

Chapter 12

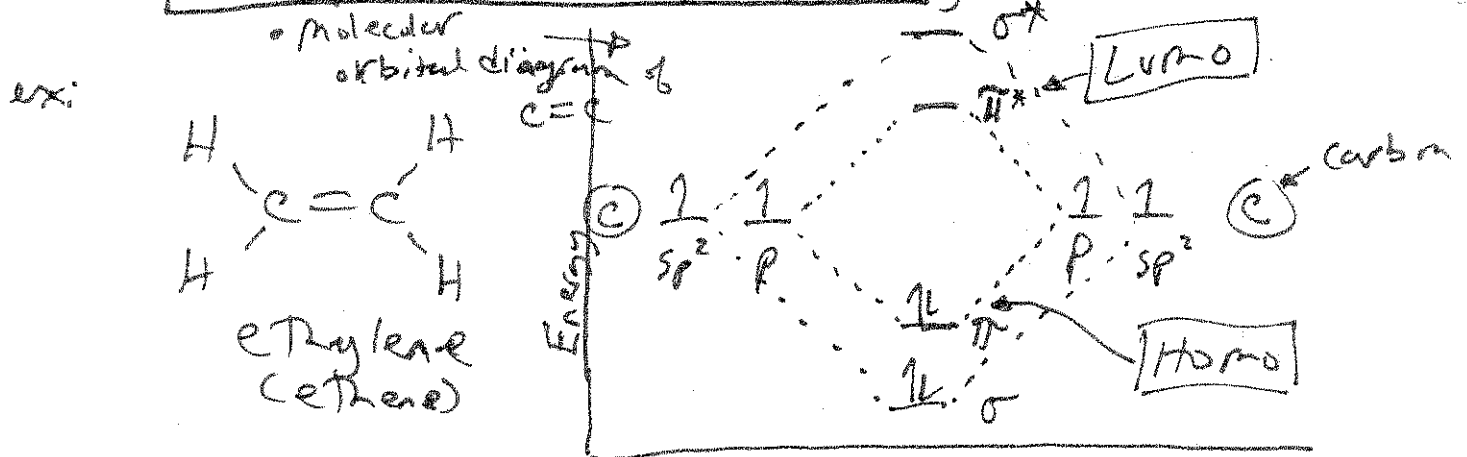
Ultra violet-Visible and Infrared Spectroscopy, Mass Spectrometry

• Ultraviolet-visible (uv-vis) spectroscopy

→ In uv-vis spectroscopy a molecule absorbs ^(400-700nm) UV or visible electromagnetic radiation (200-400nm) where the specific wavelength absorbed is determined by the energy differences (ΔE) between the occupied and unoccupied orbitals in a molecule.

→ When uv-vis absorption occurs, electrons in lower energy orbitals (occupied) are promoted to higher energy orbitals (unoccupied).

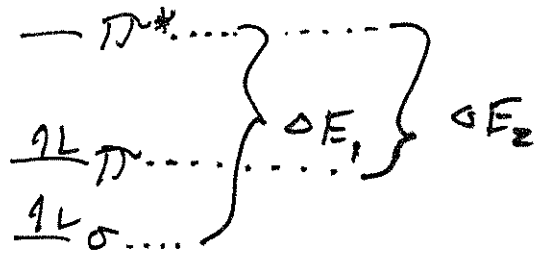
Remember molecular orbital Theory?



Homo - highest occupied m.o.
Lumo - lowest unoccupied m.o.

Compare a $\sigma \rightarrow \pi^*$ transition to a $\pi \rightarrow \pi^*$ transition

$\sigma \rightarrow \pi^*$ transition



- larger ΔE_1
- so larger ν , shorter λ

(Remember: $\Delta E = h\nu$
 $c = \lambda\nu$)

$\pi \rightarrow \pi^*$ transition

- smaller ΔE_2
- so smaller ν , longer λ

$\sigma \rightarrow \pi^*$ transition \rightarrow wavelength very short (much less than 200 nm); can't be detected by UV-vis spectroscopy

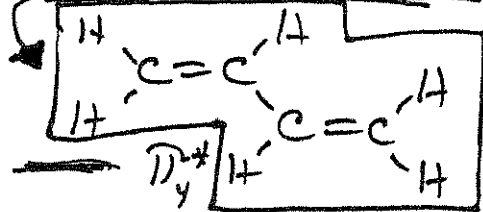
$\pi \rightarrow \pi^*$ transition

- absorbs at $\lambda = 165 \text{ nm}$ (but still too low to be detected by UV-vis)

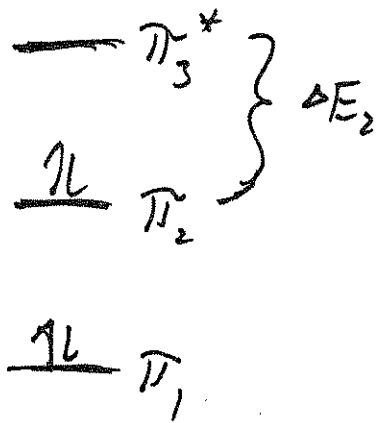
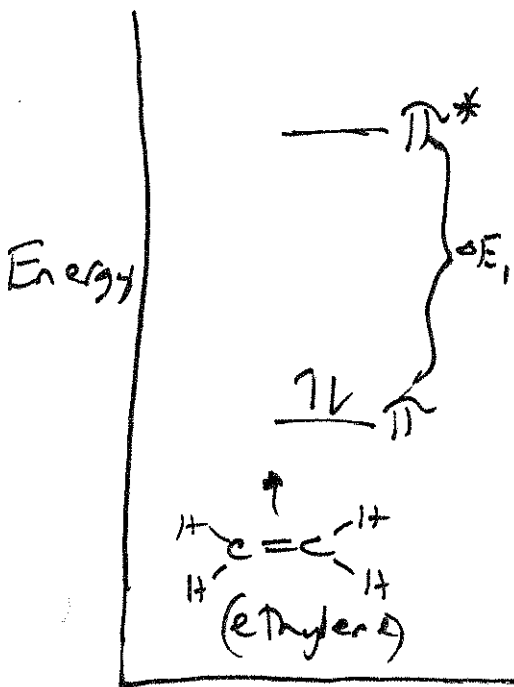
Conjugated Systems

- have 2 or more multiple bonds separated by a single bond. ex:

1,3-butadiene



\rightarrow has a smaller ΔE between the HOMO & the LUMO compared to ethylene



$\pi_2 \rightarrow \pi_3^*$ transition

ΔE_2 is lower, so ν lower, so λ is longer

\Downarrow
in the UV-vis region

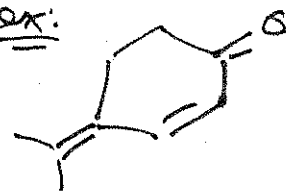
$\lambda = 217 \text{ nm}$

→ In more highly conjugated systems The HOMO + LUMO gap is even smaller, therefore λ is even longer. $C=C-C=C-C\equiv C-$ etc
250, 300nm, 350nm etc

→ eventually, in very highly conjugated systems, get absorptions in the visible region (400-700nm)

• UV-vis spectroscopy detects chromophores gives rise to colored empls

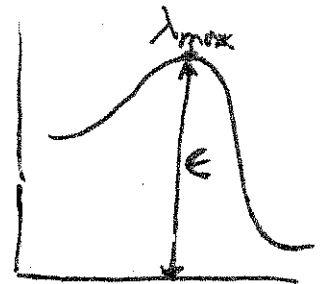
Chromophores - have double bonds, carbonyl groups, aromatic rings in conjugation ex:



(styrene)

The Absorption Spectrum

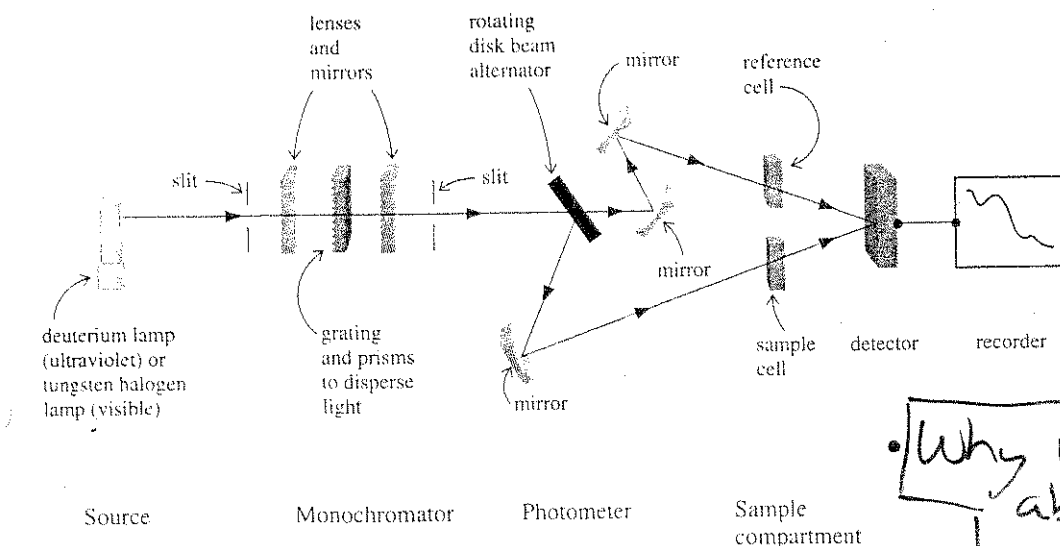
↳ get a broad absorption band with a λ_{max}



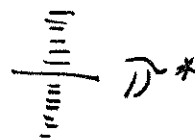
$\epsilon = \text{molar absorptivity}$
measure of the intensity of absorp

• Why is the absorption band so BROAD? (12-3)

Figure 11.2 Schematic diagram of a typical ultraviolet-visible spectrophotometer.

