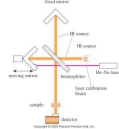


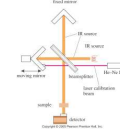
Organic Chemistry, 6th Edition
L. G. Wade, Jr.



Chapter 12 Mass Spectrometry and Infrared Spectroscopy

Jo Blackburn
Richland College, Dallas, TX
Dallas County Community College District
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Introduction



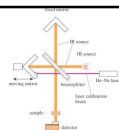
- Spectroscopy is an analytical technique which helps determine structure.
- It destroys little or no sample.
- The amount of light absorbed by the sample is measured as wavelength is varied.

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Types of Spectroscopy

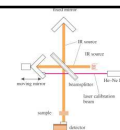


- Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.
- Mass spectrometry (MS) fragments the molecule and measures the masses.
- Nuclear magnetic resonance (NMR) spectroscopy detects signals from active nuclei and can be used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

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Electromagnetic Spectrum



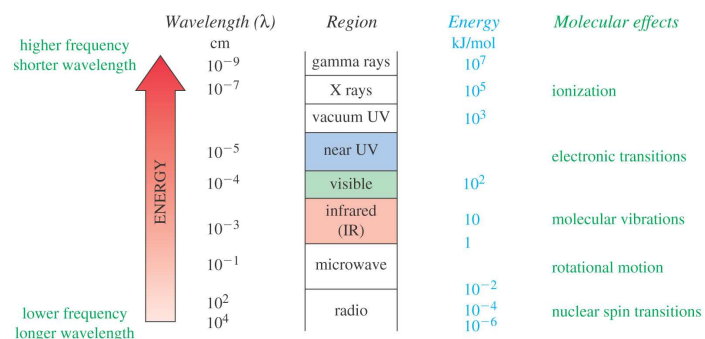
- Examples: X rays, microwaves, radio waves, visible light, IR, and UV.
- Frequency and wavelength are inversely proportional.
- $c = \lambda \nu$, where c is the speed of light ($3.00 \times 10^8 \text{ m/s}$)
- Energy per photon = $h\nu$, where h is Planck's constant, $6.62 \times 10^{-37} \text{ kJ}\cdot\text{sec}$.

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The Spectrum and Molecular Effects



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Mass Spectrometry

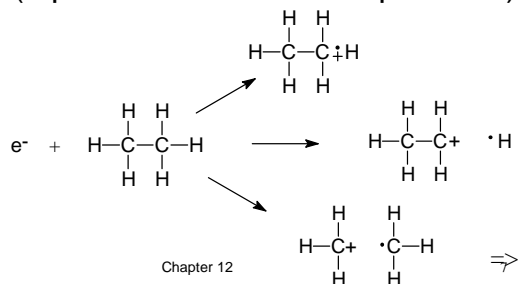
- Molecular weight can be obtained from a very small sample (but it is destroyed).
- It does not involve the absorption or emission of light.
- A beam of high-energy electrons breaks the molecule apart.
- The masses of the fragments and their relative abundance reveal information about the structure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

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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^-).



