



University of Baghdad, College of Pharmacy, Department of Pharmaceutical Chemistry

Advanced Pharmaceutical Analysis

Fifth Stage

Spring-2023

Infrared (IR) Spectroscopy

Textbook: Spectrometric Identification of Organic Compounds, Robert M. Silverstein: Eighth Edition, Chapter 2.



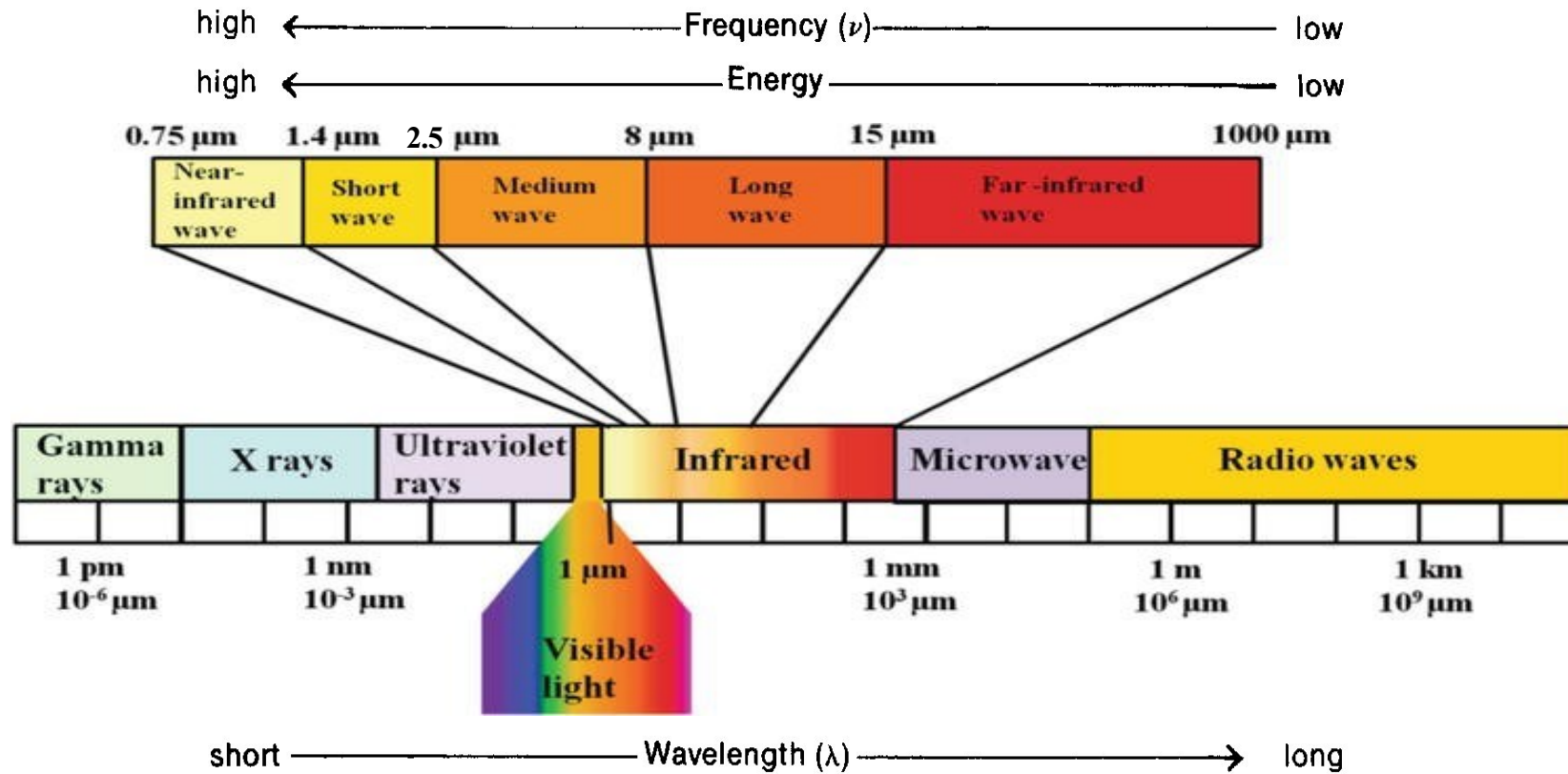
IR Spectroscopy... Outline



- ❖ Introduction
- ❖ Theory
- ❖ Sampling techniques
- ❖ H-bonding effect
- ❖ Interpretation of spectra
- ❖ Characteristic group frequencies of organic compounds
- ❖ Applications of IR spectroscopy



IR Spectroscopy



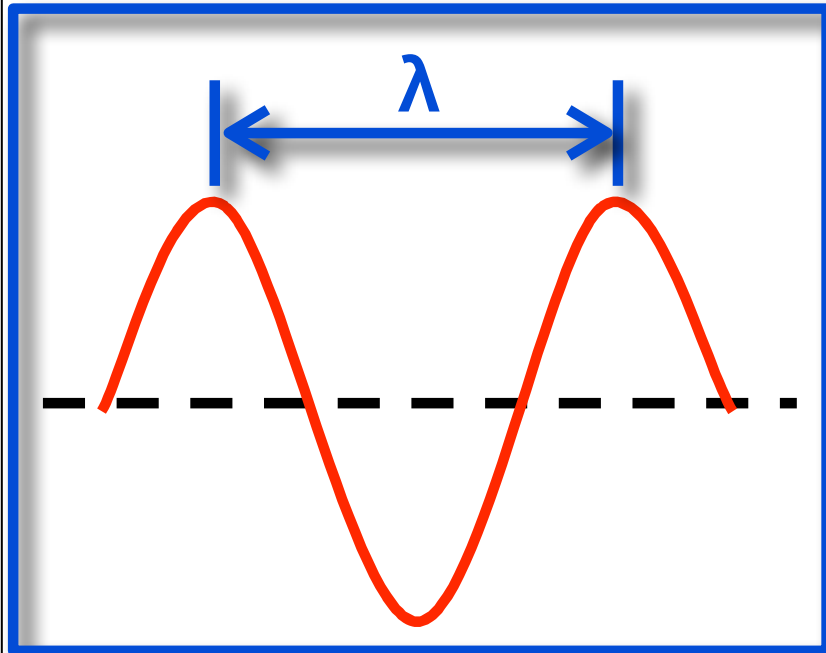


Wavelength & Frequency



- **Frequency** (ν) is **inversely** proportional to **wavelength** (λ): $\nu = c/\lambda$

c is the speed of light ($3 \times 10^8 \text{ ms}^{-1}$)



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

E = energy (J) of 1 photon

h = Planck's constant ($6.63 \times 10^{-34} \text{ Js}$)

c = speed of light ($3 \times 10^8 \text{ ms}^{-1}$)

ν = frequency (Hz)

λ = wavelength (m)

long wavelength = low energy
short wavelength = high energy



Introduction



- IR frequencies are usually expressed in units of wavenumbers ($\bar{\nu}$) whose unit is the **reciprocal centimeter** (cm^{-1});

$$\bar{\nu} (\text{cm}^{-1}) = \frac{1}{\lambda (\text{cm})} \quad \nu (\text{Hz}) = \bar{\nu} c = \frac{c (\text{cm/sec})}{\lambda (\text{cm})}$$

- E.g. $2.5 \mu\text{m} = 2.5 \times 10^{-4} \text{ cm}$ $1/2.5 \times 10^{-4} \text{ cm} = 4000 \text{ cm}^{-1}$

$$15 \mu\text{m} = 15 \times 10^{-4} \text{ cm} \quad 1/15 \times 10^{-4} \text{ cm} = 666 \text{ cm}^{-1}$$

- **Wavenumbers** (in cm^{-1}) are directly proportional to **frequency** (in Hertz), and the two are related by the speed of light; therefore, **higher frequency vibrations** correspond to **higher wavenumbers**.



