

Chapter 13: Mass Spectrometry and Infrared Spectroscopy

A. Spectroscopic Analysis—Tools for Structure Determination

We have seen many organic structures, but we have not discussed how we can figure out what these structures *are*.

Naturally, the ability to analyze a sample in the lab for its **identity and purity** is *essential*.

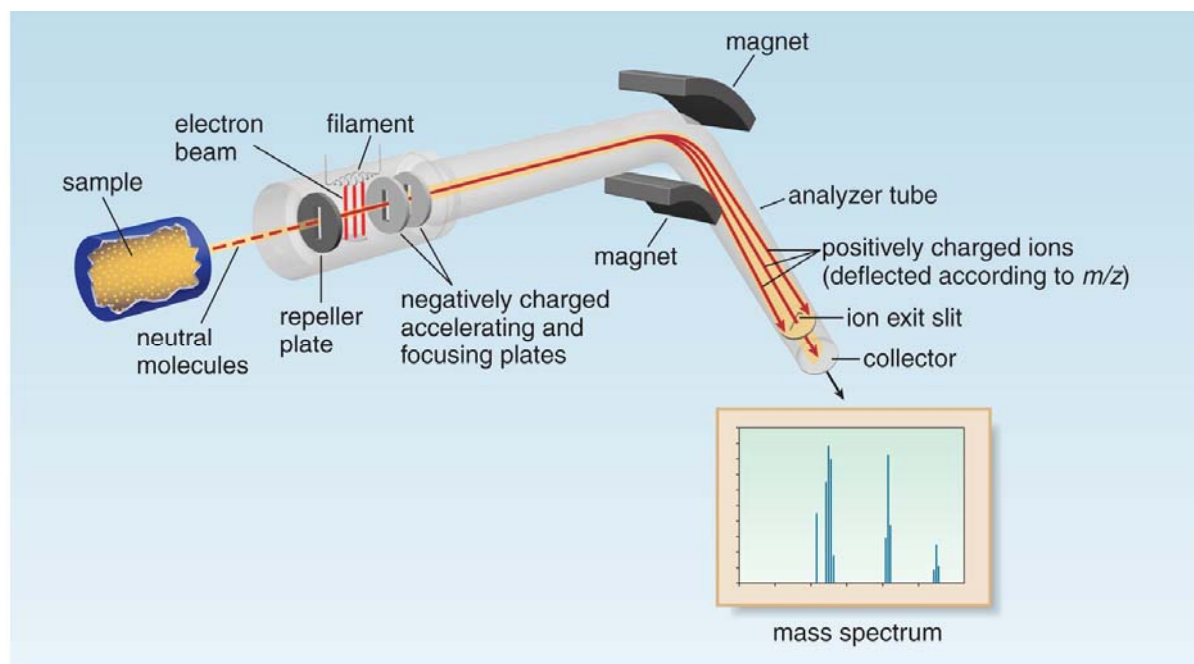
We have powerful tools that provide info about structure, but often only **indirectly**—one must know *how to interpret the data*.

Two such techniques will be introduced in this Chapter:

1. **Mass spectrometry**—info about MW and/or formula
2. **Infrared spectroscopy**—info about functional groups present

B. Mass spectrometry (MS)

- MS enables measurement of the molecular weight (MW) and, sometimes, the *formula* of a compound.
- In a **mass spectrometer**, molecules are vaporized and then blasted with energy to create ions.
- Classically, a beam of high-energy (70 eV) e^- is used, knocking off an e^- to form an unstable **radical cation**.
- The **mass-to-charge ratio** (m/z) for a charged particle can be measured—if $z = 1$, the m/z value will = its mass.



1. A “Mass Spectrum” (plural = spectra)

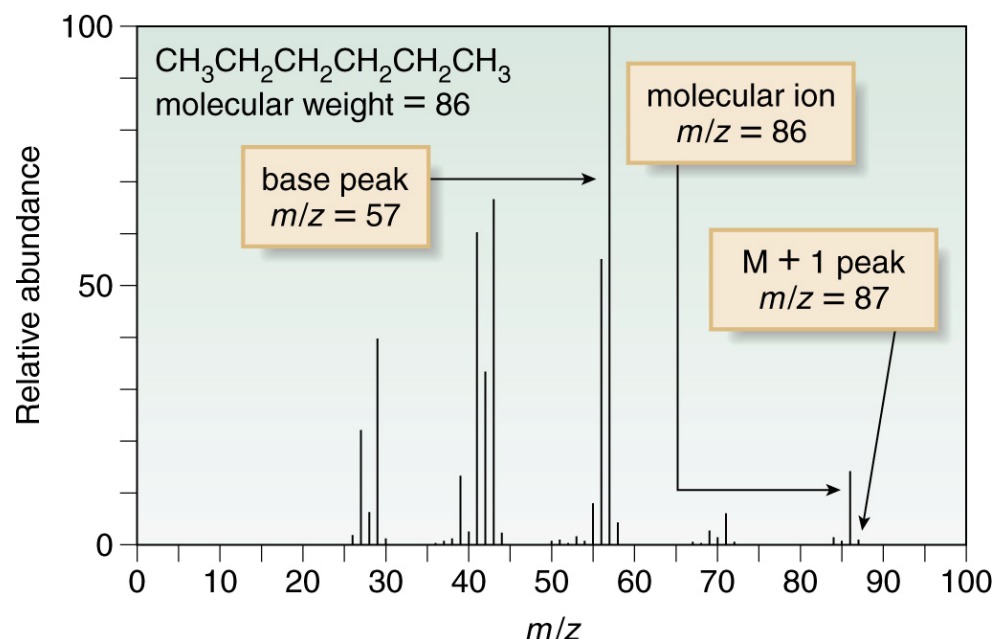
- The **radical cation** initially formed is **$M^{+\bullet}$** --called the **molecular ion** or **parent ion**. Its m/z represents the MW of M.
- **$M^{+\bullet}$** is unstable, and decomposes to form **fragments** smaller than $M^{+\bullet}$. Some of these are also **charged**, resulting in an array of ions called a **mass spectrum**.



- All **charged** species formed can be analyzed/observed—generally, the focus is on **+** ions.

An Example: the Mass Spectrum of *n*-Hexane (MW 86)

- A small M+1 peak (m/z 87) accompanies M^+ . This is called an “**isotope peak**” and is mainly due to the small 1.1% natural abundance of ^{13}C !
- The *tallest* peak (= most *abundant* ion) is at m/z 57 (C_4H_9^+). This is the “**base peak**” (such “fragment” ions may be more abundant than M^+ if they are more stable than M^+).
- Other major ions occur at m/z 43 (C_3H_7^+) and 29 (C_2H_5^+).



