NMR spectroscopy

A spinning proton creates a magnetic field.

With no external magnetic field...
The nuclear magnets are randomly oriented.

In a magnetic field...
The nuclear magnets are oriented with or against $B_0$. 
Different wavelengths of light probe different features of molecules

- **High frequency**
  - Cosmic rays
  - X-rays
  - Ultraviolet light
  - Visible light
  - Infrared radiation

- **Low frequency**
  - Microwaves
  - Radio waves

**Higher Energy**

**Lower Energy**

**IR**: bond vibrations

**NMR**: nuclear spins
1H NMR Spectroscopy
(Nuclear Magnetic Resonance = NMR)

Road map

Detailed structural information
Nuclear Magnetic Resonance (NMR) Spectroscopy

Detailed structural information about compounds

1-Nitropropane
How does this work?

The nuclei of atoms are little bar magnets

If you put a sample in a magnetic field you can observe the interactions between the nuclei and the magnet

Tells you what kind of nuclei and therefore what kinds of atoms!
These tiny bar magnets will align with or against an external magnetic field.

- A spinning proton creates a magnetic field.
- With no external magnetic field...
  - The nuclear magnets are randomly oriented.
- In a magnetic field...
  - The nuclear magnets are oriented with or against $B_0$. 
Spin States of Nuclei are Affected by Magnetic Fields

Spin states not aligned (random)

Spin states aligned:
- with magnetic field (α)
- OR against magnetic field (β)

magnetic field is applied
Energy Difference between the spin states is determined by the strength of the magnetic field.
Apply external energy source that matches $\Delta E$ to cause "spin flip" from $\alpha$ to $\beta$ spin state.

- A nucleus is in resonance when it absorbs RF radiation and "spin flips" to a higher energy state.
Use NMR to detect the difference in energy between the spin states

\[ \alpha \text{-spin states} \quad \leftrightarrow \quad \beta \text{-spin states} \]

Absorb $\Delta E$

Release $\Delta E$

Signals detected by NMR
Surroundings of a nucleus impact how much it “feels” the magnetic field.

Nuclei in different electronic environments will be “shielded” to different extents and give rise to different NMR signals.

- These protons sense a larger effective magnetic field, so come into resonance at a higher frequency.
- These protons sense a smaller effective magnetic field, so come into resonance at a lower frequency.

The diagram shows a graph with frequency on the x-axis and intensity on the y-axis. The graph is divided into two peaks, labeled as "deshielded nuclei" and "shielded nuclei." The peaks are positioned at different frequencies, labeled as "downfield" and "upfield." The intensity is shown with arrows pointing upwards from the baseline.

The diagram includes a label at the bottom left corner indicating "downfield" and at the bottom right corner indicating "upfield." The frequency range is marked from 0 ppm to 10 ppm.
Typical $^1$H NMR Spectrum:

Sample $^1$H NMR spectrum
$\text{CH}_3\text{OC(CH}_3)_3$

chemical shift (ppm) = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{v \text{ of the NMR spectrometer (in MHz)}}
Information from $^1$H NMR:

- Four different features of a $^1$H NMR spectrum provide information about a compound’s structure:
  - a. Number of signals
  - b. Position of signals
  - c. Intensity of signals.
  - d. Spin-spin splitting of signals.
a. Number of signals:

Protons in the same chemical environment will give identical signals (these protons are “chemically equivalent”; all 9 methyl protons)

Protons in different chemical environments will give rise to different signals (methyl protons vs methylene protons)
$^1$H NMR—Number of Signals

- # NMR signals = # of different types of protons in a compound.
- Protons in different environments give different NMR signals.
- Equivalent protons give the same NMR signal.
Predict the number of signals in the NMR spectrum:
Alkenes and Rings: Draw in the protons!

- Two protons are equivalent only if they are cis (or trans) to the same groups.
b. Position of Signals: tells about nearby functional groups

An isolated proton

$B_0$

The nucleus “feels” $B_0$ only.

A proton surrounded by electron density

$B_0$

magnetic field induced by the electron (opposite to $B_0$)

The induced field *decreases* the strength of the magnetic field “felt” by the nucleus.

This nucleus is shielded.
Shielding versus Deshielding

**a. Shielding effects**
- An electron shields the nucleus.
- The absorption shifts *upfield*.

**b. Deshielding effects**
- Decreased electron density deshields a nucleus.
- The absorption shifts *downfield*.

- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.
- The absorption shifts upfield.

- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance.
- The absorption shifts downfield.
Electronegative atoms deshield nearby protons - those protons will resonate downfield.

- Shielded protons absorb at lower chemical shift (to the right).
- Deshielded protons absorb at higher chemical shift (to the left).

