

Pulsed NMR of Paramagnetic Terbium

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1 - Introduction

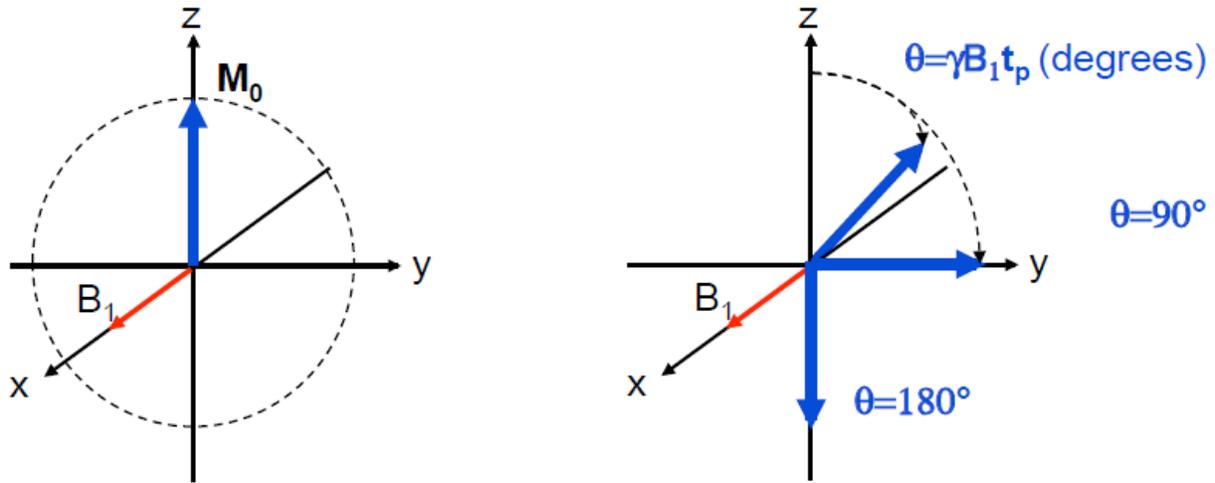
The magnetic properties of atomic nuclei have proven to provide very useful information which can directly be used in very practical applications. The parameters obtained from Nuclear magnetic resonance (NMR) spectroscopy, provide information that is widely used today in medicine, chemistry, and biological and chemical physics. One of the most commonly used NMR techniques is that of magnetic resonance imaging (MRI), which is used today by hospitals in order to capture images of internal tissues of the human body without the need of any invasive surgical procedures. NMR spectroscopy is also used to study the chemical reactivity in molecules, and is now beginning to become a useful method in determining the structures of proteins.

NMR was made possible by studying a specific property of the atomic nucleus called the magnetic moment. Most atomic nuclei, but not all, have what is called a quantum spin angular momentum. The nucleus spins about a specific axis which is referred to as the spin axis or the magnetic moment (μ). These moments, when present in a constant magnetic field (\mathbf{B}_0), will align either parallel or anti-parallel to the field; much like a compass aligning with the earth's magnetic field. In liquid or solid NMR, there will be a majority of nuclei in one direction resulting in a bulk magnetization (\mathbf{M}_0) in one direction of the magnetic field. This direction is most commonly noted as the +z direction in the reference frame. Unlike the analogy of the compass, a magnetic moment will naturally precess about the magnetic field, with an angular frequency (ω_0) proportional to the strength of the magnetic field. This state is called the resonance condition, and is given by the following equation known as the Larmor Frequency:

$$\omega_0 = \gamma \mathbf{B}_0$$

Where γ is a constant specific to each nucleus called the gyromagnetic ratio.

