

# PULSED/CW NUCLEAR MAGNETIC RESONANCE



## *“The Second Generation of TeachSpin’s Classic”*

- Explore NMR for both Hydrogen (at 21 MHz) and Fluorine Nuclei
- Magnetic Field Stabilized to 1 part in 2 million
- Homogenize Magnetic Field with Electronic Shim Coils
- Quadrature Phase-Sensitive Detection with 1° Phase Resolution
- Direct Measurement of Spin-Spin and Spin-Lattice Relaxation Times
- Carr-Purcell and Meiboom-Gill Pulse Sequences
- Observe Chemical Shifts in both Hydrogen and Fluorine Liquids
- Compare Pulsed and Continuous Wave NMR Detection
- Study Pulsed and CW NMR in Solids
- Built-in Lock-In Detection and Magnetic Field Sweeps

Instruments Designed For Teaching

TEACH  
SPIN 

# PULSED/CW NUCLEAR MAGNETIC RESONANCE

## INTRODUCTION

Nuclear Magnetic Resonance has been an important research tool for physics, chemistry, biology, and medicine since its discovery simultaneously by E. Purcell and F. Bloch in 1946. In the 1970's, pulsed NMR became the dominant paradigm for reasons your students will discover using the apparatus described in this brochure, TeachSpin's second generation of our classic PS1-A&B. This new unit was designed in response to requests for additional functions from some of the 200 users of our original unit. It has many new features and capabilities, yet it remains designed specifically for teaching. Its modular design and rugged construction, combined with sophisticated rock-stable electronics, allows students to take research-grade, publishable data on an instrument that they configure. Its outstanding reliability (backed by a two year warranty) and straightforward operation means that no "resident expert" is required to teach or maintain this apparatus.

Pulsed NMR experiments provide a rich "intellectual phase-space", bringing together important aspects of classical mechanics (torque, angular momentum, precession), quantum mechanics (time-dependent perturbation, stimulated emission, superposition of states), statistical mechanics (density matrix and relaxation), electricity and magnetism (Faraday's law, Fourier transforms, and rf magnetic fields), and chemical physics (spin-exchange, paramagnetic impurities, and dipolar coupling). Students connect these concepts, studied in separate courses, as they analyze these experiments and their data.

## THE INSTRUMENT

PS2-A is a completely redesigned spectrometer with state-of-the-art digital and analog electronics. It consists of four major "components": the permanent magnet, the rf sample probe inside it, the PS2 controller, and the mainframe. The 0.50 Tesla high-homogeneity permanent magnet is temperature stabilized so that its field is stable to 1 part in 2 million over 20 minutes. This makes it possible to do phase-sensitive detection and signal averaging in pulse experiments. The rf sample probe (residing in the magnet gap) is a single-coil, capacitively-tuned, 50-ohm, impedance-matched system with an attached set of four magnetic field-gradient coils ( $\frac{\partial B_z}{\partial x}, \frac{\partial B_z}{\partial y}, \frac{\partial B_z}{\partial z}, \frac{\partial^2 B_z}{\partial z^2}$ ). The PS2 controller provides both the servomechanism for temperature regulation and four current-regulated supplies for the field gradient coils.

The mainframe contains four independent modules, which are the heart of the spectrometer (Figure 1). The modular design enhances educational transparency. The low-noise, broadband, fast-recovery **21 MHz Receiver** includes a  $\lambda/4$  coaxial cable, protective fast-recovery diodes, a 20 dB directional coupler, as well as both envelope and quadrature phase-sensitive detectors. The receiver can be tuned for either hydrogen or fluorine NMR signals.

The **21 MHz Digital Synthesizer** produces rf power in both pulsed and cw formats. There is sufficient rf power to produce a  $\pi/2$  pulse in about 2.5 microseconds. It also produces the reference signals (in  $1^\circ$  phase steps) for the quadrature detectors. The **Pulse Programmer** digitally creates the pulsed sequences of various pulse lengths, number of pulses, time between pulses, and repetition times. The **Lock-In/Field Sweep** provides a wide range of magnetic field sweeps, as well as a lock-in detection system for examining weak cw NMR signals from solids.

