# COURSE : SC202 (CHEMISTRY)
DR. SANGITA TALUKDAR

SPECTROSCOPY

Spectroscopy: It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.

1. Infrared Spectroscopy
2. UV-Visible Spectroscopy
3. ^{1}H- NMR Spectroscopy

Electromagnetic radiation: It is a simple harmonic wave that travels in straight line until it is reflected or refracted like light and other forms of radiant energy.
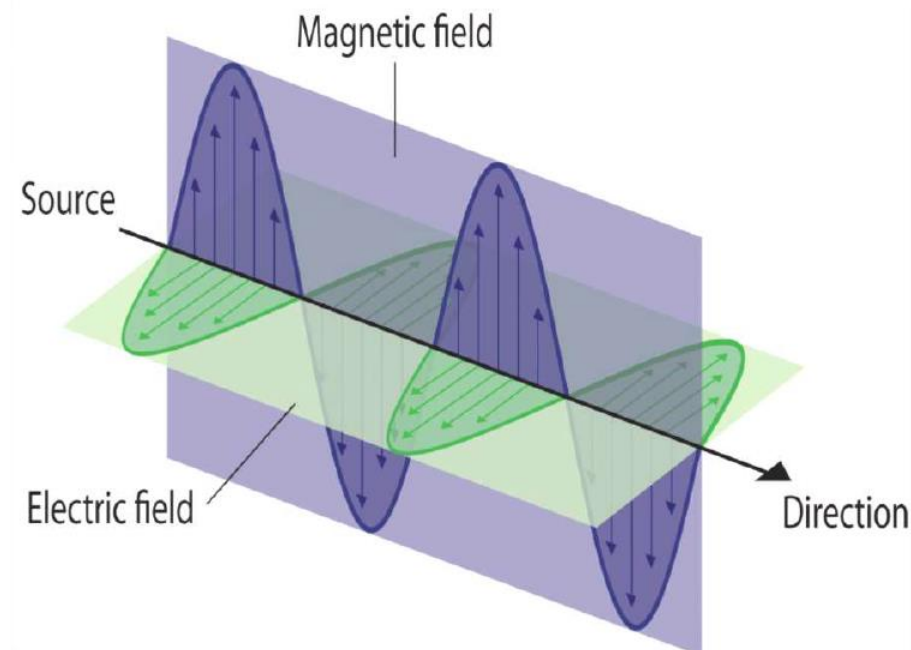
Electromagnetic Radiation

We can represent a light wave travelling through space by a sinusoidal trace as in figure 1.1. In this diagram λ is the *wavelength* of the light
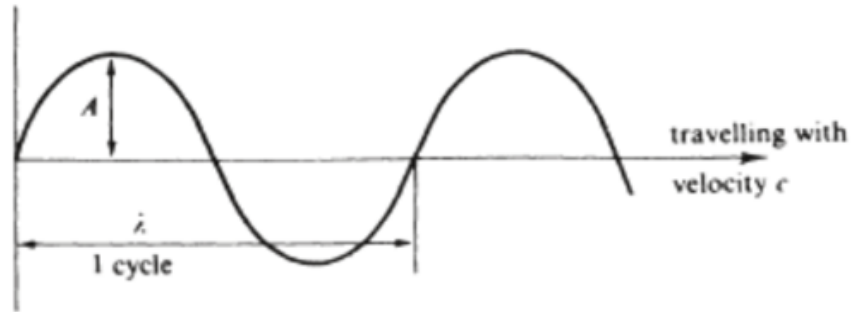
Wavelength (λ): the distance between consecutive peaks on a wave.

Frequency (v): the number of full cycles of a wave that pass a given point in a second.

**Hertz (Hz):** the unit in which radiation frequency is reported; s^{-1}

Common units used to express wavelength

Unit	Relation to Meter
Meter (m)	----
Millimeter (mm)	1 mm = 10^{-3} m
Micrometer (µm)	1 µm = 10^{-6} m
Nanometer (nm)	1 nm = 10^{-9} m
Angstrom (Å)	1 Å = 10^{-10} m

Energy of the electromagnetic radiation:

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

where E = energy of the radiation in joules/J, h = Planck's constant/6.626 x 10^{-34} J s, ν = frequency of the radiation/Hz, c = velocity of light /2.998 x 10^8 ms^{-1} , λ = wavelength/m .
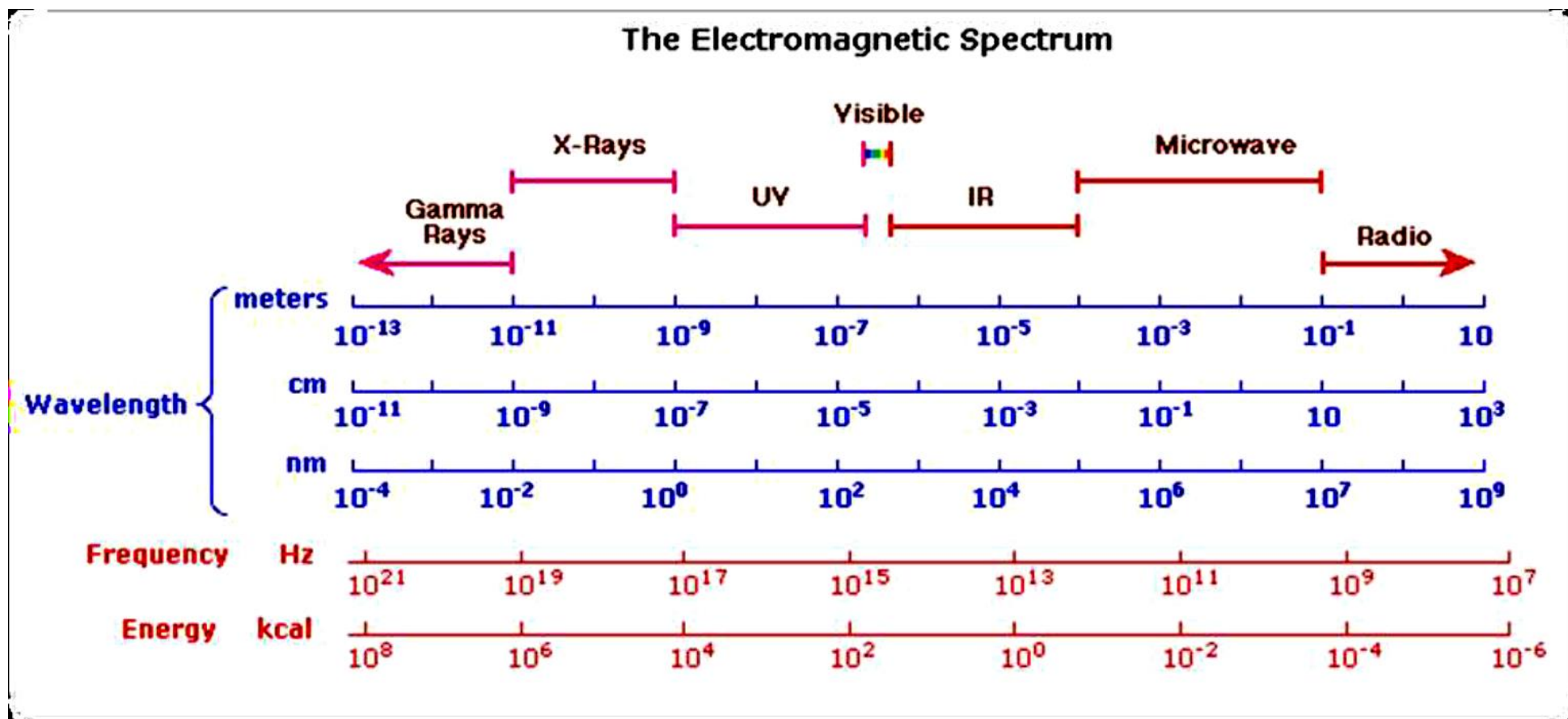
We will study three types of molecular spectroscopy

