Chapter 13

Mass Spectrometry and Infrared Spectroscopy
Overview of Mass Spectrometry

- **Mass spectrometry** is a technique used for measuring the molecular weight, which can be helpful in determining the molecular formula of an organic compound.

- In one type of mass spectrometer, a molecule is ionized by bombardment with a beam of high-energy electrons.

- The energy of the electrons is ~ 1600 kcal (or 70 eV).

- Since it takes ~ 100 kcal of energy to cleave a typical $\sigma$ bond, 1600 kcal is an enormous amount of energy to come into contact with a molecule.

- The electron beam ionizes the molecule by causing it to eject an electron.
In a mass spectrometer, a sample is vaporized and bombarded by a beam of electrons to form an unstable radical cation, which then decomposes to smaller fragments. The positively charged ions are accelerated toward a negatively charged plate, and then passed through a curved analyzer tube in a magnetic field, where they are deflected by different amounts depending on their ratio of mass to charge ($m/z$). A mass spectrum plots the intensity of each ion versus its $m/z$ ratio.
When the electron beam ionizes the molecule, the species that is formed is called a **radical cation**, and symbolized as \( \text{M}^{+\cdot} \).

The radical cation \( \text{M}^{+\cdot} \) is called the **molecular ion** or **parent ion**.

The mass of \( \text{M}^{+\cdot} \) represents the molecular weight of \( \text{M} \).

Because \( \text{M} \) is unstable, it decomposes to form fragments of radicals and cations that have a lower molecular weight than \( \text{M}^{+\cdot} \).

A mass spectrum is a plot of the amount of each cation (its relative abundance) versus its **mass-to-charge ratio** \( (m/z, \text{where } m \text{ is mass, and } z \text{ is charge}) \).
The tallest peak in the mass spectrum is called the base peak.

For methane the base peak is also the M peak (molecular ion), although this is usually not the case.

Though most C atoms have an atomic mass of 12, 1.1% have a mass of 13.

Thus, $^{13}\text{CH}_4$ is responsible for the peak at $m/z = 17$. This is called the M + 1 peak.
The mass spectrum of CH₄ consists of more peaks than just the M peak.

Since the molecular ion is unstable, it fragments into other cations and radical cations containing one, two, three, or four fewer hydrogen atoms than methane itself.

Thus, the peaks at m/z 15, 14, 13, and 12 are due to these lower molecular weight fragments.

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{e}^- & (\text{CH}_4)^{++} \\
& & \text{mass 16} \\
& \rightarrow -\text{H}^+ & \text{CH}_3^+ \\
& & \text{mass 15} \\
& \rightarrow -\text{H}^+ & \text{CH}_2^{++} \\
& & \text{mass 14} \\
& \rightarrow -\text{H}^+ & \text{CH}^+ \\
& & \text{mass 13} \\
& \rightarrow -\text{H}^+ & \text{C}^{++} \\
& & \text{mass 12}
\end{align*}
\]
Mass Spectrum of Hexane

- The molecular ion for hexane is at $m/z = 86$.
- A small $M + 1$ peak occurs at $m/z = 87$.
- The base peak occurs at $m/z = 57$ ($C_4H_9^+$).
- Major fragment peaks also occur at 43 ($C_3H_7^+$) and 29 ($C_2H_5^+$).
The Nitrogen Rule

- Hydrocarbons, as well as compounds that contain only C, H, and O atoms, always have a molecular ion with an even mass.
- An odd molecular ion generally indicates that a compound contains nitrogen.
- This effect is called the **nitrogen rule**: A compound with an odd molecular ion contains an odd number of N atoms.
- A compound that contains an even number of N atoms gives an even molecular ion.
Alkyl Halides and the M + 2 Peak

• Most elements have one major isotope.
• Chlorine has two common isotopes, $^{35}\text{Cl}$ and $^{37}\text{Cl}$, which occur naturally in a 3:1 ratio.
  • Thus, there are two peaks in a 3:1 ratio for the molecular ion of an alkyl chloride.
  • The larger peak, the M peak, corresponds to the compound containing the $^{35}\text{Cl}$. The smaller peak, the M + 2 peak, corresponds to the compound containing $^{37}\text{Cl}$.
  • When the molecular ion consists of two peaks (M and M + 2) in a 3:1 ratio, a Cl atom is present.
• Br has two common isotopes, $^{79}\text{Br}$ and $^{81}\text{Br}$, in a ratio of ~ 1:1.
  • When the molecular ion consists of two peaks (M and M + 2) in a 1:1 ratio, a Br atom is present.
Mass Spectrum of 2-Chloropropane

