

# Infrared Spectroscopy

## Characteristics

Sensitive to polar groups and antisymmetric modes

Small amounts of samples needed (mg, as low as ng)

Signal detection is simple

Special sample preparation is often needed (thin films, KBr pellets....)

# Raman Spectroscopy

## Characteristics

Sensitive to nonpolar groups and symmetric modes

Inefficient detection scheme (1 photon out of a million)

Special site-specific techniques available

- resonance Raman spectroscopy

- surface enhanced Raman spectroscopy

Sampling method is often simple

Highly focused laser beam

# NMR Spectroscopy

## Characteristics

### Solution NMR

Signal intensity can be directly and quantitatively related to chemical group concentration

Sensitive to molecular mobility

Sensitive to surrounding electronic environment

Sensitivity depends on the nucleus of interest (natural abundance and magnetogyric ratio)

Some nuclei show little signal overlap

# NMR Spectroscopy

## Characteristics

### Solid-state NMR

In addition to the characteristics in solution-state NMR....

Can study frozen solid state conformation

Ability to determine the position of proton

Ability to determine the correlation among nuclei

# Mass Spectrometry

## Characteristics

Very sensitive (amount of detectable sample, pg and fg)

Ability to determine precise mass of a molecular fragment  
or mother molecule (MALDI)

Needs to be vaporized and ionized (fragmentation)

Various sampling and ionization techniques

# IR SPECTROSCOPY



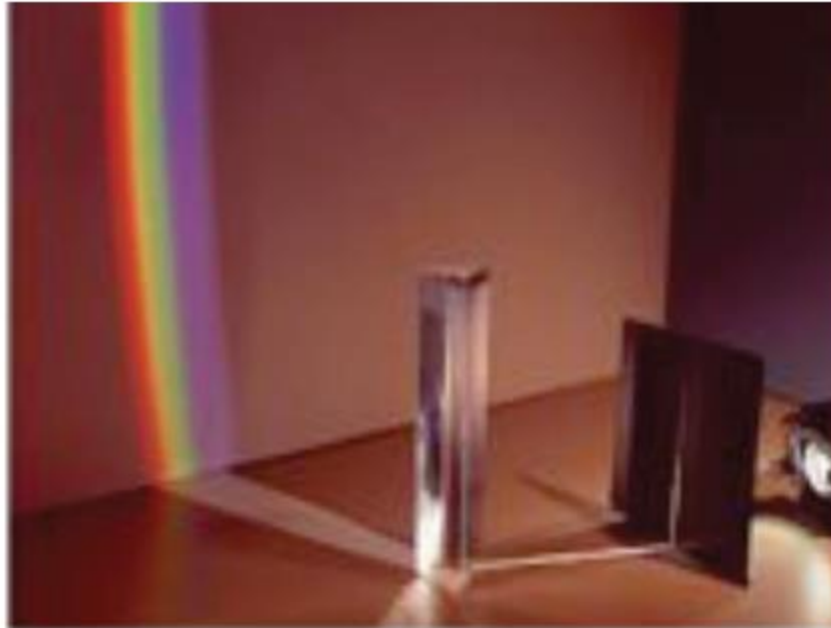
# Interaction of light with matter

# White light

- Light sources are most of the time “white”
- Newton proved that white light is a mixture of different types of light
- Light of different colors are “basic” types of light
- Newton proved this in the 1660's by using two prisms to decompose white light



# White light



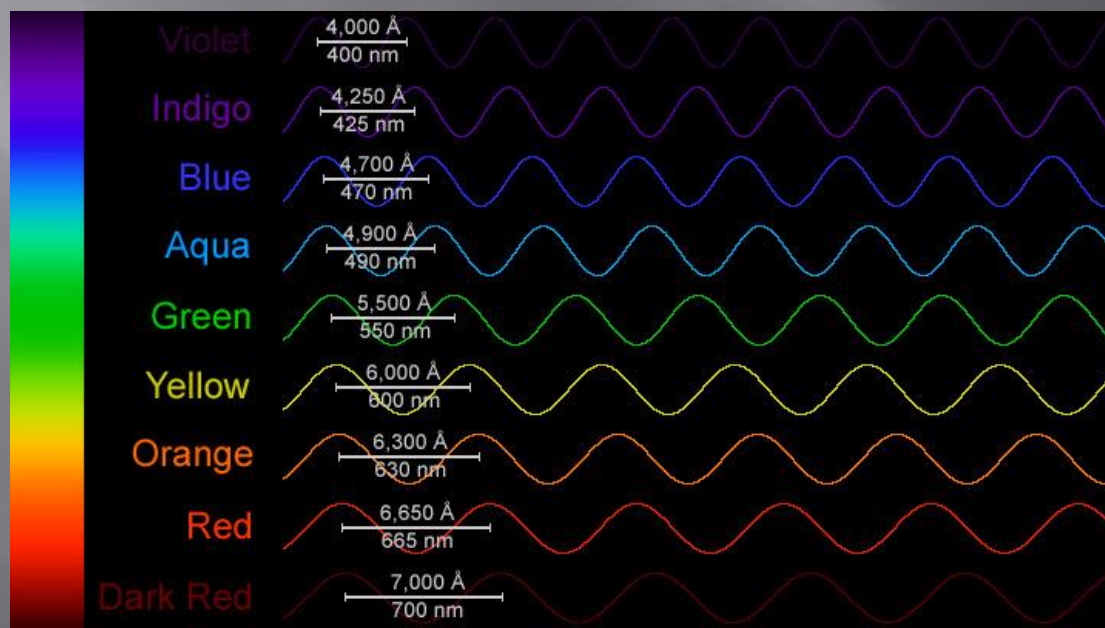
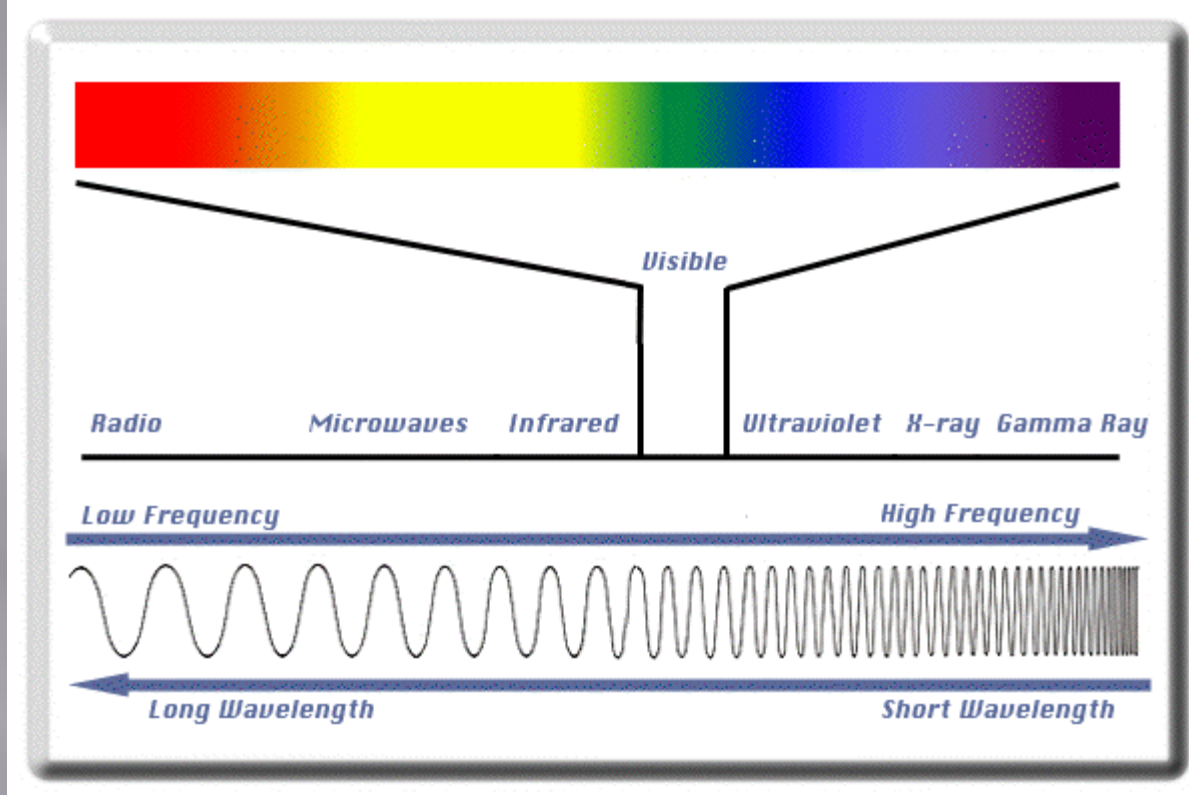


Magnetic field

Electric field

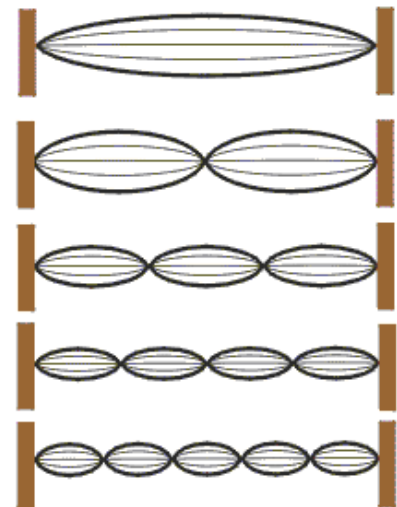
# Light

- Light is an electromagnetic wave (Electric and Magnetic fields oscillation and propagating)
- Visible light is only a particular type, with a particular of oscillation
- The complete spectrum of electromagnetic radiation is referred to as Electromagnetic Spectrum.



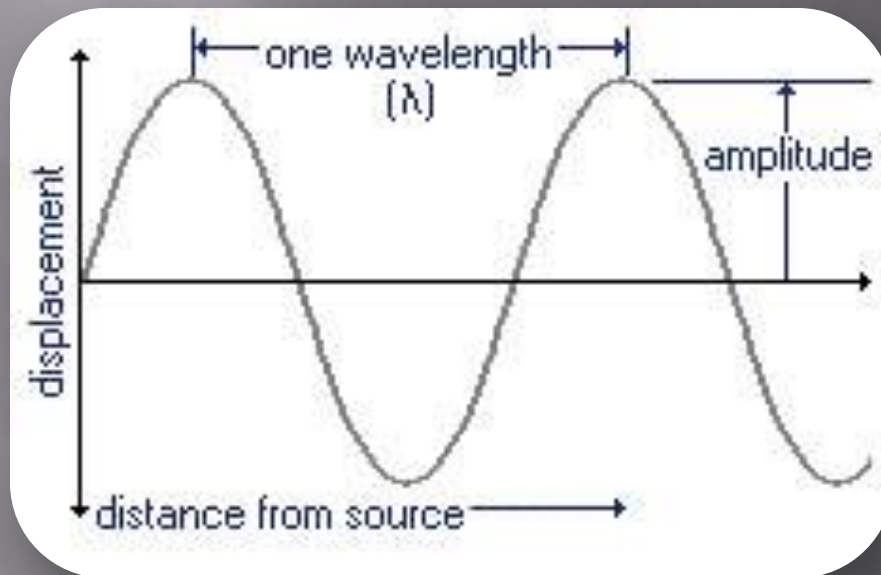
# Characteristics of waves

- Waves transfer energy without transporting any of the oscillating “stuff”
- Example: String oscillating



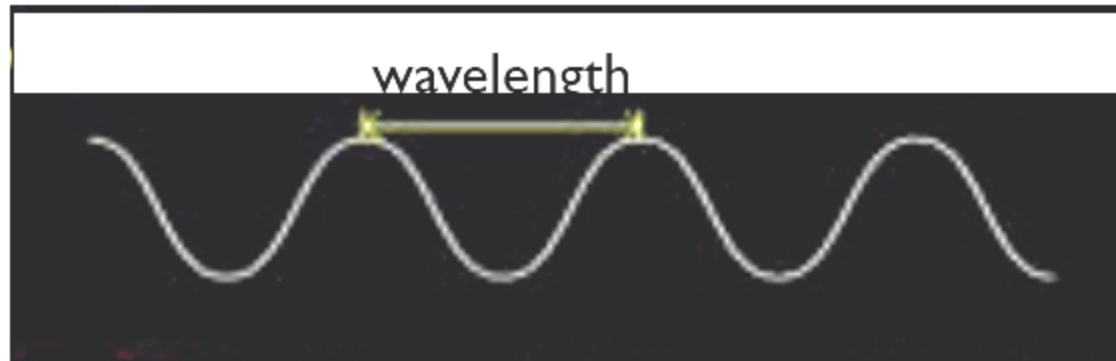
# Characteristics of waves

## ▣ Amplitude



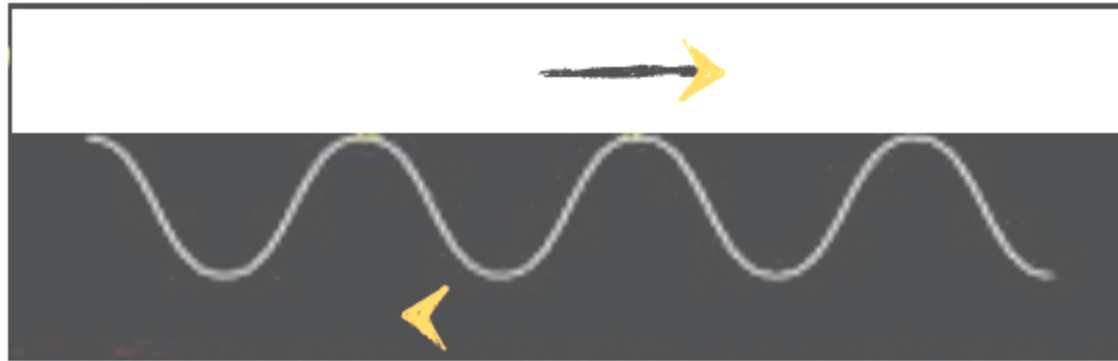
Maximum height of the oscillating stuff

# Characteristics of waves



- Wavelength: Distance between adjacent

# Characteristics of waves

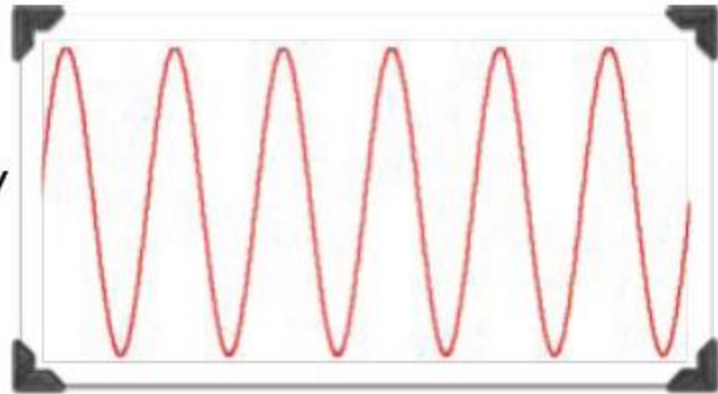


- The **SHAPE** moves, the oscillating stuff stays (the wave *propagates*, carries energy)
- Frequency: number of crests passing a point each second. Units = Hertz (Hz) = cycles/s

