Chapter 13 - Spectroscopy

YSU 400 MHz Nuclear Magnetic Resonance Spectrometer(s)

Techniques used to find structures of organic molecules

**NMR spectroscopy:** Based on the response of magnetic nuclei to an external magnetic field and an energy source (Radio frequency)

**IR spectroscopy:** Response of bonds within organic molecules to externally applied Infra Red light

**UV/Vis spectroscopy:** Response of electrons within bonds to externally applied UV or Visible light

**Mass spectrometry:** Response of molecules to being bombarded with high energy particles such as electrons
13.1 The Electromagnetic spectrum - Figure 13.1

13.2 Two (quantized) energy states - Figure 13.2

\[ \Delta E = E_2 - E_1 = h\nu \]
13.2 Physics Concepts

\[ E = h\nu \]

i.e. Energy of the radiation is directly proportional to its frequency \((n = \text{Planck's constant})\)

\[ \nu = c/\lambda \]

i.e. Frequency of the radiation is inversely proportional to its wavelength \((c = \text{speed of light})\)

\[ E = hc/\lambda \]

i.e. Energy of the radiation is inversely proportional to its wavelength

*Take home:*

- Longer wavelength, lower energy
- Higher frequency, higher energy

13.3 Introduction to \(^1\text{H} \text{NMR} – \text{Nuclear Spin}\)

- (a) No external magnetic field
- (b) Apply external magnetic field \(B_0\)

Nuclear spins of protons \((^1\text{H} \text{nucleus})\) - Figure 13.3
Energy difference between states increases with field strength (Fig. 13.4)

No energy difference in nuclear spin states in absence of external magnetic field.

Increasing strength of external magnetic field.

Nuclear magnetic moment antiparallel to $B_0$

Nuclear magnetic moment parallel to $B_0$.

Schematic diagram of a Nuclear Magnetic Resonance spectrometer.
Basic operation of a Fourier Transform (FT) NMR Instrument (Fig. 13.5)

13.4 NMR Spectrum Characteristics – Chemical Shift

Position of signal is the chemical shift
**13.4 NMR Spectrum Characteristics – Chemical Shift**

Chemical shift ($\delta$) = position of signal – position of TMS peak $\times 10^6$

Enables us to use same scale for different size spectrometers (60 MHz, 400 MHz, 850 MHz, etc.) throughout the world

TMS = (CH$_3$)$_4$Si, signal appears at 0 Hz on spectrum, therefore used as reference

Chemical shifts are reported as ppm (parts per million) relative to TMS and usually occur in the 0-12 ppm range for $^1$H spectra

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**13.5 Effect of molecular structure on $^1$H Chemical Shift**

<table>
<thead>
<tr>
<th>CH$_3$F</th>
<th>CH$_3$OCH$_3$</th>
<th>(CH$_3$)$_3$N</th>
<th>CH$_3$CH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3</td>
<td>3.2</td>
<td>2.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

i.e. electronegativity of other atoms plays a role in shift

CH$_3$CH$_3$ ~0.9 ppm

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13.5 Effect of E.N. on Chemical Shift

\[ \text{CH}_3 \]

\[ \text{H}_3\text{C}^\text{N}\text{CH}_3 \]

~2.2 ppm

13.5 Effect of E.N. on Chemical Shift

\[ \text{H}_3\text{C}^\text{O}\text{CH}_3 \]

~3.2 ppm
### 13.5 Effect of E.N. on Chemical Shift

**CH₃F**

~4.3 ppm

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### 13.5 Effect of molecular structure on ¹H Chemical Shift

<table>
<thead>
<tr>
<th>Structure</th>
<th>¹H Chemical Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td>7.3</td>
</tr>
<tr>
<td><img src="image2" alt="Structure" /></td>
<td>5.3</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>0.9</td>
</tr>
</tbody>
</table>

Pi electrons reinforce external field and signals show *downfield*.