The array of ions observed is called the “**fragmentation pattern**”, and is characteristic of the structure.

2. Halides and $M + 2$ Ions—More “Isotope Peaks”

Most elements have one *major* isotope (^1H , ^{12}C , ^{14}N , ^{16}O , etc.)

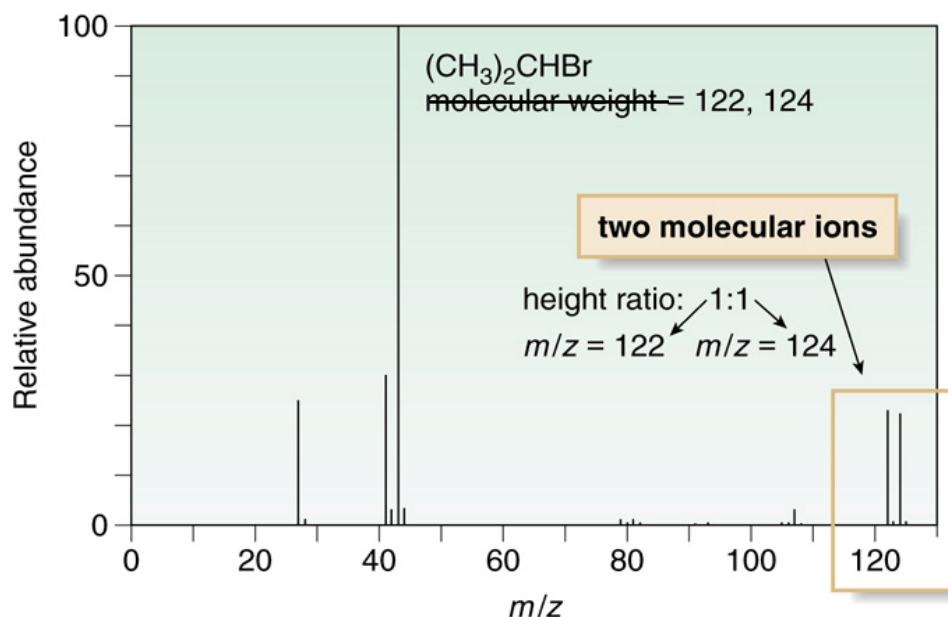
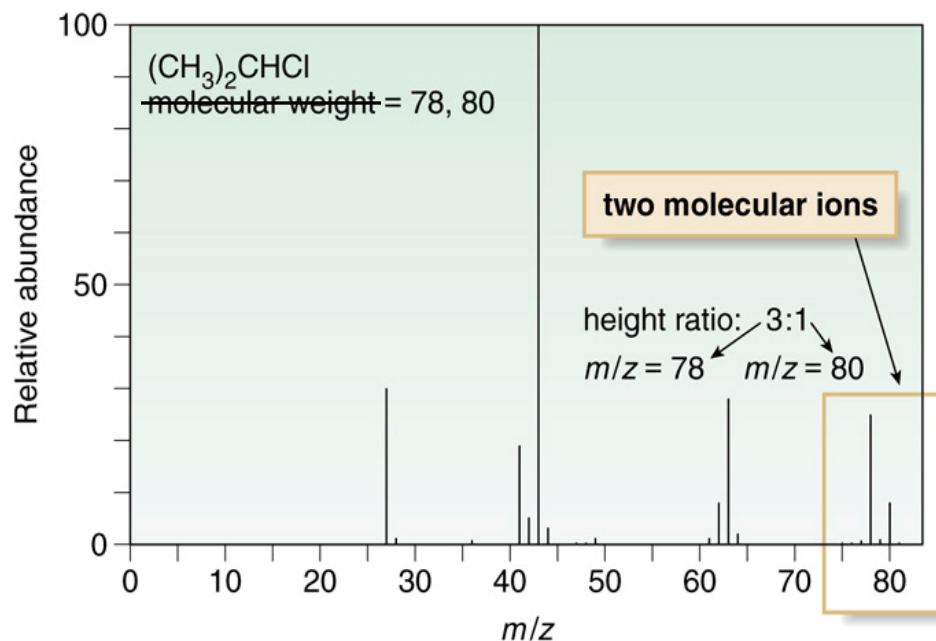
Cl has *two*; ^{35}Cl and ^{37}Cl , which occur naturally in a **3:1 ratio**.

- The M peak contains ^{35}Cl . The **$M + 2$** peak, corresponds to the molecules that contain ^{37}Cl .
- Thus, the presence of molecular ion M and $M + 2$ peaks in a **3:1 ratio** is diagnostic for the presence of **Cl** (e.g., in RCl).

Br also has two; ^{79}Br and ^{81}Br , occurring in a ratio of **$\sim 1:1$** .

- So....when the M^+ range consists of M and $M + 2$ peaks in a 1:1 ratio, a **Br** atom is likely to be present.

Examples: MS Data for 2-Chloropropane and 2-Bromopropane



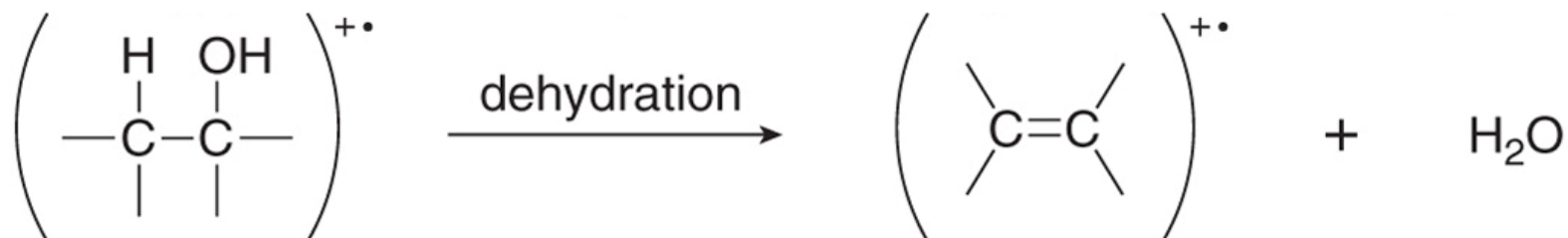
- Most **fragments** here do not have the $M + 2$ partner because the Cl or Br has been lost in getting to them.
- MS provides a good way to determine whether a compound has Cl or Br in it.
- Note: the “atomic wt” for an element in the periodic table is a **weighted average of the natural isotopes**

3. Fragmentations Useful in Structure Analysis

Some of the **fragment ions** observed in a spectrum may be useful in elucidating further details about the structure.