Introduction



- Three typical spectral regions for IR spectroscopy:
 1. **Near-IR**: excites **overtones** or **harmonics** of fundamental vibrations (multiple level transition).
 2. **Mid-IR**: excites the **fundamental vibrations** (single level transition). This region is the **most widely used for IR spectroscopy**, because it generates spectral fingerprints in which most of organic molecules.
 3. **Far-IR**: excites low-energy vibrations and higher energy rotations. The far-IR is a **difficult spectral region** for IR spectroscopy, and thus has **few analytical uses**.

Region	Energy (kJ/mol)	Wavenumber (cm ⁻¹)	Wavelength (μm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-400	2.5-25
Far IR	2.5-0.1	400-10	25-1000

- **Higher wavenumber** corresponds to a **higher energy** absorption



Introduction



- Spectroscopy provide the information about **molecular structure**. As IR is very useful in identifying **functional groups**.
- A **peak-by- peak correlation** is excellent evidence for identity. Any two compounds, except enantiomers, are **unlikely to give exactly the same IR spectrum**.
- IR spectra usually used in **conjunction with other spectral data** in order to determine or confirm molecular structure.
- Even a very simple molecule can give an **extremely complex spectrum**.



Theory



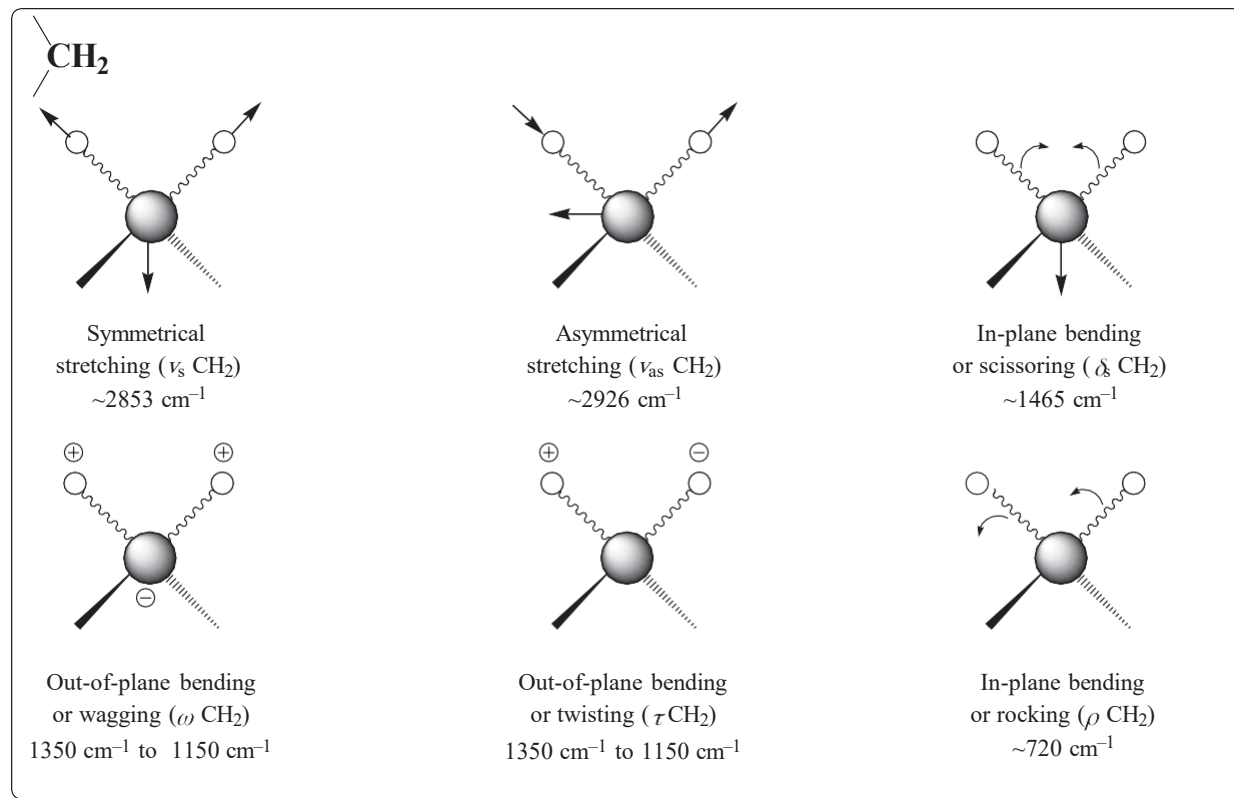
- Infrared radiation is absorbed and converted by an organic molecule into **energy of molecular vibration**. And the vibrational spectra appear as **bands**.
- The **vibrational–rotational bands** occurring between 4000 cm^{-1} and 400 cm^{-1} .
- The frequency or wavelength of absorption depends on the
 1. the **relative masses of the atoms**,
 2. the **force constants of the bonds**,
 3. the **geometrical arrangement of the atoms** (i.e., the molecular structure).



Theory



- Two of the most important types of molecular vibrations are **stretching** and **bending**.
- A **stretching** vibration is a rhythmical movement along the bond axis such that the **interatomic distance is increasing or decreasing**.
- **Stretching** can be **symmetrical** or **asymmetrical**.
- A **bending** vibration may consist of a **change in angle between bonds**
- For example, **scissoring**, **rocking**, **wagging**, or **twisting**, vibrations involve a change in bond angles within the molecule.

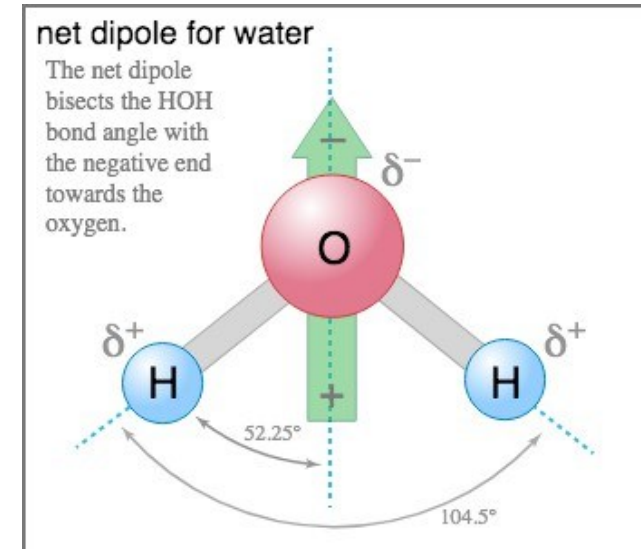




Theory



- Only those vibrations that result in a change in the **net dipole moment of the molecule** are observed in the IR spectrum.
- The alternating **electric field**, produced by the **changing charge distribution** accompanying a **vibration**, couples the molecular vibration with the oscillating electric field of the electromagnetic radiation.
- The **positions** and **relative sizes** of the **peaks** (also called **bands**) give clues about the structure of a compound.
- Functional groups that have a **strong dipole** give rise to **strong absorptions** in the IR.

