Introduction to Absorption Spectroscopy

• Absorption spectroscopy is the measurement of the amount of light which is absorbed by a molecule as a function of wavelength
• Experimentally, a sample is irradiated by a light source
• Light is transmitted by the sample at different wavelengths, detected, and plotted
• This is a non-destructive way of analyzing an organic compound

Electromagnetic Radiation and Organic Compounds

• When an organic compound absorbs light, some wavelengths are absorbed, while others are not
• When the energy of the light absorbed occurs in the region of $8 \times 10^{-5}$ cm to $1 \times 10^{-2}$ cm, molecular motions occur
• These molecular motions cause bonds to stretch, bend, and rotate
• This range of wavelengths occurs within the Infrared region of the electromagnetic spectrum

Electromagnetic Spectrum

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Energy (kJ/mol)</th>
<th>Molecular effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^7$</td>
<td>$10^6$</td>
<td>ionization</td>
</tr>
<tr>
<td>$10^6$</td>
<td>$10^5$</td>
<td>electronic transitions</td>
</tr>
<tr>
<td>$10^5$</td>
<td>$10^3$</td>
<td>molecular vibrations</td>
</tr>
<tr>
<td>$10^2$</td>
<td>$10^{-7}$</td>
<td>rotational motion</td>
</tr>
<tr>
<td>$10^1$</td>
<td>$10^{-8}$</td>
<td>nuclear spin transitions</td>
</tr>
</tbody>
</table>
**Light Energy**

\[ E = h \nu = \frac{hc}{\lambda} \]

- \( E \) = Energy
- \( h \) = Planck's constant
- \( \nu \) = Frequency (hertz)
- \( c \) = Speed of light
- \( \lambda \) = Wavelength

**Molecular Vibrations**

- Covalent bonds act like a spring between two spheres.
- The frequency of the stretching vibration depends on the mass of the atoms and the stiffness or bond strength.
- When heavier atoms are bonded together, the frequency of the vibration decreases.
- Stronger or stiffer bonds require a greater force to vibrate, so vibration will occur at higher frequency.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Approximate Bond Energy (kcal/mol)</th>
<th>Approximate Stretching Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>100 (420)</td>
<td>3000</td>
</tr>
<tr>
<td>C-D</td>
<td>100 (420)</td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>83 (350)</td>
<td>1200</td>
</tr>
</tbody>
</table>

**Frequency dependence on atomic masses**

- C—C: 83 (350) ~ 1200
- C—N: 75 (380) ~ 1200
- C—O: 86 (380) ~ 1100
- C—O: 178 (745) ~ 1700

**Frequency dependence on bond energies**

- C—C: 148 (611) ~ 1660
- C—N: 147 (615) ~ 1650
- C—N: 213 (891) ~ 2200
Units of Frequency
- The energy of light is related through frequency (ν) and wavelength (λ).
- The more common unit in Infrared spectroscopy is wavenumber or ν which is cm⁻¹ and is related to wavelength
  \[ ν (\text{cm}^{-1}) = \frac{1}{\lambda} (\text{cm}) \]
- Because Infrared spectra are commonly measured between 2.4 x 10⁻⁴ cm and 25 x 10⁻⁴ cm, the micron (µ, 10⁻⁶ m) is used for wavelength
- The relationship still holds, high frequency, low wavelength, high energy

Basic Modes of Vibration
- Bending, scissoring, rocking, and wagging vibrations create absorptions that appear between 600 and 1400 cm⁻¹
- The region between 600 and 1400 cm⁻¹ is called the fingerprint region

Dipole Moment and IR Activity
- Light is composed of a magnetic field and an electric field
- It is the electric field that interacts with the bonds in a molecule
- In particular, the electric field interacts with the dipole moment of a bond
- This interaction changes the dipole moment of the bond
- The greater the change in the dipole moment, the more intense the absorption by the bond
- The more intense the absorption, the greater the IR activity
**Dipole Moment and IR Activity**

When a bond has no dipole moment, there is no interaction with the electric field. Without the interaction, the absorption may be very weak, and possibly non-detectable. In general, symmetric bonds with no net dipole show weak or no IR activity. Unsymmetric bonds with a net dipole show IR activity.

\[
\begin{align*}
\text{H} & \text{C} & \text{C} & \text{CH}_3 \\
\text{IR Active} & & & & & \\
\end{align*}
\]

**IR Inactivity**

- When a bond has no dipole moment, there is no interaction with the electric field.
- Without the interaction, the absorption may be very weak, and possibly non-detectable.
- In general, symmetric bonds with no net dipole show weak or no IR activity.
- Unsymmetric bonds with a net dipole show IR activity.