Region of the Electromagnetic Spectrum	Type of Spectroscopy	Absorption of Electromagnetic Radiation Results in Transition Between
Radio fequency	Nuclear magnetic resonance	Nuclear spin states
Infrared	Infrared	Vibrational energy levels
Ultraviolet-visible	Ultraviolet-visible	Electronic energy levels

Interaction of EMR with matter

1. Electronic Energy Levels:

• At room temperature the molecules are in the lowest energy levels E_o.

• When the molecules absorb UV-visible light from EMR, one of the outermost bond / lone pair electron is promoted to higher energy state such as E_1, E_2, …E_n, etc is called as electronic transition and the difference is as: $\Delta E = h\nu = E_n - E_0$ where (n = 1, 2, 3, … etc) $\Delta E = 35$ to 71 kcal/mole.

2. Vibrational Energy Levels:

- The spacing between energy levels are relatively small i.e. 0.01 to 10 kcal/mole.

- e.g. when IR radiation is absorbed, molecules are excited from one vibrational level to another or it vibrates with higher amplitude.

3. Rotational Energy Levels:

• These energy levels are quantized & discrete.

• The spacing between energy levels are even smaller than vibrational energy levels.

$$\Delta E_{rotational} < \Delta E_{vibrational} < \Delta E_{electronic}$$

UV – Visible Spectroscopy

- It is also known as electronic spectroscopy.
- **The strength of electronic spectroscopy lies in its ability to measure the extent of multiple bond or aromatic conjugation within molecules.**
- Electronic spectroscopy can, in general, differentiate conjugated dienes from non conjugated dienes, conjugated dienes from conjugated trienes, αβ-unsaturated ketones from their γδ-analogs, etc.
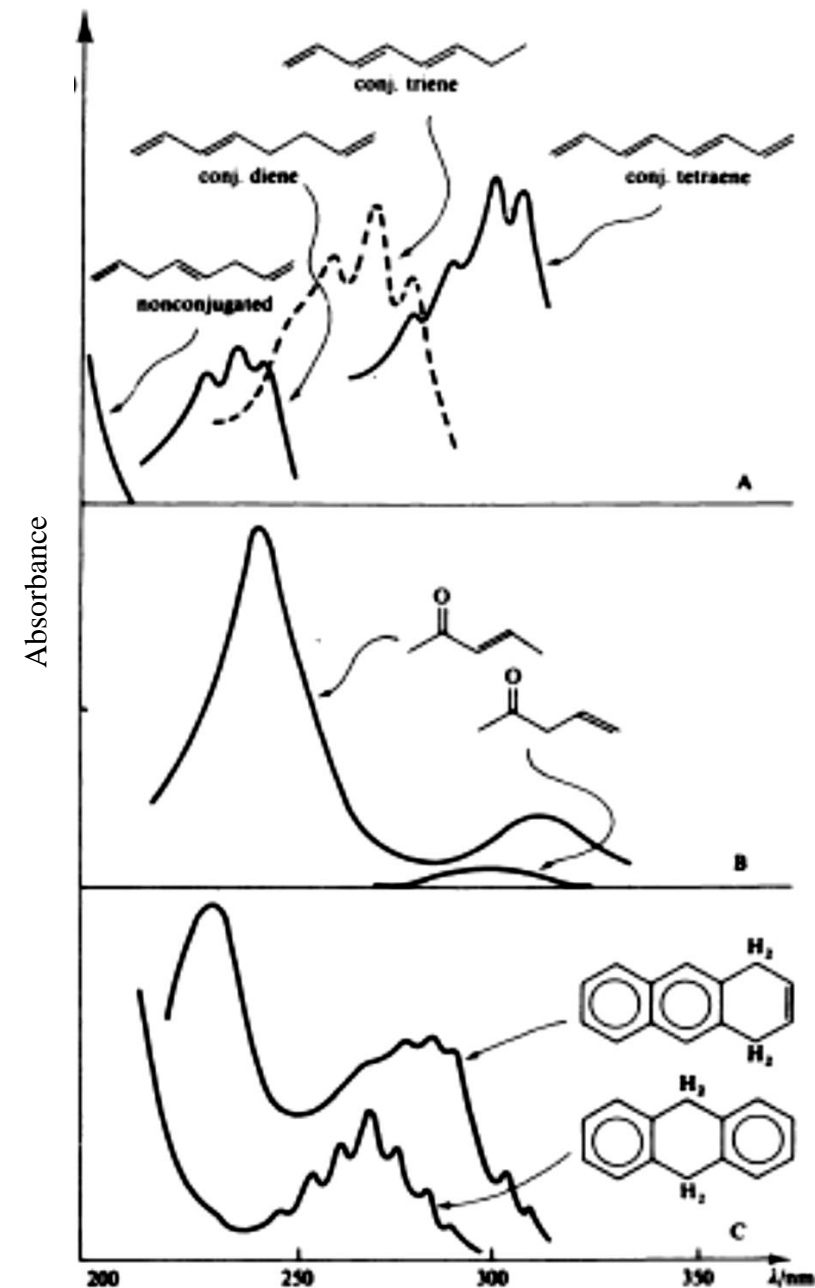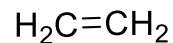
Terms used in UV / Visible Spectroscopy

Chromophores : The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n → π* & π → π* transitions.
 e.g. NO_2, C=O, C≡N, C=C, C=S, etc.
Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.
e.g.

$H_2C=CH_2$
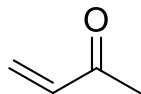
$\lambda = 171$ nm $\lambda = 279$ nm $\lambda = 290$ nm

Auxochrome refers to the functional group that could enhance the color-imparting properties of a chromophore without being itself a chromophore, e.g. - OR, $-NH_2$, $-NR_2$, etc .

Bathochromic shift: When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
• The effect is due to presence of an auxochrome or by the change of solvent.
• e.g. An auxochrome group like –OH, $-OCH_3$ causes absorption of compound at longer wavelength.

