplitude** menu item. The duration of the sweep is determined by the value selected in the **Sweep Duration** menu item. Sweeps are linear ramps with a rapid fly back. At the beginning of each sweep a 2.5 µs, 5 V pulse is output from the **Trig I/O** connector. A voltage is also output from the **Sweep I/O** connector spanning -10 V to + 10 V corresponding to the entire sweep range.
- Triggered - The triggered mode is similar to the Auto mode, except the sweep does not commence until triggered, either by a rising logic edge on the Sweep Sync I/O connector or pressing the **Manual Start** button of the front panel. If a sweep is already in progress trigger inputs are ignored. The **Sweep I/O** output signal is the same as in **Auto** mode.
- External - In external mode the **Sweep I/O** connector is an input. The input range spans -10 V to +10 V corresponding to a current range of -250 mA to + 250 mA. This is a fixed range and is *not* controlled by the **Sweep Amplitude** setting. **The Field Offset** and **Modulation** signals operate normally and are summed with the external input.
- Manual - Manual mode allows the value of the field sweep to be adjusted using the Master Selector knob on the lock-in front panel. After selecting this mode by pressing the Master Selector knob, the lower display line indicates the sweep value as a percentage of full scale, adjustable in 1% steps from -100% to + 100%, while the upper display line displays the lock-in outputs. The scale of the sweep is determined by the value selected in the Sweep Amplitude menu. The value of the **Sweep I/O** output varies from -10 V to + 10 V, corresponding to the entire sweep range. Pressing the Master Selector knob will return the user to the top menu.
- Rapid Scan (RSxx) - The **Rapid Scan** modes are used when observing the output of the receiver directly without lock-in demodulation. In this mode lock-in functions, including the field modulation are disabled. The field repetitively sweeps in a triangle waveform with peak amplitude as selected by the **Sweep Amplitude** menu item. The frequency of the Rapid Scan sweep can be set to 1, 2, 5, 10, 20, 50 or 100 Hz. The **Sweep I/O** output varies from -10 V to + 10 V, corresponding to the entire sweep range, with a snyc trigger of 50 µs, 5 V output at the Trig I/O connector.

D.4c A - Sweep Amplitude

The sweep amplitude menu item selects the amplitude of the sweep range for the **Auto, Triggered, Manual** and **Rapid Scan** modes. Sweep ranges of ±1.953, ±3.906, ±7.812, ±15.625, ±31.25, ±62.5, ±125, and ±250 mA are supported.

D.4d D - Sweep Duration

The sweep duration menu item selects the duration of the field sweep for the Auto and Triggered modes. Sweep durations of 10, 20, 50, 100, 200 and 500 seconds are allowed.

E. THE PERMANENT MAGNET

E.1 Overview

The PS2-A spectrometer comes with a uniquely designed permanent magnet described in this section. The physical specifications of the magnet are as follows:

Field Strength in Gap: 0.50 ± .01 Tesla
Homogeneity (minimum): 0.5 mT over 0.125 cm^3
Gap Width: 1.78 cm
Pole Diameter: 10.1 cm
Permanent Magnet Material: NdFeB
Weight: 15 kg

Figure 2.5 The Permanent Magnet

Removing the wooden top and insulation exposes the basic "H" – frame geometry of the magnet assembly. Soft iron is used for the frame members and the NdFeB permanently magnetized disks are mounted on each side behind the pole tips. Neodymium-Iron-Boron material was selected as the permanent magnet because of its large magnetization and its ability to retain that magnetization. Simply put, the magnet will likely outlast the electronics, the professors, and even the students.

However, NdFeB has one characteristic that can be a problem. Its magnetization is temperature dependent. Thus, the field in the air gap depends on the temperature of the magnetic material. For many experiments, this drifting magnetic field will cause only a small error in the data. For other experiments, the drift is intolerable. In order to provide a wide range of experimental possibilities, TeachSpin designed a complete temperature control system that is easy to use and will regulate the temperature of the NdFeB magnets. The temperature of the magnetic material is kept so stable that the field in the gap remains essentially constant. Within 50 minutes after the regulation loop has been closed, the gap field will reach an impressive stability.

Field Stability: $\pm 5 \times 10^{-4}$ mT over 15 minutes

(In frequency units, for proton resonance, the stability is ± 20 Hz.)

This, or even better, field stability is obtained if and only if the magnet is used in a reasonable laboratory environment.

The following is a list of "Do's and Don'ts" that must be respected for the optimum performance of this high stability-high homogeneity magnet.

Do:

1. Place the magnet in a reasonably temperature stable location.
2. Place the magnet on a non-ferromagnetic table.
3. Check all electrical connections to the magnet, temperature controller and spectrometer main frame carefully before attempting any experiment.

DO NOT:

1. Place the magnet in a draft or near an open window.
2. Place the magnet near a vent or a radiator heater.
3. Place the magnet near AC high power lines.
4. Place the magnet near a power transformer – particularly the transformer at the right rear of the main frame of the spectrometer. (There is a reason why we always show the instrument with the magnet to the left of the controller!)
5. Place anything under the magnet that might obstruct the flow of air to the thermoelectric heat sinks.
6. Direct a strong light onto the magnet, especially light from an incandescent source.
7. Keep any significant ferromagnetic materials nearby such as a screw driver, a student belt buckle, steel chain . . . Be particularly careful with items that can move.
8. Move the magnet to a new location during or close to the time of starting an experiment, especially if you want to retain the maximum field stability.
9. Place your hand or other objects on the exposed heat sinks of the thermoelectric coolers.
10. Drop the magnet or give it a large mechanical shock
11. Let ferromagnetic "stuff" fall into the magnet gap - paper clips, pins, small tools, etc

12. **DO NOT** leave the thermal servo loops on overnight – or on for several days. This will not damage the magnet or the servo electronics, but it may mean that the system will be keeping the magnet at a temperature very far from the current ambient temperature of its surroundings. Part of what makes the PS2-A system so effective at keeping the temperature stable is that the magnet temperature is being locked to the temperature of the local environment at the time the loop was closed. Using a magnet with a servo that has been on too long is not an optimum starting condition for a set of experiments that require maximum field stability.