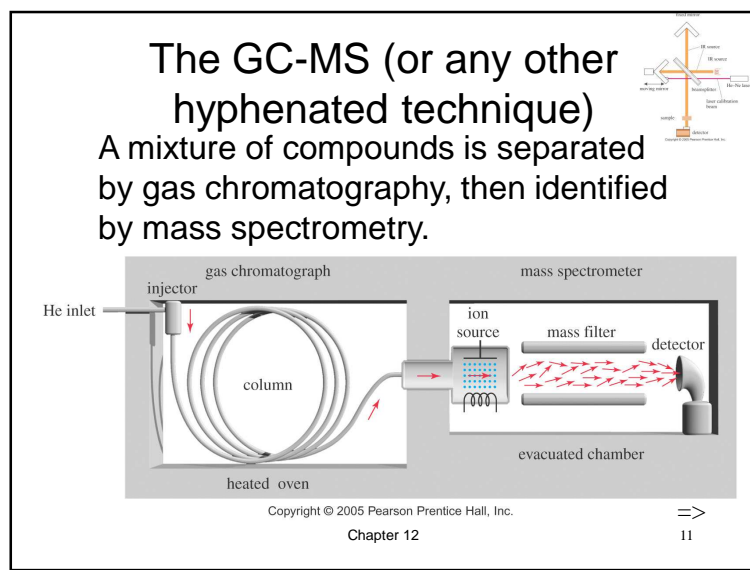
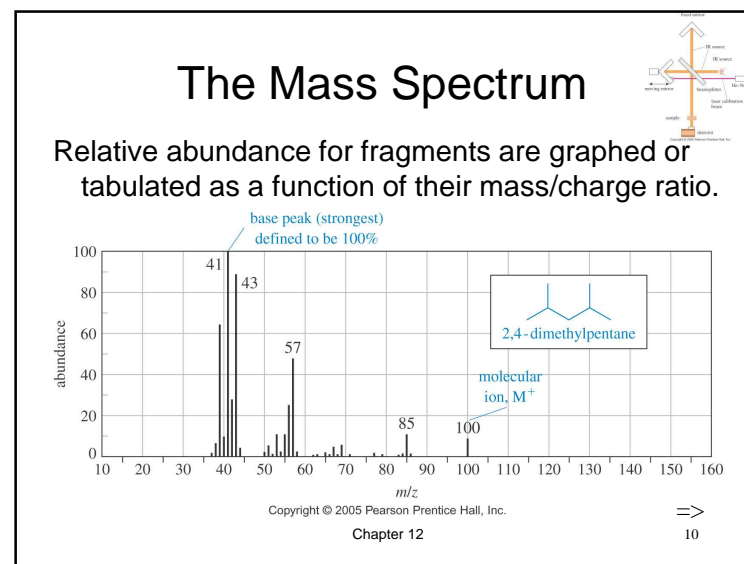
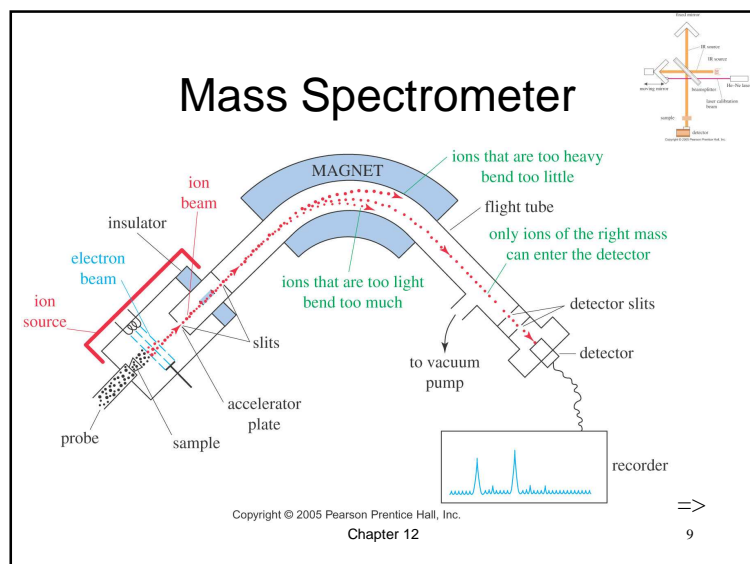
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Separation of Ions

- 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. =>

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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

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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⁺. =>

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Isotopic Abundance

TABLE 12-4 Isotopic Composition of Some Common Elements

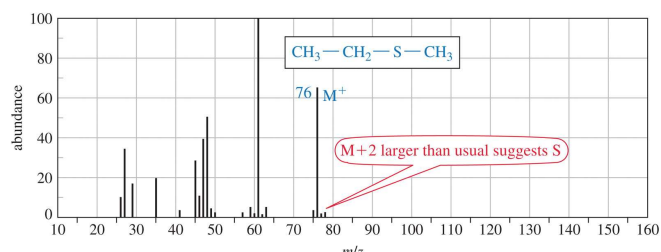
Element	M ⁺	M+1	M+2
hydrogen	¹ H	100.0%	
carbon	¹² C	98.9%	¹³ C 1.1%
nitrogen	¹⁴ N	99.6%	¹⁵ N 0.4%
oxygen	¹⁶ O	99.8%	¹⁸ O 0.2%
sulfur	³² S	95.0%	³³ S 0.8%
chlorine	³⁵ Cl	75.5%	³⁷ Cl 24.5%
bromine	⁷⁹ Br	50.5%	⁸¹ Br 49.5%
iodine	¹²⁷ I	100.0%	