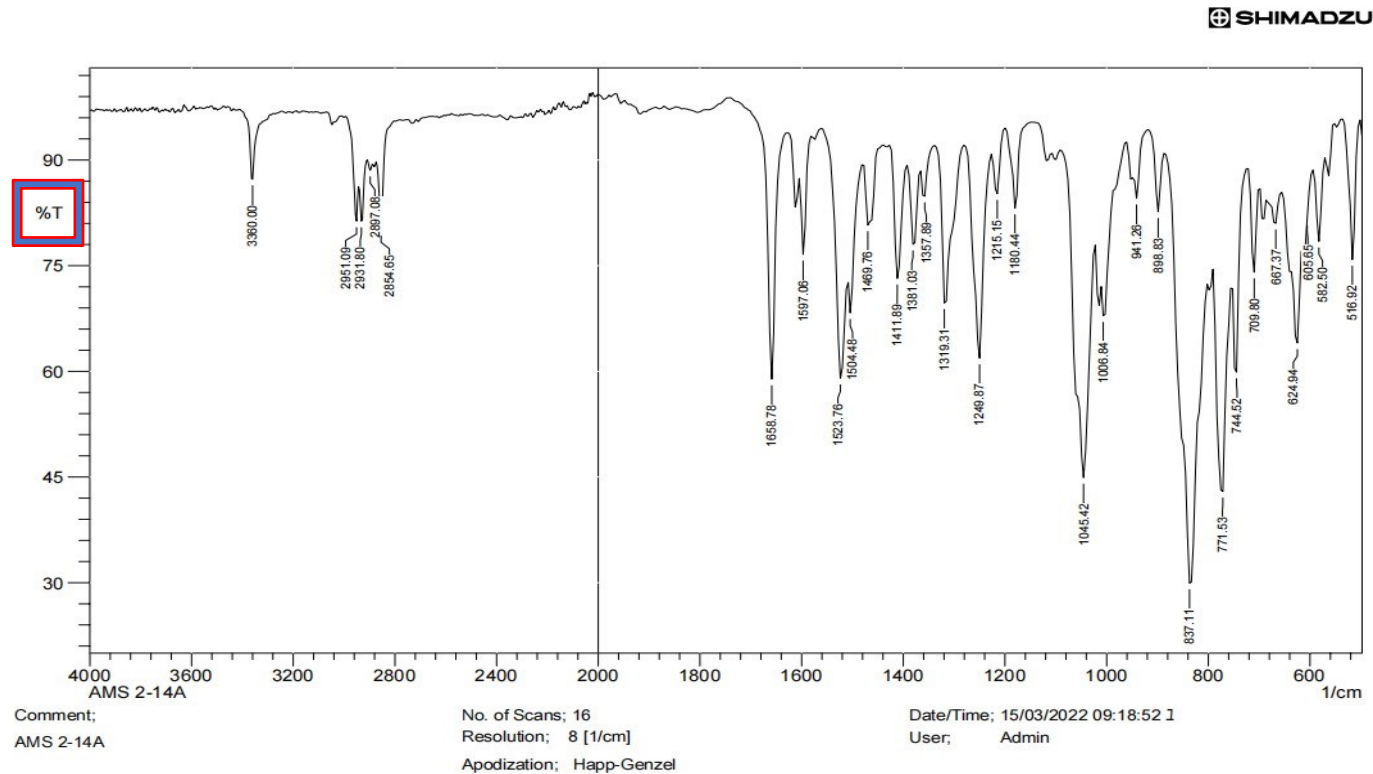




Theory



- Band intensities can be expressed either as **transmittance** (T) or **absorbance** (A).
- **Transmittance** : $T = I/I_0$ (Intensity of light out/intensity of incident light)
- **Absorbance**: $A = \log_{10} (1/T)$

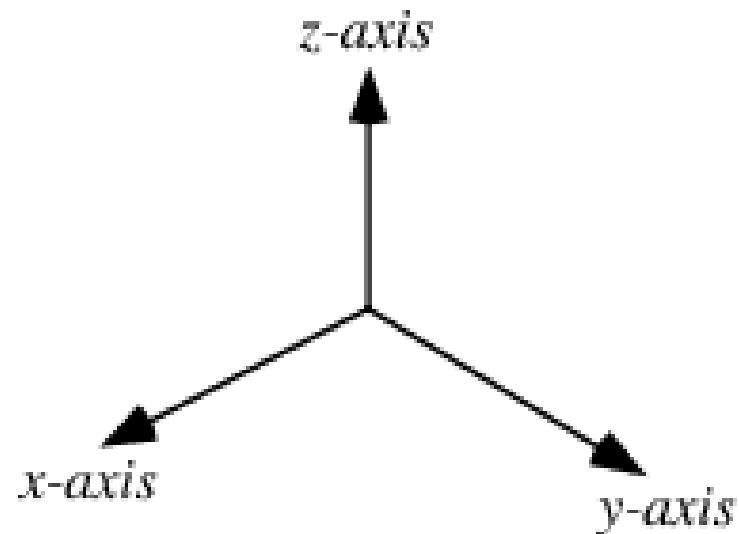




Theory



- A **molecule** has as **many degrees of freedom** as the total degrees of freedom of its **individual atoms**.
- Each atom has three degrees of freedom corresponding to the **Cartesian coordinates** (x , y , z) necessary to describe its position relative to other atoms in the molecule.

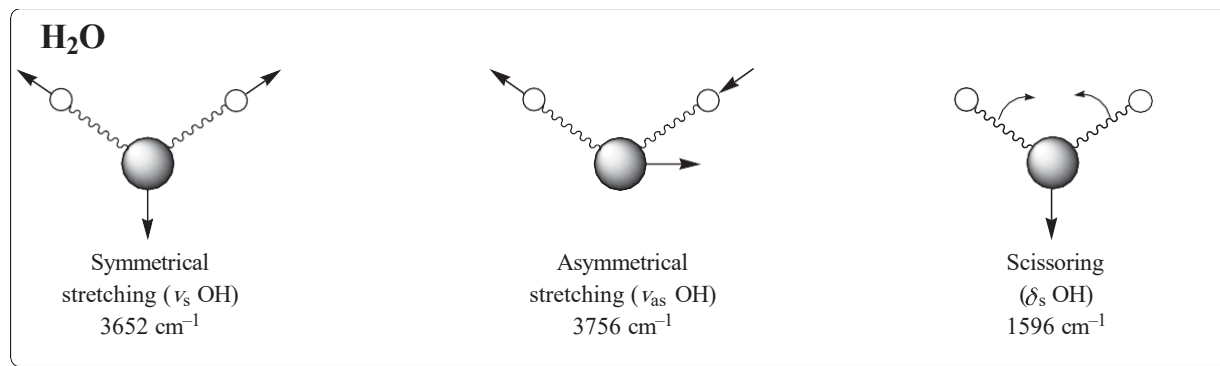




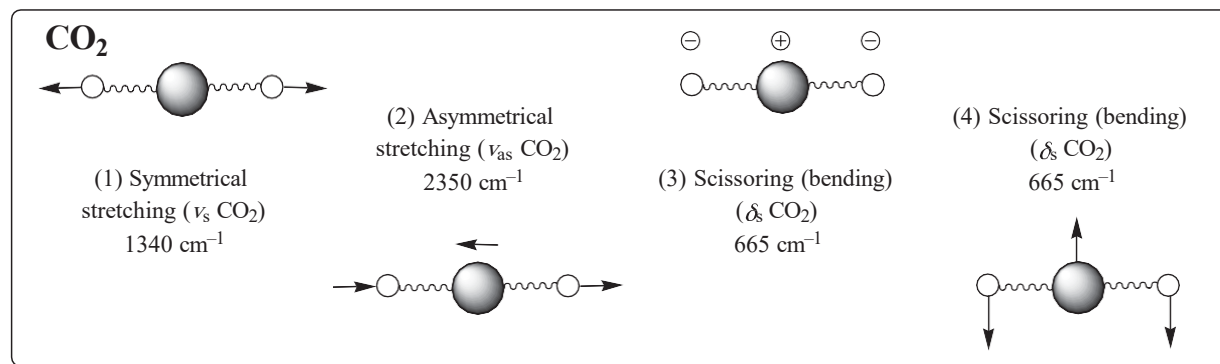
Theory



- For nonlinear molecules, three degrees of freedom describe rotation and three describe translation; the remaining $3n - 6$ degrees. H_2O has $(3 \times 3) - 6 = 3$ fundamental vibrations



- Linear molecules have $3n - 5$ vibrational degrees of freedom, since only two independent degrees of freedom are required to describe rotation. H_2O has $(3 \times 3) - 5 = 4$ fundamental vibrations





Theory



- The the observed vibrations might be **larger** than the theoretical number of fundamental vibrations because of **overtones**.
- The following will **reduce** the number of observed bands:
 1. Fundamental wavenumbers that fall **outside of the 4000 cm⁻¹ to 400 cm⁻¹ region**.
 2. Fundamental bands that are **too weak** to be observed.
 3. Fundamental vibrational wavenumbers that are so close that the **bands coalesce**.
 4. The occurrence of a **degenerate band** from several absorptions of the same frequency in highly **symmetrical molecules**.
 5. The failure of certain fundamental vibrations to appear in the IR because of the **lack of change in molecular dipole**.



Theory



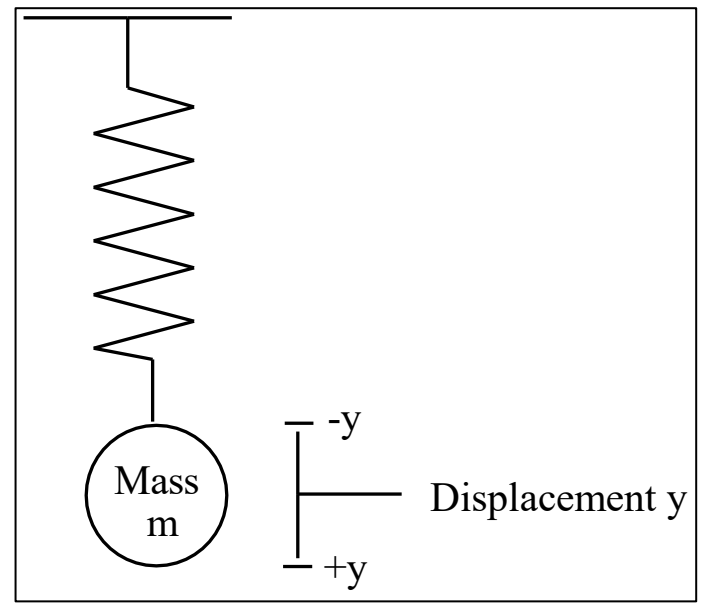
- Assignments for **stretching frequencies** can be **approximated** by the application of **Hooke's law**.
- **Hooke's law** calculate the relationship between **wavenumber of oscillation**, **atomic masses**, and **bond force constant**.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{(M_x M_y)/(M_x + M_y)}}$$

$\bar{\nu}$ = the vibrational frequency (cm⁻¹)
 c = velocity of light (cm/s)
 f = force constant of bond (dyne/cm)
 M_x and M_y = mass (g) of atom x and atom y , respectively.



- single bond 5 x10⁵ dyne/cm
- double bond 10 x10⁵ dyne/cm
- triple bond 15 x10⁵ dyne/cm



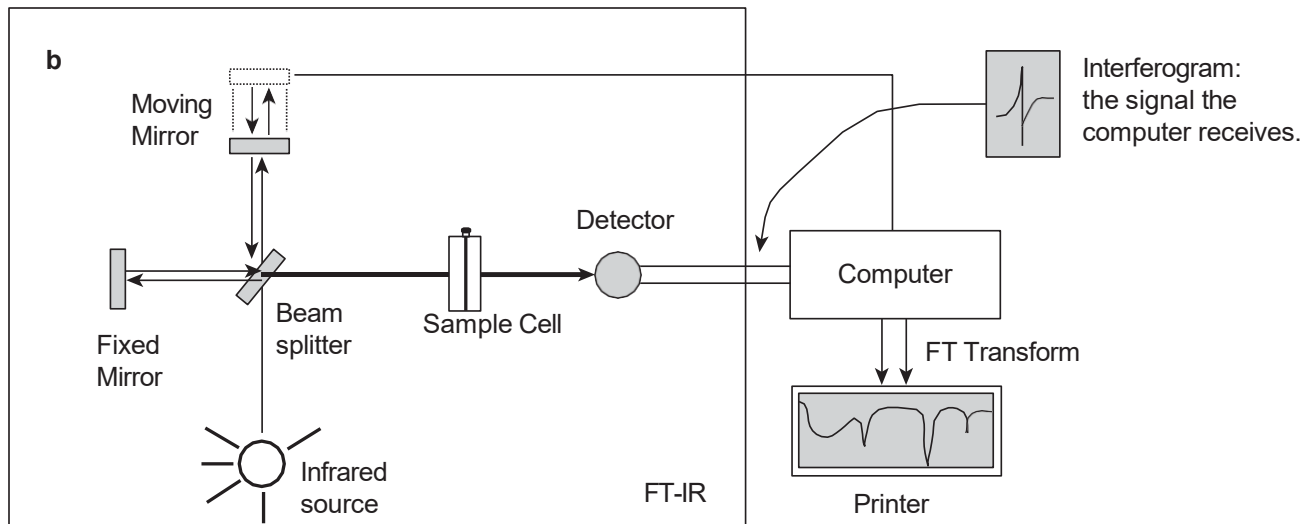
.The calculation is **not highly accurate** because effects arising from the **molecule environment**.



IR Instrumentation



- **Fourier-Transform Infrared (FT-IR)** instrument uses a system called an **interferometer**.
- The interferometer consists of a **source**, **beam-splitter**, **two mirrors**, and a **detector**.
- This interferogram goes from the beam-splitter to the sample, the energy either **absorbed** or **transmitted**. Then the transmitted portion reaches the detector.
- The detector reads information about every wavelength in the infrared range.
- The detector signal is sent to the computer, and an algorithm called a **Fourier transform** is performed on the **interferogram** to convert it into a **single beam spectrum**.





Advantages of FT-IR



- **High S/N ratios**, so it is excellent spectra from **very small samples** can be obtained.
- **Rapid** (<10 s). The entire radiation range is passed through the sample simultaneously and much time is saved.
- **Reproducible.**
- **High resolution** (<0.001 cm⁻¹)
- **Inexpensive**
- **FT-IR can be interfaced with chromatographic instrumentation,**



Sample preparation

Infrared spectra may be obtained for **gases**, **liquids**, or **solids**.

