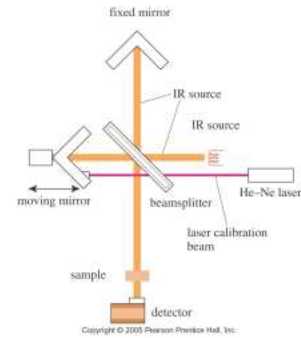

Organic Chemistry, 6th Edition
L. G. Wade, Jr.

Chapter 12
Mass Spectrometry and Infrared Spectroscopy

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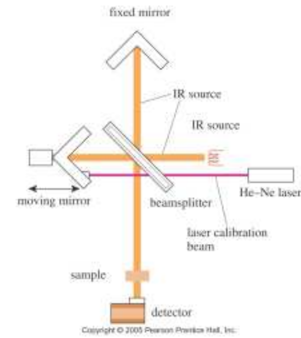
Introduction



- Spectroscopy is an analytical technique which helps determine structure.
- It destroys little or no sample.
- The amount of light absorbed by the sample is measured as wavelength is varied.

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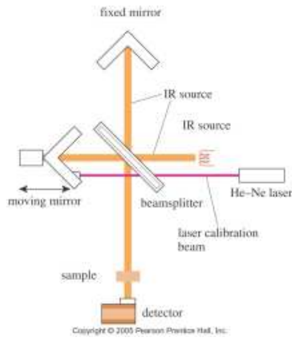
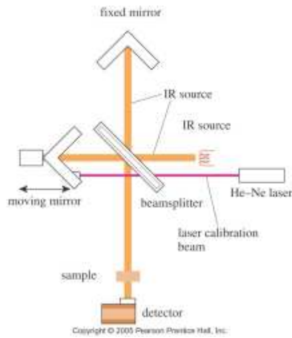
Types of Spectroscopy



- Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.
- Mass spectrometry (MS) fragments the molecule and measures the masses.
- Nuclear magnetic resonance (NMR) spectroscopy detects signals from active nuclei and can be used to distinguish isomers.
- Ultraviolet (UV) spectroscopy uses electron transitions to determine bonding patterns. =>

Electromagnetic Spectrum



- Examples: X rays, microwaves, radio waves, visible light, IR, and UV.
- Frequency and wavelength are inversely proportional.
- $c = \lambda\nu$, where c is the speed of light (3.00×10^8 m/s)
- Energy per photon = $h\nu$, where h is Planck's constant, 6.62×10^{-37} kJ•sec.

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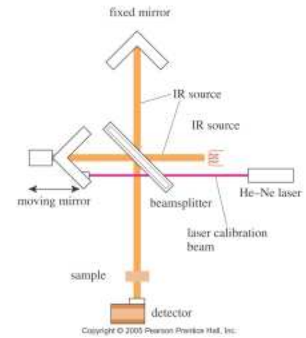
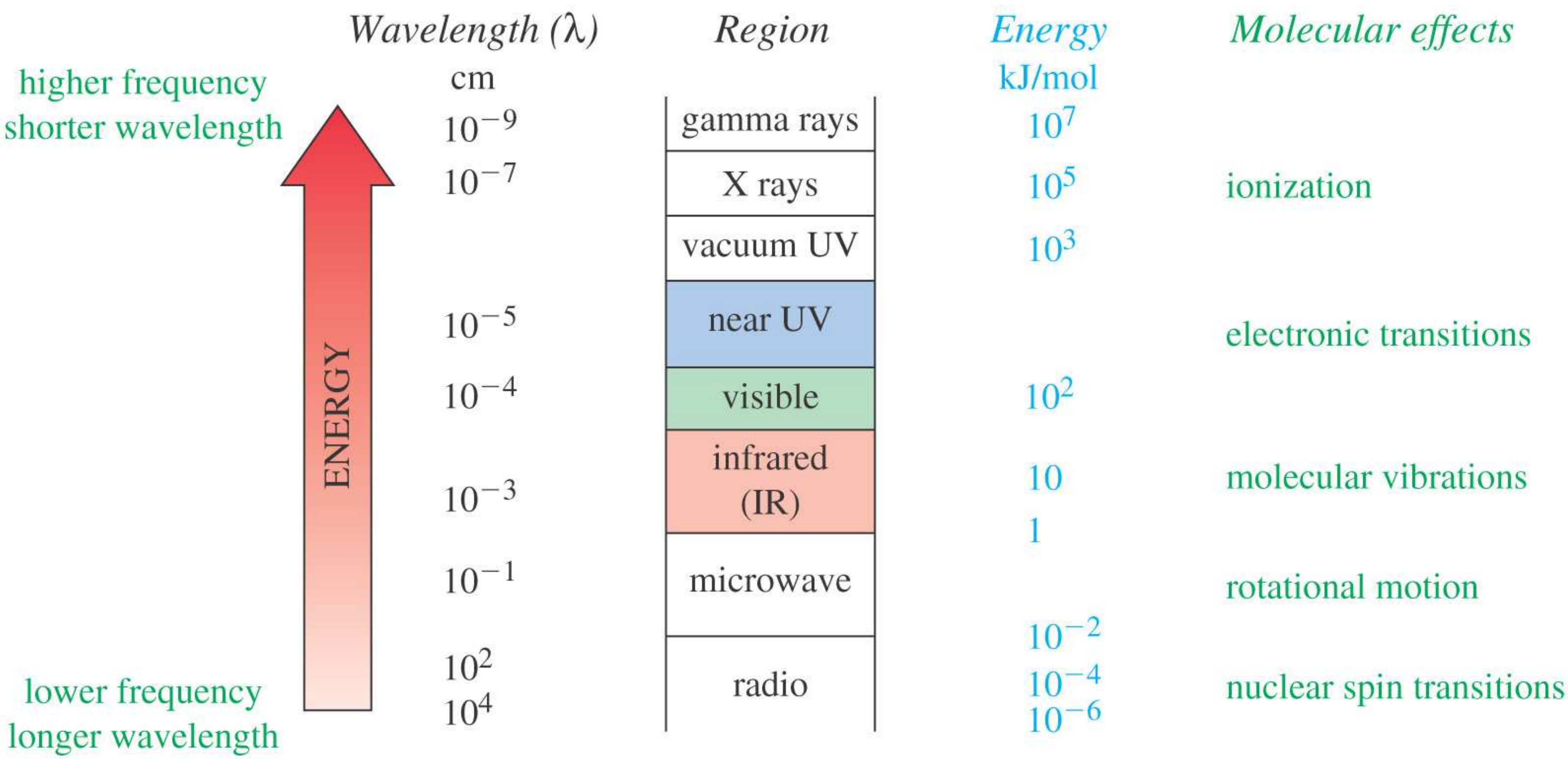
The Spectrum and Molecular Effects





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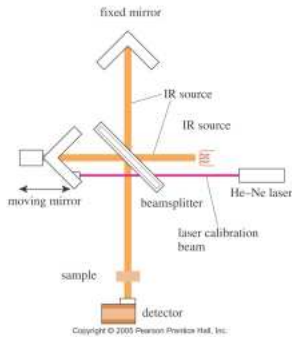
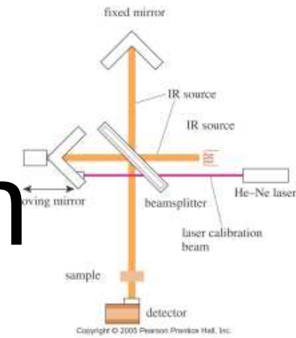


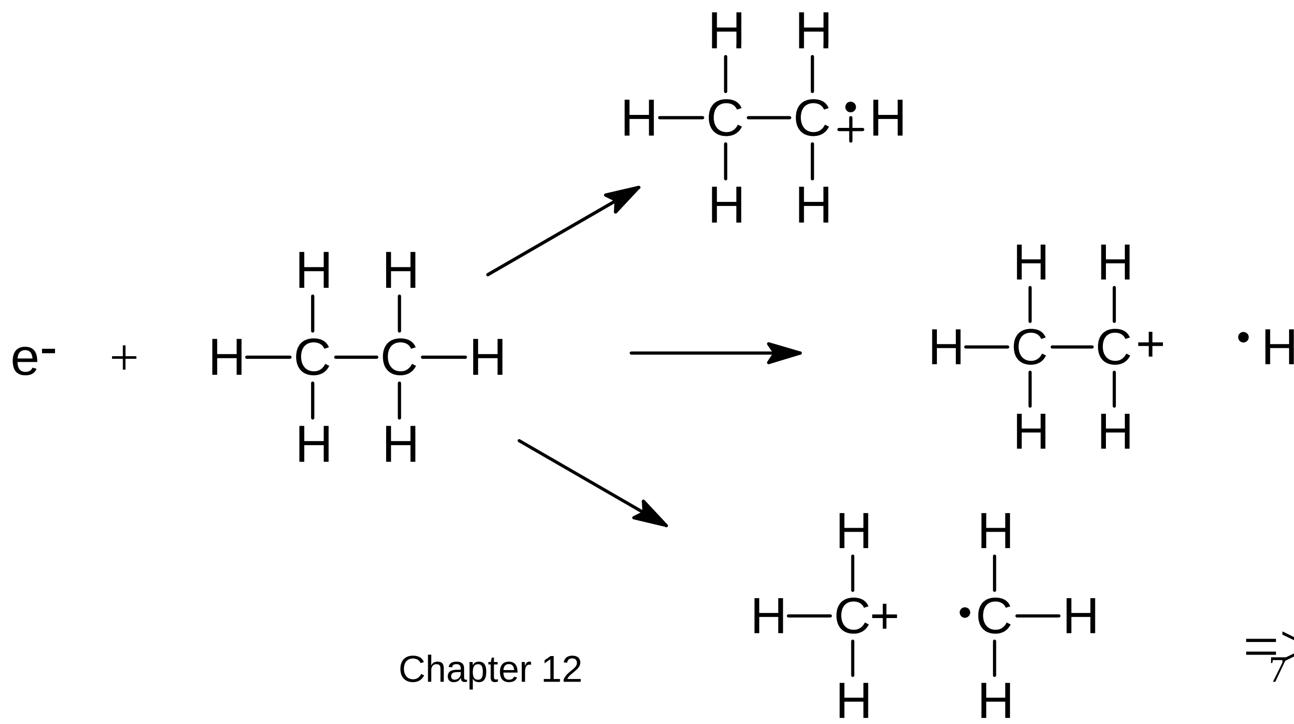
Mass Spectrometry

- Molecular weight can be obtained from a very small sample (but it is destroyed).
- It does not involve the absorption or emission of light.
- A beam of high-energy electrons breaks the molecule apart.
- The masses of the fragments and their relative abundance reveal information about the structure of the molecule. =>

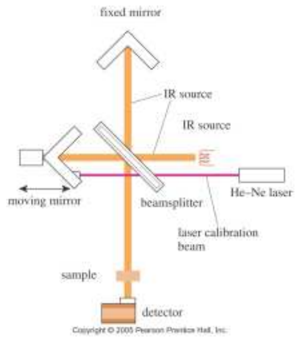
Electron Impact Ionization



A high-energy electron can dislodge an electron from a bond, creating a radical cation (a positive ion with an unpaired e^-).

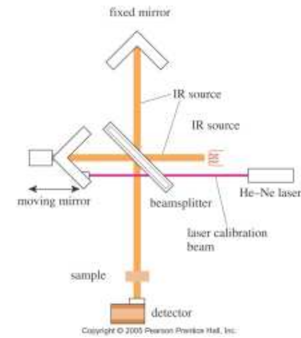


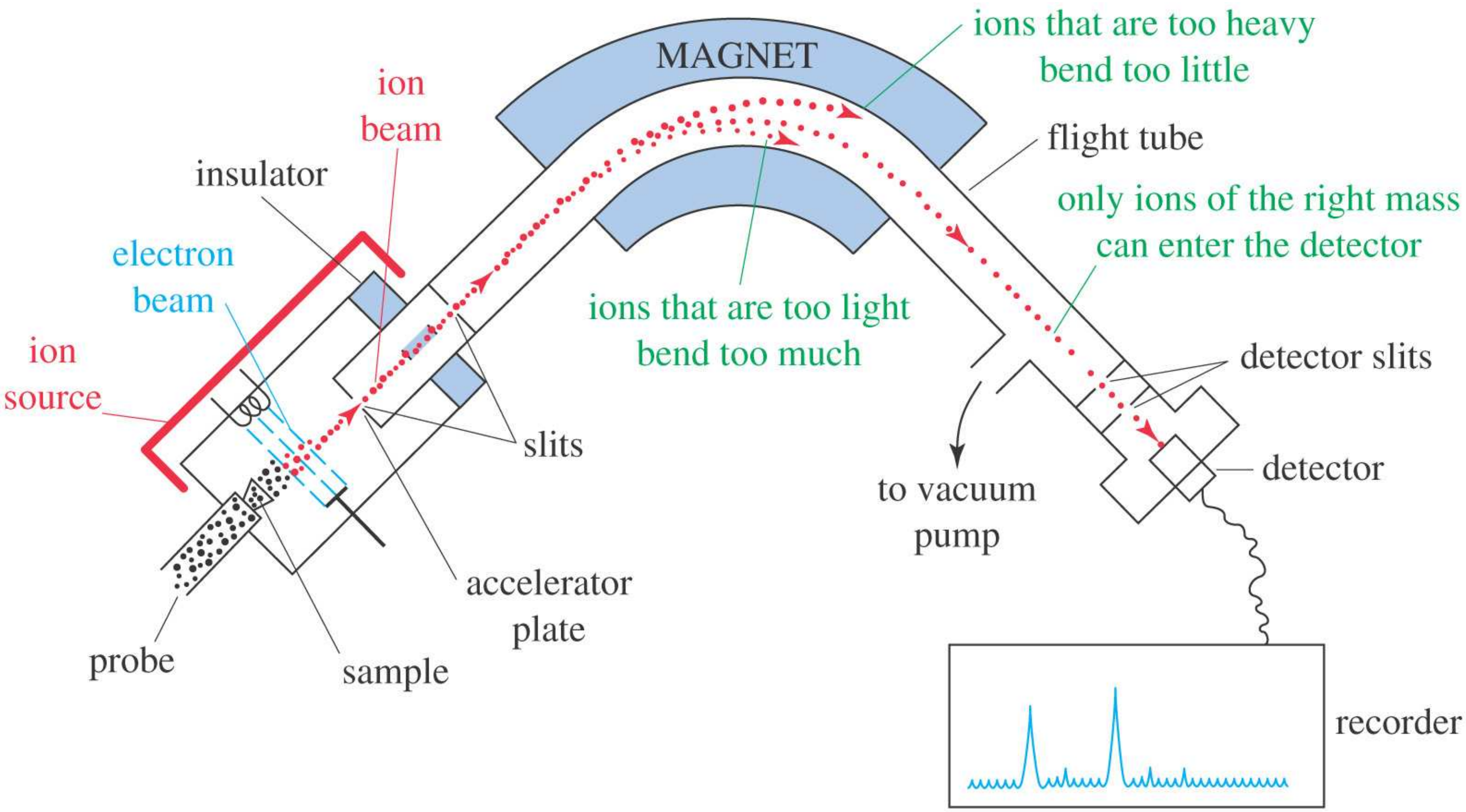
Separation of Ions



- Only the cations are deflected by the magnetic field.
- Amount of deflection depends on ***m/z***.
- The detector signal is proportional to the number of ions hitting it.
- By varying the magnetic field, ions of all masses are collected and counted. =>

