Spectroscopy- help determine the structure of organic molecules.

In the past use reactions.

15 need a large sample
16 hard for complex molecules
17 destructive

IR

1. IR- absorption spectroscopy- light is absorbed, a specific wavelength absorbed is measured. Based on the vibrations of bonds and provides evidence of functional groups.

\[ \lambda \]

\[ \lambda = \text{wavelength} \]
\[ \nu = \text{frequency} \]
\[ c = \lambda \times \nu \]

low energy and high energy related to wavelength. Short wavelength = high energy.

\[ \varepsilon = \text{photon energy} \quad \varepsilon = h \nu = \frac{hc}{\lambda} \quad h = \text{Plank’s constant} \]

\[ \varepsilon = \text{matches the difference between ground state and excited state} \]

IR must have a dipole moment.

IR = Cause atoms to vibrate.

Microwave = rotations

Radio wave = nuclear spin transitions.

IR measures wave numbers = number of wave lengths in a centimeter.

\[ 1 \text{ cm} = 10,000 \mu \text{m} \quad \text{wavelength measured in } \mu \text{m} \]

wavenumber \((\text{cm}^{-1}) = \frac{1}{\lambda} \text{ (cm)} \)

Assume two weights on a spring.

frequency of the stretching Vibrations dependent on:

1. Mass of atoms- heavier atoms, frequency decreases
2. Strength of bond. – stronger bonds require more force so vibrate faster so frequency increases with bond strength.
3. Conjugation decreases e’ density and decreases wavenumber.
4. Hybridization, greater s character higher the wavenumber. sp 3300 cm⁻¹, sp² 3000 cm⁻¹, sp³ 3000-2800 cm⁻¹

Need a polar bond to be IR active. N₂ is IR inactive. Alkyne can be inactive. More dipole stronger the absorption.

\[3n-6 = \text{fundamental vibrations} \quad n = \text{atoms}\]

amines and alcohols. Single,double peak.

Need a dipole moment to be IR active, in an electrical field will not be compressed or stretched if a non-polar bond.

Ex.
\[
\begin{align*}
\text{H}_3\text{C} & \quad \equiv \text{C} & \quad \equiv \text{C} & \quad \text{C-H} & \quad \text{N}_2 \\
\text{Not IR active} & \quad \text{IR active} & \quad \text{IR active} & \quad \text{Not IR active}
\end{align*}
\]
Different Functional groups:

1. C-C stretching

\[
\begin{align*}
\text{C—C} & : 1200 \\
\text{C=C} & : 1660 \text{ conjugated systems} \\
\text{C=O} & : 2200 \\
\end{align*}
\]

1620-1640 delocalization
1600 aromatic

2. C-H stretch

\[
\begin{align*}
\text{C—H} & : 2800-3000 \\
\equiv\text{C—H} & : 3000-3100 \\
\equiv\text{C—H} & : 3300 \\
\end{align*}
\]

3. –O-H stretch

\[
\begin{align*}
\text{H} & : 3300 \text{ broad H-bond} \\
\text{O—H} & : 3000 \text{ broad} \\
\text{N—H} & : 3300 \text{ broad if 2H get two spikes} \\
\end{align*}
\]

4. C=O stretch

\[
\begin{align*}
\text{R—C─OR} & : 1710 \\
\text{R—C─OH} & : 2700, 2800 \\
\text{R—C─O─H} & : 2500-3500 \\
\end{align*}
\]

5. C-N bonds, more polar so give greater absorption than C-C bonds.

\[
\begin{align*}
\text{C—N} & : 1200 \\
\text{C≡N} & : 1600 \\
\text{C≡N} & : >2200 \\
\text{C=O} & : <2200 \\
\end{align*}
\]
Resonance lowers carbonyl frequency, reduce e’ density.

\[
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{O} \\
1680
\end{array}
\quad
\begin{array}{c}
\text{O} \\
1685
\end{array}
\]

Ring strain increases frequency, rigid system.

\[
\begin{array}{c}
\text{O} \\
1785
\end{array}
\]

**Mass Spec**

Gives molecular weight, possible molecular formula. (HRMS)

Works by hitting a molecule with energy e’ to possibly fragment the molecule. Measure the resulting mass of charged species. M^+ or M^-.  

