CHEM / BCMB  4190/6190/8189

Introductory NMR

Lecture 9
Introduction to Complex Pulse Sequences

**Beyond simple 1D spectra:**

Simple 1D $^1$H and $^{13}$C spectra are not always sufficient for assigning even small organic compounds. The main problems are:
1) Assignment of the 1D spectra
2) Low S/N in spectra of insensitive nuclei with low natural abundance (e.g. $^{13}$C, $^{15}$N)

**Example: Neuraminic Acid derivative 1**
We would also like to use the following information:

1) $^{13}$C-$^1$H correlations
2) The number of protons attach to one carbon
3) $^1$H-$^1$H correlations
4) $^{13}$C-$^{13}$C correlations

etc.

SOLUTION: Complex pulse sequences

Use multiple pulses, delays and decoupling schemes

- Various pulses: hard pulses: 90°x, 90°y, 180°x, 180°y, etc.
  selective pulses: 90°x, 90°y, 180°x, 180°y, etc.
  pulse field gradients

- Various delays: fixed or variable delays

- Decoupling: for selective or broadband decoupling
To analyze the effect of complex pulse sequences we use:

A) Vector Diagrams:

• They are EXTREMELY useful, but it is important to know that they have certain limitations i.e. difficult to explain 2nd order spectra, population transfer, zero or multiple quantum coherence, etc.

• For ease of representation, usually in the rotating frame (x', y', and z) instead of the laboratory frame (x, y, and z). Very important to know what is the frequency (ν) of the rotating frame.

![Vector Diagram](image)

B) Energy Diagrams:

• EXTREMELY useful for understanding energy transfer in certain experiments (e.g.: SPT, INEPT, HSQC)

For \(^1\)H at equilibrium:

\[
\begin{align*}
\beta & \quad (m = -1/2) \\
E_\beta &= +1/2\gamma\hbar B_0 \\
N_\beta &= (N_\alpha + N_\beta)/2 - \delta = N
\end{align*}
\]

Single quantum transition (\(\Delta m = 1\))

\[
\begin{align*}
\alpha & \quad (m = +1/2) \\
E_\alpha &= -1/2\gamma\hbar B_0 \\
N_\alpha &= (N_\alpha + N_\beta)/2 + \delta = N + \Delta H
\end{align*}
\]
Effect of a pulse on the longitudinal magnetization (Mz):

- At equilibrium (Mz):
  ♦ Bulk magnetization along z caused by Bo
  ♦ Excess population in the α state

- After 90°, 270° pulses:

**Vector diagrams:** B1 field brings Mz to the x'-y' plane

**Energy diagram:** The populations of α and β are now equal

For $^1\text{H}$:

$$
E \quad \begin{array}{c}
\frac{N}{\beta} \\
\frac{N + \Delta H}{\alpha}
\end{array} \quad \begin{array}{c}
\frac{N + \Delta H/2}{\beta} \\
\frac{N + \Delta H/2}{\alpha}
\end{array}$$

90°, 270°
• After 180° pulses:

Vector diagrams: B1 field inverts Mz

Energy diagram: The populations of α and β are inverted

For $^1\text{H}$:
Effect of a pulse on the transverse magnetization (Mx', My'):

- The transverse magnetization (Mx', My') is not at equilibrium
  - Bulk magnetization in the x'-y' plane
  - Equal populations in the \( \alpha \) and \( \beta \) states

- Effect of 90° and 180° x and y pulses on transverse magnetization with My' component only

**Vector diagrams:**

Energy diagrams: It all depends where the final magnetization ends up (See above).
• Effect of $90^\circ$ and $180^\circ$ x and y pulses on transverse magnetization with Mx' component only

Vector diagrams:

Energy diagrams: It all depends where the final magnetization ends up (See above).
• Transverse magnetization with $M_{x'}$ and $M_{y'}$ components:

Where does it come from?

Let's consider a simple pulse sequence:

\[ 90^\circ \times \]

\[ ^1H \quad \text{Delay} \]

Vector diagrams:

A) Effect of Chemical Shift Evolution:

Example:

\[ \nu_H = \nu_{rf} + 200 \text{ Hz} \]

B) Effect of J coupling:

Example:

\[ \nu_H = \nu_{rf} \]

\[ \nu = \nu_H - \frac{1}{2}J \]

\[ \nu = \nu_H + \frac{1}{2}J \]
Effect of $90^\circ x$ pulse on transverse magnetization with $Mx'$ and $My'$ components

Vector diagrams:

Initial Magnetization:

After $90^\circ x'$ pulse:

After $90^\circ y'$ pulse:
• Effect of $180^\circ$ x and y pulses on transverse magnetization with Mx' and My' components

Vector diagrams: