Nuclear Magnetic Resonance

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1 Goal

To measure the g-factor of the proton and the Fluorine nucleus and investigate transient effects of the NMR signal.

2 Introduction/Background

Nuclear magnetic resonance is the process of irradiating a sample of protons, in the presence a magnetic field B_o, with photons of energy on resonance with the transition energy for spin flips

$$\Delta E = g\mu_N B_o \tag{1}$$

where $g = 5.5857$ is the g-factor for the proton and $\mu_N = 5.05 \times 10^{-27}$ J/T is the nuclear magneton. Due to the B_o induced Zeeman splitting, incoming electromagnetic radiation can interact with the protons to produce an upward transition (from spin up to spin down) via absorption, or downward transitions (from spin down to spin up) through stimulated emission and spontaneous emission. For a container of atoms in thermal equilibrium with an ambient field, the spontaneous emission rate is dependent on the cube of the radiation frequency and is proportional, by a factor of $\sim 10^{-6}$ for radio frequencies, to the stimulated emission rate [1]. On the other hand, for higher frequencies, such as visible light, spontaneous emission dominates over stimulated emission, since light photons of frequency f, carrying energy hf, are not near the resonance as determined by Equation 1, which requires $f_{RF} = g\mu_N B_o/h$, where h is Planck's constant.

The ratio of spin-down protons to spin-up protons can be found from statistical mechanics by taking the ratio of the Boltzmann factors for each state

$$\frac{N_-}{N_+} = \frac{e^{-E_-/k_b T}}{e^{-E_+/k_b T}} = e^{-\Delta E/kT} \tag{2}$$

where E_- and E_+ are the energies of the spin down and spin up states, respectively, and their difference forms Equation 1. At a room temperature of 300 K and for the typical magnetic field strengths applied in this experiment of 0.5 T, $\Delta E \ll k_b T$, and more precisely, $\frac{N_-}{N_+} = 0.999997$, therefore, the spin up/down states are nearly equally populated. Then, since absorption and stimulated emission share the same probability amplitude (and spontaneous emission is negligible), there is only a minuscule loss of electromagnetic energy as resonant RF photons permeate the sample. Through proper

instrumentation, this energy loss can be detected, indicating the RF photons are on resonance, and used to determine an experimental value for the quantity $g\mu_N$.

3   Procedures and Data

As seen in Figure 1, we used a solenoid pair to introduce the Zeeman splitting that distinguishes spin states by controlling B_o of Equation 1. Inside the region of horizontal field created by the solenoid pair is the solenoid inductor of a *marginal oscillator* LC circuit, which stores electromagnetic energy within its coil and, when oscillating at frequency $f_1 = 1/2\pi\sqrt{LC}$, where C was determined by a variable capacitor, subjects the sample placed within its coils to a bath of photons of frequency f_1. The inductance, and thus the impedance of the coil, is then partly determined by the magnetic permeability of the sample substance, which is approximately constant for all frequencies not equal to the resonant frequency of the sample and has a sharp maximum centered at the sample resonant frequency. The marginal oscillator is barely able to sustain an oscillation, and any that it does are of small amplitude, consequently, its oscillation amplitude is sensitive to the small change of magnetic permeability, which occurs due to the slight imbalance between protons in state N_+ vs. N_-, when the oscillation generated photons are in resonance with the transition energy of the proton spin flip [2]. We observed this change of LC oscillation magnitude on an oscilloscope with the assistance of a rectifier circuit, which converted the AC signal of the LC circuit output into DC, rendering a clear voltage dip from what otherwise would have been a difficult to identify disturbance in the oscillation envelope.
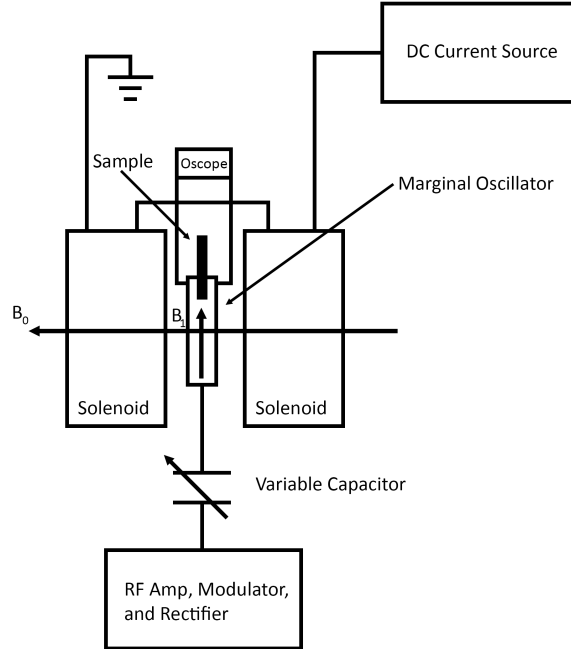