We will not explore this in depth, but two examples follow:

Alcohols often undergo a loss of H_2O in MS--**dehydration**:

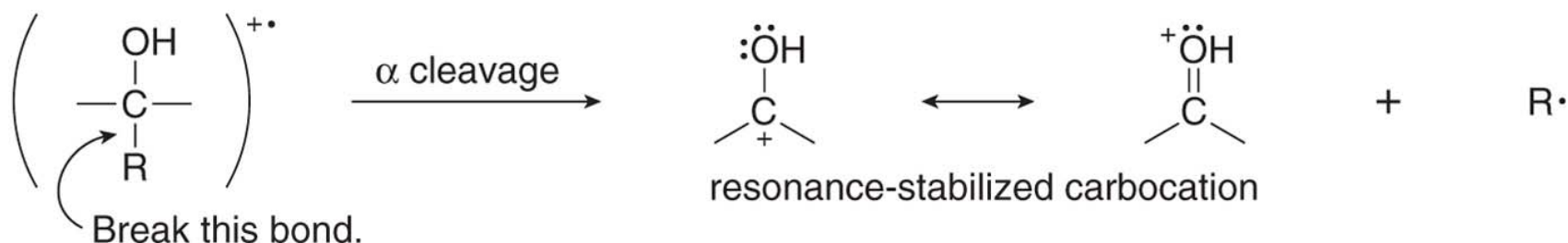


Utility? The presence of a sizable **$\text{M}-\text{H}_2\text{O}$** ion in a mass spectrum suggests that **the compound contains an alcohol group.**

Another common type of fragmentation is called **α -cleavage**.

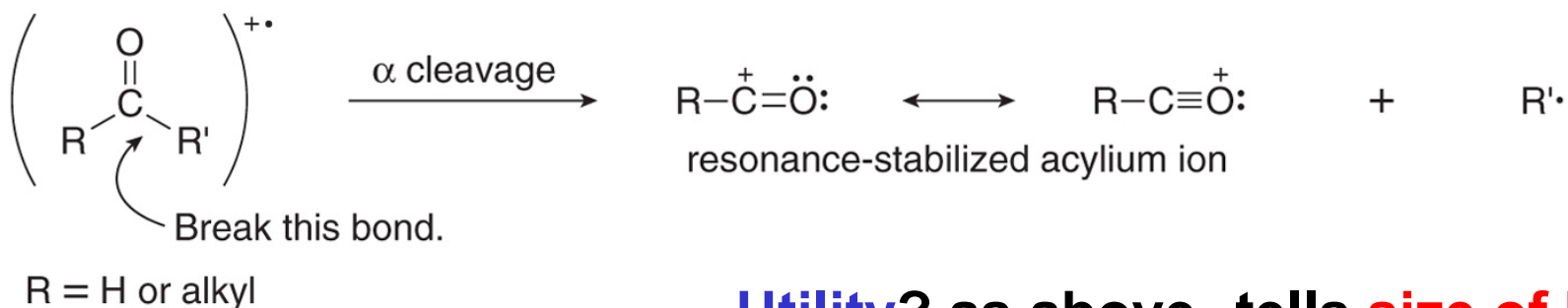
This process occurs for many functional groups, and involves a relatively favorable **cleavage of a bond “ α ” to a heteroatom**:

e.g., for alcohols:



Utility? The resulting **M-R** ion(s) can tell you **the size of R**

Carbonyl compounds can do this, too:



Utility? as above--tells **size of R**

4. High Resolution Mass Spectrometry (HRMS)

- Low resolution MS gives m/z values to the nearest whole number.
- High resolution MS gives m/z values to four (or more) decimal places.
 - Except for ^{12}C (mass = 12.0000 daltons by convention), the masses of all other nuclei are not exactly whole numbers.
 - Therefore, using the exact mass values of possible nuclei, HRMS data can be used to determine the molecular formula of an ion.

Exact masses of some common isotopes:

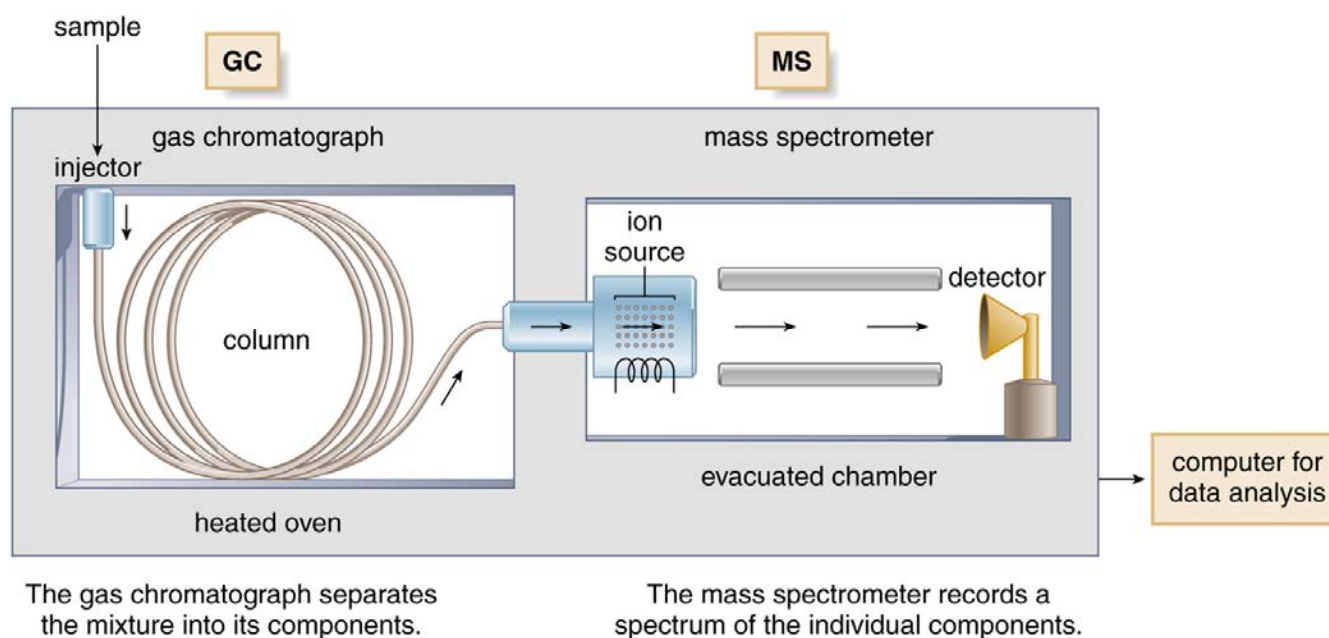
Isotope	Mass
^{12}C	12.0000
^1H	1.00783
^{16}O	15.9949
^{14}N	14.0031

Exact masses of possible formulas for m/z 60; HRMS will tell which you have!