The modules are configured by the students using the BNC cables supplied. Mistakes can be made in these interconnections yielding erroneous data, but without damaging the electronics. The high-power outputs connect through special reverse-gender BNC cables, which prevent their accidental connection to delicate electronic components. Setting the frequency to the Larmor precession frequency of the spins is done using the quadrature detectors. The rf sample probe must be tuned by the students for pulse measurements and retuned for the precise impedance-match needed for cw detection. This provides the students a good learning opportunity to understand AC circuits, especially the creation of a 50 ohm resistive impedance from essentially pure reactive components.

## EXPERIMENTS

### I. SINGLE PULSE

A good way for students to begin their exploration of NMR is to start with "single pulse" experiments. These experiments require the student to find the NMR signal, tune the rf probe and the frequency of the spectrometer, set the single pulse parameters (pulse length and repetition time), and identify  $\pi/2$ ,  $\pi$ ,  $3\pi/2$ ,  $2\pi$  pulses.

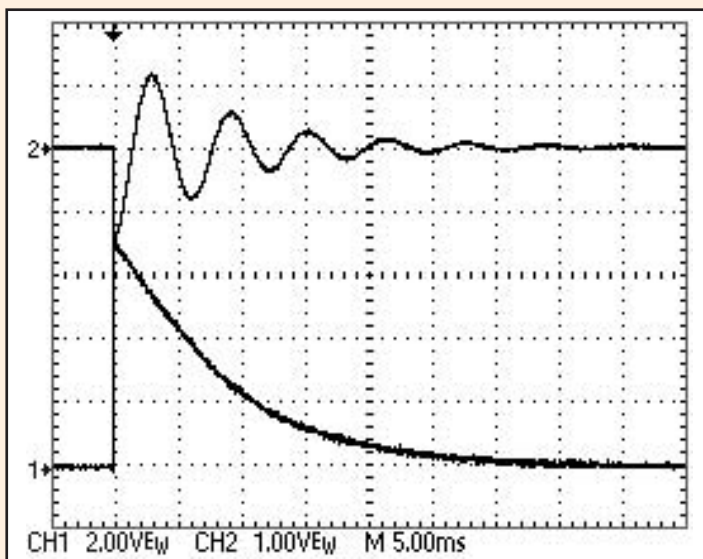


Fig. 2 Free Induction Decay (FID) of protons in mineral oil. Lower trace from envelope detector, Upper trace, Q-phase detector – slightly off resonance by 520 Hz

Figure 2 shows the free-induction decay (FID) signal following a single 90° pulse to the protons in a light mineral oil sample. The frequency synthesizer is used to tune the frequency of the rf pulse to match the Larmor Precession frequency of the protons. It can also be used to examine the magnetic field's temporal stability with the temperature servo loop activated.

Students can now easily familiarize themselves with the operation of the magnetic field gradient coils. Figure 3 shows the dramatic increase in the decay time of the FID of distilled water with proper adjustment of all four gradient coils. Since the decay time ( $T_2^*$ ) is due to the inhomogeneity in the magnetic field over the sample, the longer the  $T_2^*$ , the better the field homogeneity. The upper trace is the FID with no currents in the gradient coils and the lower is with the field homogeneity optimized.

