PHYS 360/460 Experiment 20
Nuclear Magnetic Resonance

Preparation

- Bring a USB memory stick to the lab to save experimental data
- Useful reference:
  - Fukushima, Eiichi (1981). *Experimental Pulse NMR: A Nuts and Bolts Approach*. Addison-Wesley. UW Davis Centre Call #: QC762.F85 1981

Safety

- Keep magnetically sensitive objects (e.g. watches, magnetic swipe cards) at least 1 m away from the probe to avoid potential damage.

Part A: Introduction

A.1: Basic NMR Theory

The nuclear magnetic resonance (NMR) phenomenon is dependent on a nuclear property called spin. Nuclei with spin possess a magnetic dipole moment, $\vec{\mu}$. Classically, this may be thought of as a small permanent bar magnet that has been set spinning about its long axis. If such a magnet is placed inside a magnetic field, $\vec{B}_0 = B_0\,\hat{z}$, so that the spin axis (which is in the same direction as $\vec{\mu}$), is not aligned with $\vec{B}_0$, the magnet will experience a torque, $\vec{\tau} = \vec{\mu} \times \vec{B}_0$, and precess about the magnetic field (see Figure 1, where a spherical magnet is shown). The frequency of precession is given by the Larmor relation, $f_0 = \frac{\omega_0}{2\pi} = \frac{\gamma B_0}{2\pi}$, where $\gamma \equiv$ gyromagnetic ratio = (magnetic moment/angular momentum). The gyromagnetic ratio is unique to a particular nucleus. For example, for protons (^{1}H nuclei, the nucleus commonly utilized in MRI), γ is such that in a 1 Tesla magnetic field, $f_0 = 42.57\ MHz$.

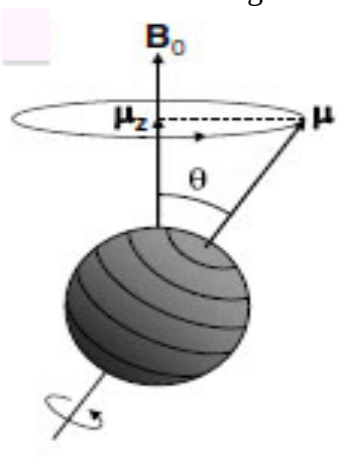

Figure 1: *Precession of magnetic moment $\vec{\mu}$ about the magnetic field $\vec{B}_0$.*

Quantum mechanically, the nuclear spin is quantized; a particular nucleus possesses its one, fixed intrinsic spin. This quantization leads to the precessional motion of $\vec{\mu}$ in the presence of a uniform, external magnetic field, $\vec{B}_0$, occurring only at well-defined, discrete angles between $\vec{\mu}$ and $\vec{B}_0$. For protons, $\vec{\mu}$ can only take on two orientations relative to $\vec{B}_0$ so that $\vec{\mu}_z$, the component of $\vec{\mu}$ along $\vec{B}_0$, is either parallel (spin "up", as in Figure 1) or antiparallel (spin "down") to $\vec{B}_0$. The two orientations of

the proton spin have slightly different energies in the $\vec{B}_0$ field, which results in the number of "up" spins in the lower energy level is slightly greater than that of the "down" spins in the higher energy level. In a sample containing a large number of spins, this produces a macroscopic magnetization $\vec{M}$ along $\vec{B}_0$.

By applying an additional magnetic field, $\vec{B}_1$, to the sample at the Larmor (resonant) frequency, f_0, the populations within the two spin energy levels can be changed. This population shift results in $\vec{M}$ being tipped away from the z-direction and precessing about $\vec{B}_0$ at f_0. It is often convenient to discuss the motion of $\vec{M}$ classically. $\vec{B}_1$ is applied in such a way that it rotates about the z-axis at the resonant frequency so that a constant torque $\vec{\tau} = \vec{M} \times \vec{B}_1$ is felt by the magnetization and it rotates about $\vec{B}_1$, effectively tipping $\vec{M}$ towards the xy-plane. While $\vec{M}$ is precessing about $\vec{B}_1$, it is also is precessing about $\vec{B}_0$, resulting in the spiral motion of $\vec{M}$ (see Figure 2a). Since the frequency of f_0 in nearly all NMR applications is in the radio-frequency range, these short-duration $\vec{B}_1$ fields are referred to as rf pulses.