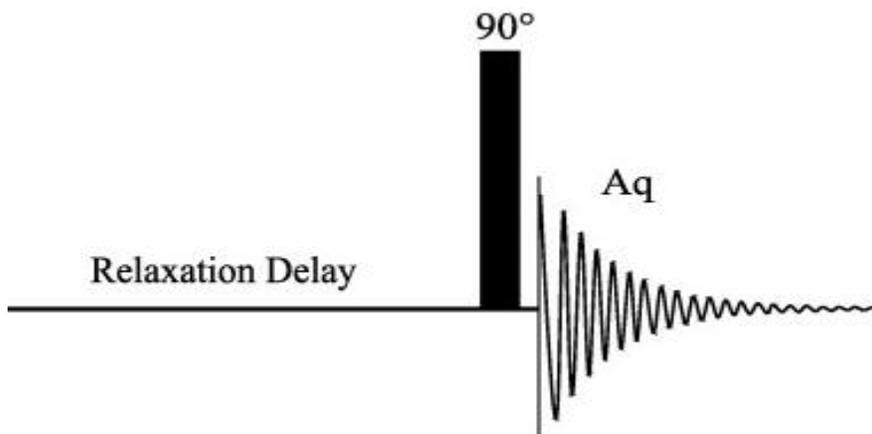
In pulsed NMR, a torque force is applied, perpendicular to the magnetic moment, tipping it towards the x-y plane. This torque is applied as a radio frequency (rf) pulse, denoted as \mathbf{B}_1 . The effect on the bulk magnetization is mainly determined by the magnitude, and duration that the rf pulse is applied. A vector representation of this can be seen in the figure below:



Effect of an RF pulse on M_0 with B_0 in the +z direction

As seen in the figure above, two important rf pulses to examine are the 90° pulse which points M_0 parallel to the x-y plane, and the 180° pulse which reverses the direction of M_0 . Once excited by the pulse, the moments dephase back to the original resonance condition; this dephasing process is referred to as relaxation.

It is common in NMR spectroscopy, that the net magnetization be measured along the x-axis, thus after a 90° pulse, the magnetization will be at a maximum and as it dephases around the z-axis, the spectrum is represented as a free induction decay (FID). An example of this can be seen in the figure below:



NMR spectrum following a 90° rf pulse

1.1 - Relaxation Times & the Bloch Equations

The information that becomes useful from NMR spectra are the time constants in the dephasing of a given solution. The 2 relaxation processes measured are called the T1 (longitudinal, spin-lattice) relaxation, and T2 (spin-spin) relaxation.

Spin-lattice relaxation is comprised of many different mechanisms such as dipole-dipole interactions, chemical shift anisotropy, scalar interactions and a few other minor components. T1 results in recovery to equilibrium to 63%, and is therefore usually much larger than measured T2. Spin-spin relaxation is related to the imperfections in the magnetic field. Inhomogeneity in the field causes imperfect dephasing and as a result, the spins of the individual nuclei interact with one another, causing faster decay. Thus, T2 is the measure of the individual spins and their interactions with each other causing a faster decay to equilibrium. This T2 causes 37% of recovery to equilibrium.

To calculate these times, it is important to note along which axis the magnetization is being measured and the specific pulse sequences being used (further explanation in section ()). From these values we can use the famous Bloch equations presented below.

