Structure Determination:

Chapter 12: Mass Spectrometry- molecular weight of the sample; formula
Chapter 12: Infrared Spectroscopy- indicated which functional groups are present
Chapter 13: Nuclear Magnetic Resonance- “map” of the C-H framework
Chapter 14: Ultraviolet-Visible Spectroscopy- bond

Chapter 12: Mass Spectrometry:
molecular weight of the sample \[ \rightarrow \text{ formula} \]

The mass spectrometer gives the mass to charge ratio, therefore the sample (analyte) must be an ion.
Mass spectrometry is a gas phase technique- the sample must be “vaporized.”

Electron-impact ionization

Sample Inlet \[ 10^{-7} - 10^{-8} \text{ torr} \]

ionization chamber

electron beam 70 eV (6700 KJ/mol)

R-H \[ \rightarrow \text{ R-H}^+ \] (M+)

mass analyzer

proton 1.00728 u
neutron 1.00866 u
electron 0.00055 u
Magnetic Field, $B_o$

\[
\frac{\text{mass}}{\text{charge}} = \frac{m}{z} = \frac{B^2 r^2}{2V}
\]

- $B =$ magnetic field strength
- $r =$ radius of the analyzer tube
- $V =$ voltage (accelerator plate)

**Molecular Ion** (parent ion, $M$) = molecular mass of the analyte; sample minus an electron

**Nitrogen rule**: organic molecules with an odd mass must have an odd number of nitrogens. Organic molecules with an even mass have an even number of nitrogens (0 is an even number)

**Base peak**: largest (most abundant) peak in a mass spectra; arbitrarily assigned a relative abundance of 100%.

If the mass can be determined accurately enough, then the molecular formula can be determined (high resolution mass spectrometry) - double focusing mass spectrometer
### Exact Masses of Common Natural Isotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>mass</th>
<th>natural abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1.00782</td>
<td>99.985</td>
</tr>
<tr>
<td>$^2$H</td>
<td>2.01410</td>
<td>0.015</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>12.0000</td>
<td>98.892</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>13.00335</td>
<td>1.108 (1.11%)</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>14.00307</td>
<td>99.634</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>15.00010</td>
<td>0.366 (0.38%)</td>
</tr>
<tr>
<td>$^{16}$O</td>
<td>15.99491</td>
<td>99.763</td>
</tr>
<tr>
<td>$^{17}$O</td>
<td>16.99913</td>
<td>0.037 (0.04%)</td>
</tr>
<tr>
<td>$^{18}$O</td>
<td>17.99916</td>
<td>0.200 (0.20%)</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>18.99840</td>
<td>100.00</td>
</tr>
<tr>
<td>$^{35}$Cl</td>
<td>34.96885</td>
<td>75.77</td>
</tr>
<tr>
<td>$^{37}$Cl</td>
<td>36.96590</td>
<td>24.23 (32.5%)</td>
</tr>
<tr>
<td>$^{79}$Br</td>
<td>78.91839</td>
<td>50.69</td>
</tr>
<tr>
<td>$^{81}$Br</td>
<td>80.91642</td>
<td>49.31 (98%)</td>
</tr>
<tr>
<td>$^{127}$I</td>
<td>126.90447</td>
<td>100.00</td>
</tr>
</tbody>
</table>

High resolution mass spectrometry can give the formula of the sample

**mass = 58**

- $N_3O$  58.0042
- $N_4H_2$  58.0280
- CNO$_2$  57.9929
- CH$_2$N$_2$O  58.0167
- CH$_2$N$_3$  58.0406
- C$_2$H$_2$O$_2$  58.0054
- C$_2$H$_4$NO  58.0293
- C$_2$H$_6$N$_2$  58.0532
- C$_3$H$_6$O  58.0419
- C$_3$H$_6$N  58.0657
- C$_4$H$_{10}$  58.0783

For mass = 200, there are at least 51 empirical formulas with C,H,N,O
The radical cation (M⁺) is unstable and will fragment into smaller ions:

\[
\begin{align*}
\text{H} & \quad - \text{e}^- \quad \text{[H-\text{C-H}]}^+ \quad m/z = 15 \\
\text{H} & \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad + \quad \text{H}^+ \\
\text{charge neutral} & \quad \text{not detected} \\
\text{m/z} & = 14 \\
\text{H} & \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad + \quad \text{H}^+ \\
\text{charge neutral} & \quad \text{not detected}
\end{align*}
\]
Mass spectra can be quite complicated and interpretation difficult.