It is useful in NMR/MRI to discuss the motion of $\vec{M}$ in the "rotating frame". This is a frame of reference, or coordinate system, that is rotating at the Larmor frequency about $\vec{B}_0$ (the z-axis). The three axes in this rotating frame are indicated by x', y' and z'. Since $\vec{B}_0$ is stationary in both the laboratory frame and the rotating frame, the z'-axis in the rotating frame is the same as the z-axis in the laboratory frame. Then, the application of $\vec{B}_1$, which is stationary in the rotating frame, causes the $\vec{M}$ vector to rotate about $\vec{B}_1$, while staying in the z'y'-plane (see Figure 2b).

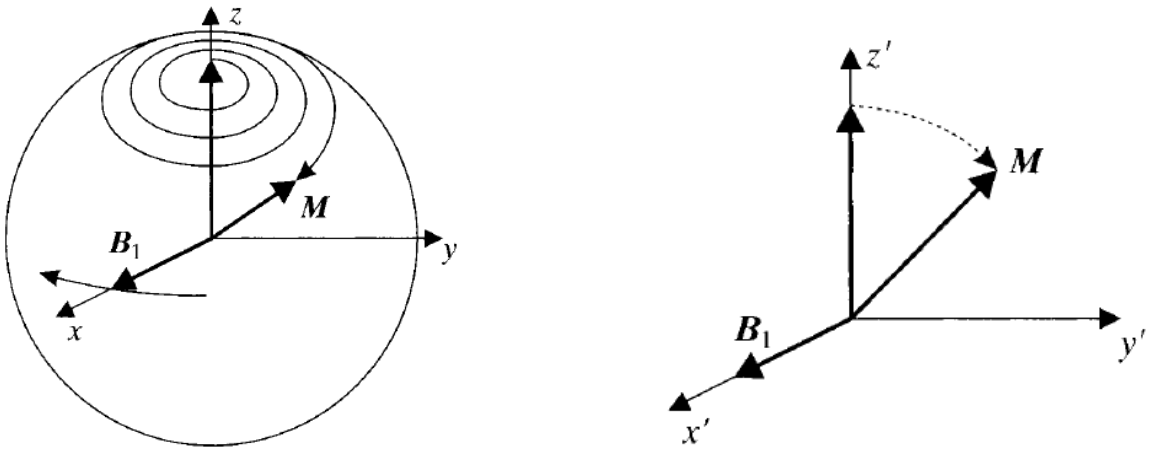

Figure 2: *a) Motion of $\vec{M}$, acted upon by $\vec{B}_1$, while precessing about $\vec{B}_0$, which is directed along z. b) The action of $\vec{B}_1$ on $\vec{M}$ as viewed in the rotating frame. (taken from Medical Imaging: Signals and Systems by J.L. Prince and J.M. Links, Pearson Prentice Hall)*

$\vec{M}$ can be manipulated using various rf pulse schemes. For example, if we apply a rf pulse of amplitude B_1 and duration τ_P such that $\vec{M}$ is rotated into the xy-plane, we call such a pulse a $\frac{\pi}{2}$ pulse; by doubling τ_P, a π pulse is produced, rotating $\vec{M}$ into the negative z-direction.

The characteristic time for the magnetization in the xy-plane, M_{xy}, to decay is called T_2, the

spin-spin relaxation time. As time progresses, the spins will give up the energy they gained through the application of the $\frac{\pi}{2}$ pulse and return to their equilibrium populations of up and down spins. At this point we say that the magnetization has regrown along the z-axis to its equilibrium value B_0. The characteristic time for this regrowth is called T_1, the spin-lattice relaxation time and will be elaborated upon below.

As $\vec{M}$ (and the associated magnetic field resulting from the vector sum of fields produced by all the up spins and all the down spins) precesses about $\vec{B}_0$, any component in the xy-plane induces an emf in a receiving coil around the sample (typically the sample coil that generates the B_1 field). According to Faraday's Law, $emf = -N \frac{d\phi_{B-due\ to\ \vec{M}}}{dt}$. The recorded signal of this precessing magnetisation is called the free induction decay (FID).