$$M_x(t) = [M_x(0)\cos\omega t - M_y(0)\sin\omega t]e^{(-t/T2)}$$

$$M_y(t) = [M_x(0)\sin\omega t + M_y(0)\cos\omega t]e^{(-t/T2)}$$

$$M_z(t) = M_{eq} + [M_z(0) - M_{eq}]e^{(-t/(T1))}$$

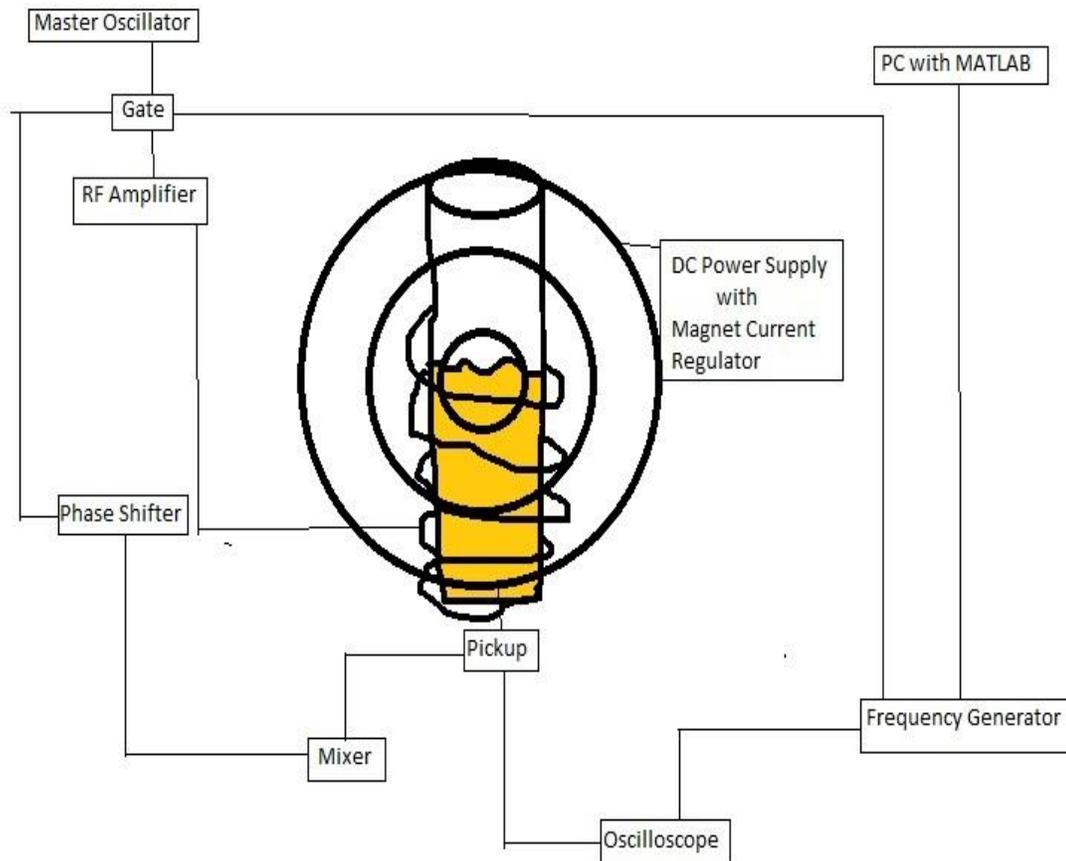
2 - Experiment

In regards to magnetization, an element can be of three main types. The first is diamagnetic which means that in the presence of a magnetic field, the element will not become magnetized or act as a magnetic dipole. If an element is classified as paramagnetic, then it will become magnetized but only while in the presence of a magnetic field. The third type is ferromagnetic, which means that the element will become magnetized in a magnetic field and also maintain its magnetic properties after it has been removed from the field. In paramagnetic elements, there is a measure of magnetization which is called the magnetic susceptibility. This could be given in terms of mass, molar or volume magnetic susceptibility.

For this experiment we will be taking a look at the NMR spectra and measuring the relaxation times of Terbium, which has the highest constant in magnetic susceptibility. Then comparing these values to Calcium, which has a lower magnetic susceptibility, and Iron, which is a ferromagnetic element. The values of the molar magnetic susceptibilities can be seen below.

Element Name	Molar Magnetic Susceptibility
Terbium	2.131685×10^{-6}
Calcium	5.531×10^{-10}
Iron	N/A

2.1 - Experimental setup



The diagram above represents the setup of components used in this NMR experiment. As seen, the sample is placed in-between two Helmholtz coils which create the magnetic field. The coils are powered by a DC power supply with a voltage of 30.6V and a Magnet Current Regulator adjusted to provide a current of 2.356A. Wrapped around the sample test tube, is the pickup coil which both sends out the rf pulses and also detects the magnetization within the sample.

A PC with MATLAB controls a waveform generator to output pulses at 5V which allows the signals from a master oscillator at 10MHz and RF Power Amplifier to be transmitted to the pickup coil.

The mixer allows for filtering of noise coming from the master oscillator and the pickup coil, while the phase shifter tunes and synchronizes the simultaneous signals.

Finally, the magnetization signal flows through a low-pass filter, then into an oscilloscope to be displayed in terms of voltage. All data came from the signal output of the oscilloscope.