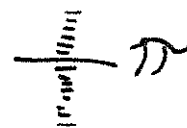


- The absorption band is so broad because of the vibrational energy levels.

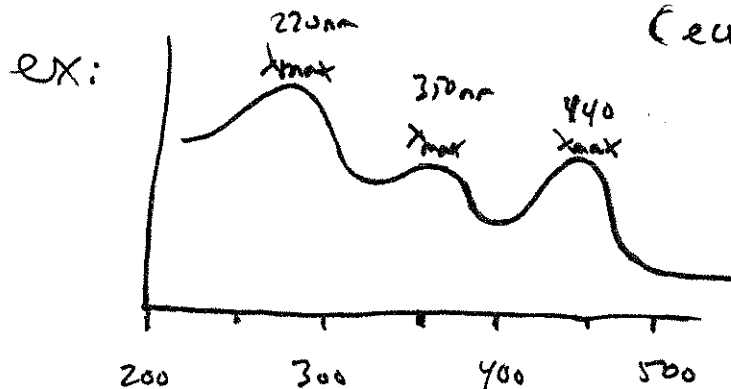


- Report a UV-vis spectrum like

This: $\lambda_{\text{max}}^{\text{solvent}} 240 (\epsilon = 12,000)$
 units = $\frac{\text{L}}{\text{mol} \cdot \text{cm}}$



- A compound can have more than 1 λ_{max} (each λ_{max} for a different transition)



- We can use the molar absorptivity of a compound in Beer's Law to determine concentrations

$$A = \epsilon b c$$

Labels for the equation: A is absorption, ϵ is molar absorptivity, b is path length, and c is concentration.

→ can also use UV-vis spectroscopy to measure the kinetics of a rxn - if a chromophore is consumed during the course of a rxn the λ_{max} will decrease

Structure and λ_{max} Relationship

- λ_{max} is dependent on the extent of conjugation and the degree of substitution on the conjugated system (alkyl groups)

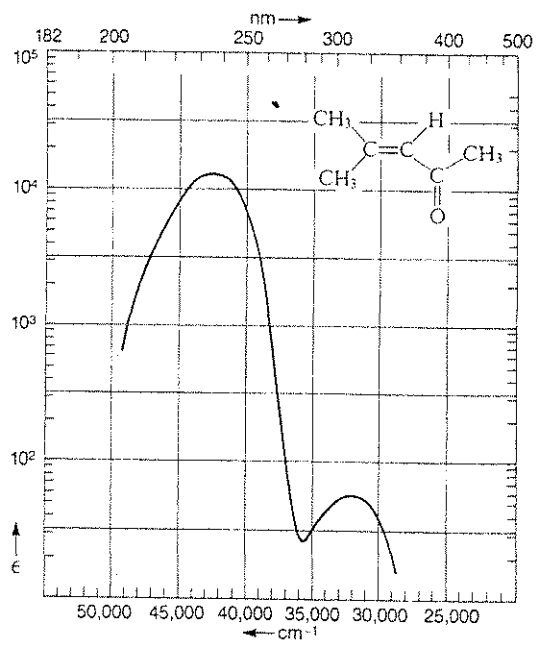
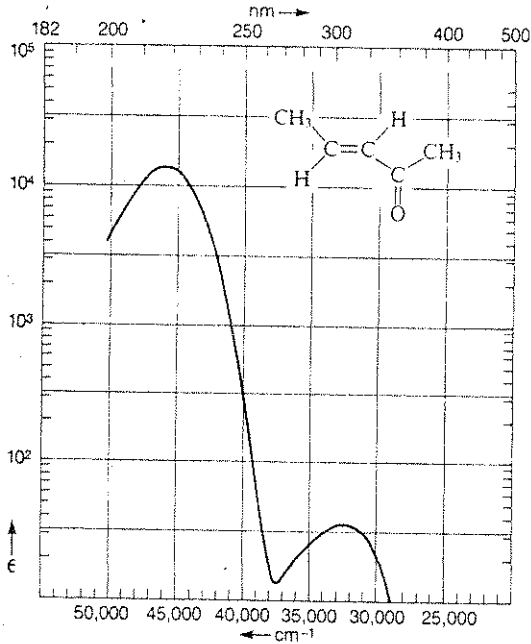


Figure 11.5 (p 403)

Ultraviolet spectra of 3-penten-2-one and 4-methyl-3-penten-2-one in ethanol.

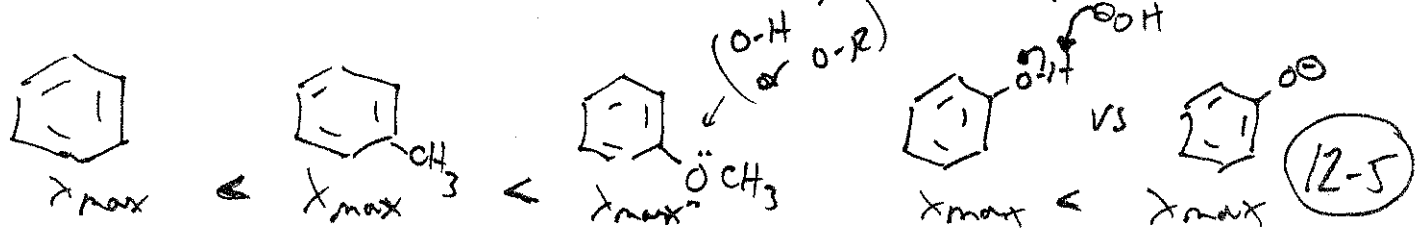
From the UV Atlas of Organic Compounds.

General TRENDS

- as conjugation increases, λ_{max} increases and ϵ is larger
- as degree of substitution on the conjugated system increases, λ_{max} increases

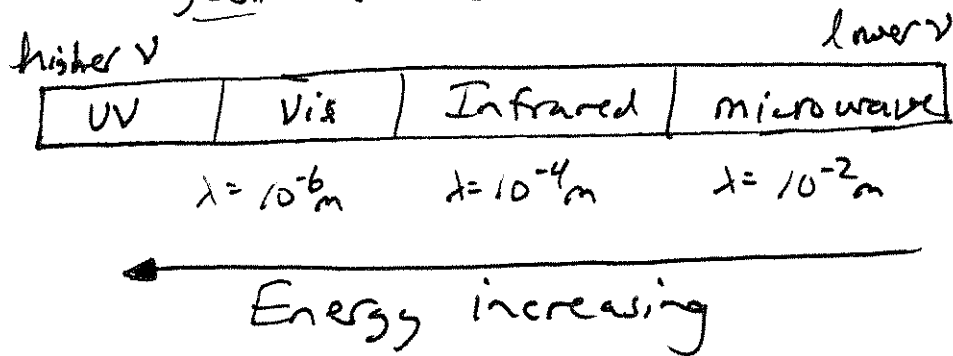
Benzene (benzene ring) also a chromophore

→ add substituents, shifts λ_{max}



Infrared Spectroscopy

Infrared: frequencies just below visible and just above microwave



- Infrared frequencies Do NOT have enough energy to cause electronic transitions (like in UV-Vis) but instead they cause groups of atoms to vibrate.
(w/ respect to the bonds that connect them)
- Like electronic transitions, vibrational transitions correspond to distinct energies. Molecules absorb IR radiation at certain frequencies (or wavelengths).
- Use units of wavenumbers ($\bar{\nu}$, cm^{-1}) for IR spectroscopy

$$\bar{\nu} (\text{cm}^{-1}) = \frac{1}{\lambda (\text{cm})}$$

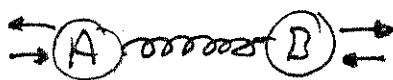
Molecular Vibrations

→ Vibrations occur at certain frequencies which depend on

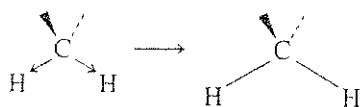
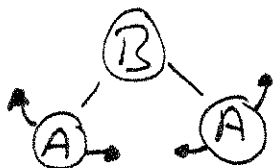
A) mass of (A) and (B)

B) strength of the bond

stretching



bending

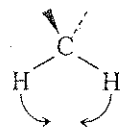


symmetric stretching

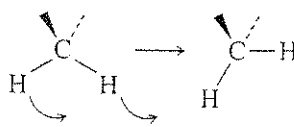


antisymmetric stretching

Figure 11.9
Typical stretching vibrations of a methylene group.