Mass Spectrometer





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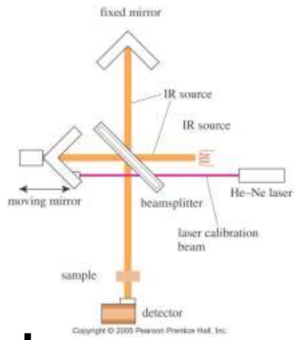
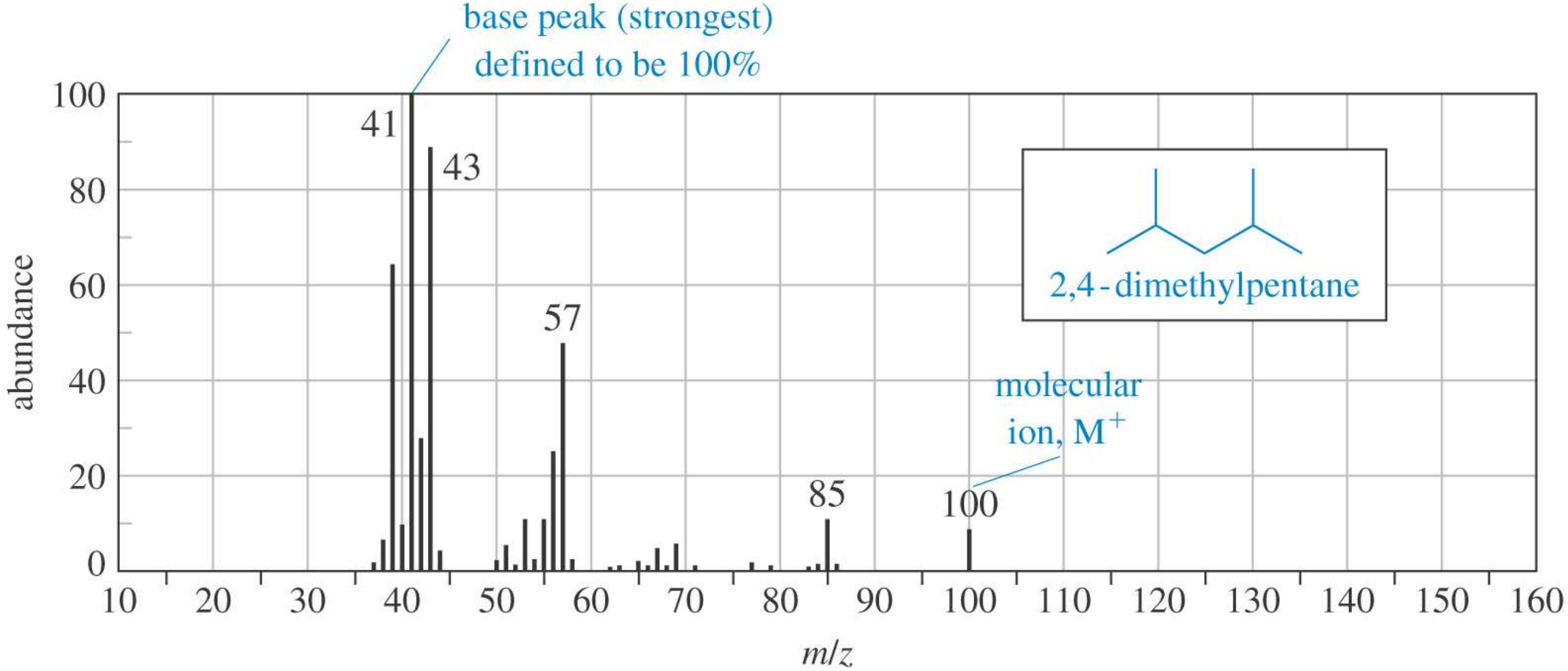
The Mass Spectrum



Relative abundance for fragments are graphed or tabulated as a function of their mass/charge ratio.



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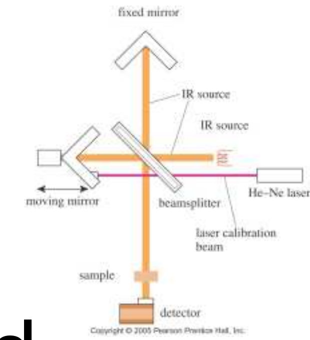
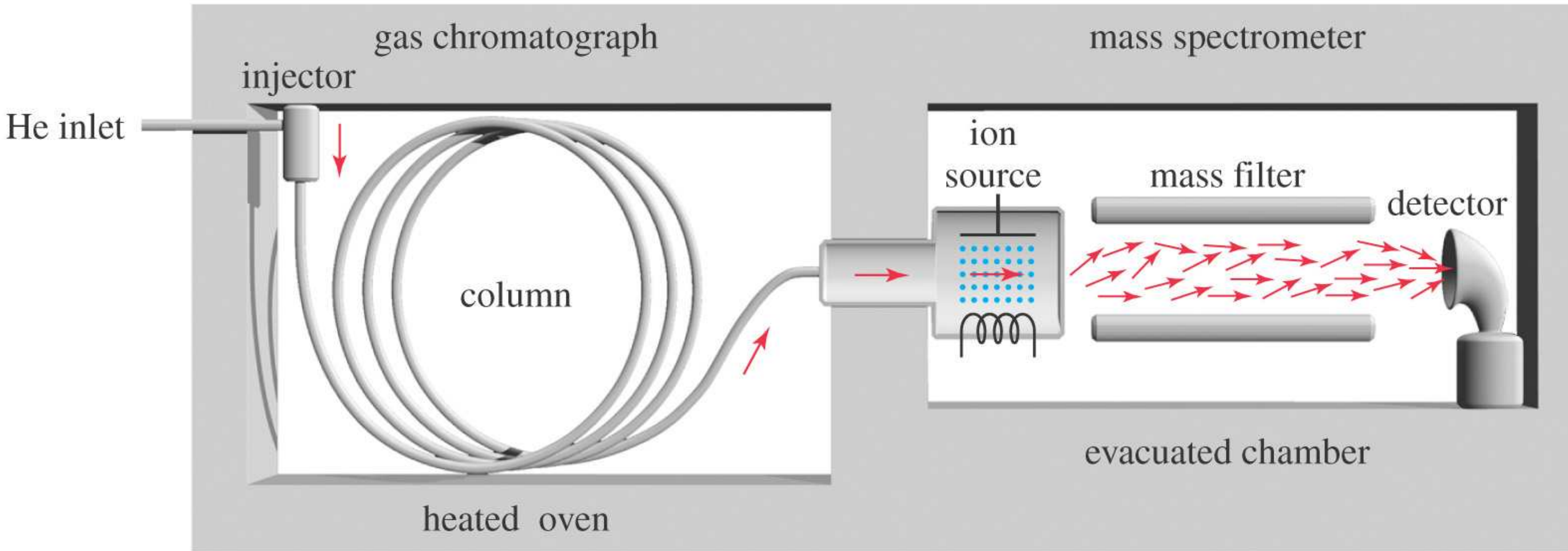
The GC-MS (or any other hyphenated technique)



A mixture of compounds is separated by gas chromatography, then identified by mass spectrometry.



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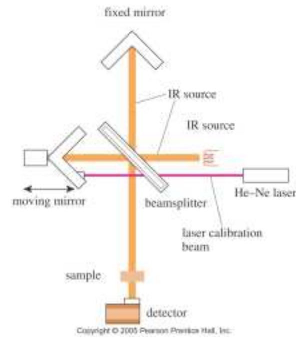


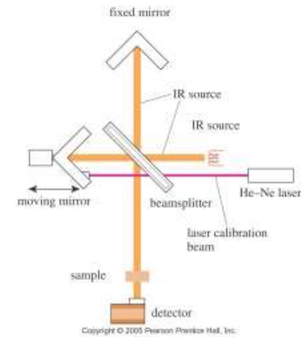
High Resolution MS

- Masses measured to 1 part in 20,000.
- A molecule with mass of 44 could be C_3H_8, C_2H_4O, CO_2, or CN_2H_4.
- If a more exact mass is 44.029, pick the correct structure from the table:

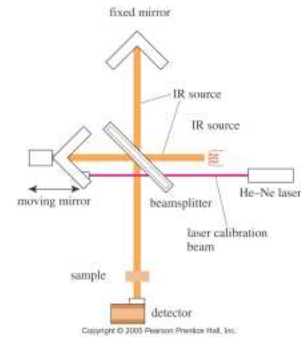
C_3H_8	C_2H_4O	CO_2	CN_2H_4
44.06260	44.02620	43.98983	44.03740

=>

Molecules with Heteroatoms



- Isotopes: present in their usual abundance.
- Hydrocarbons contain 1.1% C-13, so there will be a small M+1 peak.
- If Br is present, M+2 is equal to M^+.
- If Cl is present, M+2 is one-third of M^+.
- If iodine is present, peak at 127, large gap.
- If N is present, M^+ will be an odd number.
- If S is present, M+2 will be 4% of M^+. =>



Isotopic Abundance

TABLE 12-4 Isotopic Composition of Some Common Elements

Element	M^+		M+1		M+2	
hydrogen	^{1}H	100.0%				
carbon	^{12}C	98.9%	^{13}C	1.1%		
nitrogen	^{14}N	99.6%	^{15}N	0.4%		
oxygen	^{16}O	99.8%			^{18}O	0.2%
sulfur	^{32}S	95.0%	^{33}S	0.8%	^{34}S	4.2%
chlorine	^{35}Cl	75.5%			^{37}Cl	24.5%
bromine	^{79}Br	50.5%			^{81}Br	49.5%
iodine	^{127}I	100.0%				

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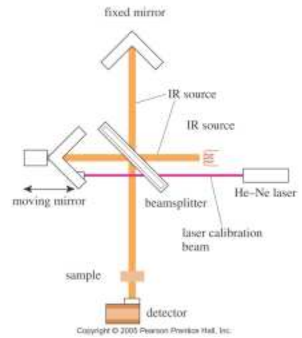
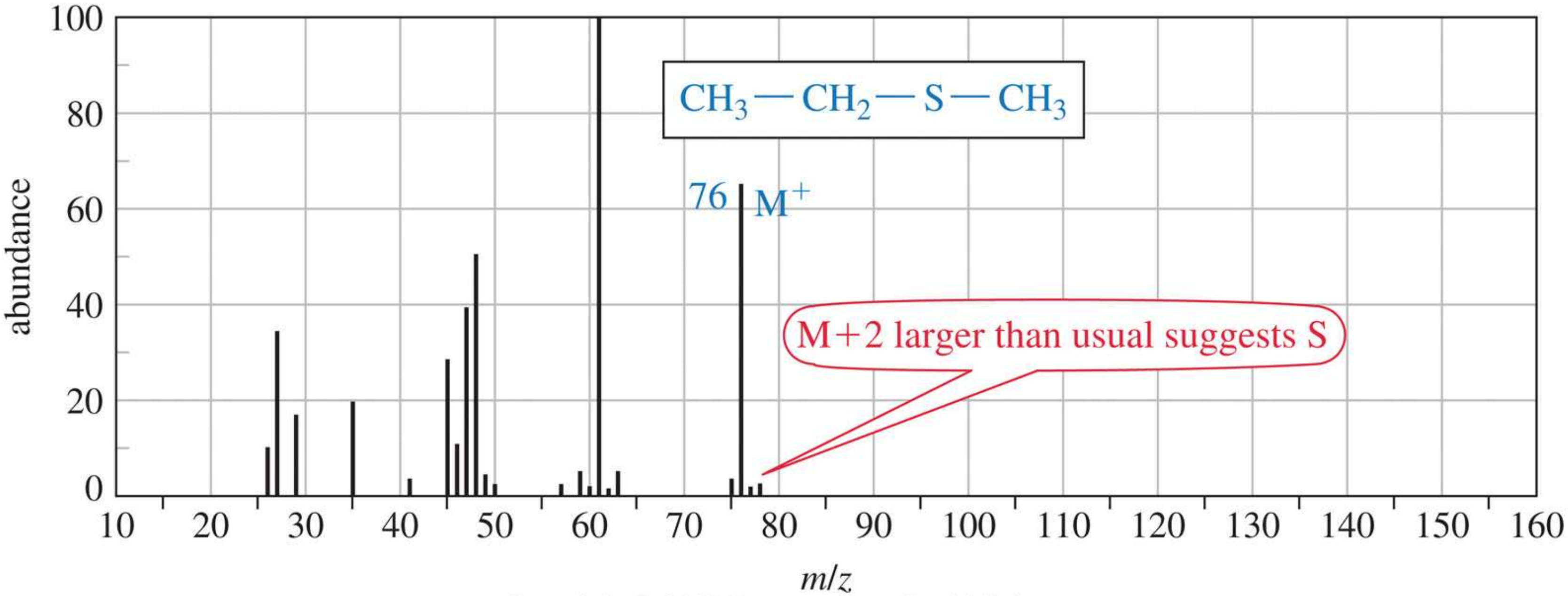
Mass Spectrum with Sulfur





