Physical Chemistry

18: NMR
Inversion recovery ($T_1$)

The signal matrix is $s(\tau, t)$

The relaxation delay needs to be $5T_1$. 

The arrayed experiment is shown with pulses at time $\tau$, $\frac{\pi}{2}$, and $\pi$.
Inversion recovery ($T_1$)

Relaxation along the z-axis

\[ M_z(t) = M_0 - 2M_0e^{-t/T_1} \]
Inversion recovery ($T_1$)

Relaxation along the z-axis

$$M_z(t) = M_0 - 2M_0 e^{-t/T_1}$$
Moving tube

Moving tube

Faster data acquisition, quantitative carbon spectra.

Spin-spin relaxation ($T_2$)

Relaxation in the xy plane, involves relative orientation of spins

Determines the linewidth

$$v_{\frac{1}{2}} = \frac{1}{\pi T_2} \quad T_2 \leq T_1$$

For protons, $T_2$ is usually between 1 and 10 seconds

$T_2 = 1$ sec, $v_{\frac{1}{2}} = \frac{1}{\pi} = 0.3$ Hz

$T_2 = 10$ sec, $v_{\frac{1}{2}} = \frac{1}{10 \cdot \pi} = 0.03$ Hz

$$M_y(t) \propto e^{-t/T_2}$$
Spin echo ($T_2$)

The signal matrix is $s(\tau, t)$

This experiment refocuses chemical shift.
Each resonance has a pattern that gives information about its neighbors
1. Equivalent protons do not split each other’s signals.

2. A set of \( n \) nonequivalent protons splits the signal of a nearby proton into \( n + 1 \) peaks.

3. Splitting is observed for nonequivalent protons on the same carbon or adjacent carbons.

If \( \text{H}_a \) and \( \text{H}_b \) are not equivalent, splitting is observed when:

\( \text{H}_a \) and \( \text{H}_b \) are on the **same** carbon.

\( \text{H}_a \) and \( \text{H}_b \) are on **adjacent** carbons.
Splitting is not generally observed between protons separated by more than three $\sigma$ bonds.
# The n+1 rule (for “simple” compounds)

<table>
<thead>
<tr>
<th># of non-equivalent protons</th>
<th># of peaks</th>
<th>Name</th>
<th>Looks like</th>
</tr>
</thead>
<tbody>
<tr>
<td>on adjacent carbon:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>doublet</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>triplet</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>quartet</td>
<td></td>
</tr>
</tbody>
</table>
J-coupling: product basis

Two spins are coupled through the scalar (J) coupling:

$$|\psi\rangle = c_{\alpha\alpha} |\alpha\alpha\rangle + c_{\alpha\beta} |\alpha\beta\rangle + c_{\beta\alpha} |\beta\alpha\rangle + c_{\beta\beta} |\beta\beta\rangle$$

If the spins are far apart in chemical shift, they are called A and X (or more generically $I_1$ and $I_2$).
J-coupling: Hamiltonian

The Hamiltonian for weakly coupled spins has a J-coupling term.

\[ \hat{H}_0 = \omega_1^0 \hat{I}_{1z} + \omega_2^0 \hat{I}_{2z} + 2\pi J_{12} \hat{I}_{1z} \hat{I}_{2z} \]

\[ \hat{H}_0 |\alpha\alpha\rangle = \omega_{\alpha\alpha} |\alpha\alpha\rangle \quad \omega_{\alpha\alpha} = \frac{1}{2} \omega_1^0 + \frac{1}{2} \omega_2^0 + \frac{\pi}{2} J_{12} \]

\[ \hat{H}_0 |\alpha\beta\rangle = \omega_{\alpha\beta} |\alpha\beta\rangle \quad \omega_{\alpha\beta} = \frac{1}{2} \omega_1^0 - \frac{1}{2} \omega_2^0 - \frac{\pi}{2} J_{12} \]

\[ \hat{H}_0 |\beta\alpha\rangle = \omega_{\beta\alpha} |\beta\alpha\rangle \quad \omega_{\beta\alpha} = -\frac{1}{2} \omega_1^0 + \frac{1}{2} \omega_2^0 - \frac{\pi}{2} J_{12} \]

\[ \hat{H}_0 |\beta\beta\rangle = \omega_{\beta\beta} |\beta\beta\rangle \quad \omega_{\beta\beta} = -\frac{1}{2} \omega_1^0 - \frac{1}{2} \omega_2^0 + \frac{\pi}{2} J_{12} \]
J-coupling: product basis
Magnetically inequivalent spins split each others’ signals

