Chemistry 431
Lecture 23

Introduction
The Larmor Frequency
The Bloch Equations
Measuring $T_1$: Inversion Recovery
Measuring $T_2$: the Spin Echo

NC State University
NMR spectroscopy

- The Nuclear Magnetic Resonance Phenomenon
- The Magnetization Vector
- Spin Relaxation
- The Chemical Shift
- Scalar Coupling
- Linewidths and Rate Processes
- The Nuclear Overhauser Effect
The Nuclear Magnetic Resonance Phenomenon

- Nuclei may possess a spin angular momentum of magnitude \( \sqrt{I(I+1)}\hbar \).
- The component around an arbitrary axis is \( m_I \hbar \) where \( m_I = I, I-1, \ldots, -I \).
- The nucleus behaves like a magnet in that it tends to align in a magnetic field.
- The nuclear magnetic moment \( \mu \) has a component along the z-axis \( \mu_z = \gamma m_I \hbar \).
The magnetogyric ratio and nuclear magneton

The magnetogyric ratio is $\gamma$ where $\gamma \hbar = g_I \mu_N$. The nuclear g-factor ranges from ca. -10 to 10. Typical g-factors $^1$H $g=5.585$, $^{13}$C $g=1.405$ $^{14}$N $g=0.404$

The nuclear magneton is $\mu_N$ where

$$\mu_N = \frac{e\hbar}{2m_p} = 5.05 \times 10^{-27} \text{ J T}^{-1}$$

Nuclear magnetic moments are about 2000 times smaller than the electron spin magnetic moment because $\mu_N$ is 2000 times smaller than the Bohr magneton.
The Larmor frequency

- Application of magnetic field, $B$ to a spin-1/2 system splits the energy levels.
- $E_{m_I} = -\mu_z B = -\gamma \hbar B m_I$
- The Larmor frequency $\nu_L$ is the precession frequency of the spins $E_{m_I} = -m_I \hbar \nu_L$
- \[ \nu_L = \frac{\gamma B}{2\pi} \]
- For spin 1/2 nuclei the resonance condition is $E_{m_I} = \hbar \nu_L$
The classical vs. quantum view

- According to a classical picture the nuclei precess around the axis of the applied magnetic field \( B_z \) or \( B_0 \).
- In the quantum view a sample is composed of many nuclei of spin \( I = 1/2 \). The angular momentum is a vector of length \( \sqrt{I(I+1)} \) and a component of length \( m_I \) along the z-axis.
- The uncertainty principle does not allow us to specify the x- and y- components.
- In either case the energy difference between the two states is very small and therefore the population difference is also small.

\[
\frac{N_\beta}{N_\alpha} = e^{-\frac{h\nu L}{kT}}
\]

This small population difference gives rise to the measured magnetization in a NMR experiment.
The bulk magnetization vector

The applied magnetic field $\mathbf{B}$ causes spins to precess at the Larmor frequency resulting in a bulk magnetization $M_0$. 
The Bloch Equations

The magnetization vector $M$ obeys a classical torque equation:

$$\frac{dM}{dt} = M \times B$$

where $B$ is the magnetic field vector. $M$ precesses about the direction of an applied field $B$ with an angular frequency $\gamma B$ radians/second.
The Vector Components of the Bloch Equations

\[
\frac{dM_x}{dt} = \gamma \left( M_y B_z - M_z B_y \right)
\]
\[
\frac{dM_y}{dt} = \gamma \left( M_z B_x - M_x B_z \right)
\]
\[
\frac{dM_z}{dt} = \gamma \left( M_x B_y - M_y B_x \right)
\]

If no radiofrequency fields are present then \( \frac{dM_x}{dt} = 0 \) and \( \frac{dM_y}{dt} = 0 \) and we simply have rotation about the static field \( B_z \). We will also call this \( B_0 \).
The static field causes precession of nuclear spins.

The magnetic field vector $\mathbf{M}$ precesses about $B_0$. The spins precess at the Larmor frequency $\omega = -\gamma B_0$. 
The effect of a radiofrequency field

The static magnetic field $B_0$.
The magnetic field due to an applied rf pulse is $B_1$.
The magnetization along the z-axis is zero after a saturating $\pi/2$ pulse and precesses in the x,y plane.

Equilibrium Effect of a $\pi/2$ pulse is to rotate M into the x,y plane
Precession in the x,y plane leads to an oscillating magnetic field called a free induction decay.
Relaxation times $T_1$ and $T_2$

The longitudinal relaxation time governs relaxation back to the equilibrium magnetization along the z-axis.

The transverse relaxation time is the time required for spin dephasing in the x,y plane as the spins precess.

Spins that precess at different rates due to spin-spin coupling and they dephase due to spin flips.
In order to obtain phase information detection along both x and y directions is required. Instead of using two coils to detect the radiofrequency signals one uses two detectors in which one has the phase of the reference frequency shifted by $90^\circ$. These correspond to the real and imaginary components of the free induction decay (FID). The observed spectrum is the Fourier transform of the FID.
Experimental aspects of quadrature detection

Illustration of receiver coils at 90° to one another.
The free induction decay

Real part

\[ FID(t) = \exp(-t/T_2)\cos(\omega t) \]

Imaginary part

\[ FID(t) = \exp(-t/T_2)\sin(\omega t) \]

Here \( \omega = \pi \)
The free induction decay

Note that in this modeling the sample rate is One point per millisecond. The period is $1/\pi$ So there are approximately 3 points per period. Note that the sampling does capture the sinusoidal Character.
Nyquist Theorem ("Fundamental Theorem of DSP")

If $f(t)$ is bandlimited to $[-\Omega_B, \Omega_B]$, we can reconstruct it perfectly from its samples for $\Omega_s = 2\pi T > 2\Omega_B$.

$\Omega_N = 2 \Omega_B$ is called the "Nyquist frequency" for $f(t)$. For perfect reconstruction to be possible $\Omega_s \geq 2\Omega_B$ where $\Omega_s$ is the sampling frequency and $\Omega_B$ is the highest frequency in the signal.

Below is the same “data set” with 4 times the sampling rate.
Measuring relaxation

• Relaxation is the rate of return to the ground state. In magnetic resonance this means restoration of the M vector to its initial position.
• There is longitudinal relaxation ($T_1$) and tranverse relaxation ($T_2$)

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$

• $T_2^*$ is also called the pure dephasing
• $T_1$ is also called the spin-lattice relaxation time
• $T_2$ is also called the spin-spin relaxation time
Measurement of $T_1$: Inversion Recovery

**Equilibrium**
- Effect of a $\pi$ pulse is to rotate $M$ into the $-z$ direction

With time the magnetization decreases along $-z$

The magnitude of the signal in the $x,y$ plane depends on delay
Measurement of $T_2$: Spin Echo

Equilibrium

A $\pi/2$ pulse rotates $M$ into the $x,y$ plane

$\pi/2$ pulse rotates $M$ into the $x,y$ plane and dephases for a time $\tau$

$\pi$ pulse reverse the order of the fast and slow spins

Spin rephasing will occur after a time $\tau$.

During spin evolution in the $x,y$ plane there are differing precession rates of spins due to spin flips and due to magnetic field inhomogeneity. The spin echo produces a signal whose magnitude depends on the delay time $\tau$. This gives a measurement of $T_2$. 
The chemical shift

- The local magnetic field is the field felt by a particular nucleus.
- The applied field $B$ induces currents in the electrons surrounding the nucleus give rise to a shielding. The shielding constant is $\sigma$.
- The local magnetic field is reduced by shielding by a factor $1 - \sigma$.

$$B_{loc} = B + \delta B = (1 - \sigma)B$$

- The chemical shift is the difference between the resonance frequency of a nucleus and that of a standard.
Chemical shifts are reported on the $\delta$-scale

- The Larmor frequency of a shielded nucleus is:
  \[ \nu_L = \frac{\gamma B_{loc}}{2\pi} \]

- Chemical shifts are reported on the $\delta$-scale.
  \[ \delta = \frac{\nu - \nu^0}{\nu^0} \times 10^6 \]

- The resonance frequency of the standard is $\nu^0$. 
Origin of shielding constants

- The shielding constant is the sum of three contributions.

\[ \sigma = \sigma(\text{local}) + \sigma(\text{molecule}) + \sigma(\text{solvent}) \]

- The local contribution is due to electrons on the atom that contains the nucleus.
- The molecular contribution is from the rest of the molecule.
- The solvent contribution is from surrounding solvent molecules.
The local contribution

• The local contribution is a sum of both diamagnetic $\sigma_d$ and paramagnetic $\sigma_p$ parts.
• The diamagnetic part arises from circulation of the electrons in response to $B$.
• The Lamb formula gives the magnitude of $\sigma_d$,

$$\sigma_d = \frac{e^2 \mu_0}{3m_e} \int_0^\infty \rho(r)rdr$$

where $\rho$ is the electron probability density $|\Psi|^2$. $\sigma_d$ is inversely proportional to the Bohr radius. The magnetic moment of a current loop $\propto a_o^2$. The magnetic field generated at the nucleus $\propto 1/a_o^3$. 
The molecular contribution

- The applied magnetic field generates currents in neighboring groups proportional to the magnetic susceptibility $\chi$ of a group.
- The induced magnetic moment gives rise to a magnetic field that is inversely proportional to the cube of the distance from the nucleus.
Scalar coupling

- A neighboring nucleus contributes to the local field resulting in splitting or fine structure.
- The strength of the interaction is expressed in terms of the scalar coupling constant \( J \) (in Hz).
- Coupling is shown for two nuclei \( A \) and \( X \) with difference chemical shifts.
- Coupling constants are independent of \( B \).
The energy levels of coupled systems

• For a spin-1/2 AX system there are four spin states:
  \[ \alpha_A\alpha_X \quad \alpha_A\beta_X \quad \beta_A\alpha_X \quad \beta_A\beta_X \]

• Neglecting spin-spin coupling the transition energies are
  \[ E = -\gamma(1-\sigma_A)hBm_A -\gamma(1-\sigma_X)hBm_X \] where \( m_A \) and \( m_X \) are the spin quantum numbers.

• Spin-spin coupling depends on the relative orientation of the two nuclear spins and is proportional to the product \( m_A m_X \)

• Including spin-spin coupling \( E = -h\nu_A m_A -h\nu_X m_X +hJm_A m_X \)

• When a transition of nucleus A occurs X remains unchanged \( \Delta m_A = +1 \) \( \Delta m_X = 0 \) and the transition energies are
  \[ \Delta E = h\nu_A - \frac{1}{2}hJ \] and \( \Delta E = h\nu_A + \frac{1}{2}hJ \)
The four energy levels of an AX system

Energy:

1/2hν_A + 1/2 hν_X

1/2hν_A - 1/2 hν_X

-1/2hν_A + 1/2 hν_X

-1/2hν_A - 1/2 hν_X

No spin-spin coupling:

\[ \beta_A \beta_X \]

\[ \beta_A \alpha_X \]

\[ \alpha_A \beta_X \]

\[ \alpha_A \alpha_X \]

With spin-spin coupling:

\[ \alpha_X \rightarrow \beta_X \]

\[ \alpha_A \rightarrow \beta_A \]

\[ \alpha_X \rightarrow \beta_X \]

\[ \alpha_A \rightarrow \beta_A \]