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*.

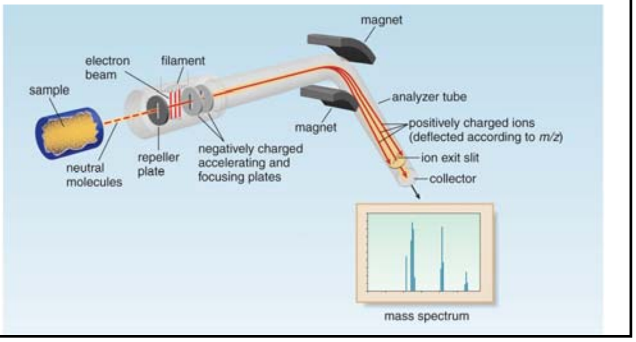
We have powerful tools that provide info about structure, but often only indirectly—one must know *how to interpret the data*.

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**

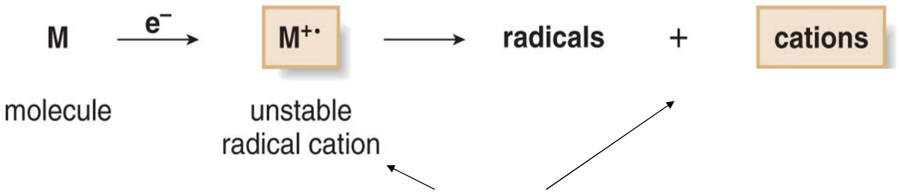
B. Mass spectrometry (MS)

- **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 = spectr<u>a</u>)

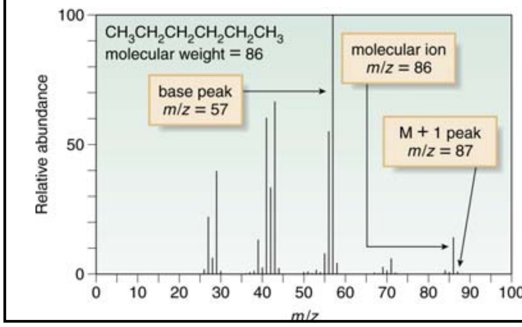
- **The radical cation initially formed is $M^{+\bullet}$ --called the molecular ion or parent ion. Its *m/z* represents the MW of M.**
- **$M^{+\bullet}$ is unstable, and decomposes to form fragments smaller than $M^{+\bullet}$. Some of these are also charged, resulting in an array of ions called a 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 $M^{+\cdot}$. 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 $M^{+\cdot}$ if they are <u>*more stable*</u> than $M^{+\cdot}$).**
- **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 (^{1}H, ^{12}C, ^{14}N, ^{16}O, etc.)

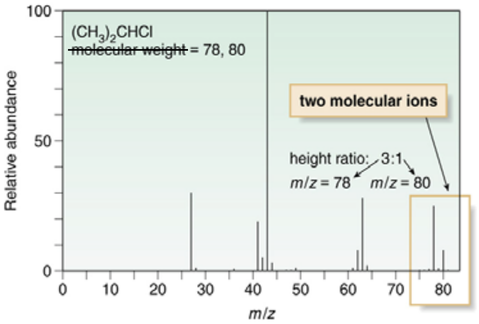
Cl has *two*; ^{35}Cl and ^{37}Cl, which occur naturally in a 3:1 ratio.

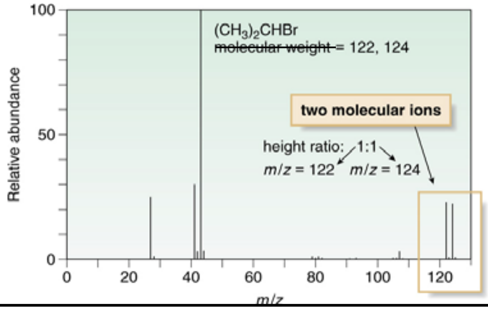
- The M peak contains ^{35}Cl. The M + 2 peak, corresponds to the molecules that contain ^{37}Cl.
- Thus, the presence of molecular ion M and M + 2 peaks in a 3:1 ratio is diagnostic for the presence of Cl (e.g., in RCl).