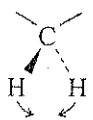


scissoring

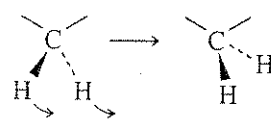


rocking

in-plane bending



twisting



wagging

out-of-plane bending

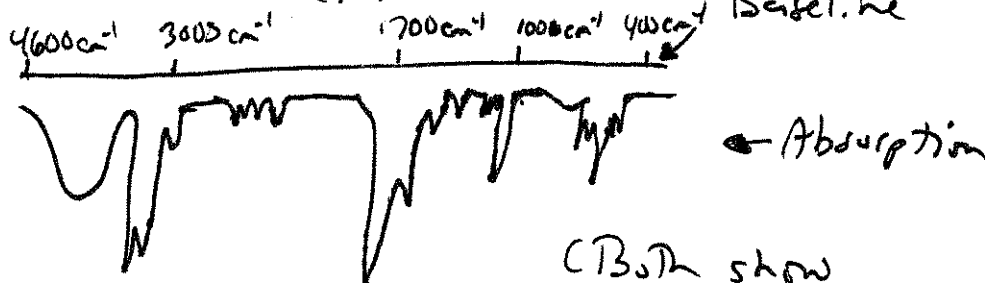
Figure 11.10
Different kinds of bending vibrations for a methylene group.

- Add IR radiation of the correct frequency for a particular bond → The molecule ABSORBS this energy and the molecular vibration INCREASES at this frequency.

NMR spectra



IR spectra



Why is IR useful?

Both show absorption, but plotted differently

⇒ Because different functional groups absorb at different frequencies and intensities. In many cases, one can tell what functional groups are present in a molecule based upon the IR spectrum.

Remember: The stretching frequency is related to

- The mass of the bonded atoms and
- The strength of the bond so:

weakest bond: C-C lower $\bar{\nu}$

C=C @ $\approx 1650 \text{ cm}^{-1}$

strongest bond: C≡C higher $\bar{\nu}$ @ $\approx 2200 \text{ cm}^{-1}$

• Heavier atoms vibrate more slowly than lighter ones so frequency decreases with increasing atomic weight

C-Br $\bar{\nu}$ lower

C-H $\bar{\nu}$ higher

- To show an absorption peak in IR spectroscopy, a particular bond must have a change in dipole moment

⇒ If a bond has a larger change in dipole moment when stretching occurs

The bond will absorb IR radiation more strongly

i.e. (more polar bonds will absorb more energy)



- smaller or no dipole moment change when stretched, smaller peak or no absorption

- larger dipole moment change when stretched, so stronger absorption peak

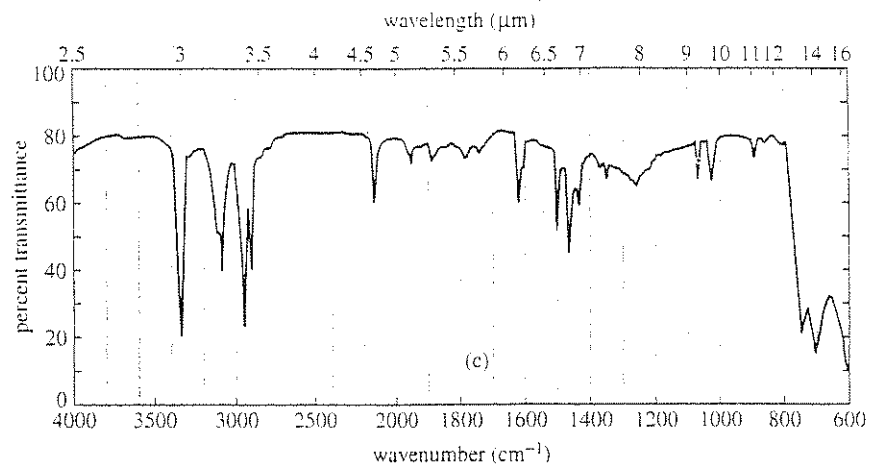
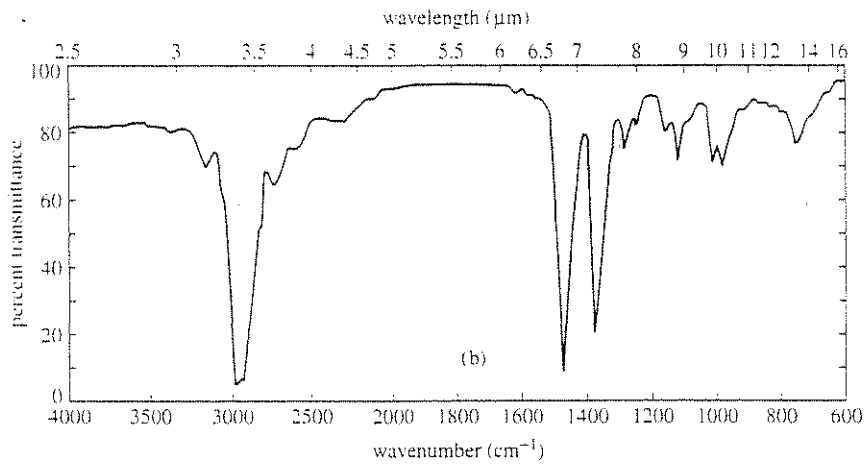
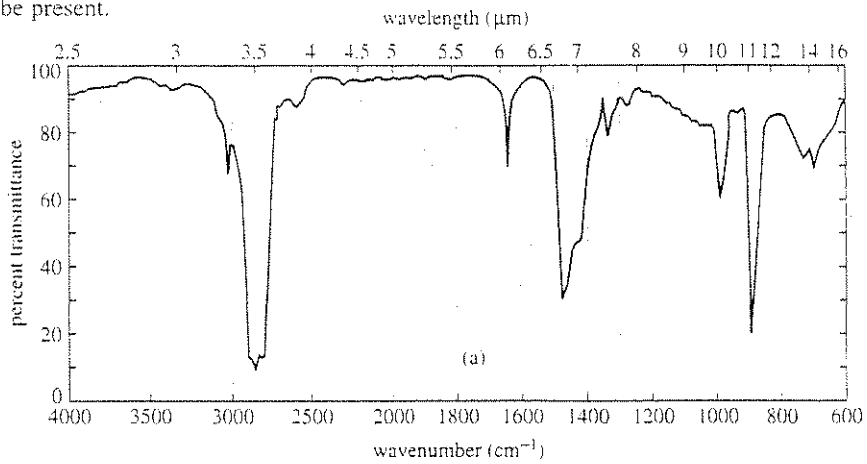
Summary: 3 Factors That Effect Bond Stretching Frequency and Intensity

- 1) Bond Strength
- 2) Mass of Bonded Atoms
- 3) Change in Dipole Moment

- if there is no change in dipole moment during stretching, the bond will not absorb IR radiation

Problem:

For each hydrocarbon spectrum, determine whether the compound is an alkane, an alkene, an alkyne, or an aromatic hydrocarbon. More than one unsaturated group may be present.



- IR spectra can be used to identify an unknown substance by comparison with a database of spectra
 - if exactly the same IR spectrum they are the same compound
 - (1400 cm^{-1} - 200 cm^{-1})
called the fingerprint region (12-11)

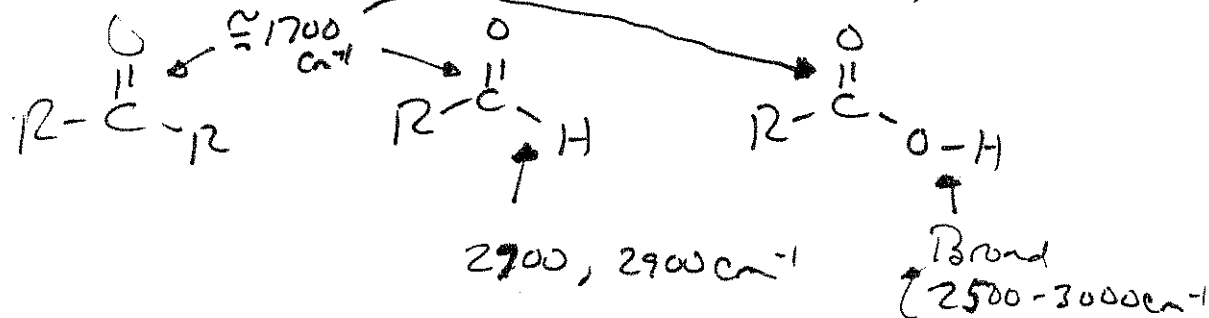
Carbonyl Groups

(intense, strong peaks because large changes of dipole moment when stretching occur)