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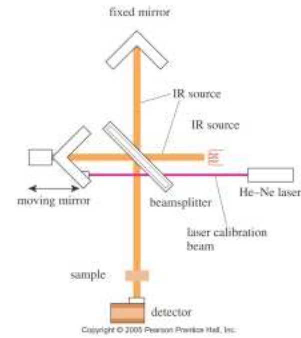
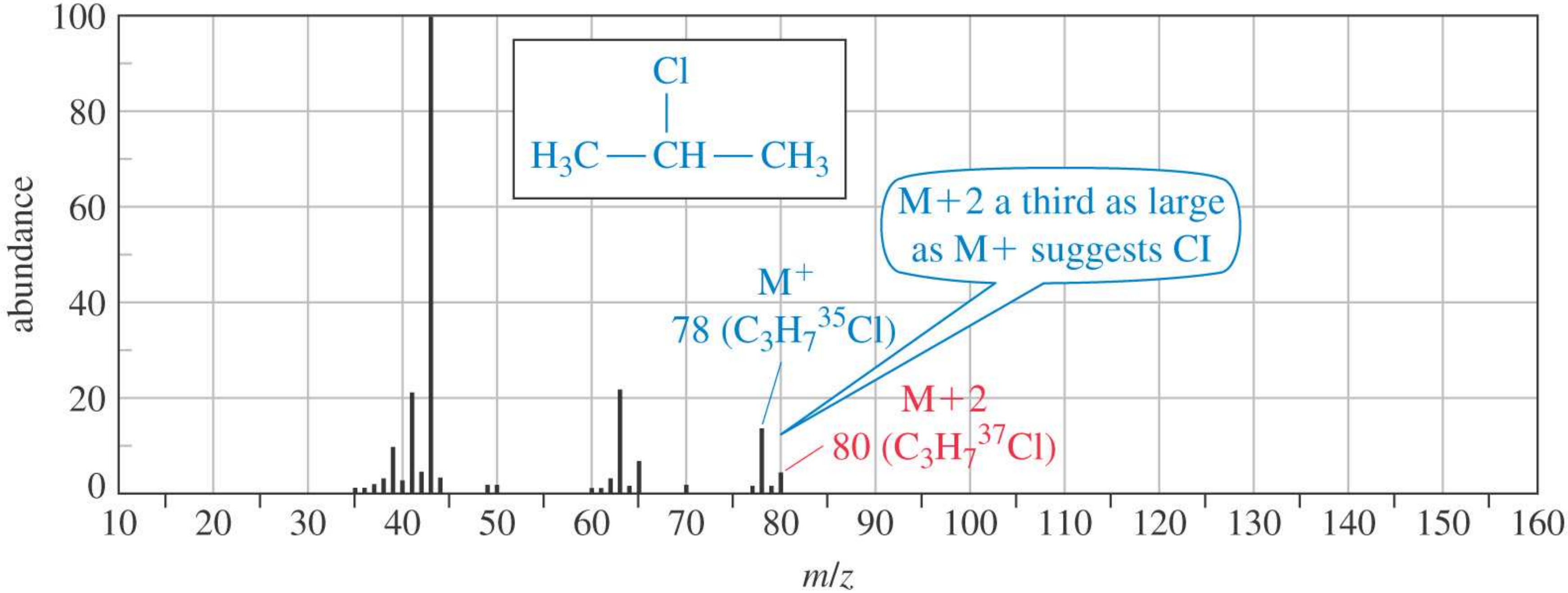


Mass Spectrum with Chlorine



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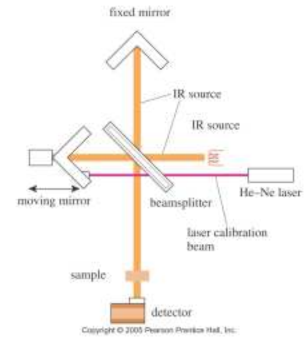
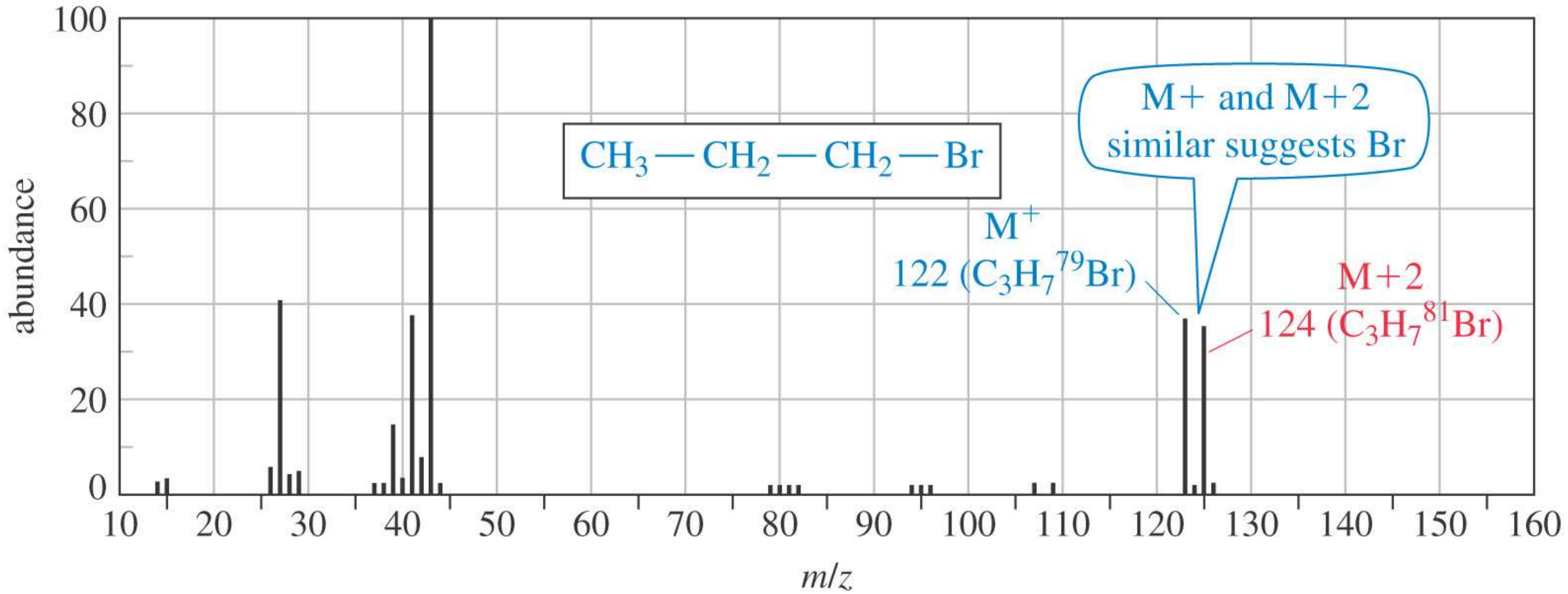
Mass Spectrum with Bromine





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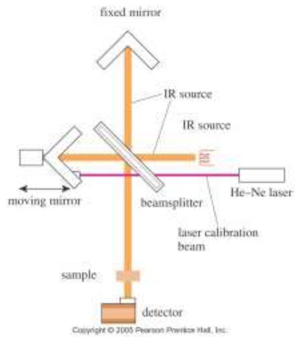
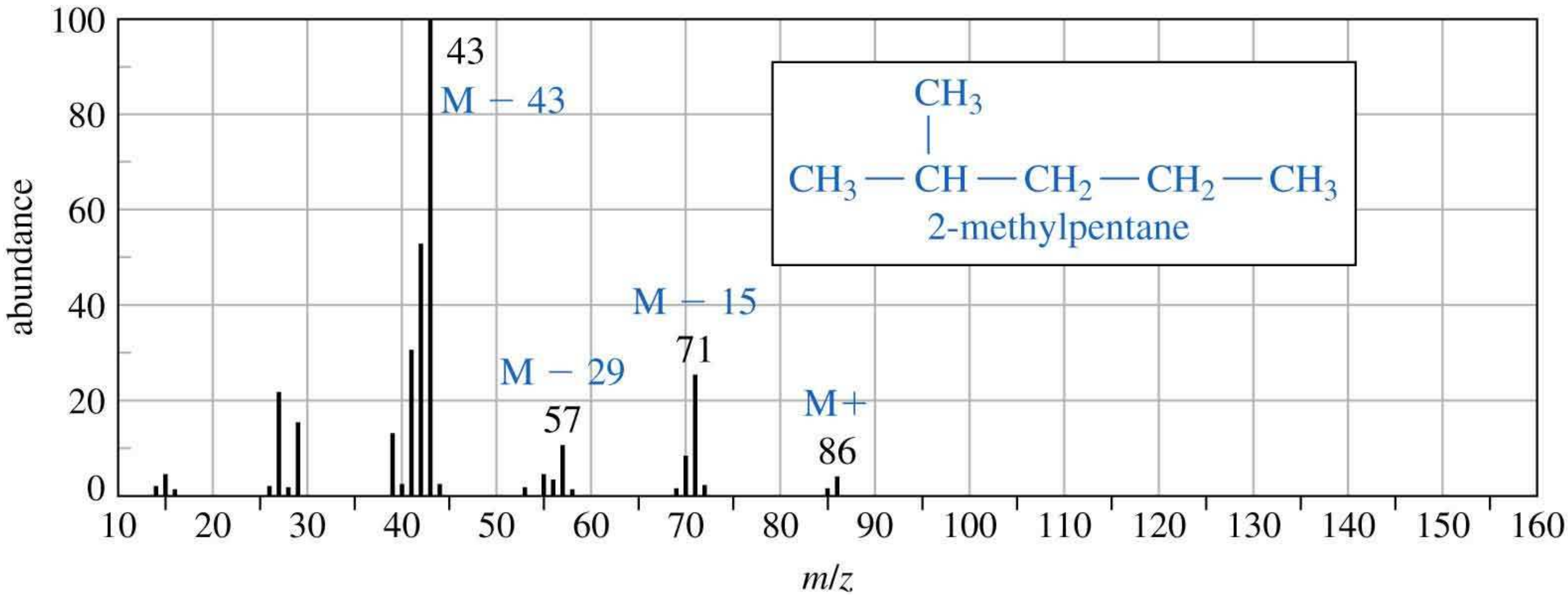
Mass Spectra of Alkanes



More stable carbocations will be more abundant.



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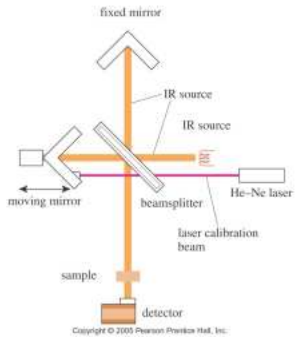
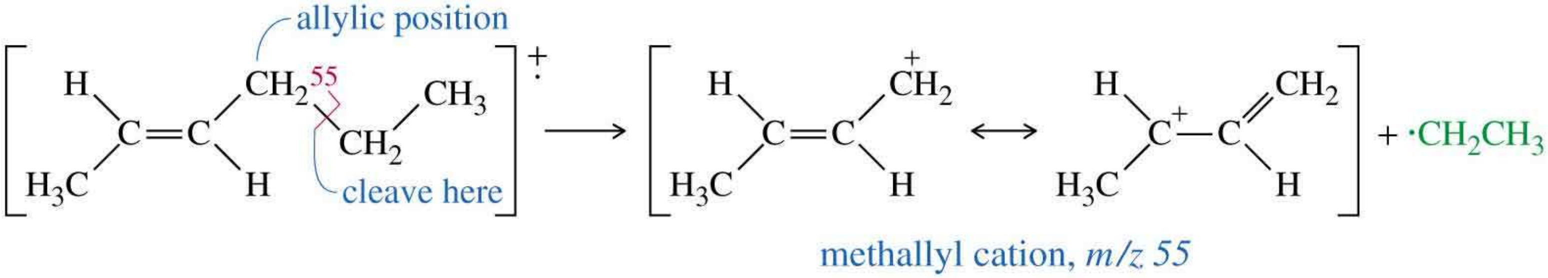
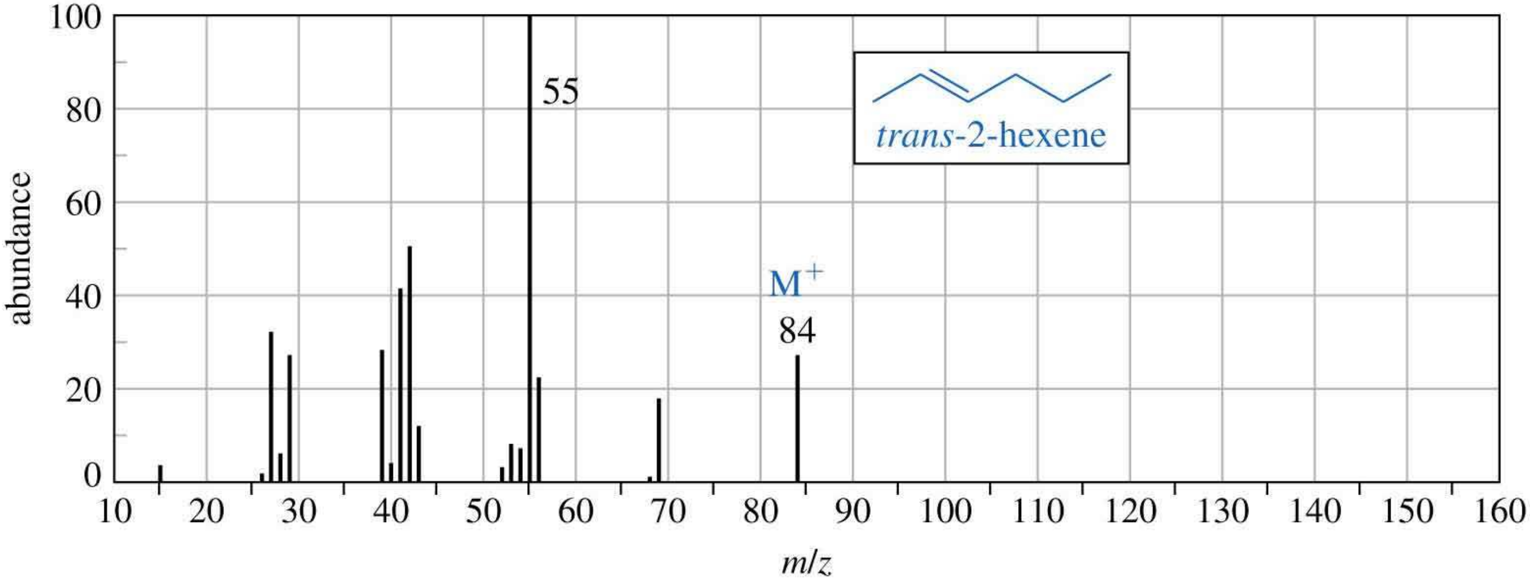


Mass Spectra of Alkenes

Resonance-stabilized cations favored.





