**T1 and T2 NMR**

**Physical Chemistry II Lab**

**CHM4111L**

**Dr. Clark**

**1. Objective and Relation to Lecture**

Provide a brief description of the purpose of the experiment. What are you trying to achieve or learn?

**2. Introduction / Theory**

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful analytical tool in chemistry and biochemistry, with applications ranging from structural determination of molecules to exploring dynamic processes in materials. NMR relies on the fact that certain atomic nuclei possess an intrinsic angular momentum, or spin, which gives rise to a magnetic moment. The interaction of these nuclear magnetic moments with an external magnetic field forms the basis of NMR. In this experiment, we focus on two important NMR relaxation processes: **spin-lattice relaxation (T₁)** and **spin-spin relaxation (T₂)**, both of which provide insight into the interactions of nuclei with their surroundings.

**Basic Principles of NMR**

Nuclei such as protons (¹H) have an intrinsic angular momentum, or spin, denoted by **I**. The magnetic moment, **μ**, associated with this spin is proportional to the spin angular momentum vector, and is given by:

where **γ** is the gyromagnetic ratio, a constant specific to each nucleus. When placed in an external magnetic field **B₀**, the magnetic moments of the nuclei tend to align either with (parallel) or against (antiparallel) the field, leading to two distinct energy levels for nuclei with spin ½. The energy difference between these two orientations is given by:

where **ΔE** is the energy difference, ℏ is the reduced Planck’s constant, and **B₀** is the strength of the magnetic field. The population of nuclei in the two energy states follows a Boltzmann distribution, with slightly more nuclei in the lower energy state at thermal equilibrium.

The application of a radiofrequency (RF) pulse at the resonance frequency, **ν₀**, causes transitions between the two energy levels, flipping the spin populations. This frequency is related to the strength of the external magnetic field by the **Larmor equation**:

After the RF pulse is turned off, the system returns to equilibrium through relaxation processes, characterized by two timescales: **spin-lattice relaxation (T₁)** and **spin-spin relaxation (T₂)**.

**Spin-Lattice Relaxation (T₁)**

Spin-lattice relaxation, or longitudinal relaxation, is the process by which the nuclear magnetization vector returns to its equilibrium value along the direction of the applied magnetic field (**z-axis**). During this process, energy is transferred from the excited nuclear spins to their surrounding environment, or lattice. The recovery of magnetization follows an exponential behavior, described by the equation:

where **M\_z(t)** is the magnetization at time **t**, **M₀** is the equilibrium magnetization, and **T₁** is the spin-lattice relaxation time. A longer **T₁** indicates slower energy transfer between the spins and the lattice.

**Spin-Spin Relaxation (T₂)**

Spin-spin relaxation, or transverse relaxation, refers to the loss of phase coherence between nuclear spins in the transverse plane (perpendicular to the magnetic field). This process occurs due to interactions between neighboring nuclear spins, leading to a dephasing of the magnetization. The decay of transverse magnetization is also exponential, given by:

at time **t**, and **T₂** is the spin-spin relaxation time. Unlike **T₁**, **T₂** is sensitive to interactions between spins and provides information on the local molecular environment.

**Relationship Between T₁ and T₂**

While **T₁** is typically longer than **T₂**, the two relaxation times are independent, and each reveals different aspects of molecular dynamics. In general, **T₁** reflects the rate of energy exchange between nuclear spins and their surroundings, whereas **T₂** relates to the coherence of spin states due to interactions within the system.

In this experiment, we will use a table-top NMR instrument to measure **T₁** and **T₂** for protons in three different samples: mineral oil, glycerin, and water doped with a small amount of CuSO₄. The presence of CuSO₄ acts as a paramagnetic relaxation agent, influencing the relaxation times by enhancing the rate of energy transfer.

These measurements will provide insights into how different environments affect the relaxation mechanisms of nuclear spins and help us better understand the molecular interactions at play in each sample.