E.2 Controlling the Temperature

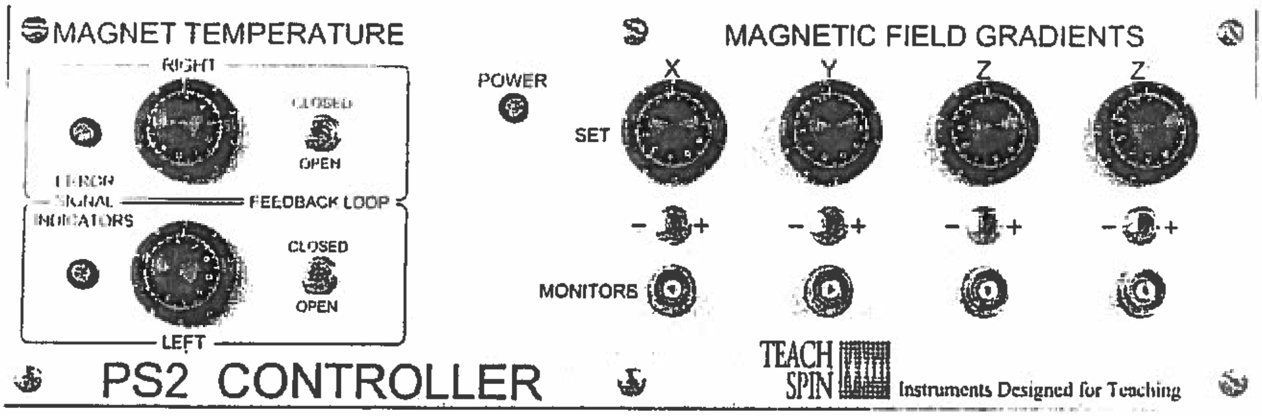


Figure 2.6 Control Panel

The temperature of the NdFeB magnets on the two pole pieces are controlled by two identical and independent thermal servo units, one for each pole. These servo units are designed to keep the temperature of the individual magnetic disc on each pole at a constant temperature. Note that the specific temperature of an individual pole piece is not important. What is essential is that the temperature of each NdFeB disc remains constant for the duration of the experiment.

To accomplish this stability, a special thermistor temperature sensor is put in good thermal contact with each NdFeB disc. A thermistor is a special material whose resistance varies in a predictable and reproducible way with temperature. Thus, the value of the thermistor resistance is a measure of the temperature of the NdFeB disc, which is also a measure of its magnetization. The temperature of the disc is then modulated (controlled) by a thermoelectric cooler, which has the remarkable property of either cooling or heating a surface depending on the polarity of the current through it. Heat is transferred from the NdFeB magnetic to the heat sinks which exchange heat to the room by both convection and radiation. These heat sinks also masquerade as the side panel labels of the unit. Students should not put their hands on these heat sinks during critical runs where optimum temperature stability is required. Some care should be taken with these panels. Letting heavy objects hit them could damage the thermoelectric cooler.

Operating the servo loop temperature controller is straight forward. The last student who used the unit should have left the loop OPEN! This is easily done with the two toggle switches on the front panel. It can also be accomplished by turning the power off, using the power switch on the power entry module at the rear of the Mainframe. Using the power switch, however, is not the best practice because it will also turn off the electric field shim gradient coils. If you are using the shim coils for the experiment, they should have been left ON. The shim coils can be left on indefinitely without damage to either the coils or controller. Keeping the fields of the shim coils on requires that the spectrometer also be left on. However, we recommend that both the A and B pulses on the pulse programmer be turned off.

Gradient coils ON and loop OPEN is the best way to leave the apparatus during a semester, where it is important to obtain optimum field stability in the shortest time. In this configuration, the magnet comes to steady state equilibrium in the shortest time with its ambient temperature.

The objective is now to lock the temperature of each magnetic disc at its existing temperature – or as near to it as is possible. Since each magnet might be at a slightly different temperature, or, more likely, since the temperature sensing thermistors are not exactly matched, it is essential to find the temperature set point for each side. With the loop OPEN, adjust both set point potentiometers on the front panel until the corresponding LED becomes dark. Red means the set point is too high, blue that it is too low. At the correct value, the LED goes dark. Figure 2.7 is a simplified block diagram of the controller which shows how this works. The thermistor is in one arm of a Wheatstone bridge and the output of the bridge is compared to the adjustable reference voltage. The difference is amplified by the instrument amplifier. Both the actual bridge signal from the thermistor and the reference voltage are available on BNC connectors on the back panel. You may monitor the thermistor bridge signal to assure yourself that the loop is stabilizing the temperature of the magnets.

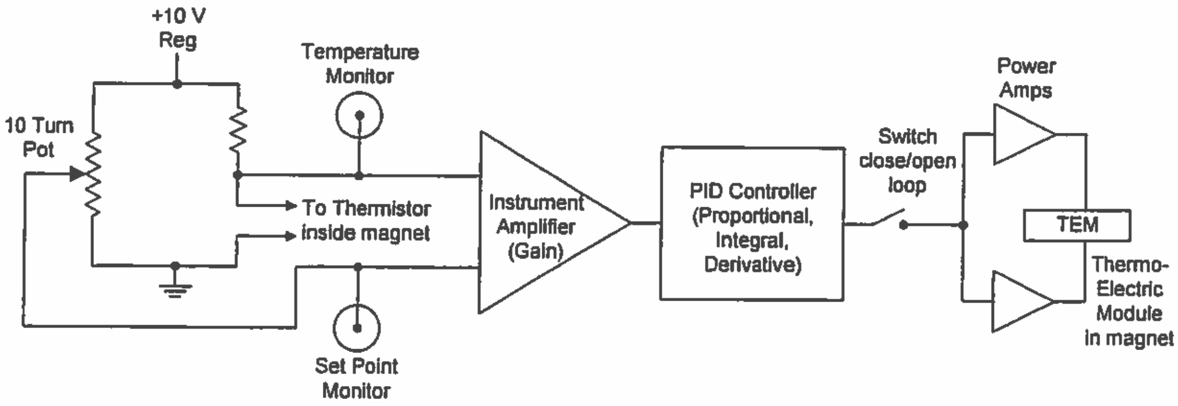


Figure 2.7 Simplified Block Diagram of the Controller

Once the two reference voltages have been carefully set and locked on the ten turn knobs, both loops should be closed simultaneously. You will likely notice some oscillation in the current to the TEC's but this should settle down in a minute or so as the loop PID (Proportions, integral, differential) establishes a fixed temperature. The LED should remain dark as long as the servo is doing its job and keeping the magnets at a fixed temperature. Also the temperature monitor voltage should remain constant and the same as the reference voltage. If this does not occur, repeat the starting procedure. If this system still does not lock the temperature, there may be loose cables or the system may need repair.

Because of the rather slow thermal response times for the entire magnet assembly, it takes about 45 minutes for the magnetic field to achieve optimum stability. Each magnet is slightly different and students may wish to measure this characteristic time as well as the stability of the one they are using. After making sure the field is homogenized and the gradient coils optimized (this can easily be done using a single pulse FID signal with a mineral oil sample), drifts in the magnetic field of as little as 10 Hz can be detected. This drift can be monitored using a two channel scope to compare the envelope output with the output of either of the phase sensitive detectors. (The phase and gain must be adjusted so that the two signals are equal.)