A C—H bond becomes more deshielded as it gets closer to electronegative atoms.
Which proton will be more deshielded and resonate further downfield, $H_a$ or $H_b$?
$^1$H NMR—Chemical Shift Values

- The chemical shift of a C—H bond increases with increasing alkyl substitution.

<table>
<thead>
<tr>
<th>Substitution</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH$_2$—H</td>
<td>~ 0.9 ppm</td>
</tr>
<tr>
<td>R$_2$CH—H</td>
<td>~ 1.3 ppm</td>
</tr>
<tr>
<td>R$_3$C—H</td>
<td>~ 1.7 ppm</td>
</tr>
</tbody>
</table>

Increasing alkyl substitution
Increasing chemical shift
Chemical Shift: protons in given environment absorb in predictable region of NMR spectrum. 

Tells you about nearby functional groups
Rank $H_a$, $H_b$, and $H_c$ from deshielded to shielded
c. Intensity of the signals

The area under an NMR signal is proportional to the number of absorbing protons.

The ratio of integrals to one another gives the ratio of absorbing protons in a spectrum. Note that this gives a ratio, and not the absolute number, of absorbing protons.
Integration = area under the signal
= number of protons that give rise to the signal

Integration = 3

Integration = 9

CH₃OC(CH₃)₃

NMR integration

chemical shift (ppm)
Predict integration:

1-bromo-2,2-dimethylpropane

methylene protons

methyl protons

TMS signal

δ (ppm)

frequency
Predict integration:

Integration = 9

Integration = 2

1-bromo-2,2-dimethylpropane
Predict the $^1$H NMR integration of the illustrated hydrogens in the following spicy compounds

<table>
<thead>
<tr>
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<tr>
<td>Integration</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Splitting pattern</td>
<td></td>
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cinnamaldehyde
- cinnamon flavor
Predict the $^1$H NMR splitting patterns and integration of the illustrated hydrogens in the following spicy compounds

**capsaicin**
- chili peppers

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</table>
d. Spin-Spin Splitting of Signals

“Splitting Patterns”

Each resonance has a complex shape that gives information about its environment (its neighbors)
\(^1\)H NMR—Spin-Spin Splitting

**Spin-spin splitting** occurs only between nonequivalent protons on the same carbon or adjacent carbons.

An example:

![Chemical structure](image)

1,1-dichloroethane:
- would show 2 signals in \(^1\)H NMR
- The non-equivalent protons are on adjacent carbons
- Therefore, we should observe spin-spin splitting between the red and blue H’s
$^1\text{H NMR—Spin-Spin Splitting: An example}$

Consider the signal for the \( \text{CH}_3 \)
The adjacent H impacts the applied magnetic field “felt” by CH₃

• The adjacent proton (CHCl₂) can be aligned with (↑) or against (↓) B₀ (the applied magnetic field).

• Thus, the absorbing CH₃ protons feel two slightly different magnetic fields—one slightly larger than B₀, and one slightly smaller than B₀.

• Since the absorbing CH₃ protons feel two different magnetic fields, they absorb at two different frequencies in the NMR spectrum, thus splitting a single absorption into a doublet.


$^1$H NMR—Spin-Spin Splitting: An example

Consider the signal for the CH$_3$Cl

- With no adjacent H's: The absorbing H's feel only one magnetic field.
- With one adjacent H: The absorbing H's feel two different fields, so they absorb at two different frequencies.

The NMR signal is a single peak.

The NMR signal is split into a doublet.

- One adjacent proton splits an NMR signal into a doublet.
A closer look at the methyl doublet
(a splitting diagram)

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
$^1$H NMR Spectrum of 1,1-Dichloroethane
Rules for Splitting Patterns

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 $H_a$ and $H_b$ are not equivalent, splitting is observed when:

- $H_a$ and $H_b$ are on the same carbon.
- $H_a$ and $H_b$ are on adjacent carbons.
Splitting is not generally observed between protons separated by more than three $\sigma$ bonds.