Hypsochromic shift: When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.
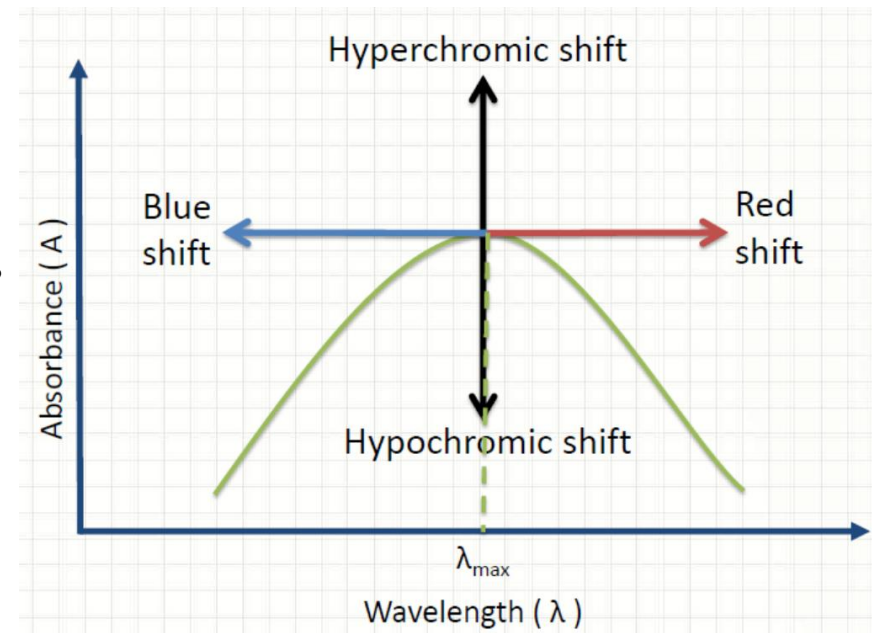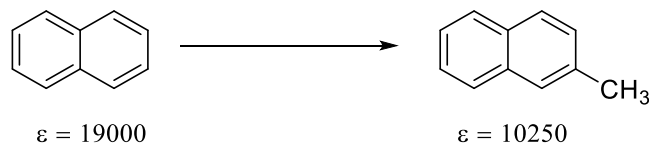
e.g. aniline shows blue shift in acidic medium as it loses conjugation.

Aniline
$\lambda = 280$ nm

$\lambda = 265$ nm
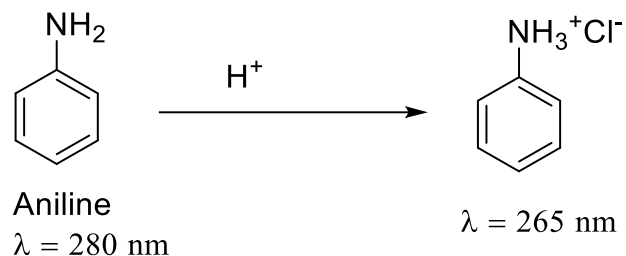
Hyperchromic Shift: When the absorption intensity of a compound is increased, it is called hyperchromic shift.

Pyridine
$\varepsilon = 2750$

2-methyl pyridine
$\varepsilon = 3560$
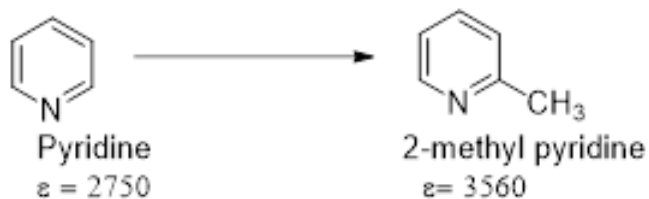
Hypochromic Shift: When the absorption intensity of a compound is decreased, it is called hypochromic shift.

$\varepsilon = 19000$

$\varepsilon = 10250$

Theory of electronic transitions
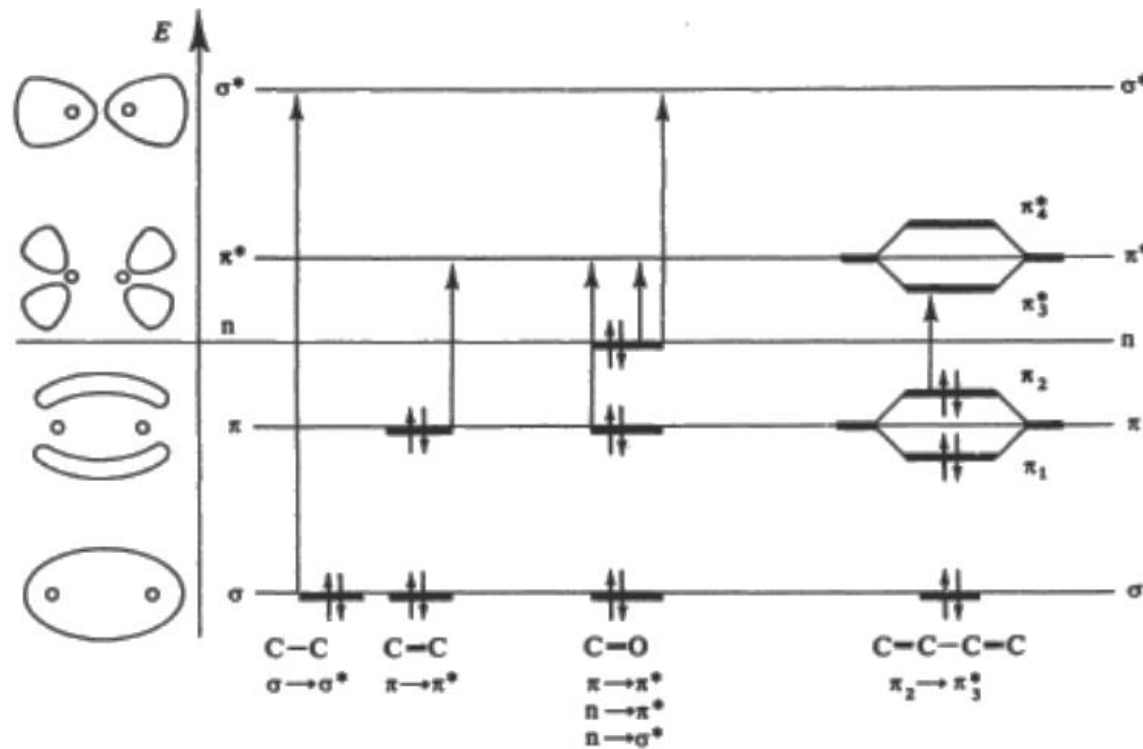
a. σ- σ^* transitions: e.g. Methane (CH_4) has C-H bond only and can undergo $\sigma \rightarrow \sigma^*$ transition. It is a high-energy process, and requires very -short-wavelength ultraviolet light (around 150 nm).

b. π-π^* transition: Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo $\pi \rightarrow \pi^*$ transitions

c. n-σ^* transition: Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of n $\rightarrow \sigma^*$ transition.

d. n-π^* transition: this n -π^* transition is 'forbidden' in symmetry terms and therefore the intensity is low, although the wavelength is long (around 280 nm).

e. **Conjugated dienes show absorption at much longer wavelength than do isolated alkene groups**, a typical value being around 217 nm.

Lambert's Law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light.

$$A = \epsilon l$$

Beer's Law

When a monochromatic radiation is passed through a solution, the decrease in the intensity of the radiation with the thickness of the solution is directly proportional to the intensity of the incident light as well as concentration of the solution.