- have very intense absorptions around

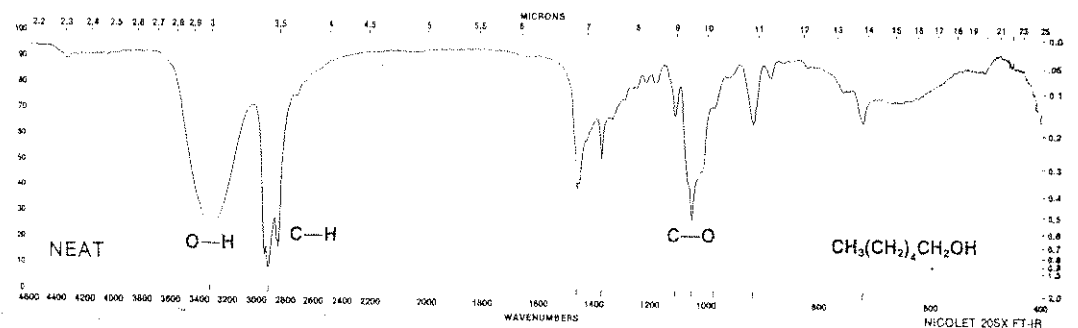
1700 cm^{-1}

• simple ketones, aldehydes & carboxylic acids

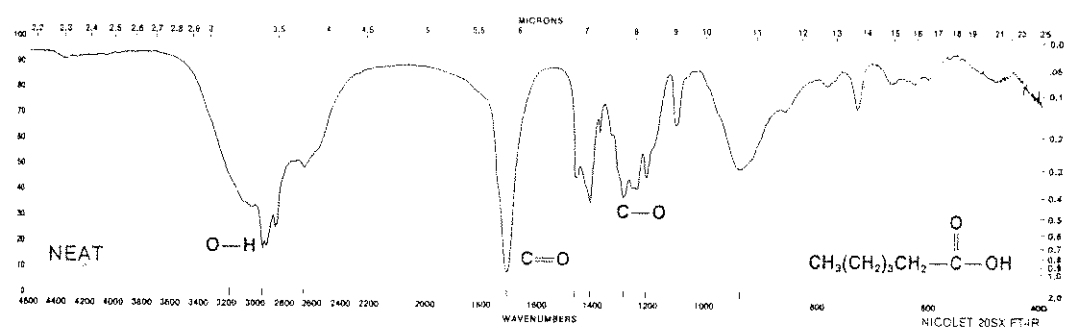


• Hydrogen bonded alcohols also have a very broad O-H stretch at $\approx 3200-3600 \text{ cm}^{-1}$ (because Hydrogen bonded)

(Note: higher frequency than O-H of carboxylic acid)



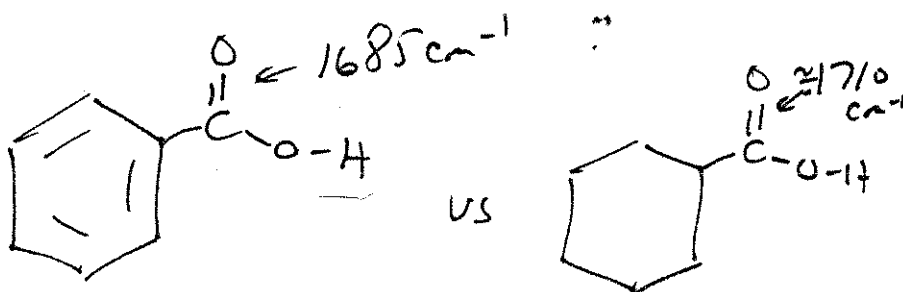
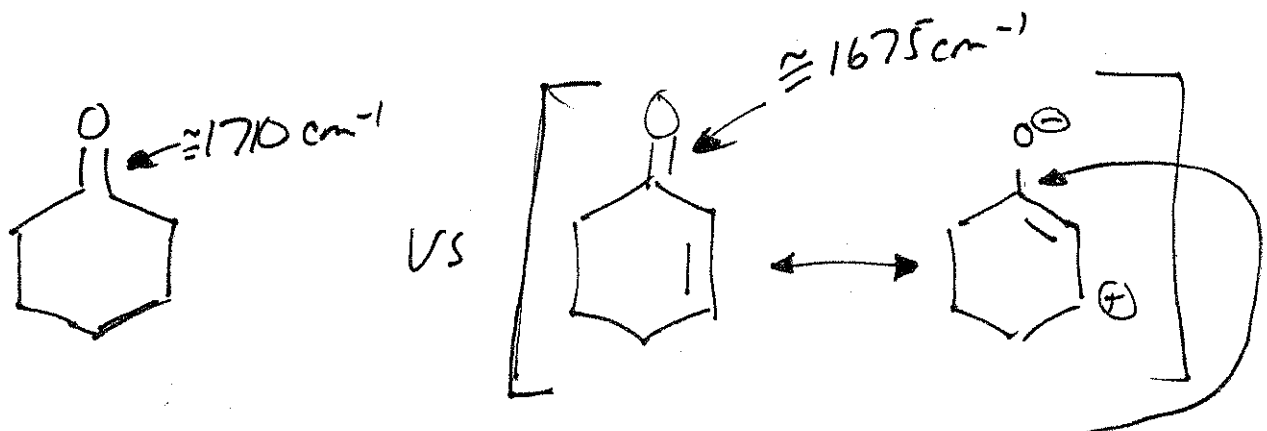
From The Aldrich Library of FT-IR Spectra.



From The Aldrich Library of FT-IR Spectra.

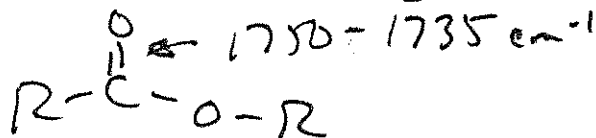
• When have conjugated carbonyl compounds

$\bar{\nu}$ is lowered because of resonance



single bond character, therefore lowers $\bar{\nu}$

⊕ Stretching frequency of esters a bit different than ketones, aldehydes + carboxylic acids → usually a bit higher $\bar{\nu}$



Note: also have C-O stretching w/



$1300 - 1000 \text{ cm}^{-1}$ STRONG

ps 456 in text

Table 11.1 Characteristic Infrared Absorption Frequencies

Bond Type	Stretching, cm^{-1}	Bending, cm^{-1}
C—H alkanes	2960–2850 (s)	1470–1350 (s)
C—H alkenes	3080–3020 (m)	1000–675 (s)
C—H aromatic	3100–3000 (v)	870–675 (v)
C—H aldehyde	2900, 2700 (m, 2 bands)	
C—H alkyne	3300 (s)	
C≡C alkyne	2260–2100 (v)	
C≡N nitrile	2260–2220 (v)	
C=C alkene	1680–1620 (v)	
C=C aromatic	1600–1450 (v)	
C=O ketone	1725–1705 (s)	
C=O aldehyde	1740–1720 (s)	
C=O α , β -unsaturated ketone	1685–1665 (s)	
C=O aryl ketone	1700–1680 (s)	
C=O ester	1750–1735 (s)	
C=O acid	1725–1700 (s)	
C=O amide	1690–1650 (s)	
O—H alcohols (not hydrogen bonded)	3650–3590 (v)	
O—H alcohols (hydrogen bonded)	3600–3200 (s, broad)	1620–1590 (v)
O—H acids	3000–2500 (s, broad)	1655–1510 (s)
N—H amines	3500–3300 (m)	
N—H amides	3500–3350 (m)	
C—O alcohols, ethers, esters	1300–1000 (s)	
C—N amines, alkyl	1220–1020 (w)	
C—N amines, aromatic	1360–1250 (s)	
NO ₂ nitro	1560–1515 (s)	
	1385–1345 (s)	

You will be given Table 11.1 + Fig 11.13 on quiz + exams

s = strong absorption w = weak absorption
 m = medium absorption v = variable absorption