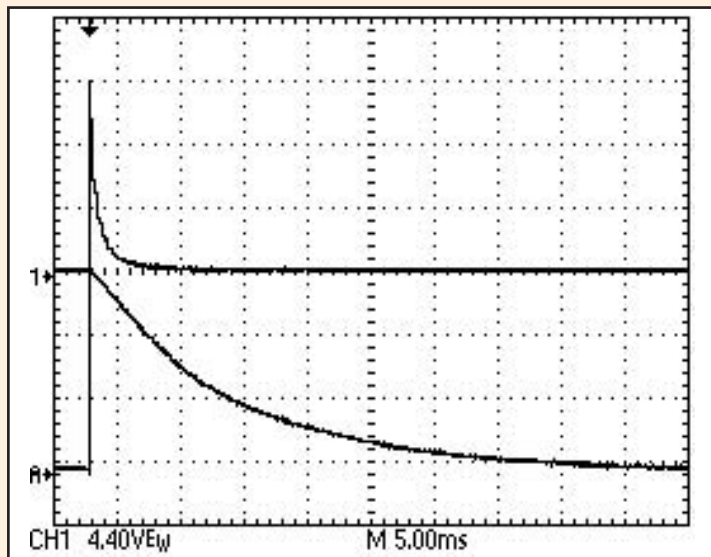


Fig. 3 FID of distilled water. Upper trace magnet without gradient field, lower trace gradients optimized

Next, the student might search for FID signals from one of the fluorine liquids provided. This requires reducing the synthesizer frequency approximately 6%, switching bands on the receiver, and retuning the rf sample probe. The FID signals from Fluorinert FC-70 are shown in Figure 4.

The FID signal can also be recorded in frequency space by taking the FFT (Fast Fourier Transform) of the phase detector signal. Figure 5 shows this data with a vertical logarithmic scale of 10 dB/division.

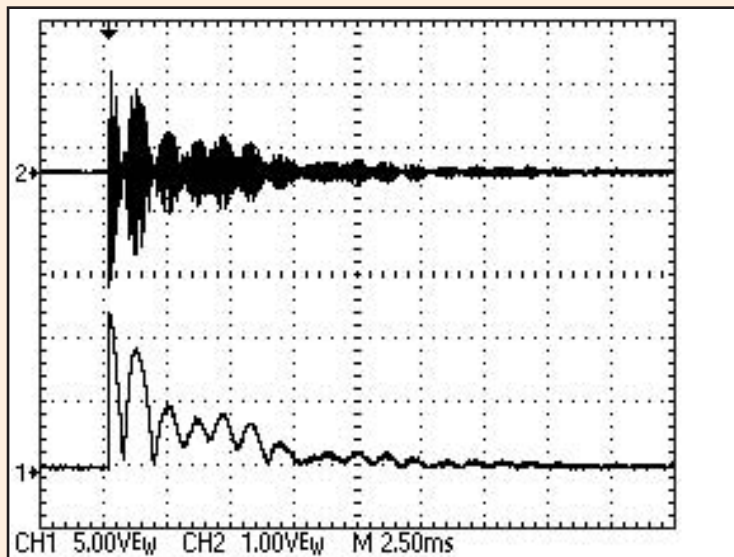


Fig. 4 FID of Fluorinert FC-70. Upper trace phase detector, Lower trace envelope detector

Note the multiple peaks indicating at least two (possibly five) inequivalent fluorine sites. The addition of the field gradient coils makes it possible to observe signals from inequivalent nuclear spins in **both** fluorine and hydrogen liquids. We have measured these chemical shifts in ethyl alcohol and toluene (see Fig. 12).

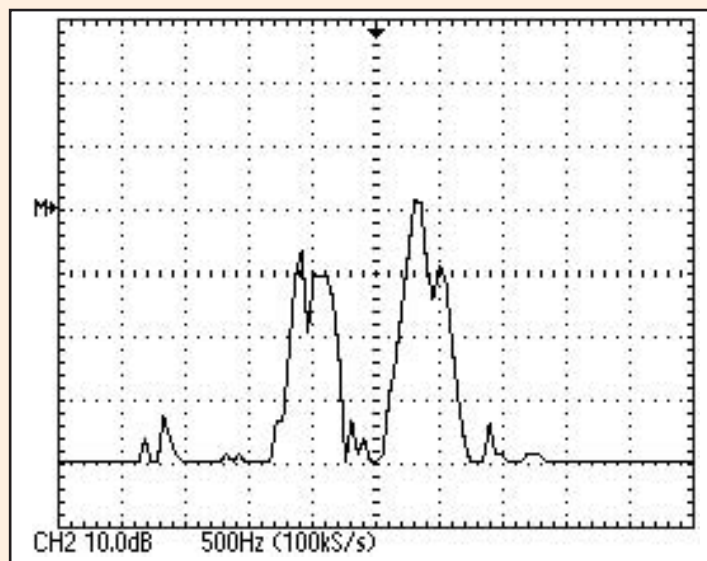


Fig. 5 FFT of the FID of Fluorinert FC-70. Vertical scale 10 dB/div, Horizontal scale 500 Hz/div



