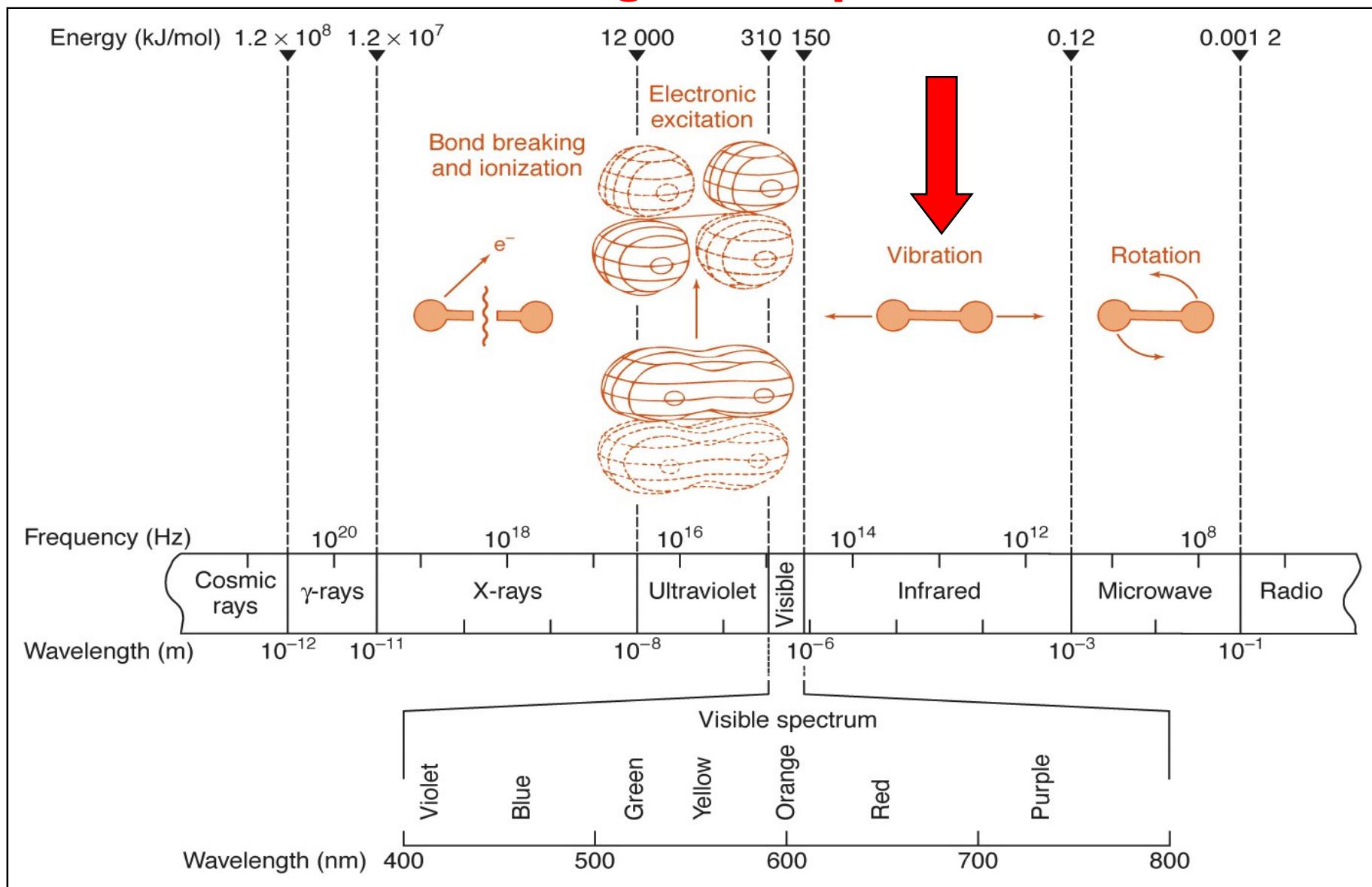


INFRARED ABSORPTION SPECTROSCOPY

What is spectroscopy?

- **Spectroscopy is an analytical technique which helps to determine structure.**
- **It is basically the study of the interaction of matter and electromagnetic radiation.**
- **It destroys little or no sample.**

Electromagnetic Spectrum



- Energy of IR photon insufficient to cause electronic excitation but can cause vibrational excitation

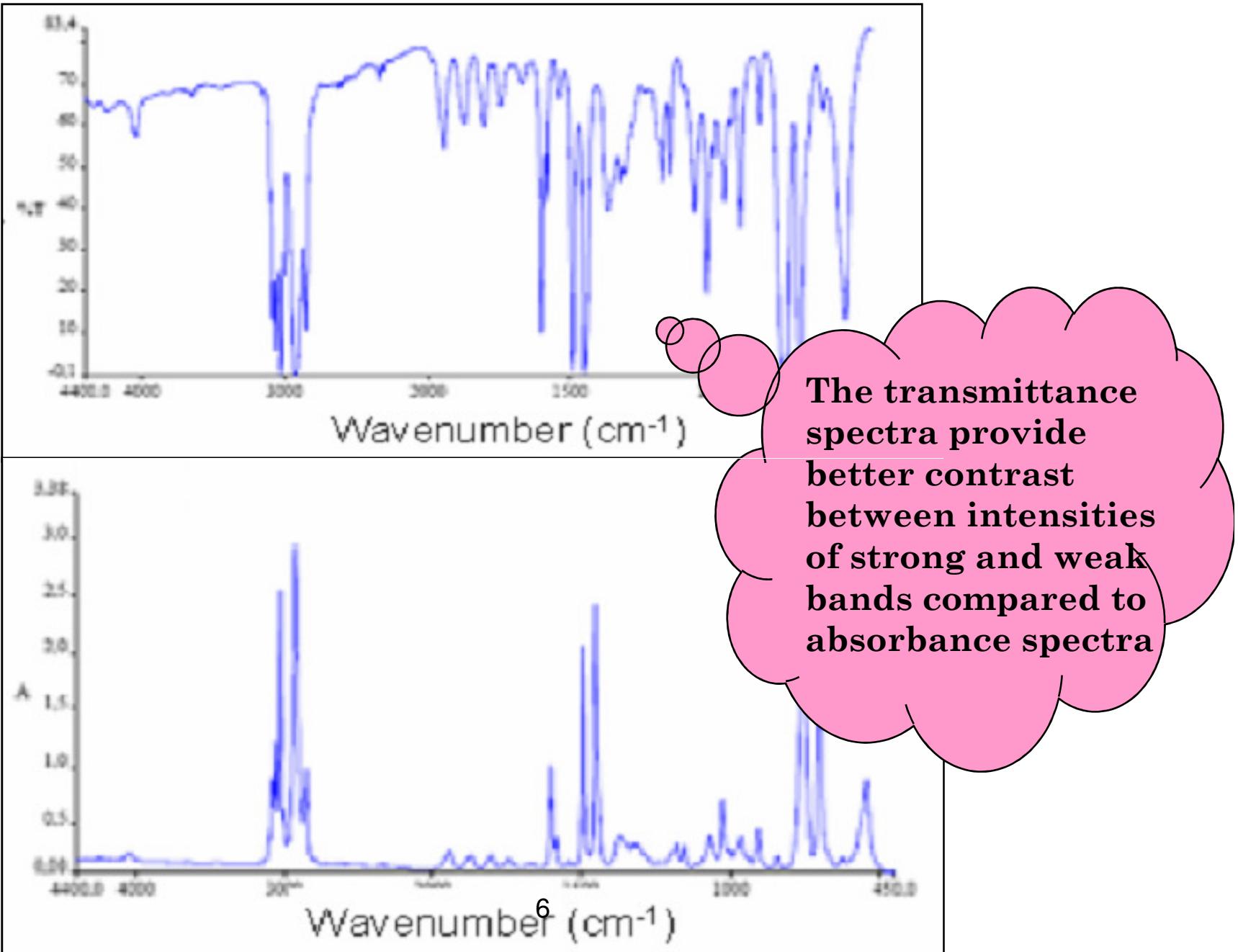
Principles

- When the certain molecules are exposed to IR light, it will absorb the energy to make the atoms of molecules vibrate
- The vibration frequency depend on the mass of atoms, bond length and the bond strength
- Molecule vibration is stimulated by absorption of radiation in the same frequency with the frequency of its origin vibrations

Infrared spectroscopy

- Mostly for qualitative analysis
- Absorption spectra is recorded as transmittance spectra
- Absorption occurs at specific wavelengths
- IR spectra is called “fingerprints”
- No other chemical species will have identical IR spectrum

Comparison between transmittance (upper) vs



Energy Expression

The relationship between the energy (E) of a photon and the frequency (or the wavelength) of the electromagnetic radiation is described by the equation

$$E = h\nu = \frac{hc}{\lambda}$$

Wavenumber ($\tilde{\nu}$) is another way to describe the *frequency* of electromagnetic radiation, and the one most often used in infrared spectroscopy. It is the number of waves in one centimeter, so it has units of reciprocal centimeters (cm^{-1}). Scientists use wavenumbers in preference to wavelengths because, unlike wavelengths, wavenumbers are directly proportional to energy. The relationship between wavenumber (in cm^{-1}) and wavelength (in μm) is given by the equation

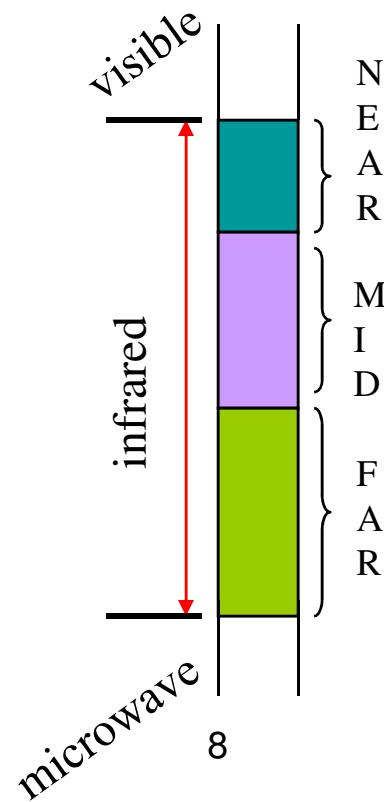
$$\tilde{\nu}(\text{cm}^{-1}) = \frac{10^4}{\lambda(\mu\text{m})} \quad (\text{because } 1 \mu\text{m} = 10^{-4} \text{ cm})$$

So *high frequencies, large wavenumbers, and short wavelengths* are associated with *high energy*.

- IR region of EM spectrum:
 - λ : 780 nm – 1000 nm
 - Wavenumber: 12,800 – 10 cm^{-1}

- IR region subdivided into 3 subregions:

1. **Near IR region (Nearest to the visible)**
(12,800 to 4000 cm^{-1})
2. **Mid IR region**
(4000 – 200 cm^{-1})
3. **Far IR region**
(200 – 10 cm^{-1})

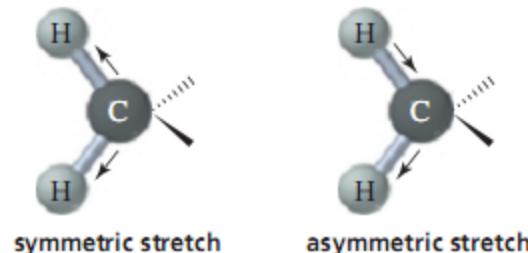
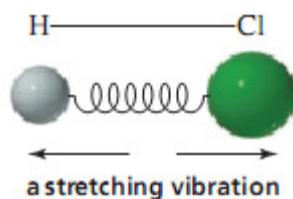


13.7 Infrared Spectroscopy

Stretching and Bending Vibrations

A **Stretch** is a vibration occurring along the line of the bond that changes the bond length

Stretching vibrations

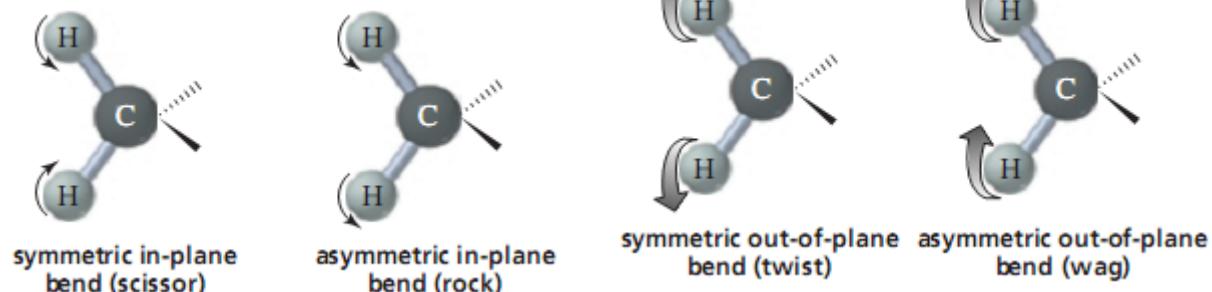


A **bend** is a vibration that does not occur along the line of the bond, but changes the bond angle.

A **Tri atomic** molecule can experience **symmetric** and **asymmetric** stretches and **bends**

Bending vibrations can be either **in-plane** or **out-of-plane** they are often referred to as **rock**, **scissor**, **wag** and **twist**.