Figure 13.3

(CH₃)₂CHCl
molecular weight = 78, 80

two molecular ions

height ratio: 3:1
m/z = 78  m/z = 80

Relative abundance

m/z
Mass Spectrum of 2-Bromopropane

Figure 13.4

$$(\text{CH}_3)_2\text{CHBr}$$
molecular weight = 122, 124

two molecular ions

height ratio: 1:1

$m/z = 122$  $m/z = 124$
Fragmentation Patterns

• Cleavage of C – C bonds forms lower molecular weight fragments that correspond to lines in the mass spectrum.

Figure 13.5
Some Common Fragmentation Patterns

**Carbonyls**

$(\text{RC}R')^+$

$\xrightarrow{\alpha \text{ cleavage}}$

$R^+\text{C}=\text{O}$: $\leftrightarrow$ $R^-\text{C}=\text{O}^+$ + $R'^\cdot$

resonance-stabilized acylium ion

$R = \text{H or alkyl}$

**Alcohols**

$(\text{OH})^+$

$\xrightarrow{\alpha \text{ cleavage}}$

$\text{C}^+\text{O}\leftrightarrow\text{C}^+\text{OH}$ + $R'^\cdot$

resonance-stabilized carbocation

$R = \text{H or alkyl}$

**Dehydration**

$(\text{H}\text{OH})^+$

$\xrightarrow{\text{dehydration}}$

$\text{C}^+\text{C}$ + $\text{H}_2\text{O}$
High Resolution Mass Spectrometers

- **Low resolution** mass spectrometers report \( m/z \) values to the nearest whole number.  
  - Thus, the mass of a given molecular ion can correspond to many different molecular formulas.
- **High resolution** mass spectrometers measure \( m/z \) ratios to four (or more) decimal places.  
  - This is valuable because except for \(^{12}\text{C} \) whose mass is defined as 12.0000, the masses of all other nuclei are very close—but not exactly—whole numbers.
  - Using the mass values of common nuclei, it is possible to determine the single molecular formula that gives rise to a molecular ion.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{12}\text{C} )</td>
<td>12.0000</td>
</tr>
<tr>
<td>(^{1}\text{H} )</td>
<td>1.00783</td>
</tr>
<tr>
<td>(^{16}\text{O} )</td>
<td>15.9949</td>
</tr>
<tr>
<td>(^{14}\text{N} )</td>
<td>14.0031</td>
</tr>
</tbody>
</table>
Exact Mass in High-Res Mass Spectra

• A molecule having a molecular ion at $m/z = 60$ using a low-resolution mass spectrometer could have any one of the following molecular formulas.

• A high-resolution mass spectrometer would differentiate between these to give only one possible formula.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Exact mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3H_8O$</td>
<td>60.0575</td>
</tr>
<tr>
<td>$C_2H_4O_2$</td>
<td>60.0211</td>
</tr>
<tr>
<td>$C_2H_8N_2$</td>
<td>60.0688</td>
</tr>
</tbody>
</table>
Electromagnetic Radiation

• **Electromagnetic radiation** is radiant energy having dual properties of both waves and particles.

• Particles of electromagnetic radiation are called **photons**, and each has a discrete amount of energy called a quantum.

• Electromagnetic radiation can be characterized by its **wavelength** and **frequency**.

• **Wavelength** (λ) is the distance from one point on a wave to the same point on an adjacent wave.

• **Frequency** (ν) is the number of waves passing per unit time. It is reported in cycles per second (s⁻¹), which is also called **hertz** (Hz).

<table>
<thead>
<tr>
<th>Unit</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>meter (m)</td>
<td>1 m</td>
</tr>
<tr>
<td>centimeter (cm)</td>
<td>10⁻² m</td>
</tr>
<tr>
<td>micrometer (µm)</td>
<td>10⁻⁶ m</td>
</tr>
<tr>
<td>nanometer (nm)</td>
<td>10⁻⁹ m</td>
</tr>
<tr>
<td>Angstrom (Å)</td>
<td>10⁻¹⁰ m</td>
</tr>
</tbody>
</table>
The electromagnetic spectrum is arbitrarily divided into different regions, ranging from gamma rays to radio waves.

