Chapter 12
Structure Determination: UV-Vis, Mass Spectrometry and Infrared Spectroscopy

Hovig Kouyoumdjian
What’s Next?

- Now that we have an idea about how to synthesize a molecule...
- Can we see what we made?
- How can we be sure that we synthesized a certain molecule
- Is there a magical instrument that can tell us about the structure of the product?
Determining the Structure of an Organic Compound

- The analysis of the outcome of a reaction requires that we know the full structure of the products as well as the reactants.

- Different methods now permit structures to be determined directly:
  - ultraviolet-visible spectroscopy (UV-VIS)
  - mass spectrometry (MS)
  - infrared (IR) spectroscopy
  - nuclear magnetic resonance spectroscopy (NMR)
The Electromagnetic Spectrum

Human Eye Response

- 400 nanometers
- 700 nanometers
- 10,000 nanometers (10 micro-meters)

- Cosmic and gamma rays
- Increasing energy
- Increasing frequency
- Decreasing wavelength
- Decreasing energy
- Increasing wavelength
- Increasing energy
- Increasing frequency
- Decreasing wavelength

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What Kind of Data We See?

- $\lambda_{\text{max}} = 217 \text{ nm}$
- LUMO $\rightarrow$ E$_2$ $\rightarrow$ $\pi^*$
- HOMO $\rightarrow$ E$_1$ $\rightarrow$ $\pi$

Electronic excitation $\rightarrow$ $h\nu$

$E = h\nu = h \frac{c}{\lambda}$

- E: energy (J)
- $h$: Planck's constant (J*s)
- $\nu$: frequency (1/s)
- c: speed of light (m/s)
- $\lambda$: wavelength (m)
Organic Molecules and Absorbance

- Nature of the \( \pi \rightarrow \pi^* \) transition is crucial for absorbance.
- The most important factor is the extent of the conjugation.

- Any conjugated molecule will have an absorbance between 200-400 nm (UV range). However, that range can extend to 400 - 800 nm (Visible range) for highly conjugated molecules.

Red pigment found in tomatoes

Lycopene, a conjugated polyene
Which of the following compounds is most likely to absorb in the visible region of the electromagnetic spectrum?

A. \[
\begin{array}{c}
\text{\includegraphics{diagram1}}
\end{array}
\]

B. \[
\begin{array}{c}
\text{\includegraphics{diagram2}}
\end{array}
\]

C. \[
\begin{array}{c}
\text{\includegraphics{diagram3}}
\end{array}
\]

D. \[
\begin{array}{c}
\text{\includegraphics{diagram4}}
\end{array}
\]

E. \[
\begin{array}{c}
\text{\includegraphics{diagram5}}
\end{array}
\]
UV/Visible spectroscopy is based on _____ excitation.

A) electronic
B) rotational
C) nuclear
D) vibrational
Electromagnetic Spectrum Revisited

- Radiant energy is proportional to its frequency (cycles/s = Hz) as a wave (Amplitude is its height)

![Diagram of the electromagnetic spectrum showing different regions such as gamma rays, X-rays, ultraviolet, infrared, microwaves, and radio waves, along with their corresponding frequencies and wavelengths. The visible spectrum is also highlighted with wavelengths ranging from 380 nm to 780 nm.]
Infrared Spectroscopy

- IR region lower energy than visible light (below red – produces heating as with a heat lamp)

- $2.5 \times 10^{-6}$ m to $2.5 \times 10^{-5}$ m region used by organic chemists for structural analysis

- IR energy in a spectrum is usually measured as wavenumber (cm$^{-1}$), the inverse of wavelength and proportional to frequency

- Specific IR absorbed by an organic molecule is related to its structure
Infrared Energy Modes

- IR energy absorption corresponds to specific modes, corresponding to combinations of atomic movements, such as bending and stretching of bonds between groups of atoms called “normal modes”
- Energy is characteristic of the atoms in the group and their bonding
- Corresponds to vibrations

Symmetric stretching
Antisymmetric stretching
In-plane bending
Out-of-plane bending
Infrared spectroscopy is based on _____ energy.

A) electronic  
B) rotational  
C) nuclear  
D) vibrational
Interpreting Infrared Spectra

- Most functional groups absorb at about the same energy and intensity independent of the molecule they are in.

- Characteristic higher energy IR absorptions in Table 12.1 can be used to confirm the existence of the presence of a functional group in a molecule.