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

- So….when the M$^{+\cdot}$ 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





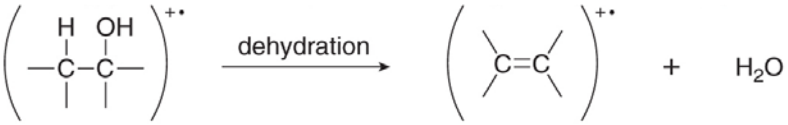
- Most *fragments* here do not have the M + 2 partner because the Cl or Br has been lost in getting to them.
- MS provides a good way to determine whether a compound has Cl or Br in it.
- Note: the “atomic wt” for an element in the periodic table is a weighted average of the natural isotopes

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**:

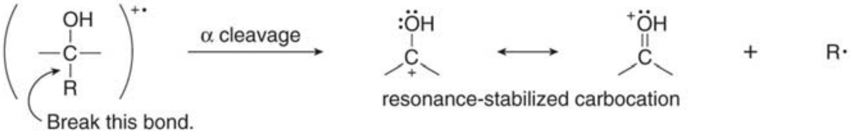


Utility? The presence of a sizable **M-H_2O** ion in a mass spectrum suggests that **the compound contains an alcohol group.**

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:

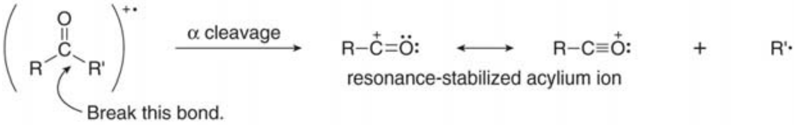


Break this bond.

resonance-stabilized carbocation

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

Carbonyl compounds can do this, too:



Break this bond.

resonance-stabilized acylium ion

R = H or alkyl

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:

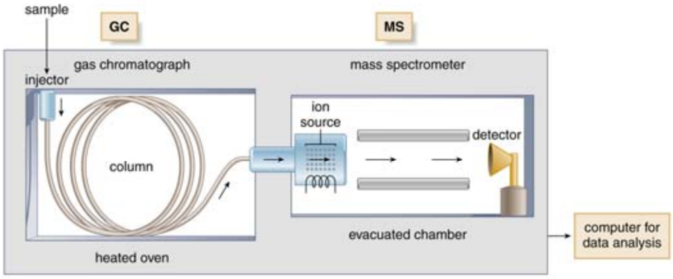
Isotope	Mass
^{12}C	12.0000
^{1}H	1.00783
^{16}O	15.9949
^{14}N	14.0031

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

Formula	Exact mass
C_3H_8O	60.0575
$C_2H_4O_2$	60.0211
$C_2H_8N_2$	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.**

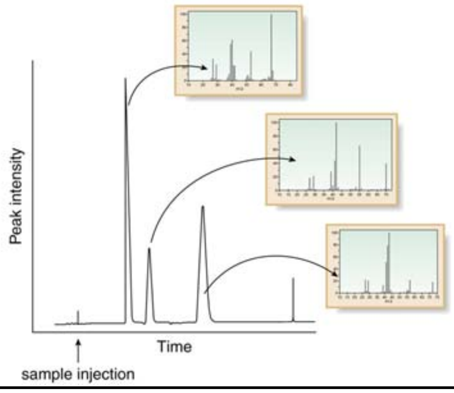


The gas chromatograph separates the mixture into its components.

The mass spectrometer records a spectrum of the individual components.

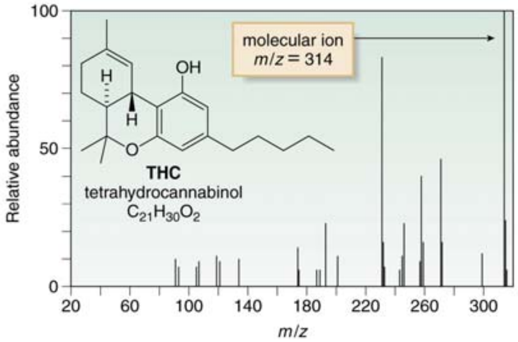
- **Sample is injected, vaporized, and swept by an inert gas through the column. Lower boiling compounds travel faster, and exit the column (“elute”) before higher boiling ones.**

- **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 $M^{+\cdot}$ and fragment ions.**
- **GCMS data for a three-component mixture are shown below.**



GCMS Analysis in Drug Screening

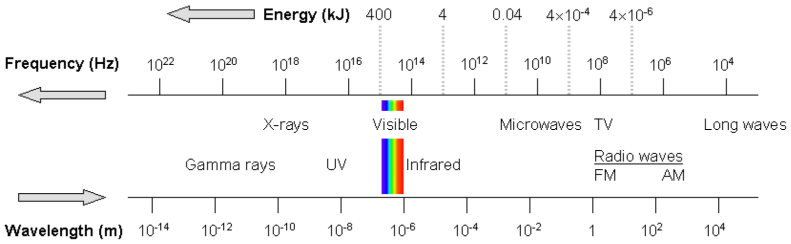
- **To analyze a urine sample for THC, the main active component of marijuana, a urine extract is made and analyzed by GCMS.**
- **If THC is present, it appears as a GC peak with a retention time matching that of THC, *and* a mass spectrum with an $M^{+\cdot}$ at *m/z* 314 (the MW of THC) and a matching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