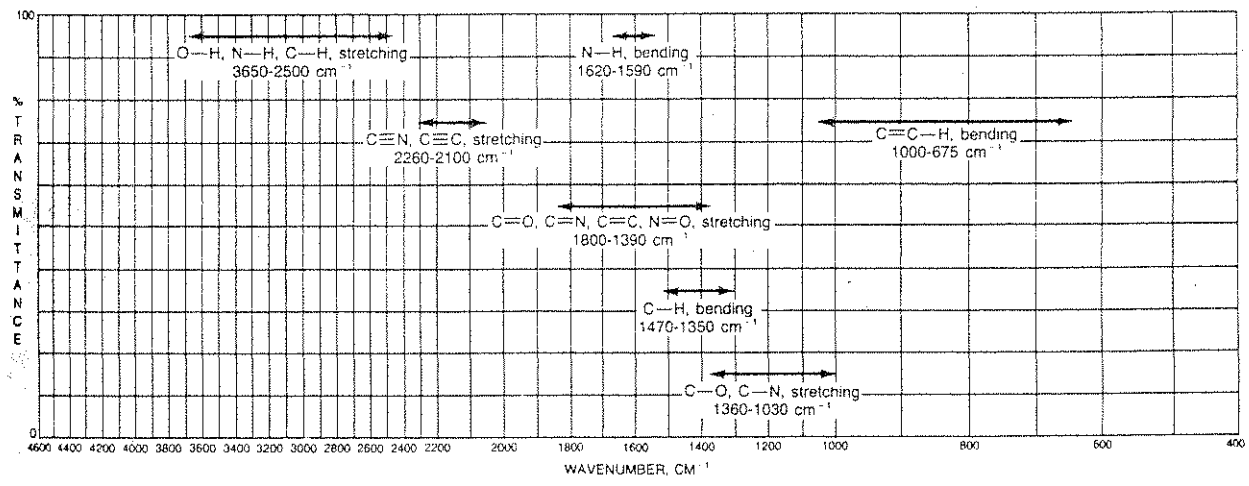
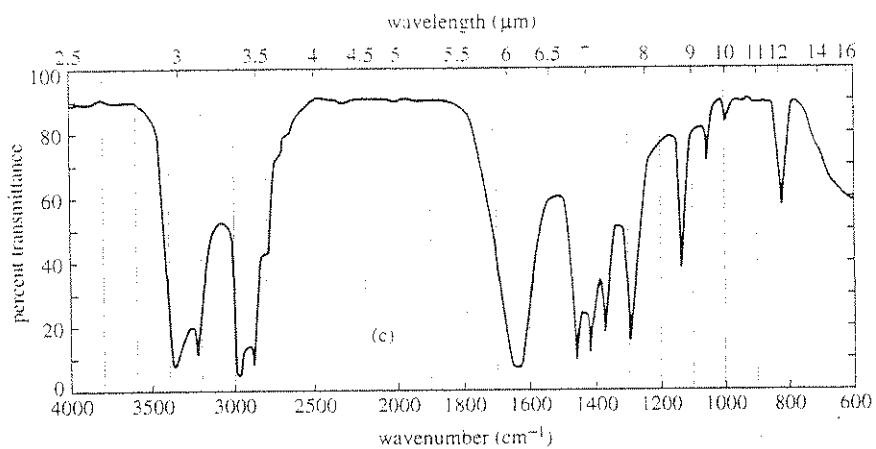
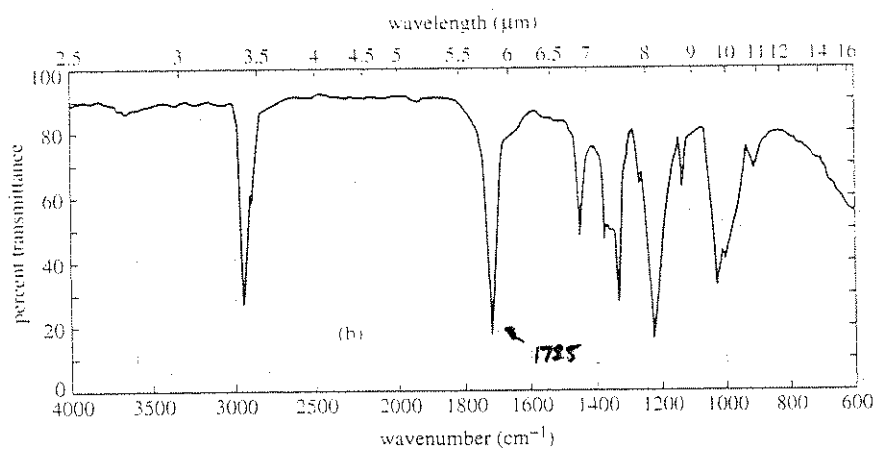
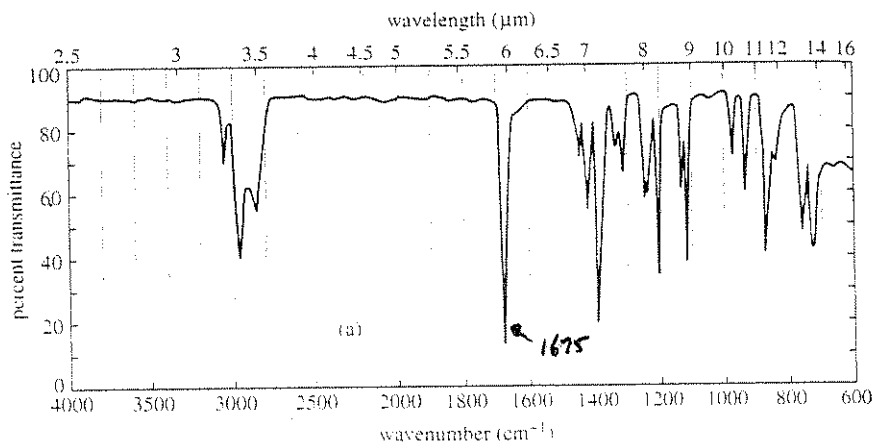


Figure 11.13 Infrared regions for different types of bonds.

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- We won't assign a unique structure with an IR spectrum (like we did w/ NMR) → we will use to identify functional groups present in a molecule. (12-10)

The infrared spectra for three compounds are provided. Each compound has one or more of the following functional groups: conjugated ketone, ester, amide, nitrile, and $C\equiv C$ triple bond. Determine the functional group(s) in each compound.



12-13.5

Mass Spectrometry

Mass spectrometry provides the molecular weight and other valuable info about the molecular formula using very small amounts of material.

- Mass spectrometry (MS) is very different ^{from} IR and UV-vis spectroscopy
 - ⇒ UV-vis + IR spectroscopy - involve absorption of electromagnetic radiation over a range of wavelengths
 - ⇒ Mass spectrometry - doesn't use electromagnetic radiation - uses high energy electrons to break the molecule apart

A mass spectrometer:

- ① ionizes molecules in a high vacuum using a high energy electron beam.
- ② sorts the ions according to their mass to charge ratio ($\frac{m}{z}$)
- ③ records the relative number of ions of each mass

A mass spectrum = graph plotted by
 The mass spectrometer
 x-axis = masses of ions
 y-axis = relative # of ions of each mass

example:

m/z	Abundance (% of base peak)
39	62
41	100 (base peak)
42	24
43	90
56	23
57	50
85	11
100 (M ⁺)	10

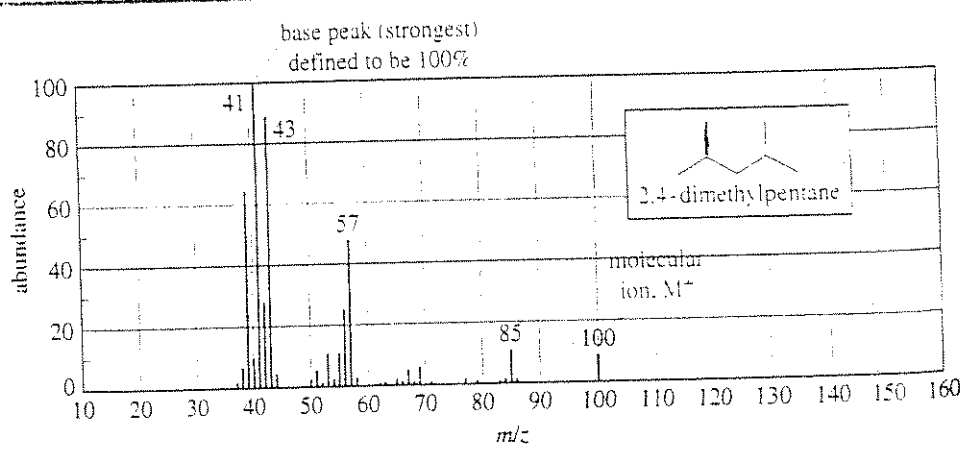
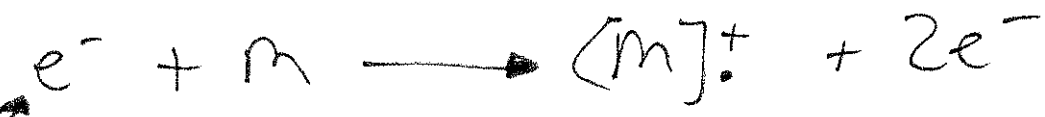


FIGURE 11-15 Mass spectrum of 2,4-dimethylpentane, given both as a bar graph and in tabular form. Notice that abundances are given as percentages of the strongest peak (the base peak). In this example, the base peak is at m/z 41 and the molecular ion ("parent peak") is at m/z 100.

