Ch. 23 Nuclear Magnetic Resonance Spectroscopy
Intro to NMR Spec.

**β-spin state**
higher energy state
very few

**applied magnetic field**

Intro to NMR Spec.

rf radiation

E₁ more

NMR

e⁻⁻ e⁻⁻ e⁻⁻
diamagnetic shielding

E₂ less

Intro to NMR Spec.

deshielded higher E

E₁

shielded lower E

E₂

signal

signal

a

b

energy

E₁

E₂

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Nuclear Magnetic Resonance Spec. 2
**Key Points**

1. Because of its charge and spin, a nucleus can behave like a magnet.
2. NMR spectroscopy operates by applying a magnetic field to nuclei and then measuring the amount of energy necessary to put various nuclei in resonance.
3. Nuclei in different electronic environments (shielded or deshielded) require different amounts of energy to bring them into resonance.
4. An NMR spectrum provides a signal or peak representing the energy necessary to bring each nuclei into resonance.

**Sample Problem**

1) How many signals would there be in the NMR spectrum of the following molecules?

- $\text{CH}_3\text{CH}_2\text{CH}_3$
- $\text{CH}_3\text{CH}\text{CH}_2\text{CH}_3$
Sample Problem 2) How many signals would there be in the NMR spectrum of the following molecule?

\[
\begin{align*}
&\text{CH}_3 \\
&\text{H}_3\text{C}-\text{CCH}_2\text{CH}_3 \\
&\text{CH}_3
\end{align*}
\]

Sample Problem 3) How many signals would there be in the NMR spectrum of the following molecule?

\[
\begin{align*}
&\text{H} \\
&\text{C}=\text{C} \\
&\text{H} \\
&\text{H}
\end{align*}
\]

Sample Problem 4) How many signals would there be in the NMR spectrum of the following molecule?

\[
\begin{align*}
&\text{CH}_3 \\
&\text{C}=\text{C} \\
&\text{H} \\
&\text{H} \\
&\text{H}
\end{align*}
\]
Sample Problem 5) How many signals would there be in the NMR spectrum of the following molecule?

![苯基甲基甲基烷基甲基](image)

Sample Problem 6) How would you use HNMR spectroscopy to distinguish cis-1,2-dimethylcyclopropane, trans-1,2-dimethylcyclopropane, and 1,1-dimethylpropane?

![顺-1,2-二甲基环丙烷、反-1,2-二甲基环丙烷和1,1-二甲基丙烷](image)

1st Aspect of NMR - # of Peaks

![1,1-二甲基环丙烷](image)
cis-1,2-dimethylcyclopropane

trans-1,2-dimethylcyclopropane

Sample Problem 7) How many signals would there be in the NMR spectrum of the following molecule?
1st Aspect of NMR - # of Peaks

4 Aspects of NMR
1. The number of peaks in the NMR spectrum equal the number/type of hydrogens/other atoms in the molecule

2nd Aspect of NMR - Shifting

NMR

ClCH₂CH₃

<table>
<thead>
<tr>
<th>Cl</th>
<th>CH₂</th>
<th>CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
<td></td>
</tr>
</tbody>
</table>

Energy

a  b 0
Sample Problem 1) Provide a rough sketch of the HNMR spectrum of the following molecule:

\[
\text{O}_2\text{NCH}_2\text{CH}_2\text{CH}_3
\]
Sample Problem 2) Provide a rough sketch of the HNMR spectrum of the following molecule:

\[ \text{CH}_3 \text{H}_3\text{C-CH-CH}_3 \text{CH}_3 \]

Sample Problem 3) Provide a rough sketch of the HNMR spectrum of the following molecule:

\[ \text{CH}_3 \text{HCCCH}_2\text{CH}_3 \text{CH}_3 \]

shifting:
\[ 3^\circ > 2^\circ > 1^\circ \]

Sample Problem 4) Provide a rough sketch of the HNMR spectrum of the following molecule:

\[ \text{CH}_3\text{CH}==\text{CH}_2 \]
Sample Problem 5) Provide a rough sketch of the HNMR spectrum of the following molecule:

\[
\text{CH}_3
\]

