Investigation of T_1 and T_2 of Glycerol with Pulsed NMR

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This experiment utilizes pulsed nuclear magnetic resonance to determine characteristic spin-relaxation properties of glycerin. A quick, order-of-magnitude estimate was used to measure the Spin-Lattice Relaxation Time T_1 of our sample to be 50 ± 6 ms. The Spin-Spin Relaxation Time T_2 was observed with the Carr–Purcell–Meiboom–Gill (CPMG) technique, which we measured to be 54 ± 5 ms. The T_1 and T_2 values of water is several orders of magnitude greater ($T_1 \approx 3$ s) than our measurement as expected, since the protons on glycerin have less rotational freedom compared to those on water due to greater steric hindrance.

I. INTRODUTION

Many nuclei, notably the proton, have spin angular momentum, and these magnetic moments will tend to align with an applied DC magnetic field. With the application of a radio frequency (RF) magnetic field pulse of radio, the net magnetization of a sample can be rotated to an arbitrary angle, from where it will precess while decaying back to equilibrium to re-align with the DC field. The timescales for growth toward equilibrium (parallel to the field) and decay of the transverse component of the magnetization are different. These relaxation times T_1 and T_2 can be used to characterize the sample, and can provide information about the nuclei's environments.

II. THEORY

In order to understand NMR, both classical and quantum mechanics is required. From the classical point of view, a proton can be modelled as a rotating magnetic bar with an associated magnetic moment μ. From classical mechanics, we know that $\mu = \gamma \mathbf{J}$, where $\mathbf{J}$ is the angular momentum and γ is the gyromagnetic ratio. Two spin states exist for the proton, spin up and spin down. When a sample containing protons is placed in a magnetic field, most of the spins of the protons will align with the magnetic field and occupy the lower energy state corresponding to the direction of the magnetic field. This will create a net magnetization M_z of the sample in the same direction.

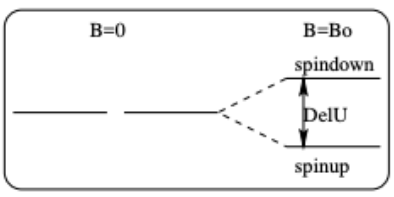

FIG. 1. Splitting in energy for the spin up and spin down states of a proton. The lower energy state in an external magnetic field B_0 is spin-up (parallel to B_0, while the higher energy state is spin-down (anti-parallel to B_0).

When an orthogonal radio frequency pulse is applied on the sample near the resonant frequency of the sample, this will excite the proton from being in the ground state to the excited state as seen in Fig. 1. The pulse supplies the population with enough energy ΔU to make the transition. Classically, this is shown with the rotation the spin of the proton being purely in the z direction to the spin precessing about the z axis with a non-zero component in the xy plane. The length of the applied pulse is proportional to the angle of rotation. This excited state will decay to equilibrium, which is the state where the spins are aligned with the magnetic field.

The rate at which the states decay back to equilibrium heavily depends on the rotational freedoms and steric hindrance of the atoms in the populations. From past NMR experiments, we see that pure liquids have long decay times compared to dense solids. Hence, NMR has often been used as a tool in chemistry to probe the structure of molecules. Another common application of NMR is in magnetic resonance imaging, a medical imaging staple in radiology.

III. METHODS

Apparatus. For the following experiments, a pulsed NMR spectrometer was used. A system-level diagram of the apparatus is shown in Fig. 2.

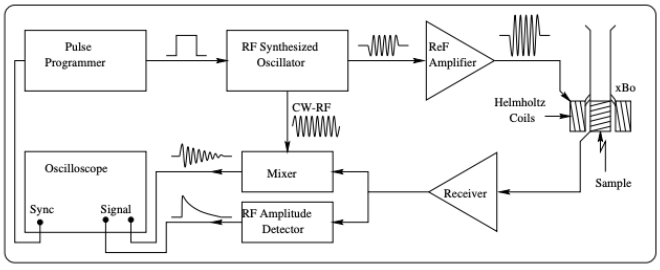

FIG. 2. System level diagram of pulsed NMR spectrometer.