Figure 1: Schematic of the experimental apparatus.

In order to avoid saturating the transition, which occurs when the sample is provided enough time to reach thermal equilibrium with the resonant radiation and forces the states to be distributed equally (as far as the detector is concerned), since the RF

bath overwhelms the natural thermal effects, we introduced a modulation field in addition to B_o, so that the external applied field becomes

$$B_{ext} = B_o + B_{mod}\cos\left(2\pi f_{mod}t\right) \tag{3}$$

where B_{mod} is the modulation amplitude, and $f_{mod} \approx 30$ Hz is the modulation frequency. For marginal oscillation frequency f_1, modulation at ≈ 30 Hz causes the B_{ext} to cross the resonant amplitude B_o twice per cycle at a rate that does not allow the sample the relaxation time necessary for it to reach equilibrium. We observed resonant crossings on the oscilloscope as a time periodic series of voltage dips from the rectifier output.

We determined the magnitude of B_o produced by the solenoid pair as a function of the current through the coils by measuring the magnetic field strength with a Gauss meter for a set of current values and performed a quadratic fit of the form $B_o = bI + cI^2$, where b, c are fit parameters, and I is the applied current, which is shown in Figure 2.
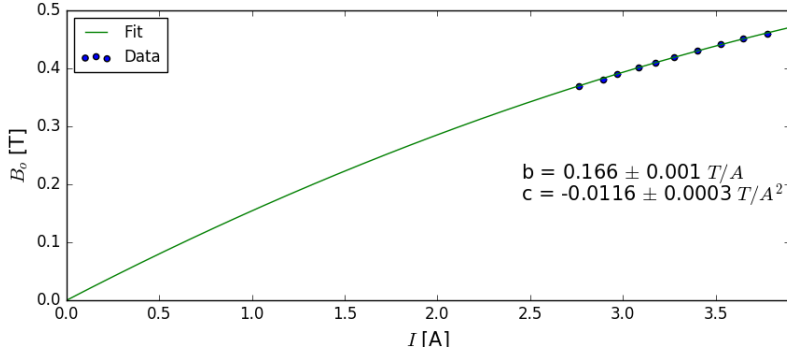

Figure 2: Quadratic curve fit relating the value of B_o to the current I through the solenoid pair.

Then, we placed a sample of water within the marginal oscillator coils and tuned the oscillation frequency f_1 to resonance at various applied fields B_o; these data pairs are shown in Table 1, which we expect to be related according to Equation 1.

Table 1: Data pairs (B_o, f_1) for a water sample, where the uncertainty in f_1 is estimated to be 0.02 MHz and is due to the fluctuating output of our frequency measuring meter. Uncertainty in the value of B_o comes from the fitting algorithm and an uncertainty of 0.001 A in the current reading, which gives an uncertainty of 0.004 T for the first three columns of the Table, and 0.005 T for the remaining columns.

