Chapter 13:
NMR Spectroscopy
NMR Spectroscopy

• By far the most important and useful technique to identify organic molecules. Often the only technique necessary.

• NMR spectrum can be recorded for many different nuclei (they need to have magnetic properties) such as: $^1$H, $^3$H, $^{13}$C, $^{15}$N, $^{19}$F, $^{31}$P

• We will focus only on proton ($^1$H) nmr here
Nuclear Spin

- A nucleus with an odd atomic number or an odd mass number has a nuclear spin.
- The spinning charged nucleus generates a magnetic field.
• An external magnetic field \((B_0)\) applies a force to a small bar magnet, twisting the bar magnet to align it with the external field.

• The arrangement of the bar magnet aligned with the field is lower in energy than the arrangement aligned against the field.
• The lower energy state with the proton aligned with the field is called the *alpha-spin state*.

• The higher energy state with the proton aligned against the external magnetic field is called the *beta-spin state*. 
A nucleus is in resonance when it is irradiated with radio-frequency photons having energy equal to the energy difference between the spin states. Under these conditions, a proton in the alpha-spin state can absorb a photon and flip to the beta-spin state.
**Chemical shift** (13.5-13.7)

- Is the position of a nmr absorption. It depends on:
  - **Electron density** in the vicinity of an hydrogen atom...this electron density is affected by the molecular structure of the molecule

- Chemical shifts are reported on the horizontal axis of the spectrum (the $\delta$ scale is in ppm) from the reference (TMS).
Tetramethylsilane (TMS) is added to a solution and arbitrarily assigned a chemical shift of “0”. All other signals are reported relative to that position.
Since electron density is the determining factor in the chemical shifts observed, dipole in the molecule will have an effect in donating or removing electrons from the vicinity of a given proton. This effect is described as

- **Shielding**: more electron in the proton’s vicinity (dipole effect minimum)

- **Deshielding**: less electron in the proton’s vicinity (dipole effect is increased)
**Shielding and Deshielding** (13.3)

No dipole, therefore, maximum electron density near the protons in CH₃  

Shielded

- More shielded, absorb at a higher field

Strong dipole pulling electrons away from hydrogen atom, therefore, electron density is reduced near protons Deshielded

- Less shielded, absorbs at a lower field

The conclusion is that shielded protons absorb radiation at higher fields (frequency) while the deshielded protons will absorb at lower fields (frequency).
• **Therefore, protons affected by the proximity of different functional groups will absorb at different fields** (because of the difference in dipole moment). This can be used to identify the structure of molecules.

• **The chemical shift:**
  - Measured in parts per million.
  - Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (MHz).
  - The chemical shift has the same value regardless of the machines (same value for 60, 100, or 300 MHz machine).
  - Called the delta scale.
The Delta Scale

The chemical shift, ppm $\delta$, is defined as:

$$\delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$

**60 MHz**

<table>
<thead>
<tr>
<th>600 Hz</th>
<th>480 Hz</th>
<th>360 Hz</th>
<th>240 Hz</th>
<th>120 Hz</th>
<th>0 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

**300 MHz**

<table>
<thead>
<tr>
<th>3000 Hz</th>
<th>2400 Hz</th>
<th>1800 Hz</th>
<th>1200 Hz</th>
<th>600 Hz</th>
<th>0 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9</td>
<td>8</td>
<td>7</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

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Different tables and graphs exist describing the general effect of functional groups on NMR absorptions. These represent only guidelines to follow. Effects of more than one functional group will normally be additive.