In a typical sample, the individual magnetic moments that contribute to $\vec{M}$ find themselves in slightly different magnetic environments due to local, internal magnetic fields produced by the neighboring spins, as well as by inhomogeneities in the B_0 field. Thus, after the magnetization has been turned into the xy-plane, spins start to dephase, decreasing the net M vector in the xy-plane, which results in a decrease/decay in the induced signal. A typical FID and the dephasing process is shown in Fig. 3.

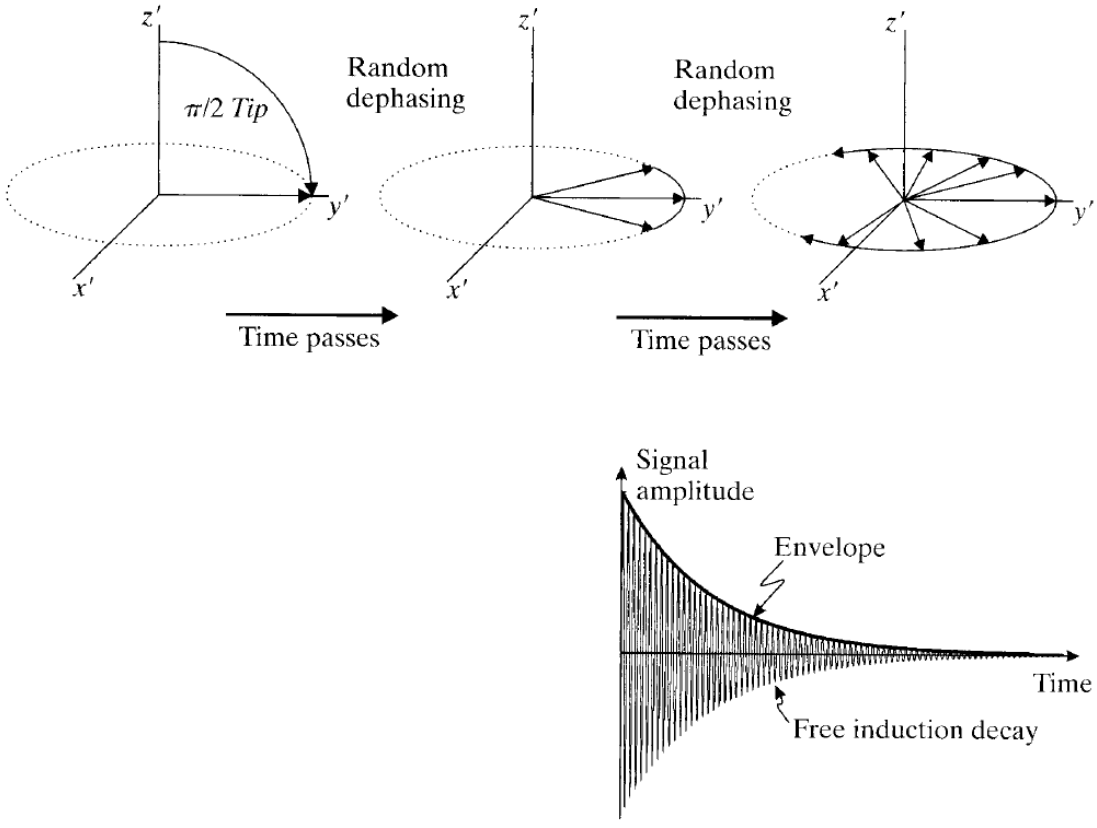

Figure 3: *The emf induced in the coil following the application of a rf pulse. This is the free induction decay (induced emf decays as a function of time), or FID. Note that the envelope of the decay is exponential and will have a time constant T_2. (Image taken from Medical Imaging: Signals and Systems by J.L. Prince and J.M. Links, Pearson Prentice Hall)*

A.2: Apparatus

The main equipment used is a self-contained, pulse NMR spectrometer consisting of the following subunits:

- Pulse programmer
- Frequency source
- Radio frequency pulse modulator
- Transmitter
- NMR probe
- NMR receiver and detector
- Permanent magnet (no cooling required)
- Power supply

The parameters relevant for NMR experiments are varied by the operator from the front panel of the spectrometer, shown in Figure 1.