B_o (T)	0.392	0.397	0.406	0.416	0.423	0.430	0.436	0.444
f_1 (MHz)	17.06	17.26	17.65	18.11	18.35	18.64	18.94	19.28

We performed the same process with a sample of Polytetrafluorethylene (PTFE) to acquire the data shown in Table 2, which allows us to determine the g-factor of fluorine by using the accepted value of μ_N and Equation 1.

Since the sweeping applied magnetic field is on resonance only briefly, the NMR signal is not simply a single peak, instead, it is an oscillation with an exponential decaying amplitude. Indeed, the lifetime of the NMR response is determined by a combination of the spin-lattice relaxation time, which characterizes the elapsed time before the net

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Table 2: Data pairs (B_o, f_1) for a PTFE sample, where the uncertainty in f_1 is again estimated to be 0.02 MHz. The uncertainty in B_o is 0.004 T for the first three columns of the Table, 0.005 T for columns four through nine, and 0.006 T for the remaining columns.

B_o (T)	0.384	0.393	0.403	0.418	0.418	0.425	0.434	0.442	0.451	0.460	0.467	0.474
f_1 (MHz)	15.77	16.15	16.53	17.32	17.33	17.51	17.86	18.02	18.34	18.67	18.93	19.19

magnetization vector of the sample realigns itself with $\vec{B}_o$ after B_{ext} has moved off resonance, and the time required for the individual spins to become dephased, meaning their directions are distributed isotropically in the plane perpendicular to $\vec{B}_o$, which is a consequence of spin-spin interactions and field inhomogeneities. When the magnetic field is aligned with $\vec{B}_o$ or the spins are dephased, there is zero time rate change in the magnetic field vector within the coil, so there is no response by the inductor, and thus no signal. [3]. To investigate this effect, we used oscilloscope cursors to measure the amplitude of each oscillation peak along with its separation in time from the beginning of the pulse, which is shown in Figure 3.
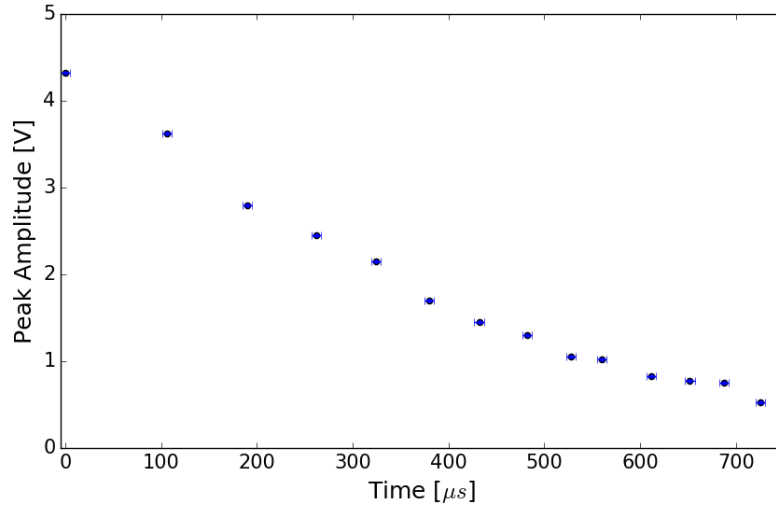

Figure 3: Exponential decay of oscillating NMR signal amplitude as a function of time elapsed since the beginning of the pulse.

The line width of the resonance signal for fluorine, which we measured to have a full width at half max of 400 ± 10 μs for PTFE, is also dependent upon the relaxation parameter. In order to convert our time scale width into one of frequency, we measured the time displacement of a set of resonance peaks, as a function of f_1 at fixed B_o, from the peak satisfying $hf_1 = g\mu_N B_o$, as seen in Table 3. For small changes in f_1, the position of the peak shifts, in an approximately linear response, in time, since a stronger B_{ext} is now necessary for resonance, which requires waiting for the oscillating B_{mod} component to bring the applied field onto resonance. The linearity of this response follows from the fact that when $B_{ext} = B_o$ is on resonance, the NMR signal appears when the B_{ext} wave is at its inflection point, thus $B_{ext} \approx B_o + B_{mod} \cdot 2\pi f_{mod} t$ for a short time interval following the moment of reaching resonance at $B_{ext} = B_o$.