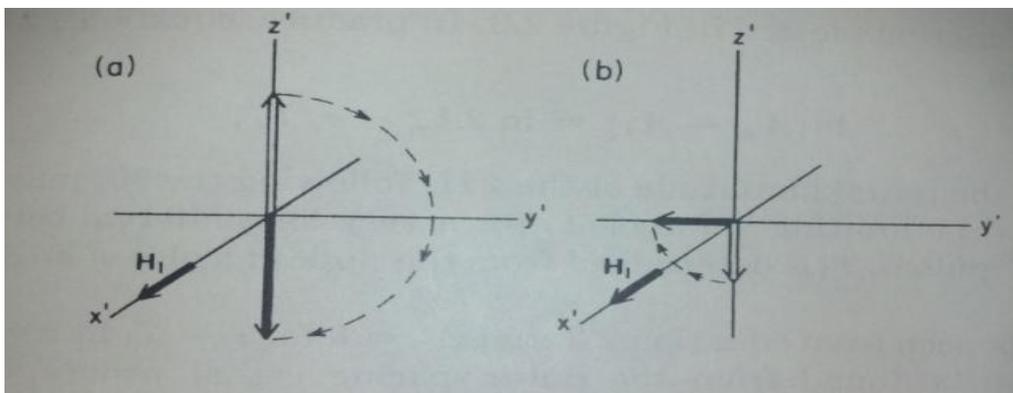
2.2 - Samples and Pulse Widths

To test the three elements, .1M (100mM) solutions of Terbium (III) Nitrate, Calcium (III) Nitrate and Iron (III) Nitrate were created with water as a solvent.

The most common method used to determine the 90° pulse, is to increase the pulse on a sample incrementally until the signal is found to be as close to 0 as possible. The time for this pulse is the 180° pulse and half that time is what is used at the 90° pulse. To test this, pulse widths close in the range of the calculated 90° pulse were used to make sure they displayed smaller maximum magnetizations.

2.3 - Measuring T1

The common $180^\circ, t, 90^\circ$ sequence was used to measure T1. The procedure works by first employing a 180° pulse to invert M_z to go from the value of $-M_0$ to M_0 . After a time t , a 90° pulse to rotate M to the y axis. At this point, a FID occurs which is proportional to the magnitude of M . The initial amplitude is plotted as a function of t , after having repeated the sequence for multiple values of t . Below is a vector representation of the process.



Using the following equation from the Bloch equations:

$$M_z = M_0(1 - 2e^{-(t/T1)})$$

We plot a log-based linear fitting using:

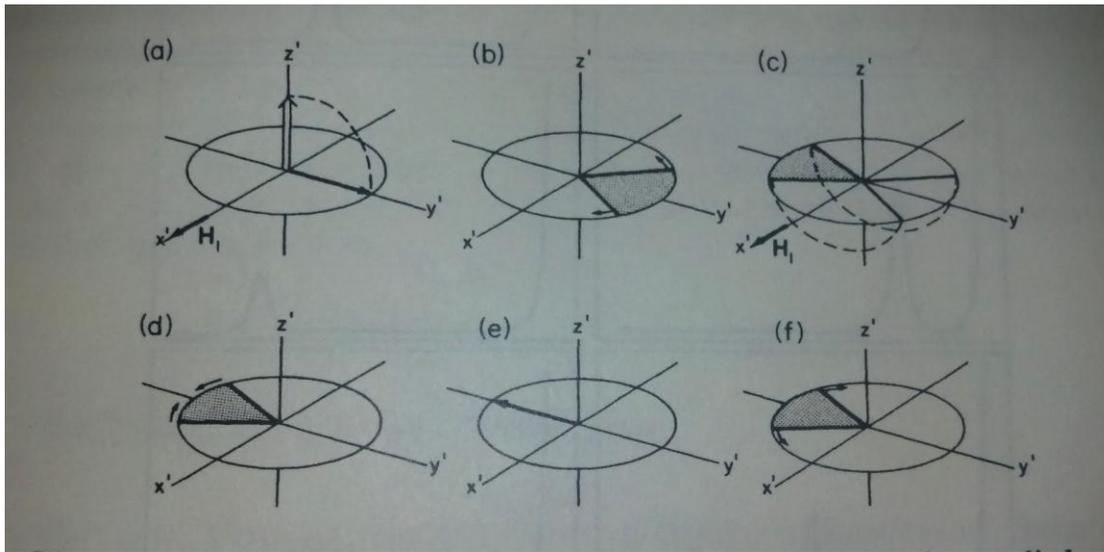
$$\ln(1 - M_z/M_0) = -t/T1$$

From this we can use the slope to calculate T1.