The controller can be operated for an indefinite time as long as the ambient temperature of the room is stable to about ± 1 C. Once the experiments are complete, the thermal loops on both of the magnetic loops should be switched to OPEN to allow the magnetic to establish equilibrium with the current room temperature. The field gradient coils should be left ON.

F. MAGNETIC FIELD GRADIENT COILS

The magnetic field homogeneity over the sample volume can be significantly enhanced by using a set of four coils that form the sides of the RF probe unit. These coils are designed to produce magnetic field **gradients** in the region around the sample when steady dc current is passed through them. There are four sets of coils producing linear field gradients in the x, y, and z directions and a quadratic field gradient in the z direction. (See Figure 2.8 for the definition of the x,y,z axes.)

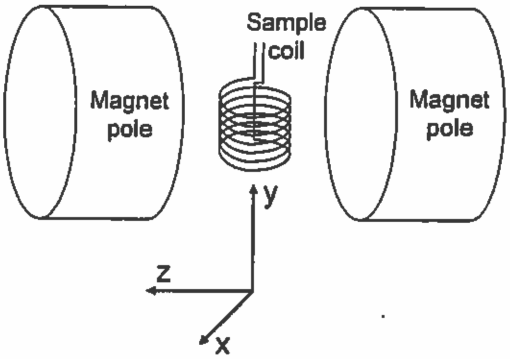


Figure 2.8 Simplified drawing of Magnetic Poles and Sample Coil showing x, y, and z axes.

Each gradient coil has two windings, one on each side of the RF probe. The coils are made on electronic circuit boards by electrochemical etching, and are therefore extremely dimensionally stable. Each is connected to a constant current regulated supply whose current is adjusted by a 10 turn potentiometer. The potentiometer shafts can be locked on the dial counter after adjustment. Current regulated supplies are used so that the current, which creates the field gradient, will not change as the resistance of the coils and leads changes with temperature.

For optimum field homogeneity, the field gradient coils should be adjusted by the students for each experiment. The gradients in the magnet may drift slightly with time and temperature, so the adjustment should be made before any critical experiment is performed. Please note that many experiments do not require optimum field homogeneity.

One can adjust the gradients with almost any liquid sample containing protons that has a "reasonable" T_1 and a $T_2 > 30$ msec. By reasonable we mean 30 – 100 msec, so that the repetition time can be 0.2 to 1.0 sec. Although ordinary water has a $T_2 >> 30$ msec, the long repetition time required (since $T_1 \sim 2$ s) makes the experiment time consuming and cumbersome. Most light mineral oil samples will serve this purpose. T_2 can easily be estimated using a two-pulse sequence and observing the spin-echo.

Optimization of the field gradients is achieved by systematically adjusting one gradient field after another while observing the Free Induction Decay (FID) envelope after a single 90° pulse - the longer the envelope, the more homogeneous the field. As good as they are, the gradient coils are not perfect. When the current is changed in the y-gradient coil, it may have some small effect on both the x and z linear gradients and may even produce a small effect on the value of the total field. Thus, one must go through the entire process several times to achieve the optimization of the field homogeneity. It is essential to optimize the field on a proton signal where the chemical shifts are small, and then use that homogenized field to observe the inequivalent fluorines in various fluorine samples.

Students should be able to obtain 5 ms T_2^* for the proton signal in light mineral oil. It may take some "fiddling around" to achieve this. Gradients can be added in either direction simply by flipping the reversing switch on the front panel. The currents in each coil can be monitored at the BNC connection under each control potentiometer. This point monitors the voltage across a 2.5 Ω precision resistor in series with the X and Y gradient coil, and a 1.25 Ω resistor for the Z and Z^2 gradient coils. These monitor points can be used to record the currents and to determine their stability as well as to trouble shoot any problems that might occur in the electronics.

Specifications:

$$\frac{\partial B_z}{\partial z} = 6.6\ (\mu T / mm)/amp \qquad \frac{\partial^2 B_z}{\partial z^2} = 20\ (\mu T / mm^2)/amp$$

$$\frac{\partial B_z}{\partial x}, \frac{\partial B_z}{\partial y} = 7.1\ (\mu T / mm)/amp$$

G. MAGNET YOKE ADJUSTMENT

The adjustment about to be explained should only be made by the faculty or staff in charge of this apparatus. ***Students should not attempt this adjustment!***

The magnet pole pieces are adjusted at the factory to reduce or nearly eliminate the X, Y linear gradients over the sample. After you have optimized the magnetic field homogeneity over the sample by adjusting the electric current gradient coils, you should notice that the X and Y linear gradient current settings are at only a small fraction of their entire range. But suppose, after many years, or after the magnet has been moved several times, students discover that they could improve the homogeneity of the field even more, but they have "run out of current" in say the Y-linear gradient. If indeed this is correct, realigning the pole pieces will greatly reduce the inherent Y-gradient of the magnet. (Please Note - This realignment of the pole pieces will primarily affect X and Y gradients and has only a very small effect on the Z-gradients).

The procedure is as follows: Place a small (few drops) light mineral oil sample in the RF sample probe. Be sure it is in the proper location. Tune the spectrometer for an FID following a single 90° pulse. Turn down the gradient coil currents to zero. Insert the 3/32" hex wrench with T-handle, into one of the three 1/8" holes in the front heat sink and engage one of the three set screws. These set screws (which were initially adjusted at the factory) press on the front pole face and are used to align the front pole face to be parallel to the rear pole face. It is the "parallelness" of the two pole pieces that determines the X and Y linear gradients.

With the FID from the light mineral oil presented on an oscilloscope, adjust each of the three set screws to achieve the longest T_2^* (decay time). Usually, this takes many iterations, because moving one screw changes the effect of the others. You should only need to turn the screws a fraction of a rotation. If you go more than a full rotation, back off all the screws and start again.

When you have achieved the longest possible T_2^*, turn on the electric shim coils and use them to optimize the field gradients. If you have made the adjustment correctly, you should only need a small fraction of the available X and Y linear gradient currents to get to a maximum T_2^*.

Once these adjustments have been made, they should not need to be repeated for at least 6 months, maybe many years. This is certainly not an adjustment that should be needed every lab period. In fact, it is highly possible that you will never need it!