**TABLE 13-3**

Typical Values of Chemical Shifts

<table>
<thead>
<tr>
<th>Type of Proton</th>
<th>Approximate δ</th>
<th>Type of Proton</th>
<th>Approximate δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkane ((-\text{CH}_3)) methyl</td>
<td>0.9</td>
<td>(\text{C}═\text{C}═\text{CH}_3) allylic</td>
<td>1.7</td>
</tr>
<tr>
<td>alkane ((-\text{CH}_2)) methylene</td>
<td>1.3</td>
<td>(\text{Ph}═\text{H}) aromatic</td>
<td>7.2</td>
</tr>
<tr>
<td>alkane ((-\text{CH})) methine</td>
<td>1.4</td>
<td>(\text{Ph}═\text{CH}_3) benzylic</td>
<td>2.3</td>
</tr>
<tr>
<td>((-\text{CH}_3)) methyl ketone</td>
<td>2.1</td>
<td>(\text{R}═\text{C}═\text{H}) aldehyde</td>
<td>9–10</td>
</tr>
<tr>
<td>(\text{C}≡\text{C}═\text{H}) acetylenic</td>
<td>2.5</td>
<td>(\text{R}═\text{C}─\text{OH}) acid</td>
<td>10–12</td>
</tr>
<tr>
<td>(\text{R}═\text{CH}_2─\text{X}) (X = halogen, O)</td>
<td>3–4</td>
<td>(\text{R}═\text{OH}) alcohol</td>
<td>variable, about 2–5</td>
</tr>
<tr>
<td>(\text{C}═\text{C}≡\text{H}) vinyl</td>
<td>5–6</td>
<td>(\text{Ar}═\text{OH}) phenol</td>
<td>variable, about 4–7</td>
</tr>
<tr>
<td>(\text{R}═\text{NH}_2) amine</td>
<td>variable, about 1.5–4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note:* These values are approximate, as all chemical shifts are affected by neighboring substituents. The numbers given here assume that alkyl groups are the only other substituents present. A more complete table of chemical shifts appears in Appendix 1.

**TABLE 13-2**

Chemical Shifts of the Chloromethanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}═\text{C}─\text{H})</td>
<td>(\delta 0.2)</td>
<td>2.8 ppm</td>
</tr>
<tr>
<td>(\text{H}═\text{C}─\text{Cl})</td>
<td>(\delta 3.0)</td>
<td>2.3 ppm</td>
</tr>
<tr>
<td>(\text{H}═\text{C}─\text{Cl})</td>
<td>(\delta 5.3)</td>
<td>1.9 ppm</td>
</tr>
<tr>
<td>(\text{H}═\text{C}─\text{Cl})</td>
<td>(\delta 7.2)</td>
<td></td>
</tr>
</tbody>
</table>

*Note:* Each chlorine atom added changes the chemical shift of the remaining methyl protons by 2 to 3 ppm. These changes are nearly additive.

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Magnetic Fields of Aromatics

- The induced magnetic field of the circulating aromatic electrons opposes the applied magnetic field along the axis of the ring.
- Protons in the region where the induced field reinforces the applied field are deshielded and will appear at lower fields in the spectrum between $\delta 7–8$. 

![Diagram of magnetic fields and molecular structure](image-url)
Magnetic Field of Alkenes

- The pi electrons of the double bond generate a magnetic field that opposes the applied magnetic field in the middle of the molecule but reinforces the applied field on the outside where the vinylic protons are located.
- This reinforcement will deshield the vinylic protons making them shift downfield in the spectrum to the range of $\delta 5–6$. 

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Magnetic Field of Alkynes

- When the terminal triple bond is aligned with the magnetic field, the cylinder of electrons circulates to create an induced magnetic field.
- The acetylenic proton lies along the axis of this field, which opposed the external field.
- The acetylenic protons are shielded and will be found at δ2.5 (higher than vinylic protons).
Deshielding of the Aldehyde Proton

- Like a vinyl proton, the aldehyde proton is deshielded by the circulation of electrons in the pi bond.
- It is also deshielded by the electron-withdrawing effect of the carbonyl (C=O) group, giving a resonance between $\delta 9-10$. 

![Diagram showing deshielding of the aldehyde proton](image_url)
O-H and N-H Signals

- The chemical shift of the acidic protons depends on concentration.
- Hydrogen bonding in concentrated solutions deshield the protons, so signal is around $\delta 3.5$ for N—H and $\delta 4.5$ for O—H.
- Proton exchanges between the molecules broaden the peak.
Carboxylic Acid Proton

- Because of the high polarity of the carboxylic acid O—H bond, the signal for the acidic proton will be at shifts greater than δ10.
Practice Questions

• For each of the following compounds, which of the protons (in red and blue) has the greater chemical shift?

\[
\begin{align*}
\text{CH}_3\text{CHCHBr} \\
\quad \text{Br} \quad \text{Br}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CHCH}_3 \\
\quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C-O-C} \\
\quad \text{H}_2
\end{align*}
\]
**Number of Signals** (13.6)

- Chemically different protons will have signals at different positions. \( \text{CH}_3\text{CH}_2\text{Br} \)

- Chemically identical protons will have different signals if they are environmentally different.
Practice Question

- How many signals would you expect to see in the $^1$H-NMR spectrum of the following compounds?
Area Under the Peaks (13.9)

- Another line (looks like steps) usually appears on a NMR spectrum. It is the integral line.