- **Gases fill cell**

- (a) transparent windows (NaCl/KBr)

- (b) long pathlength (10 cm) - few molecules

- **Liquids fill cell**

- (a) solute in transparent solvent - not water (attacks windows)

- (b) short pathlength (0.1-1 mm) - solvents absorb

- (c) Solvent may be used is CCl_4

- (d) (NaCl/AgCl) used as diluents





Sample preparation

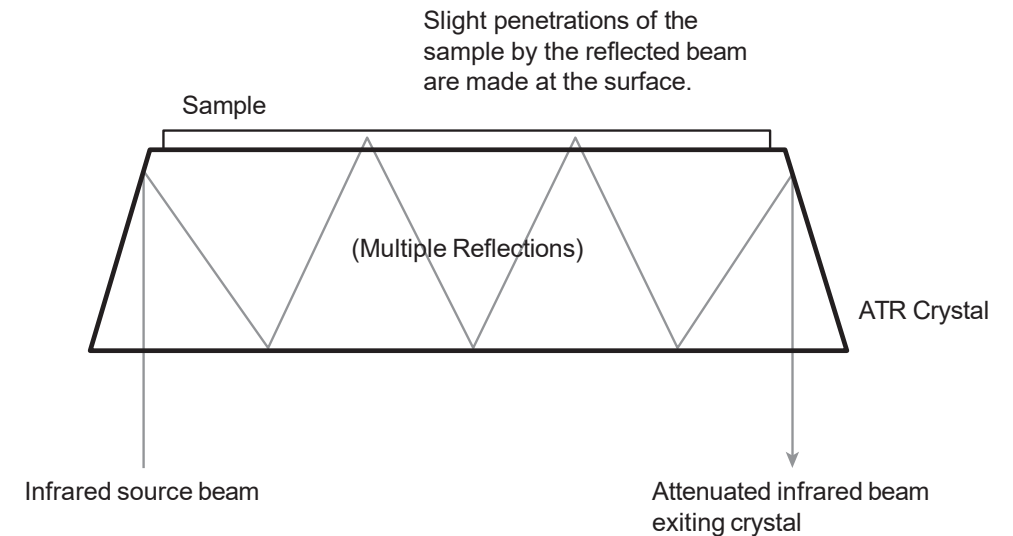


- **Solids**

(a) make semi-transparent pellet with KBr

(b) grind and mix with Nujol (hydrocarbon oil) to form mull. One drop between NaCl plates.

- The best method of determining a spectrum of samples is to make use of an **Attenuated Total Reflectance (ATR) accessory**.
- The ATR method provides a powerful sampling technique that virtually eliminates sample preparation with both liquids and solids, thus leading to **rapid analysis of samples**.





IR Spectroscopy



Factors Affecting Group Frequencies

- Hydrogen bonding
- Ring strain
- Electronic effects
- Isomerism
 - structural
 - stereoisomerism
- Symmetry
- Fermi coupling



Factors Affecting Group Frequencies



Hydrogen Bonding

- Hydrogen bonding takes place between a hydrogen atom bonded to an electronegative element and an atom with a non-bonding electron pair.



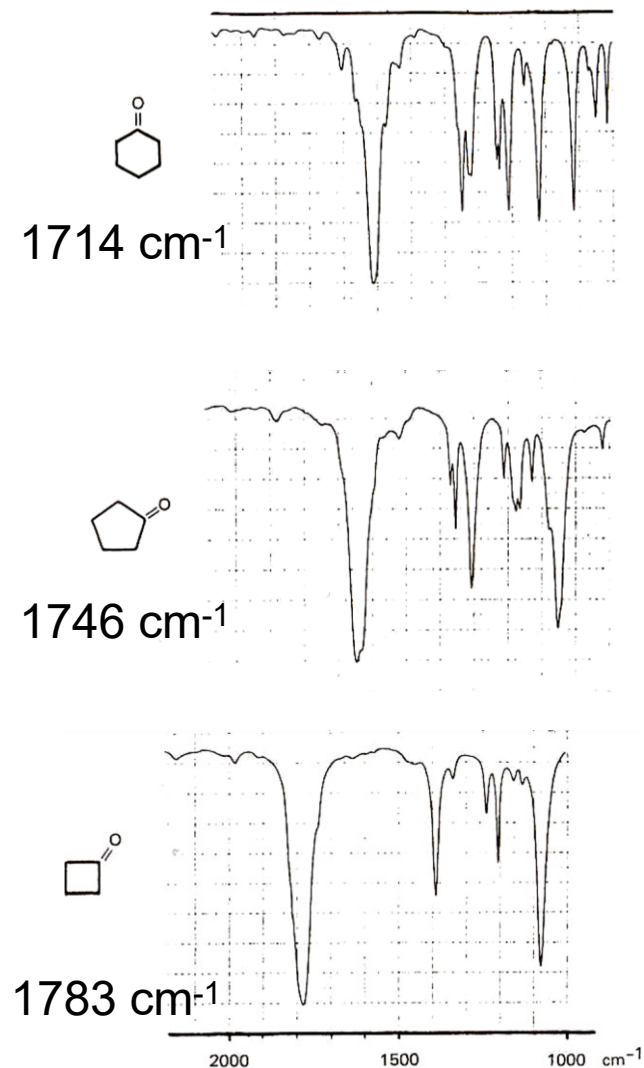
- The effect of hydrogen bonding is to cause **increasing the intensities**, **broadening peaks** and a **shift peaks to lower frequencies** in IR.



Factors Affecting Group Frequencies



Effect of Ring Strain



- Increasing ring strain causes a shift in the carbonyl stretching to higher wave numbers.
- This increase in frequency with increasing angle strain is observed for exocyclic double bonds.

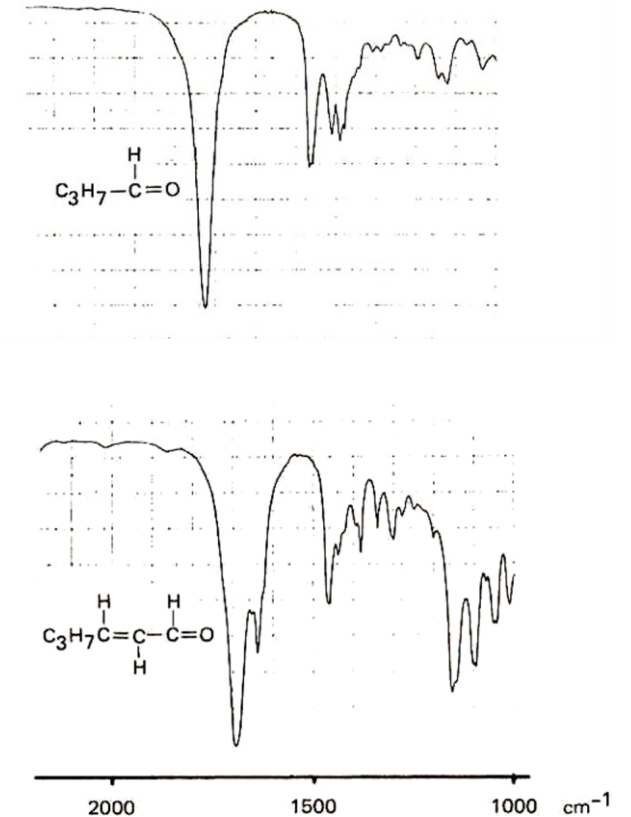


Factors Affecting Group Frequencies



Electronic Effects - Effect of Conjugation

- Effects due to the **change in the distribution of electrons** in a molecule produced by a substituent atom or group can often be detected in vibrational spectra. Include **inductive** and **resonance effects** as well as **conjugation** of double bonds.
- **Conjugation** tends to **lower the double bond character** and **increase the bond order** of the intervening single bond.
- As a consequence, the C=O stretching frequency is **lowered by 20-30 cm⁻¹** in this conjugated aldehyde.