A.  

EI: Positive mode. Electron impact ionization.

\[ e^+ + M \rightarrow [M]^+ + 2e^+ \text{ radical cation.} \]

Ex.

\[ \text{CH}_3\text{OH} + e^+ \rightarrow \text{CH}_3\text{OH} + 2e^+ \]

Measure mass/charge = m/z = 32/1 = 32 determines distance of path.

M^+ = molecular ion peak  

highest peak = base peak

B.  

High res mass spec- determines the possible molecular weight.  

mass are dependent on isotopic composition.
Ex. m/z = 32

Can be CH$_3$OH or H$_2$NNH$_2$

32.0262  32.0375

dependent on exact masses.

C = 12.000  N = 14.003050  O = 15.994914  H = 1.007825

Isotope peaks

M + 1  M + 2

Br has 50:50 isotope ration of 79 and 81.
Cl 75.5:24.5  35 and 37, gives rise to M + 1 and M + 2 peaks and also relative intensities.

Fragmentation

R:R’ + e’ → [R.R’]$^+$ + 2e’

Molecular ion

\[ R^+ + \text{R’} \text{ (not detected)} \]

Fragmentation patterns and intensities are based on the stability of the resulting cation and radical.

57 = CH$_3$-CH$_2$-CH$_2$-CH$_3$\(^+\) can also be tertbutyl.

43 = CH$_3$-CH$_2$-CH$_3$\(^+\) carbocation in 2 position also

1. = CH$_3$-CH$_2$\(^+\)

15 = CH$_3$\(^+\)

1. Fragmentation patterns- give most stable products of carbocation and radical

\[
\begin{align*}
\text{\textbullet} & \quad \rightarrow \quad \text{\textbullet}^+ \quad \text{+ CH}_2\text{CH}_3 \\
\text{\textbullet} & \quad \rightarrow \quad \text{\textbullet} \quad \text{+ CH}_2\text{CH}_3
\end{align*}
\]

2. Stabilization by resonnance.

\[
\begin{align*}
\text{\textbullet} & \quad \rightarrow \quad \text{\textbullet}^+ \quad \text{+ CH}_3\text{.}
\end{align*}
\]

3. Loss of a molecule. Even numbered peaks are double fragmentation.

\[
\begin{align*}
\text{H}_2\text{O} & = -18 \\
\text{CO}_2 & = -44 \\
m/z = 70
\end{align*}
\]

\[
\begin{align*}
\text{\textbullet} & \quad \rightarrow \quad \text{\textbullet}^+ \quad \text{+ H}_2\text{O}
\end{align*}
\]

Ethane = -28

Rings = Loss of -28
4. Ketones-

\[
\begin{align*}
\text{RCO}_2HR' \rightarrow [\text{RCO}_2R']^+ & \rightarrow [\cdot \text{O} + \text{R}^+ + \text{RCO}_2^+] + \cdot \text{R}' \\
\end{align*}
\]

Ex.

\[
\begin{align*}
\cdot \text{CH}_3 + & \quad + \text{O} \\
\text{m/z 57} & \quad \text{m/z 43}
\end{align*}
\]

McLafferty rearrangement- cyclic intramolecular transfer of a hydrogen atom, gamma to a carbonyl oxygen.

5. Amines-

\[
\begin{align*}
\text{R}^+ + \text{NH}_2 & \rightarrow [\cdot \text{H} + \text{R}^+ + \text{NH}_2^+] + \cdot \text{R} \\
\end{align*}
\]

Ex.
6. Ac ids-
   B. Common loss-

   ![Chemical structure diagram]

   Ex.

   McClaffert

   ![Chemical structure diagram]

   7. Ethers-

   Ex.