

Pulsed NMR Spectroscopy

Introduction

Nuclear Magnetic Resonance spectroscopy, or NMR spectroscopy, is one of the most valuable analytical techniques available to chemistry. An NMR spectroscopy experiment consists of irradiating an ensemble of nuclear spins in H_0 with a radio frequency magnetic field, to induce transitions from the lower Zeeman energy level to the upper Zeeman level. This task is made relatively difficult by the very small population difference between these two levels. In addition, one cannot induce transitions between the two Zeeman levels at a rate greater than the natural relaxation times that describe how the nuclear spins achieve equilibrium with their surroundings. A vital part of magnetic-resonance spectroscopy concerns the study of these relaxation times to better understand inter- and intramolecular interactions. The experiment you will conduct in the laboratory involves measurement of spin-lattice (T_1) and spin-spin (T_2) relaxation times for protons in a variety of environments. Background information on pulsed NMR spectroscopy is available in Chapter 19 “Nuclear Magnetic Resonance Spectroscopy” in *Principles of Instrumental Analysis, 5th edition* by Skoog, Holler, and Nieman and in Chapter 18 “Spectroscopy 3: Magnetic Resonance” in *Physical Chemistry, 6th edition* by Atkins.

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When a spin $1/2$ nucleus is placed in an external magnetic field, H_0 , two separate Zeeman levels result. Magnetic resonance is carried out by inducing transitions between Zeeman levels. The energy separation between adjacent levels can be used to find the transitions frequency ν

$$\Delta E = h\nu = g_n \mu_N H_0 = \gamma_n \hbar H_0. \quad (1)$$

Here g_n is the nuclear g factor for a given nucleus, $\mu_N \equiv e\hbar/2m_p c$ is the nuclear magneton, and $\gamma_n = g_n \mu_N / \hbar$ is the magnetogyric ratio. The separation between the energy levels and the transition frequency depend on the magnitude of the external magnetic field. If angular frequency units, ω (radians/second) = $2\pi\nu$, are used, the photon whose energy is equivalent to the Zeeman splitting will be

$$\omega_0 = \gamma_n H_0. \quad (2)$$

The behavior of nuclear magnetism can be described using a classical model. This model is the basis of the Bloch equations. If H_0 defines the z direction, an individual nuclear magnetic moment will precess around the z axis, as shown in Figure 1. The angular frequency of this precession is ω_0 . The number of magnetic moments contained in a typical NMR sample is not one, but roughly 10^{18} . These can be represented by a distribution of magnetic moments placed about the cone of precession shown in Figure 1 for the “spins” in the lower-energy state and similar cone-shaped distribution directed along $-z$ for the higher-energy state. The vector sum of all of these magnetic moments yields a single bulk magnetization vector, M_0 , that will be parallel to H_0 (z) at thermal equilibrium (Figure 2). (There is a slight excess of spins in the lower-energy state.) The population of Zeeman levels can be perturbed from equilibrium by an rf magnetic field H_1 of angular frequency

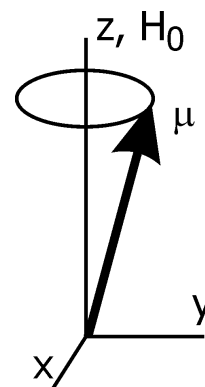


Figure 1: Precession of nuclear spin around external field.

ω_0 , applied along the x or y axis. It is much easier to understand the dynamic behavior of this system by considering a new coordinate system, having the same origin and z axis as Figure 1 but with the new axes perpendicular to z , x' and y' , that rotate at angular frequency ω_0 . In this “rotating coordinate system,” M_0 and H_1 will appear to be stationary and at right angles to one another. In a pulsed-NMR experiment, the rf field is turned on briefly to perturb M_0 from its equilibrium state. The return of M_0 to its original position along z is governed by spin relaxation processes and carries the information contained in an NMR spectrum in its time evolution.

When a resonant H_1 field is applied to the equilibrium magnetization, M_0 , of Figure 2, it produces a torque on this vector that causes precession around the H_1 field axis (x -axis). This is an identical phenomena to precession around the z -axis produced by the external magnetic field. The precessional frequency in the yz plane is given by

$$(\omega)_{yz} = \gamma_n H_1. \quad (3)$$

The H_1 field (10^{-3} -100G) is much smaller than the H_0 field, and the precessional frequency is correspondingly smaller ($3-3 \times 10^6 \text{ sec}^{-1}$). A receiver, or detector, coil is placed along the y -axis and, as the magnetization vector sweeps through this axis, an NMR signal is detected. This method of detection occurs by magnetic induction. Each magnetic moment generates a weak local field given roughly by μ_N / r^3 . The fluctuating magnetic field created by the motion of the

moments (or spins) gives rise to a dH/dt that induces a current in the receiver coil when it has a projection along y .