Bending vibrations

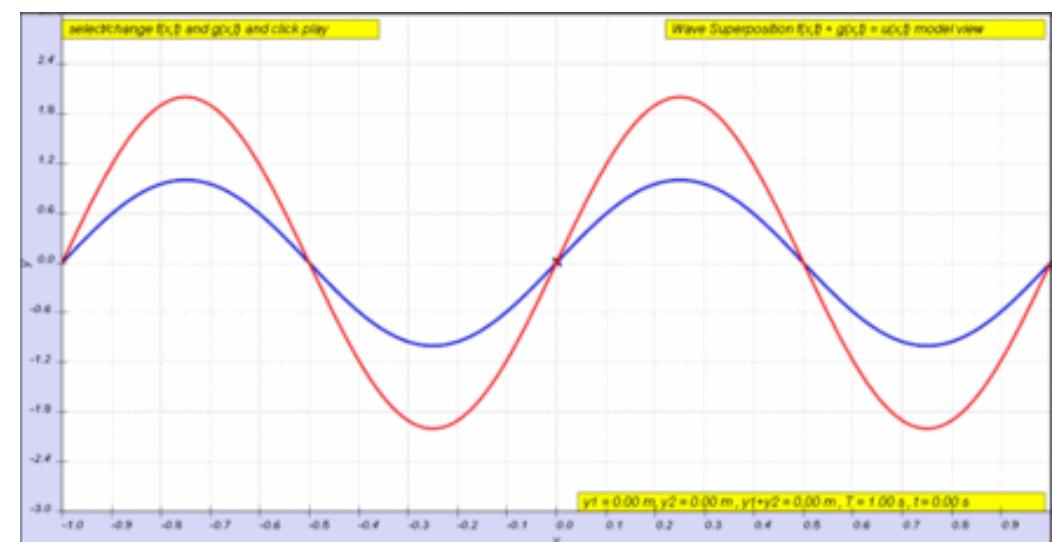
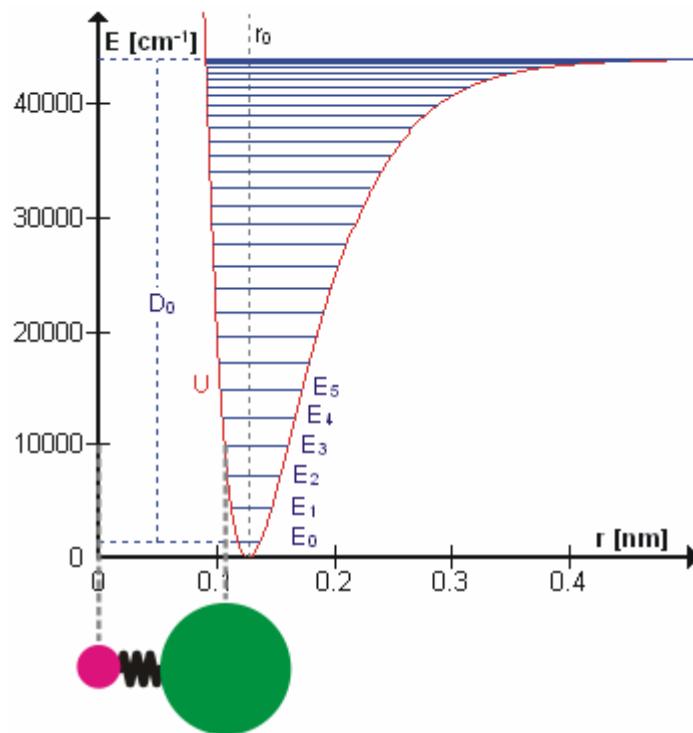


- **When IR absorption occur?**

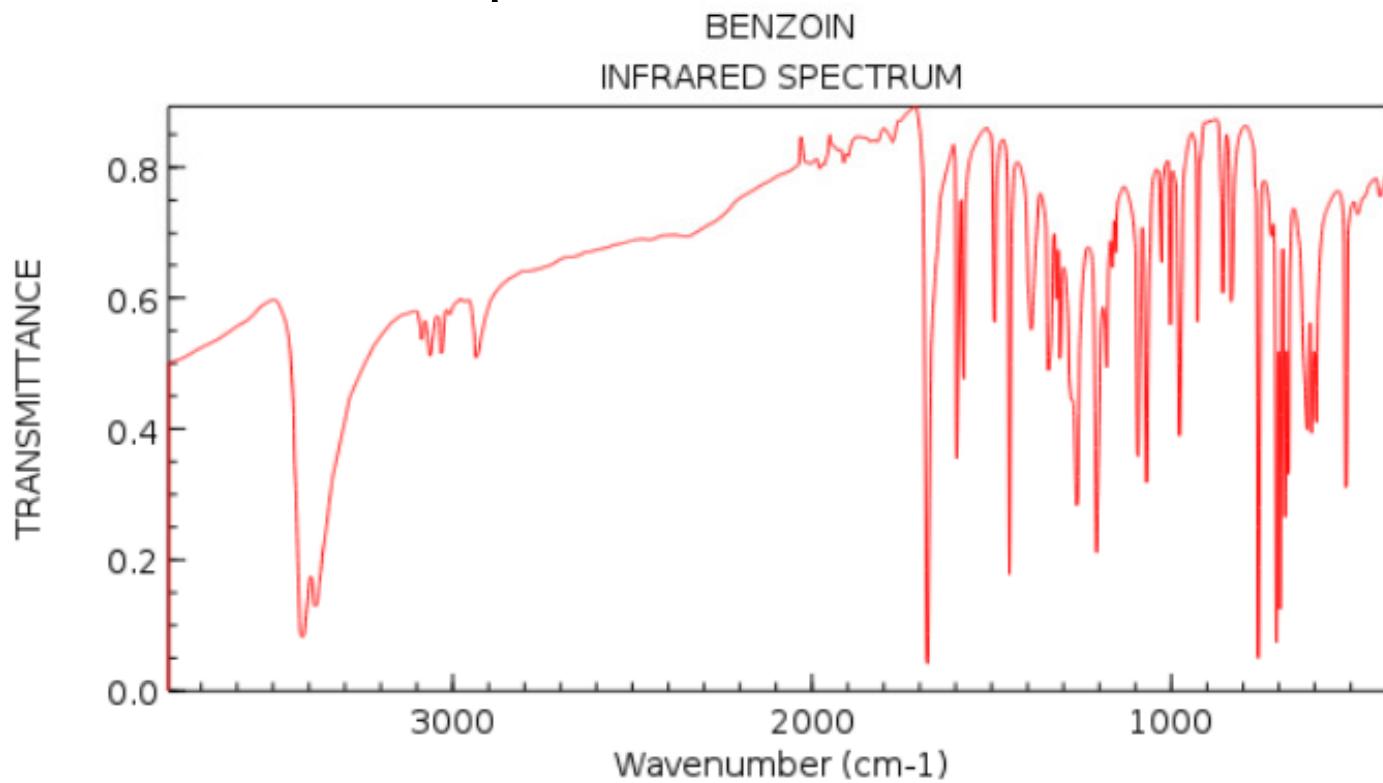
1. IR absorption only occurs when IR radiation interacts with a molecule undergoing a change in **dipole moment** as it vibrates or rotates.
2. Infrared absorption only occurs when the incoming IR photon has sufficient energy for the transition to the next allowed vibrational state

Note: If the 2 rules above are not met, **no absorption can occur**

The energy absorbed will **increase the amplitude** of the vibrational motions of the bonds in the molecule but not the **frequency**.

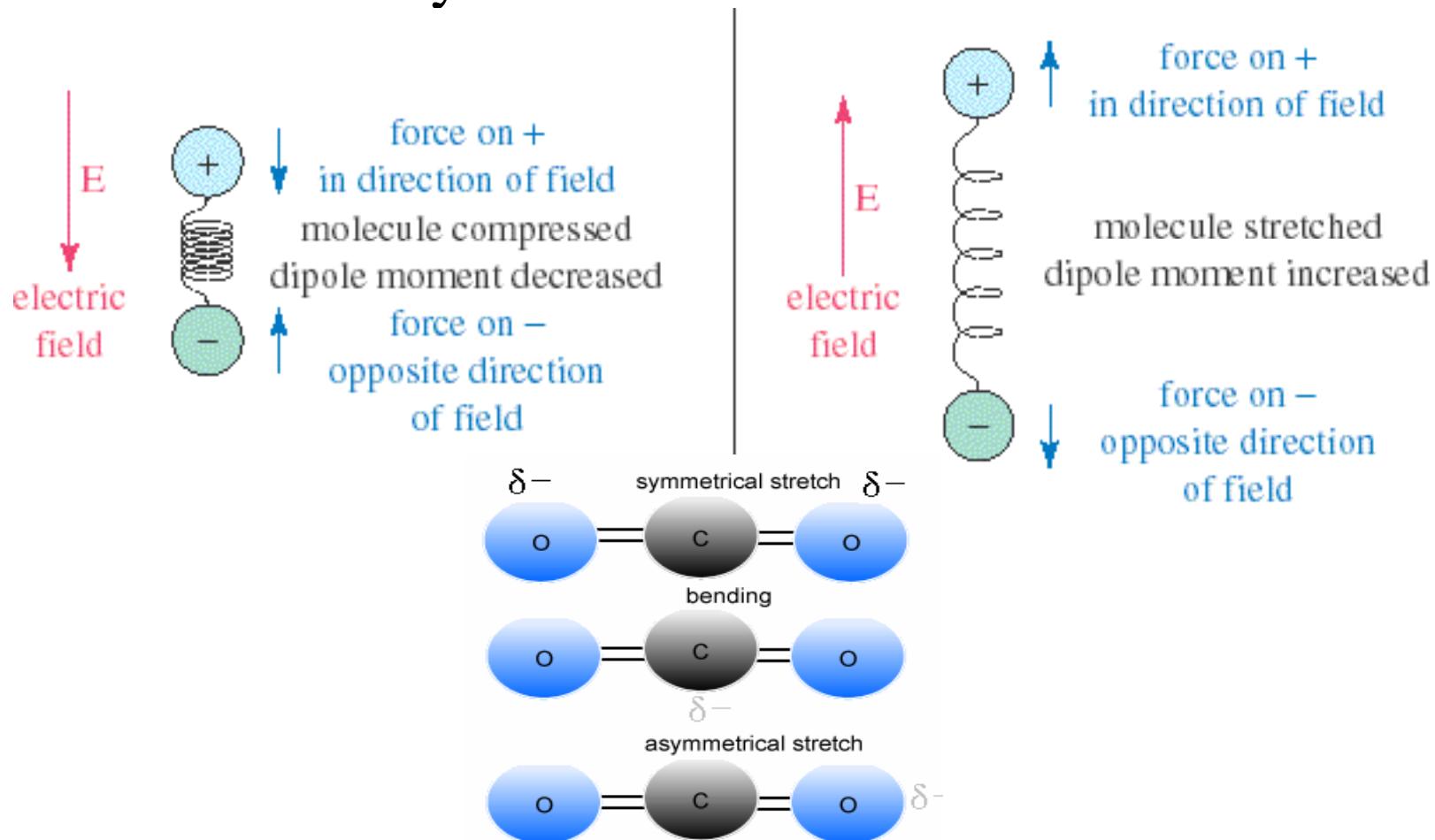


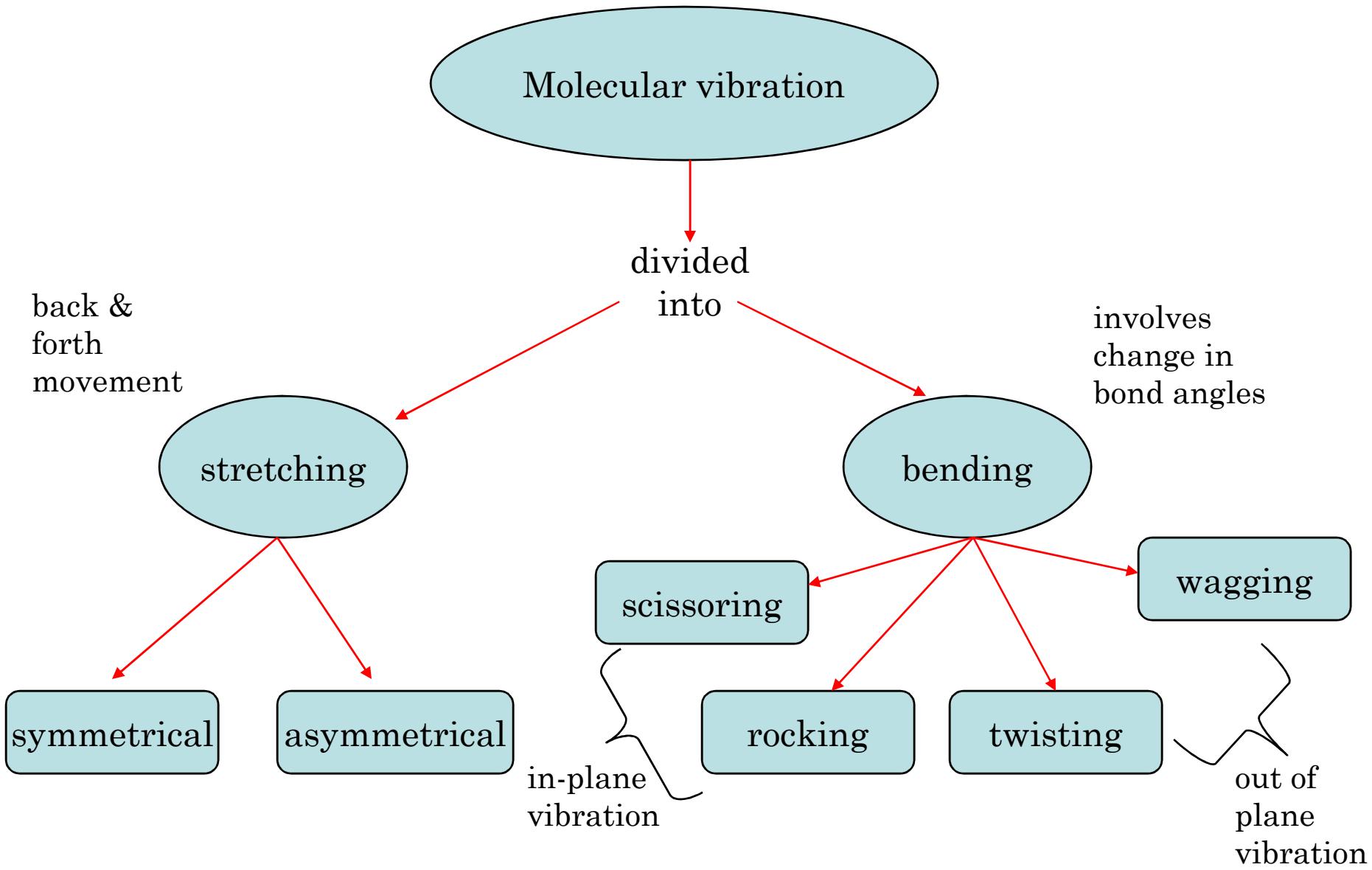
- NOT ALL bonds in a molecule are capable of absorbing IR energy. Only those bonds that have change in dipole moment are capable to absorb IR radiation.
- The larger the dipole change, the stronger the intensity of the band in an IR spectrum



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.