Figure 4: *NMR spectrometer. Numbers shown are referred to in the text as, for example, #1.*

Pulse Programmer

The built-in pulse programmer allows for five independent experiments:

- Free Induction Decay (FID), or T2*
- Inversion Tecovery (IR)
- Spin-Echo (SE)
- Carr-Purcell (CP)
- Gated Carr-Purcell (CPS)

The type of experiment performed is selected by knob #1 (Note: all #'s refer to the labels found in Figure 4). The pulse sequence is either automatically repeated, with a repetition time selected by knob #2, or is triggered manually using the single experiment push button #3. The experimental operation mode, automatic or manual, is selected by means of switch #4.

The length of the r.f. pulses applied is determined by potentiometers #5, for the 90° pulse, and #6, for the 180° pulse. Variation of the spacing between pulses, where applicable, is determined by potentiometer #7, whose numeric value is shown on its face in milliseconds, and by multiplier knob #8.

Resonance

The magnetic field value, B_0, as determined by the permanent magnet of the spectrometer, determines the Larmor frequency of the precessing spins. The spectrometer is operating at a fixed frequency of 9 MHz but does allow slight frequency adjustment (± 60 kHz) to match the applied pulse frequency to the Larmor frequency determined by the magnet. Frequency adjustment is accomplished with potentiometer #9.

NMR Probe Head

The sample is inserted into the probe holder (#10) positioned at the top of the spectrometer, and is as close as possible to the exact centre of the pole faces of the permanent magnet.

DO NOT DROP SAMPLES INTO THE SAMPLE HOLDER. If a sample will not fit into the holder, call the demonstrator. DO NOT FORCE ANYTHING INTO THE R.F. SAMPLE HOLDER AS THE R.F. COIL MAY BE DAMAGED.

NMR Receiver

The NMR signal is generated by the spins inside the sample, inside the probe head, and is amplified and detected in the receiver section of the spectrometer. The controls for the receiver parameters are found in the portion of spectrometer front panel labeled DETECTION. The variable receiver gain allows for adapting to a very broad range of samples, ie. samples of varying nucleic abundance. The gain can be varied by adjusting control knob #11. Diode or phase sensitive detection can be selected using switch #12.

The Reference Phase

In phase-sensitive detection, the FID is seen at points of constant phase. The reference phase of the NMR signal is adjusted using potentiometer #13. Changing the setting of the reference knob will change the signal being output from the spectrometer. The signal is filtered to improve the signal-to-noise ratio. The bandwidth of the output amplifier can be varied in steps, using potentiometer #14, from ~ 200 kHz to ~ 3 kHz.

Gradient

A gradient can be applied across the sample by adjusting potentiometer #15. This is used for imaging experiments. For spectroscopy and relaxometry experiments, the gradient knob should be turned to 0.

Part B: NMR Measurements

B.1: Finding Resonance

Sample: Water

Spectrometer settings :

- Place the water sample in the magnet.
- Selection knob #1 set to FID.
- Select the appropriate repetition time (about 5·T1) to maximize the signal.
- Adjust the receiver phase to maximize the signal.
- Adjust the receiver gain so that a signal of approximately 1 V appears on the oscilloscope.
- Adjust the pulse to maximize the signal, by using potentiometer #5. This is a 90° pulse.

Explain what is happening as you make the above adjustments. Why is it called a 90° pulse?

With the settings as above you should see a FID on the screen. Adjust the NMR frequency, potentiometer #9, until the NMR signal is reasonably exponential – at this point the Larmor frequency, f_0, is identical to the r.f. frequency of the spectrometer. Once this condition is met, the spin system is on resonance.

Obviously if you set the pulse width to twice its length for the 90° pulse you obtain a 180° pulse. Adjust potentiometer #5 until you obtain a 180° pulse. The 180° pulse flips the macroscopic magnetization vector to be pointing along the negative z-axis. Since there is no magnetic vector in the xy-plane, there should be no signal. You may see a small signal due to the inhomogeneity of the magnetic field.

What happens to the signal as you keep increasing the pulse width? With a pulse length of 3 x 90° = 270° the magnetic field vector would have been flipped 270° and the signal would appear as the negative of the 90° pulse signal. Explain this.

Save representative data acquired for each sample and discuss (the details of saving data to a PC for later analysis will be covered by the demonstrator at the start of the lab).

B.2: The FID and T_2

Samples: Water, alcohol, rubber

Spectrometer settings:

- Selection knob #1 set to FID.
- Select the appropriate repetition time to maximize the signal.
- Adjust the receiver gain to an appropriate value.
- Adjust the receiver phase to maximize the signal.
- Adjust the pulse to maximize the signal, by using potentiometer #5. This is a 90° pulse.