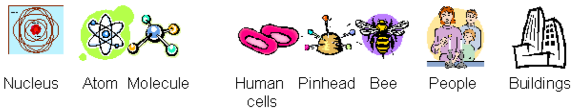
- **The size/area of the GC peak would be related to the amount present.**

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:



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).**

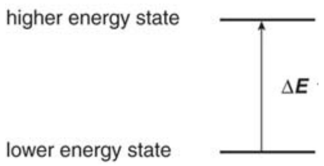
- **The energy (*E*) of a photon is proportional to its frequency (ν); $E = h\nu$, where *h* = Planck's constant**

- **E and λ are *inversely* proportional:**

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

Absorption of Electromagnetic Radiation

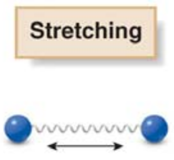
- **When radiation hits a molecule, some wavelengths, but not all, will be absorbed. Which? Depends on the structure…**
- **For absorption to occur, the energy must match the ΔE between two energy states in the molecule**

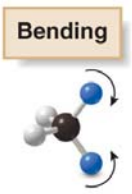


- **The larger the Δ*E* between two states, the higher the energy of radiation needed for absorption to occur.**
- **Ultraviolet (UV)-visible light causes electronic excitation (Ch. 16)**
- **Infrared (IR) light causes vibrational excitation...**

D. Infrared (IR) Spectroscopy

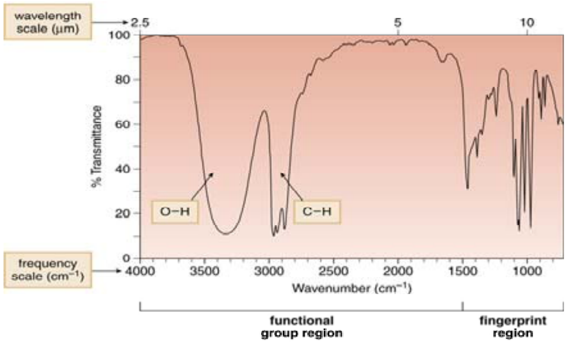
- **Absorption of IR light causes changes in the vibrational motions of a molecule.**
- **The various vibrational modes available to a molecule include bond-stretching and bending modes.**





- **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.

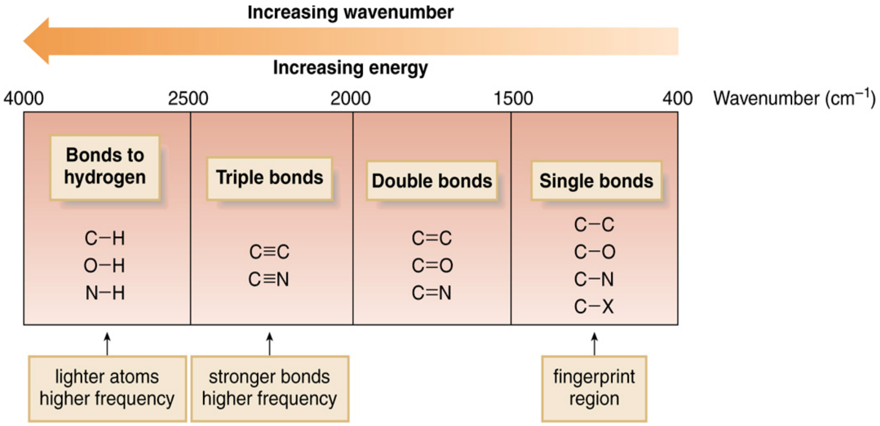
Wavenumber is not the same as wavelength—its a *frequency* term (*inverse* of wavelength)

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 ⇒ more *useful*.**



Increasing wavenumber

Increasing energy

4000 2500 2000 1500 400 Wavenumber (cm^{-1})