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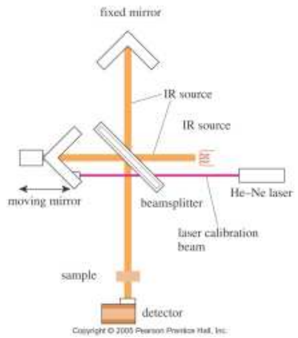
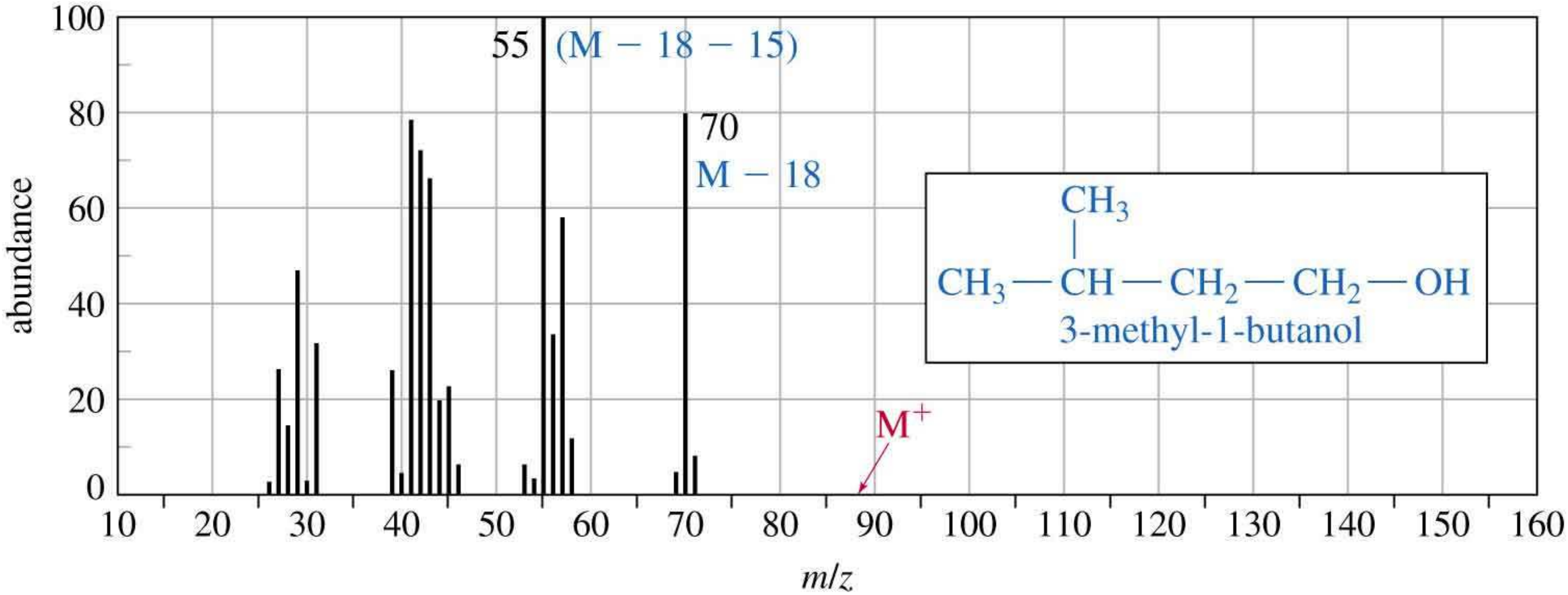
Mass Spectra of Alcohols



- Alcohols usually lose a water molecule.
- M^+ may not be visible.



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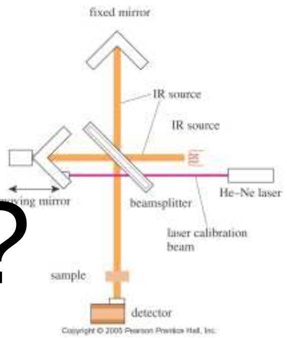
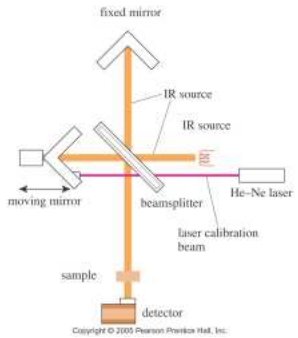
What information we will obtain from mass spectra?



- The mass of the molecular ion.
- What for?
  - ➢ To compare the mass of the molecular ion with the mass of the empirical formula of the compound under study.
  - ➢ If the molecular ion is twice as heavy as the mass of the empirical formula for the compound, then the molecular formula will be twice the empirical formula.

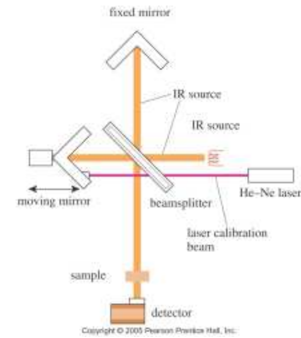
The UV-Vis Region



- Provides information regarding electronic structure.
- Just above violet in the visible region
- Wavelengths usually 200-750nm
- For wavelengths below 200nm, vacuum is required.

=>

The UV-Vis Region



- Mostly used for systems with conjugated double bonds.
- 1-octene λ_{max}=180nm
- 1,3-butadiene λ_{max}=220nm
- 1,3,5-hexatriene λ_{max}=250nm

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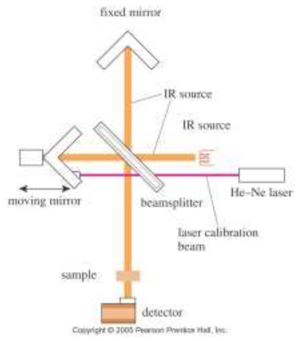
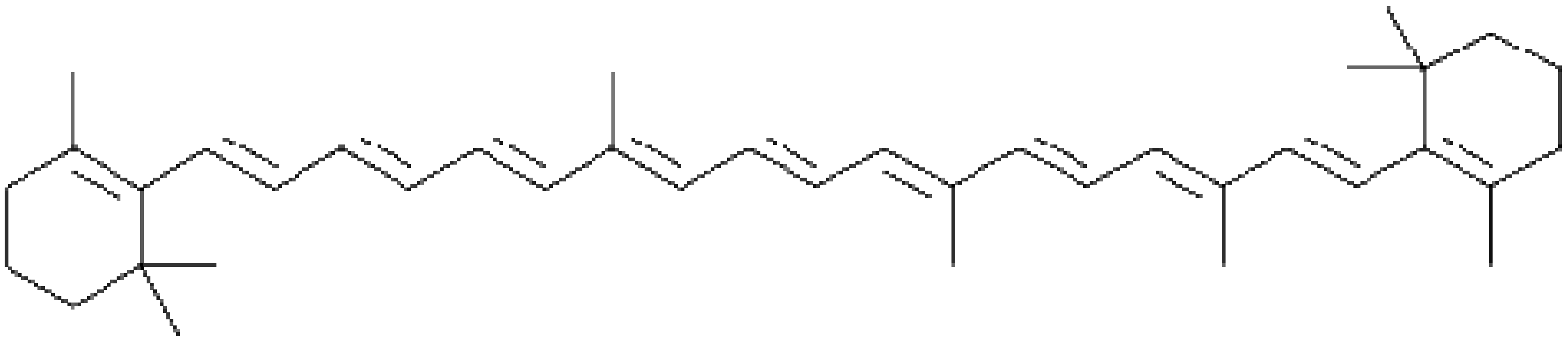
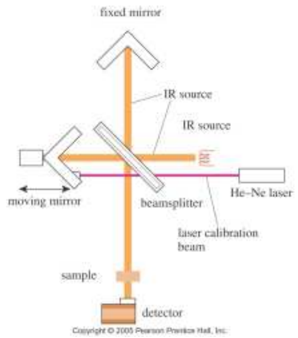
The UV-Vis Region





β-carotene λ_{max}=480nm

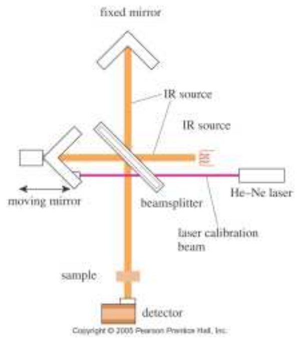
Color is between red and orange
(because it reflects those colors)



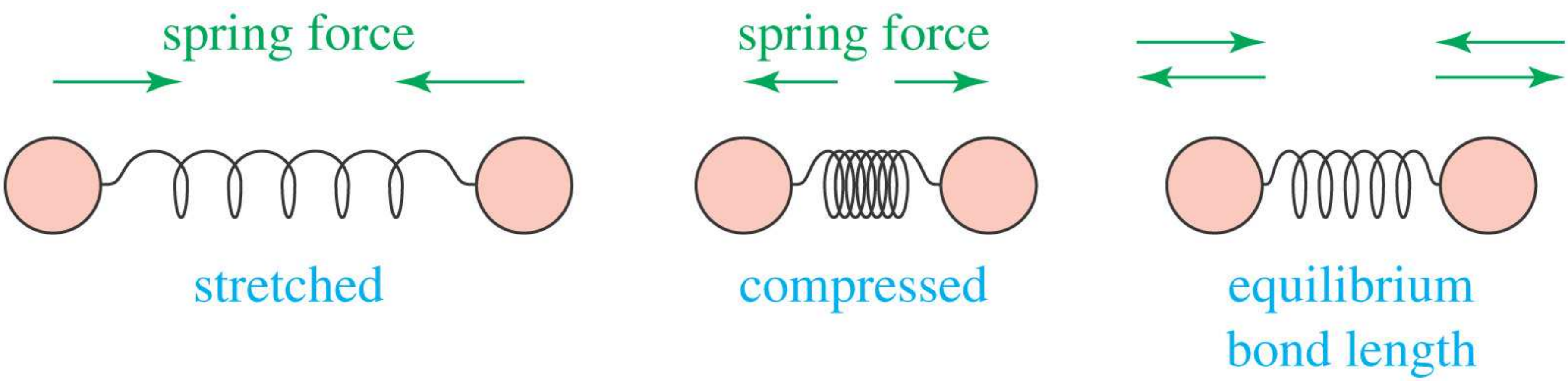
The IR Region

- Just below red in the visible region.
- Wavelengths usually 2.5-25 µm.
- More common units are wavenumbers, or cm^{-1}, the reciprocal of the wavelength in centimeters.
- Wavenumbers are proportional to frequency and energy. =>

Molecular Vibrations



Covalent bonds vibrate at only certain allowable frequencies.



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Stretching Frequencies

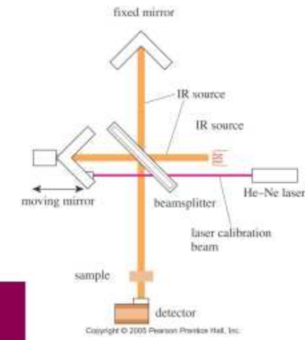


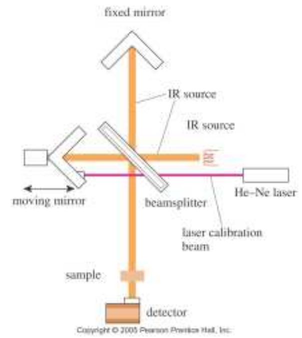
TABLE 12-1 Bond Stretching Frequencies.

Bond		Bond Energy [kJ (kcal)]		Stretching Frequency (cm^{-1})	
		Frequency decreases with increasing atomic mass			
C—H	heavier atoms ↓	420 (100) <note these are trs>		3000	$\bar{\nu}$ decreases ↓
C—D		420 (100)		2100	
C—C		350 (83)		1200	
		Frequency increases with bond energy			
C—C		350 (83)	stronger bond ↓	1200	$\bar{\nu}$ increases ↓
C=C		611 (146)		1660	
C≡C		840 (200)		2200	

- Frequency decreases with increasing atomic mass.
- Frequency increases with increasing bond energy.

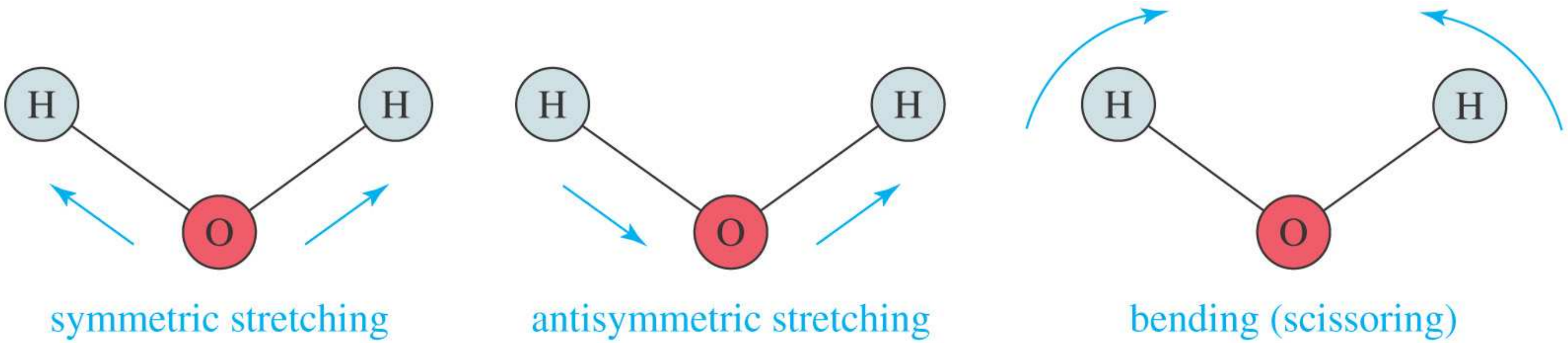
=>

Vibrational Modes

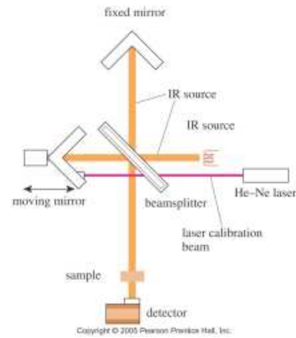


Nonlinear molecule with *n* atoms usually has 3*n* - 6 fundamental vibrational modes.

Linear molecules will have 3n – 5 modes.



Fingerprint of Molecule



- Whole-molecule vibrations and bending vibrations are also quantized.
- No two molecules will give exactly the same IR spectrum (except enantiomers).
- Simple stretching: 1600-3500 cm^{-1}.
- Complex vibrations: 600-1400 cm^{-1}, called the “fingerprint region.”