The inputs of the system are the timing and pulse parameters (number, duration, and delay time between the pulses, etc.) from the user. These inputs are given to

the pulse programmer, which generates signals that are then sent through the transmitter coil that is wrapped around the sample. This generates the RF pulses that are orthogonal to the DC field from the magnetic coils. The DC magnetic field is generated by two permanent magnets outside the sample. The sizing of the magnetics are larger than the sample, to produce a field that is as homogeneous as possible. A receiver coil is wrapped around the sample to detect the precession of the sample nuclei in the plane orthogonal to the DC magnetic field. An oscilloscope is used to display and record the voltage signals from the receiver coil.

A summary of the placement of coils can be found in Figure 3. The outer magnetic, transmitter coil, and the pickup coil are orthogonal to each other so that they are not sensitive to each other. Since the receiver coil is orthogonal to the static magnetic field, only spin precessions in the xy plane will be detected.

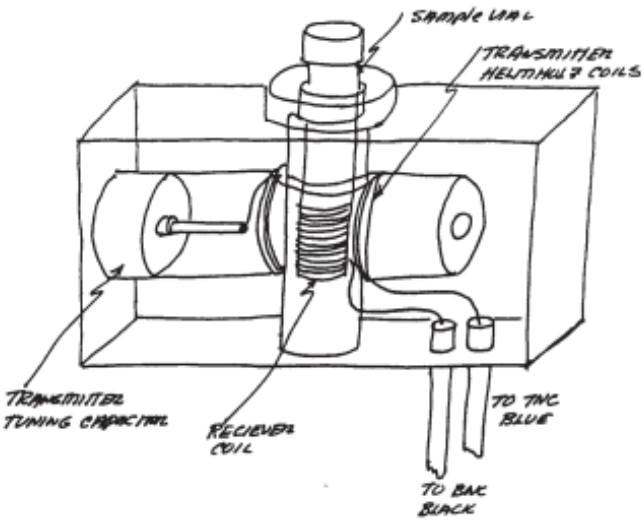

FIG. 3. Placement of coils with reference to sample. The receiver coil is wrapped around the sample to detect the Free Induction Decay. The transmitter coil is also wrapped around the sample in an orientation orthogonal to the receiver coil to deliver the RF pulses. This entire setup is placed in a solenoid that generates a magnetic field perpendicular to both coils.

Upon absorption of the radio frequency pulse, the spin states of our population will flip into the higher energy state. Once the pulse stops, the population will begin to decay back to the ground state immediately. This decay can be captured on the oscilloscope and is referred to as the Free Induction Decay (FID). There are two types of relaxations involved in this decay, and a sample can be characterized by these two relaxation times. Spin-lattice relaxation T_1 is the relaxation time for the sample to decay $1/e$ of the way back to equilibrium in the z direction. Spin-spin relation T_2 is the relaxation time for the sample to decay $1/e$ of the way back to equilibrium in the xy plane.

Spin-Lattice Time T_1 T_1 relaxation characterizes how much time a population needs to equilibriate its magnetization in the z direction. T_1 can be derived from the differential equation

$$\frac{dM_z}{dt} = -\frac{M_0 - M_z}{T_1} \tag{1}$$

where M_0 is the equilibrium magnetization, M_z is the magnetization along the z-axis, and T_1 is the characteristic spin-lattice relaxation time. When we integrate Eqn. 1 with the initial condition that at $t = 0$, $M_z = 0$, we find that

$$M_z(t) = M_0(1 - 2e^{-\frac{t}{T_1}}) \tag{2}$$

The pulse sequence required to measure T_1 is first a π rotation pulse, followed by a $\pi/2$ pulse.