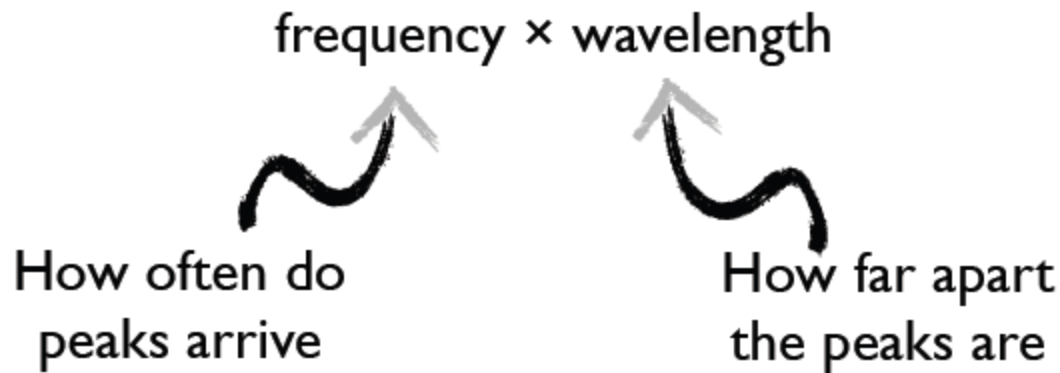


# Characteristics of waves

- Velocity of propagation: determined by frequency and wavelength of the wave



# Characteristics of waves



# Characteristics of waves

frequency  $\times$  wavelength = speed of propagation

For light, this is  $c = 300,000 \text{ km/s}$   
 $= 3 \times 10^8 \text{ m/s}$

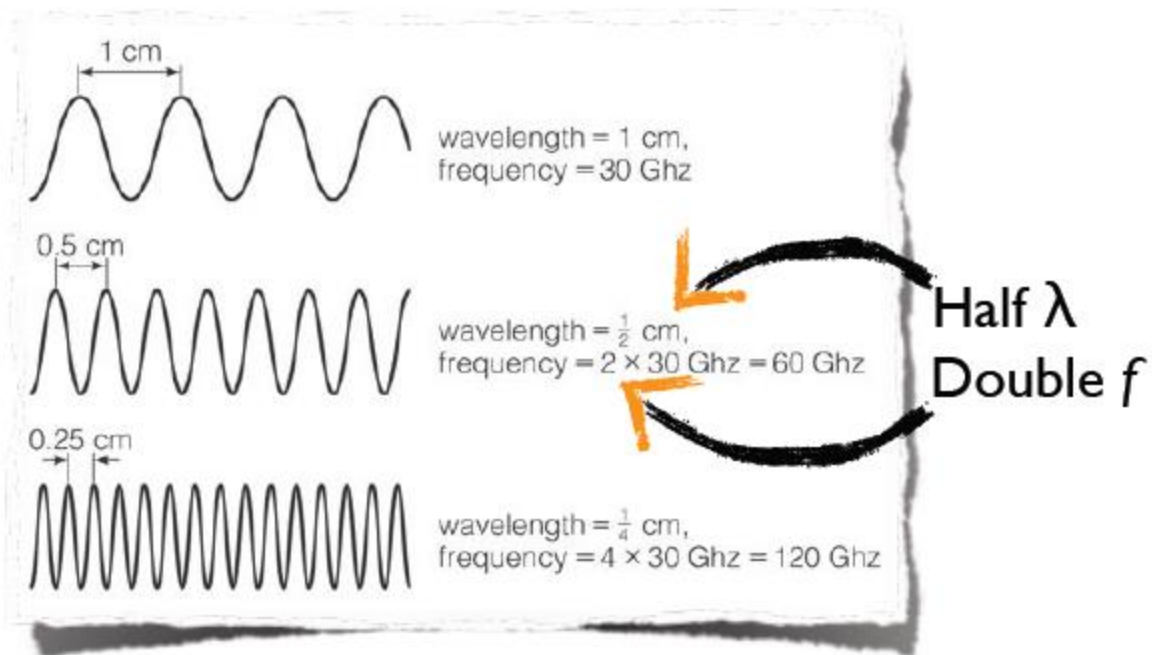
$$f \times \lambda = c$$

# Characteristics of waves

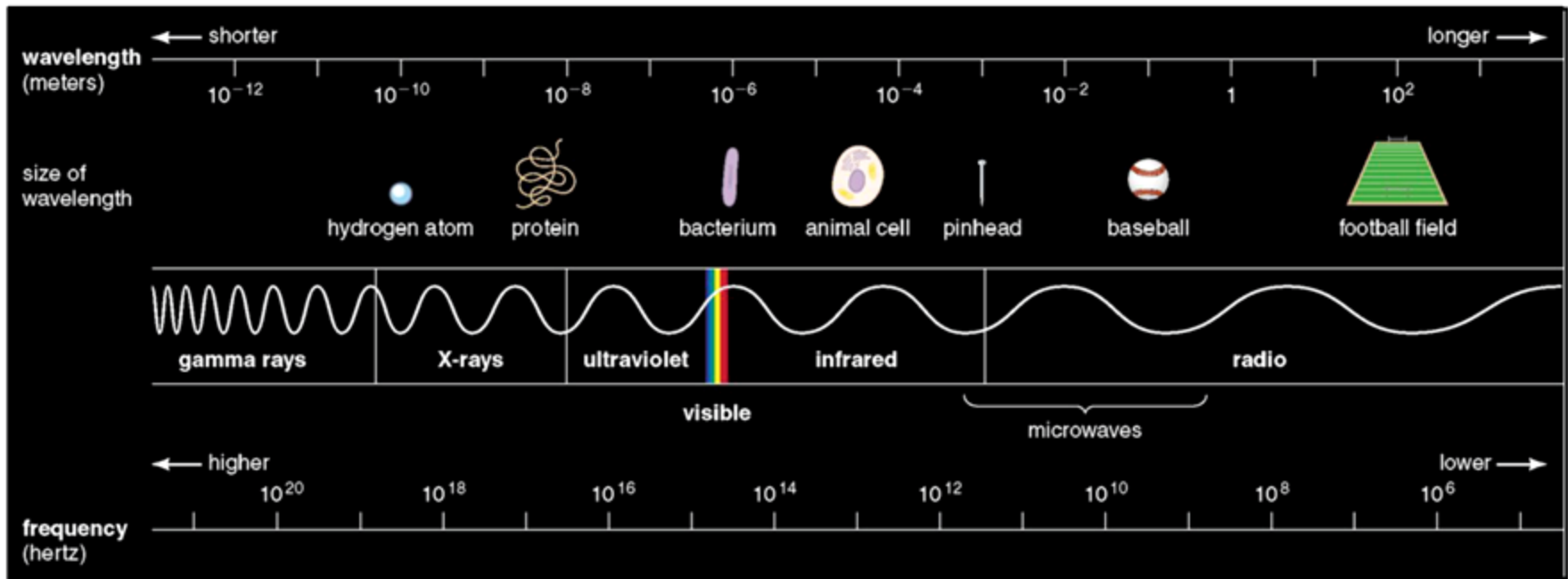
$$f \times \lambda = c$$

Since  $c$  is constant, each type of light is characterized by its wavelength (or frequency) only

# Characteristics of waves



# Different types of “light”



# Quantum Mechanics and Light

- Experiments (1902) show that light behaves both as a wave and as a particle.
- Particles (*quantum*) of light are called *photons* (Einstein 1905).

Each photon has a wavelength and a frequency.

The energy of a photon is proportional to its frequency.

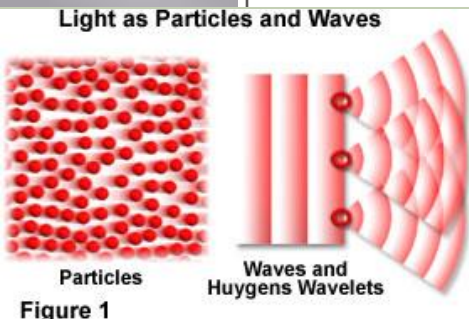
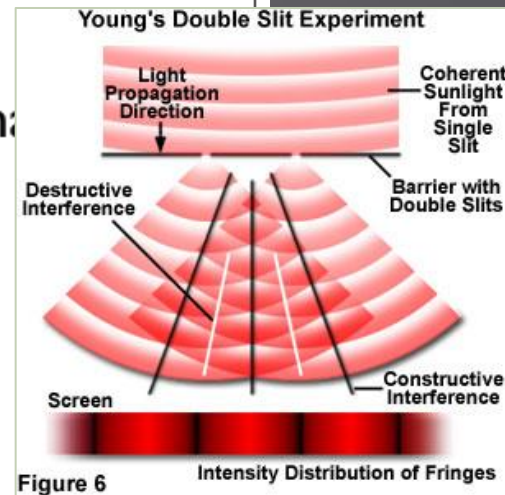
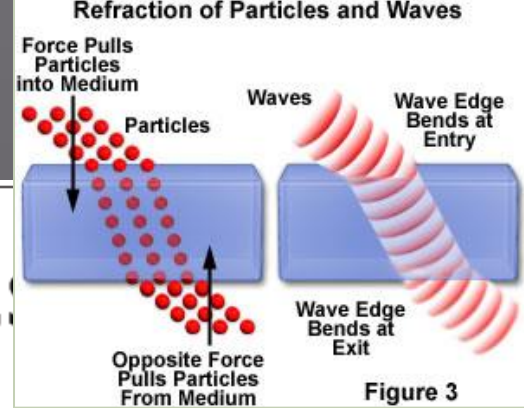
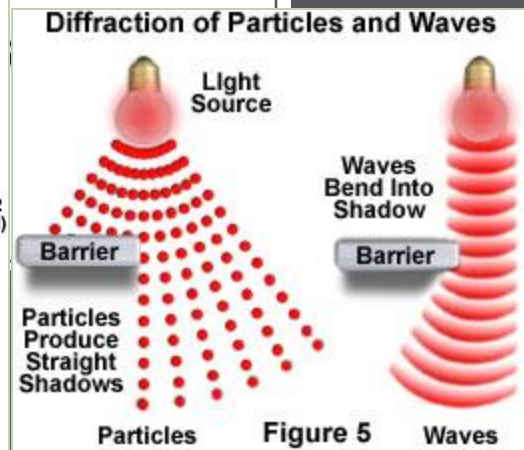
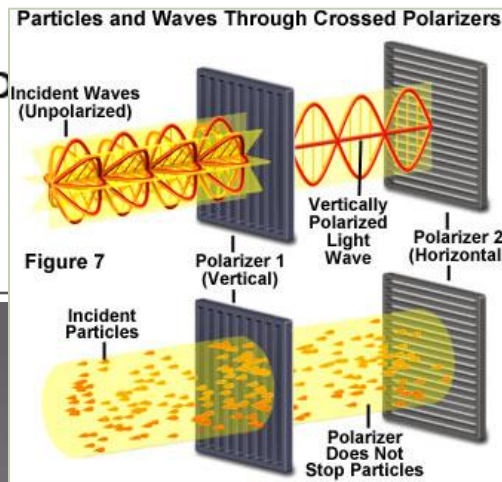
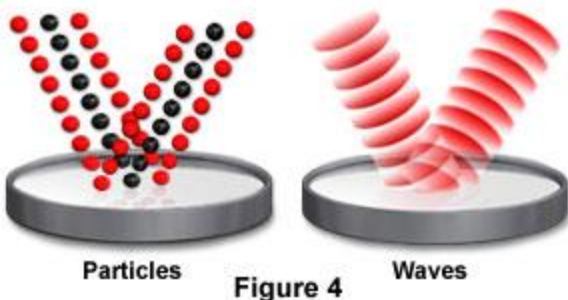


Figure 1 Particles and Waves Reflected by a Mirror





# Quantum Mechanics and Light

- $E = h f$  = energy of each photon
- $h = 6.626 \times 10^{-34}$  joules  $\times$  s



Planck's constant

# Quantum Mechanics and Light

$$E = h \times f$$

The energy of *each photon* is big in light of high frequency, but low in light of small frequency

# Light and Matter

- The interactions between light and matter determine the appearance of everything we see.



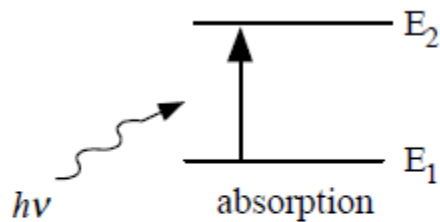
# Light and Matter

- Refraction, reflection or scattering
- Transmission:
  - Transparent objects transmit light.
  - Opaque objects block (absorb) light.
- Emission
- Absorption

# So...what is light?

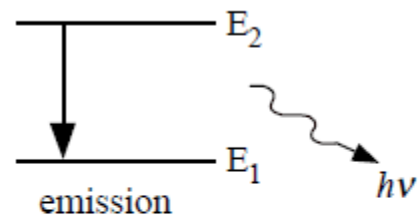
- Light is a form of energy.
- *Visible* light comes in many colors that combine to form white light.
- It is an electromagnetic wave that also comes in individual “pieces” called photons. Each photon has a precise wavelength, frequency, and energy.
- Radio waves, microwaves, infrared, visible light, ultraviolet, X rays, and gamma rays.

# Absorption and emission of light from matter



$$E_2 - E_1 = h\nu$$

must satisfy Bohr relation

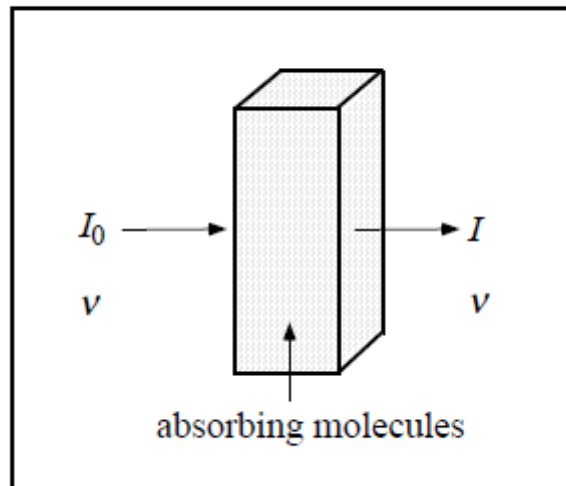


$$E_2 - E_1 = h\nu$$

emission could be induced  
or spontaneous

# The Beer-Lambert Law

Most absorbing materials satisfy the Beer-Lambert Law.



If  $I_0 \equiv$  incident light intensity at frequency  $\nu$   
 $I \equiv$  intensity of transmitted light at same frequency  
 $C \equiv$  concentration of absorbers  
 $\epsilon \equiv$  molar extinction coefficient  
 $l \equiv$  length of light path through the absorbers

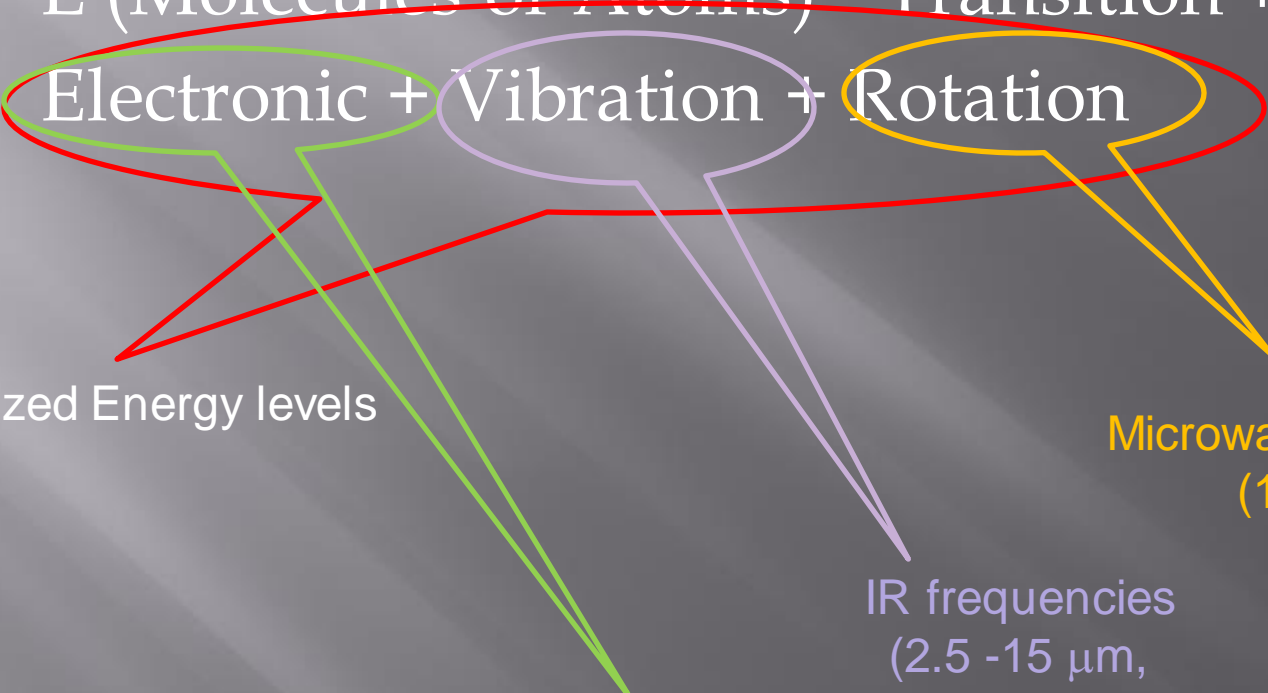
then  $\log_{10} \frac{I_0}{I} = \epsilon l C$

Quantity  $\log_{10} \frac{I_0}{I} = A$  is called the absorbance or sometimes optical density (OD).