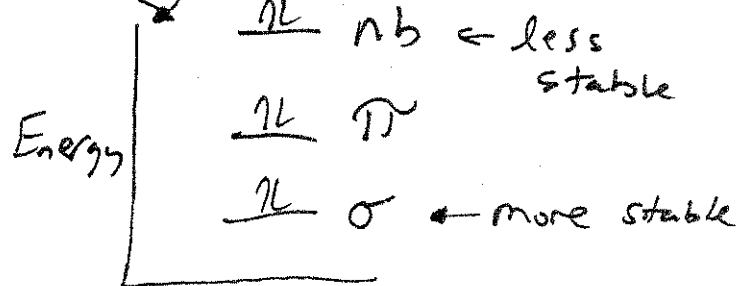
Electron Impact Ionization M = neutral molecule



formation of $[M]^+$ molecular ion (radical cation)

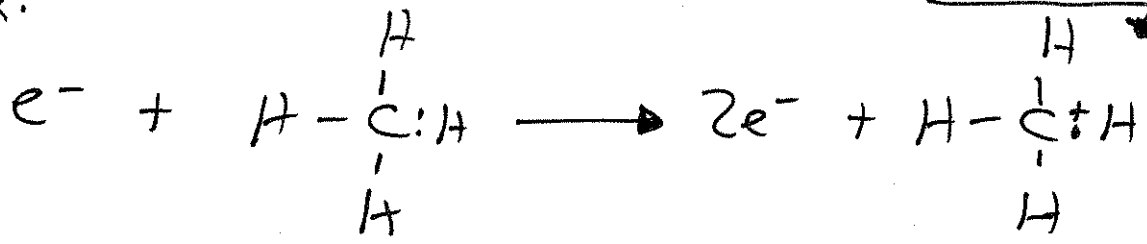
molecular orbital energies:

ease of e⁻ removal
 $\sigma < \pi < \text{nonbonding}$



e⁻ will remove electrons most easily from highest energy molecular orbital

ex:



radical cation

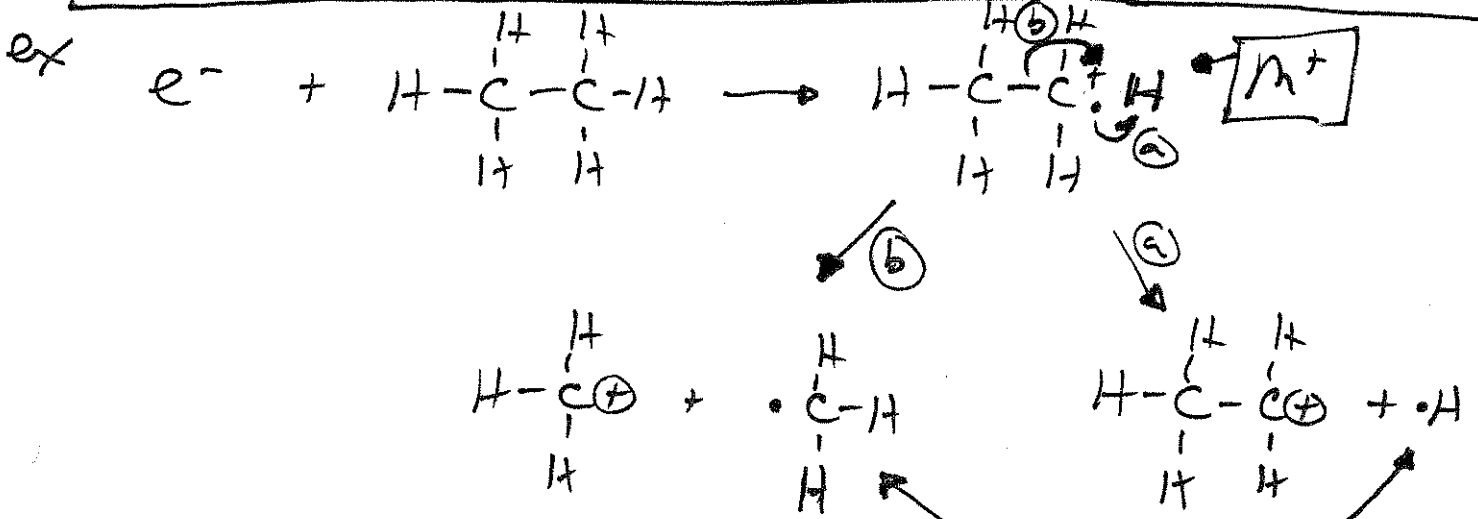
(electron removed from σ bond because there are no nonbonding or π orbitals in CH_4)

M^+ of CH_4
↑
molecular ion

- Can also break apart the molecular ion by fragmentation to form smaller molecular weight fragments
- ⇒ fragments can be other radical cations, carbocations and neutral molecules

BUT

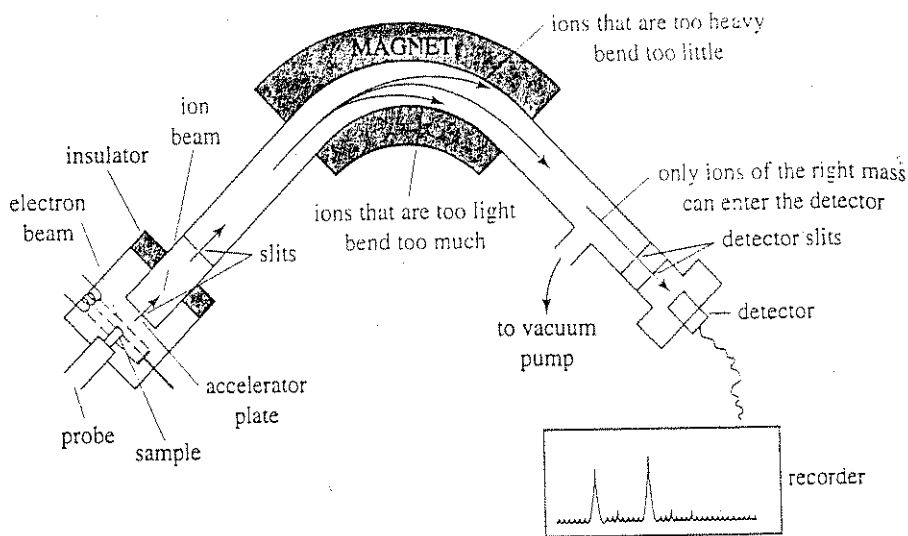
Only POSITIVELY CHARGED FRAGMENTS are detected by mass spectrometry



not detected by MS because no charge

12-16

FIGURE 11-14 Diagram of a mass spectrometer. A beam of electrons causes molecules to ionize and fragment. The mixture of ions is accelerated and passes through a magnetic field, where the paths of lighter ions are bent more than those of heavier ions. By varying the magnetic field, the spectrometer plots the abundance of ions of each mass.



How a Mass Spectrometer Works

- ① Molecules are ionized by a high energy electron beam (done in a vacuum chamber)
- ② Positively charged ions are attracted to a negatively charged plate which has a narrow slit to allow some of the ions to pass through.
- ③ The ion beam enters an evacuated flight chamber with a curved portion between the poles of a large magnet.
- ④ When the ions interact with the magnetic field, heavier ions bend less, lighter ions bend more. The exact curvature depends upon the $\frac{m}{z}$ ratio. (12-17)

⑤ At The end of The flight tube There is another slit with an ion detector. At any given magnetic field, only ions of one particular mass to charge ratio are bent exactly right to pass Thru The slit and enter The detector.

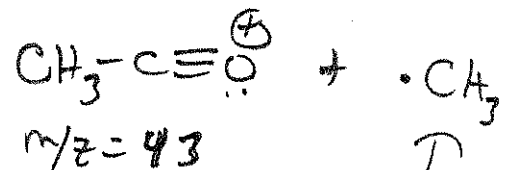
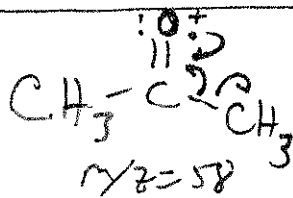
⑥ The magnetic field is varied, which produce a scan of all The possible ion masses and produces a graph of The # of ions of each mass. (Abundances)

In a mass Spectrum peaks are assigned ABUNDANCES as a percentage of The strongest peak — called The BASE PEAK

⇒ The Base Peak does NOT always correspond to The mass of The molecular ion.

Homolytic Cleavage

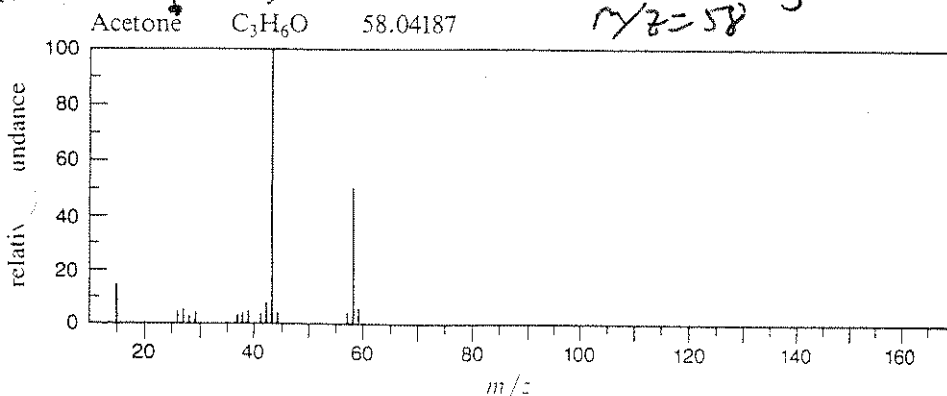
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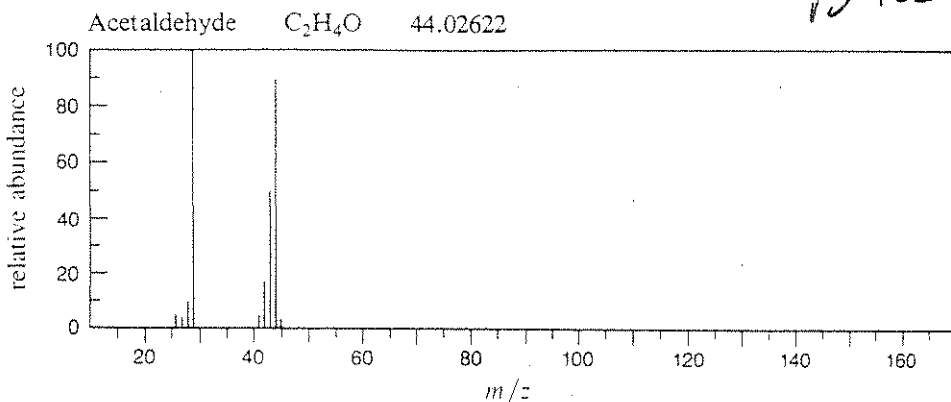


base peak

can't see in mass spectrum because

Not Charged (12-18)