Table 3: Time displacement of the NMR signal as a function of f_1 from the origin peak occurring when $f_1 = 17.48 \pm 0.02$ MHz. For these measurements our instrument failed to provide a reliable readout of f_1, so we have truncated its precision, applied a large uncertainty, and excluded the data point in the final column of this table from our analysis.

f_1 (MHz)	17.59 ±0.01	17.60 ±0.01	17.61 ±0.01	17.64 ±0.01	17.64
Time (ms)	3.18 ±0.01	4.65 ±0.01	7.25 ±0.01	9.24 ±0.01	6.00

4   Analysis and Discussion

Each water molecule contains a two Hydrogen atoms with single proton nuclei that couple to the applied magnetic field and undergo Zeeman splitting according to their g-factor. We performed a least square fit to the data of Table 1 with Equation 1 and the accepted value of $\mu_N = 5.05 \times 10^{-27}$, shown in Figure 4, to find the experimental value $g_{proton} = 5.702 \pm 0.003$, which lies many standard deviations from the accepted value of 5.5857. We expect the discrepancy between our measured results and the accepted value is due to unreliable readouts of f_{RF} and the uncertainty in B_o, which is comprised of the calibration algorithm uncertainty and experimental difficulty when using the Gauss meter probe to determine the magnetic field at the location of the sample.
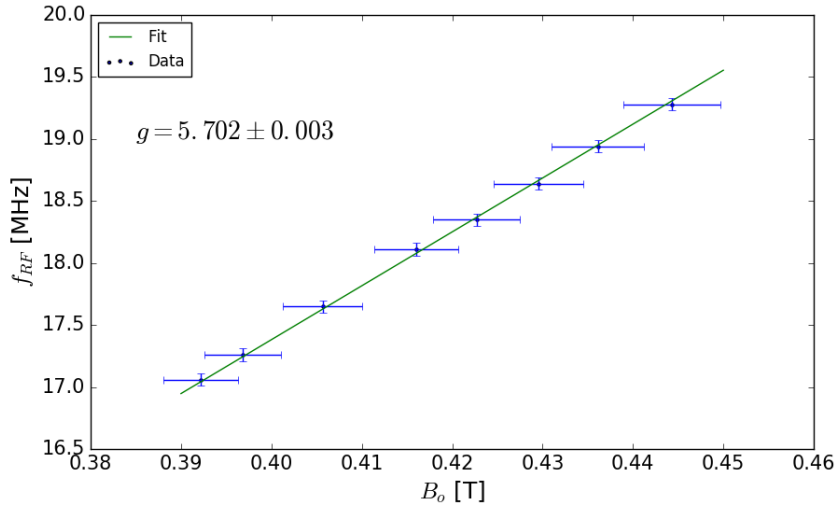

Figure 4: Linear least square fit to the data of Table 1 with Equation 1, in order to determine the slope, which provides g_{proton} for the Hydrogen nuclei of water.

We performed the same analysis the PTFE Fluorine sample, which also has a nucleus of spin 1/2, in order to determine the g-factor of fluorine, as seen in Figure 5, where we found $g = 5.37 \pm 0.01$, which carries a larger relative uncertainty than our measurement of g_{proton}. The data of Figure 5 do not appear to be well represented by the simple linear relationship of our fit, this may have been caused by complex interactions within the populated nucleus, lattice effects, or simply be the result of poor measurements/instrumentation. From these two measurements we can conclude that the nuclei of Hydrogen and Fluorine share approximately the same capacity for