2nd Aspect of NMR - Shifting

2nd Aspect of NMR - Shifting

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Nuclear Magnetic Resonance Spec. 13
2nd Aspect of NMR - Shifting

\[ \delta = \frac{\text{distance downfield from TMS (Hz)}}{\text{operating frequency of the NMR (MHz)}} \]

<table>
<thead>
<tr>
<th>proton</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₃</td>
<td>0.85</td>
</tr>
<tr>
<td>-CH₂</td>
<td>1.20</td>
</tr>
<tr>
<td>-CH⁻</td>
<td>1.55</td>
</tr>
<tr>
<td>=CH₂</td>
<td>4.7</td>
</tr>
<tr>
<td>R-OH</td>
<td>2-5 variable</td>
</tr>
</tbody>
</table>

~2.4 ppm  H=C≡
2nd Aspect of NMR - Shifting

4 Aspects of NMR
2. Proximity to an electronegative atom and/or multiple bond causes a peak to be shifted downfield

3rd Aspect of NMR - Integration

CICH₂CH₃

NMR

a  b
3rd Aspect of NMR - Integration

\[
\text{ClCH}_2\text{CH}_3
\]

\[
\frac{a}{b} = \frac{2}{3} = \frac{a}{b}
\]

4 Aspects of NMR

3. There is a relationship between the area under a peak and the number of hydrogens responsible for the peak.
Sample Problem 1) Give the multiplicity of each kind of hydrogen in the following molecule:

BrCH₂CH₂F
Sample Problem 2) Give the multiplicity of each kind of hydrogen in the following molecule:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{H}_3\text{C} & - \quad - \quad \text{CH}_2\text{Cl} \\
\text{CH}_3 &
\end{align*}
\]

Sample Problem 3) Give the multiplicity of each kind of hydrogen in the following molecule:

\[
\text{CH}_3\text{CH}_2\text{CH}_3
\]

Sample Problem 4) Give the multiplicity of each kind of hydrogen in the following molecule:

\[
\text{FCH}_2\text{CH}_2\text{CH}_2\text{Cl}
\]
Sample Problem 5) Give the multiplicity of each kind of hydrogen in the following molecule:

\[ \text{CH}_3\text{CH}_3 \]

A peak or signal cannot be split by its equivalent

Sample Problem 6) Give the multiplicity of each kind of hydrogen in the following molecule:

\[ \text{H} - \text{C} = \text{C} - \text{H} \]

\[ \text{F} - \text{C} = \text{C} - \text{F} \]

Sample Problem 7) Give the multiplicity of each kind of hydrogen in the following molecule:

\[ \text{F} - \text{C} = \text{C} - \text{H} \]

\[ \text{H} - \text{C} = \text{C} - \text{Br} \]
Sample Problem 8) Give the multiplicity of each kind of hydrogen in the following molecule:

Sample Problem 9) Give the multiplicity of each kind of hydrogen in the following molecule:

4th Aspect of NMR - Splitting
4th Aspect of NMR - Splitting

\[
\text{CH}_2\text{CH}_3
\]

8-6.5 ppm

cd be a

4th Aspect of NMR - Splitting

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} - & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} = & \\
\end{align*}
\]

4th Aspect of NMR - Splitting

\[
\begin{align*}
\text{C} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{long-range coupling} & \\
\end{align*}
\]
4th Aspect of NMR - Splitting

H \(\text{C}--\text{C}--\text{C}\) H

no splitting observed

4 Aspects of NMR
4. Peaks can be split due to neighboring/different hydrogens

Cl\(_2\)C\(\text{H}\)CH\(_3\)

\(B_{\text{effective}}\)

quartet
4th Aspect of NMR - Splitting

doublet

4th Aspect of NMR - Splitting

doublet

doublet

4 Aspects of NMR

1. The number of peaks in the NMR spectrum equal the number of hydrogens in the molecule
2. Proximity to an electronegative atom and/or multiple bond causes a peak to be shifted downfield
3. There is a relationship between the area under a peak and the number of hydrogens responsible for the peak
4. Peaks can be split due to neighboring/different hydrogens
**Key Points**

1. Coupling constants, or $J$ values, measure the distance between split peaks in Hz.
2. Coupling constants are not dependent on the field strength or the operating frequency of the spectrometer.
3. Coupling constants are useful in analyzing complex NMR spectra because protons on adjacent carbons can be identified by their identical coupling constants.

