

Pulsed NMR in Mineral Oil and Glycerin

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) is a method used by physicists, chemists, and medical professionals for a myriad of different purposes. Developed in 1942, NMR has been the subject of several Nobel Prizes including 1952 Nobel Prize in Physics awarded to Felix Bloch and Edward Mills Purcell, the 1991 Nobel Prize in Chemistry awarded to Richard R. Ernst, and most recently, the 2002 Nobel Prize in Chemistry awarded to John Fenn, Koichi Tanaka, and Kurt Wuthrich. NMR is most notably used in the medical field through Magnetic Resonance Imaging (MRI) which has been used in diagnostic medicine since 1977.

Pulsed Nuclear Magnetic Resonance (Pulsed NMR), developed in 1950 by Erwin Hahn, is very similar to the NMR but differs in the sense that an NMR is a continuous wave of radio frequency (RF) while Erwin Hahn used pulse bursts of RF when observing condensed matter subjected to magnetic fields. Rather than using condensed matter, this experiment will be using two different samples: glycerin and mineral oil. Using Pulsed NMR will bring the protons of each sample out of thermal equilibrium by using pulses of RF to observe different quantum properties of each sample.

This paper will start by explaining the theory behind Pulsed NMR in Section II including the basic quantum principles associated with this experiment, free induction decay, and the gyromagnetic ratio. Section III will explain the experimental design, the different expected signals and their meaning, and the explanation of the pi and pi/2 pulses. Section IV will illustrate the acquired results including the obtained values of T_1 , T_2 , and T_2^* for glycerin and mineral oil. The results will also include the measured values for the gyromagnetic ratio of both substances analyzed. Section V will serve as the conclusion, summing up the experiment and the results.

II. THEORY

A. Basic Quantum Principles

Similar to the electron, the proton also has a spin. The purpose of the pulsed NMR is to analyze the spin of single proton which is subjected to magnetic fields and RF. The spin of the proton gives rise to the angular momentum and the magnetic moment. The spin of the proton has a

relation to angular momentum by the equation

$$\vec{J} = \hbar \vec{I} \quad (1)$$

where $\vec{J}$ is the nuclear angular momentum and $\vec{I}$ spin of the nucleus where $I = 1/2$. The magnetic moment is related to the nuclear angular momentum through the gyromagnetic ratio given by the equation

$$\vec{\mu} = \gamma \vec{J} \quad (2)$$

where μ is the magnetic moment of the nucleus and γ is the gyromagnetic ratio, which will be further explained later.

The magnetic energy plays a key role in the relation to the magnetic moment and the magnetic field. This relation is illustrated by

$$U = \vec{\mu} \cdot \vec{B} \quad (3)$$

where U is the total magnetic energy of the system and $\vec{B}$ magnetic field applied to the system. This equation is then transformed for the system observed in this experiment which deals with the spin of the proton oriented on the z axis written

$$U = -\gamma \hbar \vec{I}_z \vec{B}_o \quad (4)$$

in which the nuclear spin vector obtains values in the z direction. The magnetic fields applied to the samples are kept at a constant rate, therefore $\vec{B}_o$ is treated as a constant. This equation then simplifies to

$$\Delta U = \gamma \hbar \vec{B}_o = \hbar \omega_o \quad (5)$$

which illustrates the energy spacing between the magnetic quantum number $m_I = +1/2$ and $m_I = -1/2$. ω_o is the angular frequency. Due to the value of $I=1/2$ for the proton in this system, there are only two magnetic energy states.

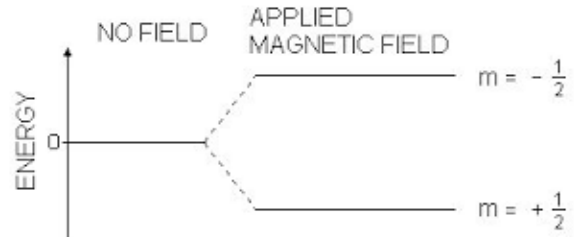


Figure 1. Magnetic quantum number level spacing for $I=1/2$

B. T_1 and Free Induction Decay

In pulsed NMR for substances in thermal equilibrium, there are key measurements of constants associated with each sample. The first is spin-lattice relaxation time constant. It describes the transitions of angular momentum for the protons in the sample in terms of time. This occurs because of the transitions in the quantum number m . Again, this is a two state system for the magnetic quantum number because the angular momentum $I=1/2$. The spin-lattice relaxation period is denoted by T_1 which is a constant. This can be described using the differential equation

$$\frac{dM_z}{dt} = \frac{M_o - M_z}{T_1} \quad (6)$$

which describes the proportional rate in which the protons approach and separate from thermal equilibrium where M_z is the magnetization in the $+z$ axis described by

$$M_z = (N_1 - N_2)\mu \quad (7)$$

N describes the number of spins per unit volume for each m_I state.