Fig. 1 The "Mainframe" with its four modules

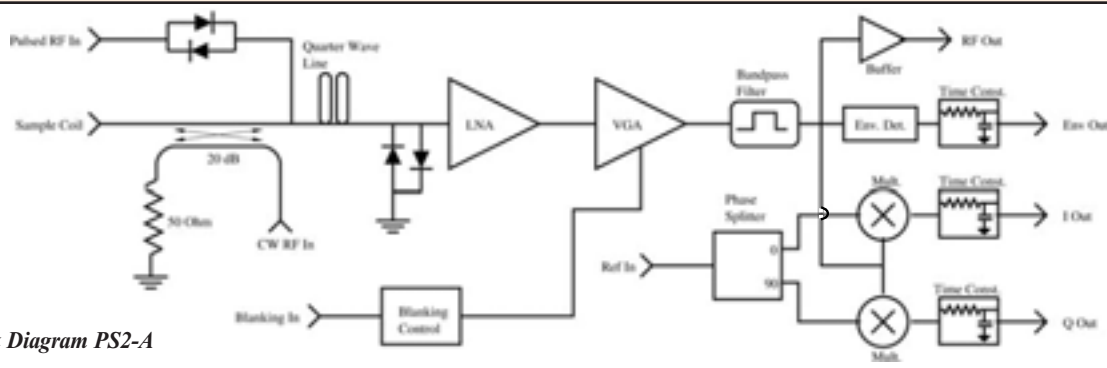


Fig. 6 – Block Diagram PS2-A

## II. CONTINUOUS WAVE (CW)

Although CW techniques inaugurated the field of magnetic resonance and remained the method of choice as a research tool for about 25 years, pulsed NMR now completely dominates nuclear magnetic spectroscopy. However, TeachSpin believes it is important for students to carry out a few CW experiments so they can compare these two methods and understand the advantages that pulsed techniques provide.

The spectrometer must be reconfigured for CW experiments. In this new configuration the 20 dB directional coupler plays a crucial role, since the continuous rf power is directed to the sample coil via this coupler (see Fig. 6). Critical to the success of these experiments is the matching of the rf sample coil to the 50 ohm line. This is done using the two quadrature phase-sensitive detectors as a reflection bridge. When the probe is “perfectly” matched, there is no reflected power to the low-noise amplifier (LNA).

The lock-in module provides magnetic field sweeps whose magnitude and sweep time can be chosen by the experimenter. It also provides an analog output voltage proportional to the sweep field. Thus, using a digital scope in x-y mode, where x is proportional to the magnetic sweep field and y is the output of one of the phase detectors, one can observe the change in bridge balance as the magnetic field is swept through the resonant conditions. Figure 7 shows the signals for fluorine in FC-70 (where no attempt has been made to separate the real and imaginary part of the nuclear susceptibility using the phase shifter).

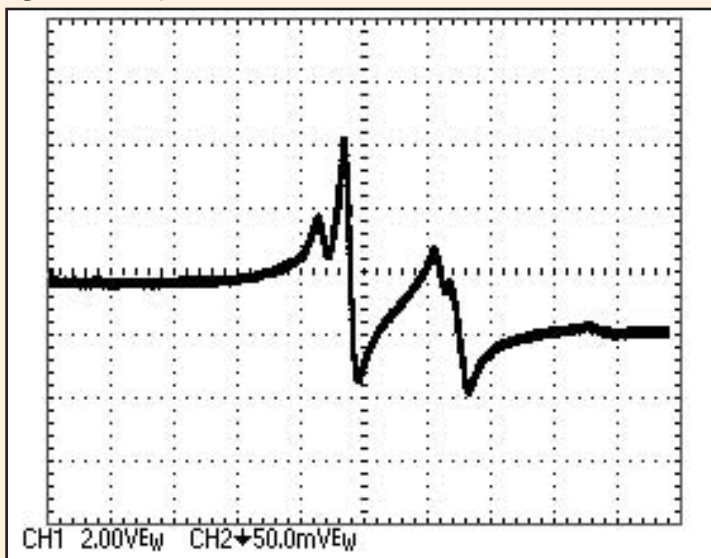


Fig. 7 CW Resonance of FC-70. The Horizontal scale is 62.5  $\mu\text{T}/\text{div}$