# Types of energies in a molecules

▣  $E(\text{Molecules or Atoms}) = \text{Transition} +$   
 $\text{Electronic} + \text{Vibration} + \text{Rotation}$



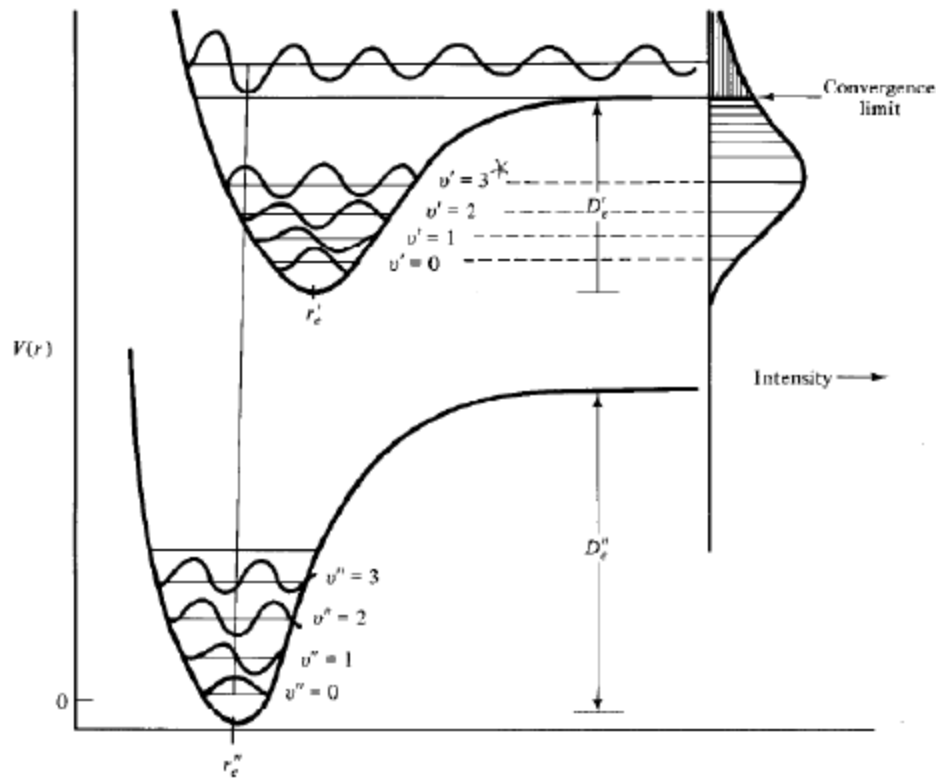
Quantized Energy levels

Uv-Visb  
frequencies  
(200-400 nm)

IR frequencies  
(2.5 -15  $\mu\text{m}$ ,  
400 - 4000  $\text{cm}^{-1}$ )

Microwave frequencies  
(1 -  $10^{-3}$  m)

# Electronic and Vibration energy levels



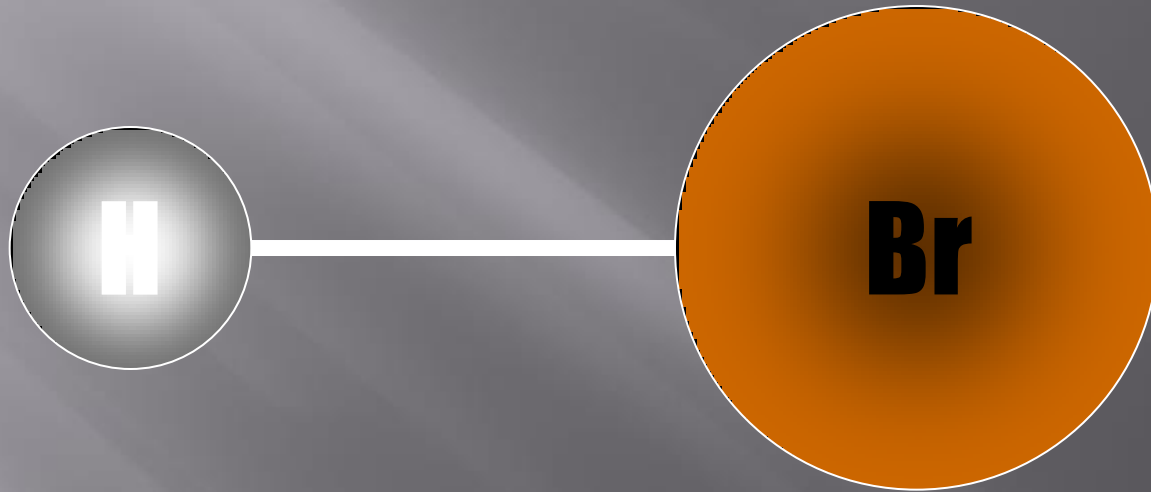
# Infrared Spectroscopy

- ✓ Substances exposed to radiation from frequency range  $10^{14}$  Hz to  $10^{13}$  Hz (wavelengths  $2.5\mu\text{m}$  -  $15\mu\text{m}$ )
- ✓ Causing vibrational energy changes in the molecule
- ✓ These absorb infrared radiation of **specific** frequencies.
- ✓ Point is to identify functional groups in the molecule

# Vibrations in Molecules and Bond Deformations

# BOND DEFORMATION

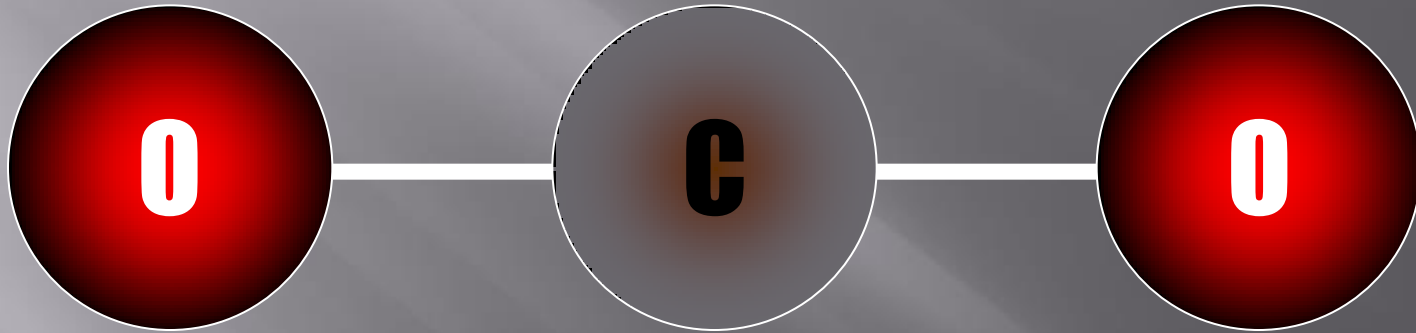
- ▣ SIMPLE diatomic molecules can only vibrate one way, by *stretching*.



For these molecules there is only **one** vibrational infrared absorption.