They are most conveniently used as the combined **Beer-Lambert law**:

$$\log I_o/I = \epsilon c l \text{ or } A = \epsilon c l$$

where I_o is the intensity of the incident light (or the light intensity passing through a reference cell),
I is the light transmitted through the sample solution ,
$\log I_o/I$ is the *absorbance (A)* of the solution (formerly called the *optical density , OD)* ,
c is the concentration of solute (in mol L^{-1}, mol dm -3) ,
I is the path length of the sample (in cm, m x 10^{-2}) and
ϵ is the *molar absorptivity* (formerly called the *molecular extinction coefficient,* in l mol^{-1} cm^{-1} , m^2 mol^{-1} x 10^{-2} .

Derivation of Beer-Lambert's Law
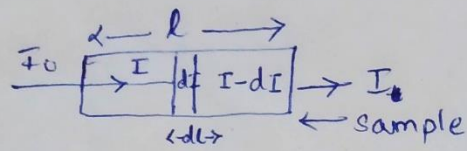
$$-\frac{dI}{I} \propto [C] \cdot dl$$

$$\frac{-dI}{I} = a[C]dl$$

Integrating the above equation

$$\int_{I_0}^{I} \frac{-dI}{I} = a \int_{0}^{l} [C]dl$$

$$\Rightarrow -\ln \frac{I}{I_0} = a[C] \cdot l$$

$$\Rightarrow 2.303 \log I/I_0 = -a[C] \cdot l$$

$$\Rightarrow \log I/I_0 = -\epsilon [C] \cdot l \longrightarrow \text{①} \quad \left[\frac{a}{2.303} = \epsilon\right.$$

$$\Rightarrow \frac{I}{I_0} = 10^{-\epsilon[C]l}$$

$$\Rightarrow I = I_0 \cdot 10^{-\epsilon Cl}$$

$$\text{Transmittance, } T = \frac{I}{I_0}$$

INFRARED SPECTROSCOPY

- The vibrational IR extends from 2.5 x 10^{-6} m (2.5 μm) to 2.5 x 10^{-5} m (25 μm)

  - the frequency of IR radiation is commonly expressed in wavenumbers

  - wavenumber ($\bar{\nu}$): the number of waves per centimeter, with units cm^{-1}

  - expressed in wavenumbers, the vibrational IR extends from 4000 cm^{-1} to 400 cm $^{-1}$

- **The transitions involved in infrared absorption are associated with *vibrational* changes within the molecule**; for example, the band near 3000 cm^{-1} (that is, corresponding to 9.3 x 1013 Hz) has exactly the same frequency as a C-H bond undergoing *stretching vibrations.*

- **Infrared spectroscopy is therefore basically vibrational spectroscopy**.

- *Different bonds* (C-C, C=C, C-O, C=O, O-H, N-H, *etc.) have different vibrational frequencies, and we can detect the presence of these bonds in an organic molecule by identifying this characteristic frequency as an absorption band in the infrared spectrum.*
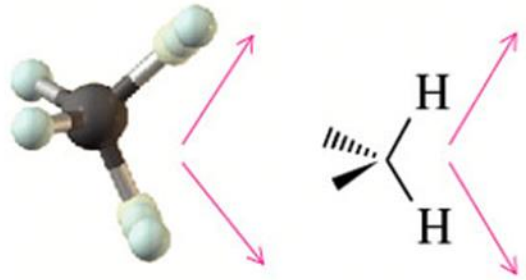
Molecular Vibrations

❑ For a molecule to absorb IR radiation

  ▪ the bond undergoing vibration must be polar and

  ▪ its vibration must cause a periodic change in the bond dipole moment

❑ Covalent bonds which do not meet these criteria are said to be IR inactive

  ▪ the C-C double and triple bonds of symmetrically substituted alkenes and alkynes,

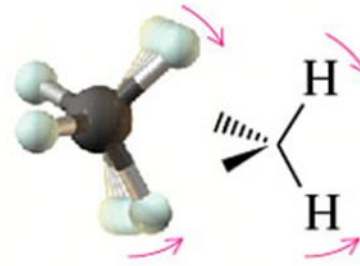   for example, are IR inactive because they are not polar bonds
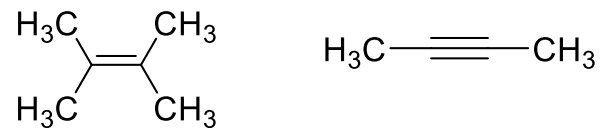
❑ For a nonlinear molecule containing *n* atoms, there are **3*n* - 6** allowed fundamental vibrations.

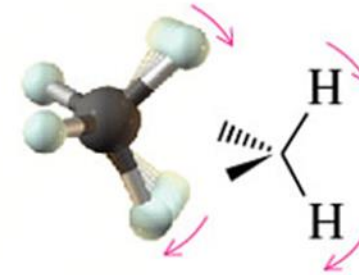 The simplest vibrational motions are bending and stretching.

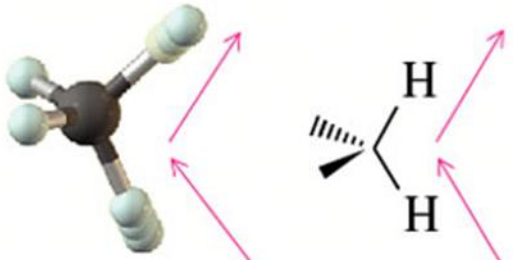# Fundamental stretching and bending vibrations for a methylene group
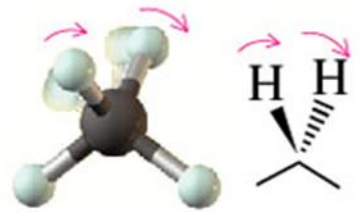

Symmetric stretching

Asymmetric stretching

Stretching vibrations

Scissoring

Rocking

Wagging
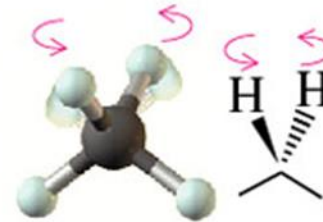
Twisting

Bending vibrations

© 2006 Brooks/Cole - Thomson

Calculation of Vibrational Frequencies

▪ Consider two covalently bonded atoms as two vibrating masses connected by a spring

- the total energy is proportional to the frequency of vibration

- the frequency of a stretching vibration is given by an equation derived from Hooke's law for a vibrating spring

$$\bar{\nu} = 4.12 \sqrt{\frac{K}{\mu}}$$

K = a force constant, which is a measure of the bonds' strength; force constants for single, double, and triple bonds are approximately 5, 10, and 15 x 10^5 dynes/cm

μ = reduced mass of the two atoms, $(m_1 m_2)/(m_1 + m_2)$, where m is the mass of the atoms in grams

- *The vibrational frequency of a bond is expected to increase when the bond strength increases, and also when the reduced mass of the system decreases.*

Thus, C=C and C=O *str* will have higher frequencies than C-C and C-O *str*, respectively: we also expect to find C-H and O-H *str* absorptions at higher frequencies than C-C and C-O *str*.