coupling to external magnetic fields through their intrinsic angular momentum. At fixed B_o, the ratio of resonant frequencies $f_F/f_{H_2O} = g_F/g_{H_2O}$, as all other variables are constant, which we see reflected in our data, since $g_F/g_{H_2O} = 0.942 \pm 0.1$, and, from the line fits of Figures 4 and 5, $f_F/f_{H_2O} = 16.38/17.382 = 0.942 \pm 0.002$ at $B_o = 0.4$ T.
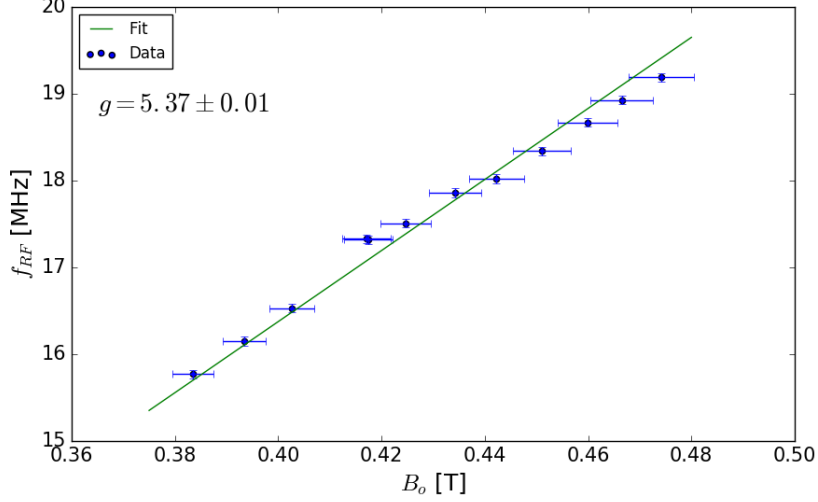

Figure 5: Linear least square fit to the data of Table 2 with Equation 1, in order to determine the slope, which provides g for the fluorine nucleus.

In order to determine the lifetime of the NMR response, we created a log amplitude vs time plot of the data in Figure 3, as seen in Figure 6, then performed a weighted linear least squares fit to an equation of the form $\ln V = \ln V_o - t/\tau$, where V_o and τ are fit parameters. We found $\tau = 389 \pm 13$ μs, which is on the order of the 1 ms value that is typical for NMR experiments and verifies that the modulation field provided the sample with sufficient time after a resonance crossing to reset back to thermal equilibrium before reaching another crossing, since a modulation frequency of ≈ 30 Hz crosses resonance every $1/60 = 0.017$ seconds. Our measured value for τ is much larger than the NMR lifetime of pure water, which is on the order of 3 s. This is the result of dissolving a small amount of copper sulfate into the water sample, which reduces the relaxation time corresponding to spin-lattice interaction, since the Hydrogen protons interact more strongly with the magnetic moment of the Copper atoms than they do with other protons. We can also conclude that both the relaxation time associated with spin-lattice interactions and the relaxation time associated with spin-spin and magnetic field inhomogeneities are greater than $\tau = 389 \pm 13$ μs, since those two processes work in concert to create the net relaxation time.