2-butanoic
$H_a$ and $H_b$ are separated by four $\sigma$ bonds.

no splitting between $H_a$ and $H_b$

ethyl methyl ether
$H_a$ and $H_b$ are separated by four $\sigma$ bonds.

no splitting between $H_a$ and $H_b$
The n+1 rule

<table>
<thead>
<tr>
<th># of non-equivalent protons on adjacent carbon:</th>
<th># of peaks:</th>
<th>Name:</th>
<th>Looks like:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>doublet</td>
<td><img src="image1.png" alt="Diagram 1" /></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>triplet</td>
<td><img src="image2.png" alt="Diagram 2" /></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>quartet</td>
<td><img src="image3.png" alt="Diagram 3" /></td>
</tr>
</tbody>
</table>
Naming Splitting Patterns

<table>
<thead>
<tr>
<th>Number of peaks</th>
<th>Name</th>
<th>Number of peaks</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>singlet</td>
<td>5</td>
<td>quintet</td>
</tr>
<tr>
<td>2</td>
<td>doublet</td>
<td>6</td>
<td>sextet</td>
</tr>
<tr>
<td>3</td>
<td>triplet</td>
<td>7</td>
<td>septet</td>
</tr>
<tr>
<td>4</td>
<td>quartet</td>
<td>&gt; 7</td>
<td>multiplet</td>
</tr>
<tr>
<td>Example</td>
<td>Pattern</td>
<td>Analysis (H&lt;sub&gt;a&lt;/sub&gt; and H&lt;sub&gt;b&lt;/sub&gt; are not equivalent.)</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>-------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>[1] C-C</td>
<td><img src="image" alt="Pattern 1" /></td>
<td>H&lt;sub&gt;a&lt;/sub&gt;: one adjacent H&lt;sub&gt;b&lt;/sub&gt; proton → two peaks → a doublet</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;b&lt;/sub&gt;: one adjacent H&lt;sub&gt;a&lt;/sub&gt; proton → two peaks → a doublet</td>
<td></td>
</tr>
<tr>
<td>[2] C-CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td><img src="image" alt="Pattern 2" /></td>
<td>H&lt;sub&gt;a&lt;/sub&gt;: two adjacent H&lt;sub&gt;b&lt;/sub&gt; protons → three peaks → a triplet</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;b&lt;/sub&gt;: one adjacent H&lt;sub&gt;a&lt;/sub&gt; proton → two peaks → a doublet</td>
<td></td>
</tr>
<tr>
<td>[3] CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td><img src="image" alt="Pattern 3" /></td>
<td>H&lt;sub&gt;a&lt;/sub&gt;: two adjacent H&lt;sub&gt;b&lt;/sub&gt; protons → three peaks → a triplet</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;b&lt;/sub&gt;: two adjacent H&lt;sub&gt;a&lt;/sub&gt; protons → three peaks → a triplet</td>
<td></td>
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<tr>
<td>[4] CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td><img src="image" alt="Pattern 4" /></td>
<td>H&lt;sub&gt;a&lt;/sub&gt;: three adjacent H&lt;sub&gt;b&lt;/sub&gt; protons → four peaks → a quartet*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;b&lt;/sub&gt;: two adjacent H&lt;sub&gt;a&lt;/sub&gt; protons → three peaks → a triplet</td>
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<tr>
<td>[5] C-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td><img src="image" alt="Pattern 5" /></td>
<td>H&lt;sub&gt;a&lt;/sub&gt;: three adjacent H&lt;sub&gt;b&lt;/sub&gt; protons → four peaks → a quartet*</td>
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<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;b&lt;/sub&gt;: one adjacent H&lt;sub&gt;a&lt;/sub&gt; proton → two peaks → a doublet</td>
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*The relative area under the peaks of a quartet is 1:3:3:1.*
Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the \( n + 1 \) rule to determine the splitting pattern.
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:

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

One nearby H splits the signal into a doublet.

The second nearby proton splits the doublet into a doublet of doublets.
Predict the $^1$H NMR splitting patterns and integration of the illustrated hydrogens in the following spicy compounds.

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*zingerol*
- causes burning sensation associated with eating ginger
Predict the $^1$H NMR splitting patterns and integration of the illustrated hydrogens in the following spicy compounds.

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cinnamaldehyde - cinnamon flavor
Predict the $^1$H NMR splitting patterns and integration of the illustrated hydrogens in the following spicy compounds.

**capsaicin**  
- chili peppers

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Protons Bound to Oxygen and Nitrogen

The greater the extent of hydrogen bonding, the greater the chemical shift (higher frequency, more desheilded)

They usually appear as broad signals and do not couple to H on adjacent carbons
$^{13}$C NMR Spectroscopy

Subway map

Information about carbon backbone
Proton-Decoupled $^{13}$C NMR of 2-Butanol

The number of signals = the number of different kinds of carbons in a compound

* Cannot integrate to get the relative ratio of carbons!
$^{13}$C NMR spectrum of

\[
\begin{array}{c}
\text{C} = \text{O} \\
\text{CH}_3
\end{array}
\]
Number of signals in $^{13}$C NMR Spectrum?

- **cinnamaldehyde**
  - cinnamon flavor

- **zingerol**
  - causes burning sensation associated with eating ginger

- **capsaicin**
  - chili peppers