Adjust the NMR signal appropriately to obtain an exponential FID. The equation that gives the magnetization as a function of time and T_2* is:

$$M_y(t) = M_0 e^{-t/T_2^*}$$

Save the data set and plot on a semi-log graph. Find T_2* from the slope of the line as indicated by the above equation. How well does the line match the values of the points plotted? Comment on any

significant deviation from exponential behaviour. Do this for each sample and discuss.

It is useful to be able to estimate T_2* directly from the FID on the screen. From the above equation we see that for t = T_2*, the ratio $M_y(t = T_2^*)/M_0 = 1/e \approx 0.37$. Thus, for an exponential decay, the time t where $M_y(t) \approx M_0/3$ is approximately equal to T_2*. Estimate T_2* this way for each sample.

B.3: Measurement of T_1

Samples: Water, alcohol, rubber

Spectrometer settings:

- Selection knob #1 set to IR.
- Select the appropriate repetition time to maximize the signal.
- Adjust the receiver gain to an appropriate value.
- Adjust the receiver phase to maximize the signal.
- Use the setting for the 90° pulse obtained previously. In this experiment two 90° pulses are used which are controlled by the potentiometers # 5 and #6. Potentiometer #6 is the first pulse and potentiometer #5 is the second pulse.

Obtain a 90° pulse for the water sample. Note that at t = $5 \cdot T_2$* there is virtually no signal. Set τ, the time interval between the two pulses, by adjusting potentiometer #7, equal to $5 \cdot T_2$*. You should see no signal. The second pulse flips whatever magnetization vector has regrown along the +Z axis towards thermal equilibrium with time constant T_1, according to :

$$M_z(\tau) = M_0(1 - e^{-\tau/T_1})$$

At $\tau << T_1$, the amount of regrowth is negligible and essentially zero signal is observed. The maximum amplitude of the FID signal varies directly with the amount of regrowth in time τ.

It may be helpful to consider the 2nd 90° pulse as a "Read Statement", the output of which is the magnitude of the magnetization vector initially along the +Z axis.

Now scan through τ by adjusting the potentiometer labeled #7, and find τ for which $M_z(\tau) = M_0/2$. Use the above equation to solve for T_1. Repeat for each sample and compare the T_1 values obtained. The important concept is that, while the signal has decayed in the xy-plane rather quickly, the regrowth along the z-axis is much slower.

The reason for needing a long repetition rate in some cases to maximize the signal should now be obvious. If the signal repeats faster than $5 \cdot T_1$, the system does not re-establish thermal equilibrium between pulses. If you were looking for the FID after a 90° pulse, the signal would not be maximal. This suggests a quick method of estimating T1 for a sample. Set up a single 90° pulse (knob #1 to FID). As the repetition time is decreased (ie. the time between subsequent pulses is shortened) the amplitude of the FID will be found to drop significantly at a particular setting. The last setting before this drop occurs can be used as a rough estimate of $5 \cdot T_1$. Use this technique to estimate T_1. How does it compare with the previous value? Estimate T_1 using this method for the other samples.

Save representative data for each sample for inclusion with your report.

B.4: Measurement of T_1 with Inversion-Recovery Sequence

Samples: Water, alcohol, rubber

Spectrometer settings:

- Selection knob #1 set to IR.
- Select the appropriate repetition time to maximize the signal.
- Adjust the receiver gain to an appropriate value.
- Adjust the receiver phase to maximize the signal.
- Use the setting for the 90° pulse obtained previously. In this experiment a 180° pulse and a 90° are used. Potentiometer #6 controls the first pulse (180° pulse) and potentiometer #5 is the second pulse (90° pulse).

Here the 180 - τ - 90 sequence is involved. The regrowth of the magnetic vector along the z-axis is given by:

$$M_z(\tau) = M_0(1 - 2e^{-\tau/T_1})$$

For the doped water sample, set up this sequence and record the FID following the 90° pulse for different values of τ, being careful to maintain good resonance throughout the experiment. Make sure the repetition time is at least $5 \cdot T_1$.

If the resonance was constant throughout the experiment, then each FID should have roughly the same T_2* measured in section B2. From each FID, extract the initial magnetization. These values plotted on a linear scale as a function of τ should yield the graph shown in Figure 5.