Hydrocarbons

Hydro-carbon	Vibration	Frequency (cm^{-1})	Intensity
Alkane			
C-H	Stretching	2850 - 3000	Medium
	Bending	1450-1475	Medium
CH$_3$	Bending	1375 and 1450	Weak to medium
C-C	(Not useful for interpretation - too many bands		
Alkene			
C-H	Stretching	3000 - 3100	Weak to medium
C=C	Stretching	1600 - 1680	Weak to medium
Alkyne			
C-H	Stretching	3300	Medium to strong
C≡C	Stretching	2100-2250	Weak
Arene			
C-H	Stretching	3030	Weak to medium
C=C	Stretching	1450-1600	Medium
C-H	Bending	690-900	Strong

Alkanes
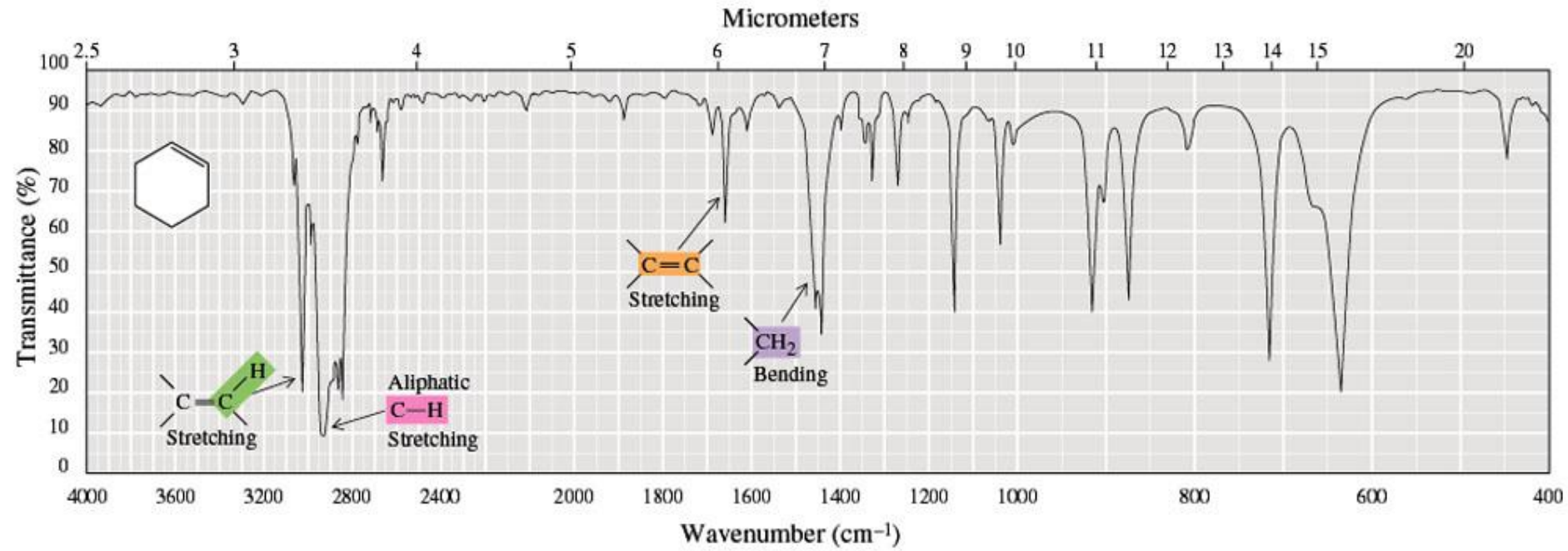
IR spectrum of decane
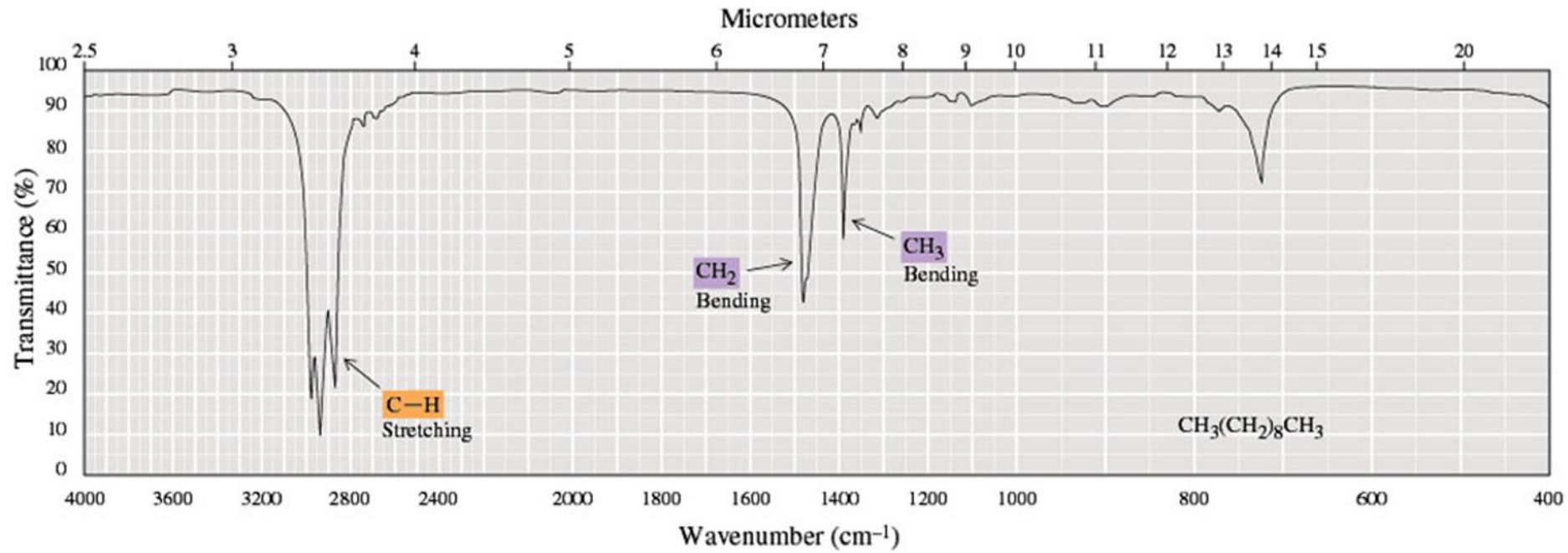
© 2006 Brooks/Cole - Thomson