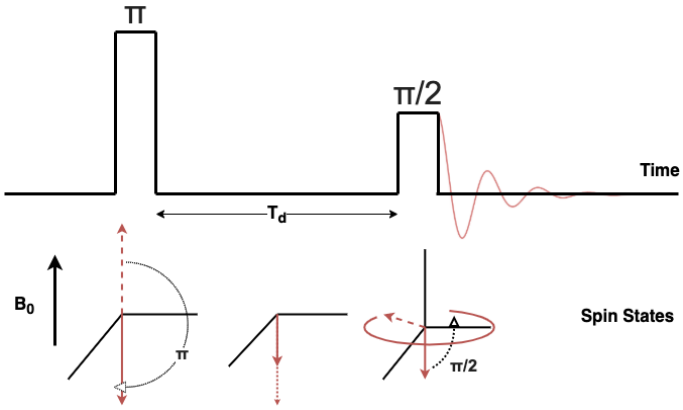

FIG. 4. T_1 Relaxation with corresponding measurement pulse sequence used. Magnetization M_z decays back to its original orientation on the z-axis. Since the receiver coil only measures the FID in the xy plane, M_z needs to be flipped into the xy plane for measurement. Initially, the spin is in the groun state, pointing in the direction of the magnetic field B_0. A π rotation pulse is applied, flipping the spin into its excited state. After some delay where M_z has had time to decay, M_z is flipped into the xy plane with a $\pi/2$ pulse. This allows us to captures the magnitude of M_z. By plotting M_z as a function of delay T_d and fitting the results to our Eqn. 2, T_1 can be found.

The main reason why T_1 relaxation occurs is the instability of the excited state. The excited state corresponds to higher entropy, and the system will reorient its spins to return to a lower entropy equilibrium state.

Spin-Spin Time T_2 T_2 relaxation is the time needed for the spins of a population to dephase from each other in the xy plane. This is also governed by the differential equations

$$\frac{dM_x}{dt} = -\frac{M_0}{T_2} \tag{3}$$

$$\frac{dM_y}{dt} = -\frac{M_0}{T_2} \tag{4}$$

where M_0 is the equilibrium magnetization, M_x is the magnetization along the x-axis, M_y is the magnetization along the y-axis and T_2 is the characteristic spin-spin relaxation time. The solutions to the differential equations in Eqn. 3 and 4 are

$$M_x(t) = M_0 e^{-\frac{t}{T_2}} \tag{5}$$

$$M_y(t) = M_0 e^{-\frac{t}{T_2}} \tag{6}$$

The pulse sequence required to measure T_2 is first a $\pi/2$ rotation pulse, followed by a repetition of π pulses.

The main reason why T_1 relaxation occurs is the inhomogeneity of the static magnetic field felt by the proton. Due to interactions with its neighbors and imperfections in the magnetic field, there will be a spatial variance in the magnetic field felt by the population. This variance will create interferences that will cancel out the signal in the xy plane over time.

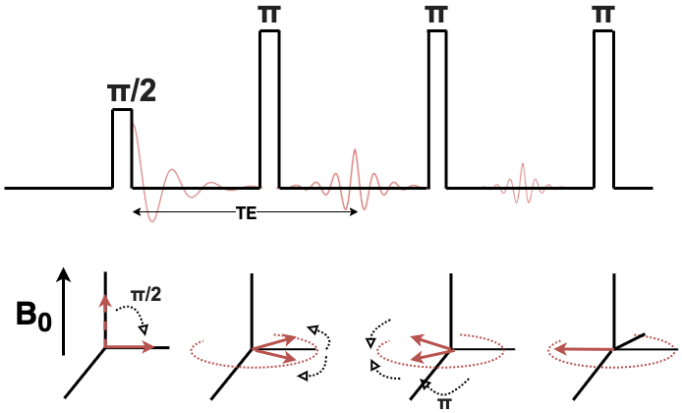

FIG. 5. T_2 Relaxation measured with Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence. Magnetization M_x and M_y decays to zero in the xy plane. Initially, the spin is in the ground state, pointing in the direction of the magnetic field B_0. A $\pi/2$ rotation pulse is applied, flipping the spin into xy plane. The inhomogeneities in the apparent magnetic field will cause the spins to dephase immediately. A π pulse is applied after a delay TE such that the dephasing becomes a rephasing. This is captured in the FID where we see a peak in M_x. The rephasing reaches a maximum magnetization, then begins to dephase again. The π pulse is repeated so that this dephasing and rephasing can be captured. By plotting M_z as a function of repetition number and fitting the results to our differential equation, T_2 can be found.