No Coupled Hydrogens

One Coupled Hydrogen

Two Coupled Hydrogens

Three Coupled Hydrogens

A Singlet

A Doublet

A Triplet

A Quartet
J-coupling: equivalent spins

No Coupled Hydrogens

One Coupled Hydrogen

Two Coupled Hydrogens

Three Coupled Hydrogens

\[ J = -\frac{1}{2} \]
Consider the signal for the CH$_3$Cl molecule.

- With no adjacent H’s: The absorbing H’s feel only one magnetic field. The NMR signal is a single peak.
- With one adjacent H: The absorbing H’s feel two different fields, so they absorb at two different frequencies. The NMR signal is split into a doublet.

- One adjacent proton splits an NMR signal into a doublet.
Protons that split each other are said to be “coupled”

The coupling constant ($J$): the amount of splitting by the methine proton

Coupled protons always have the same coupling constant

Chemical shift of the signal for the methyl protons if there were no protons on the adjacent carbon
### Standard coupling values ($J$, in Hz)

<table>
<thead>
<tr>
<th>Structural Type</th>
<th>$J$ (Hz)</th>
</tr>
</thead>
</table>
| \[
\begin{align*}
\text{H} & \quad \text{C} - (\text{C})_n - \text{C} - \text{H} \\
\text{H}_3\text{C} & \quad \text{CH}_2 - \text{X} \\
\text{H}_3\text{C} & \quad \text{CH} - \text{X} \\
\text{H}_3\text{C} & \quad \text{C} - \text{C} - \text{H} \\
\text{X} & \quad \text{Y} \\
\end{align*}
\]
| (unless in a rigid ideal orientation) |
| 0 | 6 to 8 |
| 5 to 7 | 2 to 12 |
| 2 to 12 | (depends on dihedral angle and the nature of $X$ and $Y$) |
| 0.5 to 3 | 3 to 11 |
| 12 to 15 | (must be diastereotopic) |

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</table>
| \[
\begin{align*}
\text{H} & \quad \text{C} = \text{C} \\
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\text{H} & \quad \text{C} = \text{C} \\
\text{H} & \quad \text{C} = \text{C} \\
\end{align*}
\]
| 12 to 18 |
| 7 to 12 | 0.5 to 3 |
| 3 to 11 | (depends on dihedral angle) |
| 2 to 3 | 0 to 1 |
| o 6 to 9 | m 1 to 3 |
| p 0 to 1 |
Sample spectrum

A quartet and a doublet are shown in the spectrum of a chemical compound. The quartet is observed at δ (ppm) around 6.0 and 5.8 ppm, while the doublet appears at δ (ppm) around 2.2, 2.0, and 1.8 ppm.
More complex splitting patterns: nitrobenzene

Since $H_b$ and $H_c$ are not equivalent to each other, we cannot add them together and use the $n + 1$ rule.

We must treat them separately, so $H_a$ will be a doublet of doublets.
The difference between a quartet and a doublet of doublets

- A quartet: relative intensities: 1 : 3 : 3 : 1
- A doublet of doublets: relative intensities: 1 : 1 : 1 : 1
Another example of doublets of doublets:
A closer look at the splitting pattern

$J_{bc} = 1.2 \text{ Hz (geminal)}$
$J_{cd} = 6.5 \text{ Hz (cis)}$
$J_{bd} = 14 \text{ Hz (trans)}$

One nearby H splits the signal into a doublet.

The second nearby proton splits the doublet into a doublet of doublets.
\[ {^{13}}C \text{ NMR spectrum of} \]

\[
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{C} = \text{O} \\
\text{CH}_3
\end{array}
\]
General 2D pulse sequence
$^{13}\text{C}^{15}\text{N}$ correlation of arginine