- IR spectrum has lower energy region characteristic of molecule as a whole ("fingerprint" region).
Regions of the Infrared Spectrum

- 4000-2500 cm\(^{-1}\)
  - N-H, C-H, O-H (stretching)
    - 3300-3600 N-H, O-H
    - 3000 C-H
- 2000-1500 cm\(^{-1}\)
  - double bonds (stretching)
    - C=O 1680-1750
    - C=C 1640-1680 cm\(^{-1}\)

2500-2000 cm\(^{-1}\)
- triple bonds (stretching)
  - C≡C
  - C≡N

Below 1500 cm\(^{-1}\)
- Fingerprint region
How to Interpret IR Spectra

\[ \text{CH}_3(\text{CH}_2)_4\text{CH}_3 \]

(a)

\begin{align*}
\text{Transmittance (\%)} & \\
0 & 20 & 40 & 60 & 80 & 100 \\
\end{align*}

\begin{align*}
\text{Wavenumber (cm}^{-1}\text{)} & \\
4000 & 3500 & 3000 & 2500 & 2000 & 1500 & 1000 & 500 \\
\end{align*}

- N–H
- O–H
- C–H
- C≡N
- C≡C
- C=O
- C=N

Fingerprint region
How to Interpret IR Spectra

(b)

[Graph showing IR spectrum with labeled regions for N–H, O–H, C–H, C≡N, C≡C, and C=O with corresponding frequencies and transmittance percentages.]

Fingerprint region
How to Interpret IR Spectra
Absorptions of common Hydrocarbons

**Alkanes, Alkenes, Alkynes**
- C-H, C-C, C=C, C≡C have characteristic peaks
  - absence helps rule out C=C or C≡C

<table>
<thead>
<tr>
<th>Alkanes</th>
<th>2850–2960 cm⁻¹</th>
<th>Alkenes</th>
<th>3020–3100 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td></td>
<td></td>
<td>C=H</td>
</tr>
<tr>
<td>C–C</td>
<td>800–1300 cm⁻¹</td>
<td>C=C</td>
<td>1640–1680 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RCH=CH₂</td>
<td>910 and 990 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R₂C=CH₂</td>
<td>890 cm⁻¹</td>
</tr>
<tr>
<td>Alkynes</td>
<td>2100–2260 cm⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡C–H</td>
<td>3300 cm⁻¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Draw a vertical line at 3000 cm\(^{-1}\)

- To determine whether you have alkane C-H absorption (stretching) or Alkene C-H absorption (stretching).
Absorptions of Aromatic Compounds

- Weak C–H stretch at 3030 cm\(^{-1}\)
- Weak absorptions 1660 - 2000 cm\(^{-1}\) range
- Medium-intensity absorptions 1450 to 1600 cm\(^{-1}\)

Aromatic compounds

\[ \text{C–H} \quad 3030 \text{ cm}\(^{-1}\) \text{ (weak)} \]

1660–2000 cm\(^{-1}\) \text{ (weak)}
1450–1600 cm\(^{-1}\) \text{ (medium)}
Absorptions of Alcohols and Amines

- O–H 3400 to 3650 cm\(^{-1}\)
  - Usually broad and intense
- N–H 3300 to 3500 cm\(^{-1}\)
  - Sharper and less intense than an O–H

**Alcohols**  \(\text{O–H}\)  3400–3650 cm\(^{-1}\) (broad, intense)

**Amines**  \(\text{N–H}\)  3300–3500 cm\(^{-1}\) (sharp, medium intensity)
Absorptions of carbonyls (Aldehydes)

- Exact absorption characteristic of type of carbonyl compound
  - 1730 cm\(^{-1}\) in saturated aldehydes
  - 1705 cm\(^{-1}\) in aldehydes next to double bond or aromatic ring

<table>
<thead>
<tr>
<th>Aldehydes</th>
<th>Structure</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)CH(_2)CH</td>
<td><img src="image" alt="Structure" /></td>
<td>1730 cm(^{-1})</td>
</tr>
<tr>
<td>CH(_3)CH=CHCH</td>
<td><img src="image" alt="Structure" /></td>
<td>1705 cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Structure" /></td>
<td>1705 cm(^{-1})</td>
</tr>
</tbody>
</table>

For any C=O (carbonyl) expect a strong, sharp peak 1670 to 1780 cm\(^{-1}\)
Absorptions of carbonyls (ketones & esters)

- 1715 cm⁻¹ in six-membered ring and acyclic ketones
- 1750 cm⁻¹ in 5-membered ring ketones
- 1690 cm⁻¹ in ketones next to a double bond or an aromatic ring

Ketones

<table>
<thead>
<tr>
<th>Ketones</th>
<th>CH₃CCH₃</th>
<th>CH₃CH=CHCCH₃</th>
<th>Phenyl ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image1" alt="Ketone 1" /></td>
<td><img src="image2" alt="Ketone 2" /></td>
<td><img src="image3" alt="Ketone 3" /></td>
</tr>
</tbody>
</table>

\[
\begin{array}{cccc}
1715 \text{ cm}^{-1} & 1750 \text{ cm}^{-1} & 1690 \text{ cm}^{-1} & 1690 \text{ cm}^{-1}
\end{array}
\]

- 1735 cm⁻¹ in saturated esters
- 1715 cm⁻¹ in esters next to aromatic ring or a double bond

Esters

<table>
<thead>
<tr>
<th>Esters</th>
<th>CH₃COCH₃</th>
<th>CH₃CH=CHCOCH₃</th>
<th>Phenyl ester</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image4" alt="Ester 1" /></td>
<td><img src="image5" alt="Ester 2" /></td>
<td><img src="image6" alt="Ester 3" /></td>
</tr>
</tbody>
</table>

\[
\begin{array}{ccc}
1735 \text{ cm}^{-1} & 1715 \text{ cm}^{-1} & 1715 \text{ cm}^{-1}
\end{array}
\]