IV. RESULTS AND DISCUSSION

T_1 for glycerol was measured to be 50 ± 6 ms and T_2 was measured to be 54 ± 5 ms. The uncertainty for the T_1 measurement was estimated by extracting the max deviation seen in the collected data and applying at the zero magnetization point, as seen in Eqn. 2.

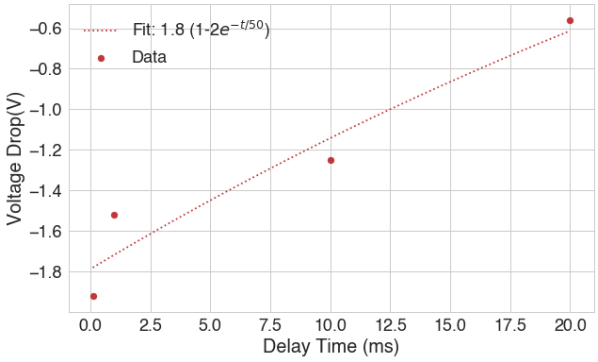

FIG. 6. Magnetization vs. delay time plot of glycerol used to extract T_1 relaxation. Due to lack of time, only a few measurements were made. Ideally, more data points should be collected, particularly around the zero magnetization region.

A scaling of 1 V was used on the oscilloscope for T_2 measurements, and the oscilloscope was able to output voltage readings on the order of 0.01 V. Applying this uncertainty of ± 0.01 V to our fit for finding T_2 with Eqn. 6, a variation of ± 5 ms was found in the exponential fit.

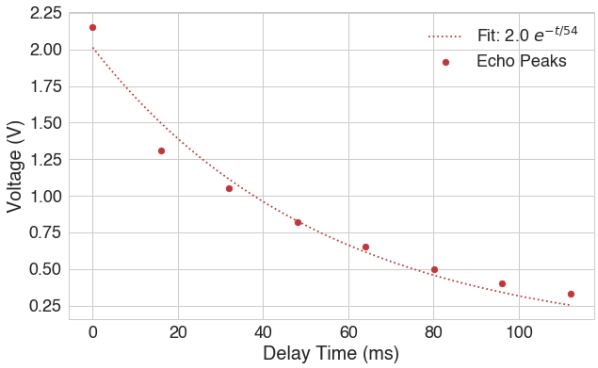

FIG. 7. Magnetization vs. echo repetition plot of glycerol used to extract T_2 relaxation.

When comparing with the long T_1 and T_2 values of water which are on the order of seconds, we can see that the protons on glycerol have less rotational freedom compared to those on water. This is expected, since the protons on glycerin have less rotational freedom compared to those on water due to greater steric hindrance, since glycerol has three hydroxide groups and water only has one.

V. CONCLUSIONS

There are several sources of error in this experiment. First, there is the uncertainty in the oscilloscope measurements. This has been taken into account by varying

exponential fits to determine the greatest variance in the relaxation time constants. Another major contributor is the dependence of relaxation times on the temperature of the sample. As temperature increases, entropy will also increase, which overall will affect at which spins relax after an excitation pulse. Over the course of the experiments, the spectrometer is hooked up to a tap water source, which cools the magnetic. Occasionally, the pressure in the tap water source fluctuates, which will also cause the temperature of spectrometer to vary. It could be possible that irradiating a sample rapidly and continuously with the RF pulses may raise its temperature as well. In the future, this experiment should be repeated as quickly as possible to avoid errors.

Another assumption was made in the analysis. Our Eqn. 2 and 6 both assume a pure sampling, with no impurities, hence the single time constant we fit to in our analysis. In reality, this may not be accurate. Impurities in the glygerol will result in a coupled system of differential equations, where there is exchange in the relaxations of the various samples. More analysis, such as fitting to a sum of exponential functions may shed more light on the purity of the glycerol.

VI. REFERENCES

[1] ENPH 352 Manual. *NMR: Spin-Spin Couple Lab.* 2018.