CHARACTERISTIC GROUP ABSORPTIONS OF ORGANIC MOLECULES



- The characteristic group absorptions expressed as **ranges** of absorption bands.
- These values have been assigned following the examination of many compounds in which the groups occur.
- Although the ranges are quite well defined, the precise frequency or wavelength at which a specific group absorbs is dependent on its **environment within the molecule and on its physical state.**



IR for Functional Groups



Alkanes

- The spectra of normal alkanes is based on the **stretching** and **bending** of **C-H** and **C-C** bonds.
- The **C-C bending** vibrations occur at **very low frequencies** (below 500 cm^{-1}) and therefore do not appear in spectra.
- The bands assigned to **C-C stretching** vibrations are **weak** and appear in the **broad region** of **1200 cm^{-1} to 800 cm^{-1}** ; they are generally of **little value** for identification.
- The most characteristic vibrations are those arising from **C-H stretching and bending**.
- The vibrational modes of alkanes are common to many organic molecules. Although the positions of C-H stretching and bending frequencies of methyl and methylene groups remain nearly constant in hydrocarbons, the attachment of CH_3 or CH_2 groups to atoms **other than carbon**, or to a carbonyl group or aromatic ring, may result in **appreciable shifts** of the C-H stretching and bending frequencies.
- **C-H stretching** in the alkanes occurs in the general region of **3000 cm^{-1} to 2840 cm^{-1}** .



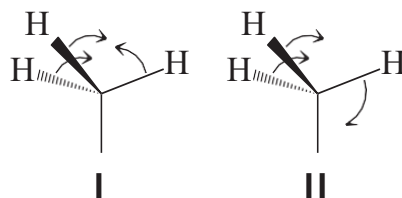
Alkanes

IR for Functional Groups



$C-H$ Bending Vibrations.

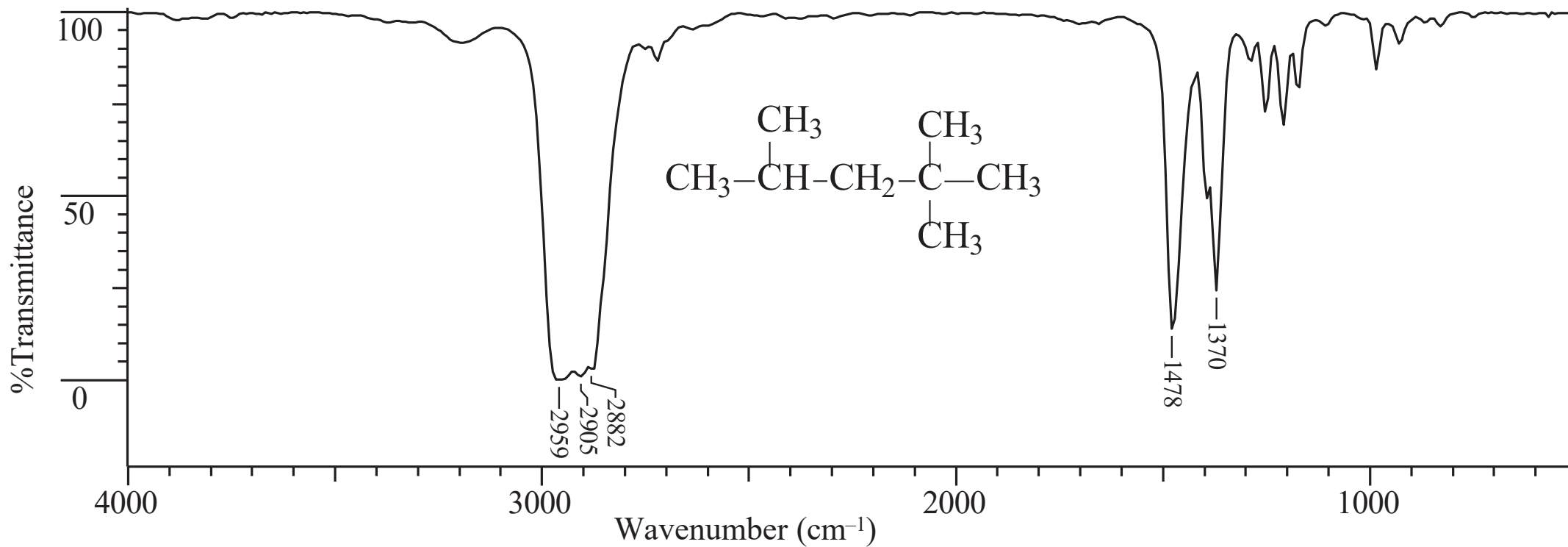
- **Methyl Groups.** Two bending vibrations can occur within a methyl group. The first of these, the **symmetrical bending vibration**, involves the **in-phase** bending of the $C-H$ bonds (I). The second, the asymmetrical bending vibration, involves **out-of-phase** bending of the $C-H$ bonds (II).



- The symmetrical bending vibration (**very stable in position**) occurs near 1375 cm^{-1} , and the asymmetrical bending vibration near 1450 cm^{-1} .
- For methyl group, **two distinct bands** occurring at approximately 2962 cm^{-1} and 2872 cm^{-1} . The first of these results from the asymmetrical stretching mode in which two $C-H$ bonds of the methyl group are extending while the third one is contracting. The second arises from symmetrical stretching in which all three of the $C-H$ bonds extend and contract in phase.



