**NMR Phenomenon**

- **Nuclear Magnetic Resonance**
  
  A spinning charged particle generates a magnetic field.
  
  A nucleus with a spin angular momentum will generate a magnetic moment ($\mu$).
  
  If these tiny magnets are placed in an applied magnetic field ($B_0$), they will adopt two different states - one aligned with the field and one aligned against the field. The energy difference between these two states is what we are observing with NMR.

**Nuclear Spin States**

- When EM waves at this energy are directed at the nuclei - it will absorb. Spins will flip from lower energy to higher energy. At that energy, nuclei are “In Resonance”.

**NMR Active Nuclei**

- Many nuclei are “NMR Active”
  - Spin Quantum Number  $I \neq 0$
  - $^1H$ -- $I = \frac{1}{2}$; $^{13}C$ -- $I = \frac{1}{2}$
  - $^{12}C$, $^{16}O$ -- $I = 0$ -- Can’t be observed

- Other nuclei that are NMR active
  - $^2H$ (D), $^{14}N$, $^{19}F$, $^{31}P$

**NMR Instrumentation**

- Sample in tube
- Radiofrequency generator
- Detector and amplifier
Magnetic Resonance Imaging

NMR is the basis for MRI

To summarize

A spinning charged particle generates a magnetic field. A nucleus with a spin angular momentum will generate a magnetic moment (m). When placed in a magnetic field ($B_0$), they will adopt two different states - one aligned with the field and one aligned against the field.

Energy difference between the states at a particular magnet strength. In the $R_f$ range of the EM Spectrum.

Methyl Acetate - Proton NMR

Methyl Acetate - Carbon NMR
**Electronic Shielding - Local Environments**

Actual magnetic field felt by the nucleus

\[
B_{\text{effective}} = B_0 - B_{\text{local}}
\]

**Methyl Acetate - Proton NMR**

**Methyl Acetate - Carbon NMR**

**Chemical Shift**

- The difference in resonance frequency of a nuclei relative to a standard
- Most Shielded
- Relatively Inert
- Volatile
- Resonance of standard is set to 0

TMS (TetraMethylSilane)
**NMR Scale**

- **X-Axis - frequency axis**

<table>
<thead>
<tr>
<th>Spectrometer Frequency (MHz)</th>
<th>Peaks measured as a shift (in Hz) away from TMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 MHz NMR</td>
<td>10 Hz</td>
</tr>
<tr>
<td>300 MHz NMR</td>
<td>0</td>
</tr>
</tbody>
</table>

**Standard Scale**

- $\delta = \text{ppm} = \text{Chemical Shift from TMS (Hz)}$
- Spectrometer Frequency (MHz)

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>100 MHz</th>
<th>300 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 MHz NMR</td>
<td>1.0 ppm</td>
<td></td>
</tr>
<tr>
<td>300 MHz NMR</td>
<td>1.0 ppm</td>
<td></td>
</tr>
</tbody>
</table>

**Different Spectrometer Frequencies**

- Each specific instrument has its own magnetic field strength - resonance occurs at different frequencies.

- 100 MHz NMR
- 300 MHz NMR

Reference TMS

- 10 Hz
- 0

Reference TMS

- 300 Hz
- 100 Hz
- 0
C13 NMR

- Difficult - Carbon 13 only 1.1% of all carbon.
- Number of different carbons
- Functional Group Regions

[Diagram showing different carbons and their chemical shifts]

13C NMR

Symmetry

- Symmetry in molecules can make carbons "Chemically Equivalent"

[Diagram showing molecules with symmetry and chemistry]

Symmetry

- Some molecules have more than one mirror plane
Substitution of Carbon

The intensity of the peaks roughly correlates with the number of hydrogens on the carbon.

C13 NMR Regions

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**Bromooctanol**

**Bromooctanal**

**Alanine Me-Ester HCl**

**Alaninol**
Alaninol - phthalimide

\[
\begin{array}{c}
\text{H} \quad \text{C} \quad \text{N} \\
\text{OH} \\
\text{O} \\
\text{O}
\end{array}
\]

DEPT-C13

A - normal C13
B - CH carbons only
C - Odd # up (CH3 and CH) Even # down (CH2)

Example from 13.7

[NH\textsubscript{2}]

Cl

KOH ethanol

or

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{N} \\
\text{O} \\
\text{O}
\end{array}
\]

A Real Example

In the alkane region there would only be 4 peaks due to symmetry

In the alkane region there would be 6 different peaks
The Answer Is . . .