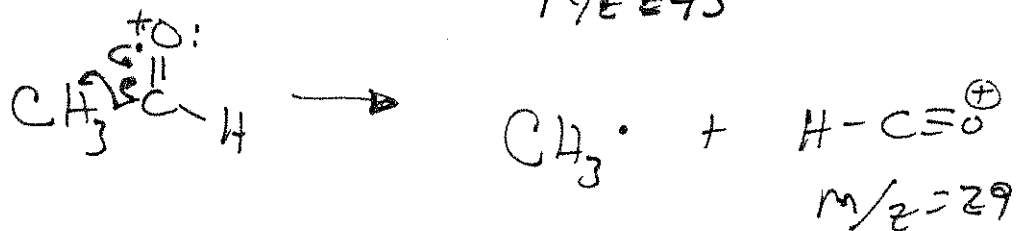
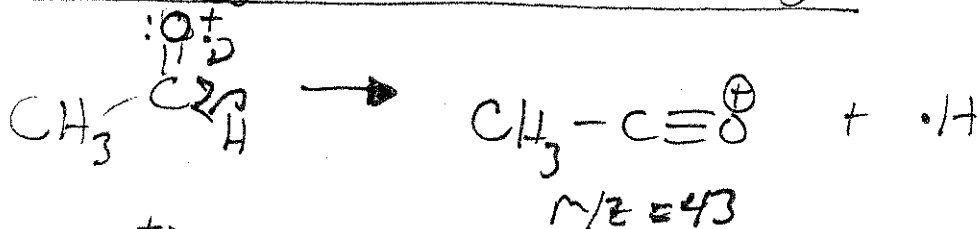


important peaks: $m/z = 43$ $m^+ = 44 \rightarrow$ CC(=O)H
 $m/z = 29$

$44 - 43 = 1$ loss of hydrogen

$44 - 29 = 15$ loss of CH₃

How? Homolytic cleavage of M⁺ of acetaldehyde



- The mass spectrum of ANY compound is unique in the pattern of peaks and relative intensities of these peaks. \rightarrow serves as a chemical fingerprint

\Rightarrow In the mass spectra of acetone + acetaldehyde acetone has a ^{small} m/z peak of (59) (MW = 58) and acetaldehyde has a ^{small} m/z peak of (45) (MW = 44)

Why??

* Because of isotopes of atoms present in these molecules

Table 11.2 Natural Isotopic Abundance of Some Elements

Element	Mass	Most Common Isotopes		
		%	Mass	%
H	1	100	2	0.016
C	12	100	13	1.08
N	14	100	15	0.36
O	16	100	18	0.20
F	19	100	—	—
Cl	35	100	37	32.5
Br	79	100	81	98.0
I	127	100	—	—

→ for carbon have ^{13}C isotope 1.08% abundant

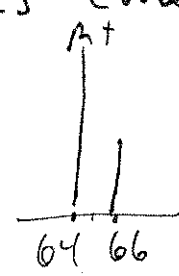
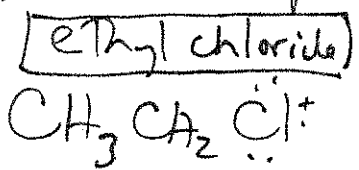
• A compound with 8 carbon atoms

has a $m+1$ peak = $8 \times 1.08 = 8.64\%$ of m^+

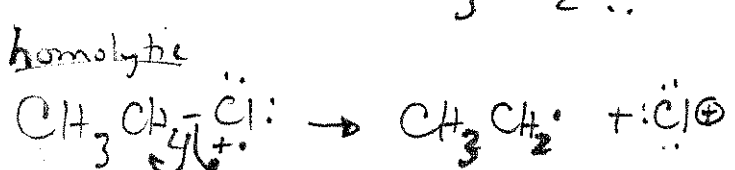
• If you have 6 oxygen atoms in a compound would increase the $m+2$ peak

$^{16}\text{O} + ^{18}\text{O}$
 $m+2 \text{ peak} = 6 \times 0.2 = 1.2\%$ of m^+

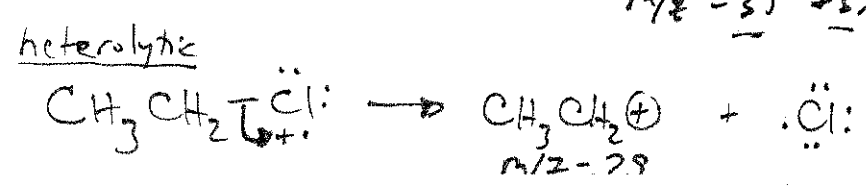
Distinctive $m+2$ peaks come from halogens in (Cl & Br) a molecule



^{35}Cl 100%
 ^{37}Cl 32.5%



$m/z = 35 + 37$ depending on isotope



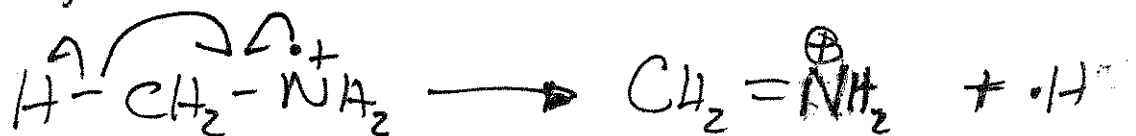
Mass Spectrometry - Shows ions of different isotopic composition as individual peaks.

- Masses can be determined to 5 decimal places with High Resolution Mass Spectrometry and can distinguish between compounds with same average molecular weights.
- Can't always see a M^+ (molecular ion) for every compound - some are too unstable

IMPORTANT FRAGMENTATION PATHWAYS

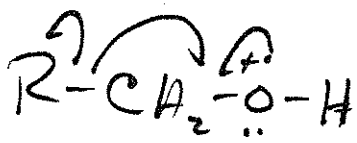
- fragment by homolytic or heterolytic cleavage of bonds adjacent to the radical cation
- abundant fragments form because of stability of radical product or ion

ex: methylamine

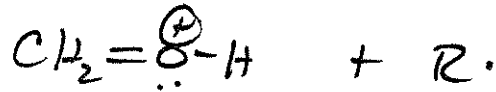


$$m/z = 30$$

base peak \rightarrow stable cation (12-21)



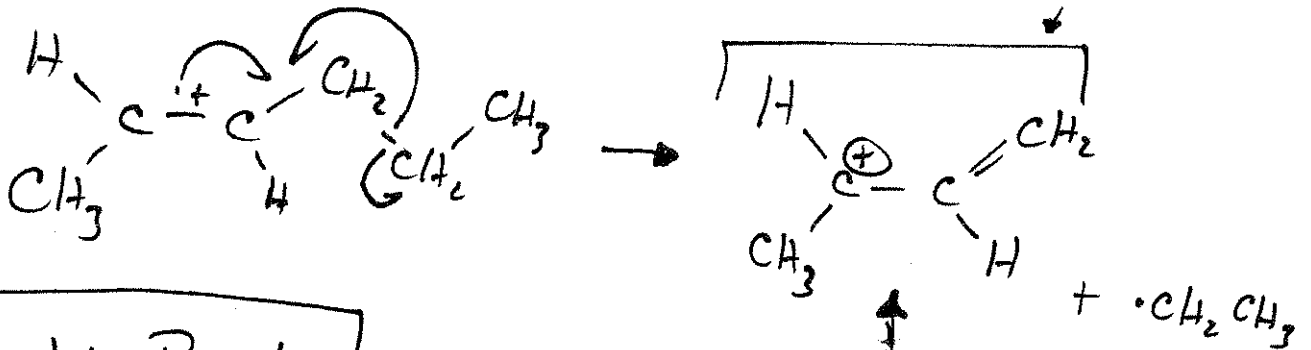
alcohols



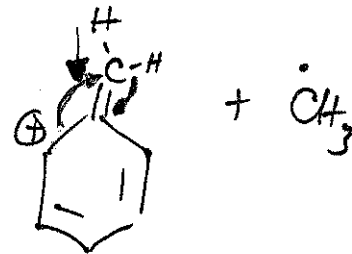
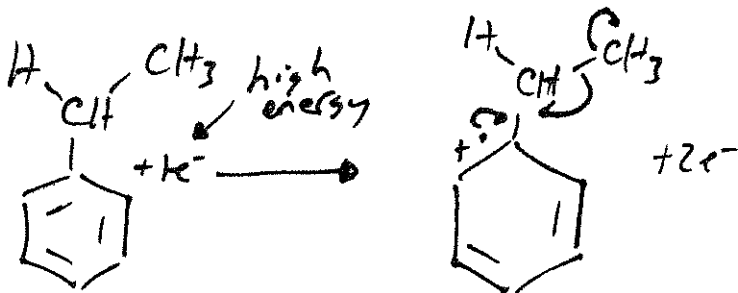
$m/z = 31$

oxonium ion → stable cation

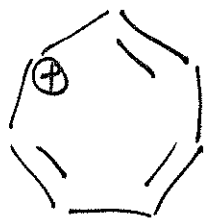
Alkenes - have α -cleavage to form allylic cations



