

## PHY451

### Pulsed Nuclear Magnetic Resonance

#### Procedure

You will be applying an rf magnetic field of frequency 10.180 MHz to the protons in water. You should calculate what magnetic field is required for this resonance. Use a Hall probe to find the current from the magnet power supply that produces this field at the sample location in the electromagnet. Knowing this current will make it much easier for you to attain the resonance condition that occurs over a very narrow field range.

1. For pulsed modulation of the rf signal, you need to set the output of the rf oscillator to +11 dB, initially. For  $\pi/2$  and  $\pi$  pulses, the pulse length should be 30  $\mu\text{s}$  and 60  $\mu\text{s}$ , respectively. Once you've been successful in obtaining a signal ("echo") from a  $\pi/2$ -  $\pi$  pulse sequence, vary the output of the rf oscillator by a dB or so in order to maximize the echo.
2. In pure water, the proton relaxation time is very long and very difficult to observe – many seconds. You will shorten this time by adding magnetic ions to the water. Start by preparing a sufficient quantity of 0.1-molar solution of  $\text{Cu}^{++}\text{SO}_4$ . After you've measured  $T_1$  and  $T_2$  at this concentration, you will then dilute this solution with water and see what happens to  $T_1$  and  $T_2$ . For a fixed molarity, changing the magnetic moment of the ionic impurity in the water will alter  $T_1$  and  $T_2$ . To see this effect, prepare a 0.05-molar solution of  $\text{Fe}^{+++}\text{Cl}_3$  that you can dilute further as needed. Make enough dilution to spread out your  $T_1$  and  $T_2$  times in order to investigate the relationship between relaxation times and the ion concentration.
3. There is a program on your computer desktop named "Nuclear Magnetic Resonance". That program will enable you to quickly and easily measure samples. Make certain, however, that you measure  $T_1$  and  $T_2$  by hand for one sample first. The program is a black box and is fallible. It is imperative to know what the software is doing, and what exactly its output means. The data is useless unless you understand the method by which it is taken. Please judiciously choose the time spacing between data points according to the expected relaxation timescale.
4. To measure  $T_2$ , your background reading will tell you to vary the time between the  $\pi/2$  and  $\pi$  pulses and measure the echo amplitude. When you plot echo amplitude vs. time, what time interval should you use? It is a good idea to measure the echo amplitude several times for a given  $\pi/2$ -  $\pi$  pulse time interval in order to have more accurate amplitude data and an estimate of the uncertainty of these data. To measure  $T_1$  effectively, you need to use a different pulse sequence:  $\pi$ -  $\pi/2$ -  $\pi$  where the time interval between the  $\pi$ -  $\pi/2$  pulses is varied and the time between the  $\pi/2$ -  $\pi$  pulses is held fixed. Compare the sign of the echo signal on the scope with that of the  $T_2$  measurement. Check to see if the echo will change sign as you further increase the delay between  $\pi$  and  $\pi/2$  pulses. It is important to set the fixed  $\pi/2$ -  $\pi$  pulse time interval correctly – smaller than the  $T_2$  time you've already measured. If you make this fixed time too long, you will be throwing away echo signal.

5. Measure the  $T_1$  and  $T_2$  times of anhydrous glycerin as a function of temperature and water content. Here you will be seeing the effects of a change in viscosity. Raising temperature is simple, but then your echoes will be time dependent as your sample cools. Varying the water content has the advantage that there will be no time dependence.
6. Many more experiments can be done. It is up to you to determine good ideas for further experimentation. Do not be afraid to bounce ideas off your instructors.

## Theory

### 1. The physics behind $T_1$ & $T_2$ .

On the previous page it was stated that  $T_1$  &  $T_2$  are shortened by adding magnetic ions to the water and also by varying the viscosity. What is the origin of these effects? In water, the magnetic impurities produce magnetic fields that fluctuate due to the random relative motion of the protons and ions. The Fourier component of the magnetic field fluctuations at  $\omega_0$  ( $= 2\pi \times 10.26$  MHz) cause these enhanced relaxations. One knows that applying a  $\pi/2$  rf pulse at  $\omega_0$  will tip the magnetization away from direction of the DC magnetic field by a large angle ( $90^\circ$ ). So it not surprising that a magnetic field fluctuating at  $\omega_0$  would have a significant impact on  $T_1$  &  $T_2$ . Also this Fourier component of the fluctuating magnetic field at  $\omega_0$  will be affected by the correlation time  $\tau_c$  for the relative motion (including tumbling) of a given proton with respect to other protons or magnetic ions. Time  $\tau_c$  is proportional to the viscosity of a liquid, so varying viscosity will affect  $T_1$  &  $T_2$ . Below are the equations for  $T_1$  &  $T_2$  in terms of  $\omega_0$  and  $\tau_c$ —based on Bloembergen-Purcell-Pound theory:

$$\frac{1}{T_1} = 2K \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \right] \quad (1)$$

$$\frac{1}{T_2} = K \left[ \tau_c + \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \right] \quad (2)$$

where  $K$  is proportional to the mean-square fluctuating magnetic field due to nearby other nuclei and/or magnetic ions. Thus, as  $K$  increases,  $T_1$  &  $T_2$  decrease, as expected when the concentration of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  are increased. For water at room temperature, one has  $\omega_0 \tau_c \ll 1$ . Take this limit in Eqs. (1) & (2) and obtain the relationship between  $T_1$  and  $T_2$  that you can test experimentally.

As stated above, changing the viscosity will alter  $\tau_c$ . For glycerin, raising its temperature (or diluting it with water) will lower its viscosity, causing  $\tau_c$  to decrease. So what do you expect  $T_1$  &  $T_2$  to do in this case (that you can test by experiment), assuming that  $\omega_0 \tau_c \ll 1$ ? In the case of watching epoxy cure over time, its viscosity will increase, causing  $\tau_c$  to get larger. What do Eqs. (1) & (2) predict about the behavior of  $T_1$  &  $T_2$  when  $\omega_0 \tau_c$  goes from  $\approx 1$  to  $\gg 1$  during curing?

## 2. How does $T_1$ affect your $T_2$ measurement with the $\pi/2$ - $\pi$ pulses?

Your background-reading materials implicitly assume that  $T_1 \gg T_2$ , which is not the case in your experiments. It turns out that having  $T_1$  closer to  $T_2$  does not affect the  $T_2$  value that you obtain in your experiments. Why? To answer this question, let us use the limit  $T_1 \ll T_2$ . If the  $T_2$  value is unaffected by having a short  $T_1$ , then  $T_2$  will also be unaffected as  $T_1 \Rightarrow T_2$ .

Fig. 1 shows the lab frame-of-reference view with  $B_{DC}$  along  $z$  and  $B_{rf}$  along  $x$ . Magnetization is in equilibrium along  $z$ , just before  $B_{rf}$  is turned

Fig. 2 shows a rotating-frame view (about  $z$  at just after the end of the  $\pi/2$  pulse where  $M$  has rotated in the  $z$ - $y$  plane by  $90^\circ$ . The  $z$  component  $M$  ( $M_z$ ) is zero here.

In Fig.3 one sees the relaxation of  $M$  during the time between the  $\pi/2$  and  $\pi$  pulses ( $\Delta t_{\pi/2-\pi}$ ). In addition to the spreading out of the nuclear moments the  $x$ - $y$  plane (that you should understand), the  $T_1$  effect also causes  $M_z$  to be non-zero (along positive  $z$ ) as  $M$  relaxes back toward equilibrium.

In Fig. 4 the effect of the  $\pi$  pulse is seen. Compare dotted arrows in the  $y$ - $z$  plane of Figs. 3 & 4 to observe the effect of the  $\pi$  pulse where each moment reversed by  $180^\circ$  about the  $x$  axis. Now  $M_z$  is negative, and it will begin relaxing toward zero.