Proton NMR
- Number of chemically different hydrogens
- Relative Ratios of protons (peak size)
- How many neighboring hydrogens
- Chemical shifts and functional groups

Proton Equivalency

Homotopic

Enantiotopic

Diastereotopic

Proton NMR Scale
Range 0-10 ppm
## NMR Correlation Chart

### Typical NMR Chemical Shifts

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Type</th>
<th>$^1\text{H}$ Chemical Shift (ppm)</th>
<th>$^{13}\text{C}$ Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td></td>
<td>0.7 - 1.8</td>
<td>10 - 60</td>
</tr>
<tr>
<td>Allylic or next to carbonyl</td>
<td></td>
<td>1.6 - 2.4</td>
<td>30 - 60</td>
</tr>
<tr>
<td>vinyl</td>
<td></td>
<td>2.5 - 4.0</td>
<td>20 - 65</td>
</tr>
<tr>
<td>carbonyl of an ester</td>
<td></td>
<td>4.0 - 5.0</td>
<td>50 - 85</td>
</tr>
<tr>
<td>vinyl</td>
<td></td>
<td>4.5 - 6.5</td>
<td>110 - 150</td>
</tr>
<tr>
<td>aromatic</td>
<td></td>
<td>6.5 - 8.0</td>
<td>110 - 140</td>
</tr>
<tr>
<td>aldehyde</td>
<td></td>
<td>9.7 - 10.0</td>
<td>190 - 220</td>
</tr>
<tr>
<td>alcoholic</td>
<td></td>
<td>varies widely will exchange with D$_2$O</td>
<td>N/A</td>
</tr>
<tr>
<td>carboxylic of water, amide, or carboxylic acid (X = O, N)</td>
<td></td>
<td>N/A</td>
<td>165 - 185</td>
</tr>
<tr>
<td>carboxylic of ketone or aldehyde</td>
<td></td>
<td>N/A</td>
<td>190 - 220</td>
</tr>
</tbody>
</table>

### Examples

#### Methyl Acetate

Area under peak corresponds to the number of H's for that resonance.

#### Triphenyl Methanol

#### Ethyl Acetate
Protons on adjacent carbons also have an effect
Resonances will split into n+1 number of peaks

Spin Spin Splitting

Two hydrogens split neighbors into a triplet

Every splitting can be broken down into a series of doublets

Three neighbors - Quartet
Higher Spin Spin Splitting

Pascal’s Triangle

<table>
<thead>
<tr>
<th>Spin State</th>
<th>Combinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>singlet</td>
<td>1</td>
</tr>
<tr>
<td>doublet</td>
<td>1</td>
</tr>
<tr>
<td>triplet</td>
<td>2</td>
</tr>
<tr>
<td>quartet</td>
<td>3</td>
</tr>
<tr>
<td>quintet</td>
<td>4</td>
</tr>
<tr>
<td>sextet</td>
<td>5</td>
</tr>
<tr>
<td>septet</td>
<td>6</td>
</tr>
</tbody>
</table>

H_b will split into 7 peaks

64 different combinations of 6 spins

Summary of Spin Spin Splitting

- Proton resonance split into n+1 number of peaks
- Relative ratio of peaks depends on number of spin states of the neighbors.
- Adjacent protons will couple with the same coupling constant.
- Protons farther away usually do not couple.
- Chemically equivalent protons cannot couple (e.g., ClCH_2CH_2Cl).

Doublet Splitting

Methyl sees 1 neighbor, Methine sees 3

Ethanol

Note that the OH (and NH) usually don’t couple.
1,1,2-Trichloroethane

2-Bromopropane

Butanone

para-Methoxypropiophenone
Toluene

Sometimes peaks overlap

Cinnamaldehyde

Multiple Coupling

Spin Spin Splitting

Every splitting can be broken down into a series of doublets

\[ ^1H\text{ NMR (without coupling)} \]

\[ \begin{align*}
H_a & \quad H_b \\
C & \quad C & \quad H_b \\
H_b & \\
\end{align*} \]

\[ ^1H\text{ NMR (with coupling)} \]

\[ \begin{align*}
H_a & \quad H_b \\
C & \quad C & \quad H_b \\
H_b & \\
\end{align*} \]

Coupling with the same J

\[ J_{a-b} = 5\text{ Hz} \quad J_{a-c} = 5\text{ Hz} \]

\[ \begin{align*}
H_b & \quad H_a & \quad H_c \\
C & \quad C & \quad C \\
H_a & \\
\end{align*} \]

Coupling with \( H_b \)

Coupling with \( H_c \)
Coupling with different $J$ values

$J_{a-b} = 5$ Hz, $J_{a-c} = 10$ Hz

Cinnamaldehyde

Multiple Coupling

$J_{H1-H2} = 6$ Hz, $H2-H3 = 12$ Hz

Cinnamaldehyde

Multiple Coupling - Identical $J$

$J_{a-b} = 5$ Hz, $J_{a-c} = 5$ Hz

Cinnamaldehyde
Multiple Coupling - Different $J$

$J_{a,b} = 10$ Hz
$J_{b,c} = 5$ Hz

$J_{a,b} = 10$ Hz $J_{b,c} = 5$ Hz

Nitropropane

$\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NO}_2$

Strategies for Determining Unknowns

- Given the Molecular Formula - calculate degrees of unsaturation.
- Identify functional groups
- Identify pieces of the structure
- Put the pieces together in a reasonable way
- Double check that your structure matches all the data given.