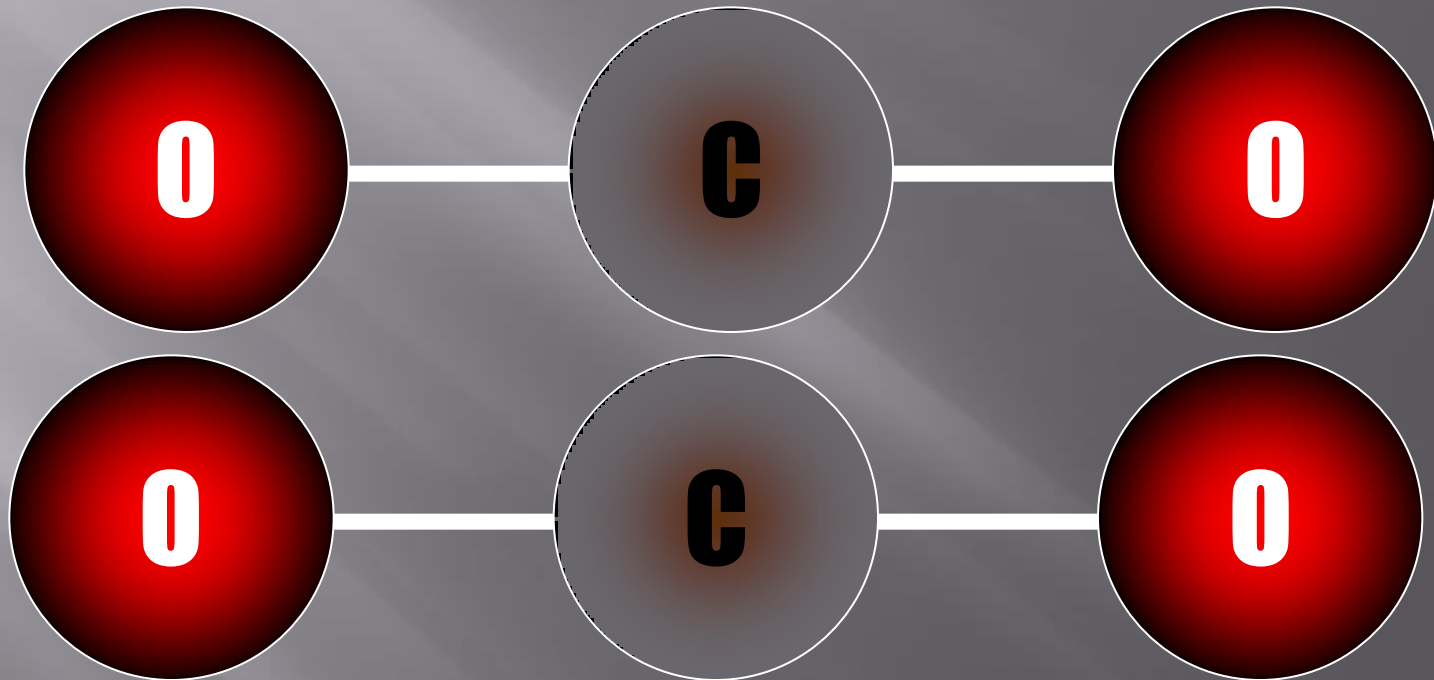
# BOND DEFORMATION

- More complex molecules have more possible deformations



symmetric stretch

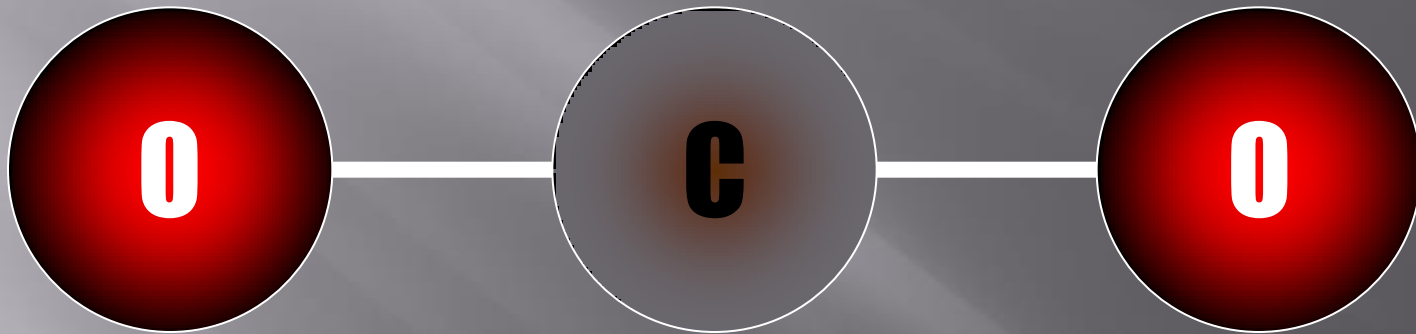
# BOND DEFORMATION



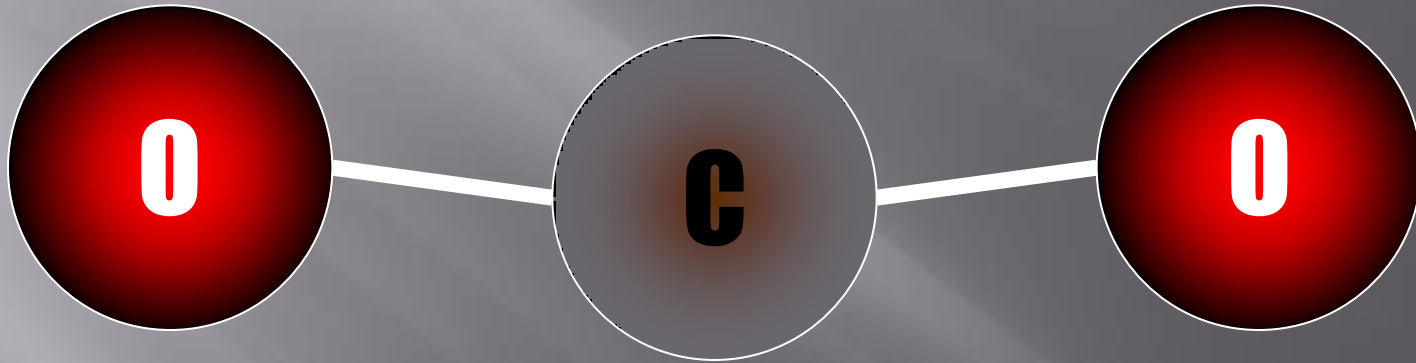
asymmetric stretch



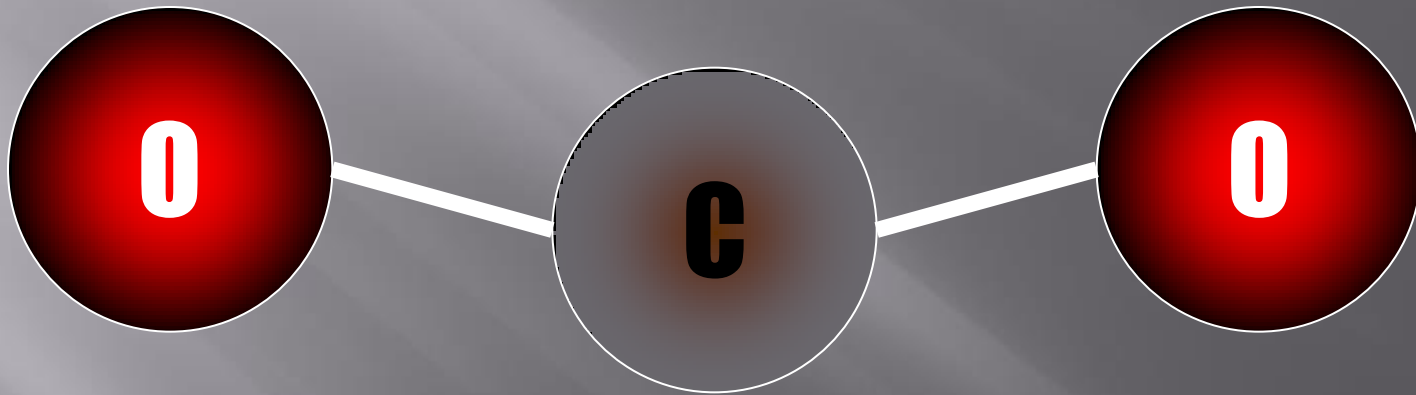
# BOND DEFORMATION



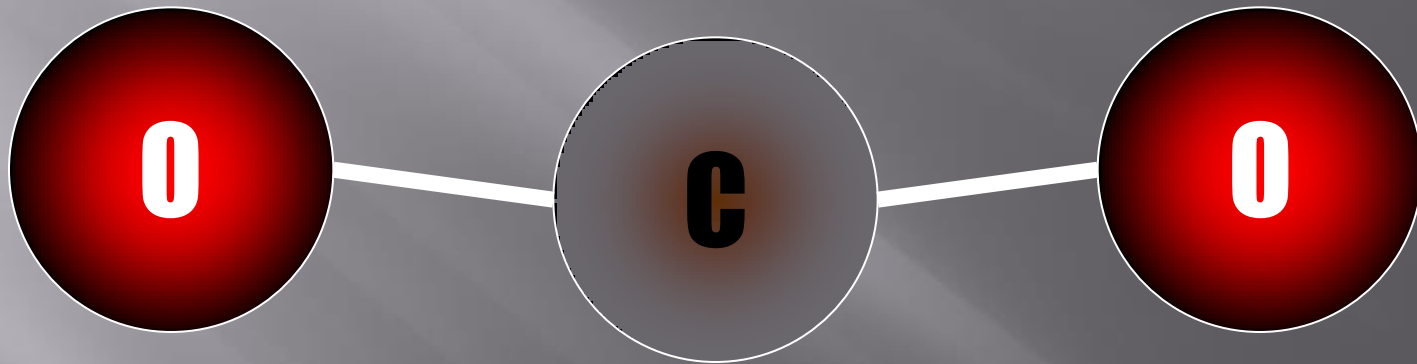
# BOND DEFORMATION



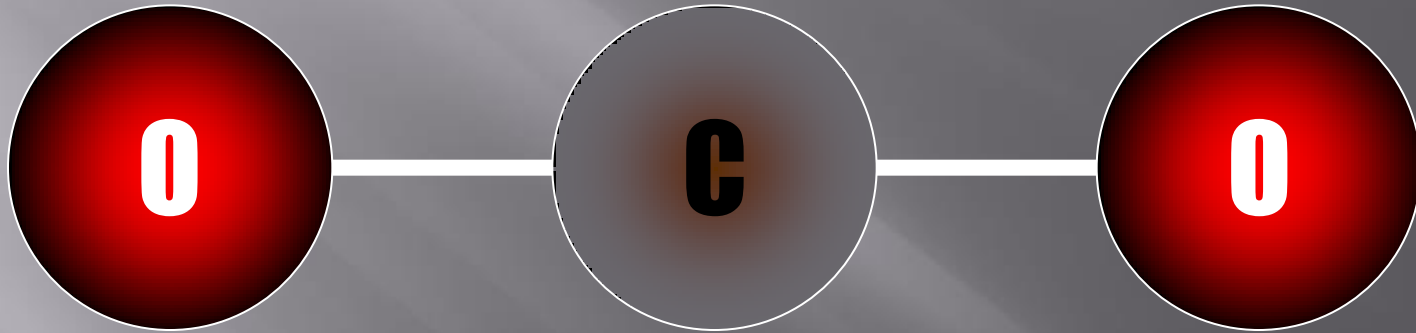
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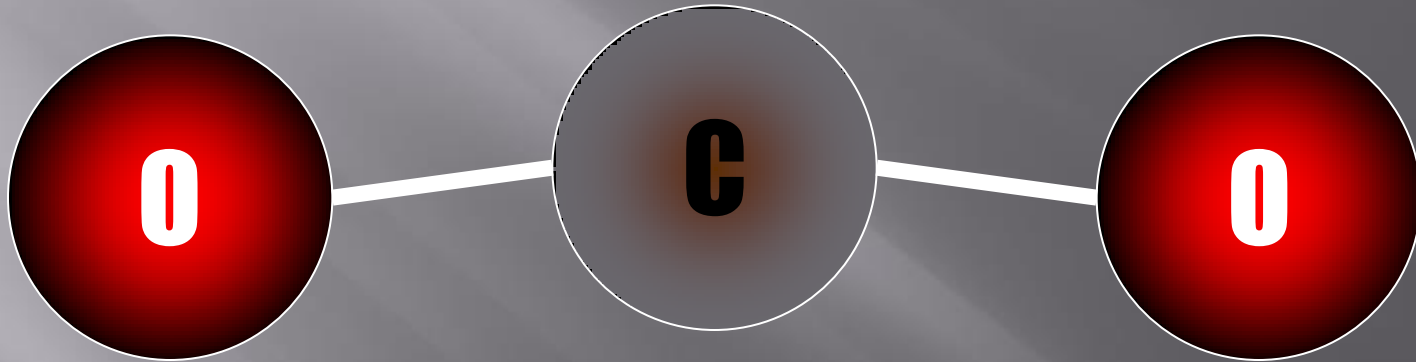
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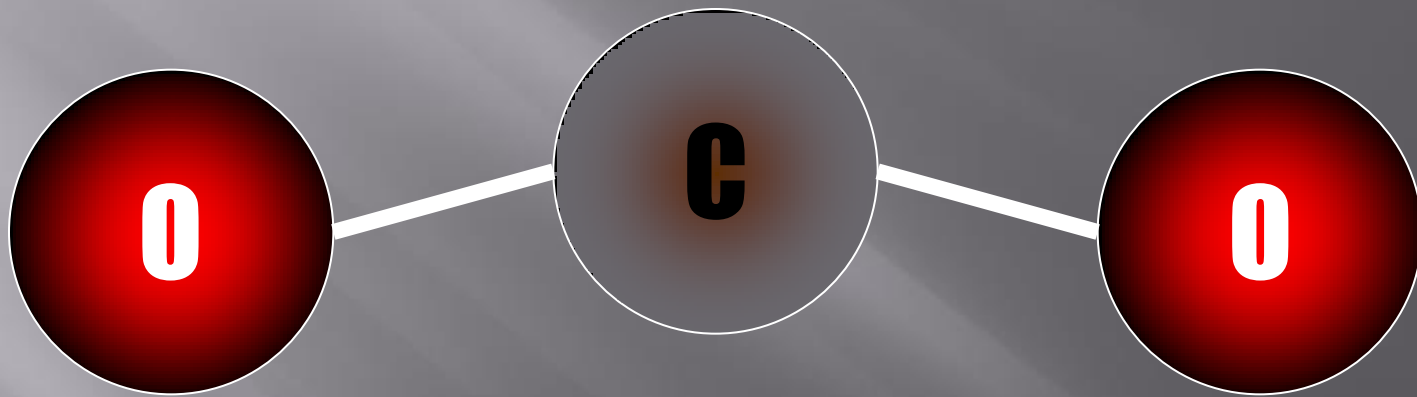
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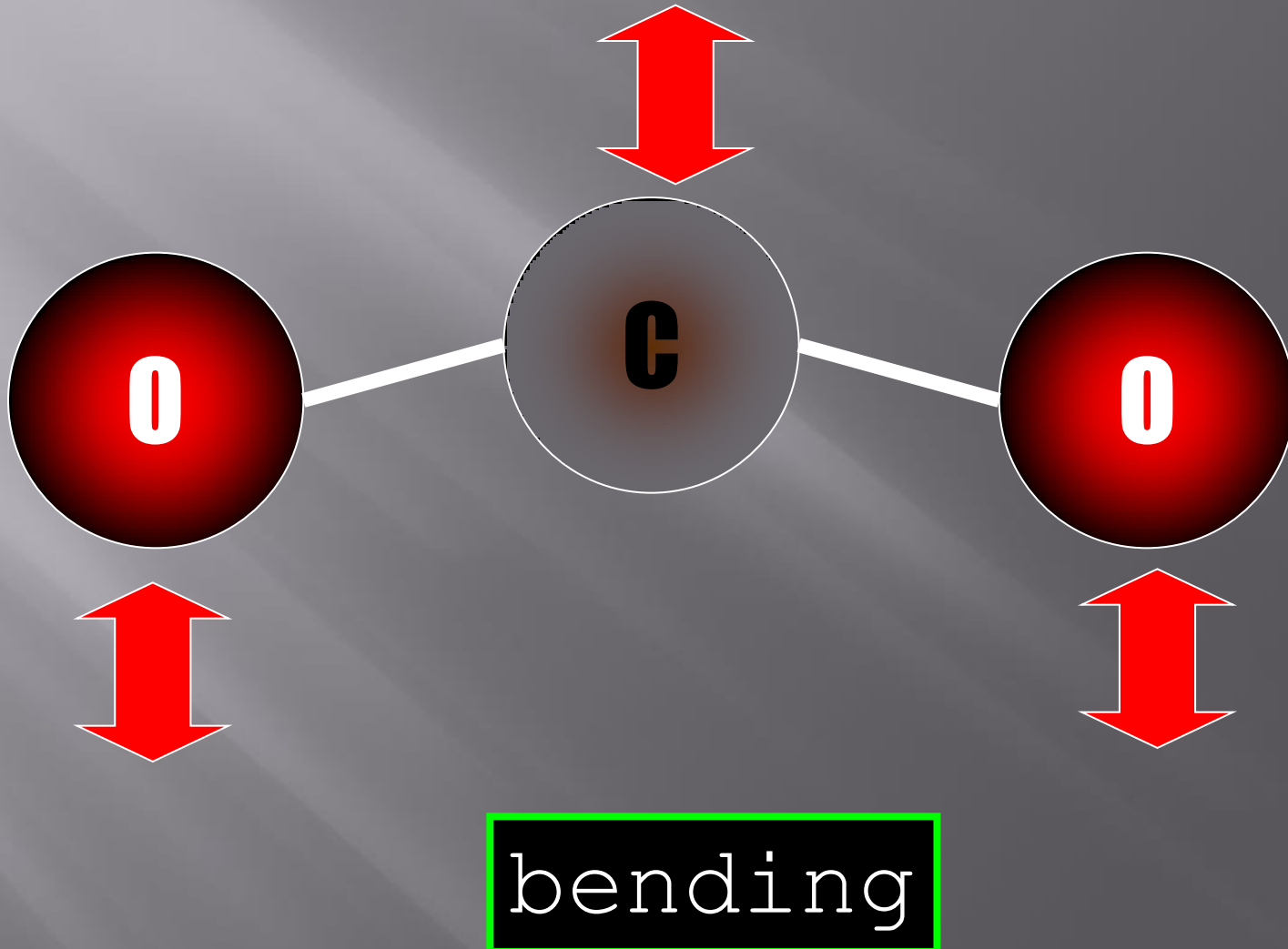
# BOND DEFORMATION



# BOND DEFORMATION



# BOND DEFORMATION





# Wavenumber ( $\text{cm}^{-1}$ )

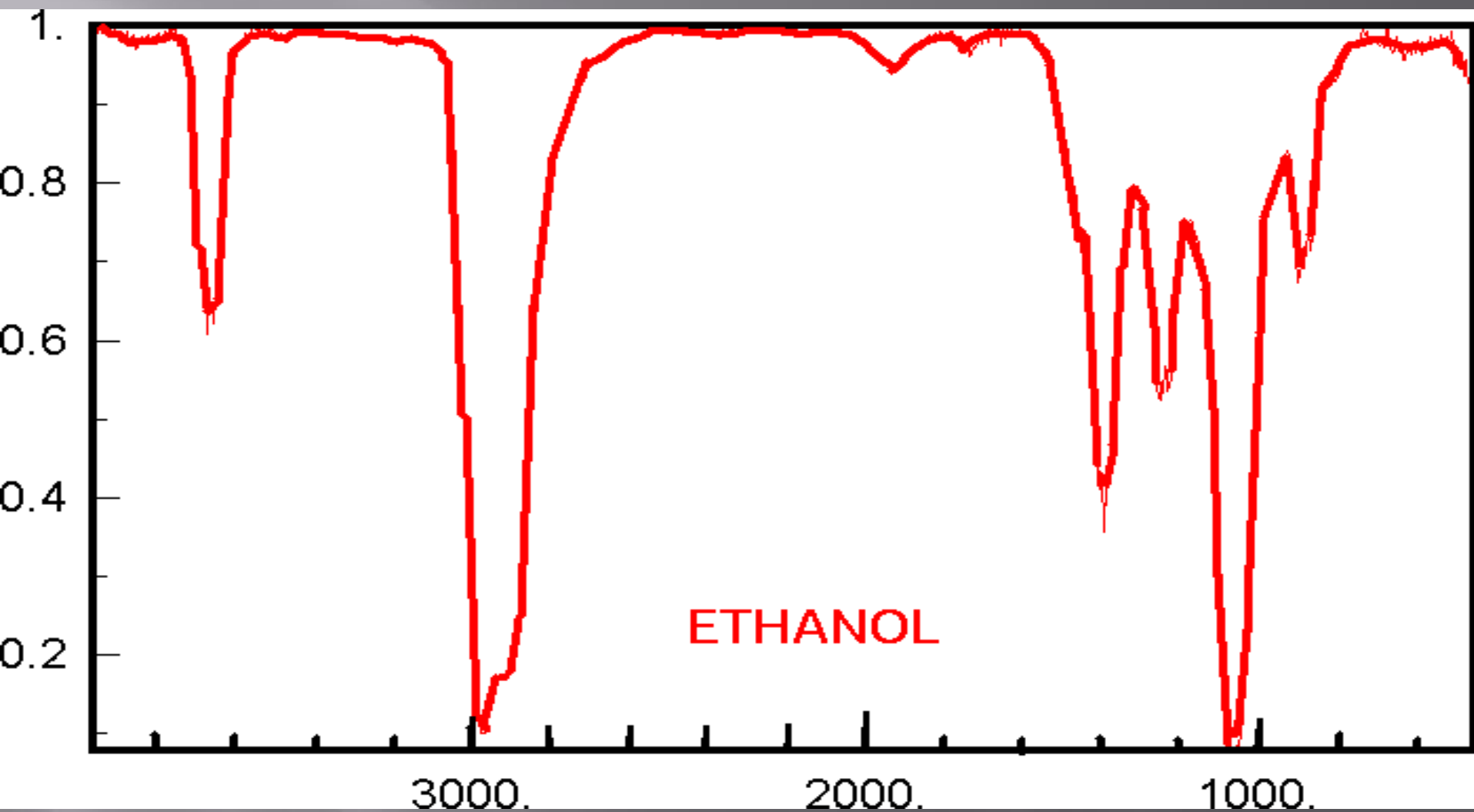
$$c = \lambda f$$

from this equation we can get the  
reciprocal of the wavelength ( $1/\lambda$ )  
this is a direct measure of the frequency

the reciprocal is described as the  
wavenumber

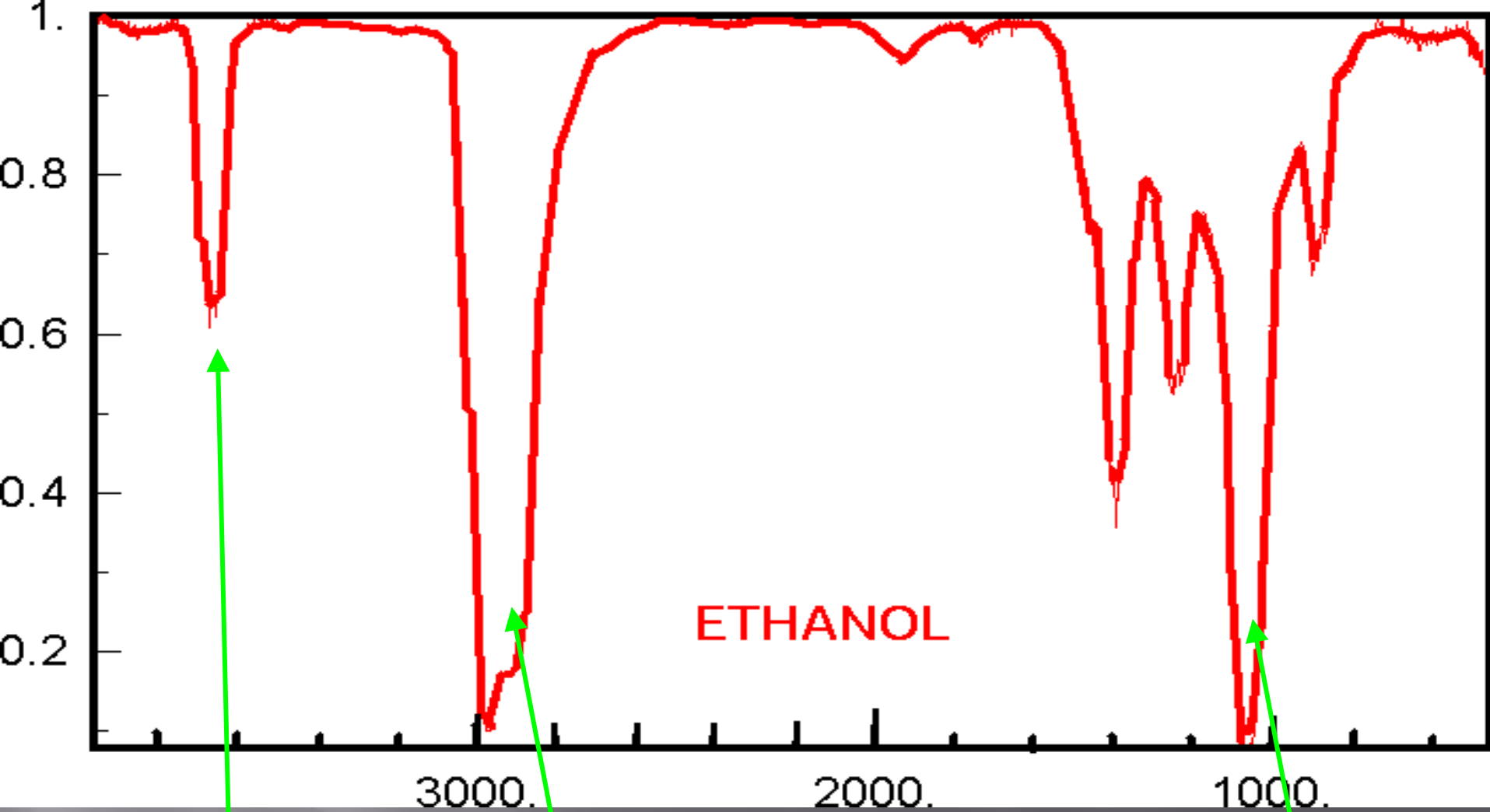
it is the wavenumber, measured in  $\text{cm}^{-1}$   
that is recorded on an infrared  
spectrum





Important ...

