Chapter 13 - Spectroscopy

YSU 400 MHz Nuclear Magnetic Resonance Spectrometers

Techniques used to find structures of organic molecules

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
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<tbody>
<tr>
<td>NMR spectroscopy</td>
<td>Based on the response of magnetic nuclei to an external magnetic field and an energy source (Radio frequency)</td>
</tr>
<tr>
<td>IR spectroscopy</td>
<td>Response of bonds within organic molecules to externally applied Infra Red light</td>
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<tr>
<td>UV/Vis spectroscopy</td>
<td>Response of electrons within bonds to externally applied UV or Visible light</td>
</tr>
<tr>
<td>Mass spectrometry</td>
<td>Response of molecules to being bombarded with high energy particles such as electrons</td>
</tr>
</tbody>
</table>

13.1 The Electromagnetic spectrum Figure 13.1
### 13.2 Two (quantized) energy states

**Figure 13.2**

<table>
<thead>
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<td><strong>Take home</strong>:</td>
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<td></td>
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<tr>
<td>Higher frequency, higher energy</td>
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### 13.2 Physics Concepts

**Figure 13.2**

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### 13.3 Introduction to ¹H NMR – Nuclear Spin

**Figure 13.3**

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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Nuclear spins of protons (¹H nucleus)</strong></td>
<td></td>
</tr>
</tbody>
</table>
Energy difference between states increases with field strength (Fig. 13.4)

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**

\[ \text{Chemical shift (δ)} = \frac{\text{position of signal} - \text{position of TMS peak} \times 10^6}{\text{spectrometer frequency}} \]

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

- TMS = (CH₃)₄Si, 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 ¹H spectra

13.5 Effect of molecular structure on ¹H Chemical Shift

- \( \text{CH}_3\text{F} \) = 4.3 ppm
- \( \text{CH}_2\text{OCH}_3 \) = 3.2 ppm
- \( \text{CH}_3\text{N} \) = 2.2 ppm
- \( \text{CH}_3\text{CH}_3 \) = 0.9 ppm

\( \text{i.e. electronegativity of other atoms plays a role in shift} \)
- $\text{CH}_3\text{NCH}_2\text{CH}_3$ at ~2.2 ppm
- $\text{H}_2\text{C}^\text{O-CH}_3$ at ~3.2 ppm
- $\text{CH}_3\text{F}$ at ~4.3 ppm
Pi electrons reinforce external field and signals show downfield.

Spectra typically have multiple signals the number depending on the number of unique types of protons.
**Table 13.1 – Chemical Shift Values**

<table>
<thead>
<tr>
<th>0 ppm</th>
<th>1 ppm</th>
<th>2 ppm</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

**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)

Aldehyde proton -CHO
From spectroscopy sheet – chemical shift ~ 9-10 ppm
3 types of Ar-H proton – chemical shift ~ 6.5-8.5 ppm
13.5 Typical \(^1\)H NMR Spectra

- Carboxylic acid proton -CO\(_2\)H
- From spectroscopy sheet – chemical shift ~ 10-13 ppm
- 3 types of Ar-H proton – chemical shift ~ 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 neighbouring H on shape
13.7 Spin-Spin Splitting – Effect of neighbouring H on shape

General rule for splitting patterns
For simple cases, multiplicity for \( \text{H} = n + 1 \)
Where \( n \) = number of neighbours

i.e
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

For red H : neighbouring H (blue) has two possible alignments, either with, or against, the external field (Ho). This affects 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. Same applies to the blue H.
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 the *coupling constant*.
Using Coupling Constants

CH₃CH₂ but which one?

Find J and match signals

Coupling Constants – Nonequivalent Neighbours

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

13.11 Complex Splitting Patterns

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

Figure 13.20

Generally for alkene protons:

J trans > J cis
13.11 Complex Splitting Patterns

13.12 ¹H NMR Spectra of Alcohols

Acidic protons exchange with any H₂O in sample

Glycosyl amide structure from NMR - NOESY
<table>
<thead>
<tr>
<th><strong>13.14 ¹³C NMR Spectroscopy</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Figure 13.23</strong></td>
</tr>
<tr>
<td><strong>Glycosyl amide structure from NMR - COSY</strong></td>
</tr>
</tbody>
</table>