- This line is used to determine the number of hydrogen responsible for a given absorption or signal. It is a relative scale so if only one signal appear in the spectrum, this line is usually not present.
• However when more than one signal is observed, this integral line will appear and help determine the structure of certain groups.

• The integration is relative between signals: ie the more H’s of one kind (equivalent) the more intense the corresponding absorption relative to the other ones.
1) Measure each steps bottom to top in a measurable unit:

2) Divide each value by the smallest one recorded. This will give the smallest signal a value of 1 proton

\[\frac{11}{11} = 1\quad \frac{34}{11} = 3\]

3) If the ratio obtained gives fractions, multiply until you get to a value that is close to a whole number
1) Ratios are: 0.5 : 1.0 : 1.5 : 3.0

2) Since it is not possible to have 0.5 proton, multiply by 2

3) Final ratios are: 1 : 2 : 3 : 6
Practice Question (Question 13-6)

- Determine the ratios of the peak areas in the following spectra. Then use this information, together with the chemical shift, to pair up the compounds with their spectra. Assign the peaks in each spectrum to the protons they represent in the molecular structure. Possible compounds:

- ![Molecular structures](image)
Spin-Spin Splitting (13.8)

- When 2 adjacent carbon atoms have chemically or environmentally different H’s, the signals for a given set of H’s on a carbon will be coupled (split) into more than one line.

- For simple molecules, the observed pattern is predictable following the **n + 1 rule**
  
  \[
  \# \text{ lines of a signal} = n + 1
  \]
  
  where \( n = \# \text{ neighbouring H’s} \)
Both $H^b$ are identical and have one neighbouring proton ($H^a$), signal for $H^b$ will be split: $1 + 1 = 2$ lines (a doublet)

$H^a$ has 2 neighbouring Hs ($H^b$), signal for $H^a$ will be split: $2 + 1 = 3$ lines (a triplet)
• Number of lines in a signal is called multiplicity. Coupling between protons is mutual.

• The coupling effect between protons is limited to the neighbouring protons. Further away will usually have no effect (except due to conjugation). Nonequivalent protons on the same carbon will be coupled.
General Splitting Rules

- Equivalent protons do not split each other.
- Protons bonded to the same carbon will split each other if they are nonequivalent.
- Protons on adjacent carbons normally will split each other, unless they are equivalent.
- Protons separated by four or more bonds will not split each other.
The coupling effect between protons is limited to the neighbouring protons. Further away will usually have no effect (except due to conjugation). Nonequivalent protons on the same carbon will be coupled. *Bonded to nonadjacent carbons: four or more bonds between protons*

protons on these 2 carbons are not coupled (4 bonds away)

protons on these 2 carbons are coupled (3 bonds away)
Multiplicity of Signals

- The shape and intensity of the line in a signal can help determine the type of groups present in a molecule.

<table>
<thead>
<tr>
<th>Number of Equivalent Protons Causing Splitting</th>
<th>Number of Peaks (multiplicity)</th>
<th>Area Ratios (Pascal’s triangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1 (singlet)</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2 (doublet)</td>
<td>1 1</td>
</tr>
<tr>
<td>2</td>
<td>3 (triplet)</td>
<td>1 2 1</td>
</tr>
<tr>
<td>3</td>
<td>4 (quartet)</td>
<td>1 3 3 1</td>
</tr>
<tr>
<td>4</td>
<td>5 (quintet)</td>
<td>1 4 6 4 1</td>
</tr>
<tr>
<td>5</td>
<td>6 (sextet)</td>
<td>1 5 10 10 5 1</td>
</tr>
<tr>
<td>6</td>
<td>7 (septet)</td>
<td>1 6 15 20 15 6 1</td>
</tr>
</tbody>
</table>

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• Doublets always have 2 lines almost of equal heights.
• Triplets: will always have a 1:2:1 ratio for the lines in that signal
• Quartets are easy to assign with their \(1:3:3:1\) ratio.
**Second order coupling** (13.13-13.14)

- Second order coupling will be observed when a given proton has more than one non-equivalent neighbours. In this case, the number of neighbours does not add up, but must be taken separately.