**IR Spectrophotometer**
Hydrocarbons, C-C Bond Stretching

- C-C bond stretching frequencies
  - C-C: 1200 cm⁻¹
  - C≡C: 2200 cm⁻¹
- As the number of π bonds increases, the bond strength and stiffness increases
- As the bond stiffness increases, so does the amount of energy required for bond vibration

Conjugation of C=C changes the stretching frequencies

- C=C isolated: 1640-1680 cm⁻¹
- C=C, some conjugation: 1620-1640 cm⁻¹
- C=C, aromatic ring: 1600 cm⁻¹
Hydrocarbons, C-H Bond Stretching

- C-H bond stretching frequencies
  - C-H (sp\(^3\)) 2800-3000 cm\(^{-1}\)
  - C-H (sp\(^2\)) 3000-3100 cm\(^{-1}\)
  - C-H (sp) 3300 cm\(^{-1}\)
- Why does the amount of s character affect the C-H stretching frequencies?
  - As the s character increases, the electrons in the bond are held closer to the carbon nucleus.
  - As the electrons are pulled closer to the nucleus, the bond becomes shorter, stiffer, and requires more energy in order to vibrate.

Alcohols

- Alcohols are characterized by the following frequencies
  - O-H 3300 cm\(^{-1}\), very broad
  - C-O 1000-1200 cm\(^{-1}\)
- Because of the dipole moment in both the O-H and the C-O bonds, the absorptions are quite intense.
  - The O-H band is broadened due to hydrogen bonding.
Amines

- N-H bonds have a stretching frequency around 3300 cm\(^{-1}\)
- N-H absorption bands are not as intense as O-H
- Primary amines, R-NH\(_2\), generally display two bands
- Secondary amines, R\(_2\)-NH, have one band
- Tertiary amines, R-N, have no bands
- Just as with O-H, there is broadening due to hydrogen bonding
- C-N stretching occurs around 1200 cm\(^{-1}\)
Carbonyl Compounds

- Ketones, aldehydes, and carboxylic acids all contain C=O
- All three give rise to stretching frequencies around 1710 cm⁻¹
- Aldehydes also display C-H stretching which occurs as a pair of bands between 2700 and 2800 cm⁻¹
- Carboxylic acids have O-H and C-O in addition to those for C=O
Measuring the Molecular Weight of Organic Compounds

- Elemental analysis usually provide empirical formula for organic compounds
- However, empirical formulas are not necessarily identical to molecular formulas
- In order to determine molecular formulas, the molecular weight of the compound is needed
- Mass spectrometry measures molecular weights

Ionization of Neutral Organic Molecules

- A sample is introduced into the inlet chamber
- It is vaporized and a small amount is allowed to leak into a second chamber
- The neutral molecules pass through a beam of high energy electrons (70eV)
- When the electrons strike the molecules, electrons are ejected forming a radical cation, $M^+$, molecular ion, or parent ion

\[ M + e^{-} (70eV) \rightarrow M^{+} + 2 e^{-} \]

Neutral Molecule Ionizing Beam

Fragmentation of Ions

- The ionizing beam exceeds the energy necessary to break organic bonds, 1600 kcal/mol
- Some molecular ions break apart into many combinations of neutral and ionized fragments
- The most intense peak which occurs is the base peak
- The base peak is not necessarily the parent ion peak
- Only charged fragments are detected by the instrument
**Detection of Charged Fragments**

- The molecular ions are accelerated to high velocity by an electric field.
- Since both ions and neutral species are present under vacuum, the neutral species are pumped away.
- The charged species are subjected to a magnetic field.
- The magnetic field deflects the charged species along a circular path.
- Lighter species are deflected more than heavier ones.
- The magnetic field directs the charged species through a slit, and then on to the detector.
- Charged fragments are identified by an m/z value, where m is mass and z is charge.
High Resolution Mass Spectrometry

- Consider the following molecular formulas
  - C\textsubscript{7}H\textsubscript{14}
  - C\textsubscript{6}H\textsubscript{10}O\textsubscript{2}
  - C\textsubscript{5}H\textsubscript{6}O\textsubscript{2}
  - C\textsubscript{5}H\textsubscript{10}N\textsubscript{2}

- All possess the same integer mass (nearest integer)
- And would exhibit M\textsuperscript{+} at m/z = 98
- We can tell them apart by High Resolution Mass Spectroscopy (HRMS)
- By using better magnetic focusing, ions can be distinguished which differ by only a few thousands of a mass unit

\[
\begin{align*}
\text{C}_7\text{H}_{14} & : 98.1096 \\
\text{C}_6\text{H}_{10}\text{O}_2 & : 98.0732 \\
\text{C}_5\text{H}_6\text{O}_2 & : 98.0368 \\
\text{C}_5\text{H}_{10}\text{N}_2 & : 98.0845
\end{align*}
\]

Mass Spectra Reveal Presence of Isotopes

- When a mass spectrum of methane is examined, a very small peak at m/z = 17 is observed
- This is an (M + 1)\textsuperscript{+} and corresponds to \textsuperscript{13}C which has a natural abundance of 1.1%
- The (M + 1)\textsuperscript{+} Peak height is n times 1.1% where n = the number of carbons in the molecule
- Other elements give rise to identifiable patterns
  - Br (M + 2)\textsuperscript{+} as large as M\textsuperscript{+}
  - Cl (M + 2)\textsuperscript{+} 1/3 as large as M\textsuperscript{+}
  - S (M + 2)\textsuperscript{+} 4% the height of M\textsuperscript{+}
  - N odd M\textsuperscript{+}
  - I\textsuperscript{+} at m/z = 127