However, the magnetic field splittings observed in the CW spectrum can now be compared to the frequency splitting detected in the FFT spectrum of the free-induction decay (Fig. 5). Broad lines from solids can be examined using 20 Hz field modulation and lock-in detection. After performing both experiments, it should become clear to the students why modern spectrometers all use Fourier analysis of the FID signal.

## III. MEASURING $T_1$ SPIN-LATTICE RELAXATION

The spin-lattice relaxation time  $T_1$  is the characteristic time for a spin system to return to its thermal equilibrium magnetization after the magnetization has been driven away from equilibrium by some external perturbation. This time constant can be measured using several different techniques. These include saturation-recovery, zero-crossing of the magnetization inversion following a  $180^\circ$  pulse, or a least-squares fit to the entire recovery signal after magnetization inversion. Figure 8 shows the superposition of 23 experiments of  $\pi$  - delay -  $\pi/2$  pulse sequence. The  $\pi$ -pulse inverts the magnetization and the  $\pi/2$  pulse rotates the magnetization into the transverse plane. This figure shows 23 FID signals from the phase sensitive detector as a function of delay time for a light mineral oil sample.

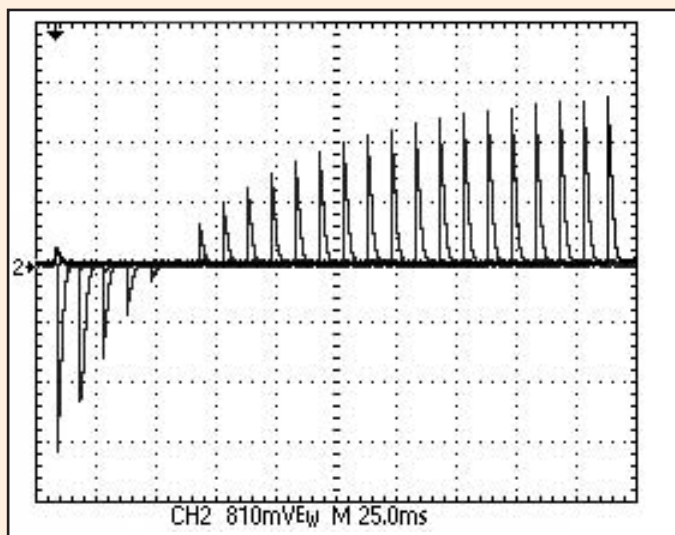


Fig. 8 Superposition of 23 experiments in a  $T_1$  measurement ( $\pi$  - delay -  $\pi/2$  sequence)

The Bloch differential equation that describes the nuclear magnetization  $M_z(t)$  returning to its thermal equilibrium value  $M_0$  is given by

$$\frac{\partial M_z}{\partial t} = \frac{M_0 - M_z(t)}{T_1}, \quad (1)$$

whose solution, for the initial condition of magnetization inversion, can be written as

$$\ln(M_0 - M_z(t)) = \ln 2M_0 - \frac{t}{T_1}. \quad (2)$$

A plot of equation (2) on a semilog graph yields a straight line whose slope can be used to extract  $T_1$ . Such a plot is shown in Figure 9.