For any C=O (carbonyl) expect a strong, sharp peak 1670 to 1780 cm⁻¹
Let’s Work a Problem

\[ \text{Transmittance} \% \]

\[ \begin{array}{c}
\text{Wavenumber (cm}^{-1}\text{)}
\end{array} \]

\[ \begin{array}{c}
3300 \text{ cm}^{-1}
\end{array} \]

\[ \begin{array}{c}
2250 \text{ cm}^{-1}
\end{array} \]

\[ \begin{array}{c}
3050 \text{ cm}^{-1}
\end{array} \]

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

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]
Let's Work a Problem

- Transmittance (%)
- Wavenumber (cm⁻¹)
- 1700 cm⁻¹
- 2900 cm⁻¹
- 3050 cm⁻¹
Mass Spectrometry of Small Molecules

- Measures molecular weight
- Sample vaporized and subjected to bombardment by electrons that remove an electron
  - Creates a cation radical
- Bonds in cation radicals begin to break (fragment)
- Charge to mass ratio is measured

\[
\text{RH} \quad \xrightarrow{\text{e}^-} \quad \text{RH}^{+} + \text{e}^- \\
\text{Organic molecule} \quad \text{Cation radical}
\]
The Mass Spectrum

- Plot mass of ions (m/z) (x-axis) versus the intensity of the signal (roughly corresponding to the number of ions) (y-axis)
- **Tallest** peak is **base peak** (100%)
  - Other peaks listed as the % of that peak
- Peak that corresponds to the **unfragmented** radical cation is **parent peak** or **molecular ion** (M⁺)

![Graph showing mass spectrum with m/z values and relative abundance]
Other Mass Spectral Features

- If parent ion not present due to electron bombardment causing breakdown, “softer” methods such as chemical ionization are used.

- Peaks above the molecular weight appear as a result of naturally occurring heavier isotopes in the sample:
  - $(M+1)$ from $^{13}\text{C}$ (around 1.1% of the $(M+)$ per carbon)
  - $(M+2)$ from $^{37}\text{Cl}$ (around 33% of the $(M+)$ per chlorine)
  - $(M+2)$ from $^{81}\text{Br}$ (around 100% of the $(M+)$ per bromine)

Isotopic Abundance
Interpreting Mass-Spectral Fragmentation Patterns

- The way molecular ions break down can produce characteristic fragments that help in identification
  - Serves as a “fingerprint” for comparison with known materials in analysis (used in forensics)
  - Positive charge goes to fragments that best can stabilize it

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 &
\end{align*}
\begin{align*}
\quad & \quad +
\end{align*}
\begin{align*}
\text{H}_3\text{C} & \quad \text{C}^+ \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\begin{align*}
\quad & \quad + \\
\cdot\text{CH}_3 &
\end{align*}

m/z = 57
Mass Spectral Fragmentation of Hexane

Hexane parent peak at m/z = 86
Other peaks at m/z = 71, 57, 43, 29

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

Hexane

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

Molecular ion, \( M^+ \)

\((m/z = 86)\)

\[ \begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+ & \quad m/z: \quad 71 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+ & \quad m/z: \quad 57 \\
\text{CH}_3\text{CH}_2\text{CH}_2^+ & \quad m/z: \quad 43 \\
\text{CH}_3\text{CH}_2^+ & \quad m/z: \quad 29
\end{align*} \]
Mass Spectrometry of Some Common Functional Groups

**Alcohols:**
- Alcohols undergo $\alpha$-cleavage (at the bond next to the C-OH) as well as loss of H-OH to give C=C.
Mass Spectral Cleavage of Amines

- Amines undergo $\alpha$-cleavage, generating radicals

\[
\begin{align*}
[RCH_2\text{N}NR_2]^+ \quad \xrightarrow{\text{Alpha cleavage}} \quad RCH_2\cdot + \quad \begin{bmatrix}
\begin{array}{c}
\text{C}^+ \\
\cdot \text{NR}_2
\end{array}
\end{bmatrix} \quad \leftrightarrow \quad \begin{bmatrix}
\begin{array}{c}
\text{C}^+ \\
\cdot \text{NR}_2
\end{array}
\end{bmatrix}
\end{align*}
\]
Fragmentation of Carbonyl Compounds

- A C-H that is three atoms away leads to an internal transfer of a proton to the C=O, called the McLafferty rearrangement.
- Carbonyl compounds can also undergo $\alpha$ cleavage.

\[
\begin{align*}
\text{ McLafferty rearrangement:} & \quad \begin{array}{c}
\text{H} \\
\bigg\{ \text{\textbf{R}} \bigg\} \\
\text{O} \\
\text{C} \\
\text{R}
\end{array} \\
\text{McLafferty rearrangement:} & \quad \begin{array}{c}
\text{C} \\
\text{C} \\
\text{O} \\
\text{C} \\
\text{R'}
\end{array}
\end{align*}
\]