We determined the change in time position of the fluorine signal as a function of change in f_{RF} from the linear least squares fit shown in Figure 7, where the second row of Table 3 forms ΔT and the difference between the entries in the first row of Table 3 and the origin frequency $f_1 = 17.48 \pm 0.02$ MHz form Δf_{RF}. From the fit, we found a slope $\Delta T/\Delta f_{RF} = 121 \pm 12$ ms/MHz, which allows calculation of the width of the resonance line, in units of Hertz, by $width = \Delta f_{RF}/\Delta T \times 400\mu s = 3.3 \pm 0.1$ kHz.
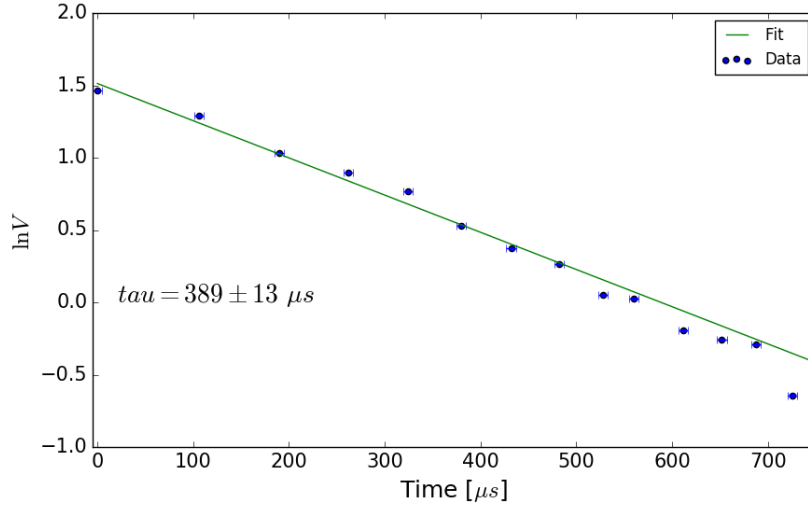
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Figure 6: Weighted linear least squares fit to a log amplitude vs time plot of the data in Figure 3 to determine the lifetime of the NMR signal in water.

5 Conclusion

We have shown that a marginal oscillator is capable of detecting a two parts in a million imbalance in the population distribution of spin states and used that information to determine the g-factor of the proton and the Fluorine nucleus by creating Zeeman splitting within these samples and then subjecting them to RF radiation that is absorbed only when it is on resonance. We found $g_{proton} = 5.702 \pm 0.003$, which is not in great agreement with the accepted value of 5.5857. And we found $g_{Fluorine} = 5.37 \pm 0.01$, a value similar in magnitude to that of g_{proton}. Additionally we determined the lifetime of the NMR response for water to be 389 ± 13 μs, which is a reasonable value for NMR experiments and gives information as to the relaxation processes of the sample. Lastly, we determined the line width of the NMR response for the Fluorine sample to be 3.3 ± 0.1 kHz.

References

[1] David J Griffiths. *Introduction to Quantum Mechanics*. Pearson, 2005.

[2] B Makarov and V Ryzhov. Advance of Marginal Oscillator. *Instrumentation, Controls, Feedback and Operational Aspects*.

[3] Adrian C. Melissinos. *Experiments in Modern Physics*. Academic Press, 2003.

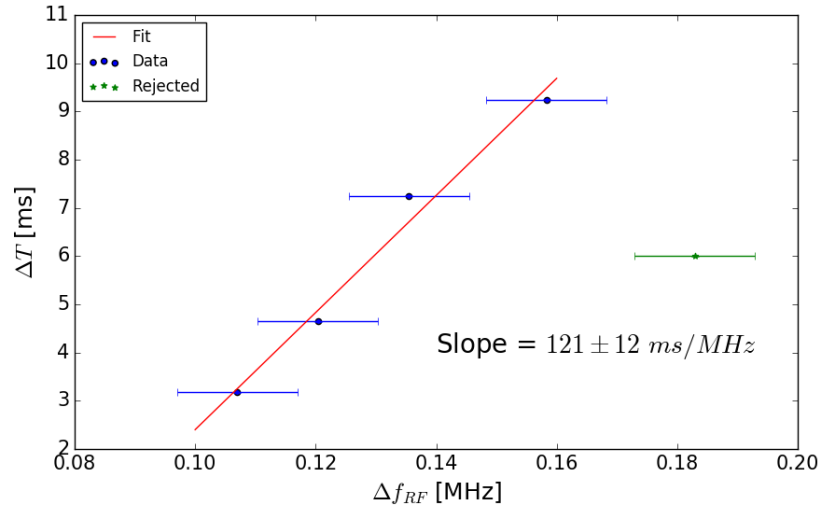Figure 7: Linear least squares fit for determining the change in time position of the NMR signal as a function of change in f_{RF}, where the out-lier data point at 0.18 MHz is excluded as previously mentioned.