Formula	Exact mass
$\text{C}_3\text{H}_8\text{O}$	60.0575
$\text{C}_2\text{H}_4\text{O}_2$	60.0211
$\text{C}_2\text{H}_8\text{N}_2$	60.0688

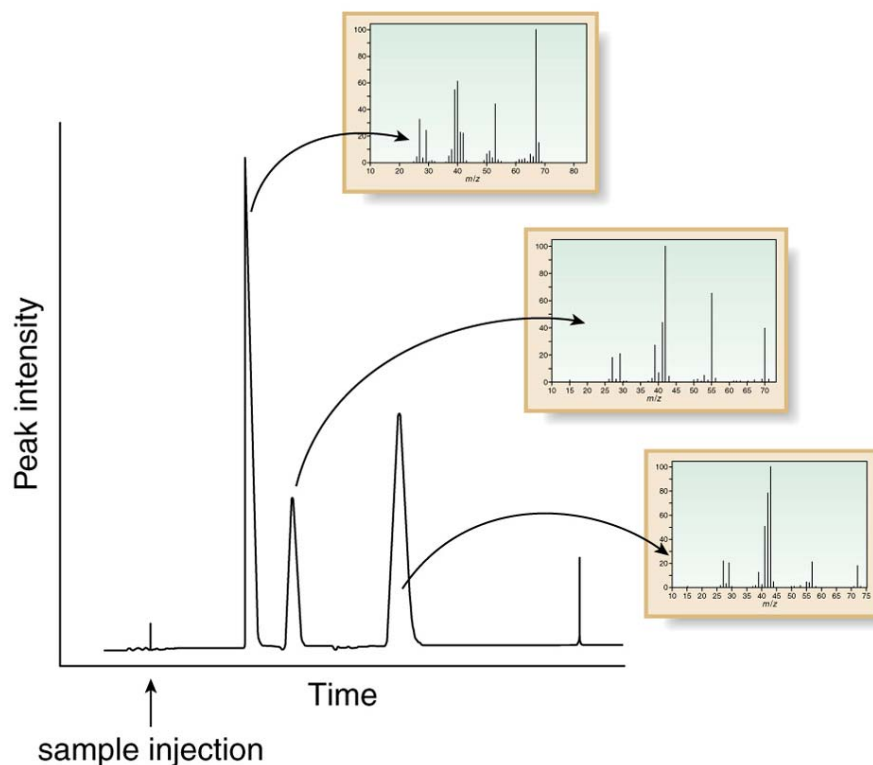
5. Gas Chromatography-Mass Spectrometry (GCMS)

- **MS** can be combined with **gas chromatography (GC)** to analyze *mixtures*. A **gas chromatograph** is a fancy oven housing a thin capillary column containing a viscous high-boiling material.



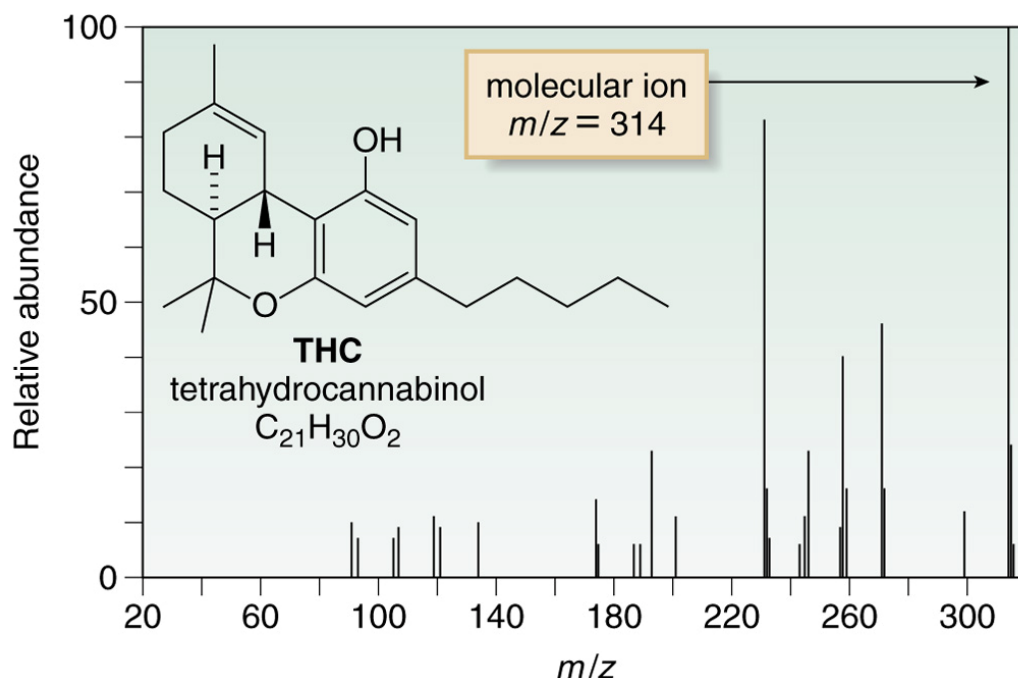
- Sample is injected, vaporized, and swept by an inert gas through the column. Lower boiling compounds travel faster, and exit the column (“**elute**”) before higher boiling ones.

- A gas chromatogram (or “**GC** trace”) of the mixture is recorded--a plot of peak intensity of each component vs. its **retention time** (the time required to travel through the column).
- Each component then enters the **MS** where it is ionized to form M^+ and fragment ions.
- GCMS data for a three-component mixture are shown below.