Visible light occupies only a small region of the electromagnetic spectrum.
Properties of Electromagnetic Radiation

• All electromagnetic radiation travels at the constant speed of light \((c)\), \(3.0 \times 10^8 \text{ m/s}\).

• The energy \((E)\) of a photon is directly proportional to its frequency (i.e., \(E\) increases as \(\nu\) increases).
  - \(E = h\nu\); \(h\) = Planck’s constant \((1.58 \times 10^{-34} \text{ cal}\cdot\text{s})\)

• Since energy and wavelength are inversely proportional, \(E\) decreases as \(\lambda\) increases.
  - \(E = h\nu = hc/\lambda\)
Absorption of Electromagnetic Radiation

• When electromagnetic radiation strikes a molecule, some wavelengths, but not all, are absorbed.
• For absorption to occur, the energy of the photon must match the difference between two energy states in the molecule (ground state to excited state).
• The larger the energy difference between two states, the higher the energy of radiation needed for absorption.
• Higher energy light (UV-visible) causes electronic excitation.
• Lower energy radiation (infrared) causes vibrational excitation.
Absorption of IR Light

• Absorption of IR light causes changes in the vibrational motions of a molecule.
• The different vibrational modes available to a molecule include stretching and bending modes.

  ![Stretching](image)
  ![Bending](image)

  A bond can stretch.  Two bonds can bend.

• The vibrational modes of a molecule are quantized, so they occur only at specific frequencies which correspond to the frequency of IR light.
Bond Stretching and Bending

• When the frequency of IR light matches the frequency of a particular vibrational mode, the IR light is absorbed, causing the amplitude of the particular bond stretch or bond bend to increase.

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When the $\nu$ of IR light = the $\nu$ of bond stretching, IR light is absorbed.

The bond stretches further. The amplitude increases.

• Different kinds of bonds vibrate at different frequencies, so they absorb different frequencies of IR light.
• IR spectroscopy distinguishes between the different kinds of bonds in a molecule, so it is possible to determine the functional groups present.
In an IR spectrometer, light passes through a sample. Frequencies that match the vibrational frequencies are absorbed, and the remaining light is transmitted to a detector. An IR spectrum is a plot of the amount of transmitted light versus its wavenumber. Most bonds in organic molecules absorb in the region of 4000 cm$^{-1}$ to 400 cm$^{-1}$.

Characteristics of an IR Spectrum
Characteristics of an IR Spectrum

• The $x$-axis is reported in frequencies using a unit called wavenumbers ($\nu$).

• Wavenumbers are inversely proportional to wavelength and reported in reciprocal centimeters (cm$^{-1}$).

• The $y$-axis is % transmittance: 100% transmittance means that all the light shone on a sample is transmitted and none is absorbed.

• 0% transmittance means that none of the light shone on the sample is transmitted and all is absorbed.

• Each peak corresponds to a particular kind of bond, and each bond type (such as O – H and C – H) occurs at a characteristic frequency.

• Infrared (IR) spectroscopy is used to identify what bonds and what functional groups are in a compound.
Regions of an IR Spectrum

- The IR spectrum is divided into two regions: the functional group region (at $\geq 1500 \text{ cm}^{-1}$), and the fingerprint region (at $< 1500 \text{ cm}^{-1}$).

Figure 13.9

- A and B show peaks in the same regions for their C=O group and $sp^3$ hybridized C–H bonds.
- A and B are different compounds, so their fingerprint regions are quite different.
Bonds and IR Absorption

• Where a particular bond absorbs in the IR depends on bond strength and atom mass.
  • Stronger bonds (i.e., triple > double > single) vibrate at a higher frequency, so they absorb at higher wavenumbers.
  • Bonds with lighter atoms vibrate at higher frequency, so they absorb at higher wavenumbers.
Bonds and IR Absorption

• Bonds can be thought of as springs with weights on each end (behavior governed by Hooke’s Law).
  • The strength of the spring is analogous to the bond strength, and the mass of the weights is analogous to atomic mass.
  • For two springs with the same weight on each end, the stronger spring vibrates at a higher frequency.
  • For two springs of the same strength, springs with lighter weights vibrate at a higher frequency than those with heavier weights.
Hooke’s Law

- **Hooke’s Law** describes the relationship of frequency to mass and bond length.