<table>
<thead>
<tr>
<th>Element</th>
<th>M\textsuperscript{+}</th>
<th>M + 1</th>
<th>M + 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>\textsuperscript{1}H</td>
<td>100.0%</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>\textsuperscript{12}C</td>
<td>98.9%</td>
<td>3\textsuperscript{13}C 1.1%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>\textsuperscript{14}N</td>
<td>99.6%</td>
<td>3\textsuperscript{15}N 0.4%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>\textsuperscript{16}O</td>
<td>99.8%</td>
<td>3\textsuperscript{17}O 0.2%</td>
</tr>
<tr>
<td>Sulphur</td>
<td>\textsuperscript{32}S</td>
<td>95.0%</td>
<td>3\textsuperscript{33}S 0.8%</td>
</tr>
<tr>
<td>Chlorine</td>
<td>\textsuperscript{35}Cl</td>
<td>75.5%</td>
<td>3\textsuperscript{37}Cl 24.5%</td>
</tr>
<tr>
<td>Bromine</td>
<td>\textsuperscript{79}Br</td>
<td>90.5%</td>
<td>3\textsuperscript{81}Br 9.5%</td>
</tr>
<tr>
<td>Iodine</td>
<td>\textsuperscript{127}I</td>
<td>100.0%</td>
<td></td>
</tr>
</tbody>
</table>
Fragmentation of Hexane

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+ + \text{CH}_3\text{CH}_2^+ \\
m/z = 57 \text{ radical}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 ^+ \xrightarrow{+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3^+ + \text{CH}_2^+ \\
m/z = 43 \text{ radical}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 ^+ \xrightarrow{+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3^+ + \text{CH}_2^+ \\
m/z = 71 \text{ radical}
\]

Fragmentation of Isomeric Alkanes

- There are three structural isomers for \( \text{C}_5\text{H}_{12} \).
- They can be distinguished by their mass spectra.
- Pentane shows a base peak at \( m/z = 43 \), but a very small \( m/z = 57 \) due to the instability of \( \text{CH}_3^+ \).
- 2-methylbutane also shows a peak at \( m/z = 43 \), but a large \( m/z = 57 \) as well.
- This is due to the formation of a secondary cation.
- Fragmentations are influenced by the stability of cations.
Fragmentation of Isomeric Alkanes

- The third isomer of C\textsubscript{5}H\textsubscript{12} is 2,2-dimethylpropane
- The base peak now is m/z = 57, not m/z = 43
- The intensity of the parent ion is also very low due to the stability of the 3\textsuperscript{o} cation formed

\[
\begin{align*}
\text{CH}_3\text{C} &\text{CH}_3 \quad \text{m/z} = 57 \\
\text{CH}_3\text{CH}_2\text{CH}_3^+ &\text{ or } \text{CH}_3\text{CHCH}_3^+ \\
\text{m/z} = 43 &\quad \text{or} \\
\text{CH}_3\text{CH}_2^+ &\quad \text{m/z} = 27 \\
\text{m/z} = 29 &
\end{align*}
\]

Lesser Fragmentations of Alkanes

- Alkanes give fragmentations of the formula C\textsubscript{n}H\textsubscript{2n+1}
- From these ions come lesser amounts of ions with the general formula C\textsubscript{n}H\textsubscript{2n-1}
- For example, in the mass spectra for the isomers of C\textsubscript{5}H\textsubscript{12}, along with m/z = 43 and 29, there also appear m/z = 27 and 41

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2^+ &\quad \text{or} \\
\text{m/z} = 43 &\quad \text{CH}_3\text{CHCH}_3^+ \\
\text{C}_3\text{H}_7^+ &\quad \text{H}_2 \\
\text{m/z} = 41 &\quad \text{m/z} = 27 \\
\end{align*}
\]

Mass Spectra of Alcohols

- The molecular ion or parent ion peak for a primary or secondary alcohol is usually quite small
- The molecular or parent ion peak is usually undetectable for tertiary alcohols
- The reason for the absence of the parent ion is that H\textsubscript{2}O is readily lost from alcohols
- Another fragmentation that is common in alcohols is the cleavage of the C-C between the carbinol carbon and its neighboring carbon
- This fragmentation is known as an alpha cleavage
Alpha Fragmentation

\[
\begin{align*}
\text{[OH]} & \rightarrow \text{[\text{OH}]} + \text{[H]}
\end{align*}
\]

- 1° alcohols give a large m/z = 31, CH₂OH⁺
- 2° alcohols give m/z = 45, 59, 73, etc.
- 3° alcohols give m/z = 59, 73, 87, etc.

\[
\begin{align*}
\text{R} & \text{H} \\
\text{OH} & + \text{H} \\
\text{R'} & \text{R''}
\end{align*}
\]