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**Splitting Diagrams**

Cl$_2$CHCH$_2$CHF$_2$

$N_{b_{left}} = 1$ \hspace{1cm} $N_{b_{right}} = 1$

$N+1=2$ \hspace{1cm} $N+1=2$

$J_{ba}$

$J_{bc}$

$J_{bc}$

---

ClCH$_2$CH$_2$CH$_3$

$N_{b_{left}} = 2$ \hspace{1cm} $N_{b_{right}} = 3$

$N+1=3$ \hspace{1cm} $N+1=4$

$J_{ba}$

$J_{bc}$

$J_{bc}$

$J_{bc}$
Sample Problem 1) Provide the splitting diagram for H_6 given that J_{HH} is 10 Hz and J_{HC} is also 10 Hz:

\[ \text{Br}_2\text{CHCH}_2\text{CHF}_2 \]

Key Points

1. Splitting diagrams can be generated for complex splitting in an NMR spectra.
2. Generating splitting diagrams involves using the N+1 rule separately for each neighboring hydrogen along with J values.
3. Splitting diagrams can determine if certain peaks will overlap, resulting in less peaks than expected.

Enantiotopic and Diastereotopic Hydrogens

\[ \begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{Br} \\
\text{H} \\
\text{H} \\
\end{array} \]
Sample Problem 1) How many signals would be observed in the HNMR for the following molecule?

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

Key Points
1. Enantiotopic hydrogens are chemically equivalent therefore they give only one NMR signal
2. Diastereotopic hydrogens are NOT chemically equivalent therefore they have different chemical shifts in an NMR spectra
OH and NH Signals in HNMR

\[
\text{HOCH}_2\text{CH}_3 \quad \text{pure and dry}
\]

\[
\text{OH and NH Signals in HNMR}
\]

\[
\text{HOCH}_2\text{CH}_3 \leftrightarrow \text{OCH}_2\text{CH}_3
\]

no splitting

proton exchange

trace acid/base

\[
\text{OH and NH Signals in HNMR}
\]

\[
\text{HOCH}_2\text{CH}_3 \quad \text{trace acid/base}
\]

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Nuclear Magnetic Resonance Spec. 30
### Key Points

1. No splitting is observed for protons on N or O if the sample is run with a trace amount of acid or base. This is due to Proton Exchange.
2. The signals for protons on N or O are usually broader than other signals on an HNMR spectra.
Deuterium in HNMR

HOCH$_2$CH$_3$ \[\xrightarrow{\text{D}_2\text{O}}\] DOCH$_2$CH$_3$

proton exchange

Deuterium in HNMR

DOCH$_2$CH$_3$ \[\text{NMR}\]

trace acid/base with D$_2$O

Key Points

1. Deuterium signals are not observed in an HNMR spectrum
2. Substituting deuterium for a hydrogen is a technique used to simplify HNMR spectra or verify signals
Key Points
1. The principles of $^{13}$C NMR are essentially the same for $^1$H NMR.
2. Fourier transform is necessary to create $^{13}$C NMR spectra.
3. $^{13}$C NMR can be run in three modes: spin-decoupled mode, proton-coupled mode, and DEPT.

![DEPT mode diagram](image)

DEPT NMR
- $\text{CH}_2 = \text{negative peak}$
- $\text{C} = \text{no peak}$
- $\text{CH}_3, \text{CH} = \text{positive peak}$
Sample Problem 1

IR

CNMR decoupled

HNMR

C₈H₁₀O₂

OCH₃

OCH₃

CH₃

OCH₂CH₃

CH₂OH

HNMR

CH₃

OCH₃

OCH₂CH₃

CH₂OH

Sample Problem 1

IR

CNMR decoupled

HNMR

C₈H₁₀O₂

OCH₃

OCH₃

CH₃

OCH₂CH₃

CH₂OH

HNMR

CH₃

OCH₃

OCH₂CH₃

CH₂OH