- Carbons 1, 2, 3, and 4 hard to distinguish just from coupling constants (all $J\approx 9$ Hz)
- Glycosyl amide structure from NMR

<table>
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<tr>
<th><strong>13.14 ¹³C NMR Spectroscopy</strong></th>
</tr>
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<tbody>
<tr>
<td>- Carbon 13 isotope and not ¹²C is observed in NMR</td>
</tr>
<tr>
<td>- ¹³C very low abundance (&lt;1%), integration not useful</td>
</tr>
<tr>
<td>- Spectra usually “decoupled” and signals are singlets</td>
</tr>
<tr>
<td>- Number of distinct signals indicates distinct carbons</td>
</tr>
<tr>
<td>- Same ideas about shielding/deshielding apply</td>
</tr>
<tr>
<td>- Spectra often measured in CDCl₃ and referenced to either the C in TMS (0 ppm) or the C in CDCl₃, which shows as a triplet at 77.0 ppm</td>
</tr>
</tbody>
</table>
13C NMR Chemical Shifts (see Sheet)

13C NMR (ppm) 21, 52, 121, 122, 120, 126, 132, 134, 148, 168, 169

13C NMR Chemical Shifts (see Sheet)

13C NMR (ppm) 23, 28, 32, 128, 151, 197

13C NMR Chemical Shifts (see Sheet)
13.15 $^{13}$C NMR – Information on Symmetry

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

13.20 Stretching and bending vibrations from Spec Sheet

 Approximate IR Absorption Frequencies (cm⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Stretching Vibrations</th>
<th></th>
<th>Bending Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-OH (alcohol)</td>
<td>2500-3600</td>
<td>R(C,H) 90</td>
</tr>
<tr>
<td></td>
<td>C=O (aldehydes)</td>
<td>1630-1690</td>
<td>Mono-substituted benzene 730-770, 690-710</td>
</tr>
<tr>
<td></td>
<td></td>
<td>770-775</td>
<td>Ortho-substituted benzene 725-775</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1770-1815</td>
<td>Para-substituted benzene 805-810, 885-730</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1700-1750</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1680-1700</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000-2050</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2260-2290</td>
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</tr>
</tbody>
</table>

Don’t memorize, learn to use as you practice problems

13.20 Interpreting IR Spectra – n-Hexane

CH₃CH₂CH₂CH₂CH₃

Figure 13.31
13.20 Interpreting IR Spectra – 1-Hexene

\[ \text{H}_2\text{C} = \text{C} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \]

Figure 13.32

13.20 Interpreting IR Spectra – t-Butylbenzene

\[
\begin{array}{c}
\text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

Figure 13.33

13.20 Interpreting IR Spectra – 2-Hexanol

\[
\begin{array}{c}
\text{OH} \\
\text{CH}_3 \text{CH} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3
\end{array}
\]

Figure 13.34
13.20 Interpreting IR Spectra – 2-Hexanone

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

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
13.22 Mass Spectrometry

Exam Problems

1. (10 pts) An unknown organic compound has the empirical formula $\text{C}_6\text{H}_8$. Given the following spectral data, provide a structure for the unknown that agrees with the data. Match the 1H NMR data to your answer.

$^1$H NMR (ppm) 1.24 (t, $J = 7.0$ Hz), 2.59 (m, 4H), 7.05 (m, 4H)

$^{13}$C NMR (ppm) 8.6, 32.7, 125.6, 128.3, 128.6, 129.4 ($\text{C} = \text{C}$ is a close to mass substrate)

Mass spectrum (m/z) 134.20 (M$^+$) (matches formula, therefore $\text{C}_6\text{H}_8$ is actual formula)

Infra Red (cm$^{-1}$) 720, 800 (due to $\text{C} = \text{C}$ substrate)

Exam Problems

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

$^1$H NMR (ppm) 1.09 (t, $J = 6.0$ Hz), 1.22 (t, $J = 7.0$ Hz), 2.69 (m, 4H), 3.52 (m, 2H), 7.50 (m, 4H)

$^{13}$C NMR (ppm) 8.4, 16.8, 25.1, 31.0, 42.4, 71.2, 134.4, 202.4

IR (cm$^{-1}$) 2.80, 5.20, 5.40, 9.20, 13.50, 13.80, 14.00, 16.20