GCMS Analysis in Drug Screening

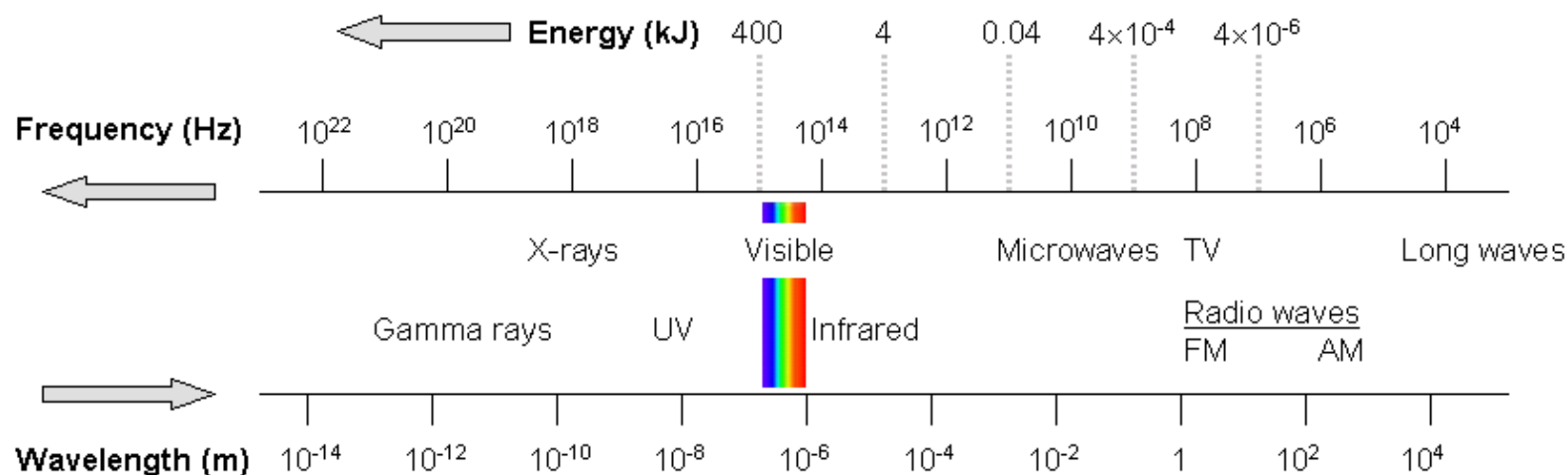
- To analyze a urine sample for THC, the main active component of marijuana, a urine extract is made and analyzed by GCMS.
- If THC is present, it appears as a GC peak with a retention time matching that of THC, **and** a mass spectrum with an M^+ at m/z 314 (the MW of THC) and a matching fragmentation pattern.



- The **size/area** of the **GC peak** would be related to the amount present.

C. The *Electromagnetic Spectrum*: More Tools for Structure Analysis

- The **electromagnetic spectrum** is divided into different regions, ranging from gamma rays to radio waves. Light visible to the human eye occupies only a small fraction.



Scale of these wavelengths:



Nucleus



Atom Molecule



Human cells



Pinhead



Bee



People



Buildings

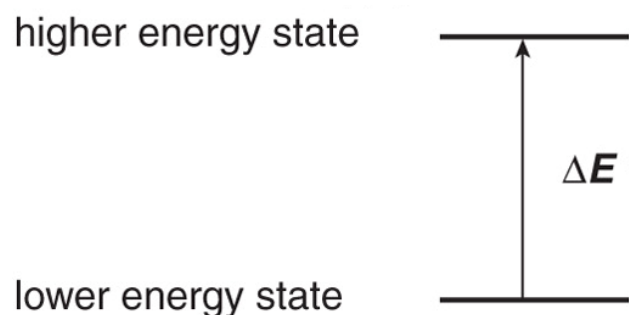
Electromagnetic radiation has properties of both waves and particles. It is characterized by **wavelength** (λ) and **frequency** (ν)

- **Wavelength** is the **distance** from one point on a wave to the analogous point on the next wave.
- **Frequency** is the # of waves passing per unit time. It is reported in cycles per second (s^{-1}), also known as **hertz (Hz)**.
- The energy (E) of a photon is **proportional to its frequency** (ν); $E = h\nu$, where h = Planck's constant
- E and λ are **inversely** proportional:

$$E = h\nu = hc/\lambda$$

Absorption of Electromagnetic Radiation

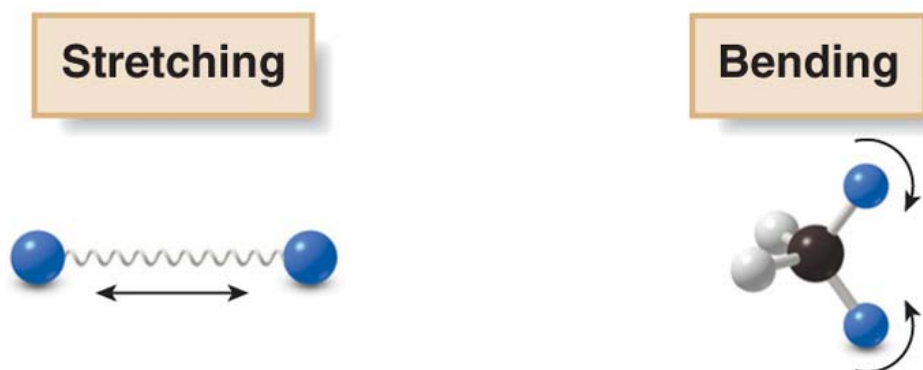
- When radiation hits a molecule, some wavelengths, but not all, will be absorbed. Which? Depends on the structure...
- For absorption to occur, the energy must match the ΔE between two energy states in the molecule



- The larger the ΔE between two states, the higher the energy of radiation needed for absorption to occur.
- **Ultraviolet (UV)-visible** light causes **electronic** excitation (Ch. 16)
- **Infrared (IR)** light causes **vibrational** excitation...

