IR Spectroscopy

- Absorption of infrared light is associated with excitation of bond vibrations

Energy absorbed ⇒ signal in spectrum ⇒ structural info

- An IR spectrum can:
  - Indicate the functional groups present
  - ‘Fingerprint’ the molecule

The frequency of vibration for IR vibration spectra are measured in wavenumbers (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Bonds</th>
<th>IR absorption (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H</td>
<td>3300</td>
</tr>
<tr>
<td>O-H (broad)</td>
<td></td>
</tr>
<tr>
<td>C-H</td>
<td>3000</td>
</tr>
<tr>
<td>C≡C</td>
<td>2200</td>
</tr>
<tr>
<td>C=N</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>1700</td>
</tr>
<tr>
<td>C=C</td>
<td>1600</td>
</tr>
</tbody>
</table>

**Example**

Which of the compounds: CH$_3$CH$_2$COCH$_3$, CH$_3$CH$_2$CHO, CH$_3$CH$_2$CH$_2$OH, is the following infrared spectrum representative of?
IR spectra of (a) cyclohexanol and (b) cyclohexanone
Questions: 1. Indicate which of the following compounds absorb around 1700 cm\(^{-1}\) and around 3300 cm\(^{-1}\) in the infrared region.

- ![Formaldehyde](image1)
- ![Alcohol](image2)
- ![Acetic Acid](image3)
- ![Cyclohexane](image4)
- ![Ethylamine](image5)

2. A compound with molecular formula C\(_3\)H\(_8\)O has a strong absorption at 3300 cm\(^{-1}\) in the infrared spectrum. Give a reasonable constitutional formula for any compound whose structure is consistent with this data.
Nuclear magnetic resonance

NMR spectroscopy is a key tool in organic chemistry
- It provides information on the structural connectivity
- Many atomic nuclei, including $^1$H and $^{13}$C, behave as if they were spinning about an axis
- As the nuclei are charged they act like a small magnet
- When placed in an external magnetic field they can align parallel or anti-parallel to it

**Principles of NMR spectroscopy**
- There is an energy difference between the two alignments
- The low energy spin is ‘flipped’ to the high energy orientation on absorption of radio frequency energy
- Many nuclei are NMR active, eg $^1$H, $^{13}$C, $^{31}$P, $^{19}$F
- For a given magnetic field, each resonate at a particular frequency
- This involves energy in the radio frequency region
- NMR is associated with ‘flipping’ the spin of a nucleus aligned in a magnetic field
- The technique is used in analysis and structure determination as well as imaging of soft tissue in animals
Structure determination by NMR spectroscopy

- most important and useful technique
- gives information about the **number** and **environments** of the hydrogens on a molecule

\[ ^1H \text{ NMR Spectroscopy} \quad (^{13}C, ^{19}F, ^{31}P \text{ etc. also possible}) \]

- frequency at which each hydrogen absorbs $E$ depends on
  (i) strength of field (size of magnet)
  (ii) immediate environment of nucleus

- All chemically equivalent protons absorb at SAME frequency; protons in different chemical environments absorb at DIFFERENT frequencies

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

- in practice, record a spectrum, $\nu$ of absorption given as **CHEMICAL SHIFT** $\delta$ (ppm) referenced to a standard $(\text{CH}_3)_4\text{Si}$ (TMS) at 0 ppm

- by a process called **INTEGRATION** one can determine the ratio of protons that give rise to each signal
FIG. 13.13
The proton nmr spectrum of methoxyacetonitrile. No signal splitting occurs with the enantiomeric protons (b). (Spectrum courtesy of Varian Associates, Palo Alto, Calif.)

FIG. 13.2
The proton nmr spectrum of p-xylene. (Spectrum courtesy of Varian Associates, Palo Alto, Calif.)
The number of signals in an NMR spectrum corresponds to the number of distinct types of hydrogen atoms in a molecule.

One signal in the $^1$H NMR spectrum:

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

Two signals in the $^1$H NMR spectrum:

\[
\text{CH}_3\text{CH}_2\text{Cl} \quad \text{CH}_3\text{CH}_2\text{O} \quad \text{CH}_2\text{CH}_3
\]

Three signals in the $^1$H NMR spectrum:

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \quad \text{C}\text{H}_3\text{CH}_2\text{OH} \quad \text{CH}_3\text{O} \text{CH}_2\text{CH}_3
\]

**NMR Spectroscopy - Question**

How many signals would be expected in the $^1$H NMR spectrum of each of the following compounds?

\[
\begin{align*}
\text{CH}_3\text{Br} & \quad \text{CH}_3\text{C} \text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{C} \text{CH}_3 & \quad \text{Br} \text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \quad \text{CH}_3\text{C} \text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]
NMR - Type of hydrogen environments

- The frequency axis ($\delta$ scale) is calibrated in parts per million (ppm)
- A reference compound, TMS, (CH$_3$)$_4$Si, taken as $\delta = 0.00$ ppm
- The frequency difference between a signal arising from a sample and the TMS signal is called the chemical shift

NMR - No. of Hs of each type

- The relative intensities of the signals is proportional to the number of hydrogen atoms which give rise to the signal.
- For example, the $^1$H NMR spectrum of (CH$_3$)$_3$CCOOCH$_3$ would exhibit two signals with intensities in the ratio 3:1
NMR Spectroscopy - Question

Give the number of environments and the ratio of signal sizes observed in the $^1H$ NMR spectrum of each of the following molecules:

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{O} & \quad \text{O} & \quad \text{CH}_3 \\
\text{O} & \quad \text{CH}_3 \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

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

NMR - Multiplicity of signal

Fine structure (splitting or multiplicity) arises from the hydrogen atoms attached to the neighbouring carbon atoms.

If a hydrogen atom has "n" equivalent hydrogen atoms on immediately adjacent carbon atoms which are in a different chemical environment, its NMR resonance will appear as a signal which is split into "n+1" lines - this is called the n+1 rule.

<table>
<thead>
<tr>
<th>Number of neighbouring hydrogen atoms (n)</th>
<th>Signal multiplicity (no. of peaks)</th>
<th>Name of signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>singlet</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>doublet</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>triplet</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>quartet</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>quintet</td>
</tr>
</tbody>
</table>
NMR Spectroscopy - Recap

<table>
<thead>
<tr>
<th>Information</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of H environments</td>
<td>No. of signals</td>
</tr>
<tr>
<td>Type of H environment</td>
<td>Position of signal</td>
</tr>
<tr>
<td>No. of H of each type</td>
<td>Size of signal</td>
</tr>
<tr>
<td>No. of adjacent H</td>
<td>Multiplicity of signal</td>
</tr>
</tbody>
</table>
NMR - Example:

\[(\text{CH}_3)_2\text{CHBr}\]

- Two signals
- Chemical shift \(\delta 2\) and \(\delta 4\) ppm.
- Relative intensity of 6:1 (from integration)
- Doublet signal for the \(\text{CH}_3\) groups and a septet signal for the \(\text{CH}\) group.

NMR Spectroscopy - Question

Give the number of signals, their relative intensities and the multiplicities in the \(^1\text{H}\) NMR spectra of each of the following compounds:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 & \quad \text{CH}_3\overset{\text{C}}{\text{O}}\overset{\text{O}}{\text{C}}\overset{\text{O}}{\text{H}}
\end{align*}
\]
NMR - MRI

The medical instrument used in magnetic resonance imaging (MRI) is in fact a specially adapted NMR machine which measures the distribution of water in body tissues.

$^1$H NMR

Detects hydrogen in water

Good for soft tissue imaging
Question: In answering questions 34 - 39, choose from the molecules A - E.

34. Which one of the molecules A - E absorbs strongly in the UV-visible region?
35. Which one of the molecules A - E absorbs in the 3200 - 3500 cm\(^{-1}\) region of the infrared spectrum?
36. Which one of the molecules A - E absorbs in the 1650 - 1800 cm\(^{-1}\) region of the infrared spectrum?
37. Which one of the molecules A - E will show two molecular ions in its mass spectrum?
38. Which one of the molecules A - E shows four signals in its \(^1\)H NMR spectrum?
39. Which one of the molecules A - E has a \(^1\)H NMR spectrum consisting of two singlet signals?

Question: In answering questions 26 and 27, choose from the molecules A - E.

26. Which of the molecules A - E shows four signals in its \(^1\)H NMR spectrum?
27. Which of the molecules A - E absorbs strongly in the UV-visible region?