If the H_1 field is turned on for a short period of time and then turned off (pulse of the rf field), the M_0 vector will precess through a fixed Θ .

$$\Theta = \gamma_n H_1 t \quad t = \text{pulse width} \quad (4)$$

For example: If the H_1 field is 10 G and the pulse width is 5.9×10^{-6} seconds, the M_0 vector for protons will turn 90 degrees. The magnetization vector will be along the y axis, and maximum NMR signal will be induced in a receiver coil placed along the y axis. After the pulse is turned off, the magnetization vector will return to its equilibrium position along the z -axis. The decay back to equilibrium is called a free-induction decay (FID), as there are no external fields (in the rotating frame) acting on the magnetization vector. The x , y , and z components will change as the M vector returns to M_0 . The time constant for reaching equilibrium along the x and y axes is the spin-spin relaxation time T_2 and the time constant for the z component to reach equilibrium is the spin-lattice relaxation time T_1 . As the magnetization vector returns to equilibrium, the y component will decrease and the NMR signal will decrease.

The z component of magnetization determines the total energy of the spin system, and the spin-lattice relaxation time determines the rate of energy transfer between the spin system and the lattice. Spin-spin relaxation does not affect the total energy of the spin system and can be thought of as a time constant for interchange of energy within the spin system. In solution, these two relaxation times are generally almost identical. In solids, the relaxation times are normally very different. Energy transfer between the spin system and the lattice is generally rather inefficient in solid samples, and the spin-lattice relaxation time

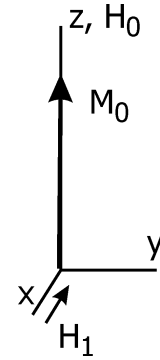


Figure 2: Bulk magnetization vector M_0 and applied rf field H_1 .

is long. Energy transfer within the spin system may be very efficient and the spin-spin relaxation time may be very short.

Dipolar Relaxation

A variety of types of interactions can lead to spin-lattice relaxation. The most common of these are dipolar interactions between nuclear spins, or between nuclear spin and electron spins and scalar spin-spin interactions. In solution, these interactions can be modulated by rotational motion of the molecules, and spin-lattice relaxation times may be rather short (e. g., 10^{-5} sec. to 5 sec.). In the solid state, energy is generally not efficiently transferred to the lattice, and the spin-lattice relaxation time may be hours. In order to determine exact equations for relaxation times, one must specify the magnetic interactions that lead to the local fields, the mechanism to produce a time dependence for the local fields, and then use statistical mechanics to derive the equations. Each proton in a sample is a magnetic dipole that can produce a dipolar field at a second type of proton in the sample. The dipolar field is given by

$$H_{dipolar} = \frac{3}{4} g_n^2 \beta_n^2 \frac{(1 - 3 \cos^2 \theta)}{r^3} \quad (5)$$

In this expression, $g_n \beta_n$ give the magnetic moment of the nuclei that are separated by a distance r . The vector connecting the two nuclear spins makes an angle θ with the direction of the external magnetic field. The local magnetic field from this interaction varies as the molecule rotates, as θ takes all possible values as the molecule assumes different orientations with respect to the field.

The equations for the relaxation times derived for rotational modulation of the dipolar interaction of two protons are given by

$$\frac{1}{T_1} = \frac{3}{20} \left(\frac{g_n^4 \beta_n^4}{2r^6} \right) \left[\frac{2\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{8\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \quad (6)$$

$$\frac{1}{T_2} = \frac{3}{40} \left(\frac{g_n^4 \beta_n^4}{2r^6} \right) \left[6\tau_c + \frac{10\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]$$

In this equation ω_0 is the nuclear Larmor frequency and τ_c is the rotational correlation time (time characteristic of molecular rotation). When $\omega_0^2 \tau_c^2 \ll 1$, both T_1 and T_2 vary as $1/\tau_c$ and are equal. This is the situation for most small molecules in low-viscosity solutions, as τ_c is about 10^{-12} s and ω_0 is about 10^9 . In solutions of higher viscosity or in cases in which molecular rotation is slow, $\omega_0^2 \tau_c^2 \gg 1$ and T_1 varies as τ_c , while T_2 varies as $1/\tau_c$. The divergence of the two relaxation times, in this case, arises from the $6\tau_c$ term in the equation for $1/T_2$. This term is due to low-frequency components of molecular motion that affect T_2 but not T_1 . A plot of T_1 and T_2 versus viscosity is given in Figure 3.