![Diagram of chemical structure and NMR peaks](image)
• Second order coupling usually give lines that do not match the simple multiplicity found in the Pascal’s triangle. Hence, while it is important to look at the number of lines, the shape will also give you clues.

• For example the signal below is not a quartet although it has 4 lines, it is a doublet of doublets since all the lines are even. A quartet would have the 1:3:3:1 ratio.
These kinds of patterns are often found in chiral molecules where protons on a given carbon appears identical, but because of the chiral center, these may actually be diastereotopic.
**Coupling constant (J)** (13.12)

- The coupling constant is the distance found between lines in a pattern due to splitting. It is measured in Hertz.
- When two different protons are coupled, the coupling constant for H\textsubscript{a} will be the same as that found for H\textsubscript{b}.
- This can help identify some groups.
The coupling constant can also help to identify specific groups

<table>
<thead>
<tr>
<th>Structure</th>
<th>Approx. ( J )</th>
<th>Structure</th>
<th>Approx. ( J )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C} - \text{C} ) (free rotation)</td>
<td>7 Hz(^a)</td>
<td>( \text{H} ) (ortho)</td>
<td>8 Hz</td>
</tr>
<tr>
<td>( \text{H} ) ( \text{H} )</td>
<td>10 Hz</td>
<td>( \text{H} ) (meta)</td>
<td>2 Hz</td>
</tr>
<tr>
<td>( \text{C} = \text{C} ) (cis)</td>
<td>15 Hz</td>
<td>( \text{C} = \text{C} ) (geminal)</td>
<td>2 Hz</td>
</tr>
<tr>
<td>( \text{H} ) ( \text{H} )</td>
<td></td>
<td>( \text{C} = \text{C} ) (allylic)</td>
<td>6 Hz</td>
</tr>
</tbody>
</table>

\(^a\)The value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon–carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

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Easily Identified patterns

**Ethyl group, **$\text{CH}_3\text{-CH}_2\text{-}$**: its position on the spectrum depends on the other groups in the molecule

quartet/triplet pattern integrating for 2 and 3
**Isopropyl group** $\text{CH}_3\text{-CH-CH}_3$

Septet/doublet pattern integrating for 1 and 6
p-disubstituted aromatics

2 doublets integrating for 2 H each
Signals for proton on heteroatoms (NH, OH) are often broad and difficult to see and may not be split. This depends on the concentration and purity of the sample.
• Usually these protons can be exchanged with D₂O.
• To verify that a particular peak is due to O—H or N—H, shake the sample with D₂O too exchange the H for a D. The deuterium is invisible in the proton NMR so the original signal for the OH will disappear.

\[
\begin{align*}
\text{R–O–H} + \text{D–O–D} & \rightleftharpoons \text{R–O–D} + \text{H–O–D} \\
\text{R–N–H} + 2 \text{D–O–D} & \rightleftharpoons \text{R–N–D} + 2 \text{H–O–D}
\end{align*}
\]
Index of Unsaturation (3.1)

- This is useful to help determine some characteristics (ring, double bonds, etc...) of the structure of an unknown compound. It represents the # of H₂ molecules one would have to add to a structure to get a fully saturated compound (see CHEM201).

<table>
<thead>
<tr>
<th>groups</th>
<th>unsaturation index</th>
</tr>
</thead>
<tbody>
<tr>
<td>— —</td>
<td>1</td>
</tr>
<tr>
<td>C=O</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>C≡N</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>

Combination adds up
Steps to determining structure

1) Determine unsaturation index from formula
2) If you have no formula, find $M^+$ in mass spectrum and note the mass
3) From IR, determine possible functional groups
4) From NMR, determine portion of structure from chemical shifts, splitting patterns, and integration
5) Substrat the groups that you have already found from the molecular formula as you go until you have found all the pieces of the puzzle. Then put pieces together.
Unknown #1: $\text{C}_3\text{H}_6\text{O}_2$
Unknown #1: C$_3$H$_6$O$_2$ Summary
Unknown #2: \( \text{C}_4\text{H}_8\text{O} \)
Unknown #2: $\text{C}_4\text{H}_8\text{O}$  Summary
Unknown #3: $\text{C}_9\text{H}_{10}\text{O}$
Unknown #3: $\text{C}_9\text{H}_{10}\text{O}$

Summary
Unknown #4: $\text{C}_{12}\text{H}_{16}\text{O}_{2}$
Unknown #6: $\text{C}_{12}\text{H}_{16}\text{O}_2$ Summary