H. MODULATION COILS

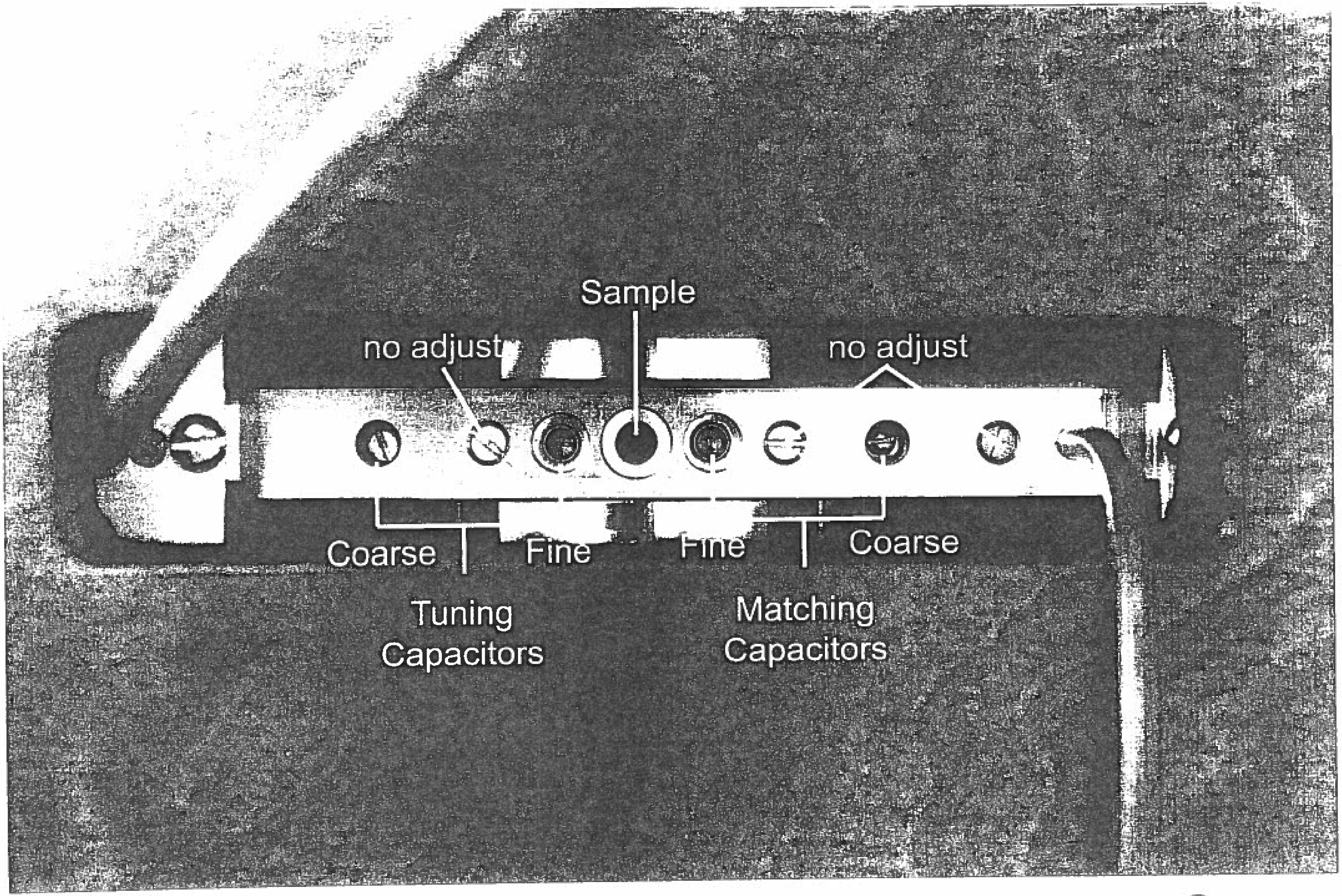
Along with the field gradient coils, a pair of Helmholtz-like coils is imbedded in the circuit boards that provide the sides to the RF probe of the spectrometer. These coils provide uniform magnetic fields in the z-direction – the direction of the main magnetic field. These coils are principally used in CW (Continuous Wave) NMR experiments. They provide a slow time-dependent sweep field as well as an AC modulating field.

The currents in the modulation coils come directly from the lock-in module on the main frame of the unit. All the controls for this unit come from the lock-in module. The electrical connection to the lock-in comes through the power cable connected from the rear of the main-frame to the back of the temperature/gradient controller unit.

The modulation coil can also be used to shift the DC field electronically. **However, along with this shift will come a change in the field homogeneity over the sample.** Care must be exercised by the user if the optimum homogeneity is to be maintained over the sweep.

Specifications:

Coil Constant: 3.1 mT/amp or 31 gauss/amp
Homogeneity: 1 part in 250
Resistance: 2 Ω


Sample
no adjust
no adjust
Coarse
Fine
Fine
Coarse
Tuning
Capacitors
Matching
Capacitors

I. RF SAMPLE PROBE HEAD

I.1 Overview

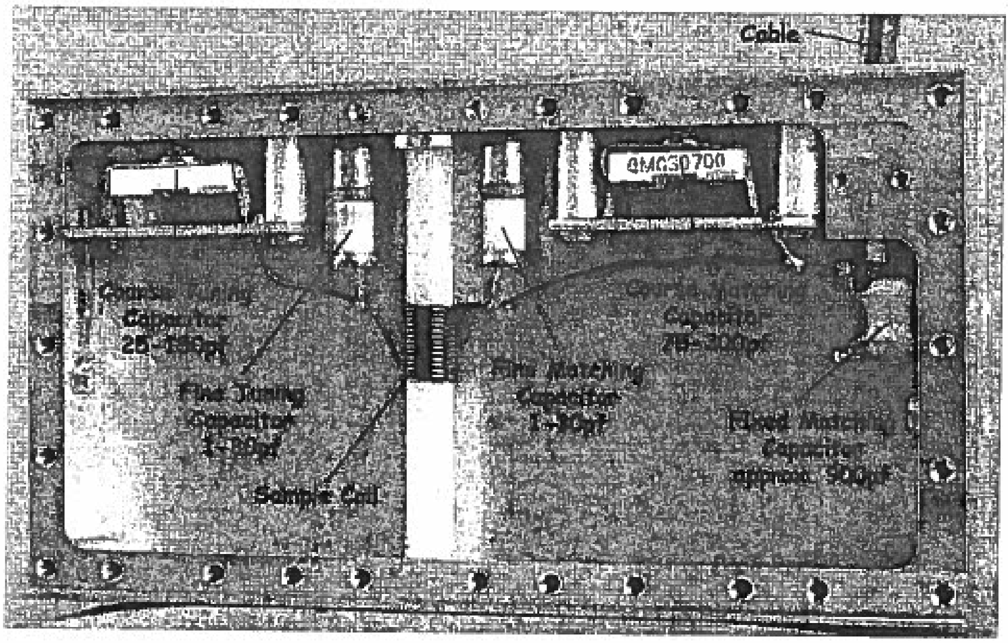


Figure 2.9 RF Sample Probe (RF Shield and Modulation and Gradient Coils not Shown)

The single coil RF sample probe is shown in Figure 2.9, without the RF shield and the modulation and gradient coils which form the side walls. The circuit diagram is shown in Figure 2.10.