Bonds to hydrogen: C–H, O–H, N–H

Triple bonds: C≡C, C≡N

Double bonds: C=C, C=O, C=N

Single bonds: C–C, C–O, C–N, C–X

lighter atoms higher frequency

stronger bonds higher frequency

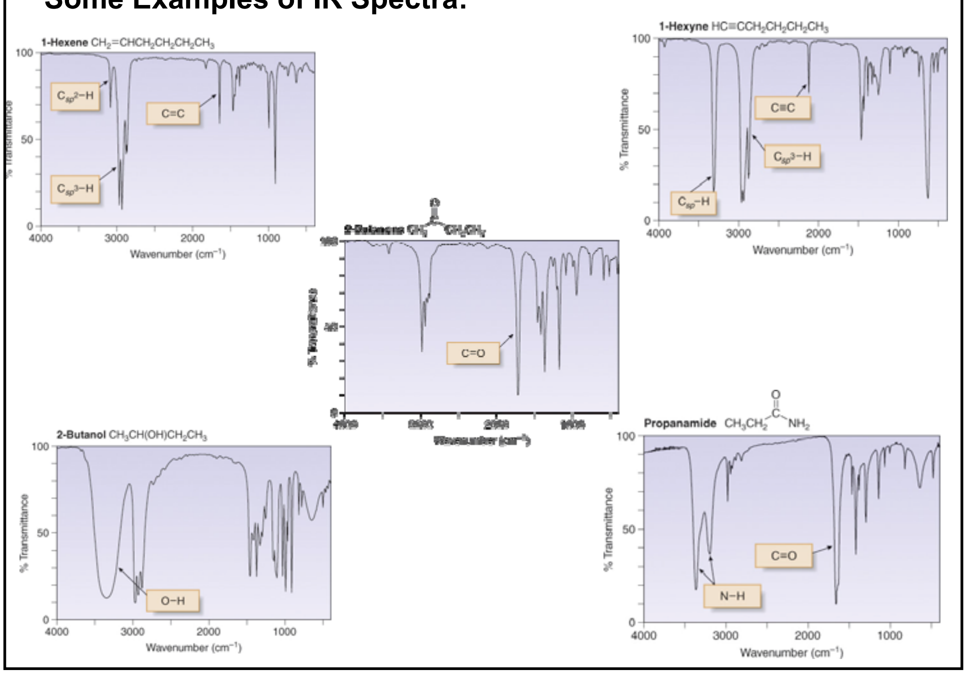
fingerprint region

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	**particularly diagnostic**
C≡N	2250	medium	
C=O	1800–1650 (often ~1700)	strong	
C=C	1650	medium	
	1600, 1500	medium	

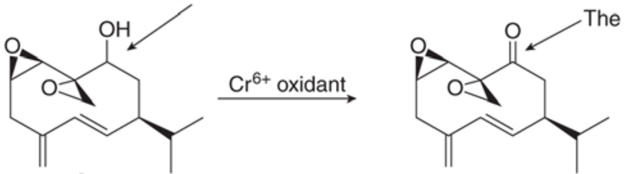
Consider how the difference in C-H absorption ranges correlates with what we know about % *s*-character & bond strength.

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.



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

The absorption at ~1700 cm^{-1} appears.

C

periplanone B

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…**

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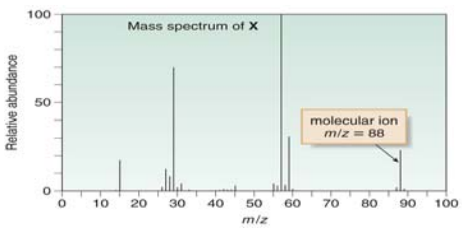
1. *IF* you know the formula of an unknown you are trying to identify, you can determine the # of degrees of unsaturation.

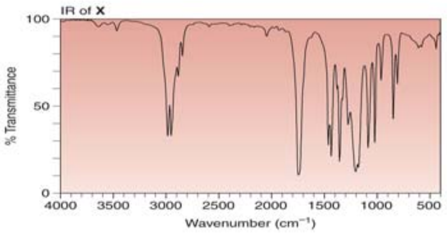
- **This tells you the total # of π-bonds and/or rings you must have in the structure.**
- **# unsats. = #C - ½ #(H+X) + ½ #N + 1 (simpler formula than the book uses, imo)**
- ***Conversely*, if you know something about the # of π-bonds and/or rings, this can be helpful in figuring out the formula.**

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; C=O absorption at 1725 cm^{-1} ⇒ at least one O atom and one unsaturation.**
- **Possible formulas with C, H, and O? C_6O not reasonable; $C_5H_{12}O$ can't work, because that formula has no unsaturations (!), but $C_4H_8O_2$ or $C_3H_4O_3$ 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 (CH_2CH_3) unit?**
- **Moreover, there is also M-31 (*m/z* 57); and 57 happens to add up to CH_2CH_3 plus C=O!**
- **Can't have a 31-mass unit piece with only C and H; could be OCH_3? Maybe structure is $CH_3CH_2COOCH_3$?**
- **Fortunately, NMR data (coming up…) will make this an easier problem to solve…**