**3. Materials and Equipment**

* TeachSpin NMR spectrometer
* Oscilloscope
* Mineral oil sample
* Glycerin sample
* Water sample doped with CuSO4
* Sample holder
* TeachSpin manual
* Metallic-free environment near the magnet

**4. Safety Precautions**

* **Magnetic Field Caution:** Avoid placing any metallic objects near the magnet to prevent hazards.
* **Electrical Safety:** Do not disconnect any leads from the control panels to the magnet during the experiment.
* **Equipment Handling:** Ensure no liquid (e.g., from the samples) comes into contact with the magnet or control panels..

**5. Experimental Procedure**

**Stage 1: Familiarization with Instrumentation**

1. Set up the TeachSpin instrument and the oscilloscope, following instructions in Sections A1 and A2 of the manual.
2. Produce a single RF pulse to observe its behavior on the oscilloscope.

**Stage 2: Pulse Sequence Generation**

1. Generate a pulse sequence using the TeachSpin pulse programmer.
2. Observe the output on the oscilloscope.

**Stage 3: Frequency Tuning and Signal Maximization**

1. Place the sample in the holder and configure the spectrometer as per the manual (e.g., set pulse width to 20%, mode to INT).
2. Use the oscilloscope to monitor the output and adjust the frequency until resonance is achieved.
3. Adjust the receiver input for maximum signal by fine-tuning the instrument knobs.

**Stage 4: Measurement of T1 Relaxation Time**

1. Set the pulse programmer to deliver a 180° pulse followed by a time delay and a 90° pulse to produce free induction decay (FID).
2. Measure the amplitude of the FID signal over varying delay times.
3. Record the data and analyze the decay curve to determine T1.

**Stage 5: Measurement of T2 Relaxation Time**

1. Set the pulse sequence to deliver a 90° pulse, followed by a time delay, a 180° pulse, and another delay to produce a spin echo.
2. Measure the echo signal over time delays, analyzing the decay curve to determine T2.

**7. Calculations and Analysis**

**Calculations and Analysis:**

1. **T1 Calculation:**
   * Plot magnetization intensity as a function of time. The intensity should follow a relaxation curve described by first-order kinetics.
   * Use Mathcad or another fitting tool to analyze the decay and extract the T1 value for each sample (mineral oil, glycerin, CuSO4-doped water).
2. **T2 Calculation:**
   * Plot the spin-echo intensity as a function of time. The echo intensities will decay over time, following a T2 relaxation curve.
   * Perform a logarithmic fit to determine the T2 value.

Graphs of magnetization intensities and spin-echo signals will be created for each sample to illustrate the relaxation processes. These relaxation times provide insights into the interaction between nuclear spins and their surrounding environments.

**Question1 Define spin-lattice (T₁) and spin-spin (T₂) relaxation times in NMR. How do these relaxation processes differ in terms of physical interactions?**

**Question2 Why is T₁ typically longer than T₂ in most samples? What molecular or environmental factors could cause these times to differ significantly?**

**Question3 In this experiment, what was the purpose of adding CuSO₄ to the water sample? How did the presence of CuSO₄ affect the relaxation times compared to the other samples?**

**Question4 Explain how the Larmor frequency is related to the external magnetic field in NMR. What role does this frequency play in the resonance condition of nuclear spins?**

**Question5 Discuss the exponential nature of the relaxation processes. How did the data you collected reflect this behavior, and what mathematical models did you use to fit your results?**

**Question6 How does molecular motion influence the T₁ and T₂ relaxation times? Compare the relaxation times for the three samples used (mineral oil, glycerin, and CuSO₄-doped water) and discuss the molecular dynamics in each.**

**Question7 Describe how temperature might affect the values of T₁ and T₂ for a given sample. What changes would you expect if you repeated this experiment at a higher or lower temperature?**

**Question8 Explain how the table-top NMR instrument measures relaxation times. What steps were involved in obtaining accurate values of T₁ and T₂ for your samples?**

**Question9 What sources of experimental error could affect the accuracy of your T₁ and T₂ measurements? Suggest potential improvements to the procedure that could minimize these errors.**

**Question10 Based on your understanding of NMR relaxation processes, how could you use the measurement of T₁ and T₂ to gain insight into the structural properties or dynamics of an unknown sample?**