The magnetic moment of an unpaired electron spin is about 1860

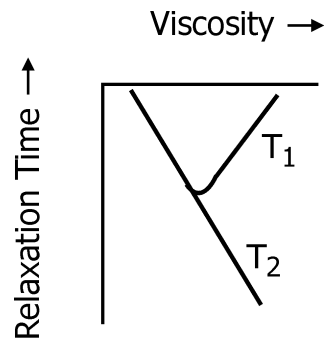


Figure 3: Behavior of T_1 and T_2 as a function of the viscosity of a solution.

times greater than that of a proton, and the dipolar interaction is correspondingly greater. Cu^{++} ions have a single unpaired electron spin that can interact with protons via a dipole-dipole interaction. The equations for the relaxation times of protons in the presence of Cu^{++} ions in solution at room temperature are given by

$$\frac{1}{T_1} = [\text{Cu}^{++}] \frac{3}{20} \left(\frac{g_n^2 \beta_n^2 g^2 \beta^2}{2r^6} \right) \left[3\tau_c + \frac{7\tau_c}{1 + \omega_s^2 \tau_c^2} \right] \quad (7)$$

$$\frac{1}{T_2} = [\text{Cu}^{++}] \frac{3}{40} \left(\frac{g_n^2 \beta_n^2 g^2 \beta^2}{2r^6} \right) \left[7\tau_c + \frac{13\tau_c}{1 + \omega_s^2 \tau_c^2} \right]$$

In this equation, $g\beta$ gives the magnetic moment of the electron spin, $g_n \beta_n$ gives the magnetic moment of the proton nuclear spin, ω_s is the Larmor frequency of the electron, and τ_c is the rotational correlation time. The Cu^{++} concentration, $[\text{Cu}^{++}]$, determines the number of electrons that are present to interact with the water molecules. The water molecules must rapidly move in and out of the coordination sphere of the Cu ions in order to have a single relaxation time.

Determining Relaxation Times

The x and y components of magnetization vector M decay exponentially and the NMR signal in the time domain will appear as an exponential decay with a time constant T_2 . T_2 is always shorter than T_1 , and the time constant characteristic of the decay after a pulse will be T_2 . If the magnetic field inhomogeneity is less than the natural line width of an NMR signal, the line width can be used to directly measure the spin-spin relaxation time T_2 .

When there is no saturation of the nuclear level populations (H_1 is sufficiently small such that $\gamma^2 H_1^2 \ll T_1 T_2$), the line shape of the absorption signal is given by

$$g(\nu) = \frac{T_2}{[1 + T_2^2 (2\pi)^2 (\nu - \nu_0)^2]} \quad (7)$$

This is the equation for a Lorentzian line. In many instances, one can, therefore, directly measure the spin-spin relaxation time from the full width at half maximum $\Delta\nu_{1/2}$ of the absorption signal

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} \quad (8)$$

The spin-lattice relaxation time can be measured by irradiating the sample with two pulses separated by a time t . The first pulse turns the magnetization vector by 180° so it is pointed along the negative z -axis. After a time (t), a 90° pulse is applied. The z component of the magnetization vector relaxes back toward its equilibrium value during the time period between pulses. If a time that is very short, compared to T_1 , is set between the pulses, the magnetization vector will remain nearly along the negative z -axis, and the 90° pulse will turn this vector to the negative y -axis. In this case, the FID will have a maximum negative value. If the time between the 180° and 90° pulse is long, compared to T_1 , the z component of magnetization will relax completely back to its equilibrium value along the positive z -axis. The 90°

pulse will then turn the magnetization vector along the positive y -axis and a maximum positive FID will be observed. If the time between pulses is set between these two extremes, the z component should vary between the maximum negative and positive values. The FID will also vary between the maximum negative and maximum positive values. The FIDs can be Fourier transformed to yield Lorentzian lines, which will initially be negative, will diminish in size, be equal to zero, become positive, and then go to a maximum positive value.