IR Components

- IR Resources
 - Quartz halogen
 - Nernst Glower lamp (run at 2000°C)
 - Globar (made from Carbide silicon, run at 1100°C)
- Sample Handling Techniques
- Gases: evacuated cylindrical cells equipped with suitable windows
- Liquid: sodium chloride windows
 - “neat” liquid
- Solid: Pellet (KBr) or Mull

Solid sample preparation

- There are three ways to prepare solid sample for IR spectroscopy.
 - Solid that is **soluble** in solvent can be dissolved in a solvent, most commonly carbon tetrachloride CCl_4 .
 - Solid that is **insoluble** in CCl_4 or any other IR solvents can be prepared either by KBr pellet or mulls.

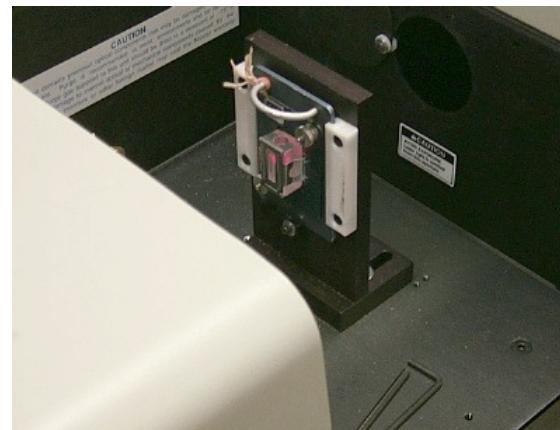
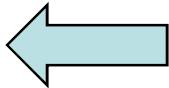
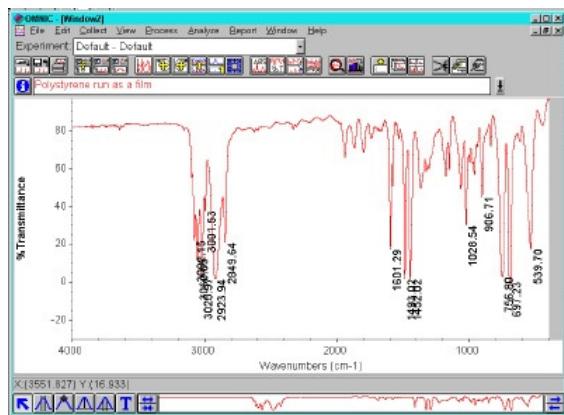
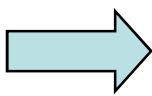
What is a mull

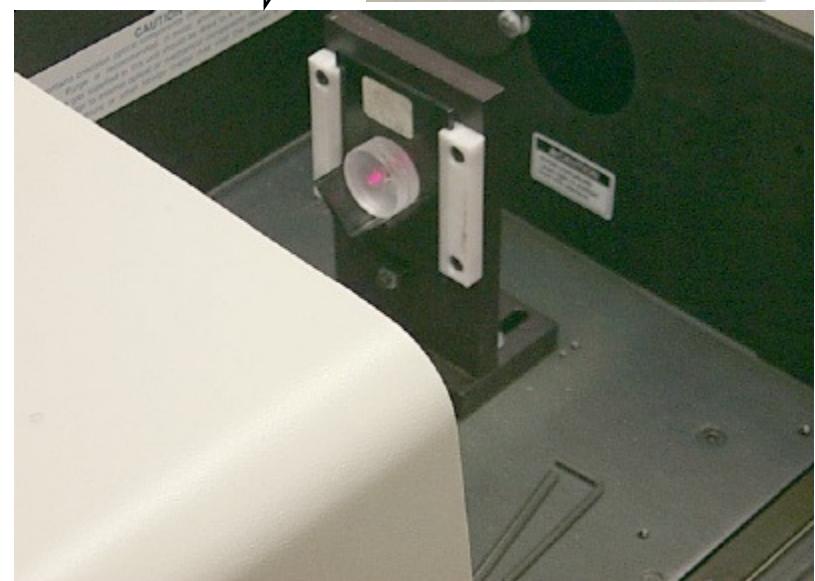
- A thick paste formed by grinding an insoluble solid with an inert liquid and used for studying spectra of the solid

What is Nujol

- A trade name for a heavy medicinal liquid paraffin. Extensively used as a mulling agent in spectroscopy

Sample preparation





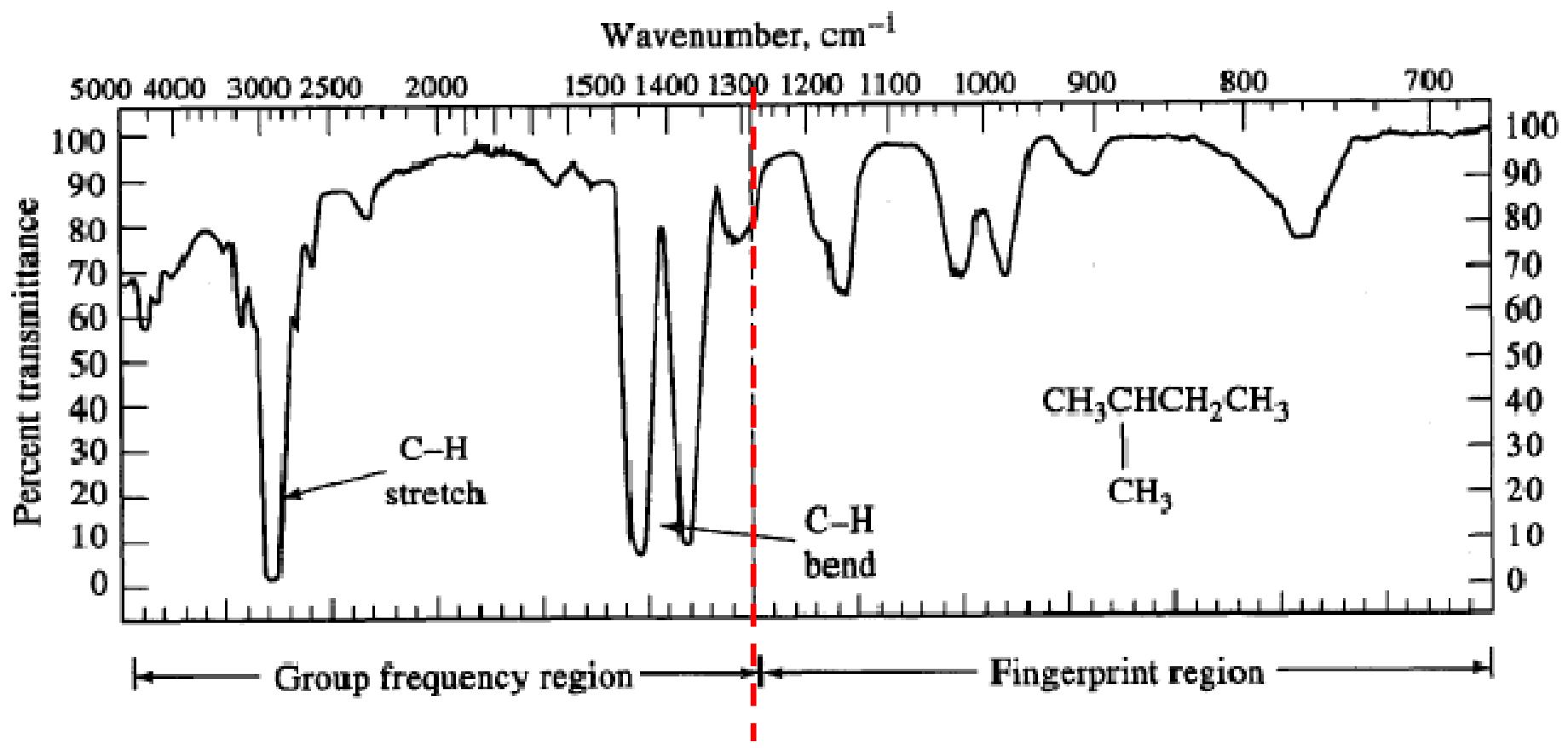
A newer type of IR spectrometer, called a Fourier transform IR (FT-IR) spectrometer, has several advantages. Its sensitivity is better because, instead of scanning through the frequencies, it measures all frequencies simultaneously. With a conventional IR spectrometer, it can take 2 to 10 minutes to scan through all the frequencies. In contrast, FT-IR spectra can be taken in 1 to 2 seconds. The information is digitized and Fourier transformed by a computer to produce the FT-IR spectrum. The spectra shown in this text are FT-IR spectra.

Interpretation Infrared Spectra

Infrared Spectra

- IR spectrum is due to specific structural features, a specific bond, within the molecule, since the vibrational states of individual bonds represent 1 vibrational transition.
- e.g. IR spectrum can tell the molecule has an O-H bond or a C=O or an aromatic ring

Infrared Spectra



How to analyze IR spectra

1. Begin by looking in the region from 4000-1300.
Look at the C–H stretching bands around 3000:

Are any or all to the **right of 3000?**

Indicates:

alkyl groups (present in most organic molecules)

Are any or all to the **left of 3000?**

a C=C bond or aromatic group in the molecule

**2. Look for a carbonyl in the region 1760-1690.
If there is such a band:**

Indicates:

Is an O–H band also present?

a carboxylic acid group

Is a C–O band also present?

an ester

Is an aldehyde C–H band also present?

an aldehyde

Is an N–H band also present?

an amide

Are none of the above present?

a ketone

(also check the exact position of the carbonyl band for clues as to the type of carbonyl compound it is)

3. Look for a broad O–H band in the region 3500–3200 cm⁻¹.
If there is such a band:

Indicates:

Is an O–H band present? an alcohol or phenol

4. Look for a single or double sharp N–H band in the region 3400–3250 cm⁻¹.

If there is such a band:

Indicates:

Are there two bands? a primary amine

Is there only one band? a secondary amine

5. Other structural features to check for:

Are there C–O stretches?

Indicates:

an ether (or an ester if there is a carbonyl band too)

Is there a C=C stretching band?

an alkene

Are there aromatic stretching bands?

an aromatic

Is there a C≡C band?

an alkyne

Are there -NO₂ bands?

a nitro compound

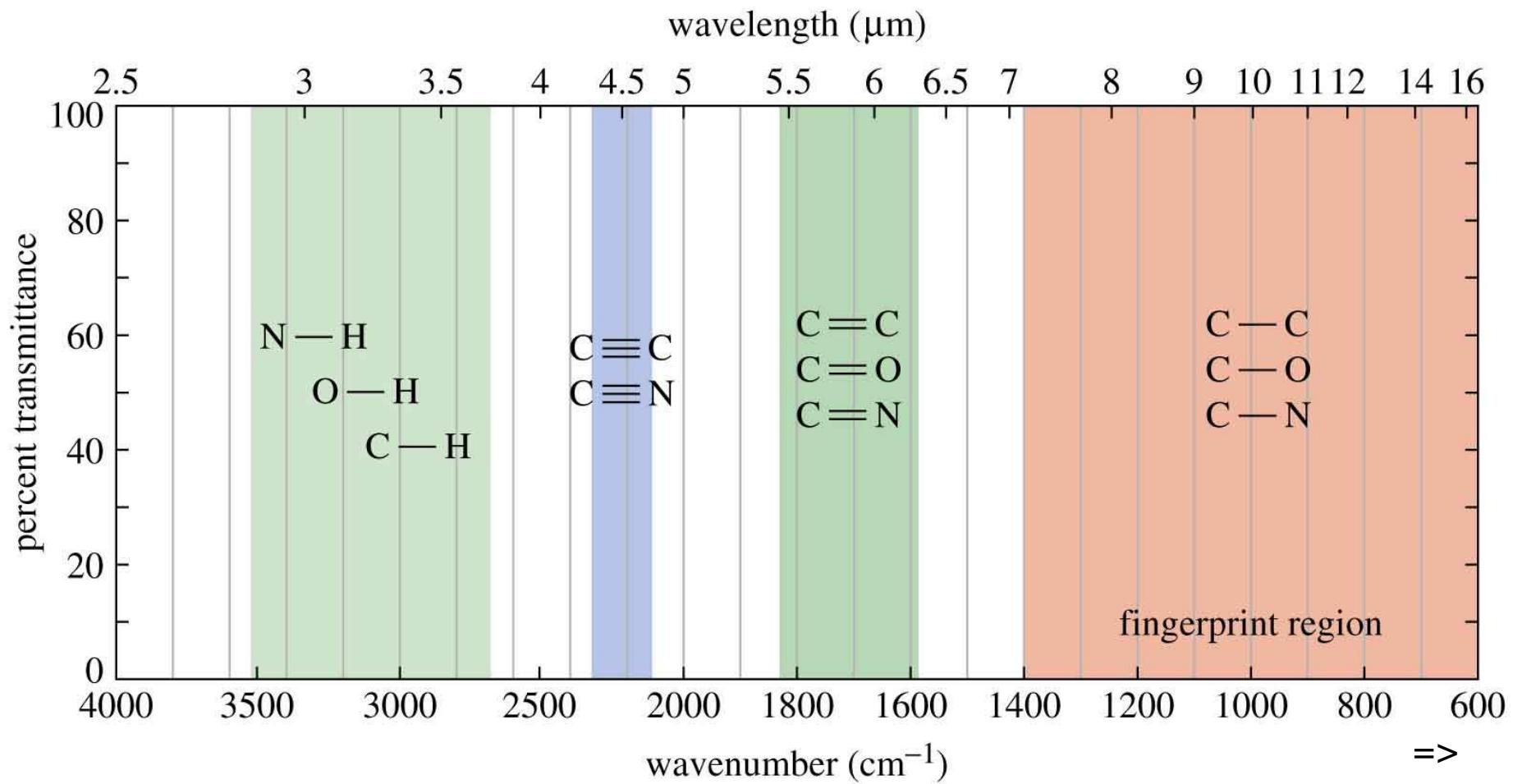
How to analyze IR spectra

- If there is an absence of major functional group bands in the region $4000\text{-}1300\text{ cm}^{-1}$ (other than C–H stretches), the compound is probably a strict hydrocarbon.
- Also check the region from $900\text{-}650\text{ cm}^{-1}$. Aromatics, alkyl halides, carboxylic acids, amines, and amides show moderate or strong absorption bands (bending vibrations) in this region.
- As a beginning student, you should not try to assign or interpret every peak in the spectrum. Concentrate on learning the major bands and recognizing their presence and absence in any given spectrum.