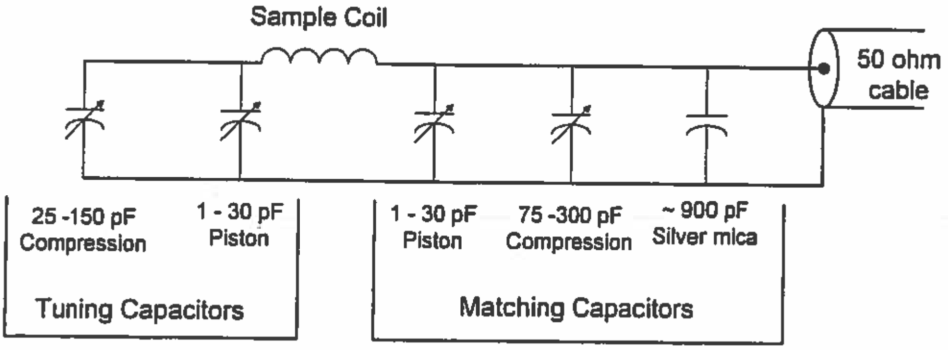


Figure 2.10 Circuit Diagram for RF Sample Probe

The two capacitors on the left side combine to tune the sample coil into series resonance at the frequency of the applied RF signal. This tuning can be observed with the "pick-up probe" that is inserted into the sample chamber. The RF field in the coil produces an emf in the two loops of the probe and that emf can be observed on an oscilloscope. Using this pick-up signal, the user can tune the sample coil to resonance by adjusting both the compression and the piston capacitors on the tuning side. Changing the impedance matching capacitors (piston, compression, and fixed 900 pf) has a small effect on optimizing the RF power to the coil, but is important when using the spectrometer in CW mode. Since there is always at least 976 pf of matching capacitance, the sample probe is usually well enough matched for most pulsed NMR experiments.

However, when searching for a signal in the pulsed mode, it is essential that the coil be on, or nearly on, resonance with the RF frequency, and that the RF frequency be at, or nearly at, the precession frequency of the nuclei being measured. This is not difficult to achieve, since the magnet has the Larmor precession frequency of a proton sample written on the serial label. This label appears on both the magnet and the electronics Mainframe. Of course, this is not an exact number since the magnetic field in the gap is temperature dependent. It is, however, close enough for a student to see a signal if the RF sample probe is properly tuned to that frequency. It is very difficult to observe a signal if the sample coil is not tuned near the RF frequency of the synthesizer.

I.2 Pickup Probe

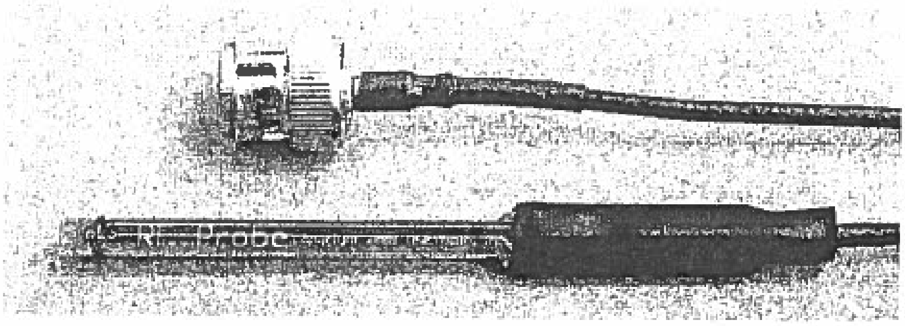
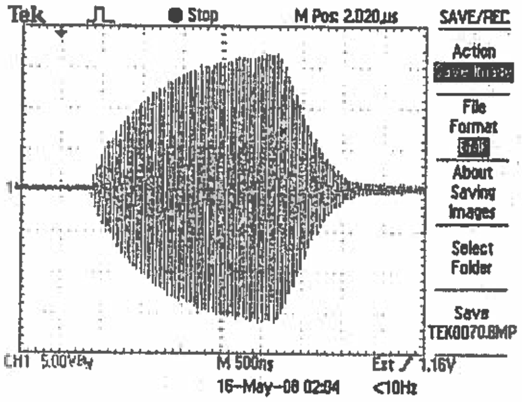


Figure 2.11 RF Pickup Probe

Figure 2.11 shows a diagram of the RF pickup probe. As described above, this probe is essential in the early stages of tuning the RF sample probe to the Larmor precession frequency. There are no test points or pickoff points in the RF circuits, so we provided the user with this probe to examine the RF field DURING THE PULSE. The oscillating RF field in the coil produces an emf in the coil, and that emf, in turn, generates an oscillating voltage across the 50 Ω load. This voltage can easily be observed on an oscilloscope, as shown in Figure 2.12.



M Pos: 2.020µs

CH1 5.00V/div

M 500ns

Ext / 1.16V

16-May-08 02:04

<10Hz

Figure 2.12 Pickup Signal During RF pulse

This voltage can be optimized primarily by adjusting the two tuning capacitors (25 – 150 pf compression, 1 – 30 pf piston) using the spectral tool provided. **BE CAREFUL NOT TO USE A STEEL SCREW DRIVER – THIS AREA HAS A LARGE MAGNETIC FIELD. YOU CAN DAMAGE THE MAGNET**

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.