**Figure 13.10**

The frequency of bond vibration can be derived from Hooke’s law, which describes the motion of a vibrating spring:

\[ \tilde{\nu} = \sqrt{\frac{k}{m}} \]

- **Hooke’s law**

- **stronger bond** → higher frequency
- **smaller mass** → higher frequency

- The force constant \( f \) is the strength of the bond (or spring). The larger the value of \( f \), the stronger the bond, and the higher the \( \tilde{\nu} \) of vibration.
- The mass \( m \) is the mass of atoms (or weights). The smaller the value of \( m \), the higher the \( \tilde{\nu} \) of vibration.
Four Regions of an IR Spectrum

- Bonds absorb in four predictable regions of an IR spectrum.

Figure 13.11
### Table 13.2 Important IR Absorptions

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Approximate $\tilde{\nu}$ (cm$^{-1}$)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H</td>
<td>3600–3200</td>
<td>strong, broad</td>
</tr>
<tr>
<td>N–H</td>
<td>3500–3200</td>
<td>medium</td>
</tr>
<tr>
<td>C–H</td>
<td>$\sim$3000</td>
<td></td>
</tr>
<tr>
<td>$\cdot$ C$_{sp}^3$–H</td>
<td>3000–2850</td>
<td>strong</td>
</tr>
<tr>
<td>$\cdot$ C$_{sp}^2$–H</td>
<td>3150–3000</td>
<td>medium</td>
</tr>
<tr>
<td>$\cdot$ C$_{sp}$–H</td>
<td>3300</td>
<td>medium</td>
</tr>
<tr>
<td>C≡C</td>
<td>2250</td>
<td>medium</td>
</tr>
<tr>
<td>C≡N</td>
<td>2250</td>
<td>medium</td>
</tr>
<tr>
<td>C=O</td>
<td>1800–1650 (often $\sim$1700)</td>
<td>strong</td>
</tr>
<tr>
<td>C=C</td>
<td>1650</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>1600, 1500</td>
<td>medium</td>
</tr>
</tbody>
</table>
Bond Strength and % s-Character

- Even subtle differences that affect bond strength affect the frequency of an IR absorption.

- The higher the percent s-character, the stronger the bond and the higher the wavenumber of absorption.
Symmetry and IR Absorption

• For a bond to absorb in the IR, there must be a change in dipole moment during the vibration.

• Symmetrical nonpolar bonds do not absorb in the IR. This type of vibration is said to be IR inactive.
IR Absorptions in Hydrocarbons

- Hexane has only C–C single bonds and \( sp^3 \) hybridized C atoms.
- Therefore, it has only one major absorption at 3000-2850 cm\(^{-1} \).
IR Spectrum of 1-Hexene

- 1-Hexene has a C=C and C_{sp^2}-H, in addition to sp^3 hybridized C atoms.
- Therefore, there are three major absorptions: C_{sp^2}-H at 3150–3000 cm\(^{-1}\); C_{sp^3}-H at 3000–2850 cm\(^{-1}\); C=C at 1650 cm\(^{-1}\).
IR Spectrum of 1-Hexyne

• 1-Hexyne has a C≡C and C\(_{sp}\)−H, in addition to \(sp^3\) hybridized C atoms.

• Therefore, there are three major absorptions: C\(_{sp}\)−H at 3300 cm\(^{-1}\); C\(_{sp^3}\)−H at 3000–2850 cm\(^{-1}\); C≡C at 2250 cm\(^{-1}\).
IR Spectrum of 2-Butanol

- The OH group of the alcohol shows a strong absorption at 3600-3200 cm\(^{-1}\).
- The peak at ~ 3000 cm\(^{-1}\) is due to \(sp^3\) hybridized C–H bonds.
IR Spectrum of 2-Butanone

- The C=O group in the ketone shows a strong absorption at \(~ 1700 \text{ cm}^{-1}\).
- The peak at \(~ 3000 \text{ cm}^{-1}\) is due to \(sp^3\) hybridized C–H bonds.
IR Spectrum of Diethyl Ether