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*Fig 13.8*
13.5 Effect of molecular structure on $^{1}$H Chemical Shift

Spectra typically have multiple signals the number depending on the
number of unique types of protons
### Table 13.1: Approximate Chemical Shifts of Representative Protons

<table>
<thead>
<tr>
<th>Compound class or type of proton</th>
<th>Chemical shift (δ, ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protons bonded to carbon</strong></td>
<td></td>
</tr>
<tr>
<td>Aliphatic</td>
<td>1.0-1.8</td>
</tr>
<tr>
<td>Terminal alkyne</td>
<td>1.8-3.1</td>
</tr>
<tr>
<td>C−H adjacent to C−O</td>
<td>2.0-2.5</td>
</tr>
<tr>
<td>C−H adjacent to C=C=N</td>
<td>2.3-2.5</td>
</tr>
<tr>
<td>Benzyllic</td>
<td>2.3-2.8</td>
</tr>
<tr>
<td>Amines</td>
<td>2.2-2.5</td>
</tr>
<tr>
<td><strong>Protons bonded to nitrogen or oxygen</strong></td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td>3.1-4.1</td>
</tr>
<tr>
<td>Acetylene</td>
<td>3.3-3.7</td>
</tr>
<tr>
<td>Vinyl</td>
<td>4.5-6.5</td>
</tr>
<tr>
<td>Aryl</td>
<td>6.0-6.6</td>
</tr>
<tr>
<td>Azide</td>
<td>9-10</td>
</tr>
</tbody>
</table>

Alkyl chloride  
Alkyl bromide  
Alcohol or ether  
Vinyl  
Aryl  
Acetylene  
Aniline  
Alcohol  
Phenol  
Carboxylic acid
13.5 Typical $^1$H NMR Spectra

Simple alkane protons – $R_2CH_2$

From spectroscopy sheet – chemical shift ~ 0.9-1.8 ppm
Ether protons -O-C-H
From spectroscopy sheet – chemical shift ~ 3.3-3.7 ppm

Two types of ether protons -O-C-H
From spectroscopy sheet – chemical shift ~ 3.3-3.7 ppm
CH₂ further downfield (two neighbouring O atoms)
13.5 Typical $^1$H NMR Spectra

**Aldehyde proton $-{\text{CHO}}$**
From spectroscopy sheet – chemical shift $\sim$ 9-10 ppm
3 types of Ar-H proton – chemical shift $\sim$ 6.5-8.5 ppm

**Carboxylic acid proton $-{\text{CO}}_2\text{H}$**
From spectroscopy sheet – chemical shift $\sim$ 10-13 ppm
3 types of Ar-H proton – chemical shift $\sim$ 6.5-8.5 ppm
13.6 Integration – Ratio of different types of H

Lines on spectra are curves
Areas underneath each curve give a reliable ratio of the different numbers of each type of proton

Areas are given as a ratio, not an absolute number
13.6 Integration – Ratio of different types of H

13.7 Spin-Spin Splitting – Effect of neighbour H on signal shape
13.7 Spin-Spin Splitting – Effect of neighbour H on signal shape
### 13.7 Spin-Spin Splitting – Effect of neighbour H on signal shape

**General rule for splitting patterns**

For simple cases, multiplicity for \( H = n + 1 \)

Where \( n \) = number of neighbouring protons

1 neighbour, signal appears as a doublet
2 neighbours, signal appears as a triplet
3 neighbours, signal appears as a quartet
4 neighbours, signal appears as a quintet, etc.

Complex splitting patterns are referred to as **multiplets**

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### 13.7-13.10 Basis of Splitting Patterns

For **red** H : neighbouring H (blue) has two possible alignments, either with, or against, the external field (Ho). This effects the local magnetic environment around the **red** H and thus there are two slightly different frequencies (and thus chemical shifts) at which the **red** H resonates. The same applies to the **blue** H.

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13.7-13.10 Basis of Splitting Patterns

**Red H will be a triplet**

**Blue H’s will be a doublet**

Red H will be split into a quartet, blue H’s will be split into a doublet.
Gaps between lines (in Hz) will be the same for adjacent protons (here ~7.4 Hz). This is known as the **coupling constant**.

Using Coupling Constants

Find J and match signals

CH₃CH₂ but which one?

CH₃CH₂O
If nonequivalent neighbours have same $J$ value then $n+1$ applies for signal.

When nonequivalent neighbours have different $J$ values then $n+1$ does not apply for signal.