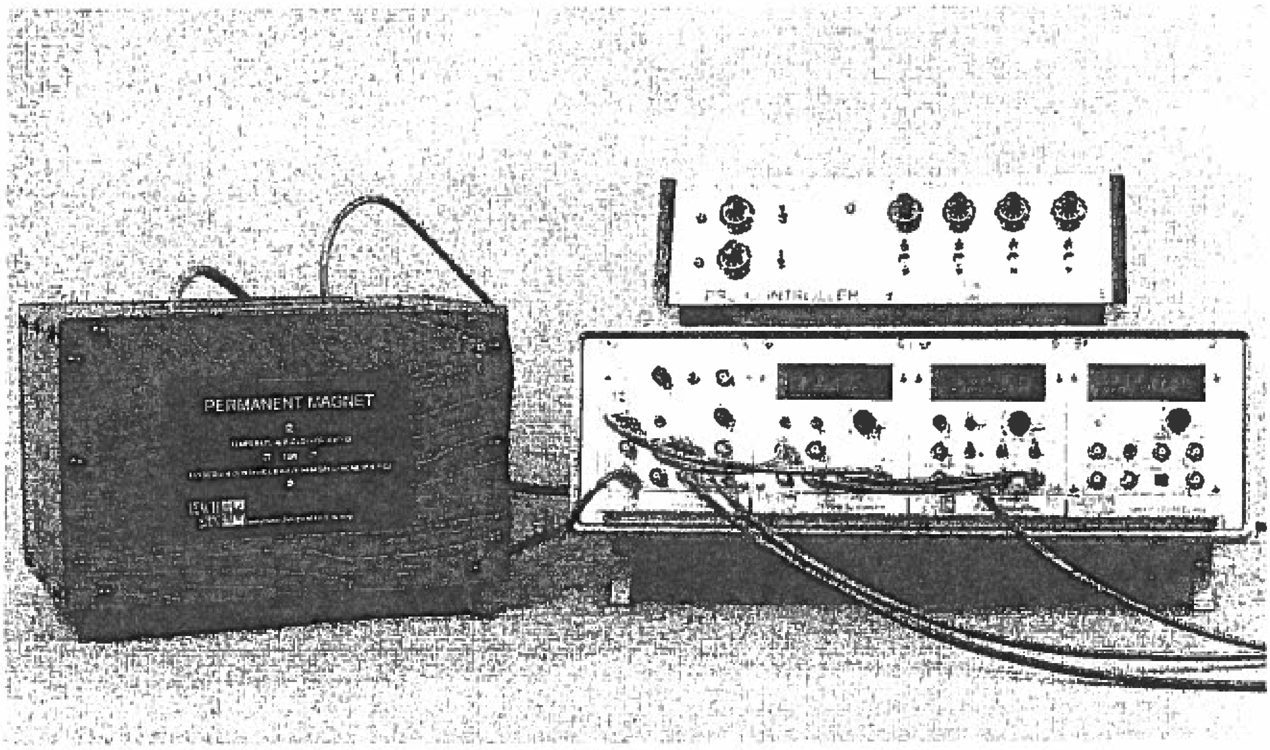


Figure 3.1 The PS2-A Spectrometer: Magnet, Mainframe and PS2 Controller

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.

✓ SYNTHESIZER	✓ PULSE PROGRAMMER	LOCK-IN / FIELD SWEEP ✓
F (flashing) – Frequency: 18.00000 mHz P Refer Phase: -180° A CW Pwr: - 10 dBm S Sweep: 0 kHz/V	A (flashing) A_len: 0.02 µs B B_len: 0. 02 µs τ tau: 0.0001 s N Num_B: 0 P Period: 0.2 ms	G (flashing) Gain: 80 V/V P Ref Phase: : -180° T Time Const: 0.5 s M Mod Amp: off H Fld off: 0.00 G S Swp Md: off A Swp Amp: 0.039 G D Swp Dur: 10 s

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.

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.

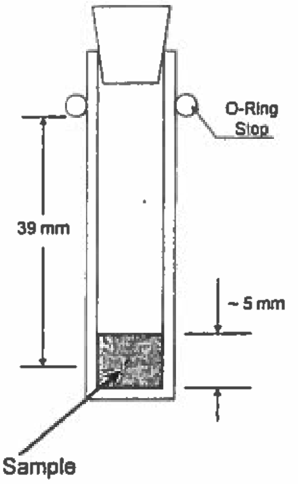


Figure 3.2 Schematic of Sample

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.

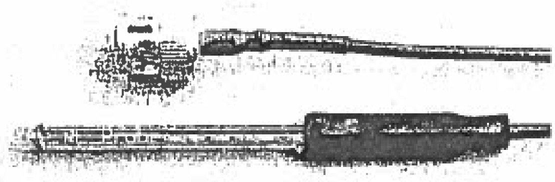


Figure 3.3 Pickup Probe

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:

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

Since the term $\omega_{ref}+\omega_{spins}$ 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.

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

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?

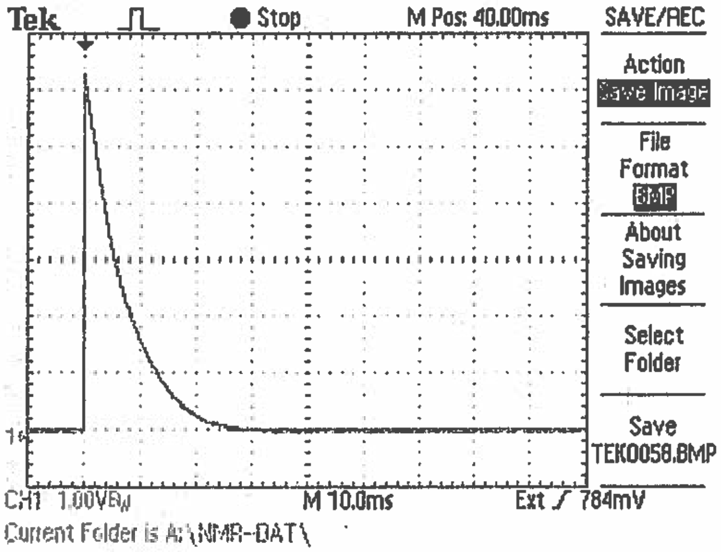


Figure 3.4 FID of Heavy Mineral Oil

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 μs) 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.

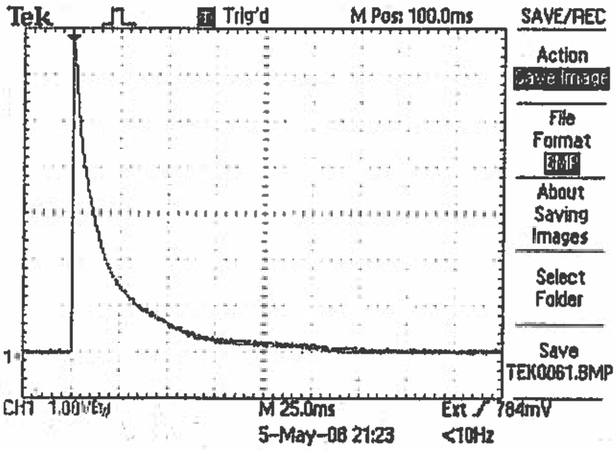


Figure 3.5 FID of Water Sample

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
Fluorine'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.