Alkenes

IR spectrum of cyclohexene

Alkynes

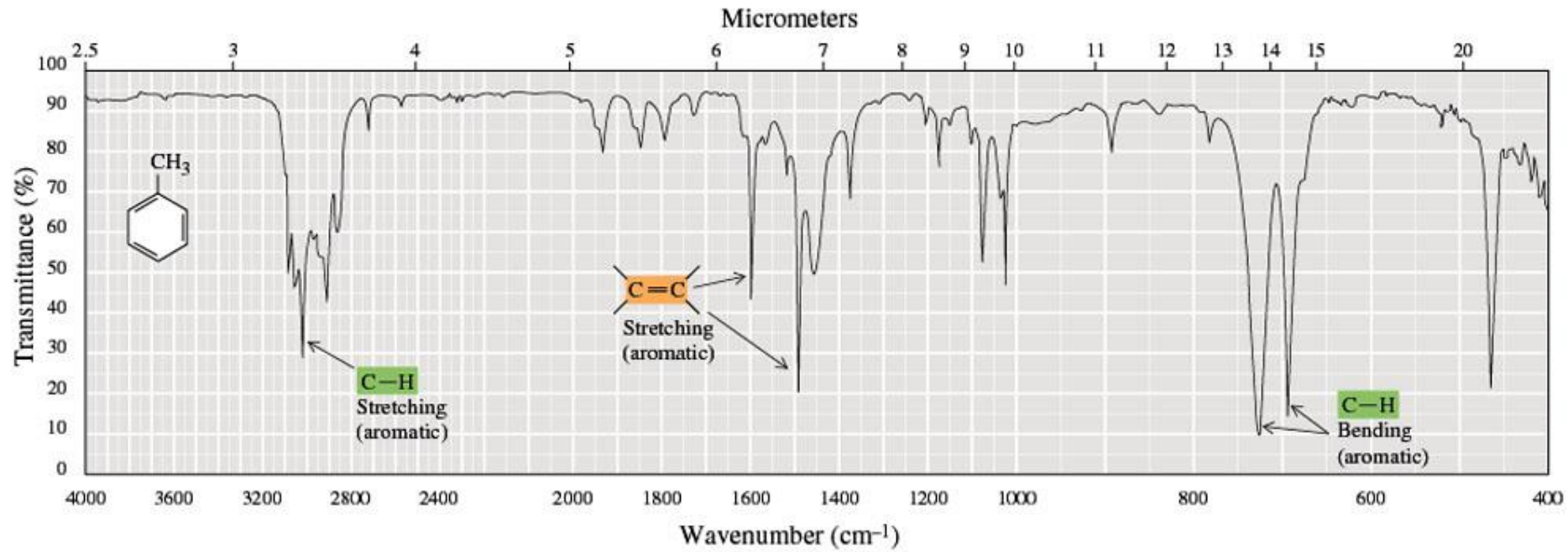## IR spectrum of 1-octyne

Micrometers

Transmittance (%) vs Wavenumber (cm^{-1})

$-C\equiv C-$ Stretching

$-C\equiv C-H$ Stretching

$CH_3(CH_2)_5C\equiv CH$
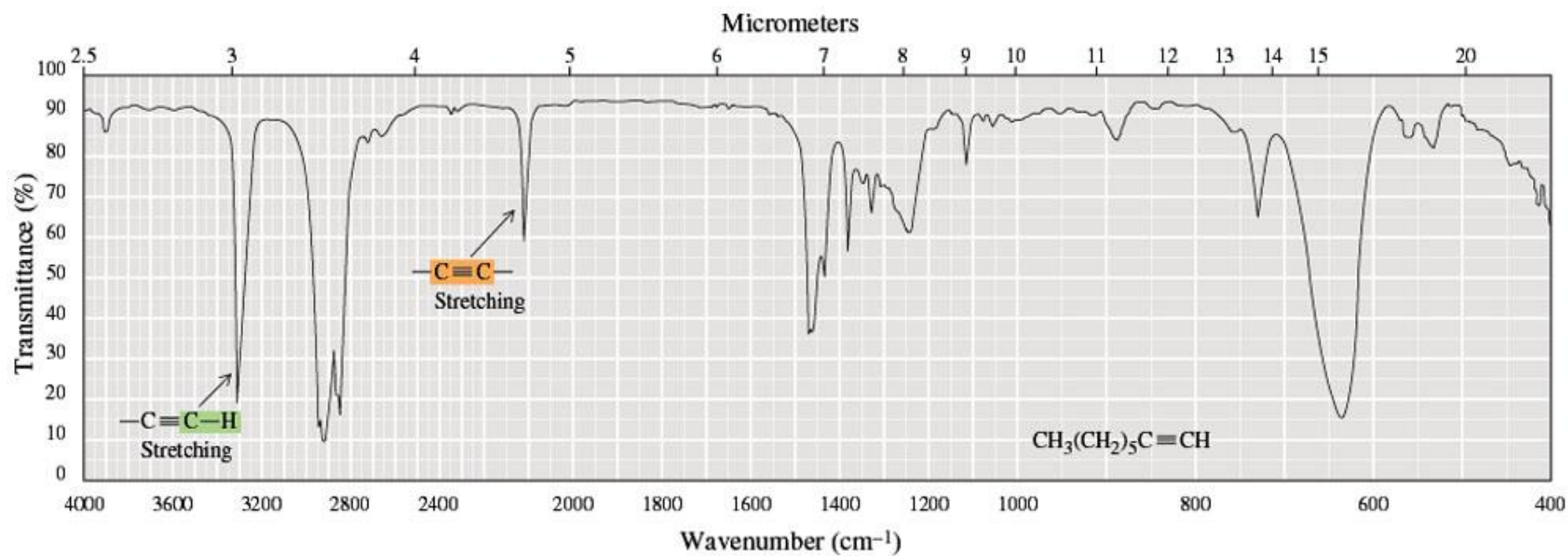
Aromatics

IR spectrum of toluene

Alcohols

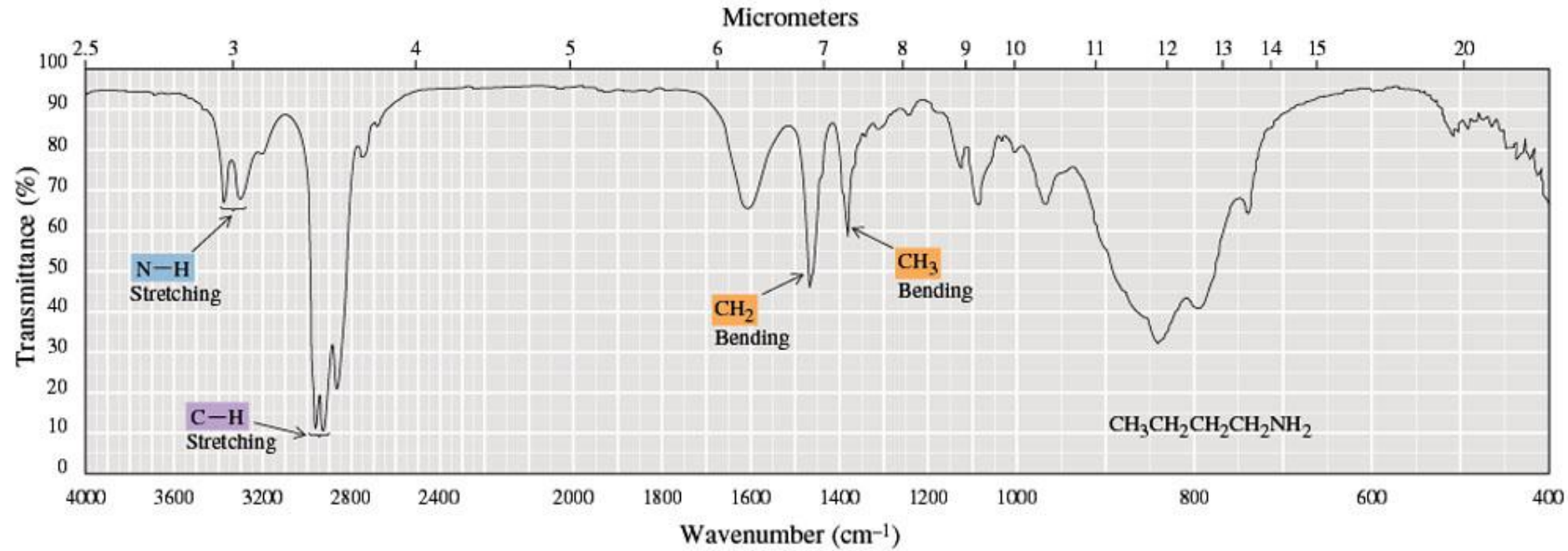| Bond	Frequency, cm^{-1}	Intensity
O-H (free)	3600-3650	Weak
O-H (H bonded)	3200 - 3500	Medium, broad
C-O	1000 - 1250	Medium