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Mass Spectrum with Sulfur

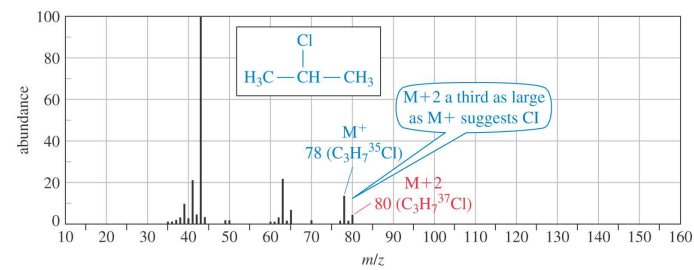


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Mass Spectrum with Chlorine

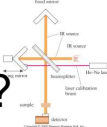


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What information we will obtain from mass spectra?

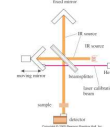


- The mass of the molecular ion.
- What for?
 - To compare the mass of the molecular ion with the mass of the empirical formula of the compound under study.
 - If the molecular ion is twice as heavy as the mass of the empirical formula for the compound, then the molecular formula will be twice the empirical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

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The UV-Vis Region



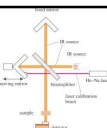
- Provides information regarding electronic structure.
- Just above violet in the visible region
- Wavelengths usually 200-750nm
- For wavelengths below 200nm, vacuum is required.

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The UV-Vis Region



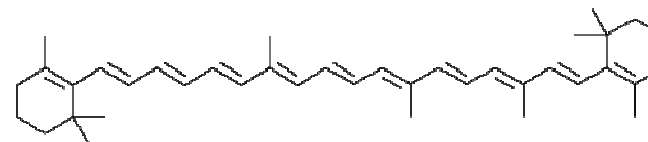
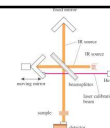
- Mostly used for systems with conjugated double bonds.
- 1-octene $\lambda_{\max}=180\text{nm}$
- 1,3-butadiene $\lambda_{\max}=220\text{nm}$
- 1,3,5-hexatriene $\lambda_{\max}=250\text{nm}$

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The UV-Vis Region

 β -carotene $\lambda_{\max}=480\text{nm}$

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

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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.

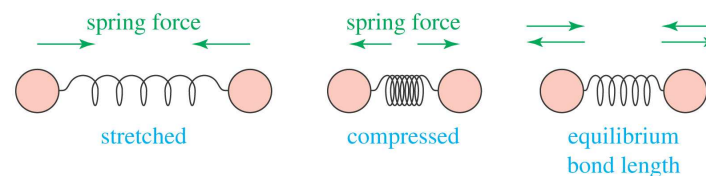
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Molecular Vibrations

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})
<i>Frequency decreases with increasing atomic mass</i>		
C—H	420 (100) <note these are trs>	3000
C—D	420 (100)	2100
C—C	350 (83)	1200
<i>Frequency increases with bond energy</i>		
C—C	350 (83)	1200
C=C	611 (146)	1660
C≡C	840 (200)	2200

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

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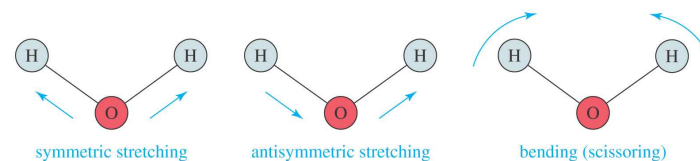
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Vibrational Modes

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

Linear molecules will have $3n - 5$ modes.



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Fingerprint of Molecule

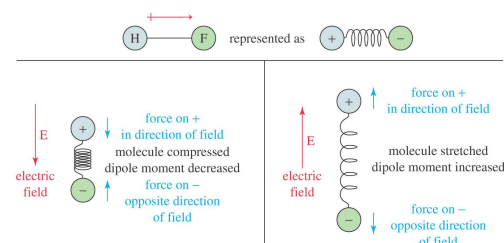
- Whole-molecule vibrations and bending vibrations are also quantized.
- No two molecules will give exactly the same IR spectrum (except enantiomers).
- Simple stretching: $1600\text{-}3500\text{ cm}^{-1}$.
- Complex vibrations: $600\text{-}1400\text{ cm}^{-1}$, called the "fingerprint region."