Alkanes



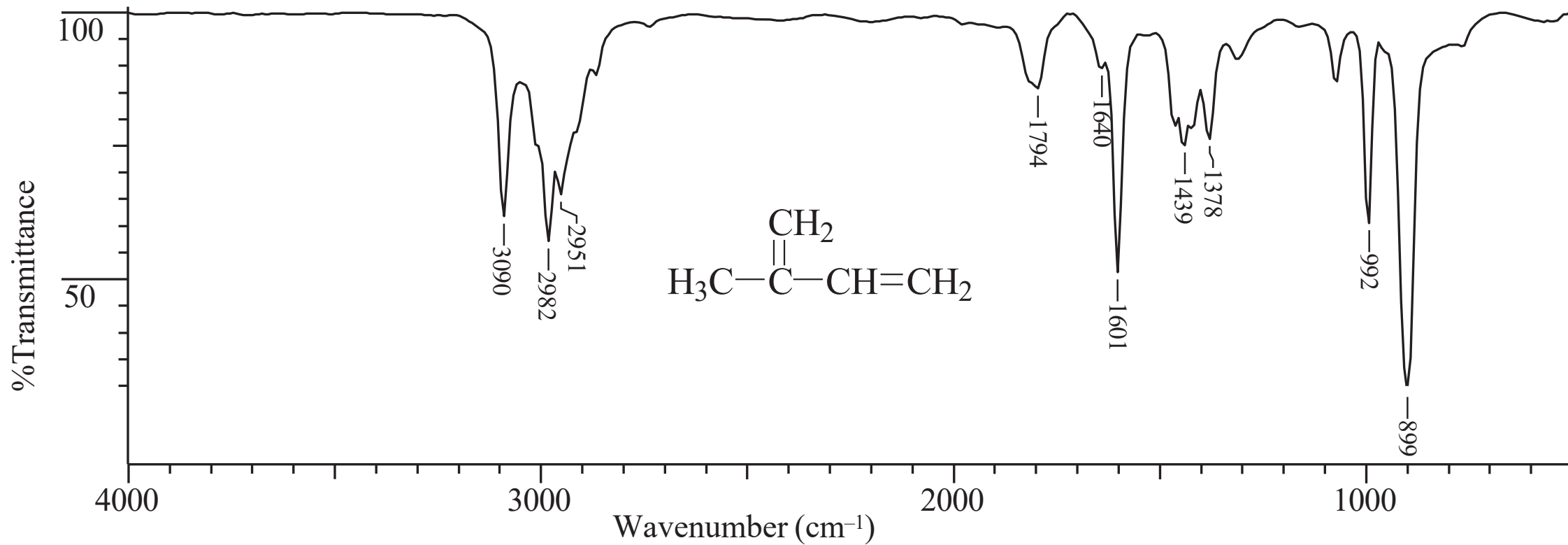


IR for Functional Groups

- **Alkenes** (olefinic) structures introduce several new modes of vibration into a hydrocarbon molecule: a **C=C stretching** vibration, **C-H stretching** vibrations in which the carbon atom is present in the alkene linkage, and **in-plane** and **out-of-plane** bending of the **alkene C-H bond**.
- **C=C Stretching Vibrations *Unconjugated Linear Alkenes***. The C=C stretching mode of unconjugated alkenes usually shows moderate to weak absorption at **1667 cm⁻¹ to 1640 cm⁻¹**.
- **C=C Stretching Vibrations *conjugated Systems***. The alkene bond stretching vibrations in conjugated dienes without a center of symmetry interact to produce two C=C stretching bands.
- The spectrum of an **unsymmetrical conjugated diene**, shows absorption near **1650 cm⁻¹** and **1600 cm⁻¹**. The symmetrical molecule diene shows only one band near **1600 cm⁻¹**.
- **Alkene C-H Stretching Vibrations**. In general, any C-H stretching bands above **3000 cm⁻¹** result from aromatic, heteroaromatic, alkyne, or alkene C-H stretching.
- The most characteristic vibrational modes of alkenes are the **out-of-plane C-H** bending vibrations between **1000 cm⁻¹ and 650 cm⁻¹**.



Alkenes





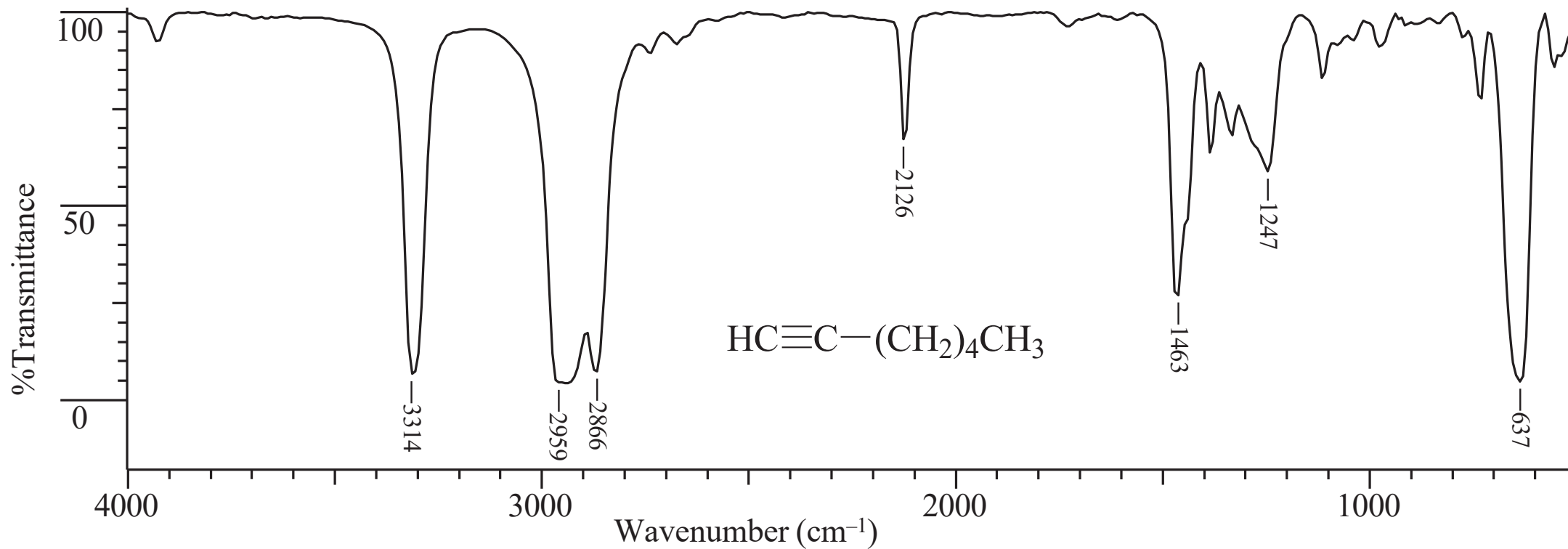
Alkynes



- The two stretching vibrations in alkynes (acetylenes) involve $C\equiv C$ and $C\equiv H$ stretching
- The **$C\equiv C$ stretching** band of alkyne molecules occurs in the region of **2260 cm^{-1} to 2100 cm^{-1}** .
- Because of symmetry, **no $C\equiv C$ band** is observed in the IR for **symmetrically substituted alkynes**.
- When the substituents are **similar in mass**, or produce **similar inductive and resonance effects**, the band may be **so weak** as to be **unobserved** in the IR spectrum.
- The **$C\equiv H$ stretching** band of monosubstituted alkynes occurs in the general region of **3333 cm^{-1} to 3267 cm^{-1}** .
- The **$C\equiv H$ bending** vibration of alkynes or monosubstituted alkynes leads to strong, broad absorption in the **700 cm^{-1} to 610 cm^{-1}** region.