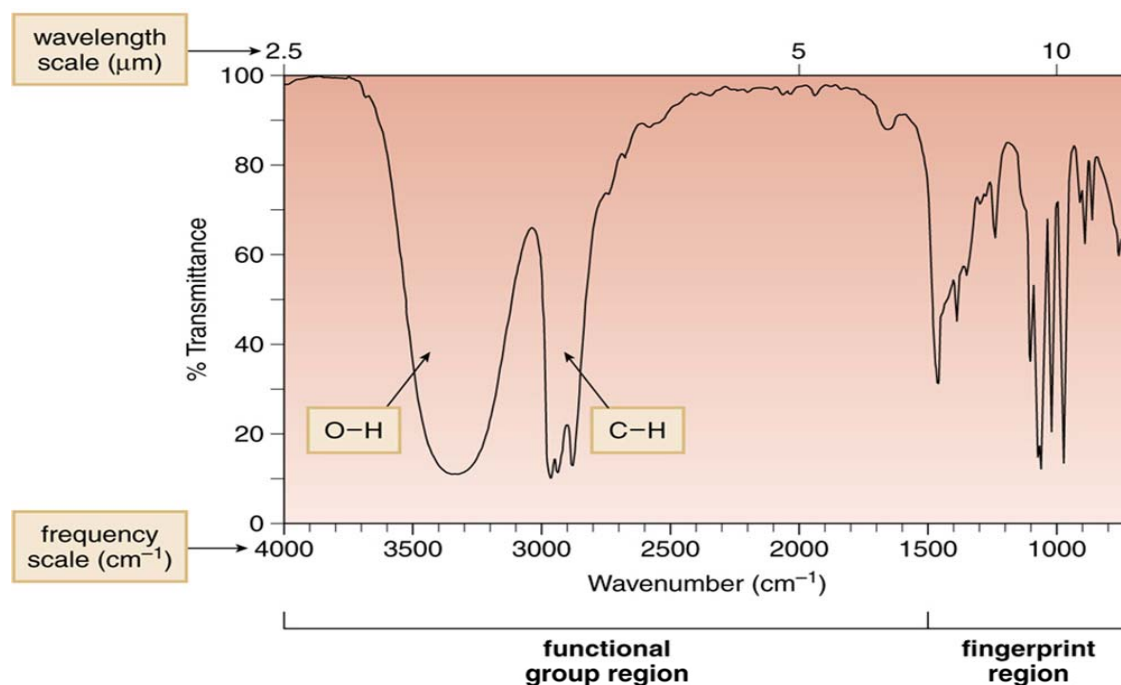
D. Infrared (IR) Spectroscopy

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



- Different kinds of bonds vibrate at different frequencies...
- These frequencies fall in the **IR range** (4000 to 400 cm^{-1}).

- In an **IR spectrophotometer**, IR light is passed through a sample.
- Some is **absorbed** (at relevant vibrational frequencies), and the remainder is transmitted to a detector.
- An **IR spectrum** is a plot of the **% transmitted light** vs. frequency, which, in IR spectra, is given in **wavenumbers (cm^{-1})**.



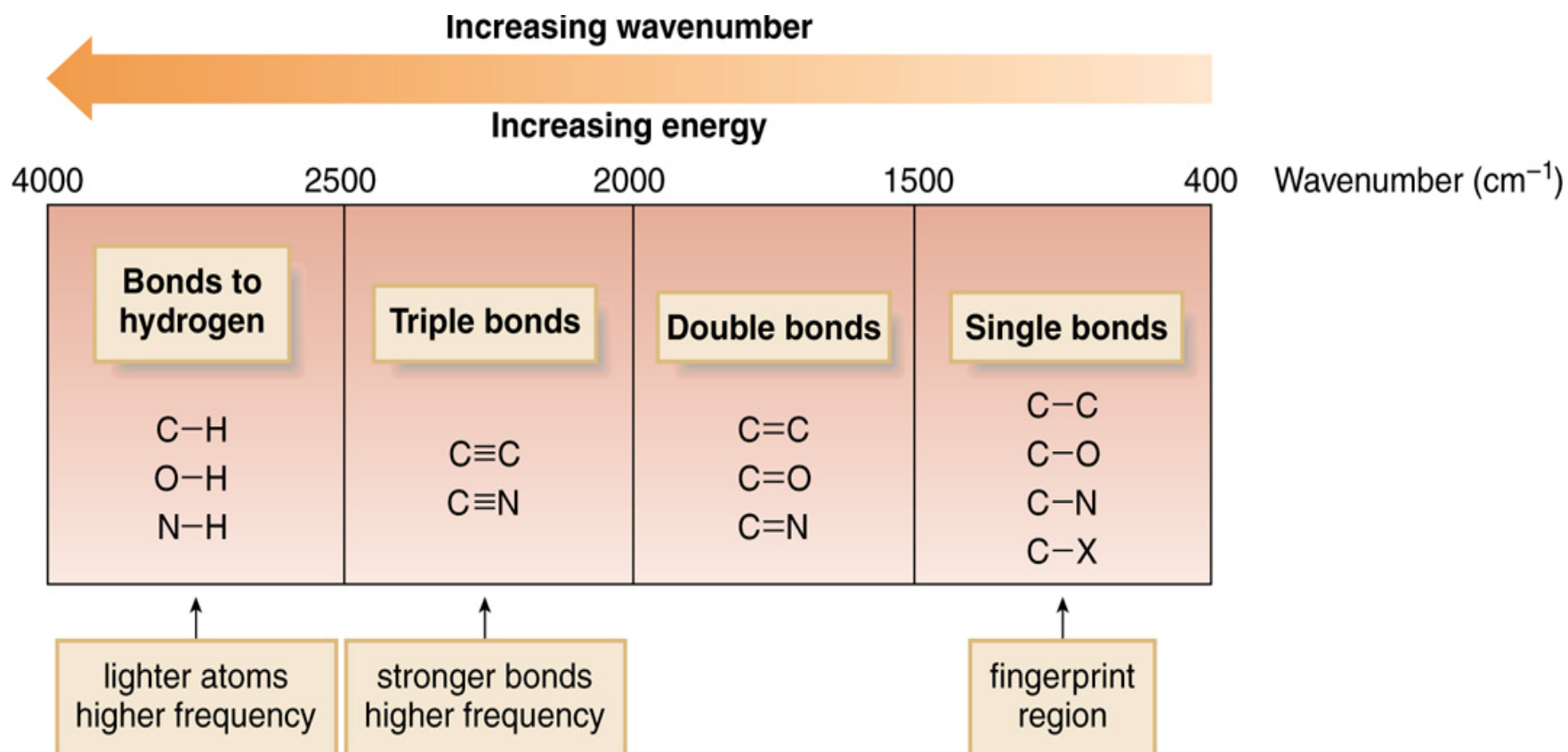
Use of **wavenumbers (cm^{-1})** is annoying, but is standard in IR.

Wavenumber is not the same as wavelength—its a **frequency** term (*inverse of wavelength*)


E. Bonds and IR Absorption

- Where a bond absorbs in the IR depends on the **bond strength** and the **mass of the atoms** involved.
- Different bond types absorb in different regions—the most diagnostic absorptions are associated with **bond stretching**.
- A potentially useful analogy involves thinking of bonds as springs with weights on each end:
 - **Stronger bonds** (i.e., triple > double > single) vibrate at a **higher frequency** (higher wavenumbers).
 - Bonds with **lighter atoms** also vibrate at **higher frequency** (higher wavenumbers).

- Most organics have many single bonds, so IR regions associated with these e.g., the “fingerprint region”) are often a *mess*.
- However, absorptions of **functional groups** (multiple bonds, O-H, N-H) **stand out** \Rightarrow more *useful*.