Fig. 5 shows that echo will occur at time  $2 \times \Delta t_{\pi/2-\pi}$  after the initial  $\pi/2$  pulse. Note that  $M_z = 0$  here, just as you had right after the  $\pi/2$  pulse in Fig. 2. **Thus  $T_1$  has no effect on your  $T_2$  measurement!**

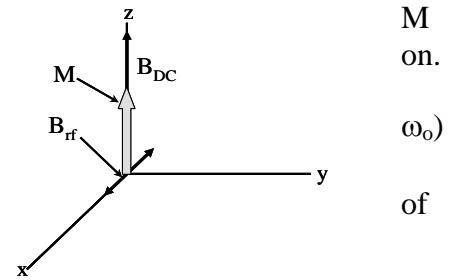


Fig. 1. Lab frame view

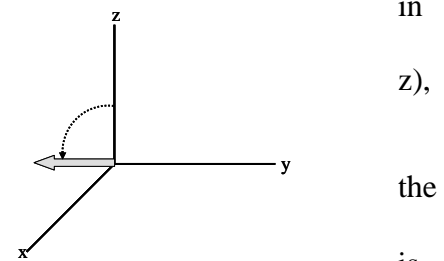


Fig. 2. Rotating frame view just after  $\pi/2$  pulse.

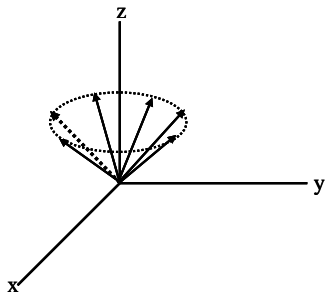


Fig. 3. Rotating-frame view just before  $\pi$  pulse.

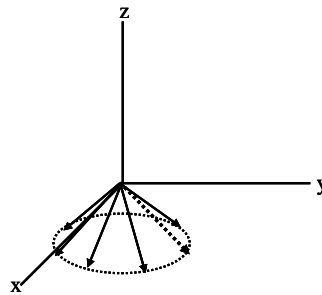


Fig. 4. Rotating-frame view just after  $\pi$  pulse.

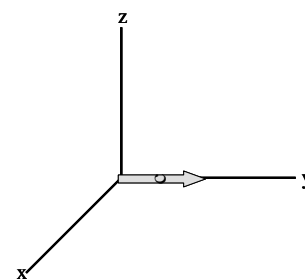
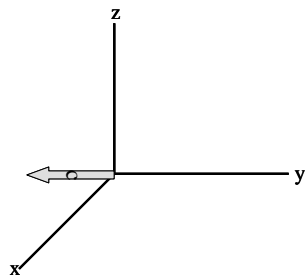


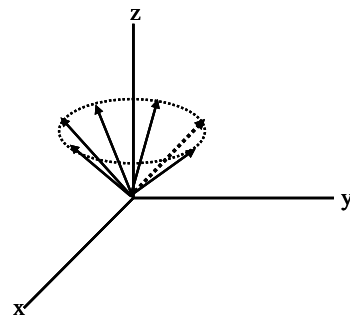
Fig. 5. Rotating-frame view at time  $2 \times \Delta t_{\pi/2-\pi}$  when the echo occurs.

For more efficient measurements of  $T_2$ , you will probably try a series of subsequent  $\pi$  pulses. Suppose you apply another  $\pi$  pulse at time  $\Delta t_{\pi/2-\pi}$  after the first echo; then you will see an opposite-sign echo after  $2 \times \Delta t_{\pi/2-\pi}$ , at which time  $M_z$  is zero again. This process is shown below, still for the case  $T_1 \ll T_2$ . So you can apply a series of  $\pi$  pulses to obtain a train of echoes where  $T_2$  is not affected by  $T_1$ .

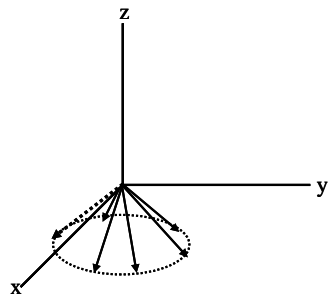
Effect of applying another  $\pi$  pulse at time  $\Delta t_{\pi/2-\pi}$  after the first echo. Follow the A-to-D sequence. Watch the dotted arrow.



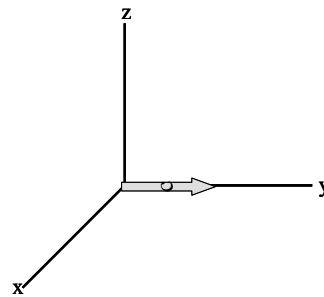
A. Repeat of Fig. 5 when first echo occurred.



B. Just before additional  $\pi$  pulse after time  $\Delta t_{\pi/2-\pi}$ .



C. Just after additional  $\pi$  pulse.



D. 2<sup>nd</sup> echo. Note reversed sign from first echo.