2.4 - Measuring T2

To measure T2, the Hahn spin-echo method was used which is composed of a $90^\circ, t, 180^\circ, t, [\text{echo}]$ sequence. The sequence begins by tipping M to the y axis with a 90° pulse. At this point, the dephasing from the inhomogeneous field causes some moments to decay faster than others. After a time t , the 180° pulse cause all moments to rotate 180 degrees about the x -axis. This “time reversal” causes the moments to all come together once again after another

period of time t . At this point $(2t)$, a spin echo is observed. This mechanism can be viewed in the diagram below.



The maxima of the spin-echoes, measured over sequences using multiple values of t , can be used just as with $T1$ except with the Bloch equation:

$$M_{xy}(t) = M_0(e^{-t/T2}).$$

Using the log-scale we get:

$$\ln(M_{xy}(t)) - \ln(M_0) = -t/T2.$$

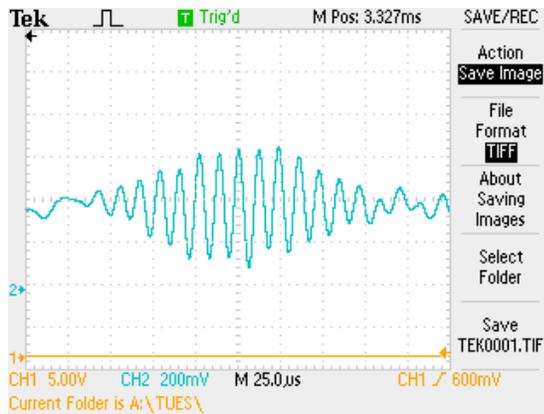
3 - Results

Using the methods described above the following $T1$ and $T2$ values were found for the solutions:

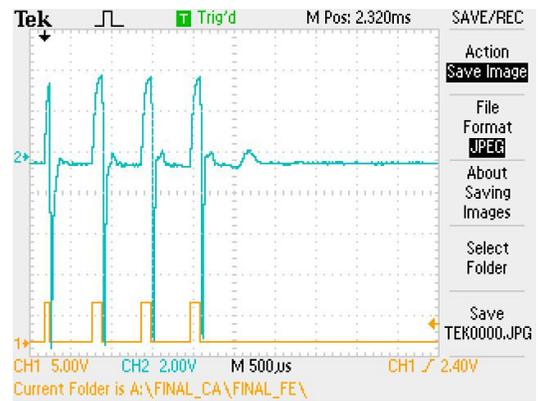
Element Name	$T1$ (ms)	$T2$ (ms)
Calcium	37.037	20.3915
Iron	30.0307	18.584
Terbium	7.402	2.6838

4 - Conclusions

Though Terbium was expected to have lower $T1$ and $T2$ values than both Calcium and Iron, the values showed to be much lower than expected. Unfortunately, no literature values for Terbium were found to compare however, the calculated values for Calcium and Iron both coincided closely to relaxation times found in other solutions containing these elements. Having noted this, the $T2$ value for Iron might not be valid given that instead of a spin-echo showing, a bump was presented instead. Below, the screenshot for an Iron spin-echo is shown compared to a spin-echo for Terbium.



(a) Terbium spin-echo



(b) Bump from Iron after 4th 180^o pulse

It is difficult to determine the validity of all results, however it should be noted that relative to each other, the values obtained were expected. Due to the high magnetic susceptibility of Terbium, the moments were more strongly attracted to the magnetic field and therefore, the overall relaxation time was less. For future experiments, it would be recommended to further analyze the effects of the ferromagnetic elements in a magnetic field in order to determine the effects on T1 and T2 relaxation times.

References

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