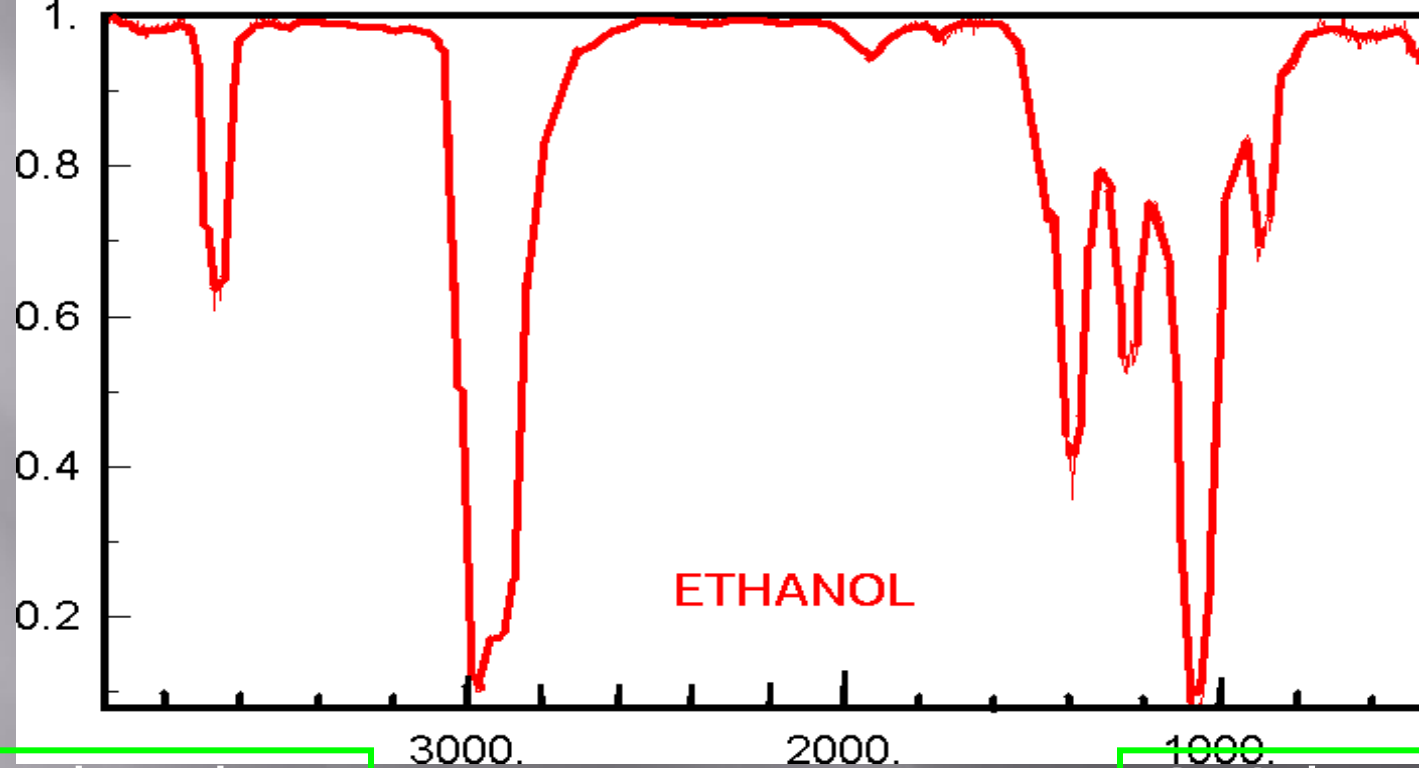
When an ir spectrum is obtained we do not try to explain the whole thing, simply look for one or two signals that are characteristic of different bonds.



O-H bond  
stretch

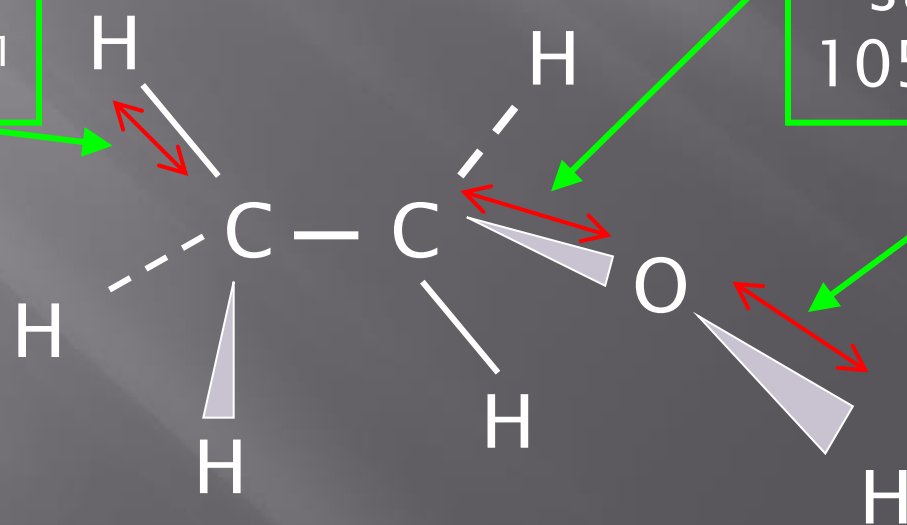
C-H bond  
stretch

C-O bond  
stretch



C-H bond  
stretch  
3010 – 2850  $\text{cm}^{-1}$

C-O bond  
stretch  
1050  $\text{cm}^{-1}$



O-H bond  
stretch  
3670  $\text{cm}^{-1}$

# Some typical absorptions

Absorption range / $\text{cm}^{-1}$	Bonds responsible	Examples
4000-2500	Single bonds to H	O-H, C-H, N-H
2500-2000	Triple bonds	$\text{C}\equiv\text{C}$ , $\text{C}\equiv\text{N}$
2000-1500	Double bonds	$\text{C}=\text{C}$ , $\text{C}=\text{O}$
Below 1500	various	C-O, C-X

- ✓ Below  $1500\text{cm}^{-1}$  the IR spectrum can be quite complex
- ✓ This region is characteristic of a particular molecule
- ✓ Hence known as '*fingerprint region*'

# INFRARED SPECTROSCOPY

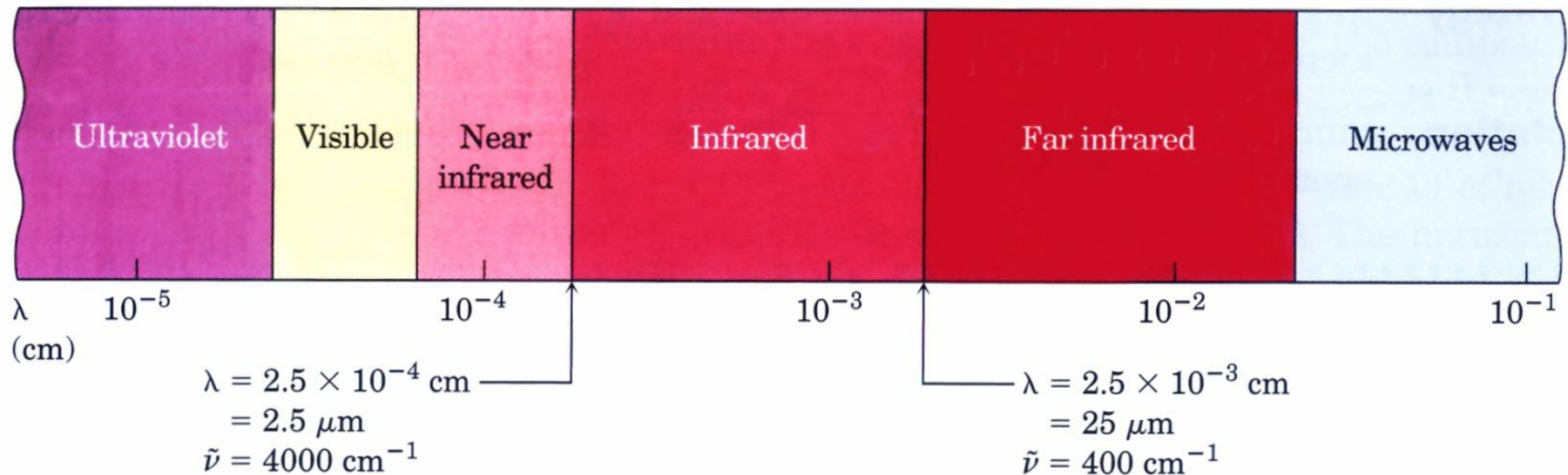
Principles and practice

# SUMMARY



# Infrared region of electromagnetic spectrum

The infrared region of the electromagnetic spectrum.



# Summary

- ▣ In the infrared region of the spectrum photons do **not excite electrons** but may induce **vibrational** excitation of covalently bonded atoms and groups.
- ▣ Molecules experience a wide variety of **vibrational motion**.
- ▣ Virtually all organic compound will absorb radiation that corresponds to these vibrations.

# Common sampling methods

## ▣ **KBr pellet**

- Good for powders; a few milligrams of the sample powder and an excess of KBr are finely ground and pressed under high pressure into a pellet. This is a useful and very general method for solids.

## ▣ **Salt cells:**

- Good for organic liquids; the liquid is placed into a reservoir milled in alkali salt windows.

## ▣ **Nujol mull:**

- The material of interest is suspended in oil, such as mineral oil, and the resulting paste is spread thinly on a salt window to form a film. This is a good technique for oils and waxy solids that do not press well into pellets.

# Different samples

- ▣ Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous).
- ▣ Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent).

# Different samples

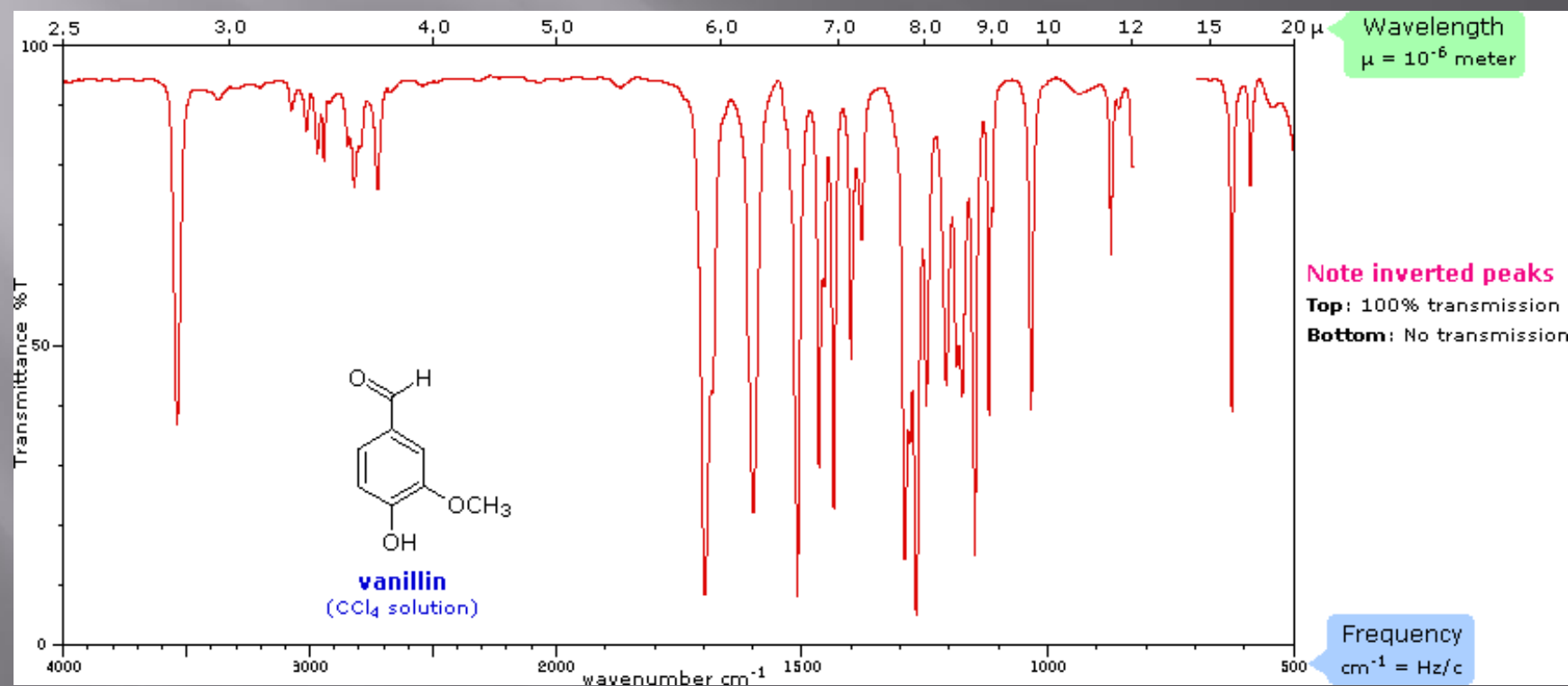
- ▣ If solvents are used to dissolve solids, care must be taken to avoid **obscuring** important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used.
- ▣ Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

# Different samples

- ▣ **Water** has a dipole moment and **absorbs** light in the infrared very strongly.
- ▣ It is difficult to measure the infrared spectrum of biological materials in water due to the spectrum of water obscuring the information.
- ▣ A combination of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  is often used to overcome this problem.

# A sample of IR Spectra

# Infrared spectrum of vanillin



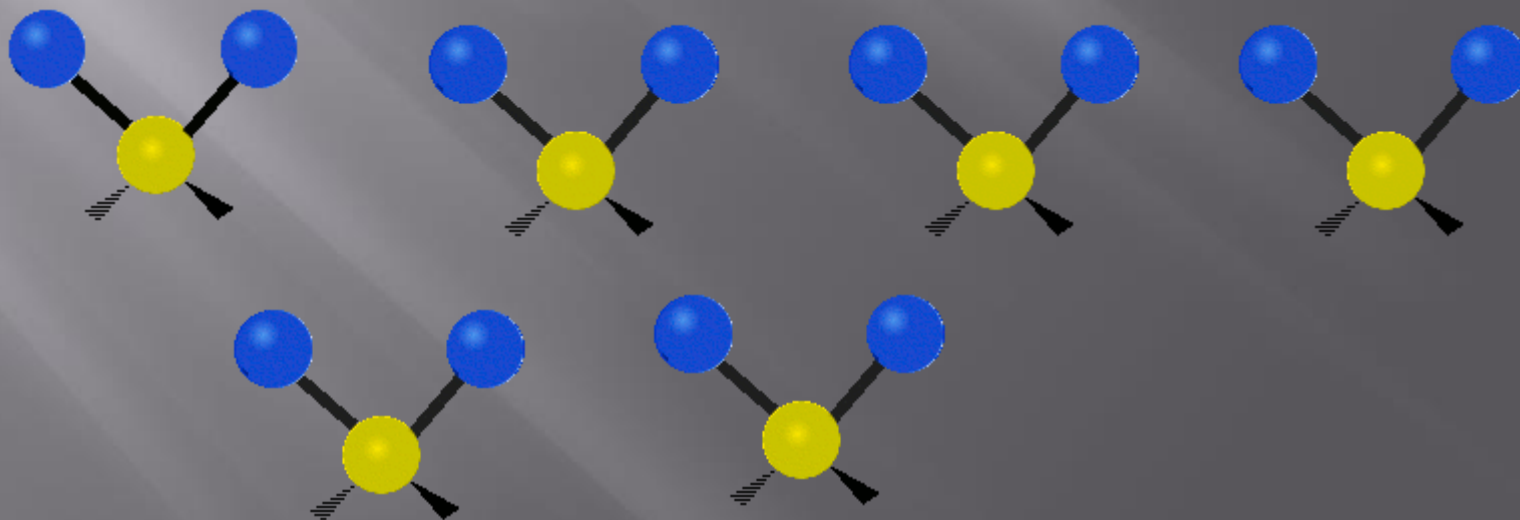


## Number of vibration modes in a molecule and number of peaks in spectra

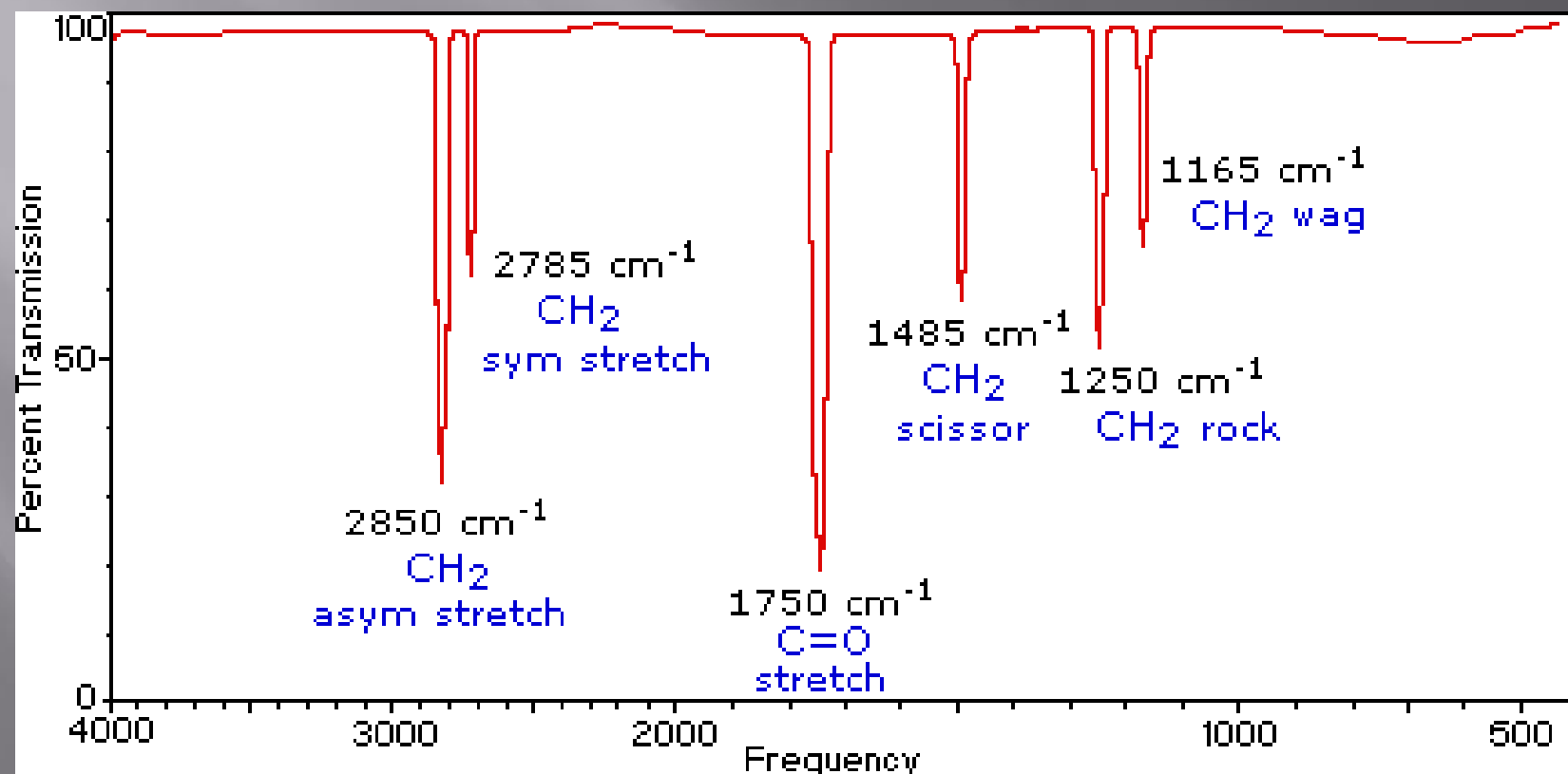
- ▣ A molecule composed of  $n$ -atoms has  $3n$  degrees of freedom, six of which are translations and rotations of the molecule itself.
- ▣ This leaves  $3n-6$  degrees of vibrational freedom ( $3n-5$  if the molecule is linear).
- ▣ Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting.