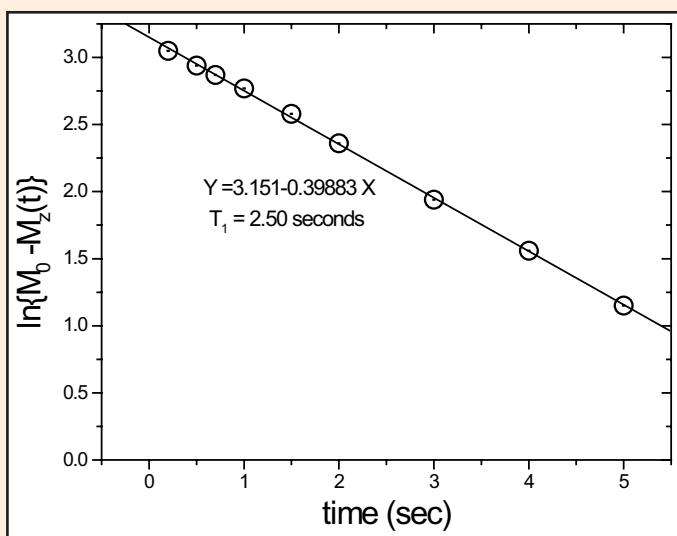


Fig. 9 Plot of Equation (2) to extract  $T_1$  for distilled water

#### IV. MEASURING $T_2$ SPIN-SPIN RELAXATION

The time characteristic of the decay of the transverse nuclear magnetization, after it has been created by a  $\pi/2$  pulse, is called the spin-spin relaxation time,  $T_2$ . It can be measured in several ways. If the magnet has sufficient field homogeneity, the decay of the FID signal gives  $T_2$  directly. Such is the case for many solids, including Teflon, as shown in Figure 13. But in most liquids,  $T_2$  is so long that the inhomogeneity of the magnetic field over the sample causes the FID to decay in a time called  $T_2^*$ , shorter than the real  $T_2$ .

The genius of Hahn's pulse techniques is that the magnet homogeneity no longer limits the measurement of  $T_2$ . Using a two-pulse sequence,  $\pi/2$ -delay- $\pi$ , the  $\pi$  pulse creates a spin-echo, rephasing the magnetization that has been dephased by the field inhomogeneities. Figure 10 shows such a two-pulse sequence for light mineral oil.

The  $\pi/2$  and  $\pi$  pulses are not fully visible in the figure because they are so short, with durations 2.5 and 5.0 microseconds respectively, but the FID and spin echo are clearly visible with a signal to noise ratio of about 100:1.

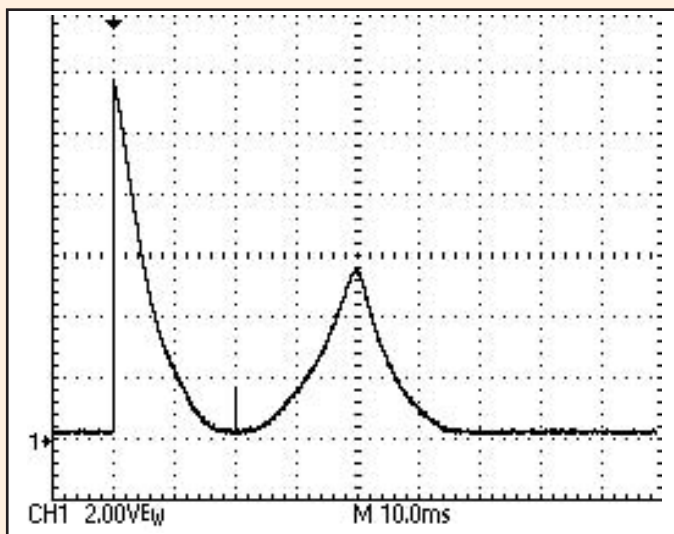


Fig. 10 Two-Pulse spin-echo measurement of  $T_2$  in light mineral oil

The Carr-Purcell pulse sequence,  $\pi/2$ -delay- $\pi$ -delay- $\pi$ -etc., can be generated to measure  $T_2$  in a "single shot". However, accumulated errors in the amplitude of the  $\pi$  pulses limit the use of this one-shot method to a few  $\pi$  pulses. The Meiboom-Gill sequence,  $\pi/2$ -delay- $90^\circ$  phase shift- $\pi$ -delay- $\pi$ -etc. eliminates the error accumulation in the  $\pi$  pulses. Figure 11 shows such a measurement of  $T_2$  for the same mineral oil sample.