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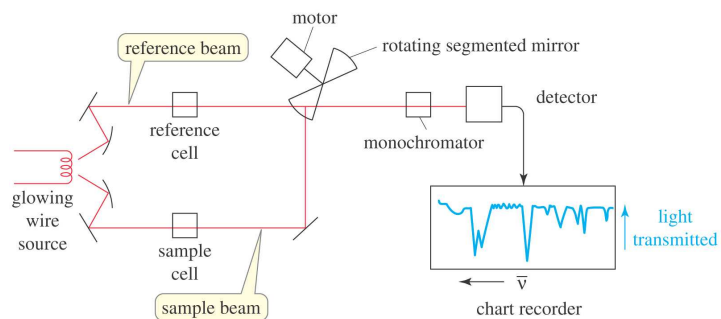
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IR-Active and Inactive

- 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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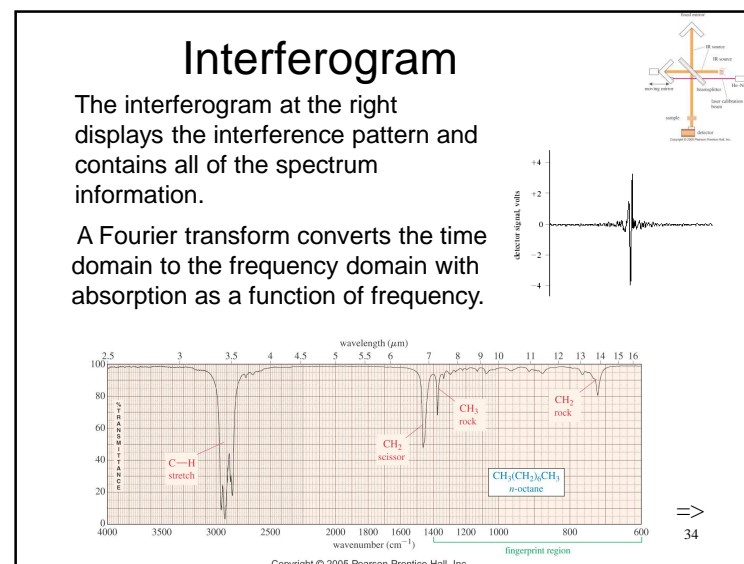
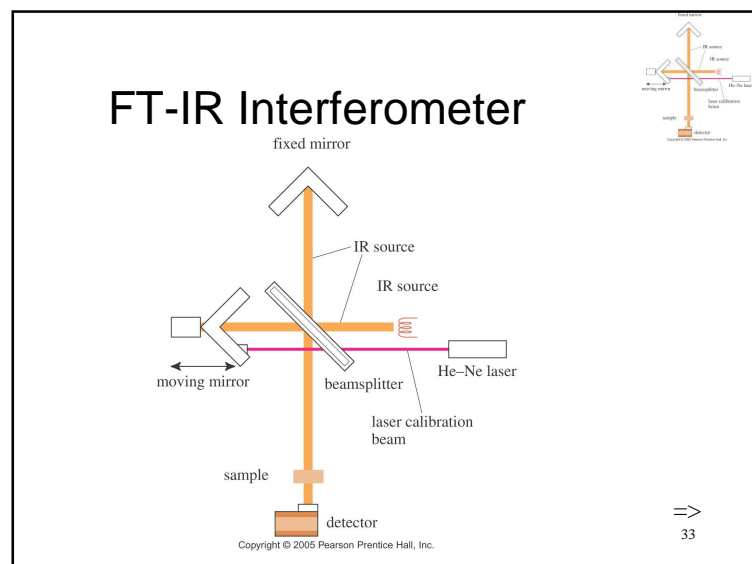
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FT-IR Spectrometer

- 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.

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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}

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Carbon-Hydrogen Stretching

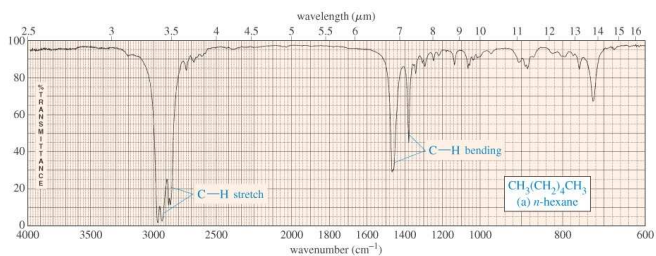
Bonds with more s character absorb at a higher frequency.