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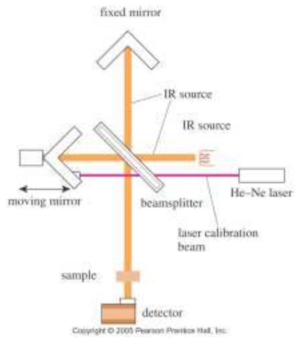
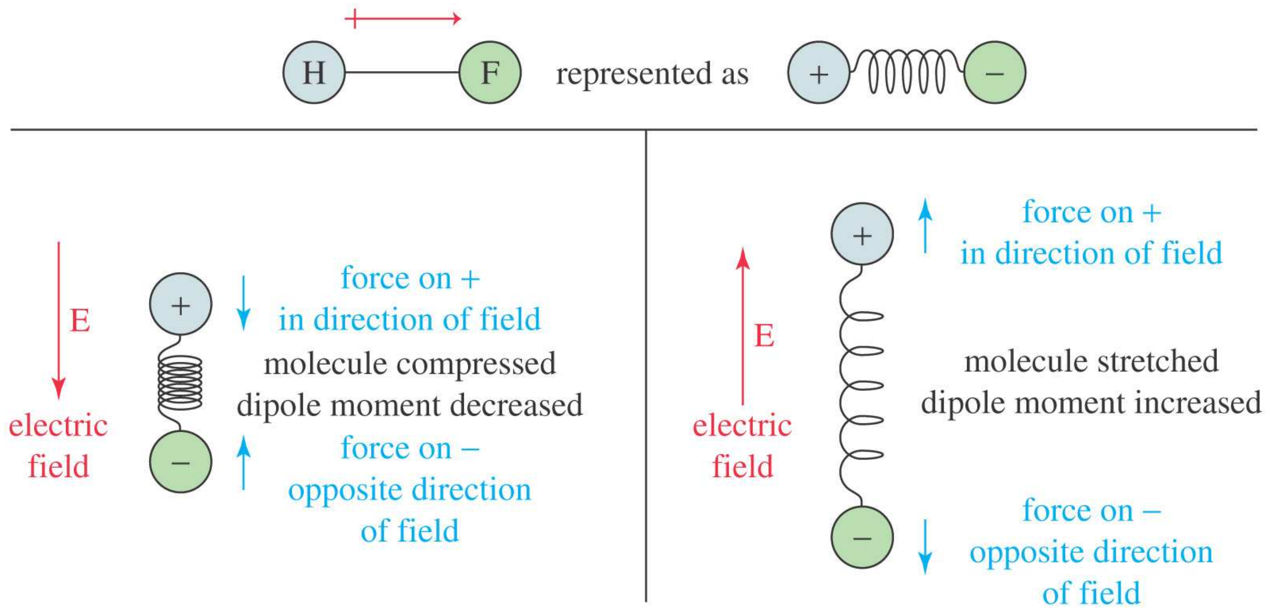


IR-Active and Inactive

- A polar bond is usually IR-active.
- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all.



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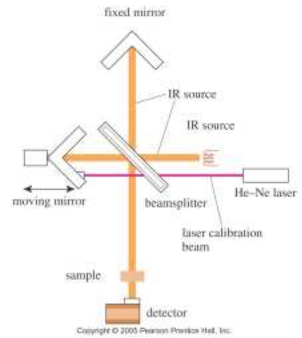
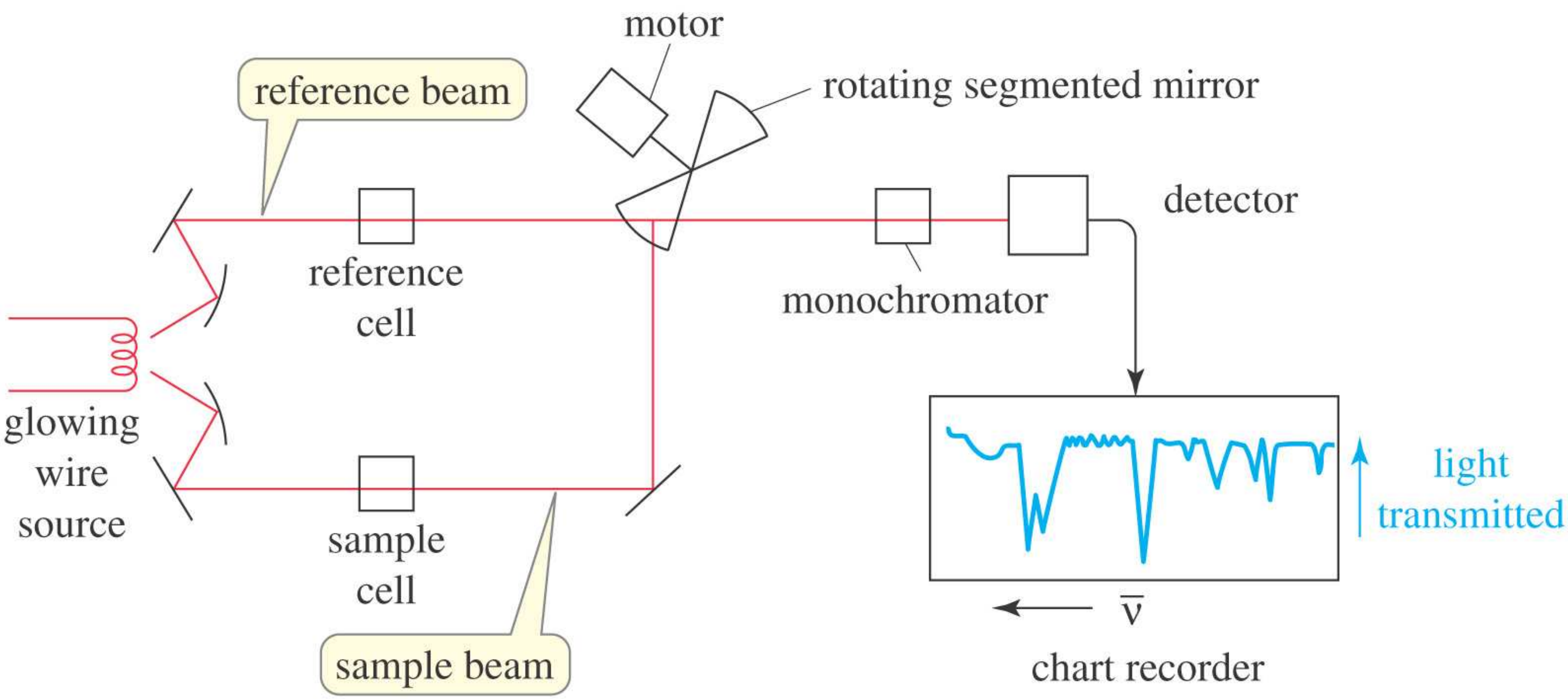
An Infrared Spectrometer





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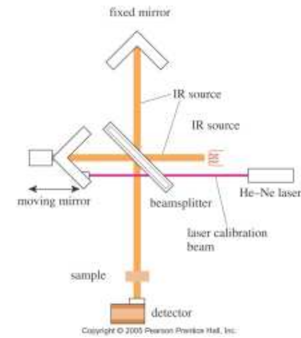
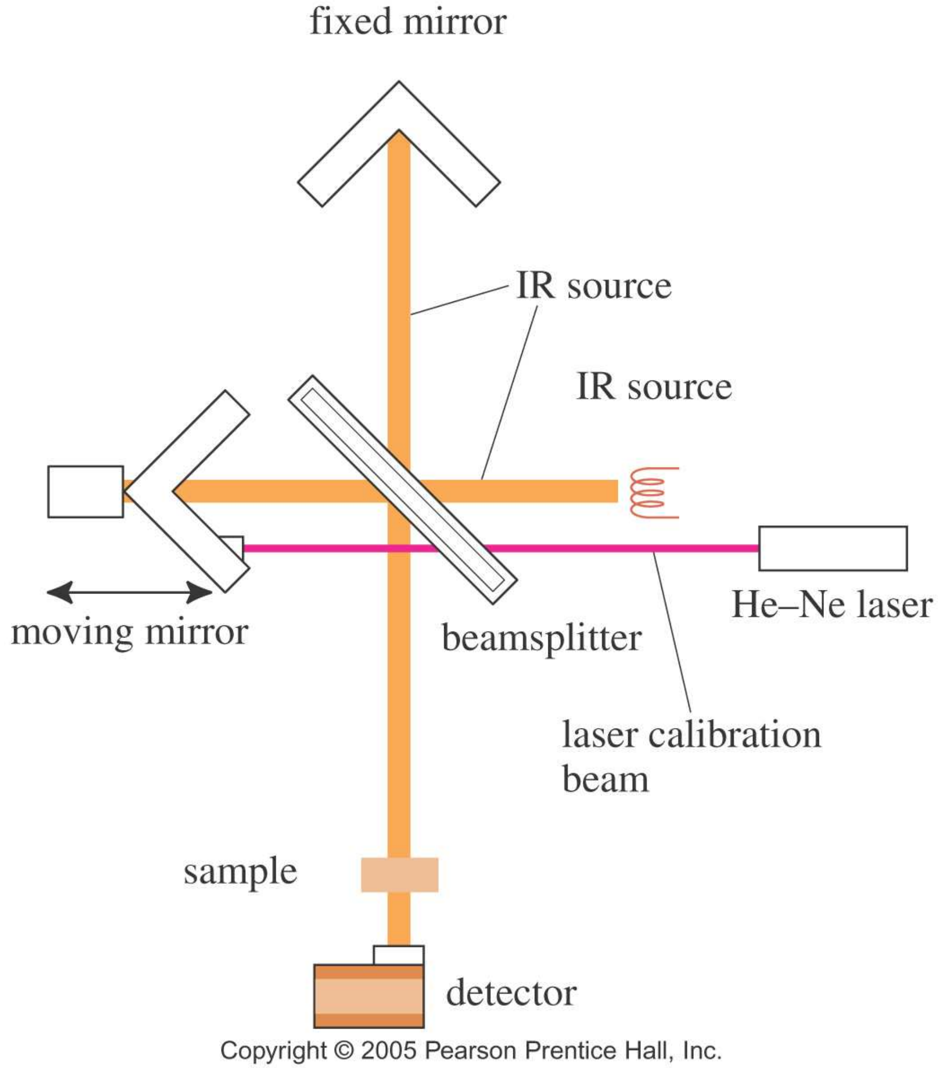
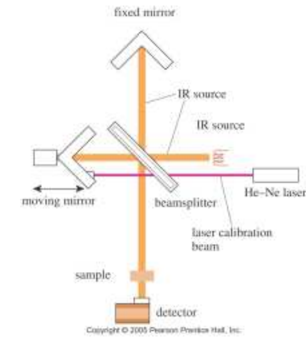
FT-IR Spectrometer



- Has better sensitivity.
- Less energy is needed from source.
- Completes a scan in 1-2 seconds.
- Takes several scans and averages them.
- Has a laser beam that keeps the instrument accurately calibrated. =>

FT-IR Interferometer





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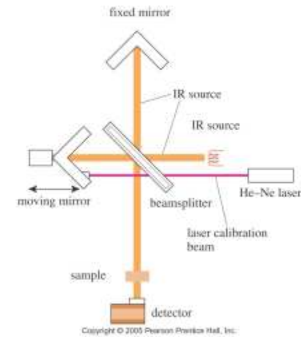
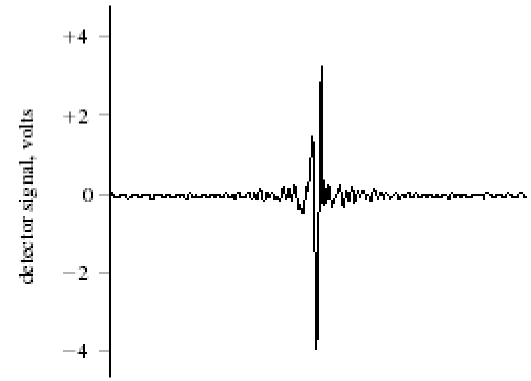
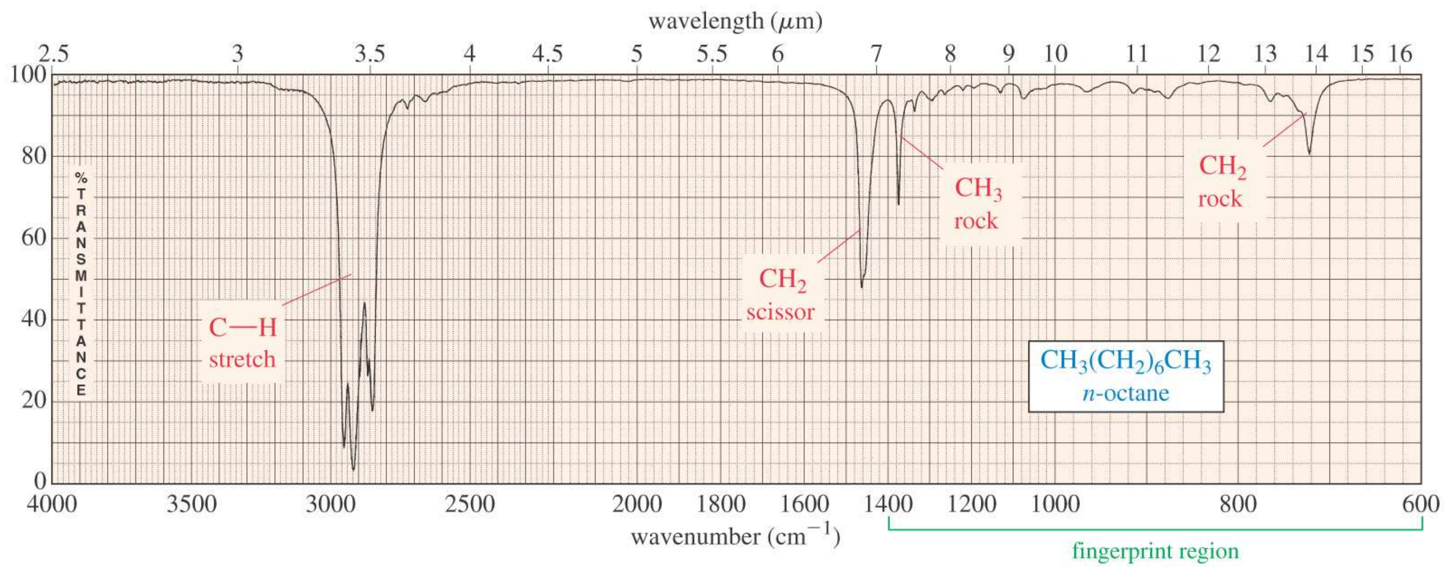
Interferogram



The interferogram at the right displays the interference pattern and contains all of the spectrum information.