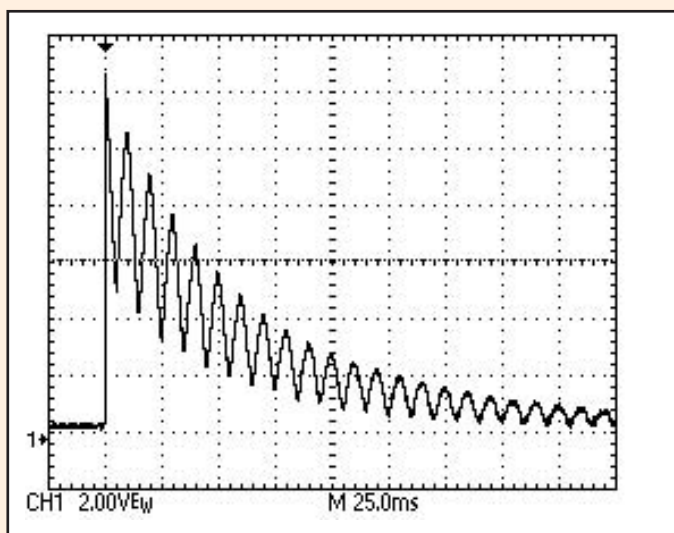


Fig. 11 Meiboom-Gill pulse sequence,  $T_2$  measurement of light mineral oil

#### V. CHEMICAL SHIFTS OF PROTONS

Chemical shifts of protons, measured by the modern high-field, high-resolution commercial spectrometer, are the "bread and butter" of chemists' application of NMR. Although this teaching apparatus cannot produce the resolution of such an instrument, it can achieve splittings that are clearly observable and measurable. Figure 12 shows the FFT of toluene, (125 Hz/div x .8 div = 100Hz splitting out of 21.2 MHz or about 4.7 ppm) The agreement with published data is excellent. With the PS2-A, students can also determine the absolute direction of the shift relative to a proton standard.

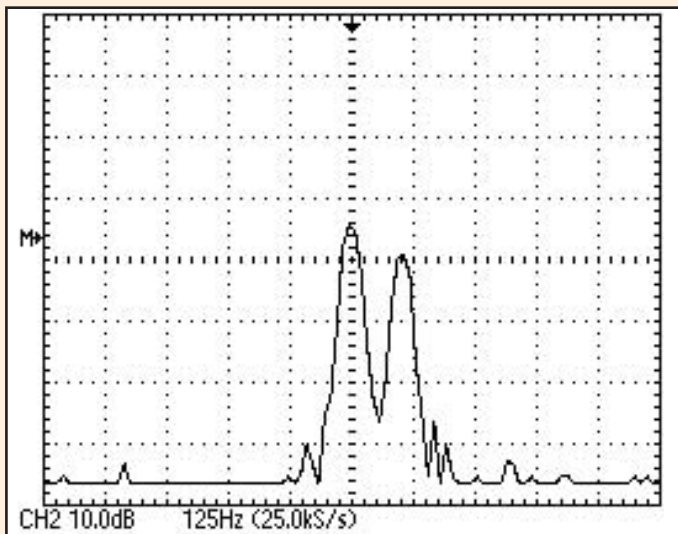


Fig. 12 FFT showing resolved chemical shifts for protons in Toluene

## VI. OTHER EXPERIMENTS

Because PS2-A was designed for short recovery times (15  $\mu$ s) the unit is also capable of observing Pulsed NMR in solids. Figure 13 shows the FID of fluorine in Teflon.