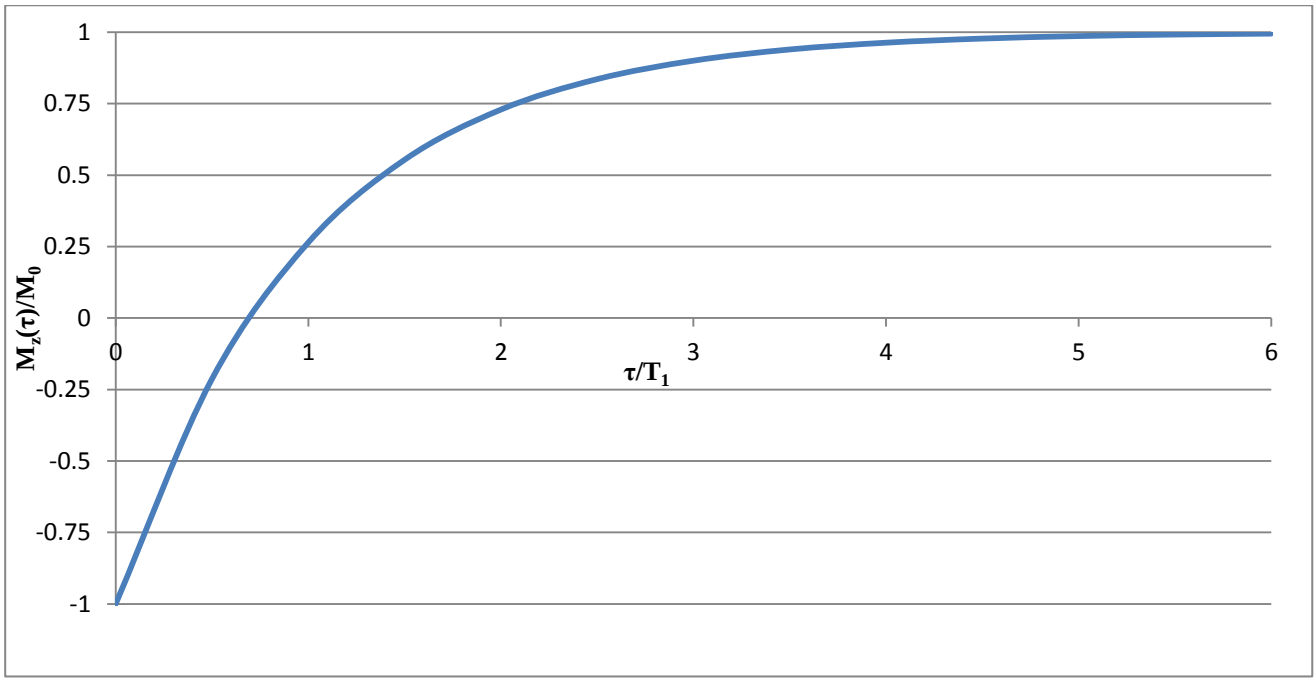

Figure 5: *Plot of magnetization in the inversion-recovery experiment.*

Arrange the parameters in the above equation so that the linear slope of a semi-log plot of your results can be used to determine T_1.

Also determine T_1 using the zero-crossing method (use value of τ for which M_z=0 in the above

equation to find T_1, using the above figure). How does it compare with the results obtained from the inversion-recovery experiment?

Using the inversion-recovery experiment determine T_1 for the 3 different samples.

Why is this sequence called the "inversion-recovery sequence"?

B.5: Hahn Echo

Samples: Water, alcohol, rubber

Spectrometer settings:

- Selection knob #1 set to SE.
- Select the appropriate repetition time to maximize the signal.
- Adjust the receiver gain to an appropriate value.
- Adjust the receiver phase to maximize the signal.
- Use the setting for the 90° pulse obtained previously. In this experiment a 90° pulse and a 180° pulse are used which are controlled by the potentiometers #5 and #6 respectively. Potentiometer #5 is the first pulse (90° pulse) and potentiometer #6 is the second pulse (180° pulse).
- Before beginning the experiment, make sure the τ value is reset to 0 by adjusting the potentiometer labeled #7.

Set up a 90° pulse for the water sample (using the selection knob #1 set to FID). By now you may have noticed that every time you change samples you have to re-adjust your pulse length and reference phase.