Generally for alkene protons: $J_{trans} > J_{cis}$
13.11 Complex Splitting Patterns

Acidic protons exchange with any H₂O in sample

13.12 ¹H NMR Spectra of Alcohols

Acidic protons exchange with any H₂O in sample
H1, H2, H3, and H4 hard to distinguish just from coupling constants (all J ~ 9 Hz)

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Carbon 13 isotope and not $^{12}$C is observed in NMR spectroscopy

$^{13}$C very low abundance (<1%), consequently integration not useful

Spectra usually “decoupled” and signals are observed as singlets

Number of distinct signals indicates distinct types of carbon

Same ideas about shielding/deshielding apply in $^{13}$C spectroscopy

Spectra often measured in CDCl$_3$ and referenced to either the C in TMS (0 ppm) or the C in CDCl$_3$, which shows as a triplet at 77.0 ppm
Not covering 13.17-13.19

13.20 Infrared Spectroscopy
Information on the types of bonds within molecules
13.20 Stretching and bending vibrations of a methylene unit

**Figure 13.25**

Don’t memorize, learn to use as you practice problems
13.20 Interpreting IR Spectra – n-Hexane

Figure 13.31

13.20 Interpreting IR Spectra – 1-Hexene

Figure 13.32
13.20 Interpreting IR Spectra – t-Butylbenzene

Figure 13.33

13.20 Interpreting IR Spectra – 2-Hexanol

Figure 13.34
13.20 Interpreting IR Spectra – 2-Hexanone

Figure 13.35

13.21 Ultraviolet-Visible (UV-Vis) Spectroscopy

Useful for identifying chromophores in molecules (benzene rings, conjugated alkene systems) - More useful in Biochemistry

Figure 13.37

Figure 13.38
13.22 Mass Spectrometry

Gives information on molecular mass and structure

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13.22 Mass Spectrometry

Exam Problems

1. (10 pts) An unknown organic compound has the empirical formula C₉H₁₄. Given the following spectral data, provide a structure for the unknown that agrees with the data. Match the \( ^1H \) NMR data to your answer:

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

1.24 (t, 6H, \( J = 7.0 \text{ Hz} \)), 2.59 (q, 4H, \( J = 7.0 \text{ Hz} \)), 7.05 (m, 4H)

\[ ^13C \text{ NMR (ppm)} \]

14.6, 32.7, 125.0, 128.3, 128.6, 139.4 (4 π-α-C is a clue to meta substitution)

Mass spectrum (m/z) 134, 20 (M⁺) (matches formula, therefore C₁₀H₁₄ is actual formula)

Infra Red (cm⁻¹) 720, 800 (close to meta substitution)
Exam Problems

6. (10 pts) Which structure below do the following spectra belong to? Explain your answer by matching the \(^1\)H NMR data to the structure you choose.

- \(^1\)H NMR (ppm): 1.06 (t, 3H, \(J = 6.9\) Hz), 1.22 (t, 3H, \(J = 7.1\) Hz), 2.00 (q, 2H, \(J = 6.9\) Hz), 2.09 (s, 3H), 3.12 (d, 2H, \(J = 7.3\) Hz), 4.00 (q, 2H, \(J = 7.1\) Hz), 4.59 (t, 1H, \(J = 7.3\) Hz)
- \(^13\)C NMR (ppm): 84.4, 15.6, 25.1, 31.0, 39.4, 62.6, 98.2, 154.4, 202.9
- IR (cm\(^{-1}\)): 1690, 1720
Exam Problems

6. (10 pts) Which structure below do the following spectra belong to? Explain your answer by matching the \(^1\)H NMR data to the structure you choose.

\(^1\)H NMR (ppm) 1.06 (t, 3H, J = 6.9 Hz), 1.22 (t, 3H, J = 7.1 Hz), 2.00 (q, 2H, J = 6.9 Hz), 2.09 (s, 3H), 3.12 (d, 2H, J = 7.3 Hz), 4.00 (q, 2H, J = 7.1 Hz), 4.59 (t, 1H, J = 7.3 Hz)

\(^13\)C NMR (ppm) 8.4, 15.6, 25.1, 31.0, 39.4, 42.6, 58.2, 134.4, 202.9

IR (cm\(^{-1}\)) 1630, 1720