# Number of vibration modes in a molecule and number of peaks in spectra

- ▣ Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking, wagging and twisting.



# Infrared spectrum of formaldehyde



# Infrared spectrum of formaldehyde

- ▣ The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown, provides an example of these terms.
- ▣ We expect **six** fundamental vibrations ( $12 - 6$ ), and these have been assigned to the spectrum absorptions.

# General features of infrared spectra

- ▣ The **exact** frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms.
- ▣ In practice, infrared spectra do not normally display separate absorption signals for **each of the  $3n-6$**  fundamental vibrational modes of a molecule.
- ▣ The number of observed absorptions may be **increased** by **additive** and **subtractive** interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact.

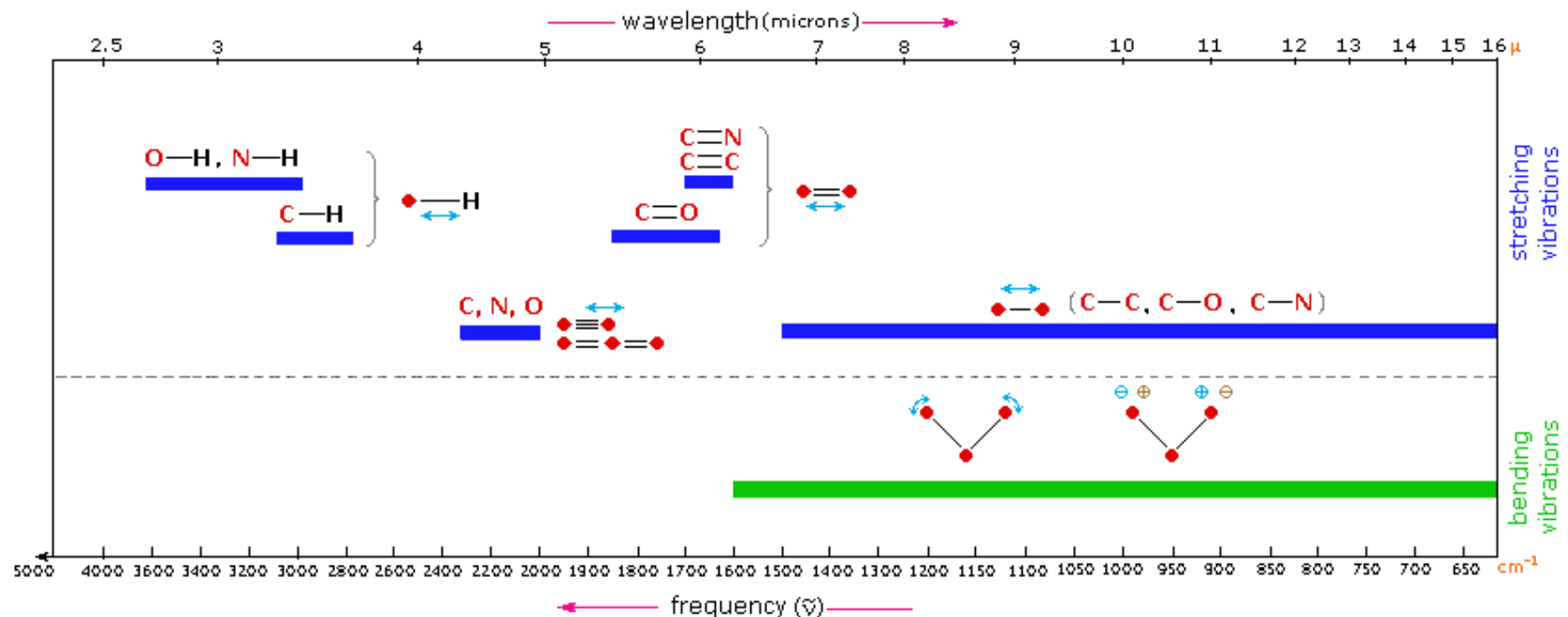
# General features of infrared spectra

- ▣ The number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules.
- ▣ One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy.
- ▣ Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.

# General features of infrared spectra

- ◉ **Stretching** frequencies are **higher** than corresponding **bending** frequencies. (It is easier to bend a bond than to stretch or compress it.)
- ◉ Bonds to **hydrogen** have higher stretching frequencies than those to **heavier** atoms.
- ◉ **Triple** bonds have higher stretching frequencies than corresponding **double** bonds, which in turn have higher frequencies than **single** bonds. (Except for bonds to hydrogen).

# General regions of an infrared spectrum





# Features of infrared spectroscopy

- ◉ It is rarely, if ever, possible to identify an **unknown** compound by using IR spectroscopy alone.
- ◉ The principal strengths are:
  - It is a quick and relatively cheap spectroscopic technique,
  - It is useful for identifying certain functional groups in molecules and
  - An IR spectrum of a given compound is unique and can therefore serve as a *fingerprint* for this compound.

# Infrared spectroscopy group frequencies

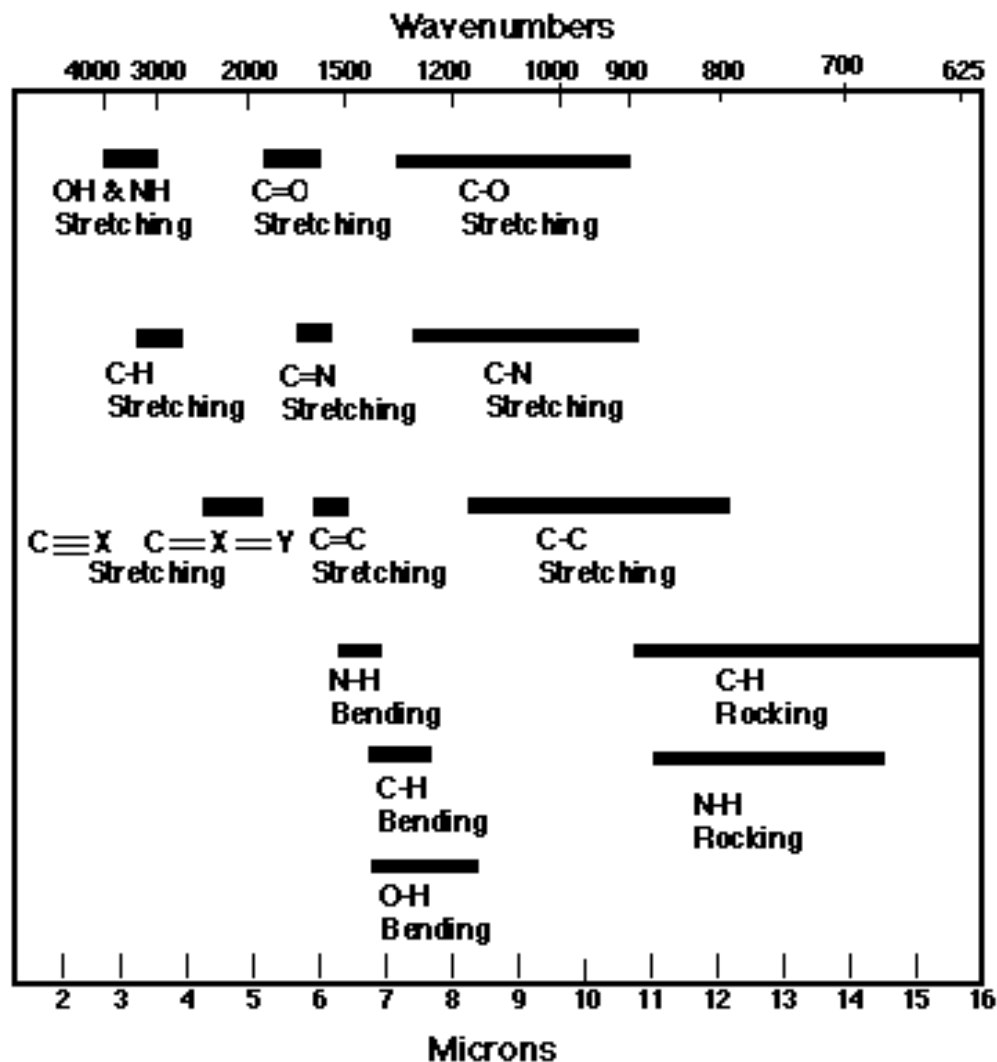
3700 – 2500  $\text{cm}^{-1}$  **Single bonds to hydrogen**

2300 – 2000  $\text{cm}^{-1}$  **Triple bonds**

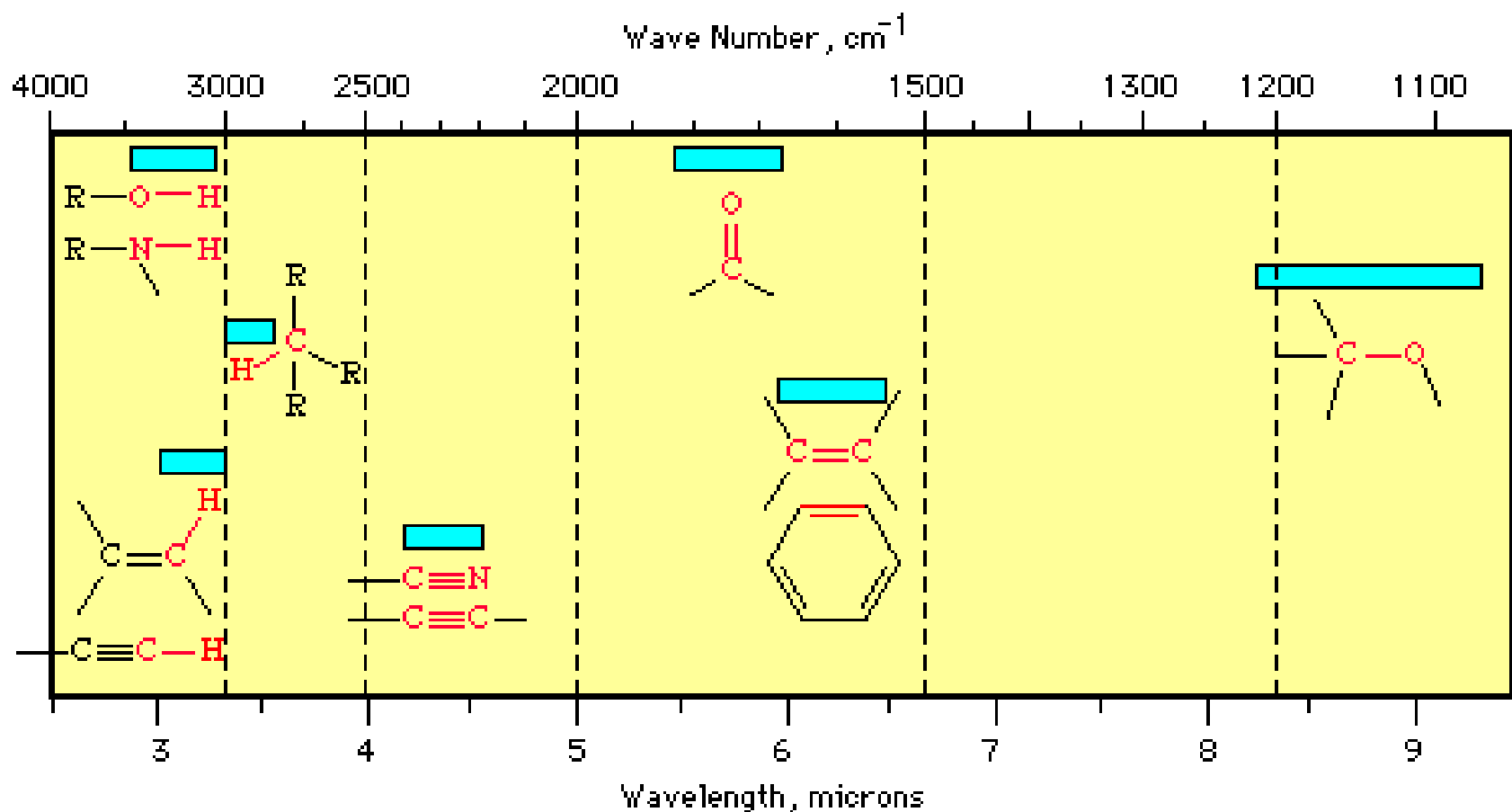
1900 - 1500  $\text{cm}^{-1}$  **Double bonds**

1400 - 650  $\text{cm}^{-1}$  **Single bonds (other than hydrogen)**



# Infrared group frequencies (correlation chart)



# Infrared group frequencies



# Infrared group frequencies

Functional group class	Band position (cm <sup>-1</sup> )	Intensity of absorption
Alkanes, alkyl groups C—H	2850–2960	Medium to strong
Alkenes =C—H C=C	3020–3100 1640–1680	Medium Medium
Alkynes ≡C—H —C≡C—	3300 2100–2260	Strong Medium
Alkyl halides C—Cl C—Br C—I	600–800 500–600 500	Strong Strong Strong
Alcohols O—H C—O	3400–3650 1050–1150	Strong, broad Strong
Aromatics 	3030	Weak
	1660–2000 1450–1600	Weak Medium
Amines N—H C—N	3300–3500 1030–1230	Medium Medium
Carbonyl compounds <sup>a</sup> C=O	1670–1780	Strong
Carboxylic acids O—H	2500–3100	Strong, very broad
Nitriles C≡N	2210–2260	Medium
Nitro compounds NO <sub>2</sub>	1540	Strong

<sup>a</sup>Carboxylic acids, esters, aldehydes, and ketones.

# Infrared group frequencies

- ▣ Alcohols and amines display strong broad O-H and N-H stretching bands in the region  $3400\text{--}3100\text{ cm}^{-1}$ . The bands are broadened due to hydrogen bonding and a sharp 'non-bonded' peak can often be seen at around  $3400\text{ cm}^{-1}$ .
- ▣ Alkene and alkyne C-H bonds display sharp stretching absorptions in the region  $3100\text{--}3000\text{ cm}^{-1}$ . The bands are of medium intensity and are often obscured by other absorbances in the region (i.e., OH).