IR spectrum of 1-hexanol
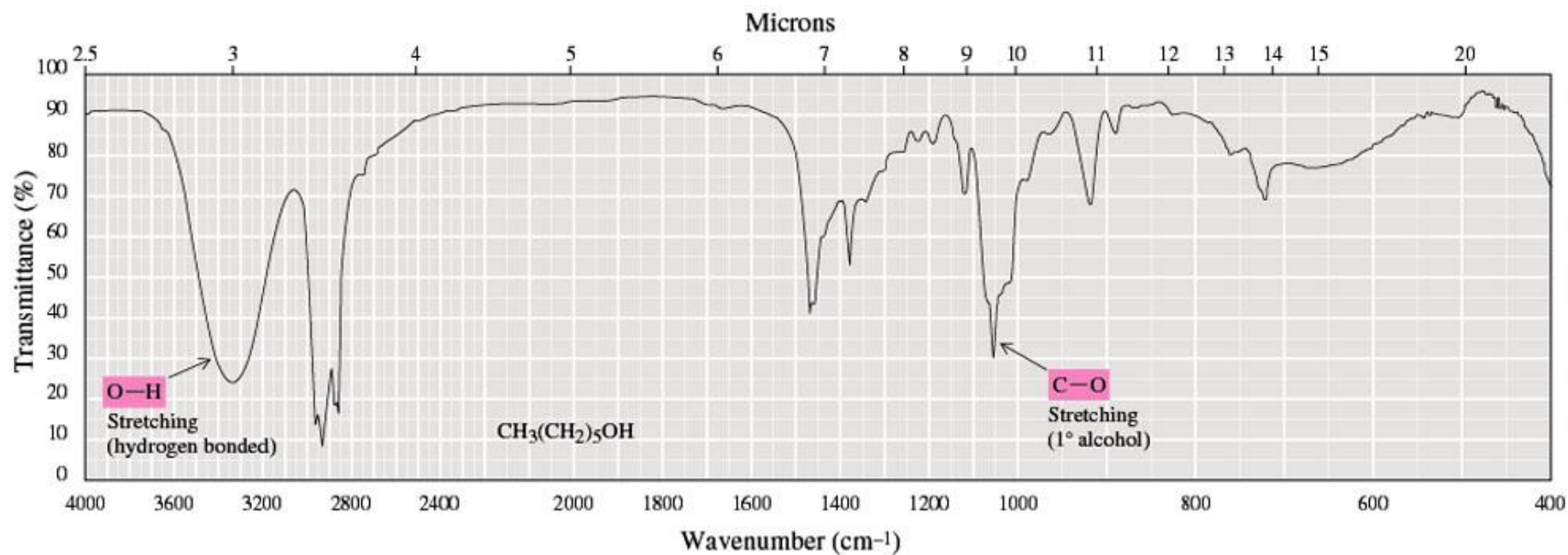
Ethers

IR spectrum of dibutyl ether
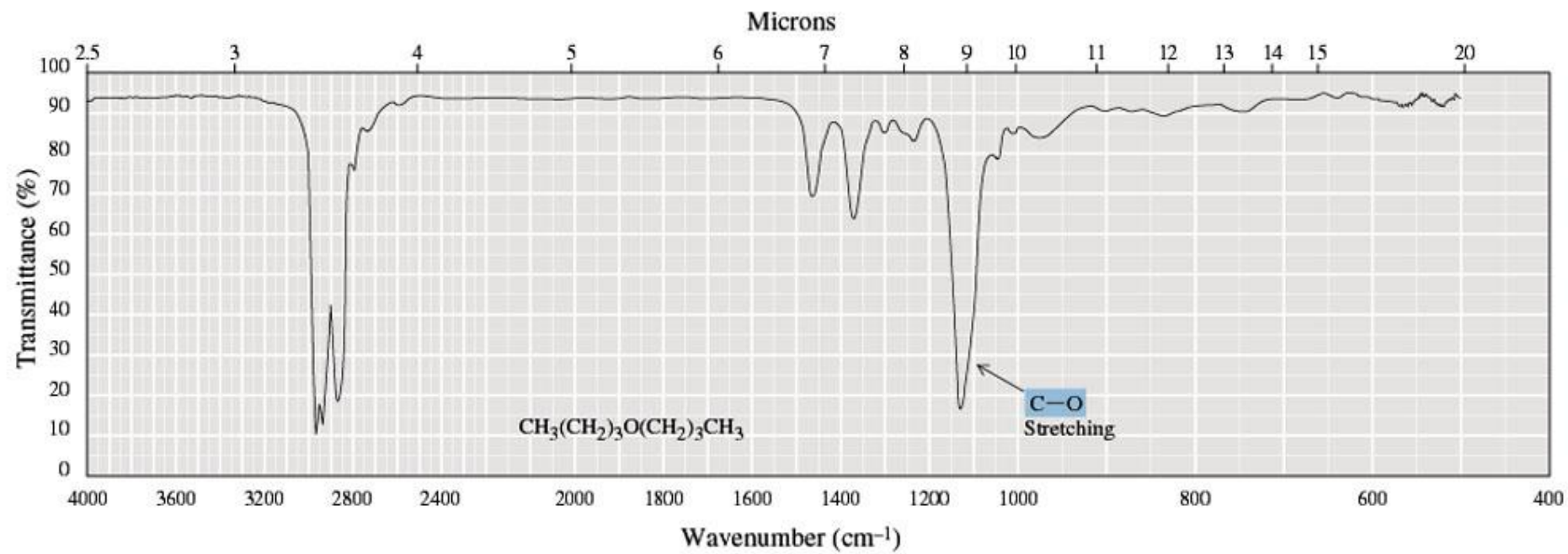
Amines

IR spectrum of 1-butanamine

© 2006 Brooks/Cole - Thomson

| Carbonyl Group		Vibration	Frequency (cm^{-1})	Intensity
O‖RCR'	Ketones C=O	Stretching	1630-1820	Strong
O‖RCH	Aldehydes C=O C-H	Stretching Stretching	1630-1820 2720	Strong Weak
O‖RCOH	Carboxylic acids C=O O–H	Stretching Stretching	1700-1725 2500-3300	Strong Strong (broad)

▪ The position of C=O stretching vibration is sensitive to its molecular environment
  • as ring size decreases and angle strain increases, absorption shifts to a higher frequency.