- 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}

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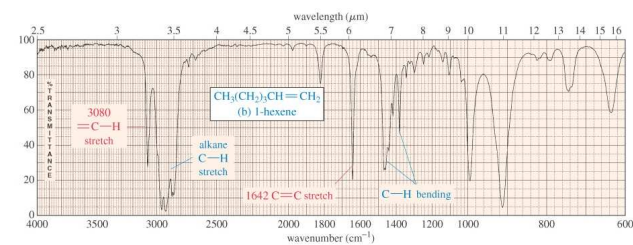
An Alkane IR Spectrum



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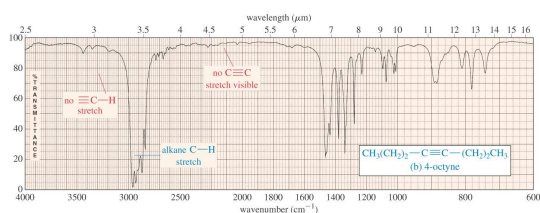
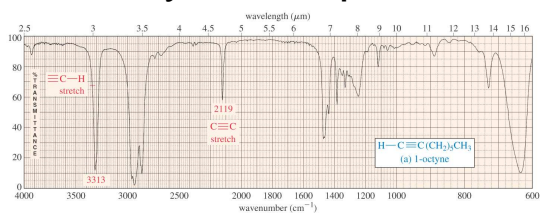
An Alkene IR Spectrum



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An Alkyne IR Spectrum



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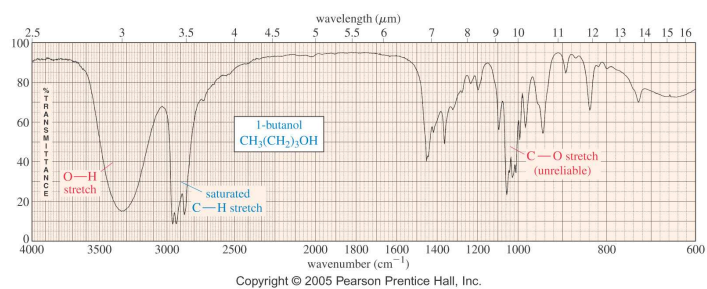
O-H and N-H Stretching

- 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).

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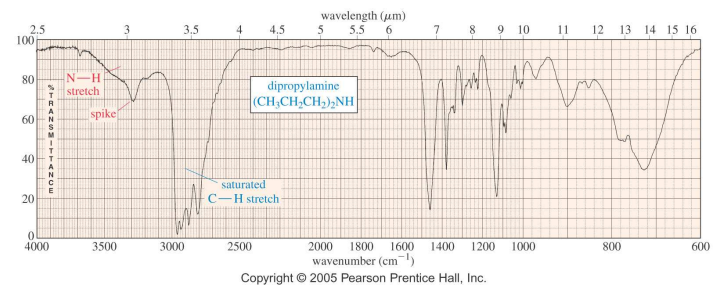
An Alcohol IR Spectrum



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An Amine IR Spectrum



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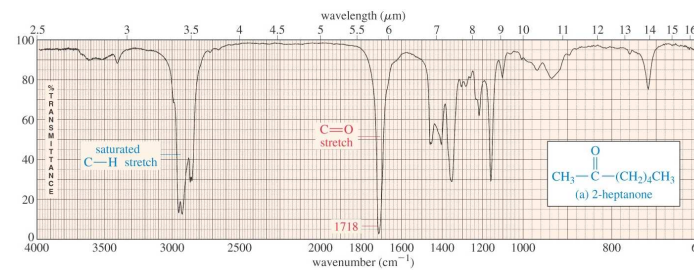
Carbonyl Stretching

- 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} .