The behavior of the z component of magnetization that is reflected in the sign and magnitude of both the FID and the frequency domain NMR signals can be analyzed to allow one to measure T_1 directly. The z component of magnetization is given by the Bloch relation

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1} \quad (9)$$

If one sets $M_z = M_0$ at time = 0 and integrates this equation, one obtains:

$$M_z = M_0 \left(1 - 2e^{-t/T_1} \right) \quad (10)$$

In this equation, M_z is the amplitude of the FID or NMR signal observed from an experiment with a pulse separation t . A plot of M_z as a function of pulse separation is given in Figure 4. M_0 is the amplitude of the FID or NMR signal observed when $t \gg T_1$. It is often replaced with A_∞ , the amplitude after the magnetization vector has completely recovered from the 180° pulse. If one takes the natural log of this equation and replaces the M_z with A_t and M_0 with A_∞ , one finds

$$\ln(A_\infty - A_t) = \ln 2A_\infty - \frac{t}{T_1} \quad (11)$$

One can plot the left side of this equation versus t and obtain T_1 from the slope of the line. Note that, when $A_t = 0$, one can solve directly for T_1 as

$$T_1 = \frac{t}{\ln 2} = \frac{t}{0.693} \quad (12)$$

This is called the T_1 null method and allows one to obtain a quick estimate of T_1 by finding the pulse separation where the FID or NMR signal has zero amplitude.

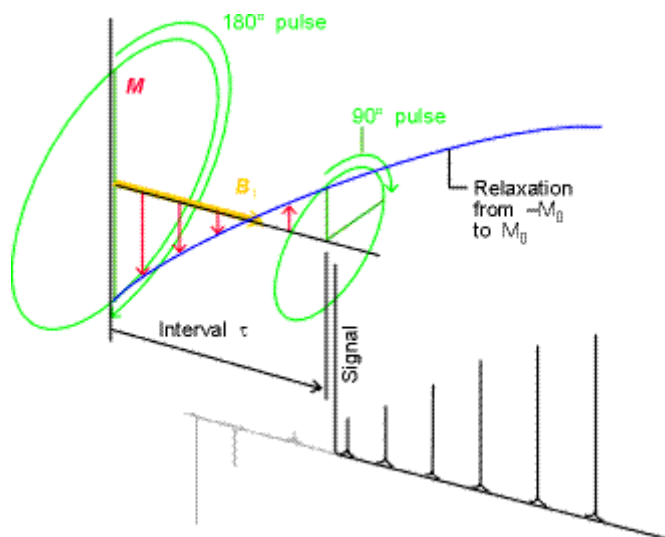


Figure 4: The result of applying a 180° pulse to the magnetization in the rotating frame and the effect of a subsequent 90° pulse. Taken from Atkins, *Physical Chemistry*, 6th edition.

Procedure

For each pulsed-NMR measurement, you should use a 180° pulse width of $70\ \mu\text{s}$ and a 90° pulse width of $35\ \mu\text{s}$. An interval of 60 s between 180° pulses can be used for all solutions.

Collect NMR spectra of 2-methyl-1-bromopropane using the following separation times (in seconds) between 180° and 90° pulses given below:

2-methyl-1-bromopropane: 30, 30, 20, 18, 16, 14, 12, 10, 8, 4, 2

Collect NMR spectra for water protons in solutions containing 0, 0.1, 0.5, and 1.0 mM Cu^{++} . Use the following separation times (in seconds) between 180° and 90° pulses given below for each solution:

0 mM Cu^{++} : 30, 30, 21, 20, 19, 18, 17, 16, 15

0.1 mM Cu^{++} : 30, 30, 18, 14, 12, 8, 4, 2

0.5 mM Cu^{++} : 30, 30, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5

1.0 mM Cu^{++} : 30, 30, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9

Collect NMR spectra for water protons in solutions containing 10% ethylene glycol/5% H_2O /85% D_2O and 50% ethylene glycol/5% H_2O /45% D_2O . Use the following separation times (in seconds) between 180° and 90° pulses given below for each solution.

10% ethylene glycol: 30, 30, 9.6, 9.4, 9.2, 9.0, 8.8, 8.6

50% ethylene glycol: 30, 30, 3.0, 2.8, 2.6, 2.4, 2.2, 1.8

Data Analysis

Estimate T_2 from the lineshapes obtained for the three different sets of protons on 2-methyl-1-bromopropane.

Use the null method to estimate T_1 for the three different classes of protons of 2-methyl-1-bromopropane.

Use the inversion recovery method to deduce T_1 for the water protons in the water-ethylene glycol mixture, the water solutions containing Cu^{++} , and the pure water solution. Include in your report a representative plot of amplitude vs. pulse delay time for the pure water solution. T_2 's for these solutions should be estimated from the lineshape of the proton resonance.