# Infrared group frequencies

- ◉ Triple bond stretching absorptions occur in the region  $2400\text{-}2200\text{ cm}^{-1}$ . Absorptions from nitriles are generally of medium intensity and are clearly defined. Alkynes absorb weakly in this region unless they are highly **asymmetric**; **symmetrical alkynes do not show absorption bands.**

# Infrared group frequencies

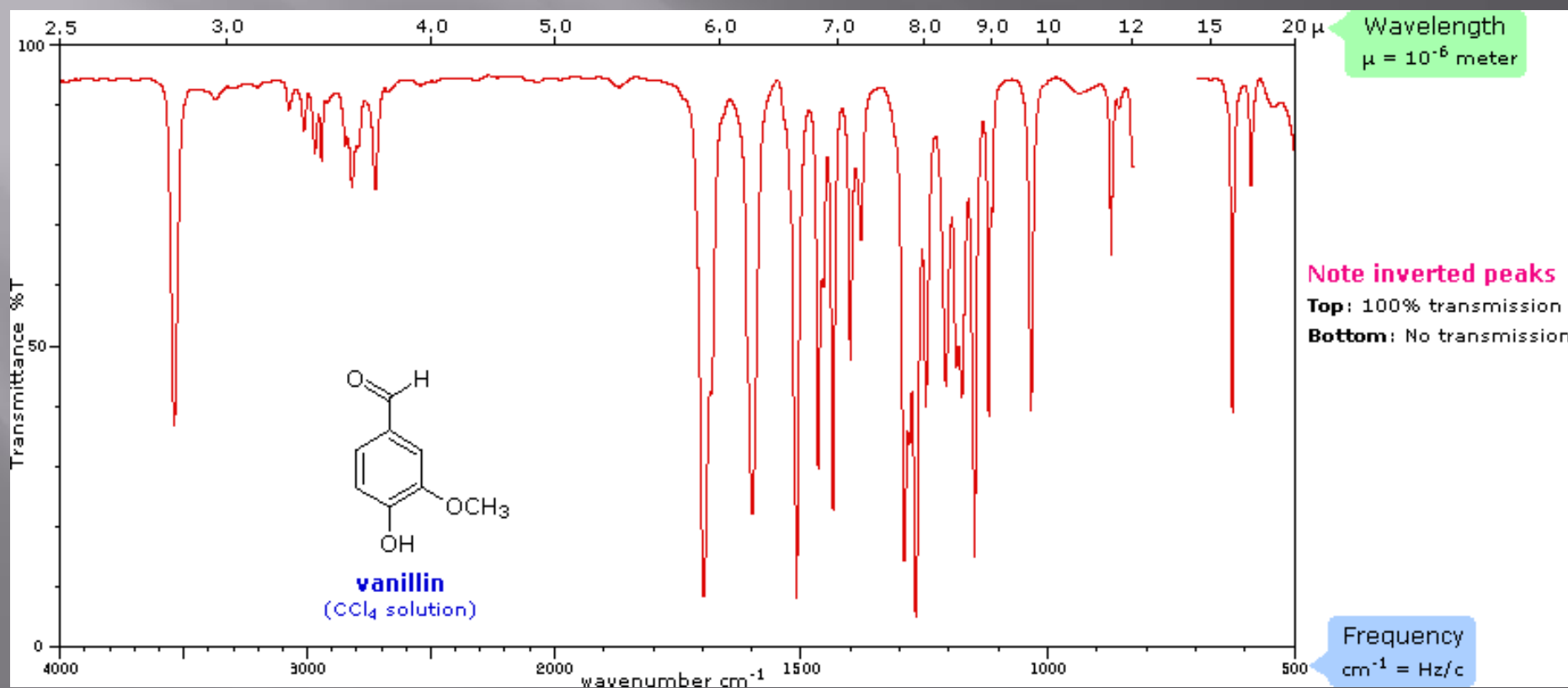
- ▣ Carbonyl stretching bands occur in the region 1800-1700  $\text{cm}^{-1}$ . The bands are generally **very strong** and **broad**. Carbonyl compounds which are more reactive in nucleophilic addition reactions (acyl halides, esters) are generally at higher wave number than simple ketones and aldehydes, and amides are the lowest, absorbing in the region 1700-1650  $\text{cm}^{-1}$ .



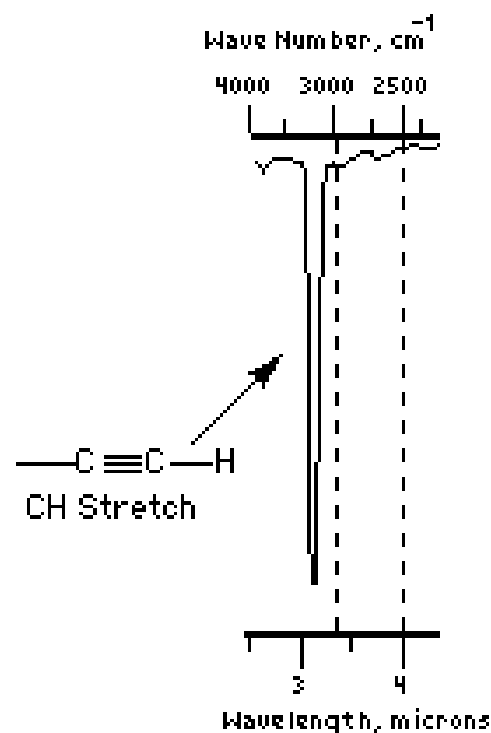
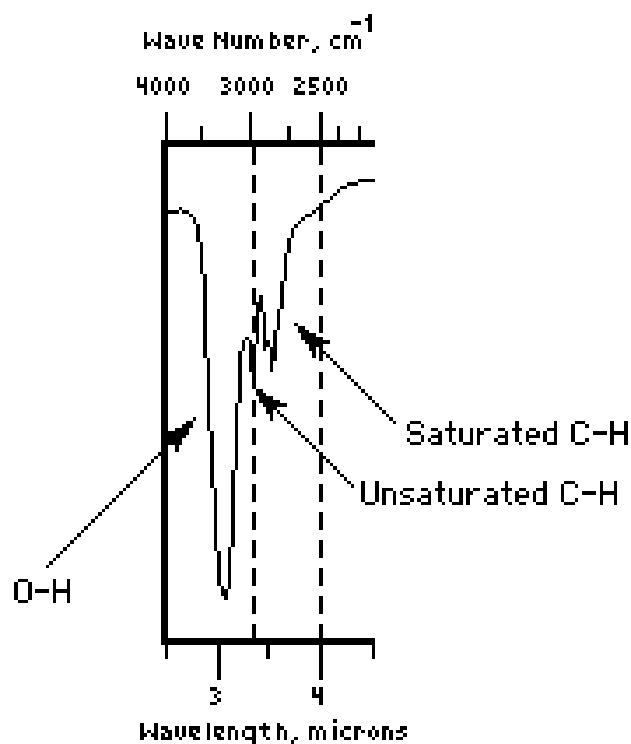
# Infrared group frequencies

- ◉ Carbon-carbon double bond stretching occurs in the region around  $1650\text{-}1600\text{ cm}^{-1}$ . The bands are generally sharp and of medium intensity. Aromatic compounds will typically display a series of sharp bands in this region.
- ◉ Carbon-oxygen single bonds display stretching bands in the region  $1200\text{-}1100\text{ cm}^{-1}$ . The bands are generally strong and broad. You should note that many other functional groups have bands in this region which appear similar.

# Infrared spectrum of vanillin



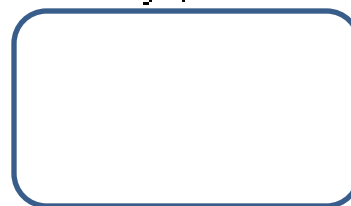
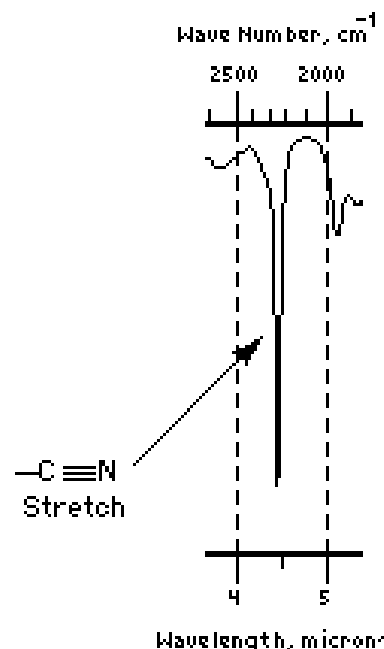
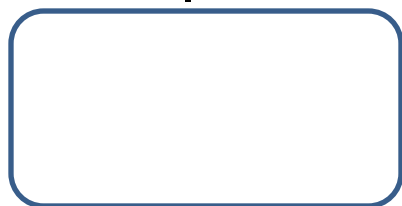
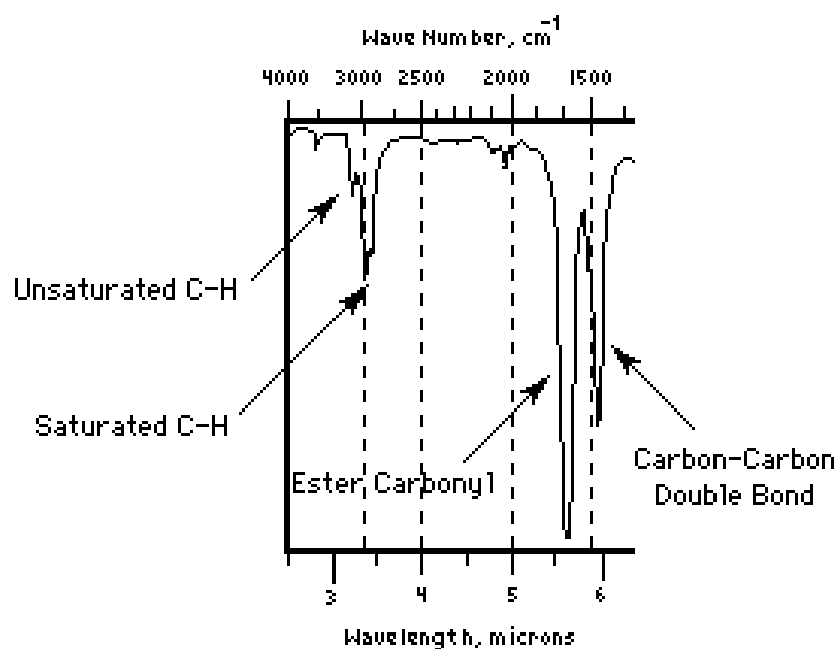
# Examples of infrared spectra



# Examples of infrared spectra

- ▣ The infrared spectrum of benzyl alcohol displays a broad, hydrogen-bonded -OH stretching band in the region  $\sim 3400\text{ cm}^{-1}$ , a sharp unsaturated ( $\text{sp}^2$ ) CH stretch at about  $3010\text{ cm}^{-1}$  and a saturated ( $\text{sp}^3$ ) CH stretch at about  $2900\text{ cm}^{-1}$ ; these bands are typical for alcohols and for aromatic compounds containing some saturated carbon.
- ▣ Acetylene (ethyne) displays a typical terminal alkyne C-H stretch.

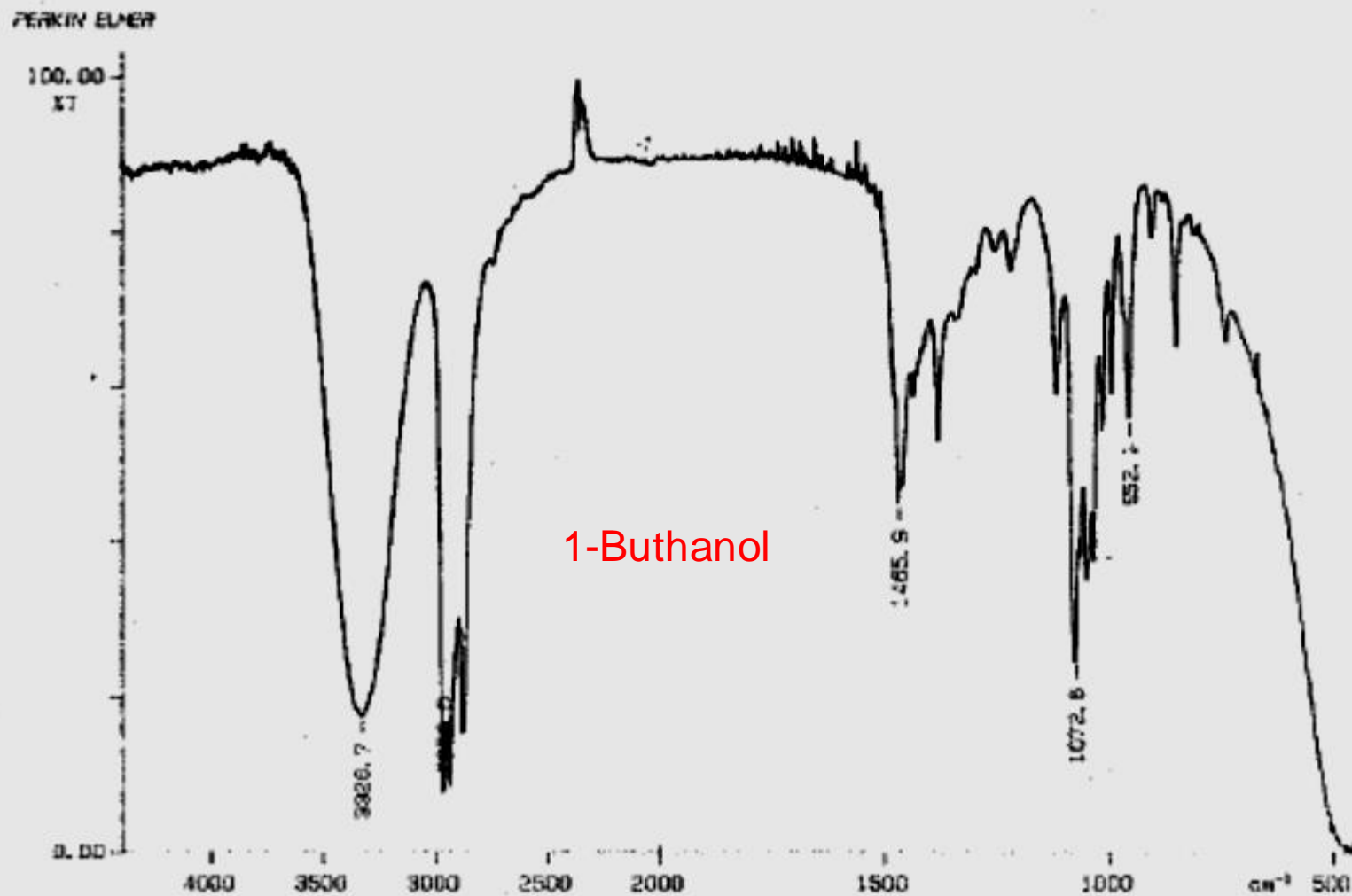
# Examples of infrared spectra



# Examples of infrared spectra

- ▣ Saturated and unsaturated CH bands are shown clearly in the spectrum of vinyl acetate (ethenyl ethanoate). This compound also shows a typical ester carbonyl at  $1700\text{ cm}^{-1}$  and an example of a carbon-carbon double bond stretch at about  $1500\text{ cm}^{-1}$ . Both of these bands are shifted to slightly lower wave numbers than are typically observed (by about  $50\text{ cm}^{-1}$ ) by **conjugation** involving the vinyl ester group.

# Example spectra (1)



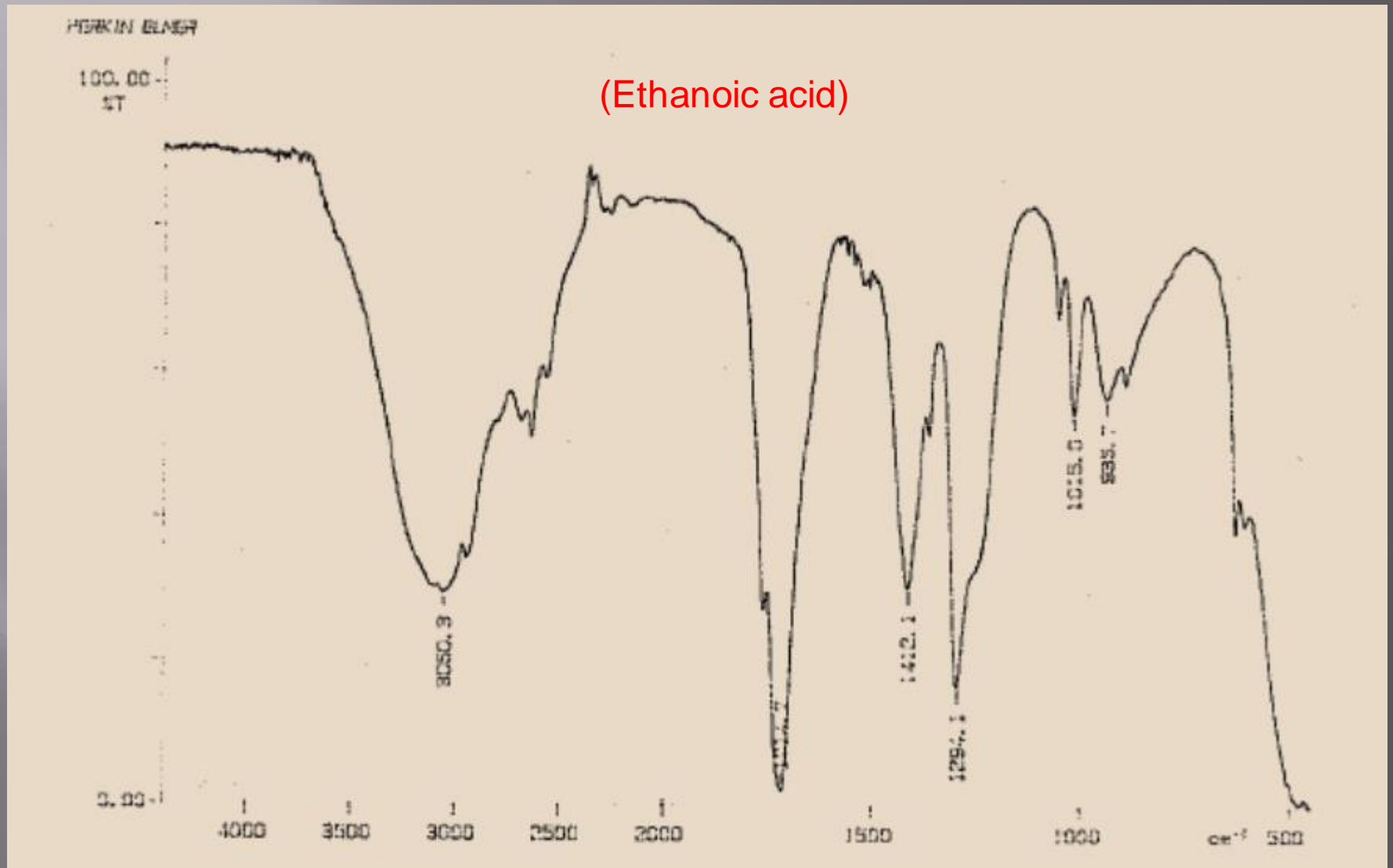
# Example spectra

- ▣ **n-Butanol  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$** 
  - O-H Stretch  $3330\text{ cm}^{-1}$
  - C-O Stretch  $1070\text{ cm}^{-1}$
  - Hydrogen Bonded