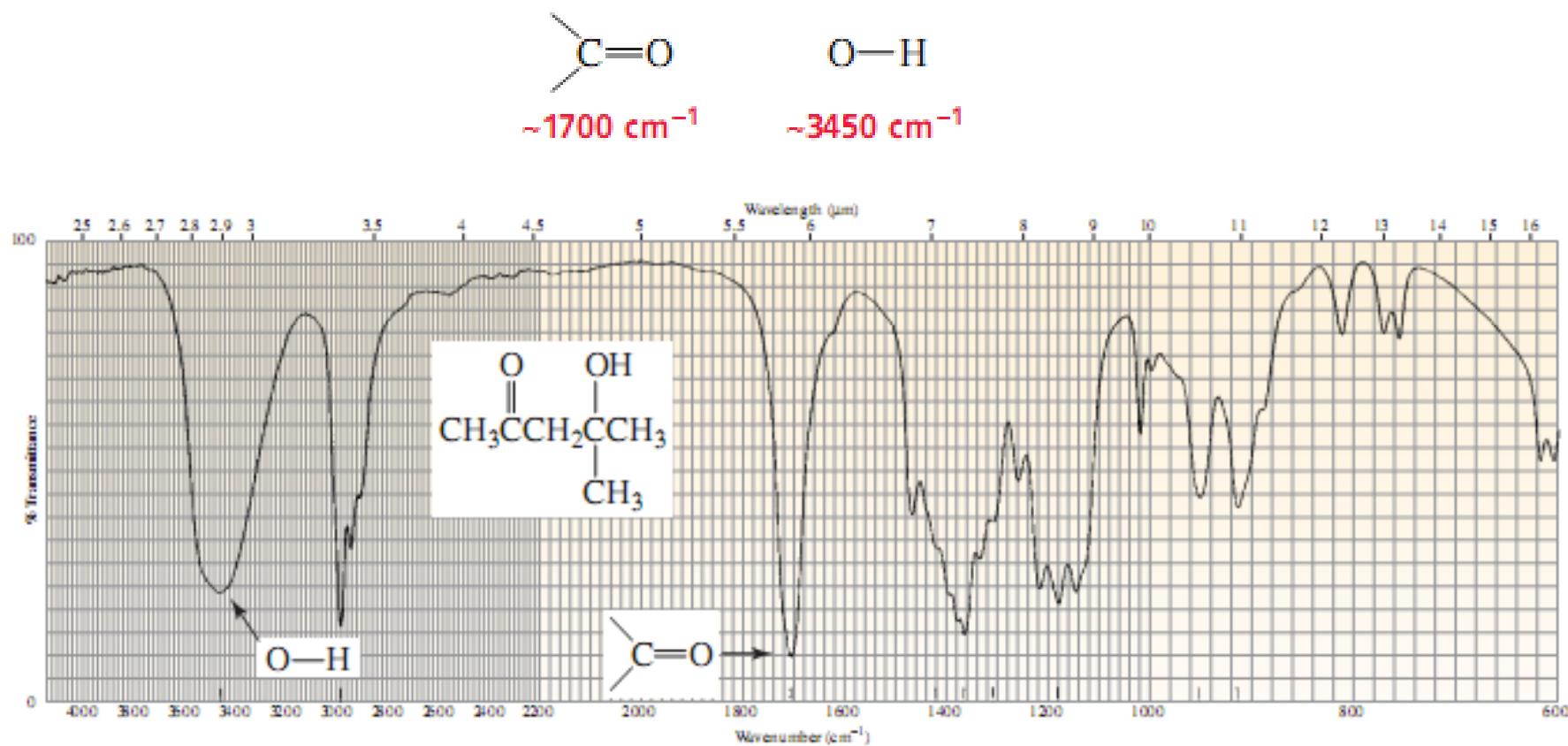
TABLE 17-2 Abbreviated Table of Group Frequencies for Organic Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes (>C=C<^{H})	3010–3095	Medium
		675–995	Strong
C—H	Alkynes ($—\text{C}\equiv\text{C—H}$)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C≡C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO ₂	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

Summary of IR Absorptions



The stretching vibration of a C=O bond absorbs energy of wave number $\sim 1700 \text{ cm}^{-1}$ whereas the stretching vibration of an O-H bond absorbs energy of wave number $\sim 3550 \text{ cm}^{-1}$

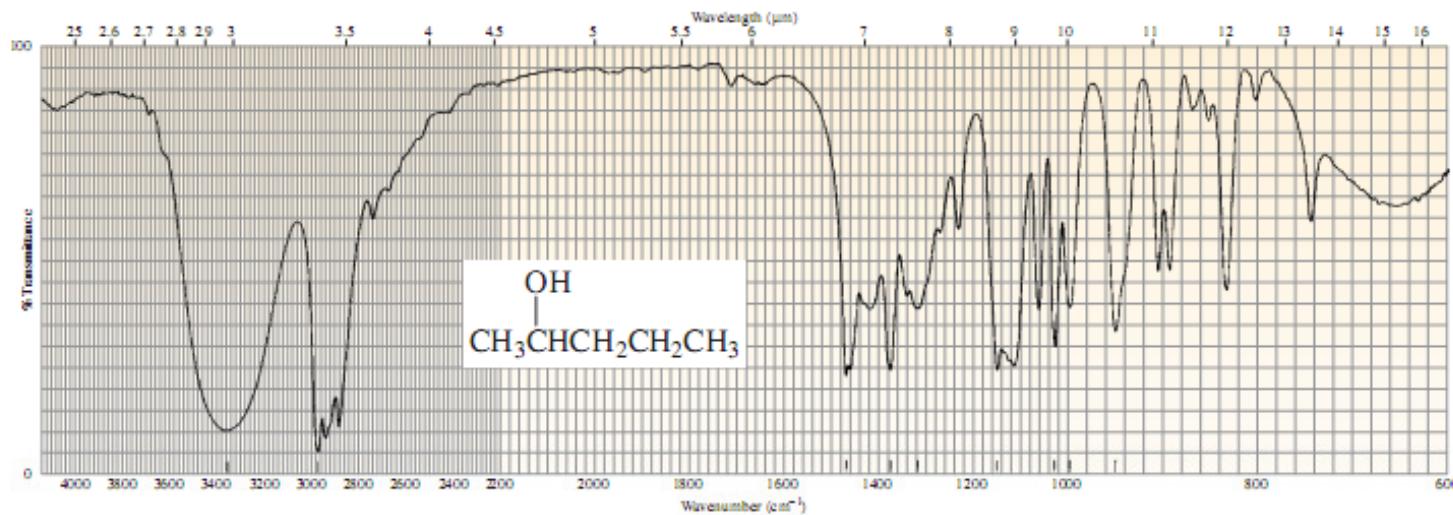


▲ **Figure 13.13**
The infrared spectrum of 4-hydroxy-4-methyl-2-pentanone.

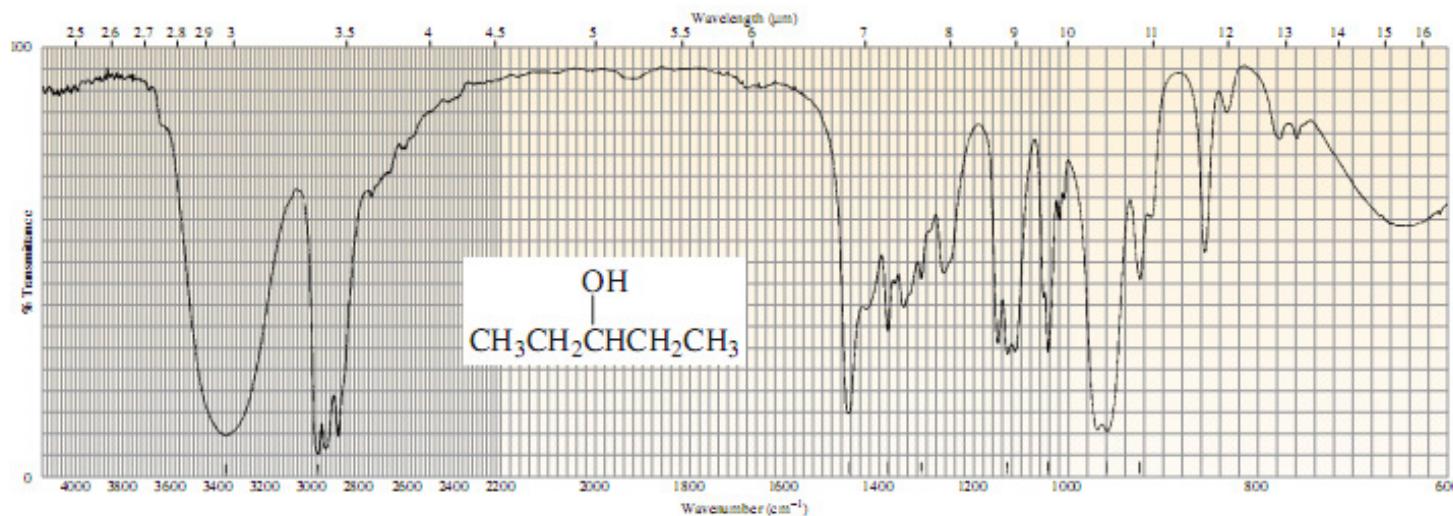
The Functional Group and Fingerprint Regions

Electromagnetic radiation with wavenumbers from 4000 to 600 cm⁻¹ has just the right energy to correspond to the stretching and bending vibrations of organic molecules.

a.



b.



13.8 Characteristic Infrared Absorption Bands

Table 13.4 Important IR Stretching Frequencies

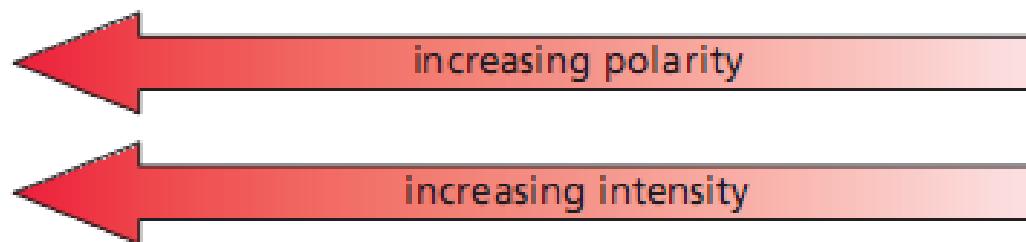
Type of bond	Wavenumber (cm^{-1})	Intensity
$\text{C}\equiv\text{N}$	2260–2220	medium
$\text{C}\equiv\text{C}$	2260–2100	medium to weak
$\text{C}=\text{C}$	1680–1600	medium
$\text{C}=\text{N}$	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
$\text{C}=\text{O}$	1780–1650	strong
$\text{C}—\text{O}$	1250–1050	strong
$\text{C}—\text{N}$	1230–1020	medium
$\text{O}—\text{H}$ (alcohol)	3650–3200	strong, broad
$\text{O}—\text{H}$ (carboxylic acid)	3300–2500	strong, very broad
$\text{N}—\text{H}$	3500–3300	medium, broad
$\text{C}—\text{H}$	3300–2700	medium

13.9 The Intensity of Absorption Bands

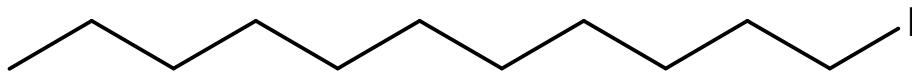
The greater the change in dipole moment, the more intense the absorption.

relative bond polarities

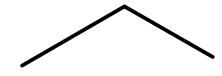
relative intensities of IR absorption



Intensity of absorption depends on the number of bonds responsible for the absorption.



23 C-H bond



5 C-H bond

I1

IITG, 8/13/2010

13.10 The Position of Absorption Bands

Hooke's Law

The amount of energy required to stretch a bond depends on the *strength* of the bond and the *masses* of the bonded atoms. The stronger the bond, the greater the energy required to stretch it, because a stronger bond corresponds to a tighter spring. The frequency of the vibration is inversely related to the mass of the atoms attached to the spring, so heavier atoms vibrate at lower frequencies.

