MCH-401: Application of Spectroscopy (Organic)

UNIT- 4th: Carbon-13 NMR Spectroscopy

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C. NMR Spectroscopy

1. General Theory

2. $^{13}\text{C}$ NMR

3. $^{1}\text{H}$ NMR
1. General Theory of NMR

A magnetic field is generated by a spinning charge.

The nucleus of many atoms is a spinning charge.
For many nuclei, an external magnetic field will cause the spinning charge to either line up **with** the external magnetic field or **against it**.
The β spin state is slightly greater in energy.

The difference in energy between α and β increases with increasing magnetic field strength.
Nuclei can absorb energy.

When nuclei in the $\alpha$ state absorb radiation equal in $E$ to the difference between the $\alpha$ and $\beta$ spin states, the $\alpha$ spin state is promoted to the $\beta$ spin state.

The radiation required for “spin flipping” has a frequency in the radio wave range.
Nuclei can emit energy.

As nuclei move from the $\beta$ spin state to the $\alpha$ spin state, energy is emitted and the frequency of that energy can be detected.

resonance = nuclei flipping back and forth between the $\alpha$ and $\beta$ spin state.
Resonance is the “Song of the Nuclei.”

Every molecule sings its own song as a result of its structure.
Analysis of an NMR spectrum may involve analyzing:

a) The **number of signals** a molecule emits

b) The **frequencies** at which signals occur

c) The **intensity** of signals

d) The **splitting** of signals
2. $^{13}$C NMR

a) Number of signals

b) Position of signals

c) DEPT data
a) The number of signals correlates with the number of types of carbon in a molecule
cyclopentane
$^{13}$C-NMR cyclopentane
Pentane

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
$^{13}$C-NMR pentane
$^{13}$C-NMR hexane
$^{13}$C-heptane
$^{13}$C-NMR chlorocyclopentane
$^{13}\text{C-NMR}$ 2,2-dimethylpropanal

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{CH}_3 \\
\text{C} \\
\text{C} \\
\text{CH}_3 \\
\text{H} \\
\text{CH}_3 \\
\end{array}
\]
$^{13}$C-NMR 2-methylbutane
$^{13}$C-NMR toluene
(Z)-3-methyl-2-pentene
(E)-3-methyl-2-pentene
Consider C₄H₉Br

Which isomers are represented by these spectra?
b) The positions of signals correlate with the extent of shielding and deshielding by electrons experienced by each C nucleus.
Diamagnetic Shielding

The greater the electron density around a C nucleus, the lower the effective magnetic field around that C nucleus.

Needs lower frequency for resonance

The carbon nucleus is “shielded”
Carbon nuclei adjacent to electronegative atoms experience a lower e- cloud density

*These carbons are “deshielded” and require greater frequencies for resonance.*
These carbons sense a larger effective magnetic field so come into resonance at a higher frequency.

These carbons sense a smaller effective magnetic field so come into resonance at a lower frequency.

Deshielded nuclei

Shielded nuclei

Less shielded "downfield"

More shielded "upfield"
Chemical Shift

The frequency at which a nucleus will resonate is dependent on the magnetic field strength.

Because this can vary from instrument to instrument, frequency is expressed relative to magnetic field strength, “chemical shift”

Chemical Shift = \frac{\text{frequency of resonance (Hz)}}{\text{frequency of instrument (MHz)}}

units = \text{parts per million} = \text{ppm}
$^{13}$C Chemical Shift Correlation Chart
<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>Approximate chemical shift (ppm)</th>
<th>Type of carbon</th>
<th>Approximate chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₄Si</td>
<td>0</td>
<td>C—I</td>
<td>0—40</td>
</tr>
<tr>
<td>R—CH₃</td>
<td>8—35</td>
<td>C—Br</td>
<td>25—65</td>
</tr>
<tr>
<td>R—CH₂—R</td>
<td>15—50</td>
<td>C—Cl</td>
<td>35—80</td>
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<tr>
<td></td>
<td></td>
<td>C—N</td>
<td>40—60</td>
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<tr>
<td></td>
<td></td>
<td>C—O</td>
<td>50—80</td>
</tr>
<tr>
<td>R—CH—R</td>
<td>20—60</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>R—C—R</td>
<td>165—175</td>
</tr>
<tr>
<td>R—C—R</td>
<td>30—40</td>
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<td></td>
</tr>
<tr>
<td>≡C</td>
<td>65—85</td>
<td>R—C=O</td>
<td>175—185</td>
</tr>
<tr>
<td>≡C</td>
<td>100—150</td>
<td>R—C=O</td>
<td>190—200</td>
</tr>
<tr>
<td></td>
<td>110—170</td>
<td>R—C=O</td>
<td>205—220</td>
</tr>
</tbody>
</table>
pentane
hexane
cyclopentane
ethyl bromide
n-propyl chloride
ethanol
2-propanol
ethyl propyl ether
Ethyl amine
Acetaldehyde
2,2-dimethylpropanal
Acetone
2-pentanone
acetic acid
Propionic acid
methyl propionate
Acetamide
N-methyl acetamide
1-pentene
(Z)-3-methyl-2-pentene
(E)-3-methyl-2-pentene
2-butyn
Benzene
toluene
Benzaldehyde
c) DEPT data

DEPT = distortionless enhancement by polarization

Distinguishes:

\[ \text{CH}_3 \] - methyl groups

\[ -\text{CH}_2- \] - methylene groups

\[ -\text{CH}- \] - methine groups

\[ -\text{C}- \text{ } \] - 4\text{o} carbons (not detected by DEPT)
DEPT $^{13}$C spectrum of citronella

$C_{10}H_{16}O$
C₄H₁₀O
$C_4H_{10}O$
C$_5$H$_{10}$O
C$_5$H$_{10}$O
C₅H₁₀O
$\text{C}_4\text{H}_8\text{O}_2$
$\text{C}_4\text{H}_8\text{O}_2$
$C_4H_8O_2$
C$_8$H$_9$Br
C₈H₉Br
C₈H₉Br
C₃H₆O₂

A

B
$^1$H NMR

CH$_3$COCH$_2$OH

CH$_3$CH$_2$COOH