Benzylic Bonds



Stabilized by resonance

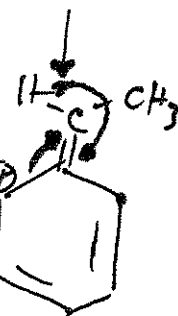
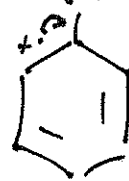


aromatic



aromatic

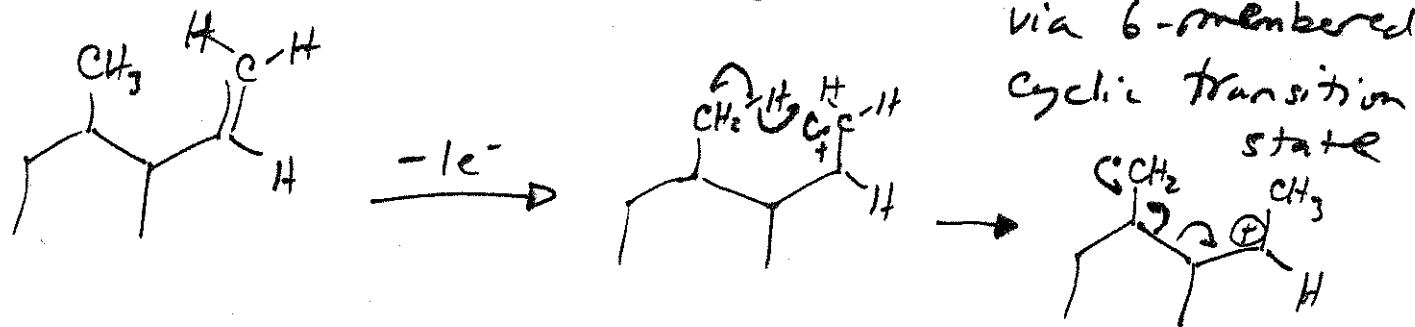
AND $\text{H}_2\text{C}(\text{CH}_3)-\overset{\oplus}{\text{C}}(\text{H})-\text{C}_6\text{H}_5$



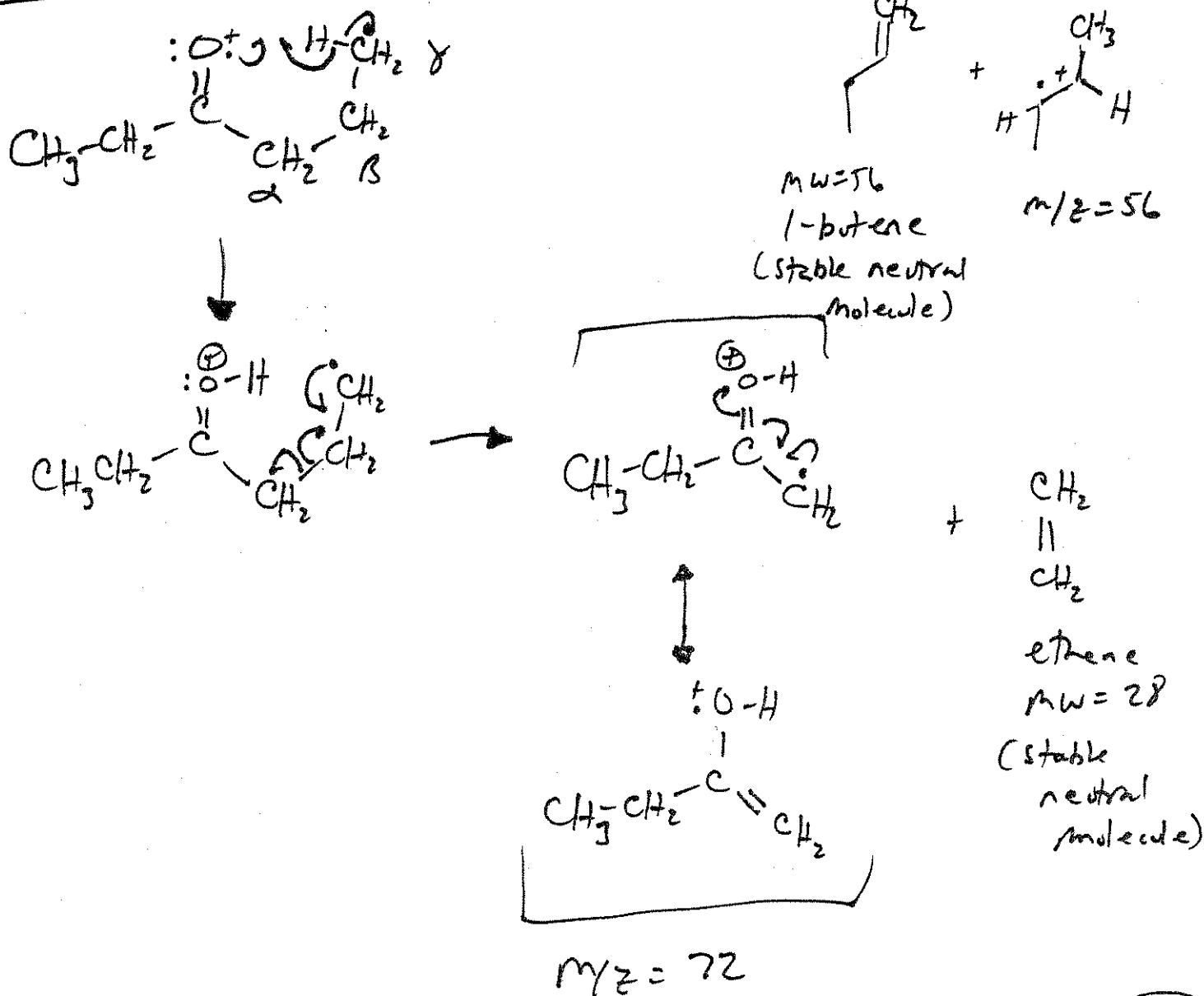
Stabilized by resonance

Rearrangement of Molecular Ions

Important alkene rearrangement - H-atom transfer via 6-membered cyclic transition state

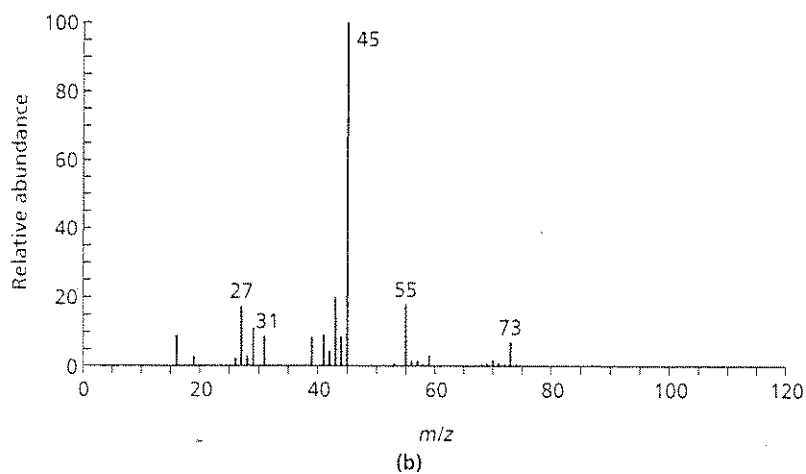
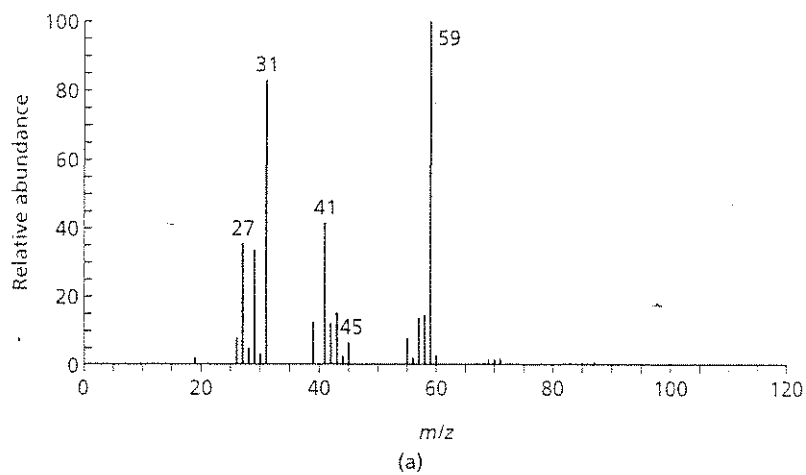


McLafferty Rearrangement



Problem

Two products are obtained from the reaction of (Z)-2-pentene with water and a trace of H_2SO_4 . The mass spectra of these products are shown in Figure 12.10. Identify the compounds responsible for the spectra.



12-24