A Fourier transform converts the time domain to the frequency domain with absorption as a function of frequency.





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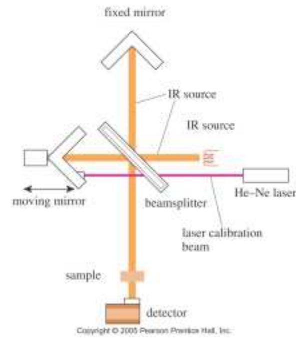
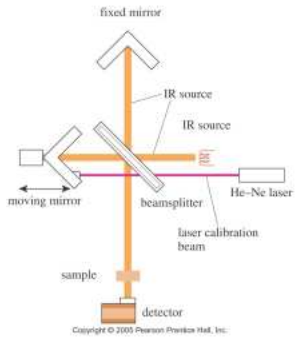
Carbon-Carbon Bond Stretching



- Stronger bonds absorb at higher frequencies:
  - C-C 1200 cm^{-1}
  - C=C 1660 cm^{-1}
  - C≡C <2200 cm^{-1} (weak or absent if internal)
- Conjugation lowers the frequency:
  - isolated C=C 1640-1680 cm^{-1}
  - conjugated C=C 1620-1640 cm^{-1}
  - aromatic C=C approx. 1600 cm^{-1}

=>

Carbon-Hydrogen Stretching

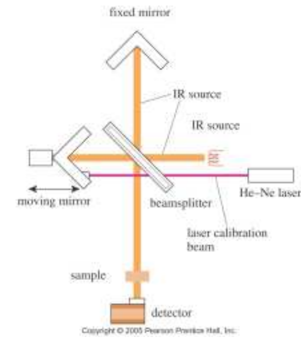


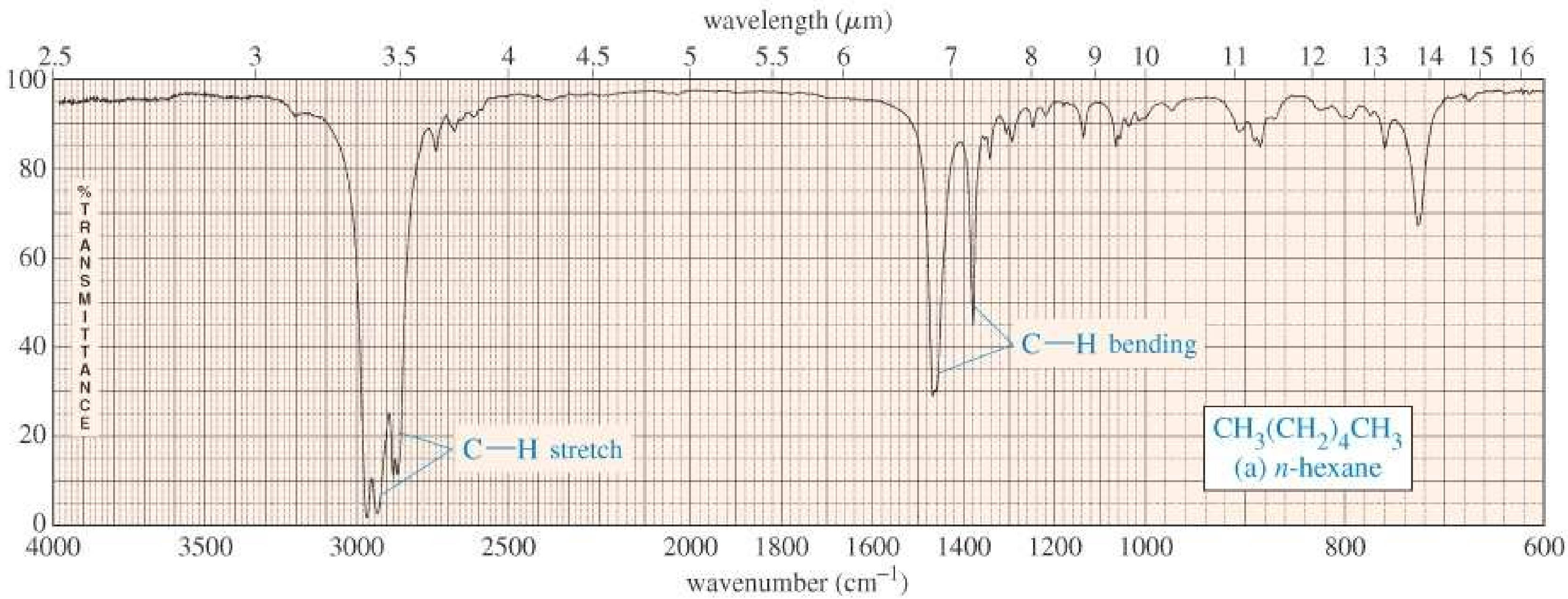
Bonds with more *s* character absorb at a higher frequency.

- *sp*^{3} C-H, just below 3000 cm^{-1} (to the right)
- *sp*^{2} C-H, just above 3000 cm^{-1} (to the left)
- *sp* C-H, at 3300 cm^{-1}

=>

An Alkane IR Spectrum





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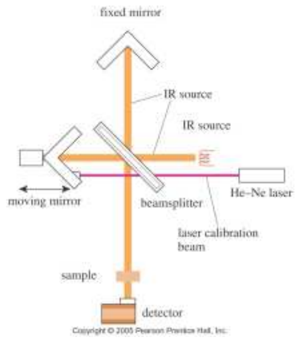
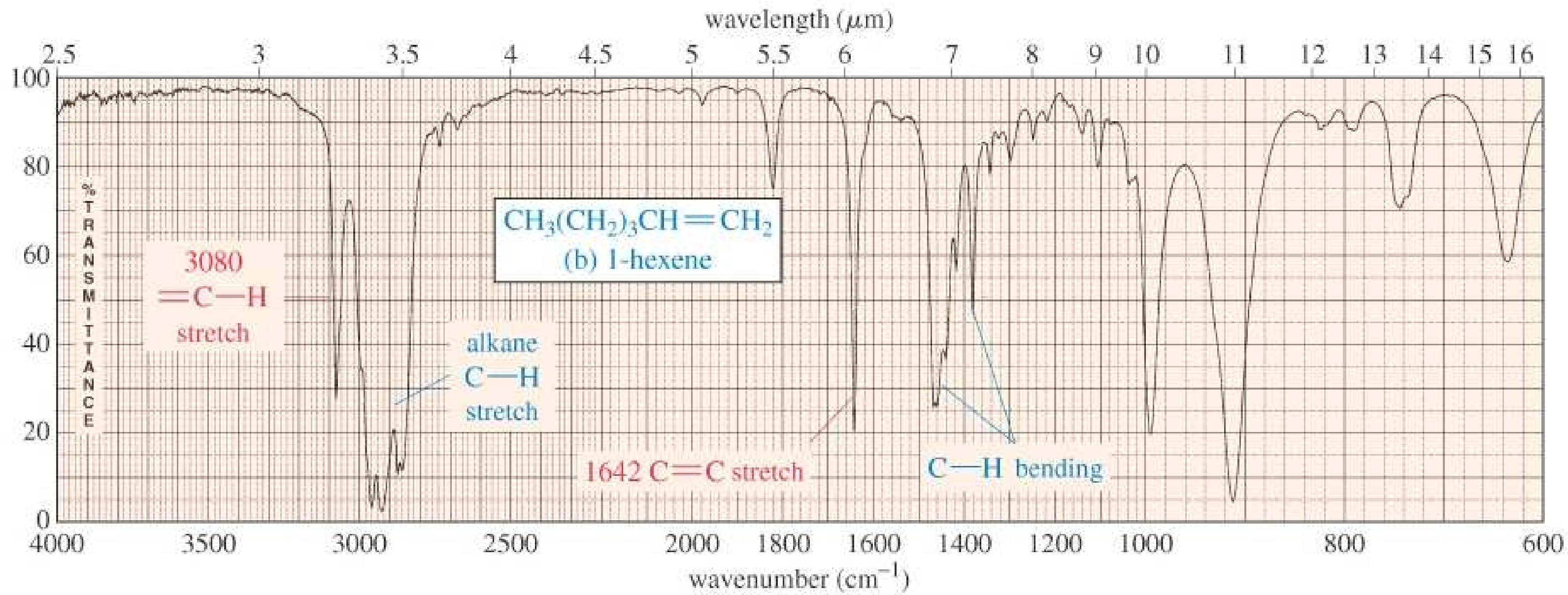
An Alkene IR Spectrum





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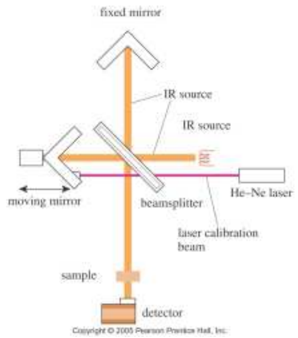
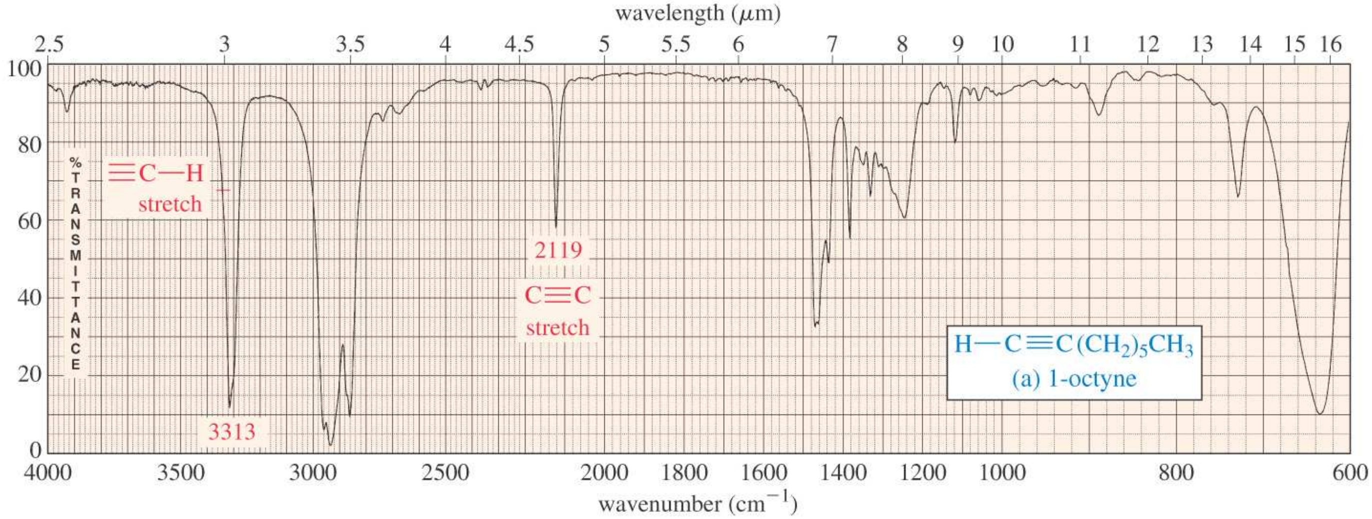
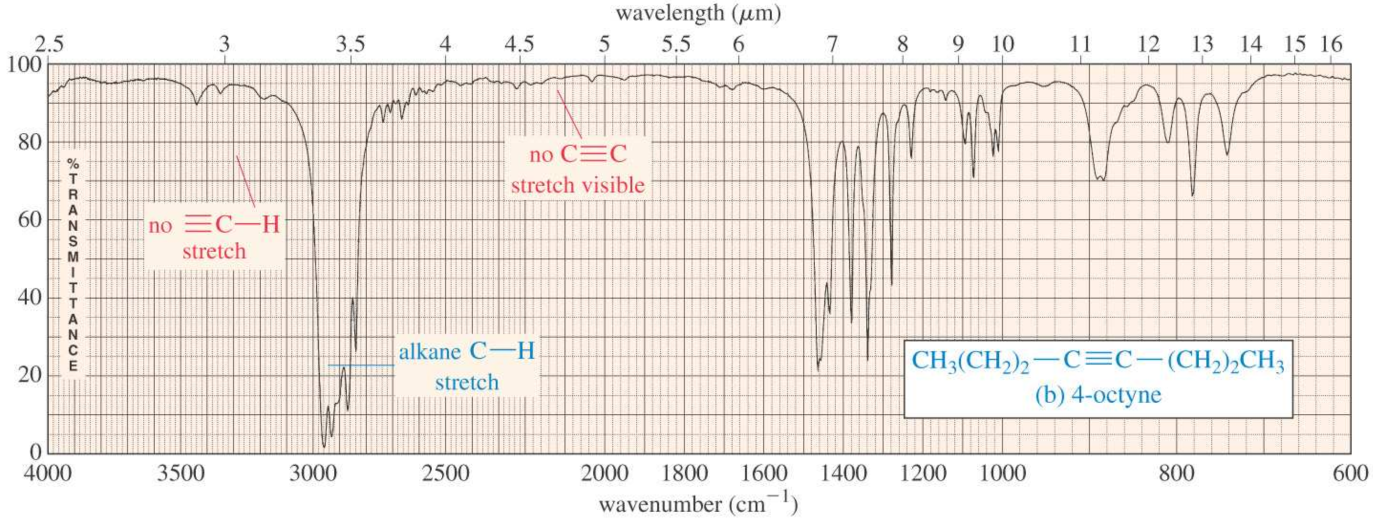
An Alkyne IR Spectrum