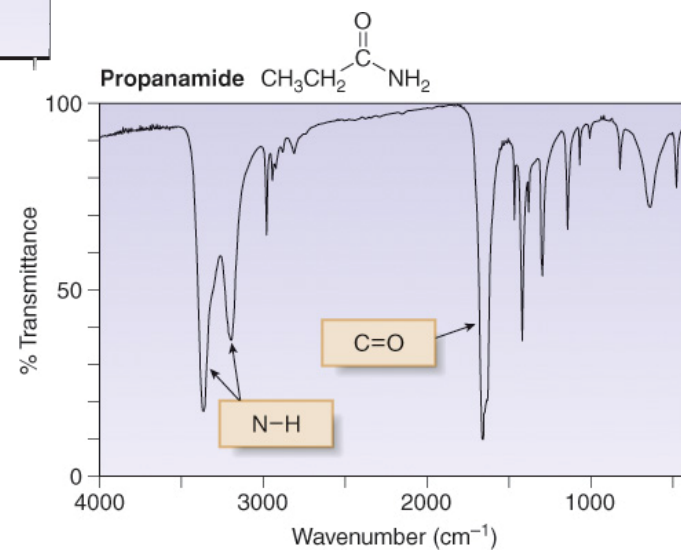
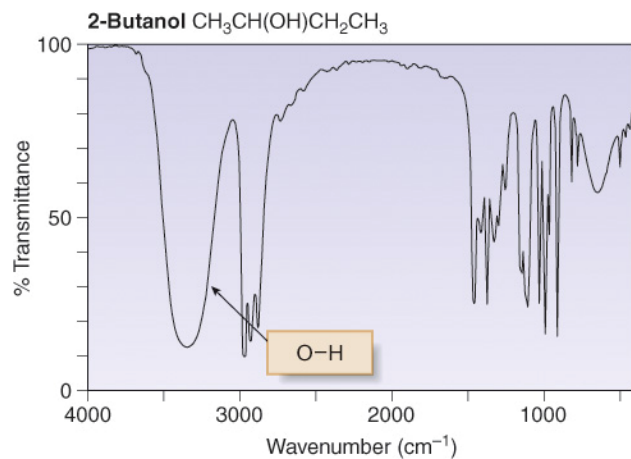
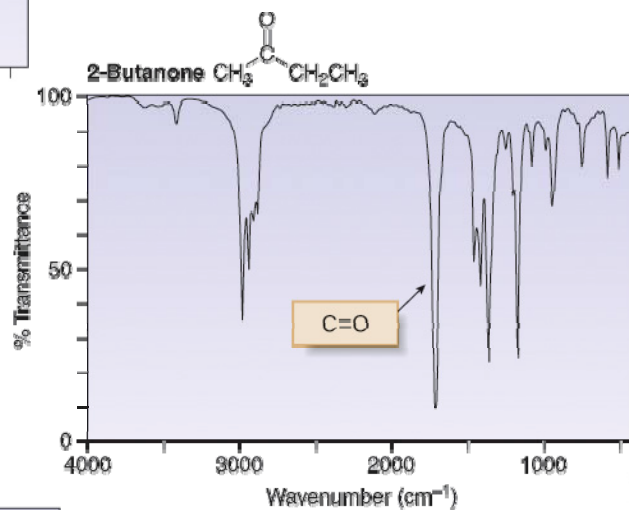
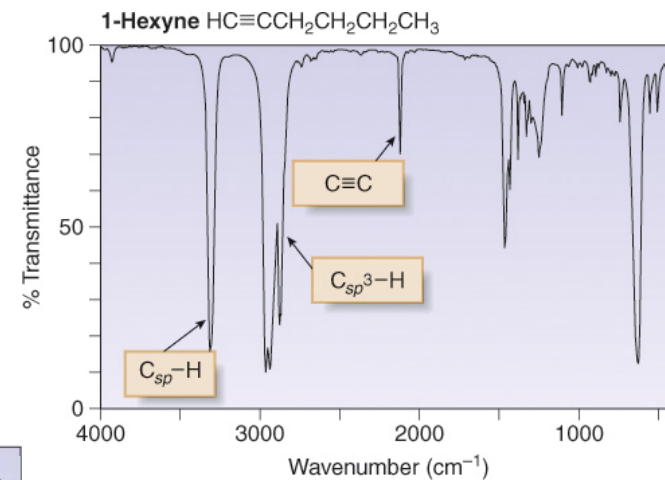
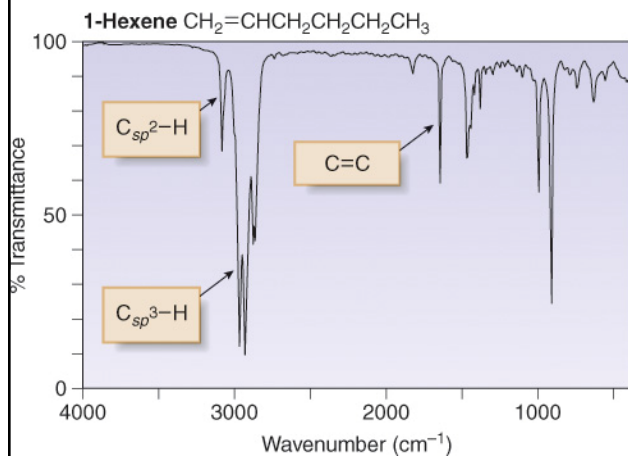


Some IR absorption ranges of note:

Bond type	Approximate $\tilde{\nu}$ (cm ⁻¹)	Intensity	
O-H	3600–3200	strong, broad	} particularly diagnostic
N-H	3500–3200	medium	
C-H	~3000		
• C _{sp} ³ -H	3000–2850	strong	
• C _{sp} ² -H	3150–3000	medium	
• C _{sp} -H	3300	medium	
C≡C	2250	medium	
C≡N	2250	medium	} particularly diagnostic
C=O	1800–1650 (often ~1700)	strong	
C=C	1650	medium	
	1600, 1500	medium	