# Example spectra (2)

(Ethanoic acid)

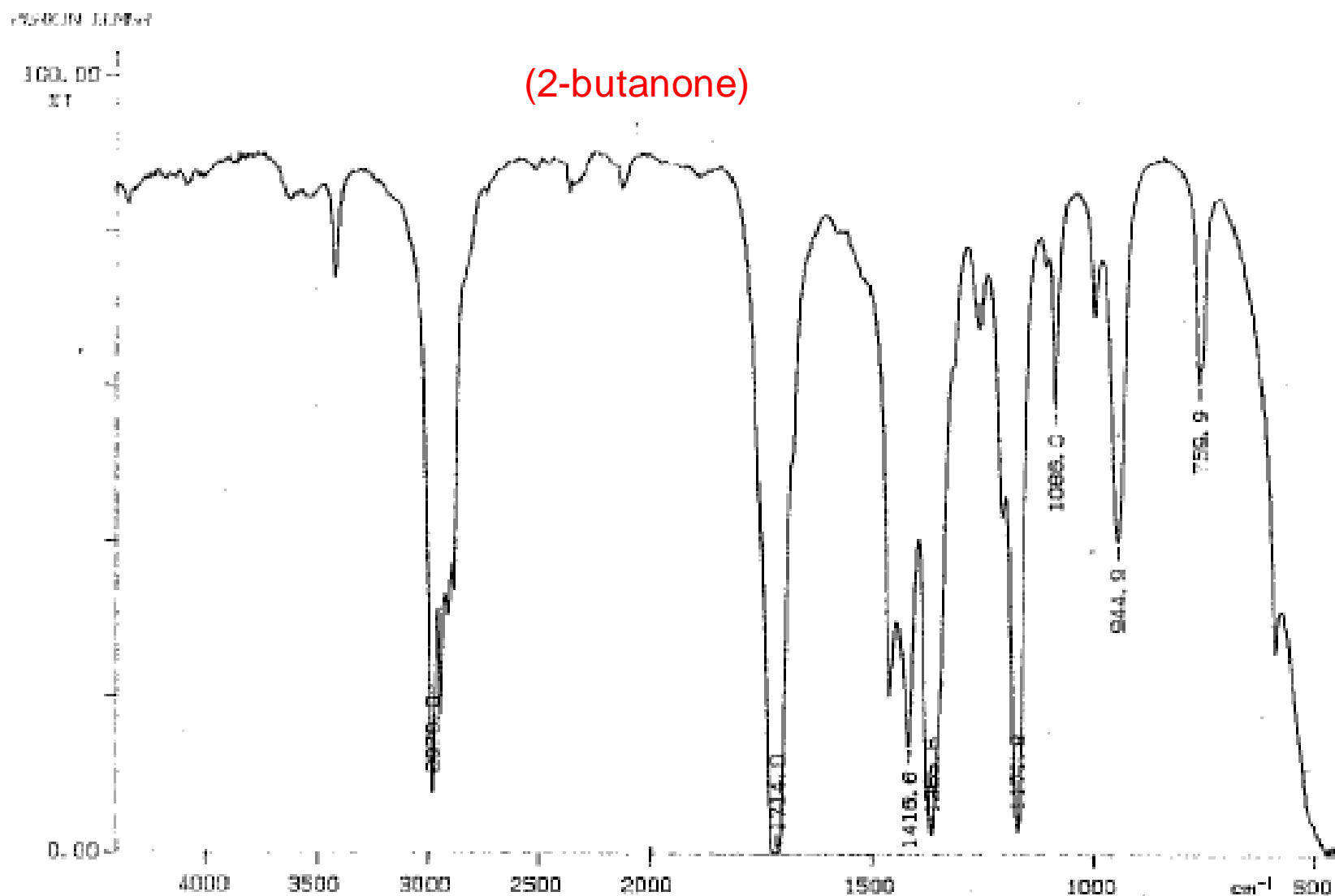


# Example spectra

## ▣ Ethanoic Acid $\text{CH}_3\text{COOH}$

- O-H Stretch  $3050\text{ cm}^{-1}$
- C=O stretch  $1715\text{ cm}^{-1}$
- C-O Stretch  $1295\text{ cm}^{-1}$
- Hydrogen Bonded

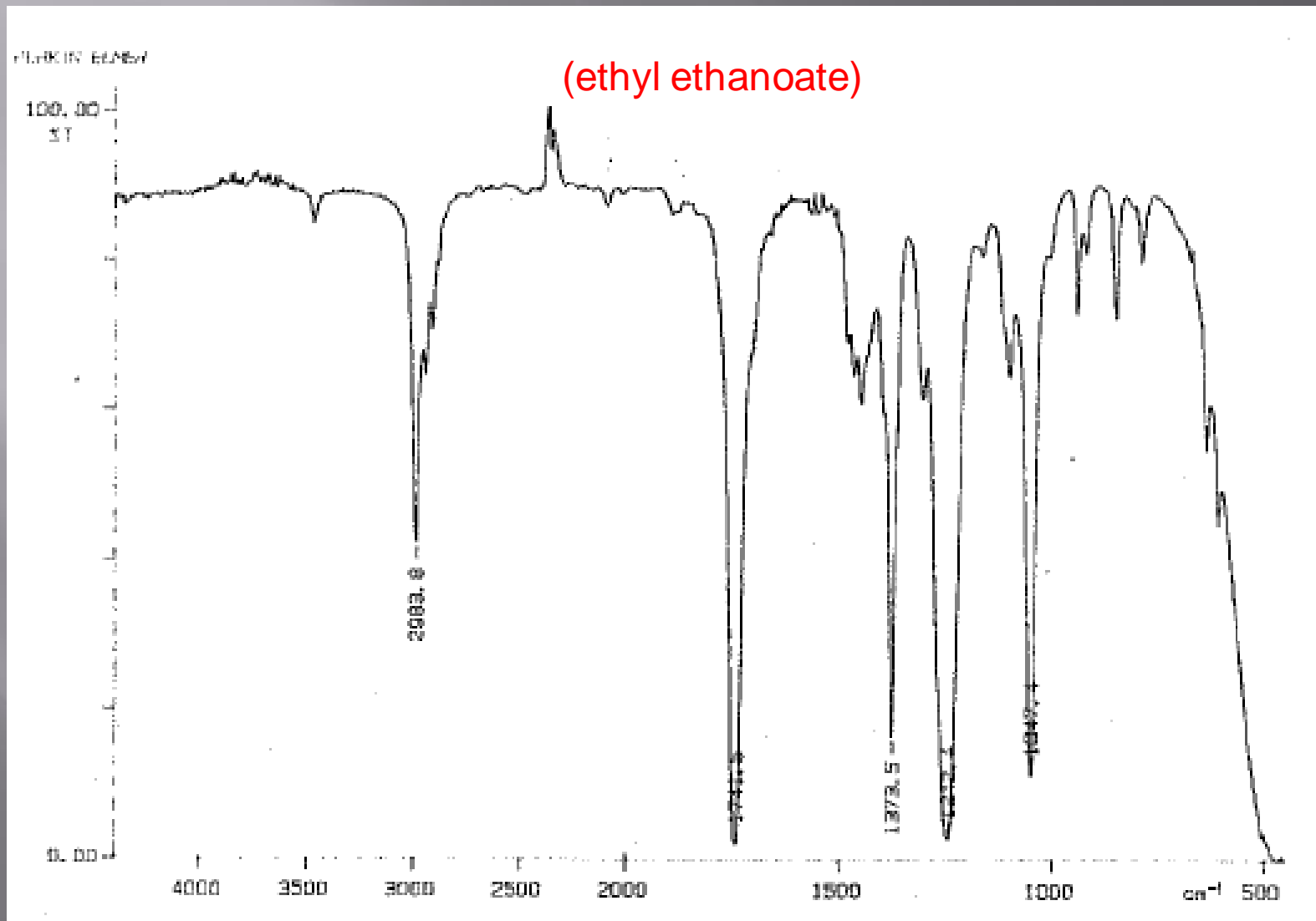
# Example spectra (3)



# Example spectra

- ▣ 2-Butanone  $\text{CH}_3\text{COCH}_2\text{CH}_3$ 
  - C=O Stretch  $1715\text{ cm}^{-1}$

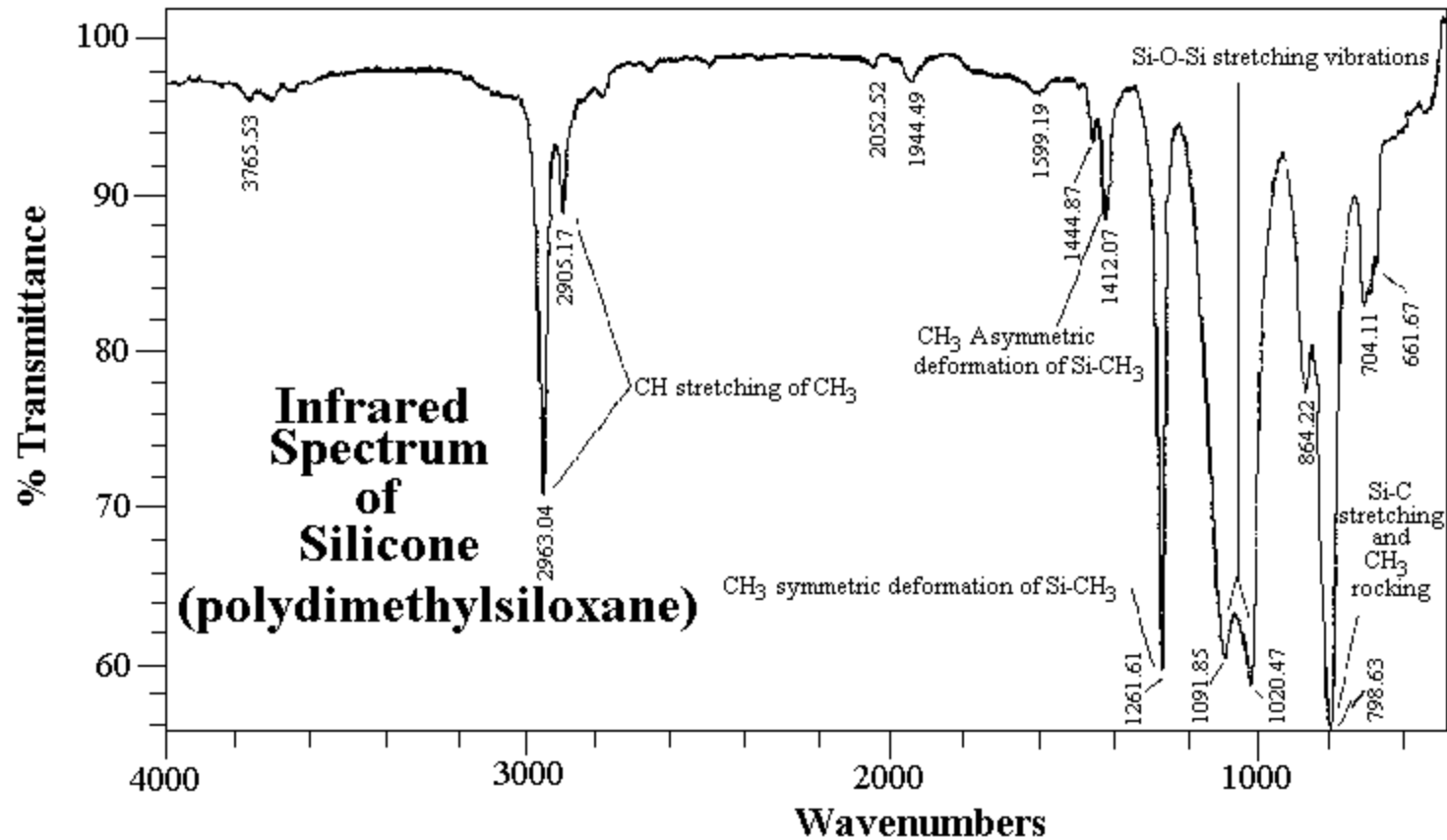
# Example spectra



# Example spectra

- ▣ Ethyl Ethanoate  $\text{CH}_3\text{COOC}_2\text{H}_5$ 
  - C=O Stretch  $1710\text{ cm}^{-1}$
  - C-O Stretch  $1240\text{ cm}^{-1}$
  - C-O Stretch  $1050\text{ cm}^{-1}$

# PDMS



# Infrared interpretation

## ▣ Step 1

- Look first for the carbonyl C=O band.
- Look for a strong band at 1820-1660  $\text{cm}^{-1}$ . This band is usually the most intense absorption band in a spectrum. It will have a medium width. If you see the carbonyl band, look for other bands associated with functional groups that contain the carbonyl by going to step 2.
- If no C=O band is present, check for alcohols and go to step 3.



# Infrared interpretation

## ▣ Step 2

- If a C=O is present you want to determine if it is part of an acid, an ester, or an aldehyde or ketone. At this time you may not be able to distinguish aldehyde from ketone.

# Infrared interpretation

## ▣ ACID

- Look for indications that an O-H is also present. It has a broad absorption near  $3300\text{-}2500\text{ cm}^{-1}$ . This actually will overlap the C-H stretch. There will also be a C-O single bond band near  $1100\text{-}1300\text{ cm}^{-1}$ . Look for the carbonyl band near  $1725\text{-}1700\text{ cm}^{-1}$ .

## ▣ ESTER

- Look for C-O absorption of medium intensity near  $1300\text{-}1000\text{ cm}^{-1}$ . There will be no O-H band.

# Infrared interpretation

## ▣ ALDEHYDE

- Look for aldehyde type C-H absorption bands. These are two weak absorptions to the right of the C-H stretch near  $2850\text{ cm}^{-1}$  and  $2750\text{ cm}^{-1}$  and are caused by the C-H bond that is part of the CHO aldehyde functional group. Look for the carbonyl band around  $1740\text{-}1720\text{ cm}^{-1}$ .

## ▣ KETONE

- The weak aldehyde CH absorption bands will be absent. Look for the carbonyl CO band around  $1725\text{-}1705\text{ cm}^{-1}$ .

# Infrared interpretation

## ▣ Step 3

- If no carbonyl band appears in the spectrum, look for an alcohol O-H band.

## ▣ ALCOHOL

- Look for the broad OH band near  $3600\text{--}3300\text{ cm}^{-1}$  and a C-O absorption band near  $1300\text{--}1000\text{ cm}^{-1}$ .

# Infrared interpretation

## ▣ Step 4

- If no carbonyl bands and no O-H bands are in the spectrum, check for double bonds, C=C, from an aromatic or an alkene.

## ▣ ALKENE

- Look for weak absorption near  $1650\text{ cm}^{-1}$  for a double bond. There will be a CH stretch band near  $3000\text{ cm}^{-1}$ .

## ▣ AROMATIC

- Look for the benzene, C=C, double bonds which appear as medium to strong absorptions in the region  $1650\text{-}1450\text{ cm}^{-1}$ . The CH stretch band is much weaker than in alkenes.

# Infrared interpretation

## ▣ Step 5

- If none of the previous groups can be identified, you may have an alkane.

## ▣ ALKANE

- The main absorption will be the C-H stretch near  $3000\text{ cm}^{-1}$ . The spectrum will be simple with another band near  $1450\text{ cm}^{-1}$ .

# Infrared interpretation

## ▣ Step 6

- If the spectrum still cannot be assigned you may have an alkyl halide.

## ▣ ALKYL BROMIDE

- Look for the C-H stretch and a relatively simple spectrum with an absorption to the right of  $667\text{ cm}^{-1}$ .