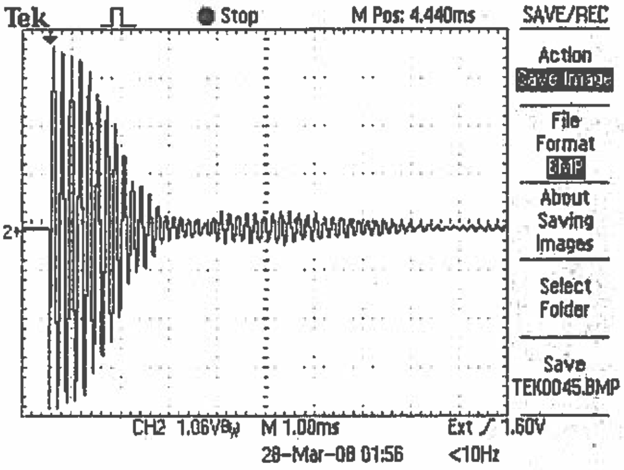


Figure 3.5 FID of FC-770

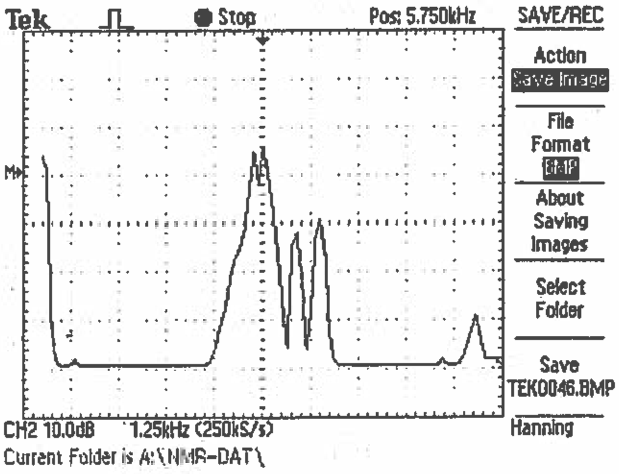


Figure 3.6 FFT of FC-770

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, τ. Thus, there are four parameters to program into the pulse programmer: A length, B length, τ (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 $P \sim 50$ ms and for other samples, the decrease was noticeable for $P \sim 1$ 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).

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z(t)}{T_1} \tag{1.13}$$

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 in then repeated with different times, τ, 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, τ_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- - 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.

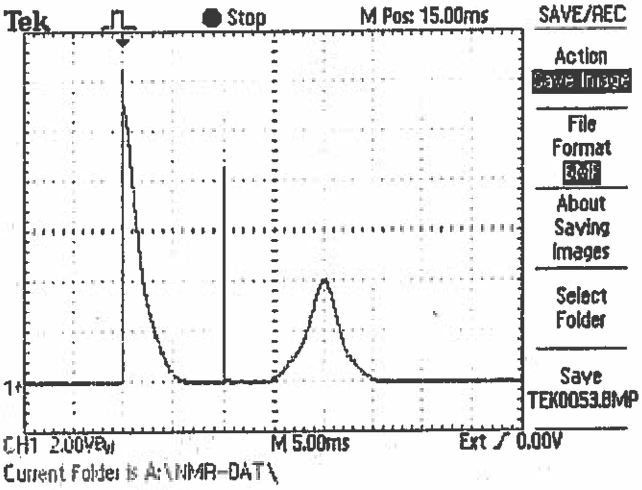


Figure 3.7

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 - - 180° - - 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-pin 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.

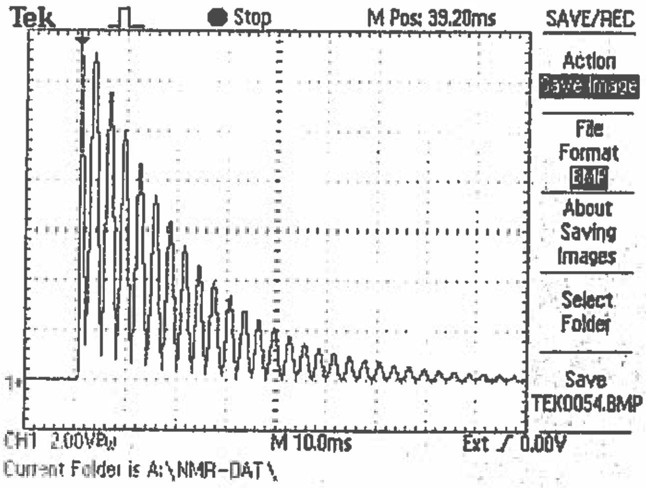


Figure 3.8 Meiboom-Gill Sequence

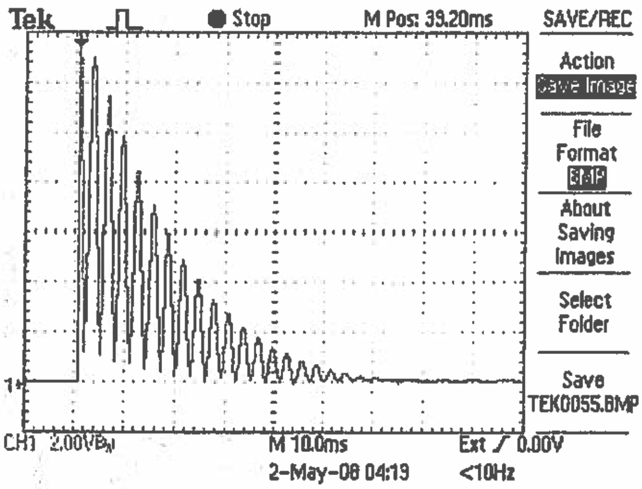


Figure 3.9 Carr-Purcell Sequence

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 τ is given by the expression:

$$M(\tau) = M_0 e^{-\gamma^2 (\frac{\partial B}{\partial z}) \frac{D\tau^3}{12}} \qquad (3.1)$$

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.

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.

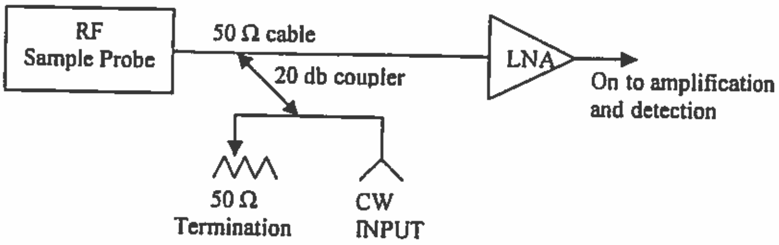


Figure 3.10 Schematic of Configuration for CW Experiments

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 Ω termination, but one hundredth of the power travels down the 50 Ω 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 Ω, 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 Ω 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 $B_0 = \omega/\gamma$ (ω = 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,

$$Z_S = Z_R + Z_C + Z_L \qquad (3.2)$$

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 theses are:

$$X_R = R \qquad (3.3)$$

$$X_C = \frac{-i}{\omega c} \qquad (3.4)$$

$$X_L = i\omega L \qquad (3.5)$$

We can write Zs in terms of resistance and reactances as:

$$Z_S = R + X_C + X_L = R + X_S \qquad (3.6)$$

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 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.)

$$Y_S = \frac{1}{Z_S} = \frac{1}{R + X_S} \qquad (3.7)$$

The admittance may be expressed as a sum of its real part, the conductance, G and its imaginary part, the susceptance, B.

$$Y_S = G_S + B_S = \frac{1}{R + X_S} = \frac{R - X_S}{R^2 - X_S^2} \qquad (3.8)$$

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 Ω + 0*i*), 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 Ω which makes the peak of G_S about $2S$. To match to 50 Ω 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, ω.

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

$$B_S = \frac{-X_S}{R^2 - X_S^2} = \frac{i(1/\omega C - \omega L)}{R^2 - X_S^2} \qquad (3.9)$$

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 a 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.