The approximate wavenumber of an absorption can be calculated from the following equation derived from Hooke's law, which describes the motion of a vibrating spring:

$$\tilde{\nu} = \frac{1}{2\pi c} \left[\frac{f(m_1 + m_2)}{m_1 m_2} \right]^{1/2} \quad c = \text{the speed of light}$$

The equation relates the wavenumber of the stretching vibration ($\tilde{\nu}$) to the force constant of the bond (f) and the masses of the atoms (in grams) joined by the bond (m_1 and m_2). The force constant is a measure of the strength of the bond. The equation shows that *stronger bonds* and *lighter atoms* give rise to higher frequencies.

Lighter atoms shows absorption bands at larger wave number

C-H	C-D	C-O	C-Cl
$\sim 3000\text{cm}^{-1}$	$\sim 2200\text{cm}^{-1}$	$\sim 1100\text{cm}^{-1}$	$\sim 700\text{cm}^{-1}$

Stretching Frequencies

Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm ⁻¹)
<i>Frequency dependence on atomic masses</i>		
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C	83 (350)	1200
<i>Frequency dependence on bond energies</i>		
C—C	83 (350)	1200
C=C	146 (611)	1660
C≡C	200 (840)	2200

heavier atoms

stronger bond

$\bar{\nu}$ decreases

$\bar{\nu}$ increases

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

Fingerprint of Molecule

- Whole-molecule vibrations and bending vibrations are also quantitized.
- No two molecules will give exactly the same IR spectrum (except enantiomers).
- Simple stretching: $1400\text{-}4000\text{ cm}^{-1}$,
“functional group region.”
- Complex vibrations: $600\text{-}1400\text{ cm}^{-1}$, called
the **“fingerprint region.”**

Effect of bond order

- Stronger bonds absorb at higher frequencies:



$\sim 2200 \text{ cm}^{-1}$

(weak or absent if internal)



$\sim 1660 \text{ cm}^{-1}$



$\sim 1100 \text{ cm}^{-1}$



$\sim 1700 \text{ cm}^{-1}$



$\sim 1100 \text{ cm}^{-1}$



$\sim 2200 \text{ cm}^{-1}$



$\sim 1600 \text{ cm}^{-1}$



$\sim 1100 \text{ cm}^{-1}$

- Conjugation lowers the frequency:

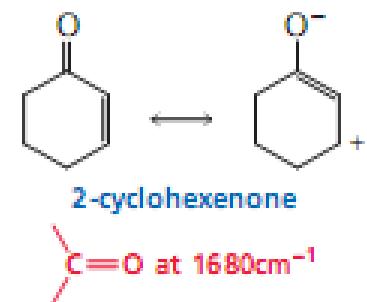
– isolated C=C $1640\text{-}1680 \text{ cm}^{-1}$

– conjugated C=C $1620\text{-}1640 \text{ cm}^{-1}$

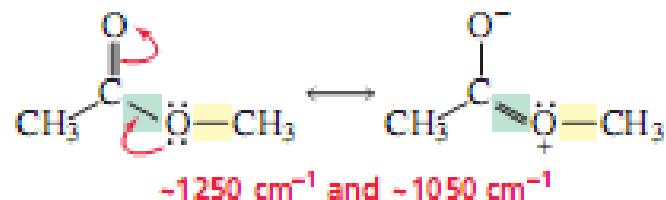
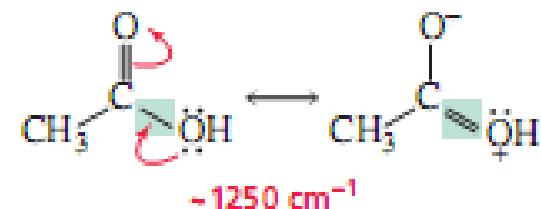
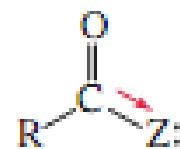
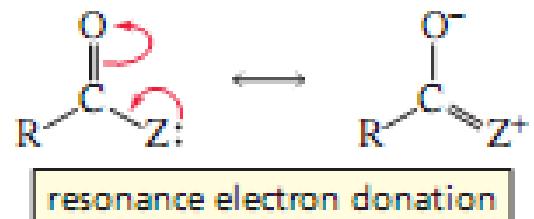
– aromatic C=C approx. 1600 cm^{-1}



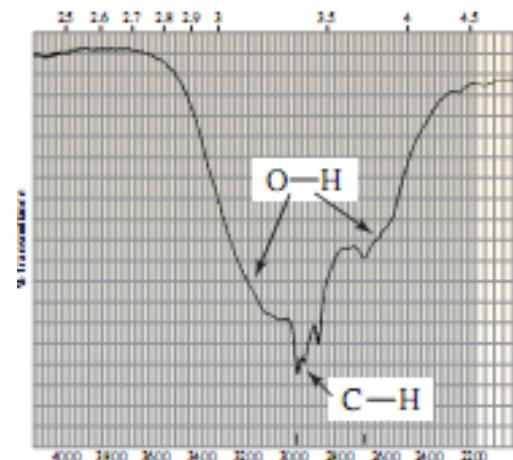
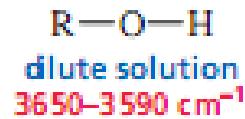
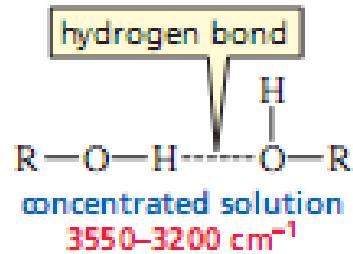
2-pentanone



Resonance and Inductive effect

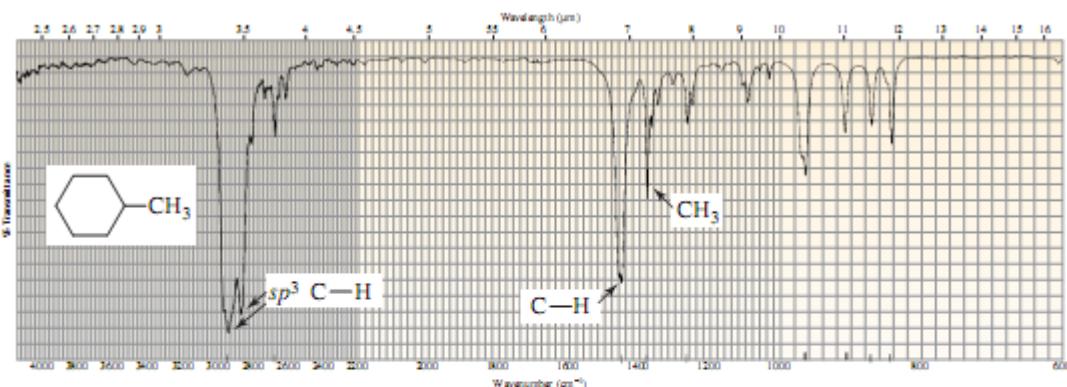


O—H Absorption Bands

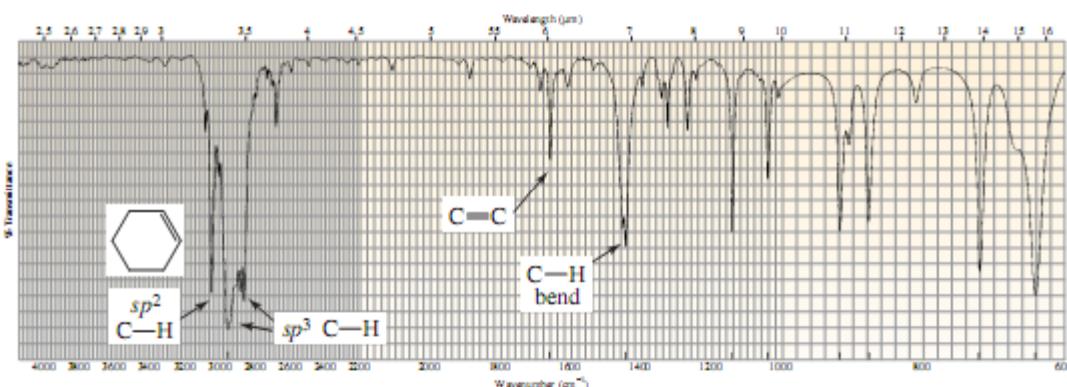


C—H Absorption Bands

The strength of C-H bond depends greater the s character of the carb opposite to the concept of acidity.



▲ Figure 13.21
The IR spectrum of methylcyclohexane.



▲ Figure 13.22
The IR spectrum of cyclohexene.

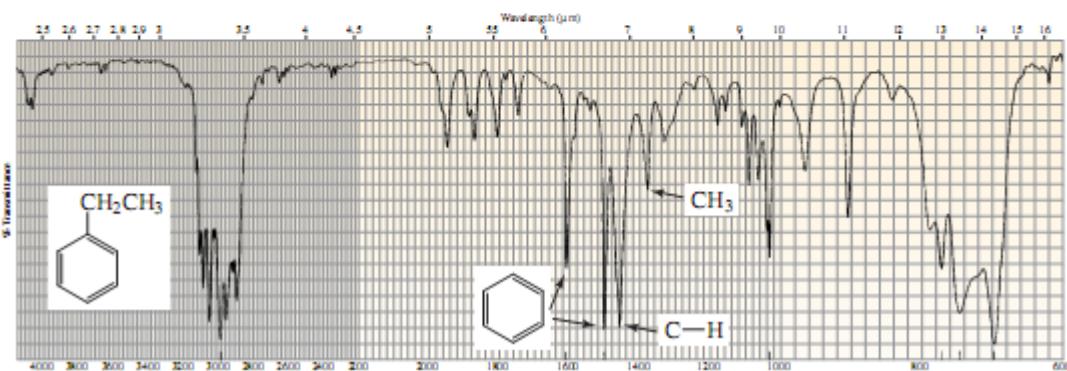


Table 13.5 IR Absorptions of Carbon–Hydrogen Bonds

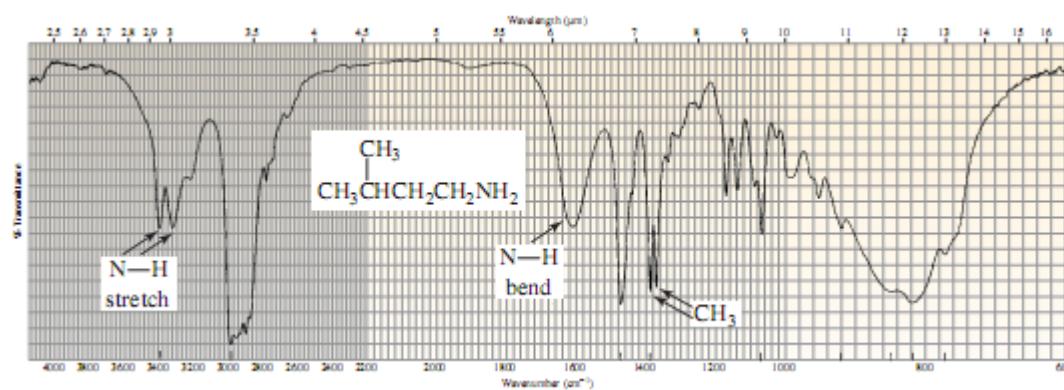
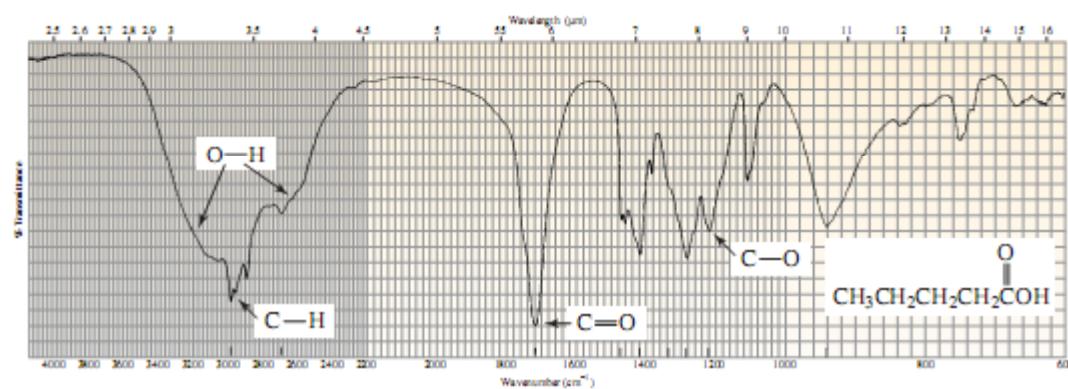
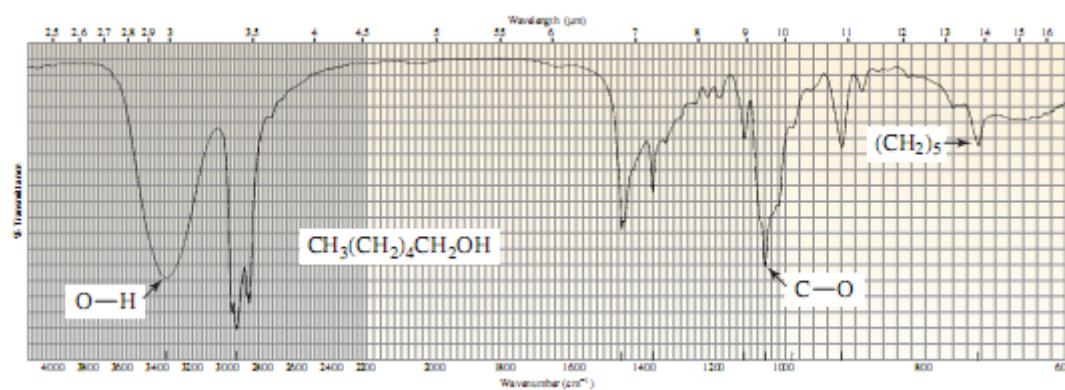
Carbon–Hydrogen Stretching Vibrations	Wavenumber (cm⁻¹)
C≡C—H	~3300
C=C—H	3100–3020
C—C—H	2960–2850
	~2820 and ~2720