Some functional groups have characteristic fragmentation (sect. 12.4)

It is difficult to assign an entire structure based only on the mass spectra. However, the mass spectra gives the mass and formula of the sample which is very important information.

To obtain the formula, the molecular ion must be observed.

soft ionization techniques (chemical ionization, fast atom bombardment)

Methods have been developed to get large molecules such as polymers and biological macromolecules (proteins, peptides, nucleic acids) into the vapor phase (matrix-assisted laser desorption ionization and electrospray ionization)
Spectroscopy and the Electromagnetic Spectrum

Electromagnetic (EM) radiation = light
  matter
  energy
  photon (quanta)

Spectroscopy: the interaction of EM radiation with matter
  (organic molecule)

\[
\text{light (h\[\nu\])} \rightarrow \text{organic molecule (ground state)} \rightarrow \begin{bmatrix} \text{organic molecule (higher energy state)} \end{bmatrix} \rightarrow \text{organic molecule (ground state)} + h\[\nu\]
\]

absorption  emission

quantized energy levels: the energy states are at discrete levels;
there is no continuum between these levels

\[
E = h\nu \\
\nu = c/\lambda \\
\nu = \frac{hc}{\lambda} \\
E \propto \lambda ^{3} \\
E \propto \lambda ^{-3}
\]

\(c = \text{speed of light (3} \times 10^{10} \text{ cm} \cdot \text{sec}^{-1})\)
\(\lambda = \text{wavelength (distance of one wave)}\)
\(\nu = \text{frequency: number of waves per unit time (sec}^{-1}, \text{ Hz})\)
\(h = \text{Planck’s constant } = 6.62 \times 10^{-34} \text{ J} \cdot \text{sec}^{-1}\)
The Electromagnetic Spectrum

Increasing Energy

Frequency ($\nu$) in Hz

- Longer wavelength ($\lambda$)

Wavelength ($\lambda$) in m

Visible

380 nm 500 nm 600 nm 700 nm 780 nm

$3.8 \times 10^{-7}$ m $7.8 \times 10^{-7}$ m

- Infrared: molecular vibrations; stretching and bending of bonds - identify functional groups (Ch. 12)

- Radiowaves: nuclear magnetic resonance spectroscopy; nuclear magnetic moments versus an external magnetic field - gives a H and C map of the molecule (Ch. 13)

- UV-vis: valance electron transitions; types of $\pi$-bonds (Ch. 14)
Infrared Spectroscopy:

<table>
<thead>
<tr>
<th>Vis</th>
<th>Near IR</th>
<th>Infrared (IR)</th>
<th>Far IR</th>
<th>microwave</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-4}</td>
<td>2.5 x 10^{-4} cm</td>
<td>2.4 x 10^{-3} cm</td>
<td>10^{-2}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 μm</td>
<td>25 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ E \square = \frac{1}{\square} \]

\( \square \) is expressed as \( \square \) (wavenumber), reciprocal cm \( (\text{cm}^{-1}) \)

\( \square = \frac{1}{\square} \) therefore \( E \square \)

Absorption of infrared radiation causes bonds within a molecule to vibrate, stretch and bend. Bonds behave like springs.

**Stretch**- deforms bond length
http://www2.chem.ucalgary.ca/Flash/photon.html

**Symmetric stretch**

**Antisymmetric stretch**

**Bend**- deforms bond angle

**In-plane bend**

**Out-of-plane bend**
**Bond Stretch:**

Hooke’s Law

\[ \omega = \frac{1}{2 \omega_c} \left( \frac{f}{\left( \frac{m_x m_y}{m_x + m_y} \right)^{1/2}} \right) \]

- \( \omega \) = vibrational frequency
- \( \omega_c \) = speed of light
- \( m_x \) = mass of X
- \( m_y \) = mass of Y

\left( \frac{m_x m_y}{m_x + m_y} \right) = \text{reduced mass} \( (\mu) \)

\[ f = \text{spring constant; type of bond between X and Y} \]

(single, double or triple)

Hooke’s law simulation:

http://www2.chem.ucalgary.ca/Flash/hooke.html

**Interpretation of an Infrared Spectra:**

organic molecules contain many atoms. As a result, there are many stretching and bending modes- IR spectra have many absorption bands