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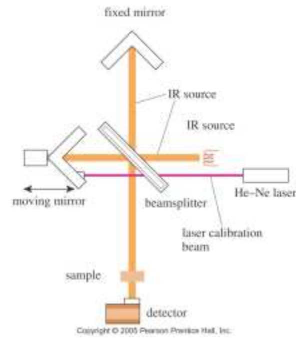
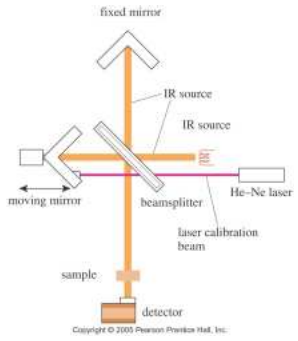
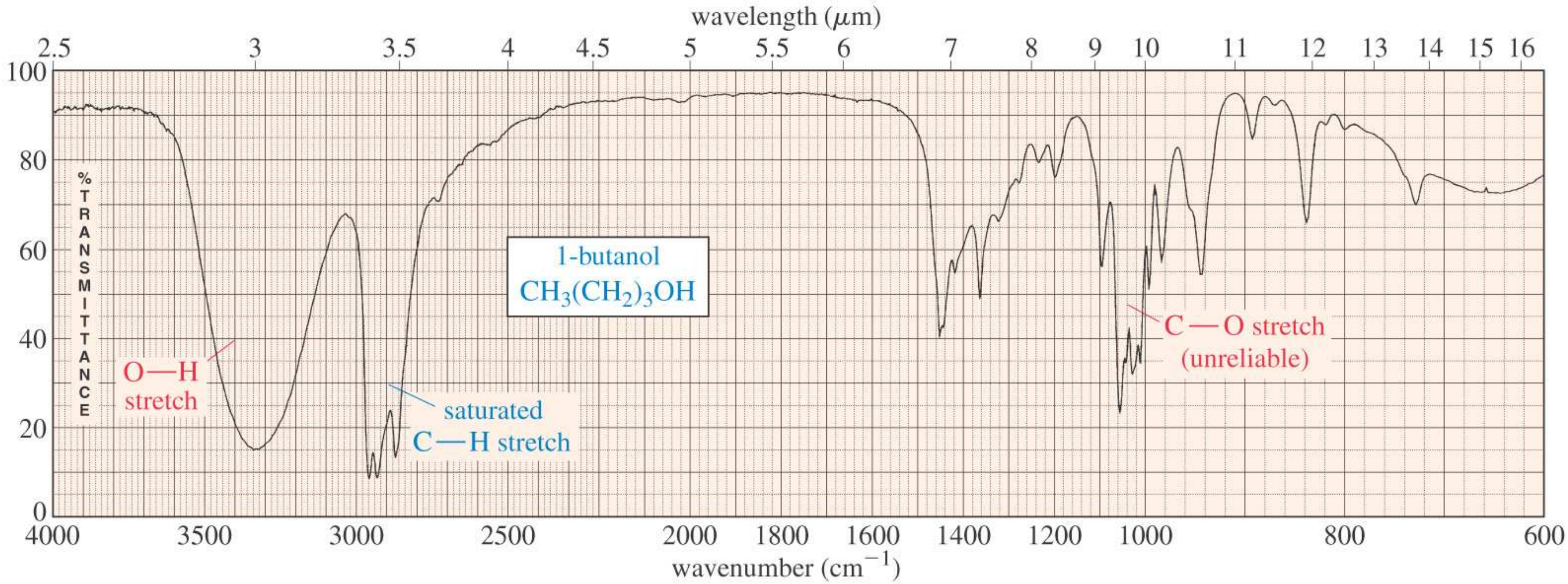
O-H and N-H Stretching



- Both of these occur around 3300 cm^{-1}, but they look different.
  - Alcohol O-H, broad with rounded tip.
  - Secondary amine (R_2NH), broad with one sharp spike.
  - Primary amine (RNH_2), broad with two sharp spikes.
  - No signal for a tertiary amine (R_3N). =>

An Alcohol IR Spectrum





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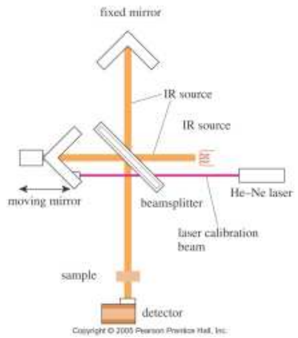
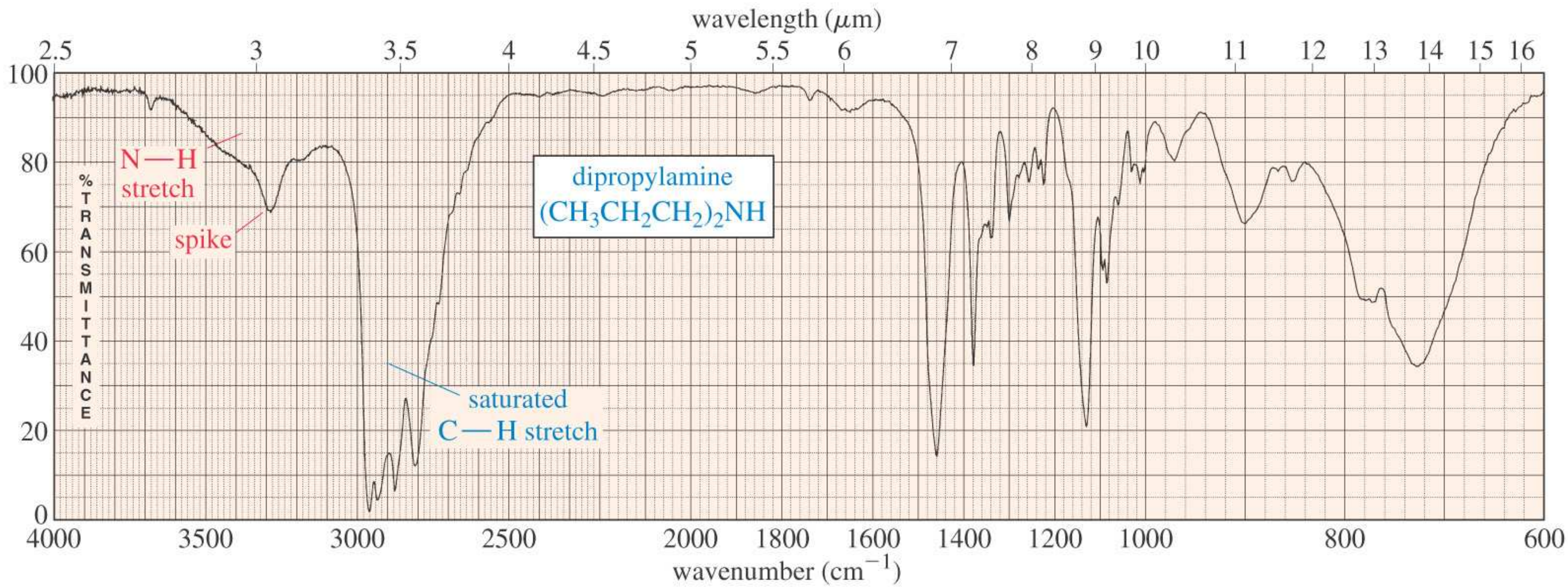
An Amine IR Spectrum





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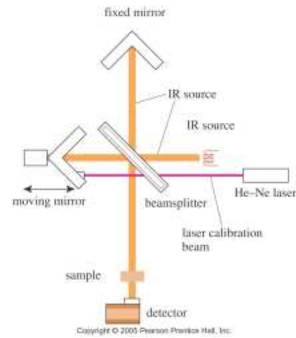
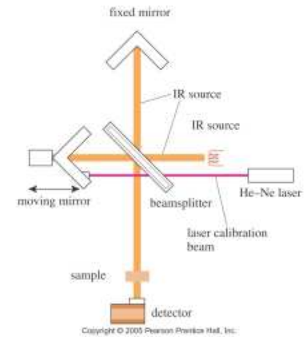
Carbonyl Stretching

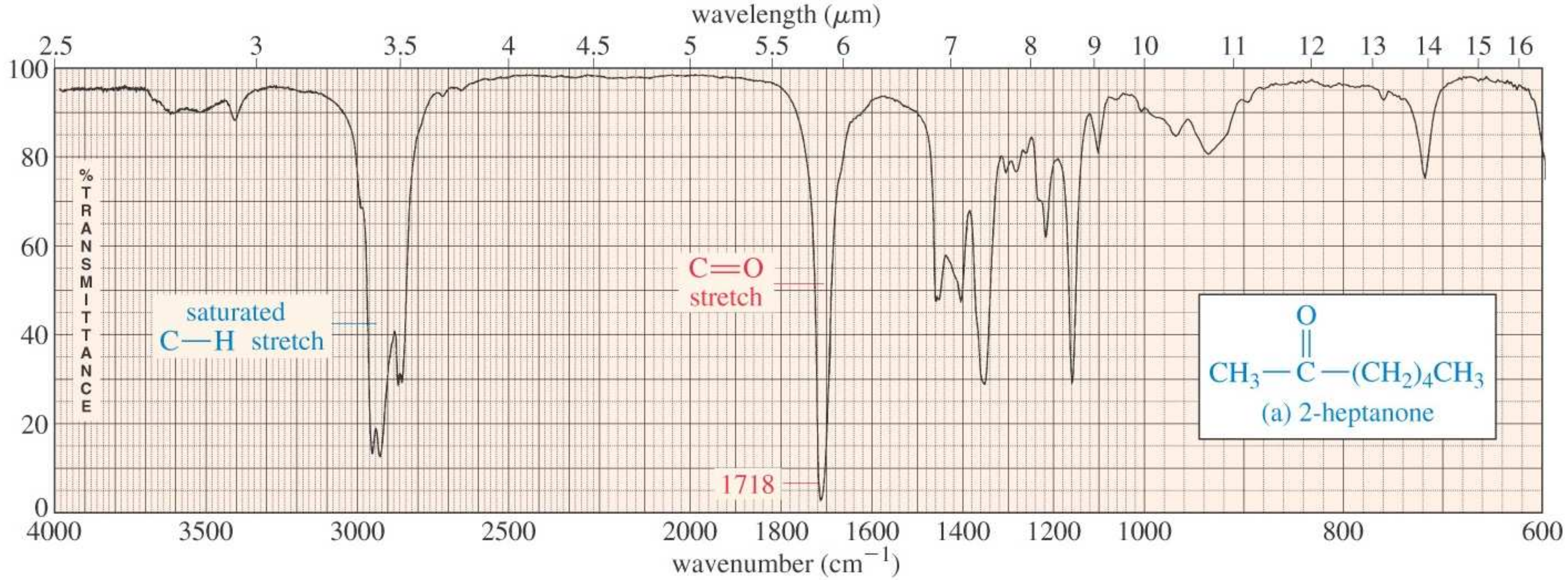


- The C=O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1}.
- Usually, it's the strongest IR signal.
- Carboxylic acids will have O-H also.
- Aldehydes have two C-H signals around 2700 and 2800 cm^{-1}.

=>

A Ketone IR Spectrum





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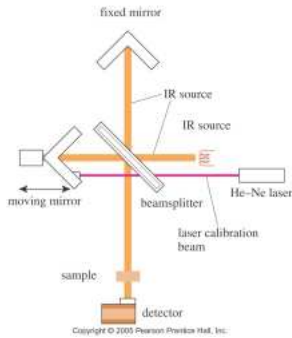
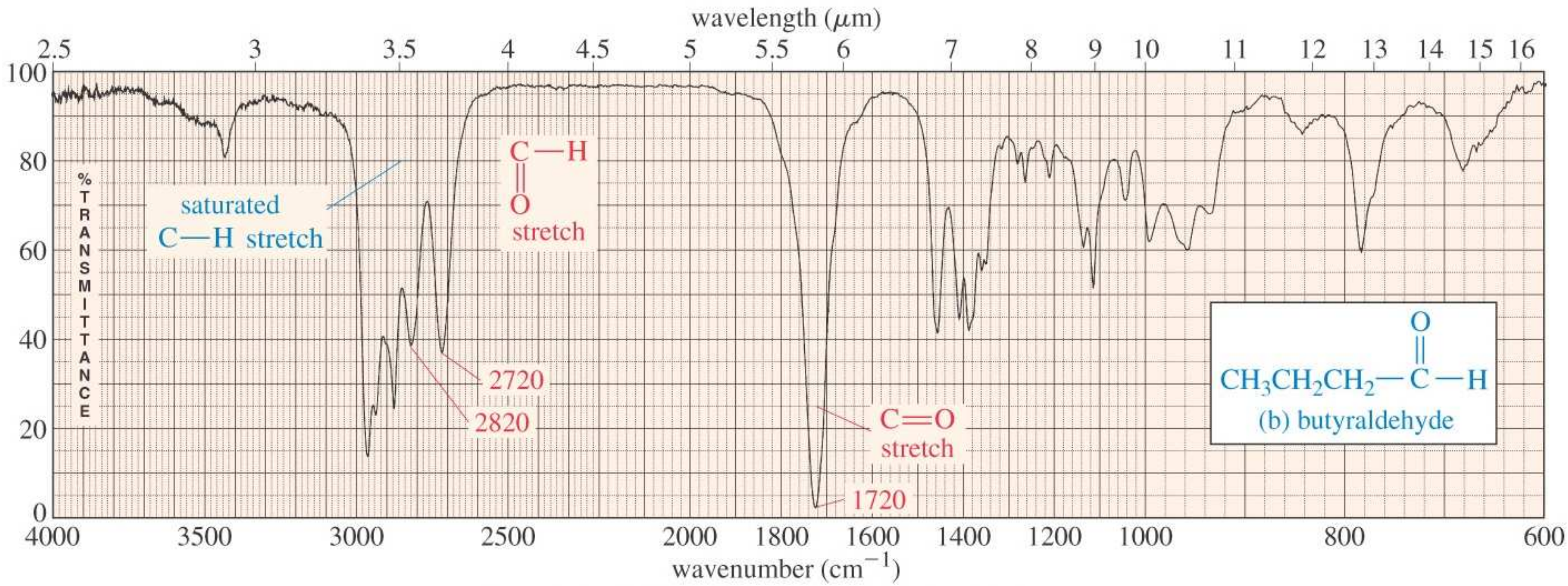
An Aldehyde IR Spectrum