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}

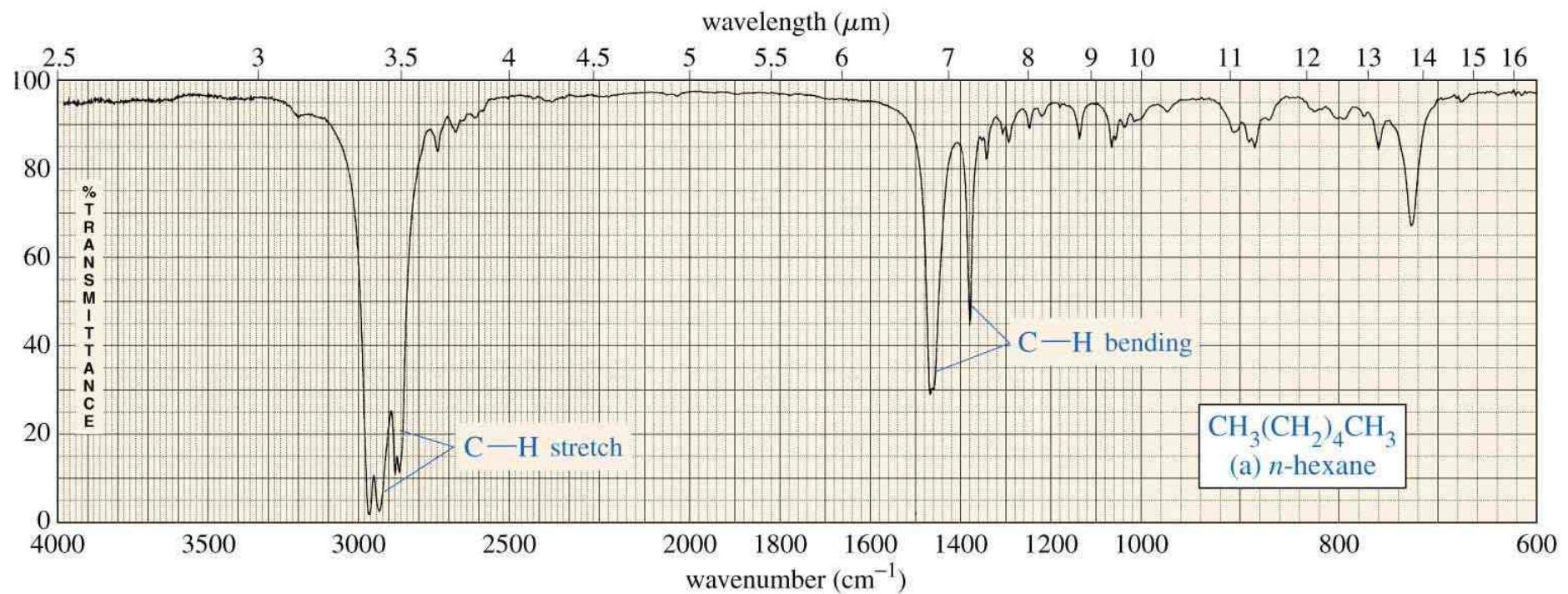
The Shape of Absorption Bands



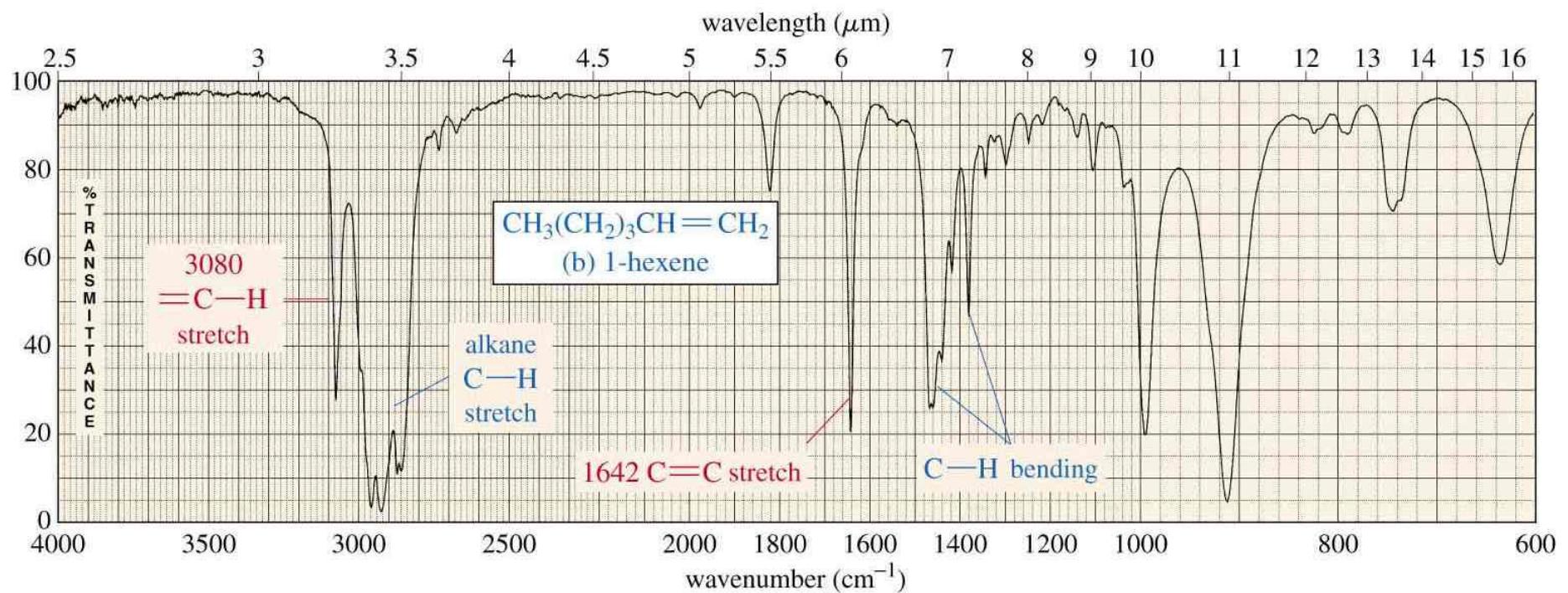
O-H and N-H Stretching

- 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)

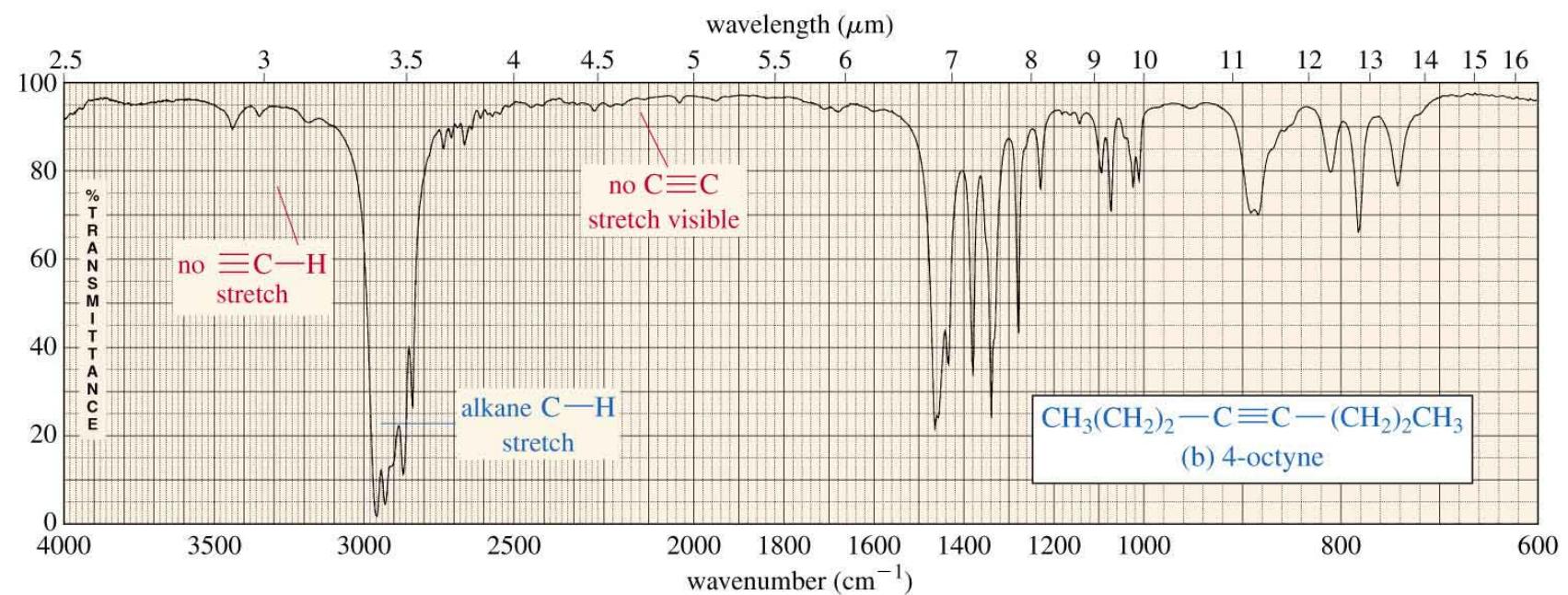
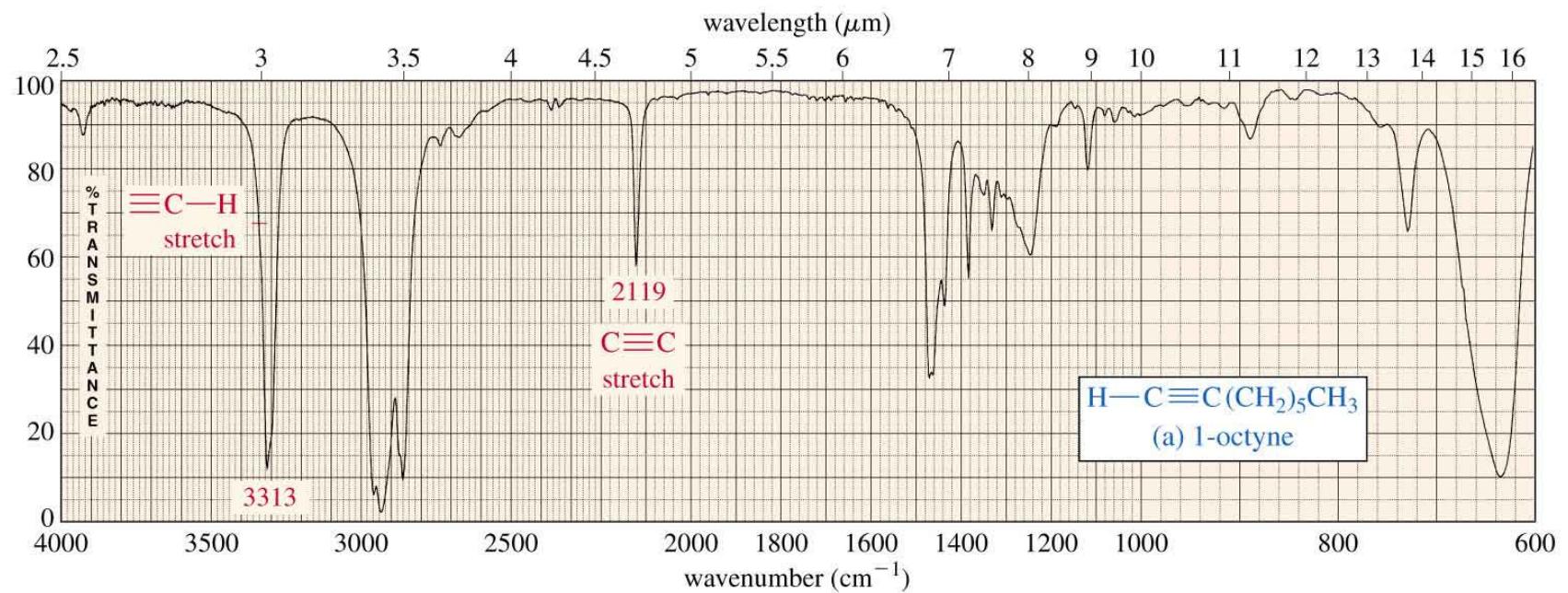
An Alkane IR Spectrum