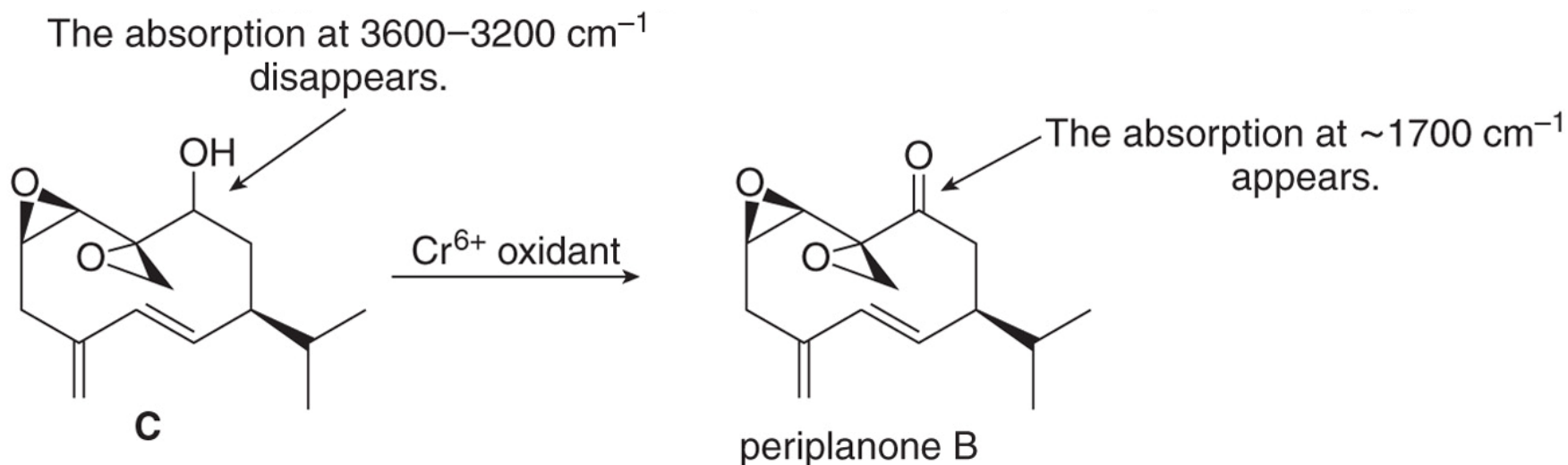
Consider how the difference in **C-H** absorption ranges correlates with what we know about % s-character & bond strength.

Some Examples of IR Spectra:



F. IR and Structure Determination

- IR does not provide a lot of *detailed* info, but can be helpful, e.g., as a quick means of confirming the outcome of a reaction.
- For example, the IR spectrum of the product below **would not** show an **OH** absorption, but **would** contain a **C=O** absorption.

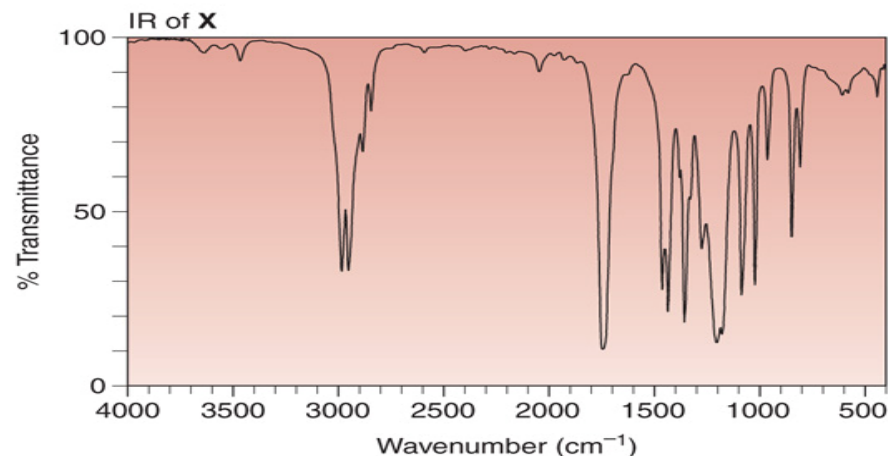
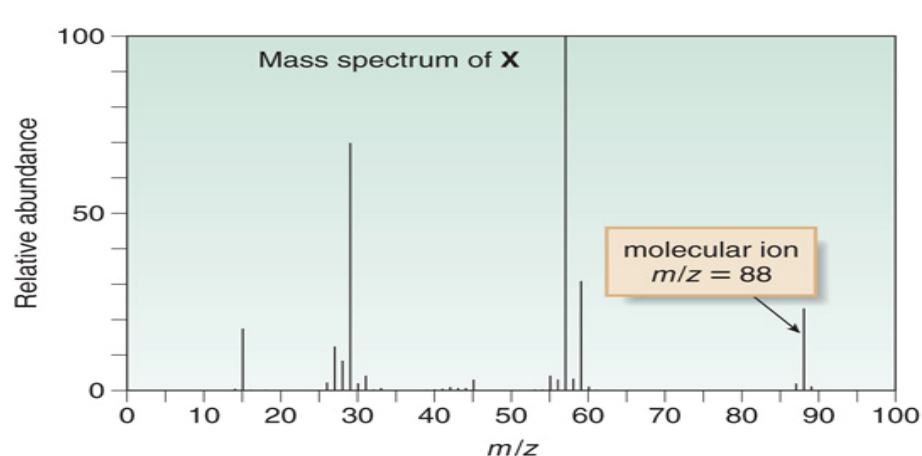


G. Structure Determination

- MS and IR can be used to *help* determine the identity of an organic compound *in the lab*.
- The process of *complete structure determination* generally requires more detailed information, especially *NMR data*, which we will cover in the next Chapter.
- However, we can *begin* to tackle such issues with MS and IR.
- Let's look at an example, but first—the next slide offers two general tips to always consider when beginning to attack a structure problem...

1. **IF** you know the formula of an unknown you are trying to identify, you can determine the # of **degrees of unsaturation**.
 - This tells you the **total # of π -bonds and/or rings you must have in the structure**.
 - **# unsats. = $\text{\#C} - \frac{1}{2} \text{\#(H+X)} + \frac{1}{2} \text{\#N} + 1$** (simpler formula than the book uses, imo)
 - ***Conversely***, if you know something about the # of **π -bonds and/or rings**, this can be helpful in **figuring out the formula**.
2. Note that a compound that contains **no N or an even # of N** atoms will always give an **even-mass molecular ion**.
 - Therefore, an **odd m/z** molecular ion indicates that a compound contains an **odd # of N** atoms...

The Use of MS and IR in Structure Determination: An Example



MW 88; what could the formula be? (Too bad we don't have HRMS)

- Clue from IR; **$\text{C}=\text{O}$ absorption at 1725 cm^{-1}** \Rightarrow at least one O atom and one unsaturation.
- Possible formulas with C, H, and O? C_6O not reasonable; $\text{C}_5\text{H}_{12}\text{O}$ can't work, because that formula has no unsaturations (!), but **$\text{C}_4\text{H}_8\text{O}_2$ or $\text{C}_3\text{H}_4\text{O}_3$** are possible.

The *book* does not expect you to go further, but you *can*...

- hmm...look at MS *fragments*. Both **M-29** and **m/z 29** are present; could indicate an **ethyl (CH₂CH₃)** unit?
- Moreover, there is also **M-31** (**m/z 57**); and 57 happens to add up to **CH₂CH₃** plus **C=O**!
- Can't have a 31-mass unit piece with only C and H; could be **OCH₃**? Maybe structure is **CH₃CH₂COOCH₃**?
- Fortunately, NMR data (coming up...) will make this an easier problem to solve...