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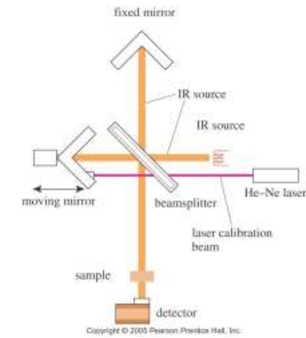
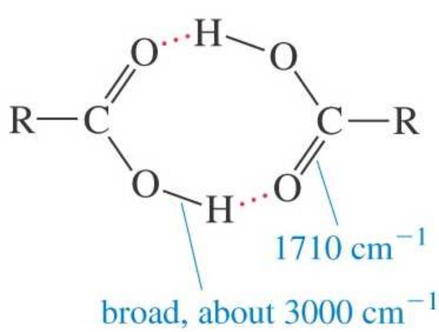
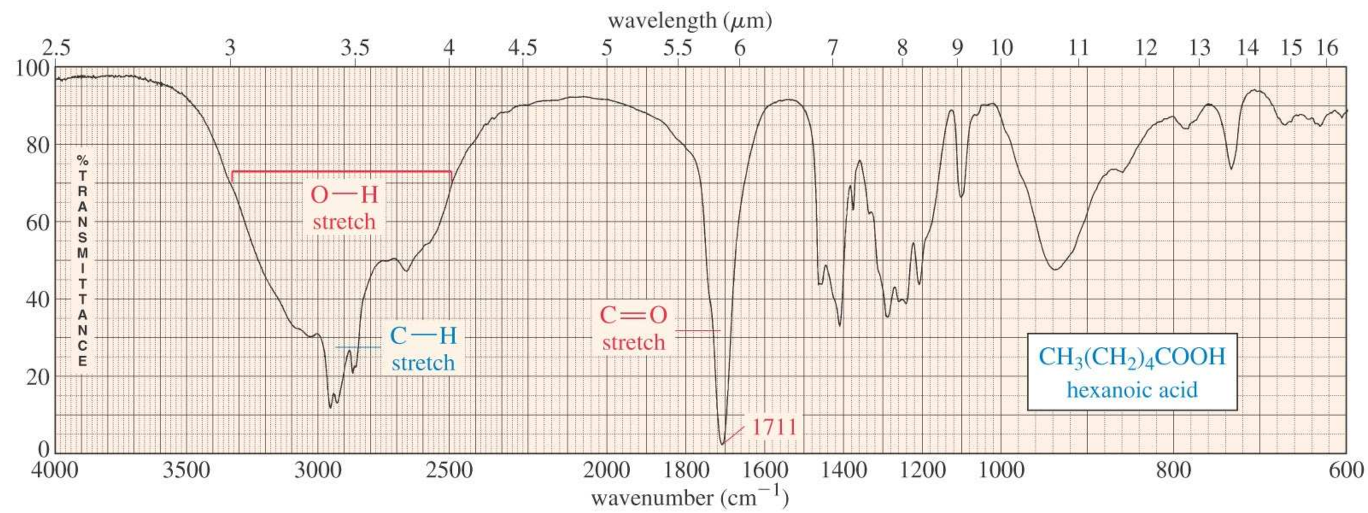


O-H Stretch of a Carboxylic Acid

This O-H absorbs broadly, 2500-3500 cm^{-1}, due to strong hydrogen bonding.





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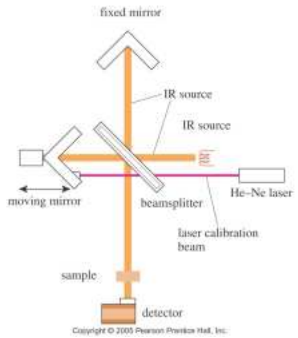
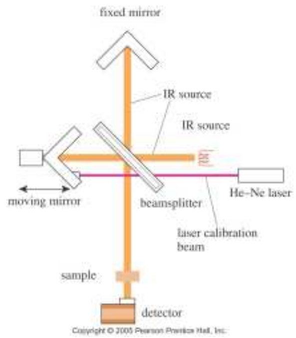
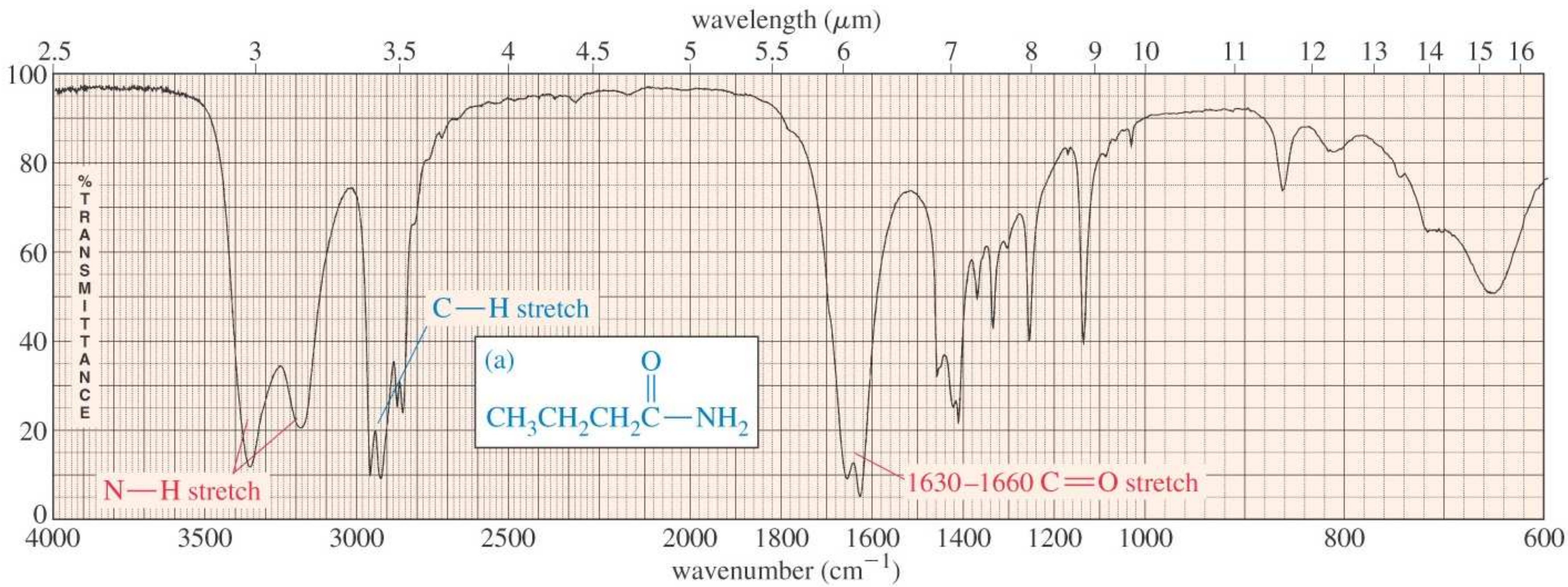
Variations in C=O Absorption



- Conjugation of C=O with C=C lowers the stretching frequency to ~1680 cm^{-1}.
- The C=O group of an amide absorbs at an even lower frequency, 1640-1680 cm^{-1}.
- The C=O of an ester absorbs at a higher frequency, ~1730-1740 cm^{-1}.
- Carbonyl groups in small rings (5 C's or less) absorb at an even higher frequency. =>

An Amide
IR Spectrum





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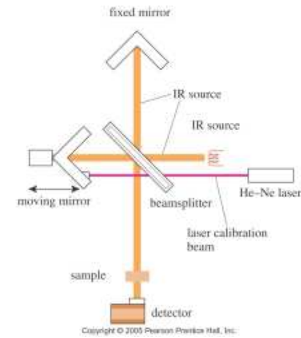
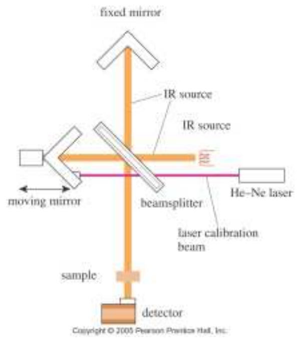
Carbon - Nitrogen Stretching

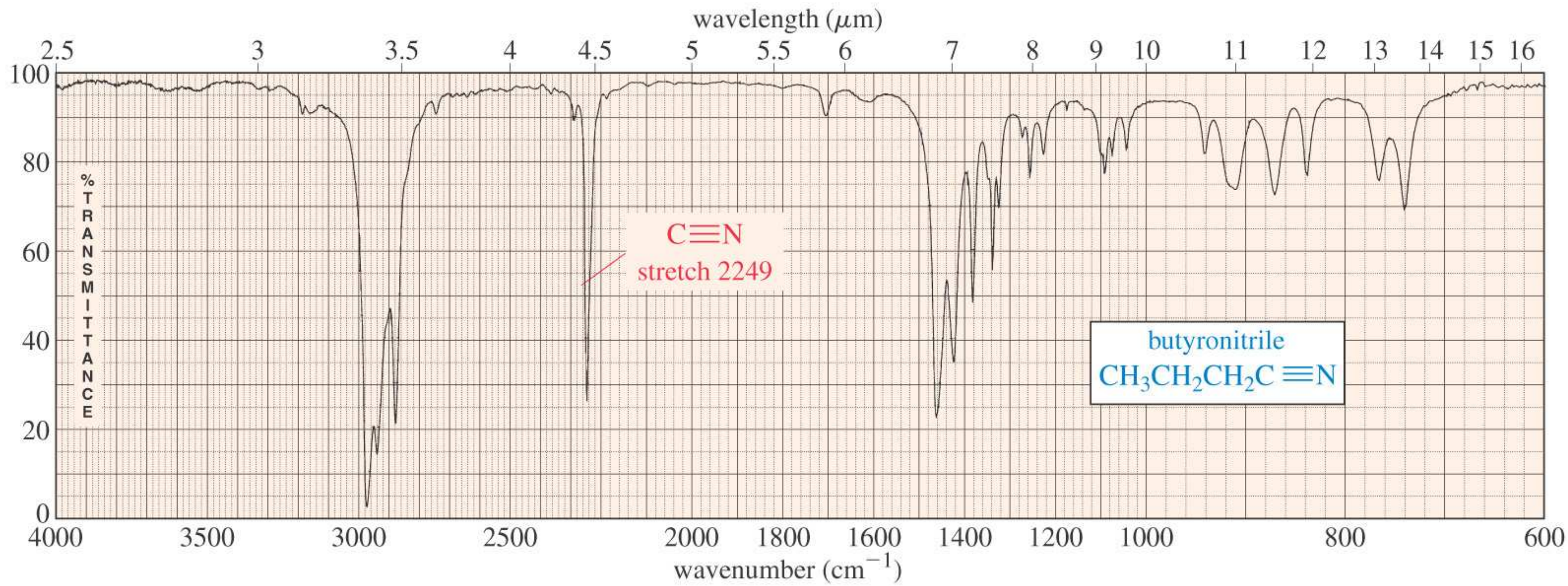


- C - N absorbs around 1200 cm^{-1}.
- C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.
- C ≡ N absorbs strongly just *above* 2200 cm^{-1}. The alkyne C ≡ C signal is much weaker and is just *below* 2200 cm^{-1} .

=>

A Nitrile
IR Spectrum





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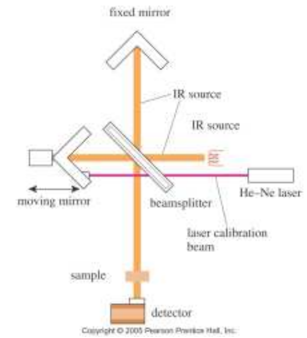
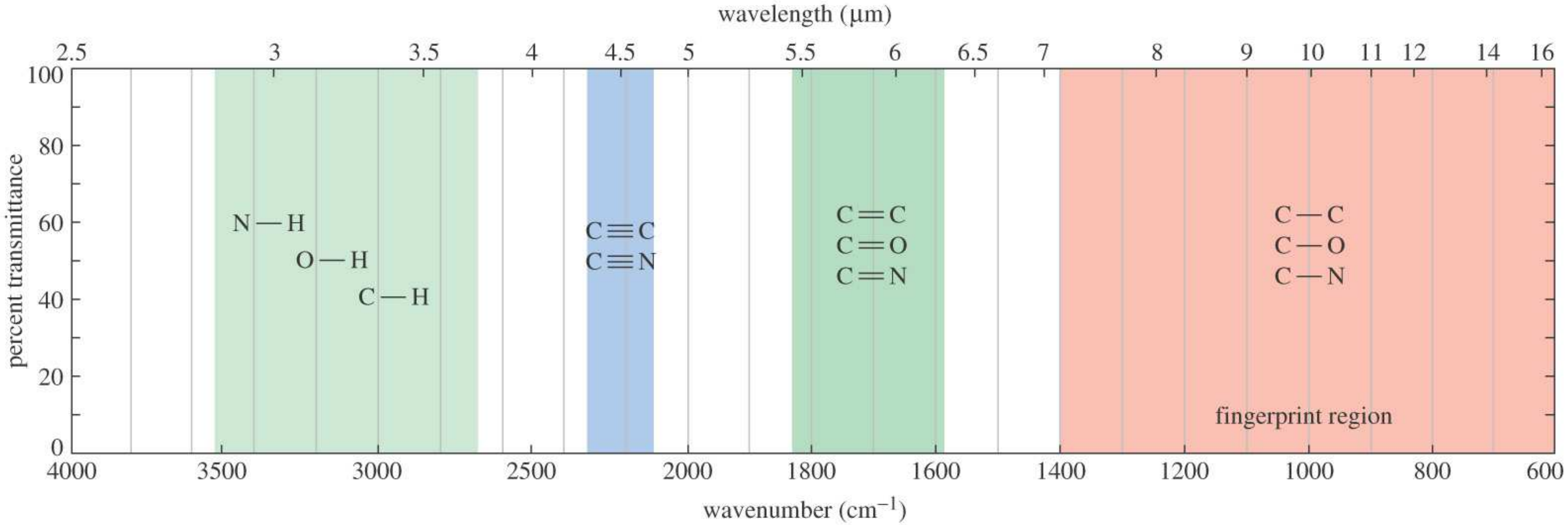
Summary of IR Absorptions





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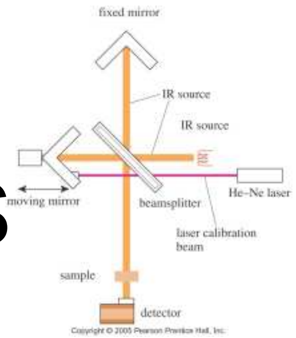
Strengths and Limitations



- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The functional group is usually indicated.
- The *absence* of a signal is definite proof that the functional group is absent.
- Correspondence with a known sample's IR spectrum confirms the identity of the compound.

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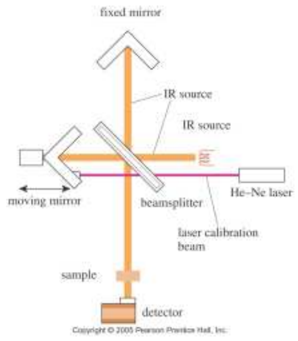

End of Chapter 12