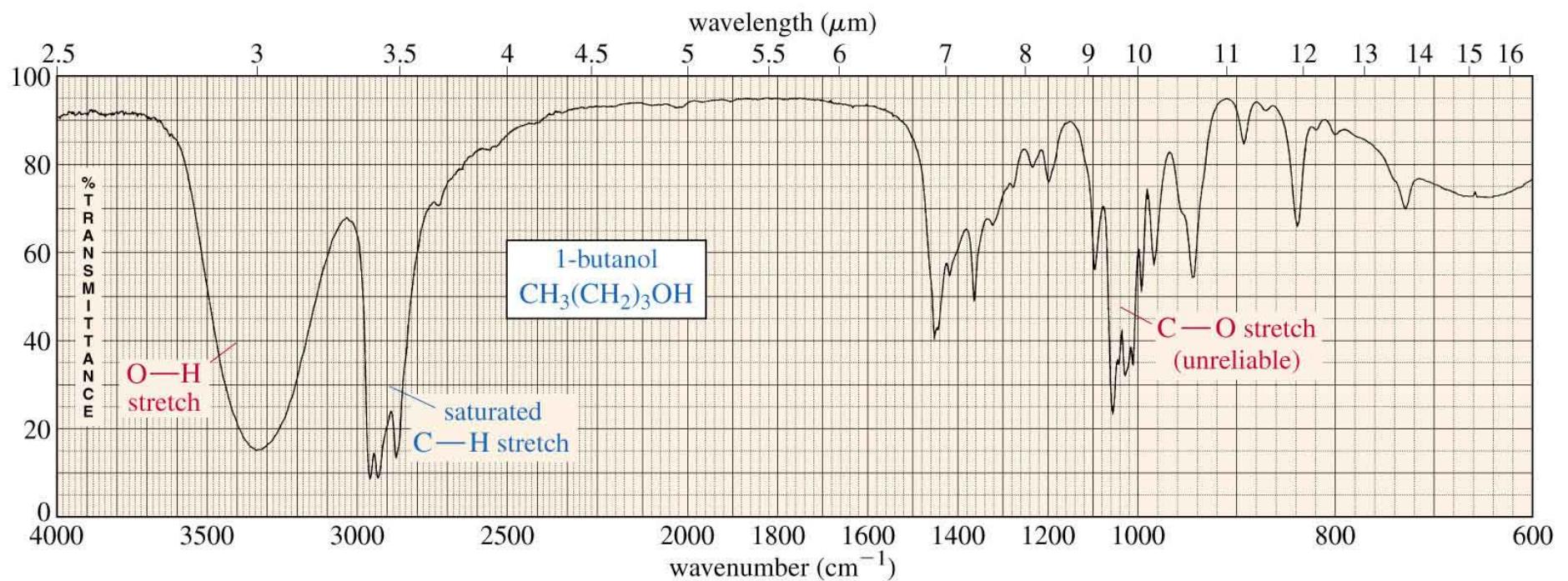
An Alkene IR Spectrum



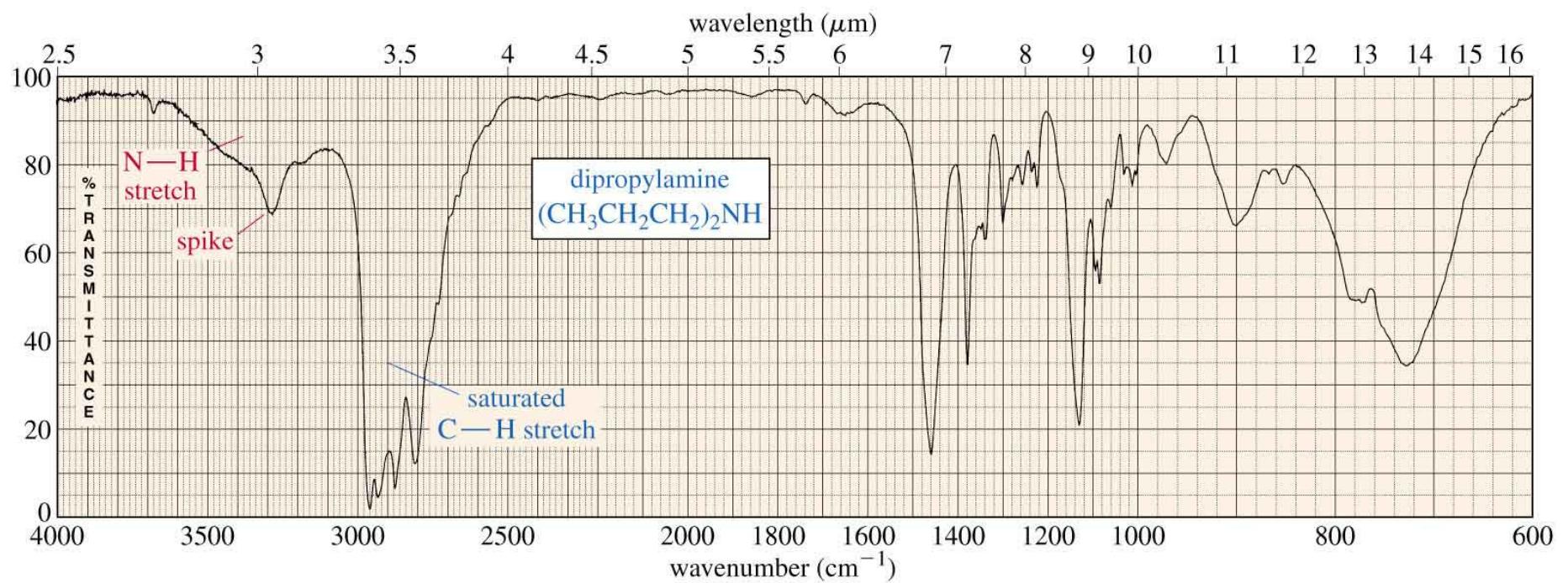
Alkyne IR Spectrum



An Alcohol IR Spectrum



An Amine IR Spectrum

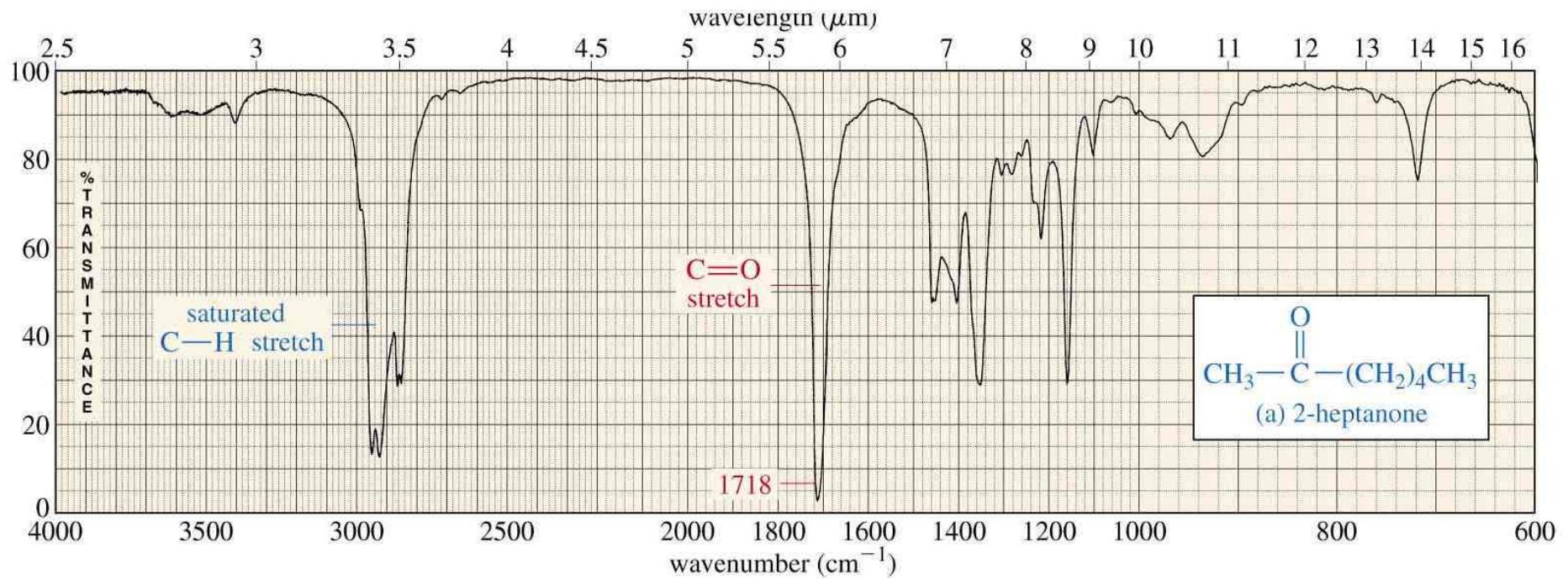


Carbonyl Stretching

- 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} .

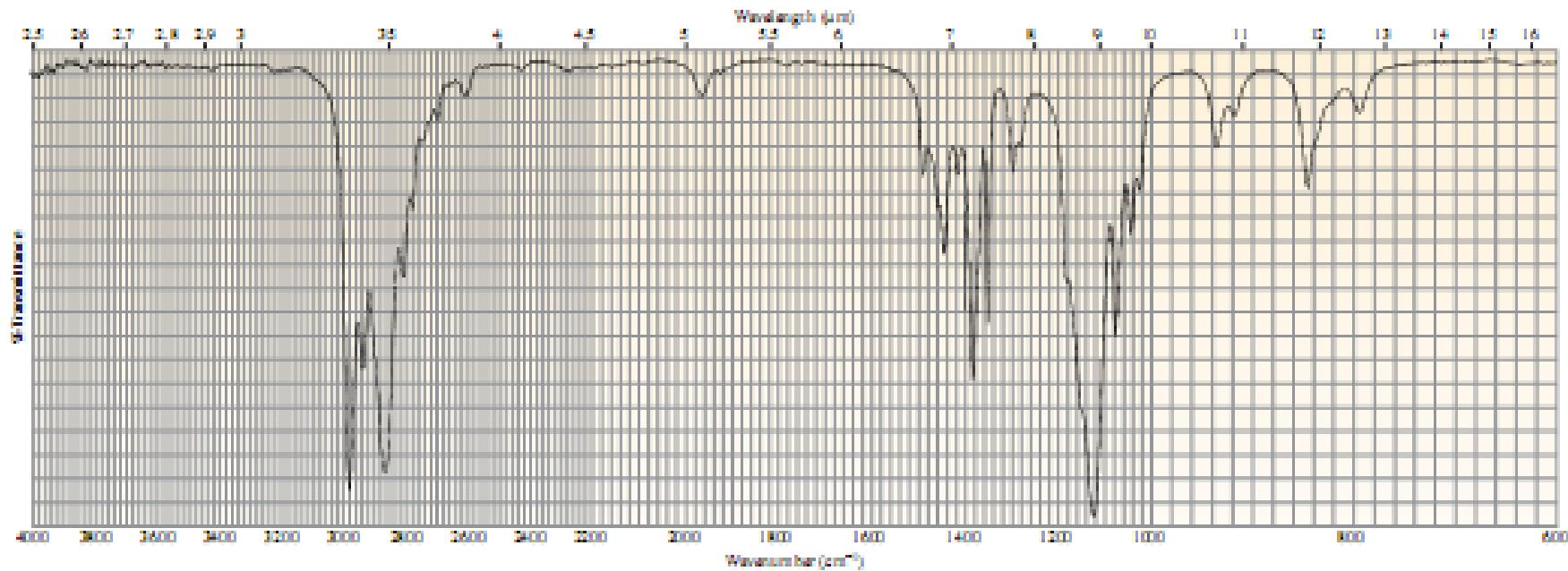
=>

A Ketone IR Spectrum



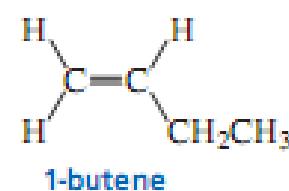
Absence of absorption band

The absence of an absorption band can be as useful as the presence of a band in identifying a compound by IR spectroscopy. For example, the spectrum in Figure 13.26 shows a strong absorption at $\sim 1100\text{ cm}^{-1}$, indicating the presence of a C—O bond. Clearly, the compound is not an alcohol because there is no absorption above 3100 cm^{-1} . Nor is it an ester or any other kind of carbonyl compound because there is no absorption at $\sim 1700\text{ cm}^{-1}$. The compound has no $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{N}$,

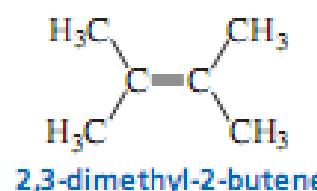


Infrared Inactive Vibrations

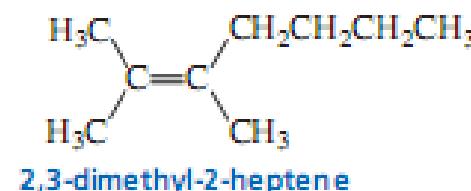
Not all vibrations give rise to absorption bands. In order for a vibration to absorb IR radiation, the dipole moment of the molecule must change when the vibration occurs.