Four distinct regions of an IR spectra

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-H single bond region</td>
<td>4000 cm(^{-1})</td>
</tr>
<tr>
<td>triple bond region</td>
<td>2500 cm(^{-1})</td>
</tr>
<tr>
<td>double bond region</td>
<td>2000 cm(^{-1})</td>
</tr>
<tr>
<td>fingerprint region</td>
<td>1500 cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td>600 cm(^{-1})</td>
</tr>
</tbody>
</table>
Fingerprint region (600 - 1500 cm\(^{-1}\)) - low energy single bond stretching and bending. The fingerprint region is unique for a given organic compound and is thus used to identify them. However there are few diagnostic absorptions.

Double-bond regions (1500 - 2000 cm\(^{-1}\))
- C=C 1650 - 1670 cm\(^{-1}\)
- C=O 1670 - 1780 cm\(^{-1}\)

Triple-bond region: (2000 - 2500 cm\(^{-1}\))
- C≡C 2100 - 2260 cm\(^{-1}\) (weak, often not observed)
- C≡N 2200 - 2260 cm\(^{-1}\)

X-H Single-bond region (2500 - 4000 cm\(^{-1}\))
- O-H 3300 - 3600 cm\(^{-1}\)
- N-H 3300 - 3600 cm\(^{-1}\)
- C-H 2700 - 3000 cm\(^{-1}\)
  - sp\(^3\) -C-H 2850 - 3000 cm\(^{-1}\)
  - sp\(^2\) -C-H 3000 - 3100 cm\(^{-1}\)
  - sp -C-H ~3300 cm\(^{-1}\)

**Carbonyl groups:**

- aliphatic aldehyde 1730 cm\(^{-1}\)
- conjugated aldehyde 1705 cm\(^{-1}\)
- aromatic aldehyde 1705 cm\(^{-1}\)
- aliphatic ketone 1715 cm\(^{-1}\)
- conjugated ketone 1690 cm\(^{-1}\)
- aromatic ketone 1690 cm\(^{-1}\)
- aliphatic ester 1735 cm\(^{-1}\)
- conjugated ester 1715 cm\(^{-1}\)
- aromatic ester 1715 cm\(^{-1}\)

*Conjugation moves the C=O stretch to lower energy (right)*
Cyclic Ketones:

![Cyclic Ketones Diagram]

Table 12.1 (page 458)

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Fundamental Frequencies</th>
<th>Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkenes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>=C-H</td>
<td>3020 - 3100 cm^{-1}</td>
<td>medium - strong</td>
</tr>
<tr>
<td>C=C</td>
<td>1640 - 1680 cm^{-1}</td>
<td>medium</td>
</tr>
<tr>
<td><strong>Aromatic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>=C-H</td>
<td>3030 cm^{-1}</td>
<td>strong</td>
</tr>
<tr>
<td>C=C</td>
<td>1660 - 2000 cm^{-1}</td>
<td>weak</td>
</tr>
<tr>
<td></td>
<td>1450 - 1600 cm^{-1}</td>
<td>strong</td>
</tr>
<tr>
<td><strong>Alkynes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>=C-H</td>
<td>3300 cm^{-1}</td>
<td>strong</td>
</tr>
<tr>
<td>C≡C</td>
<td>2100-2260</td>
<td>weak - medium</td>
</tr>
<tr>
<td><strong>Alcohols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-O</td>
<td>1050 - 1150 cm^{-1}</td>
<td>strong</td>
</tr>
<tr>
<td>O-H</td>
<td>3400 - 3600 cm^{-1}</td>
<td>strong and broad</td>
</tr>
<tr>
<td><strong>Amines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-N</td>
<td>1030 - 1230 cm^{-1}</td>
<td>medium</td>
</tr>
<tr>
<td>N-H</td>
<td>3300 - 3500 cm^{-1}</td>
<td>medium</td>
</tr>
<tr>
<td><strong>Carbonyl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>1670 - 1780 cm^{-1}</td>
<td>strong</td>
</tr>
<tr>
<td><strong>Carboxylic acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-H</td>
<td>2500 - 3500 cm^{-1}</td>
<td>strong and very broad</td>
</tr>
<tr>
<td><strong>Nitrile</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>2210 - 2260</td>
<td>medium</td>
</tr>
</tbody>
</table>
Problem 12.16