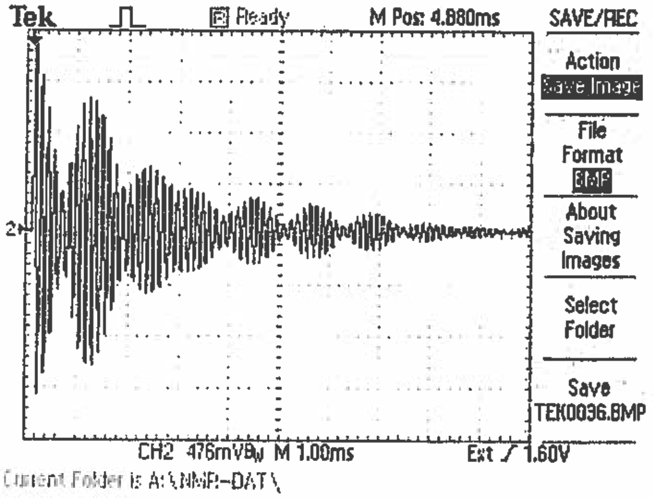


Figure 3.11 FID FC-43

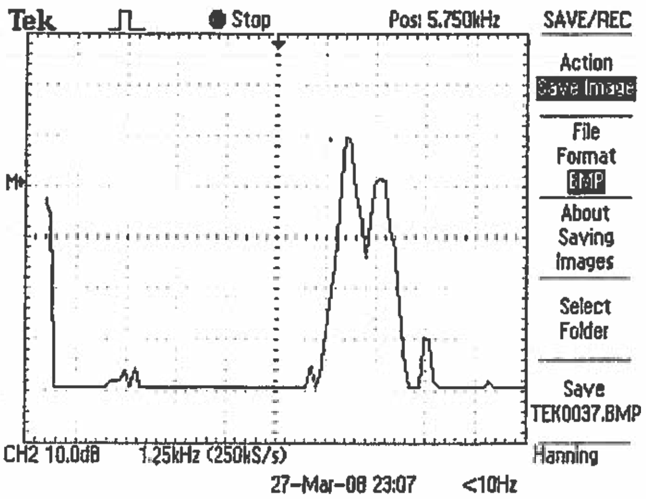


Figure 3.12 FFT FC-43

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:

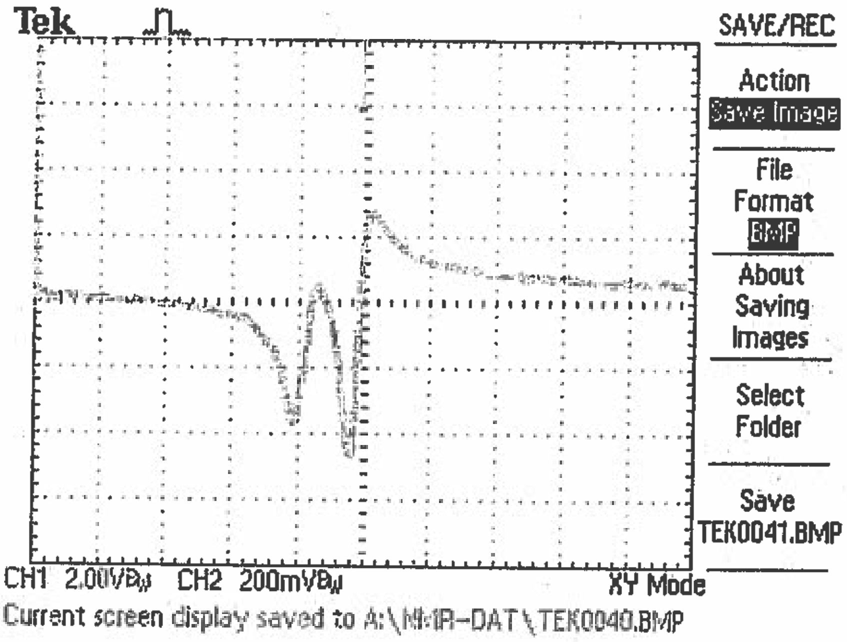
1. Set up your oscilloscope for the x-y display and adjust the offset controls so that the single spot is at the center for all gain settings with the DC coupling and the INPUT grounded.
2. Now connect the output from I and Q to inputs 1 and 2 on the 'scope. (It does not matter which output goes to which 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



Current screen display saved to A:\NMR-DAT\TEK0040.BMP

Figure 3.13 Data for FC-43

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.

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IV. EXPERIMENTS

PS2-A is a research grade Pulsed/CW NMR spectrometer capable of carrying out a wide variety of experiments and research projects. In this brief section, we are listing, in no particular order, experiments that instructors might wish to consider for their laboratory programs. This is certainly not an encyclopedic list; rather, it is a collection of experiments that will provide a challenging experience to both undergraduate and graduate students. All of the experiments require a careful reading of the literature to obtain a thorough explanation of the physics behind the experiments.

1. Measure T_1 and T_2 of water doped with paramagnetic ions over a wide concentration range. Paramagnetic ions that dissolve in water include $CuS0_4$ and $Fe(NO_3)_3$.
2. Measure T_1 and T_2 in glycerin and water mixtures.
   Glycerin and water mix in any ratio. The motion of the protons in glycerin is significantly changed by the change of the liquid viscosity with the addition of water. The relaxation times can be correlated with the viscosity of the liquid, as well as with the water concentration.
3. Measure T_1 and T_2 in mineral oil with solvents. The relaxation times of protons in mineral oil diluted with organic solvents show the effects of diffusion and correlation times.
4. Measure T_1 and T_2 in Petroleum Jelly
   Vaseline is not a solid. The two relaxation times indicate fast molecular motion which is characteristic of a liquid. Samples can be heated and T_1, as well as T_2, can be estimated as the sample cools to room temperature. Other organic greases with sufficient proton concentrations can also be studied.
5. Biological Materials
   Most biological materials have protons, usually in water molecules. Measurements of T_1 and T_2 in biological materials give detailed information about the local environment of these water molecules. This area of exploration is wide open. This might be an area appropriate for an undergraduate research participation project.
6. Discover inequivalent fluorine nuclei in the various fluorine liquids that come with the spectrometer; HT-110, FC-43, FC-70, and FC-770.
   Look up their chemical structure and identify the various fluorine sites.
7. "Watch" epoxy cure. Study T_1 and T_2 of various slow curing epoxies and explain the data.
8. Rubber is a peculiar substance. Use various pencil erasers as samples. Study T_1 and T_2 as an eraser cools. You will have to estimate the temperature, since it is difficult to measure the temperature when the eraser is in the sample coil.
9. Can you observe inequivalent protons in Ethel alcohol? What about in an echo sequence?
10. Measure spin diffusion in distilled water.
11. There are well known fluorine greases. Measure T_1 and T_2 in those salt solids.
13. Examine virgin and recycled TEFLON. Can you distinguish them from their NMR data?