Using the expressions in the lab handout, determine τ_c , the rotational correlation time, and r , the average Cu^{2+} -proton distance for $\text{Cu}(\text{H}_2\text{O})_6$. Assume $g = 2.11$ for Cu^{2+} in your calculations.

Questions

Explain the observed trend in T_1 's for the proton groups in 2-methyl-1-bromopropane. Does the trend favor inter- or intramolecular dipolar interactions as a relaxation mechanism?

How does the average Cu^{++} -proton distance compare with the equilibrium bond length for H_2O ?

What would be the effect of dissolved oxygen on the relaxation of water protons in a 95% D_2O /5% H_2O solution?

Compare the relaxation constants obtained for water protons in water-ethylene glycol mixtures with those determined for the pure water solution. Explain the changes in T_1 and T_2 as a function of the solution viscosity.

Explain the trends observed when different damping times were used for the time-domain signal in MATLAB Exercise I.

Explain the trends observed when different pulse widths were employed to explore the bandwidth of frequencies for a pulsed NMR experiment in MATLAB Exercise II.

Matlab Exercises for Pulsed NMR Experiment

In a pulsed-NMR experiment, the magnetization transverse to the lab field axis is followed as a function of time. The data are then processed by Fourier transformation to yield the familiar frequency-based NMR spectrum. These NMR signals, or free-induction decays (FIDs), take on the form of exponentially damped sinusoidal functions, where the oscillation frequencies are the frequency offsets, or chemical shifts, from the rf carrier frequency. Consider a peak in a proton NMR spectrum resolved at 5.0 ppm. For data collected with the 300-MHz spectrometer in our lab, this 5.0 ppm peak is represented in the time domain by an exponentially damped sinusoidal oscillation with an oscillation frequency of

$$\begin{aligned} 5.0 \times 10^{-6} \times 300 \text{ MHz} &= 0.0015 \text{ MHz} \\ &= 1.5 \text{ kHz} \end{aligned}$$

- I. Examine the relationship between time and frequency-domain signals, using the Fast Fourier Transform capabilities of the MATLAB math package. MATLAB can be found on the PC's in the computer lab on the first floor of the Chemistry Building. To perform this task, we will use MATLAB to generate an exponentially damped 1.5 kHz oscillating function and then take its Fourier transform. The steps for performing this task are given below, along with explanations for each step.

Procedure:

- A. Log in on the PC and go to Windows, then Matlab for Windows.
- B. Choose: Matlab 4.21c
- C. File → New → Mfile (a notepad will pop-up)
- D. The first task is to create an exponentially damped cosine function with an oscillation frequency of 1.5 kHz. Type the following commands (**DO NOT** type the step numbers):

Step

1. `time = 0:.05:100;` Creates an array of times from 0 to 100 msec in increments of 0.05 msec (we will use msec and kHz time and frequency units).
2. `y = cos (2*pi*1.5*time);` Creates cosine function with oscillation frequency of 1.5 kHz.
3. `sig = y.*exp(-time/20);` Creates “signal” function by multiplying cosine function by an exponential decay {decay time constant = 20 msec}. The dot after the y in this expression is important in that it causes the multiplication to proceed on an element-by-element basis.
4. `plot (time,sig);` Examine the decay function.
5. `xlabel ('time (msec)');` Label x-axis of plot.
6. `title ('1.5 kHz cosine function w/ 20 msec decay time');` Put title on plot.
7. `print;` Print the plot.

- | | |
|--|---|
| 4. pulse = y.*amp; | Generate pulse of 5 MHz radiation by multiplying y and amp vectors. |
| 5. plot (time (1:800), pulse (1:800)); | Examine the function |
| 6. xlabel ('time(msec)'); | Label x-axis |
| 7. title ('your title'); | |
| 8. print; | |
| 9. YY = fft (pulse); | Take Fourier Transform |
| 10. spec = abs (YY); | Take complex absolute, or magnitude spectra. |
| 11. frinc = (1/.01)/length (spec); | Compute the frequency increment for the FFT result. |
| 12. f = 0:frinc:frinc*length (spec); | Set up array of frequency values to go with data in spec. |
| 13. plot (f(1:400), spec (1:400)); | Plot frequency spectrum |
| 14. xlabel ('frequency (kHz)'); | Label x-axis |
| 15. title ('your title'); | |
| 16. print; | |
- C. Save the file. File → SaveAs → filename.m (choose an appropriate file name)
- D. Run the program. In the Matlab window: File → Run Mfile (this will cause the two plots created by this program to print)
- E. Repeat this procedure for 5 MHz pulse widths of 0.5 μsec and 5 μsec. **Explain the observed trends.**