1715 cm^{-1} 1745 cm^{-1} 1780 cm^{-1} 1850 cm^{-1}
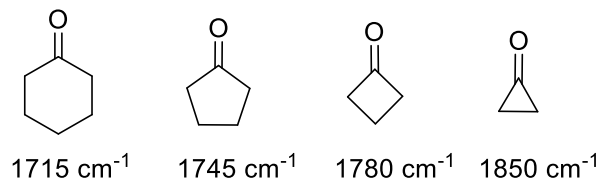
  • conjugation shifts the C=O absorption to lower frequency

1717 cm^{-1} 1690 cm^{-1} 1700 cm^{-1}
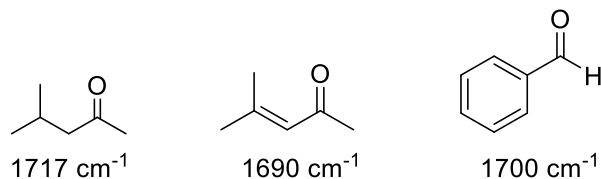
IR spectrum of pentanoic acid
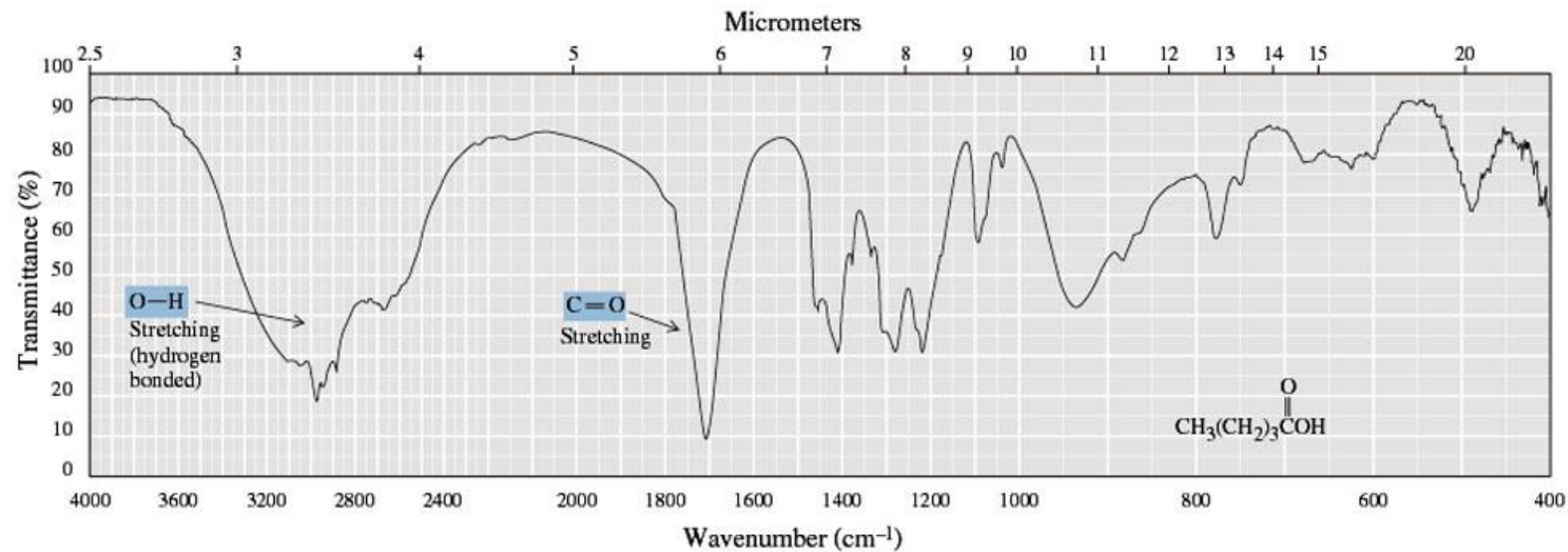
IR of ethyl butanoate
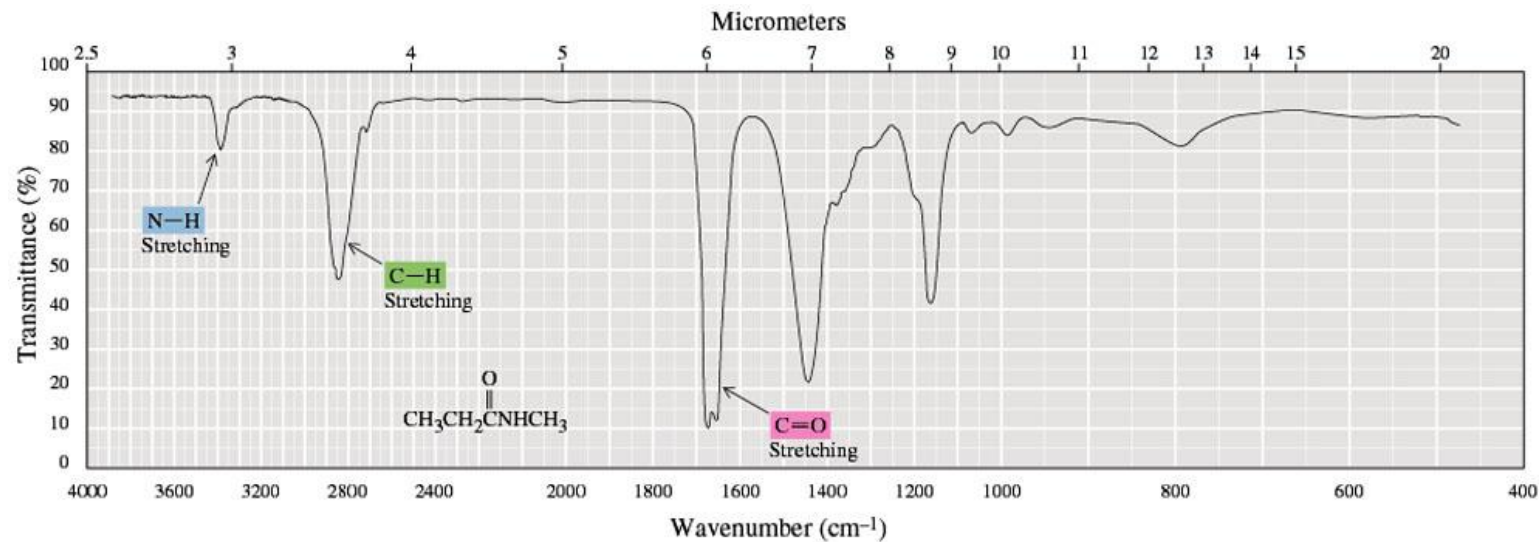
Home Assignment

1. A local radio station transmits (a) at approximately 95 MHz on its VHF transmitter and (b) at 810 kHz on medium wave. Calculate the wavelengths of these transmissions.

2. For ultraviolet light of wavelength 200 nm, calculate (a) the frequency of this light, (b) the amount of energy absorbed by one molecule when it interacts with this light, and (c) the corresponding amount of energy absorbed by one mole of substance.

3. An αβ-unsaturated ketone of relative molecular mass 110 has an absorption band with λ_{max} at 215 nm and ε 10,000. A solution of this ketone showed absorbance A = 2.0 with a 1 cm cell. Calculate the concentration of the ketone in this solution, expressed in grams per liter, gl^{-1} .

4. (a) Calculate the absorbance, A, for a solution showing 50 per cent transmittance, T. (b) Calculate the transmittance, T, for a solution showing absorbance, A, of 1.0.

5. How could infrared spectroscopy be used to distinguish the members of the following pairs? (a) natural rubber (cis-polyisoprene) and butyl rubber (polyisobutene) (b) cis and trans isomers of 3-hexane (c) 1- hexyne and 3-hexyne?