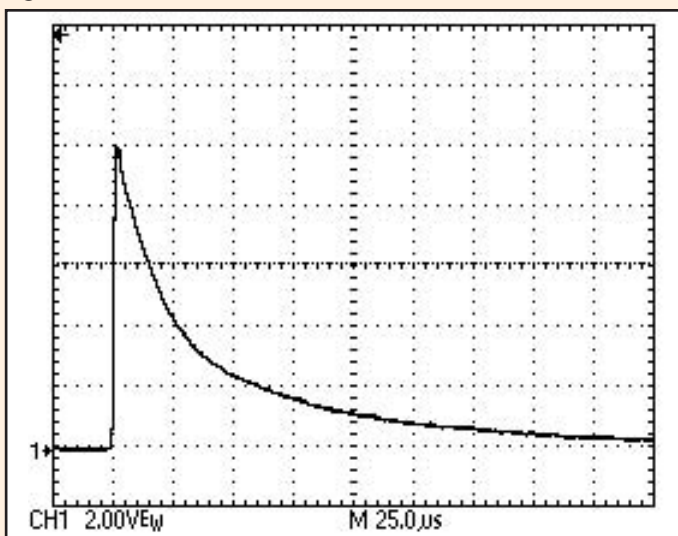


Fig. 13 FID for fluorine nuclei in solid Teflon

Students can examine the effect of paramagnetic ion concentration on relaxation times for a variety of solutes. Because the sample vials cost only a few cents, it is also practical to perform “irreversible” experiments where the vial cannot be reused. This includes measurement of  $T_1$  and  $T_2$  during slow chemical reactions, such as epoxy curing and concrete hardening. *Here is an apparatus whose possibilities are limited only by the imagination of the user. It is the ideal instrument for senior projects.*



## SPECIFICATIONS

### Magnet

Field:  $0.5 \pm 0.02$  Tesla  
 Homogeneity: (min) 0.5 mT over  $0.1 \text{ cm}^3$   
 Stability: 1 part in  $2 \times 10^6$

### Magnetic Field Gradients, Field Bias

$$\frac{\partial B_z}{\partial z} = 6.6 (\mu\text{T/mm})/\text{Amp}$$

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

$$\frac{\partial^2 B_z}{\partial z^2} = 20 (\mu\text{T/mm}^2)/\text{Amp}$$

$$\Delta B_z = 3.1 \text{ mT/Amp (sweep)}$$

### Synthesizer

Frequency: 1 – 30 MHz  
 Stability:  $\pm 50$  ppm  
 Frequency Increments: 100 kHz, 1 kHz, 10 Hz  
 Phase:  $-180^\circ$  to  $+180^\circ$  in  $1^\circ$  steps  
 CW Amplitude: -10 dBm to -65 dBm, 1dB steps  
 Sweep: 0, 1, 2, 5, 10, 20 kHz/V

### Pulse Programmer

A pulse: 0.20 – 20.0  $\mu$ s  
 B pulse: 0.20 – 20.0  $\mu$ s  
 tau: 0.0001 – 9.999 s  
 Number B: 0 – 100  
 Period: 0.2 ms – 100 s  
 External Start: TTL 4 V, 1  $\mu$ s  
 Manual Start  
 Sync: Either A or B pulse, 0.5  $\mu$ s TTL

### Receiver

LNA: Gain 20 dB, NF 2.5 dB  
 VGA: Gain 0 – 80 dB  
 Band Switch: Protons, Fluorine  
 TC: 0.001 ms – 3.3 ms  
 Outputs: RF, Env, Q, I  
 Variable Blanking

### Lock-In/Field Sweep

Modulation Freq: 20 Hz  
 Gain: 80 V/Vrms to 2650 V/Vrms  
 Phase:  $360^\circ$  in  $1^\circ$  steps  
 Time Const.: 0.5 to 10.0 s  
 Field Sweep: -250 mA to +250 mA  
 in a wide variety of formats

### RF Sample Probe

Tunable for protons and fluorine  
 Matched  $50 \Omega$  impedance

### Included

RF pickup probe  
 Complete set of BNC cables (8)  
 50 Sample Vials, caps, o-rings, case  
 Test Samples: (2 ml) FC-770, PFS-1,  
 HT-110, FC-70, FC-43,  
 Light & Heavy Mineral Oil, Glycerin  
 Instruction Manual with Sample Data

**Warranty: Two Years, Parts & Labor**

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