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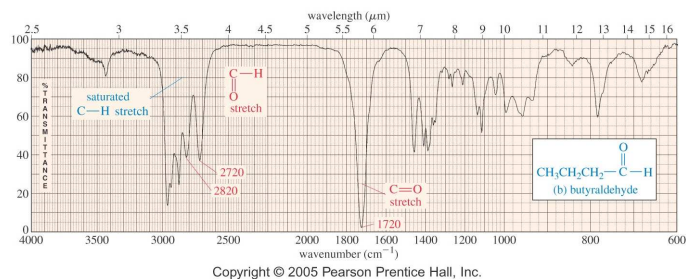
A Ketone IR Spectrum



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An Aldehyde IR Spectrum

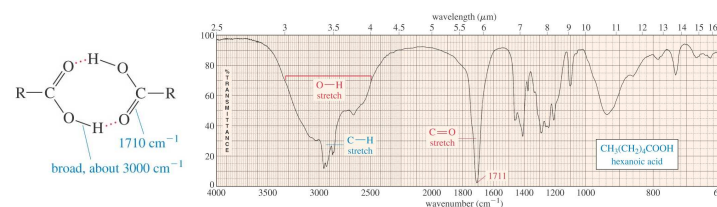


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O-H Stretch of a Carboxylic Acid

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



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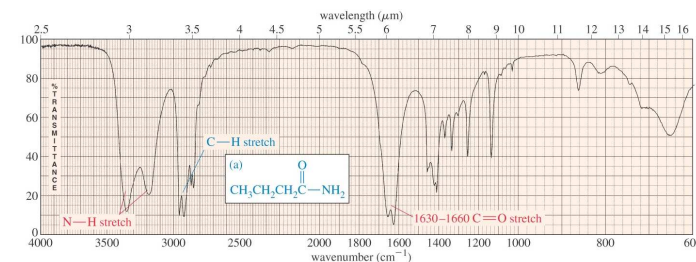
Variations in C=O Absorption

- Conjugation of C=O with C=C lowers the stretching frequency to $\sim 1680 \text{ cm}^{-1}$.
- 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, $\sim 1730\text{-}1740 \text{ cm}^{-1}$.
- Carbonyl groups in small rings (5 C's or less) absorb at an even higher frequency. =>

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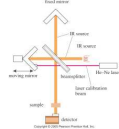
An Amide IR Spectrum



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Carbon - Nitrogen Stretching



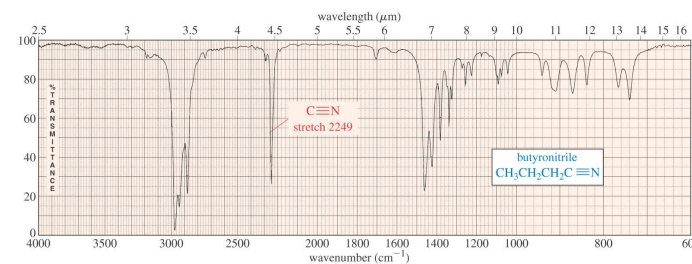
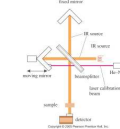
- C - N absorbs around 1200 cm^{-1} .
- C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.
- C \equiv N absorbs strongly just *above* 2200 cm^{-1} . The alkyne C \equiv C signal is much weaker and is just *below* 2200 cm^{-1} .

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A Nitrile IR Spectrum



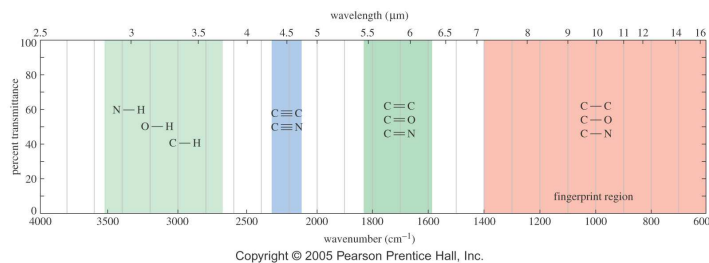
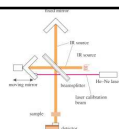
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Summary of IR Absorptions



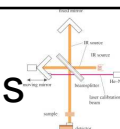
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Strengths and Limitations

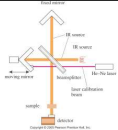


- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The functional group is usually indicated.
- The *absence* of a signal is definite proof that the functional group is absent.
- Correspondence with a known sample's IR spectrum confirms the identity of the compound.

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End of Chapter 12

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