- The ether has neither an OH or a C=O, so its only absorption above 1500 cm\(^{-1}\) occurs at ~ 3000 cm\(^{-1}\), due to \(sp^3\) hybridized C−H bonds.
• The N–H bonds in the amine give rise to two weak absorptions at 3300 and 3400 cm\(^{-1}\).
The amide exhibits absorptions above 1500 cm\(^{-1}\) for both its N–H and C=O groups: N–H (two peaks) at 3200 and 3400 cm\(^{-1}\); C=O at 1660 cm\(^{-1}\).
IR Spectrum of Octanenitrile

- The C≡N of the nitrile absorbs in the triple bond region at ~ 2250 cm⁻¹.
IR and Structure Determination

- IR spectroscopy is often used to determine the outcome of a chemical reaction.
- For example, oxidation of the hydroxy group in compound C to form the carbonyl group in periplanone B is accompanied by the disappearance of the OH absorption, and the appearance of a carbonyl absorption in the IR spectrum of the product.

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The absorption at 3600–3200 cm\(^{-1}\) disappears.

The absorption at ~1700 cm\(^{-1}\) appears.
Using MS and IR for Structure Determination

**HOW TO Use MS and IR for Structure Determination**

**Example** What information is obtained from the mass spectrum and IR spectrum of an unknown compound X? Assume X contains the elements C, H, and O.

![Mass spectrum of X](image)

- Molecular ion $m/z = 88$

![IR of X](image)

**Step [1]** Use the molecular ion to determine possible molecular formulas. Use an exact mass (when available) to determine a molecular formula.
- Use the procedure outlined in Sample Problem 13.2 to calculate possible molecular formulas. For a molecular ion at $m/z = 88$: 

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Using MS and IR for Structure Determination

**HOW TO, continued . . .**

\[
\frac{88}{12} = 7 \text{ C's} \quad \text{maximum (remainder } = 4) \quad \xrightarrow{-\text{CH}_4} \quad \text{C}_7\text{H}_4 \quad \xrightarrow{-1 \text{ C}} \quad \text{C}_6\text{O} \quad \xrightarrow{+12 \text{ H's}} \quad \text{C}_5\text{H}_{12}\text{O} \quad \xrightarrow{-\text{CH}_4} \quad \text{C}_4\text{H}_8\text{O}_2 \quad \xrightarrow{-\text{CH}_4} \quad \text{C}_3\text{H}_4\text{O}_3
\]

- Discounting \( \text{C}_7\text{H}_4 \) (a hydrocarbon) and \( \text{C}_6\text{O} \) (because it contains no H's) gives three possible formulas for \( X \).
- If high-resolution mass spectral data are available, the molecular formula can be determined directly. If the molecular ion had an exact mass of 88.0580, the molecular formula of \( X \) is \( \text{C}_4\text{H}_8\text{O}_2 \) (exact mass = 88.0524) rather than \( \text{C}_5\text{H}_{12}\text{O} \) (exact mass = 88.0888) or \( \text{C}_3\text{H}_4\text{O}_3 \) (exact mass = 88.0160).

**Step [2] Calculate the number of degrees of unsaturation (Section 10.2).**

- For a compound of molecular formula \( \text{C}_4\text{H}_8\text{O}_2 \), the maximum number of H's = \( 2n + 2 = 2(4) + 2 = 10 \).
- Because the compound contains only 8 H's, it has \( 10 - 8 = 2 \) H's fewer than the maximum number.
- Because each degree of unsaturation removes 2 H's, \( X \) has one degree of unsaturation. \( X \) has one ring or one \( \pi \) bond.

**Step [3] Determine what functional group is present from the IR spectrum.**

- The two major absorptions in the IR spectrum above 1500 cm\(^{-1}\) are due to \( sp^3 \) hybridized C–H bonds (\( \sim3000-2850\) cm\(^{-1}\)) and a C=O group (1740 cm\(^{-1}\)). Thus, the one degree of unsaturation in \( X \) is due to the presence of the C=O.
Solving IR problems

1. Check the region around 3000 cm\(^{-1}\)

2. Is there a strong, broad band in the region of 3500 cm\(^{-1}\)?  
   If yes, OH, COOH or NH\(_2\)

3. Is there a sharp peak in the region around 1700 cm\(^{-1}\)?  
   If yes, C=O

4. Is there a peak in the region around 1630 cm\(^{-1}\)?  
   If yes, C=C

5. Be aware that symmetrical alkynes and alkenes do not give IR absorbance