Once you are set-up and have selected the selection knob #1 to SE, you should see the echo, which should look something like **Figure 6**:

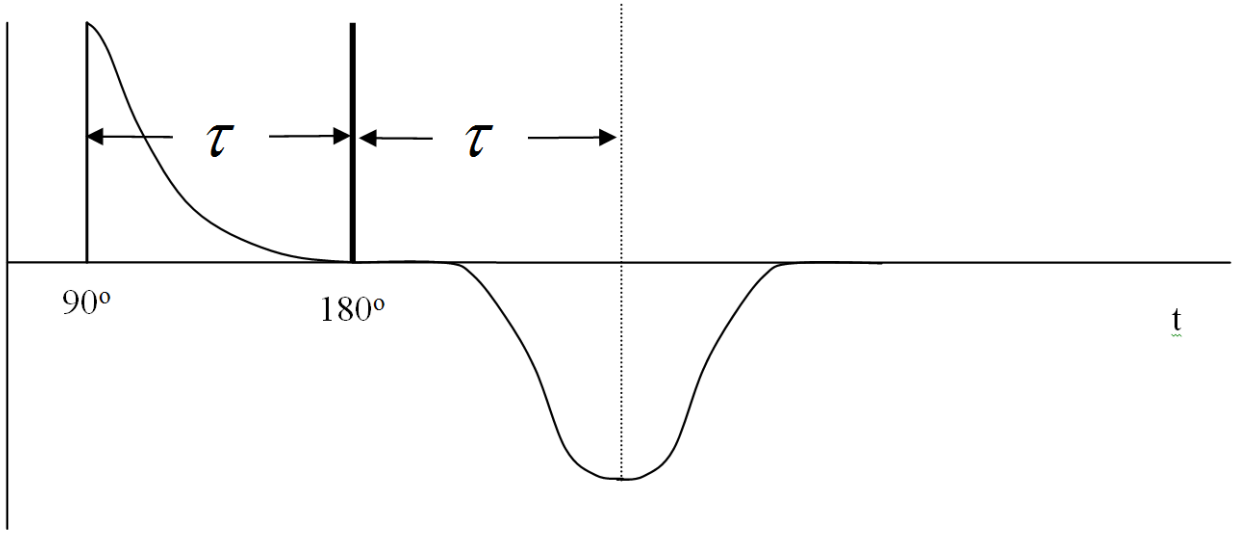

Figure 6: *Signal amplitude during Hahn Echo experiment.*

Since the magnetization is being flipped to reform on the –Y axis, it will appear negative (i.e. 180° out of phase with a 90° FID). The echo will appear at $2 \cdot \tau$ after the 90° pulse, where τ is the time between the 90° and 180° pulse. Record the echo for various τ and extract the maximum amplitude of each echo from your data. The echo peaks decay according to the equation :

$$M(t) = M_0 e^{-t/T_2}$$

Where $t = 2 \cdot \tau$. Find T_2 using the above equation for the 3 samples.

B.6: Freezing

Sample: Water

Spectrometer settings:

- Selection knob #1 set to FID.
- Select the appropriate repetition time to maximize the signal.
- Adjust the receiver gain to an appropriate value.
- Adjust the receiver phase to maximize the signal.
- Adjust the pulse to maximize the signal, by using potentiometer #5. This is a 90° pulse.

Adjust the NMR signal appropriately to obtain an exponential FID. Now get the lab demonstrator to freeze the water sample in liquid nitrogen and return the sample tube to the spectrometer. What has happened to the signal? Explain.

Part C: Report

Your write-up should include a discussion of the theory as it relates to this experiment, equipment, comments on what you have seen, done, had trouble with, and an error analysis. Include all graphs.

When several methods for finding a particular quantity (i.e. T_1) have been mentioned in the experiment, you will be expected to compare them. Can you make any suggestions about the systems under investigation (water, alcohol, rubber) from a comparison of T_1 or T_2 values in the given samples? (i.e. Discuss how the relaxation times relate to the state or phase of a sample, to the relative rates of molecular motions in a sample and to the homogeneous or inhomogeneous nature of a sample. In this discussion you may find it useful to compare T_1 and T_2 between different samples as well as T_2 to T_1 of a particular sample.) If you have trouble getting readings for a given sample using a particular technique, you will then comment on your difficulties and the error involved.