The differential equation describing the spin-lattice relaxation time constant can be integrated to yield

$$M_z(t) = M_o(1 - e^{-\frac{t}{T_1}}) \quad (8)$$

This reading is achieved by exposing the sample to a π pulse followed by a $\pi/2$ pulse.

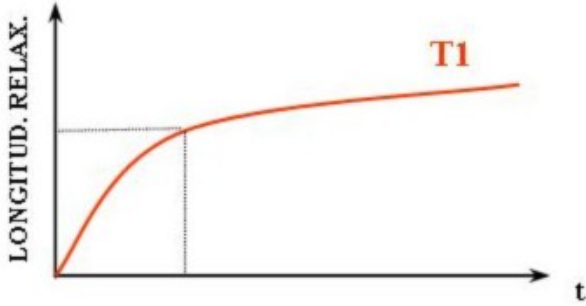


Figure 2. Illustration of expected graph of T_2 . Shows the sample approaching equilibrium.

The second constant associated with the pulsed NMR readings is the spin-spin relaxation time constant or the free induction decay (FID). FID describes the time it takes for a substance to return to thermal equilibrium. The spin-spin relaxation time is denoted by T_2 . By applying a π pulse to the sample, M_z is then oriented to M_y . Rather than remaining in the M_z axis as the spin-lattice relaxation time constant does, the spin-spin relaxation time constant is described using the differential

equations

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \quad (9)$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2} \quad (10)$$

Similar to T_1 , solutions to the differential equations yield

$$M_x(t) = M_o e^{-\frac{t}{T_2}} \quad (11)$$

$$M_y(t) = M_o e^{-\frac{t}{T_2}} \quad (12)$$

The big difference is that the terms in the exponential are negative, indicating a decay rather growth inherent in the T_1 solution.

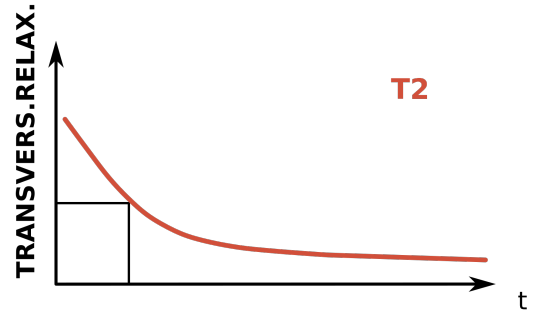


Figure 3. Illustration of the Free Induction Decay

In the obtained the spin-spin relaxation time constant, there is a spin echo produced. Through the spin echo effect, the T_2 can be obtained.

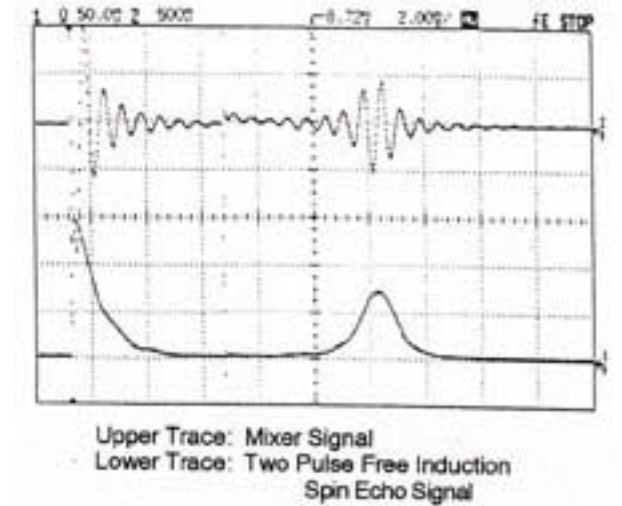


Figure 4. Illustrates the spin echo. The echo occurs after the decay has completed. The bottom line shows the readings from the spectrometer.

C. Gyromagnetic Ratio

The gyromagnetic ratio γ has the unit radians per second per gauss. The gyromagnetic ratio is ratio of the

magnetic moment of a proton to the angular momentum which is described in Equation 2. It can also be related to the angular frequency and the magnetic field

$$\omega_o = \gamma B_o \quad (13)$$

The gyromagnetic ratio for the proton is 2.675×10^4 radians per second per gauss which determines the resonant frequency

$$f_0 = 4.258 B_o \quad (14)$$

in which frequency is in MHz and the magnetic field B_o is in kilogauss.

III. EXPERIMENT

Glycerin and mineral oil are both analyzed through pulsed NMR in order to determine their gyromagnetic ratio and the T_1 , T_2 , and T_2^* values. The samples will begin at thermal equilibrium and the RF will bring the protons out of equilibrium. The protons in each sample will be tilted and the spectrometer will monitor their precession through the x-y axis. The protons are oriented in the +z axis, which means that there will be no readings in the x-y axis during these times. The protons will be precessed by two different pulses, a π pulse and a $\pi/2$ pulse. Through these pulses, there will be a precession in the protons. The π pulse, described earlier is the first pulse given to the protons in determining T_1 . After a fixed delay time, a $\pi/2$ pulse is then emitted. For determining T_2 , the opposite order is done with a $\pi/2$ pulse followed by a π pulse after a fixed delay time. Because T_1 's net magnetization is precessed only in the z direction, it is necessary to have the second $\pi/2$ pulse in order to get a reading in the x-y plane, otherwise it would be impossible to observe the relaxation time. The second π pulse in the measurement of T_2 is meant to determine the spin echo, thus improving the estimate of spin-spin relaxation time constant.