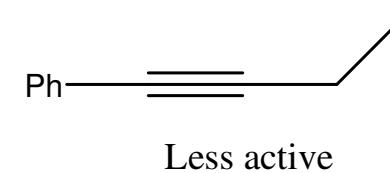
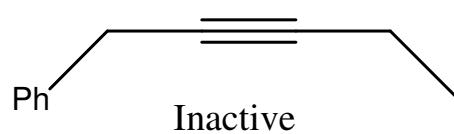
Active



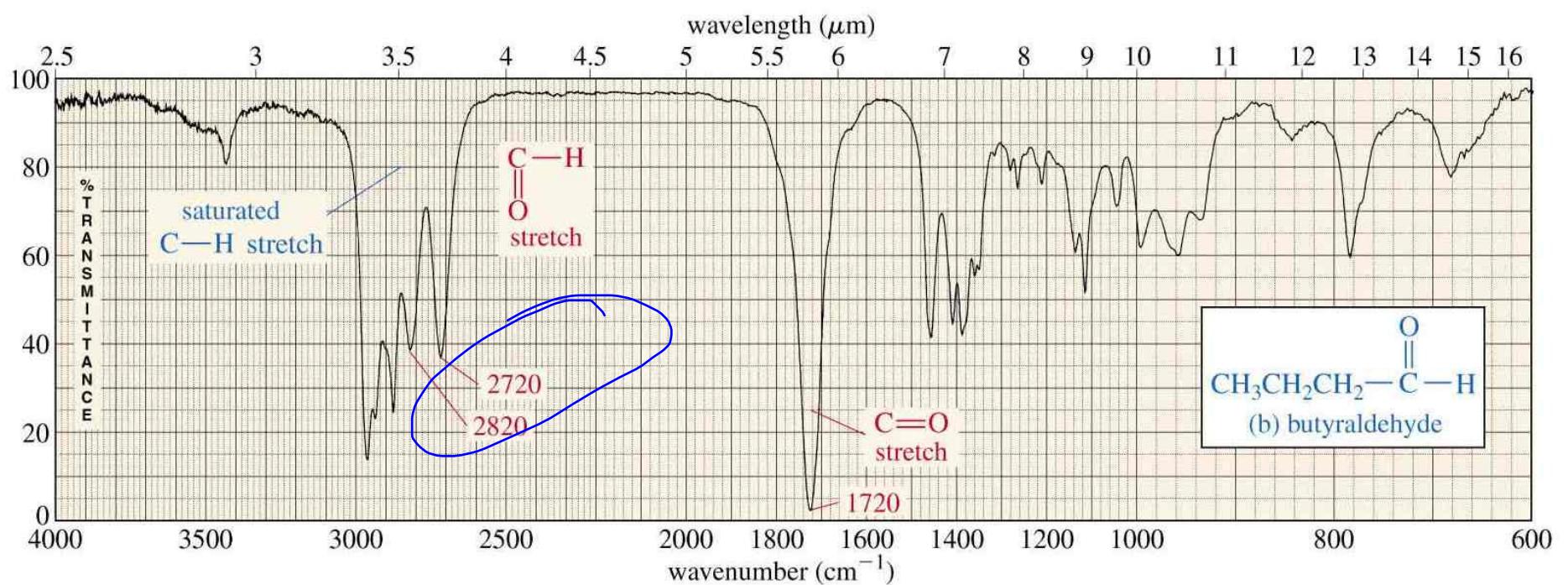
Inactive



Active

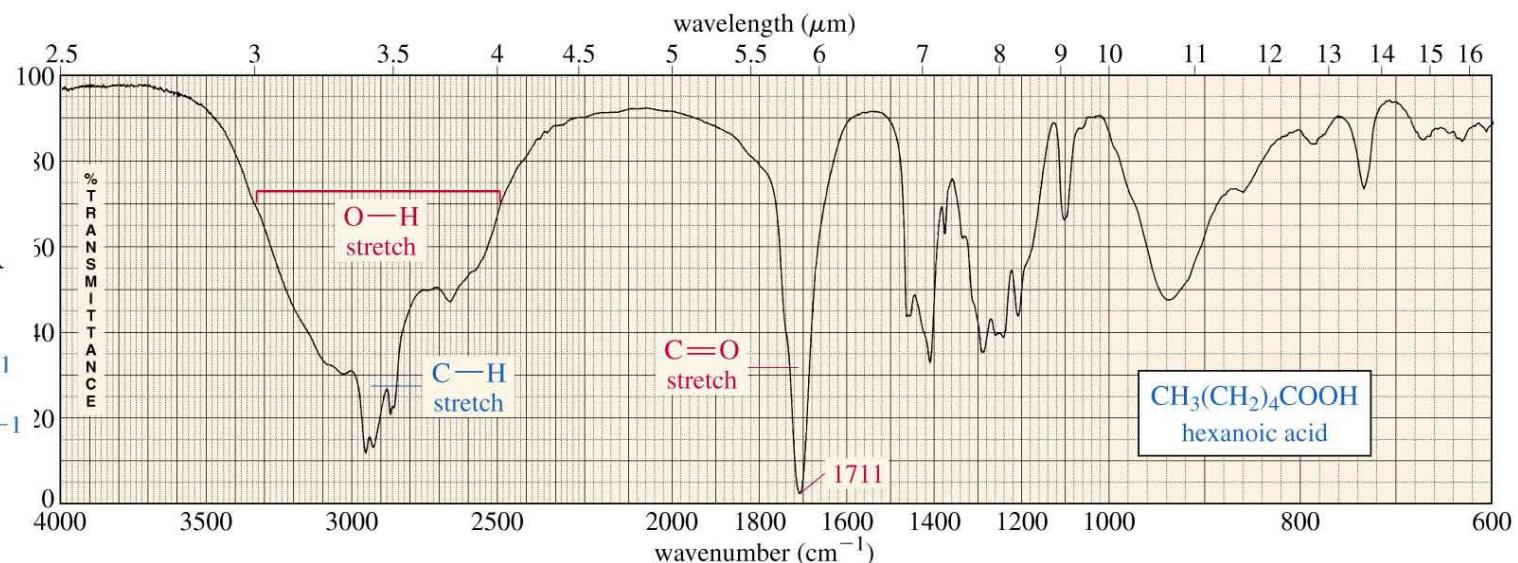
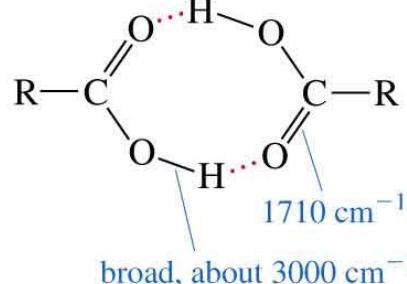


An Aldehyde IR Spectrum



O-H Stretch of a Carboxylic Acid

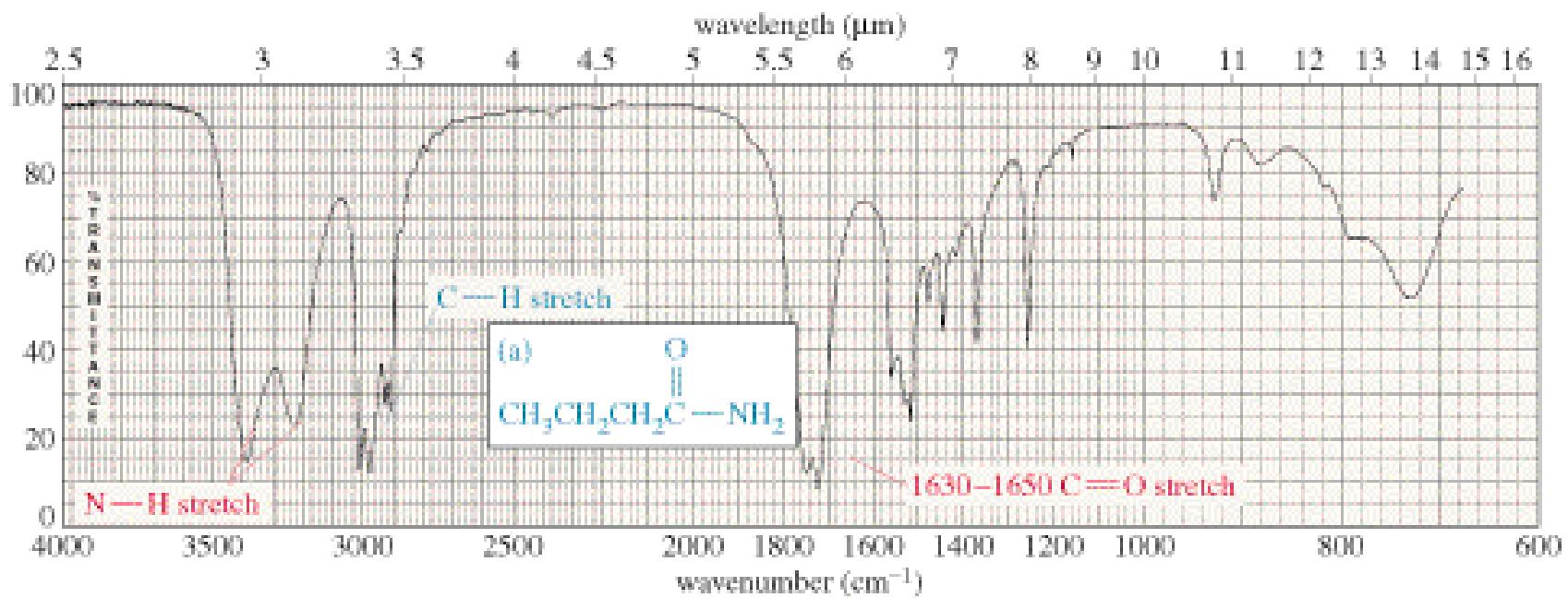
This O-H absorbs broadly, 2500-3500 cm⁻¹, due to strong hydrogen bonding.



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, $1640\text{-}1680\text{ cm}^{-1}$.
- 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.

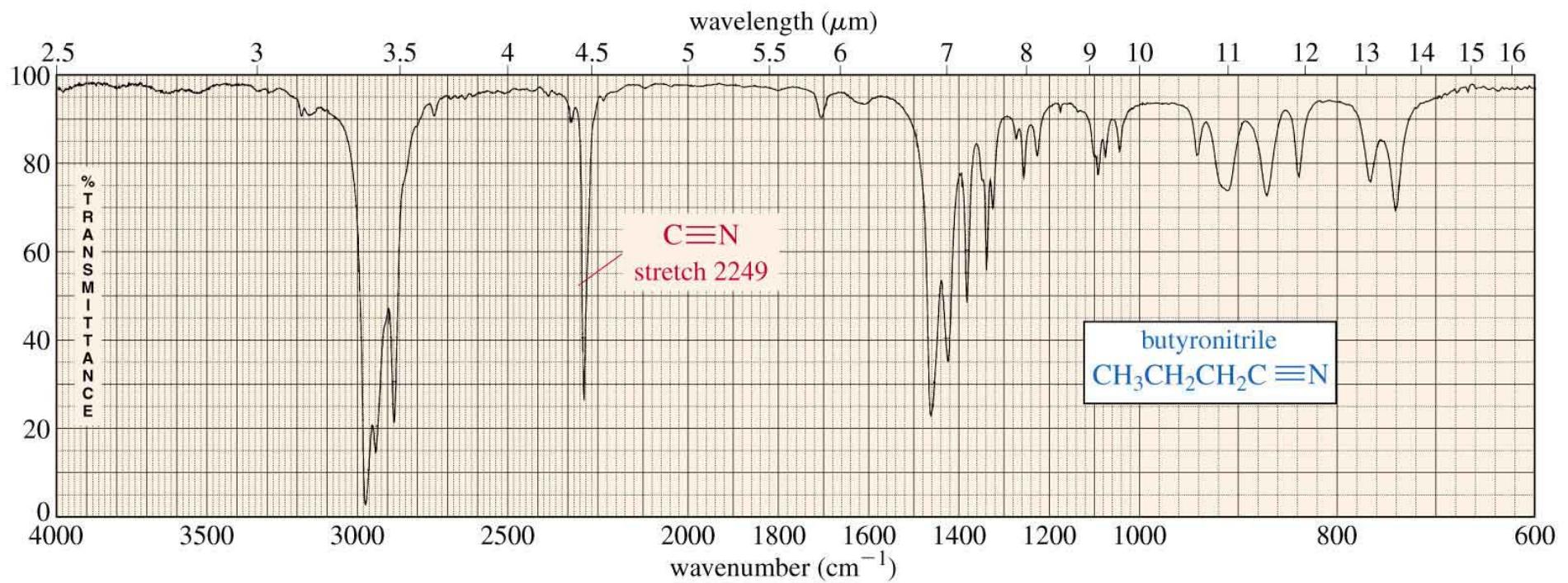
An Amide IR Spectrum



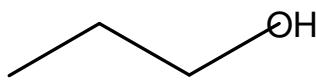
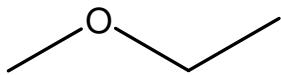
Carbon - Nitrogen Stretching

- 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} .

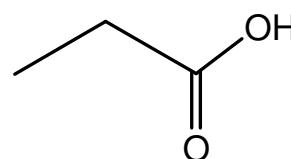
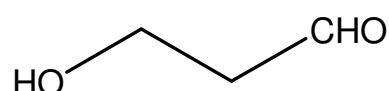
A Nitrile IR Spectrum



Q. Distinguish between the following pair of compounds .

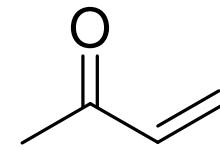
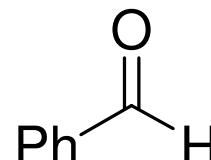
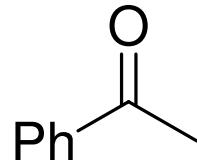
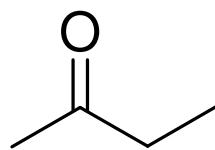


Broad –OH stretch at 3300 cm⁻¹

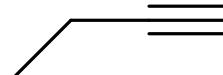
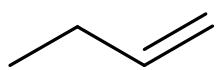
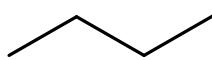
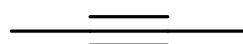


Characteristic C-H str of aldehyde

Q . Which of the following compound is expected to show strong IR absorption at 2710 and 1705.



Q . Which of the following compound is expected to show strong IR absorption at 3300.



A

B

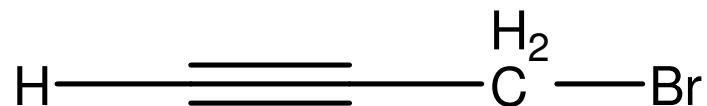
C

D

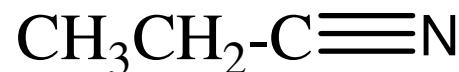
Degree of unsaturation : For a formula $C_aH_bN_cO_dX_e$:

$$\text{Degree of unsaturation} = \frac{1}{2} (2 + 2a - b + c - e)$$

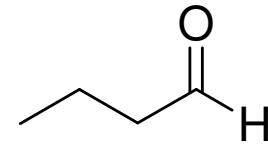
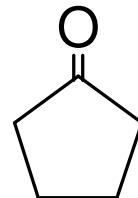
Q 1. Deduce a possible structure for the compound with the IR absorptions band at 3300, 2900, 2100 and MF C_3H_3Br



Q 2. IR absorptions band at 3000, 2250 and MF C_3H_5N



Q 3. IR absorptions band at 3000, 1750 and MF C_5H_8O



Q 4. IR absorptions band at 3000, 2715, 1715 and MF C_4H_8O

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.