The experimental set up involves a sample probe, a receiver, a detector, an oscilloscope and a mixer. The sample probe involves two sets of coils. The transmitter coil is set perpendicular to the magnetic field. The transmitter coil is responsible for providing RF pulses to the sample. The pickup coil is wrapped around the sample cell. The pickup coil detects precession in the x-y plane. The pickup coil is attached the receiver that sends the signal to the oscilloscope. In order to cancel out the frequencies produced by the RF signal in the readings, the mixer is used to determine the true frequency of the protons. This improves the readings of the resonant frequencies.

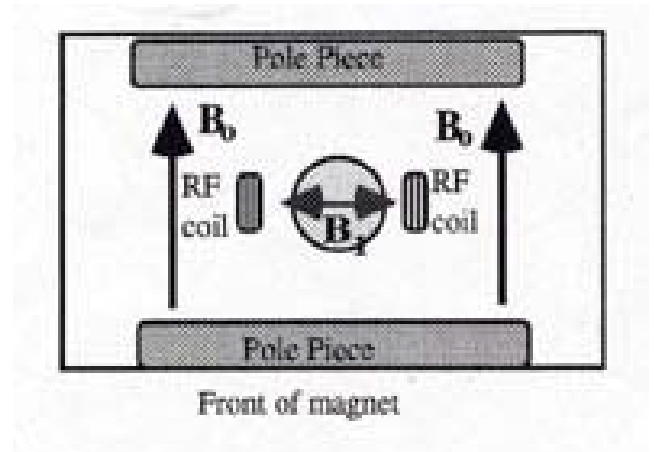


Figure 5. Experimental set up of the magnets and RF inside of the sample cell. B_o is constant where B_1 is the changing RF.

IV. RESULTS

T_1 is calculated by creating a best fit line through the data points provided in Figure 6. Uncertainty is assessed by creating error bars proportional to the amplitude of the noise at the peaks of the data points. A maximum fit, minimum fit, and a best fit line are drawn. The maximum fit line will be the upper values of the uncertainty while the minimum fit line will be the lower values of the uncertainty. In order to fully obtain the uncertainty, the equation

$$\Delta T_1 = (T_{upper} - T_{lower})/2 \quad (15)$$

T_2 is an exponential rather than a linear best fit. An exponential must be created in order to obtain the spin-spin relaxation time constant. The decay time at various times of the delay time determines the best answer for τ .

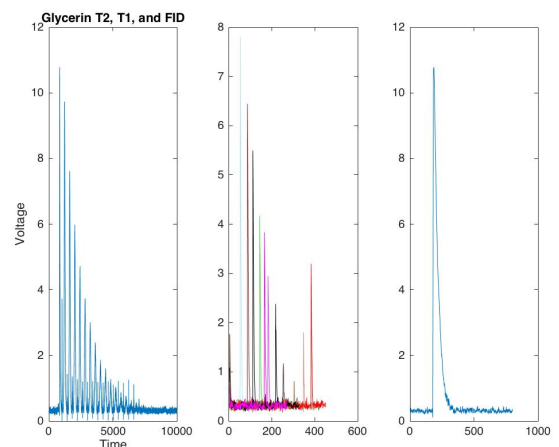


Figure 6. Left plot shows the T_2 measurements for Glycerin. Middle plot shows the T_1 measurements. Right plot shows the FID (T_2)

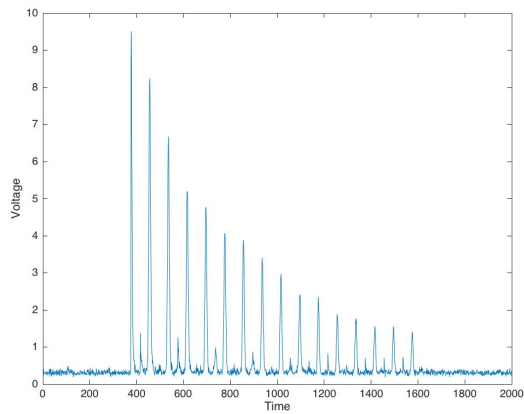


Figure 7. T2 for Mineral Oil.

Gyromagnetic ratios are calculated using the equation

$$\omega_o = \gamma B_o \quad (16)$$

where B_o is determined using the gauss meter and the angular frequency is determined by the rotation and duration of the pulses. Answer is reported in rad/s/gauss.

V. REFERENCES

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