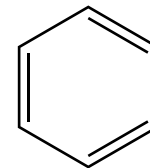


Alkynes





IR for Functional Groups



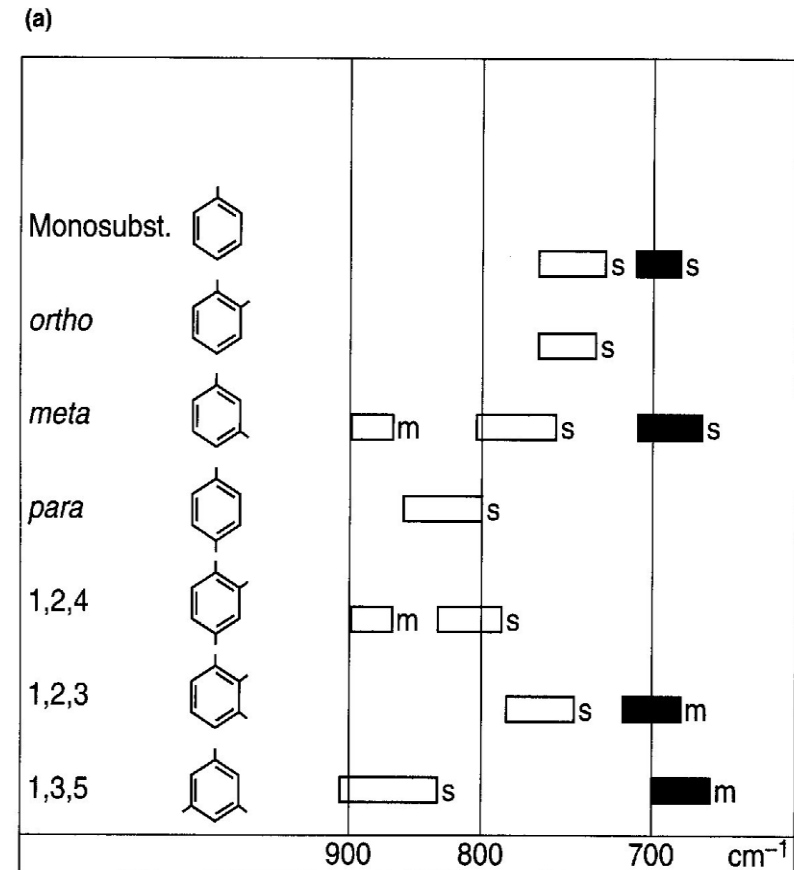
- **Aromatic Hydrocarbons**
- The most prominent and most **informative bands** in the spectra of aromatic compounds occur in the **low-frequency range from 900 cm⁻¹ to 675 cm⁻¹**.
- Skeletal vibrations, involving **carbon-carbon stretching** within the ring (aromatic C=C), absorb in the **1600 cm⁻¹ to 1585 cm⁻¹ and 1500 cm⁻¹ to 1400 cm⁻¹** regions.
- **Aromatic C-H** stretching bands occur between **3100 cm⁻¹ and 3000 cm⁻¹**.
- Weak combination and overtone bands appear in the **2000 cm⁻¹ to 1650 cm⁻¹** region.
- ***Out-of-Plane C-H Bending Vibrations.*** The in-phase, out-of-plane bending. The bands are frequently intense and appear at **900 cm⁻¹ to 675 cm⁻¹**.



IR for Functional Groups



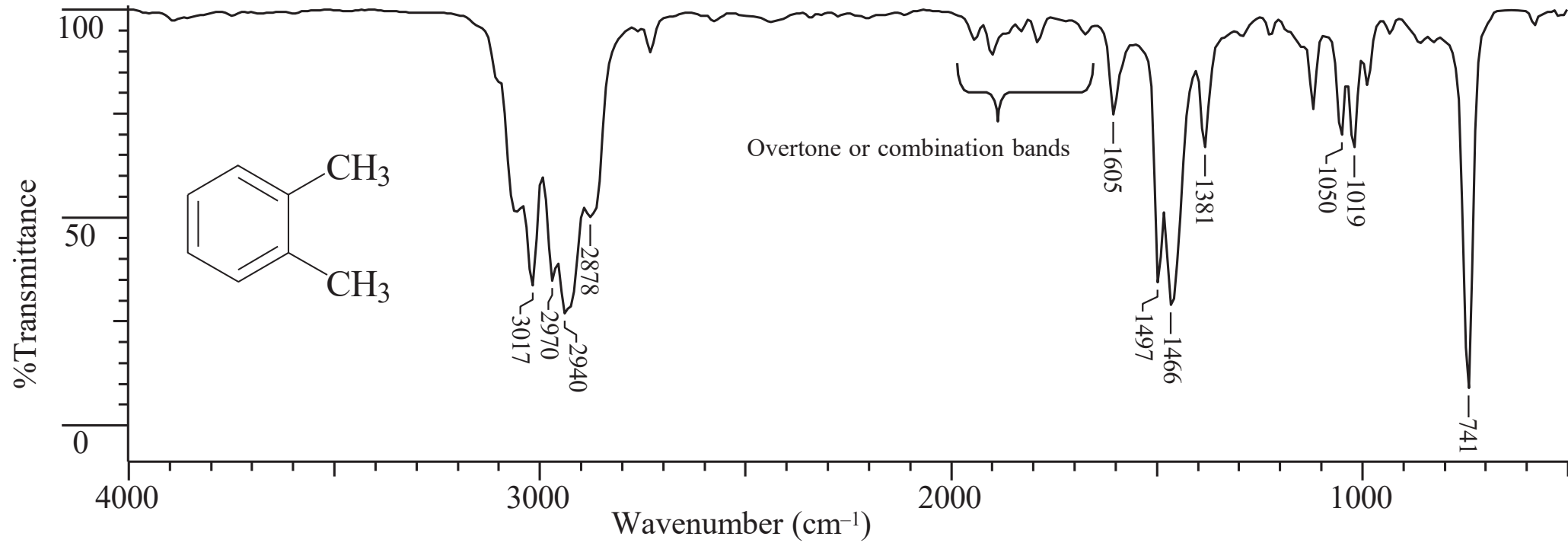
- The =C-H oops bands are usually intense
- **monosubstitution**
- 690 cm^{-1} (st) second band at 750 cm^{-1}
- **ortho-disubstituted**
- One band at 750 cm^{-1} (st)
- **meta-disubstituted**
- 690 cm^{-1} (st), one band at 780 cm^{-1} , third at 880 cm^{-1}
- **para-disubstituted**
- $800\text{-}850\text{ cm}^{-1}$ (st)
- **Combination and overtones**
- mono, di, tri, tetra, penta or hexsubstitutes



Note/ The aim of this slide is to show students that different phenyl substitution leads to different IR absorption at area $900\text{-}675\text{ cm}^{-1}$



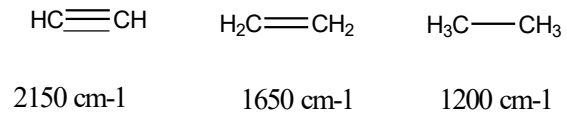
Aromatic Hydrocarbon



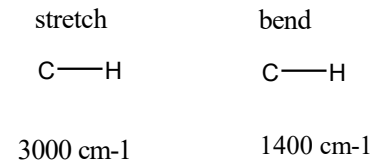


Important Rules

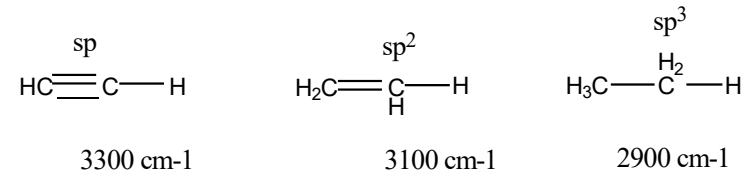
Stronger bonds vibrate at a higher frequency than weaker bonds



Bending modes occur at lower frequencies than stretching

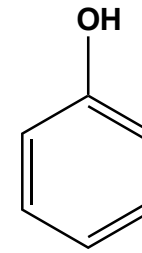


Hybridization changes the force constant (values are for the C-H stretch)

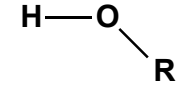




IR for Functional Groups



Phenol



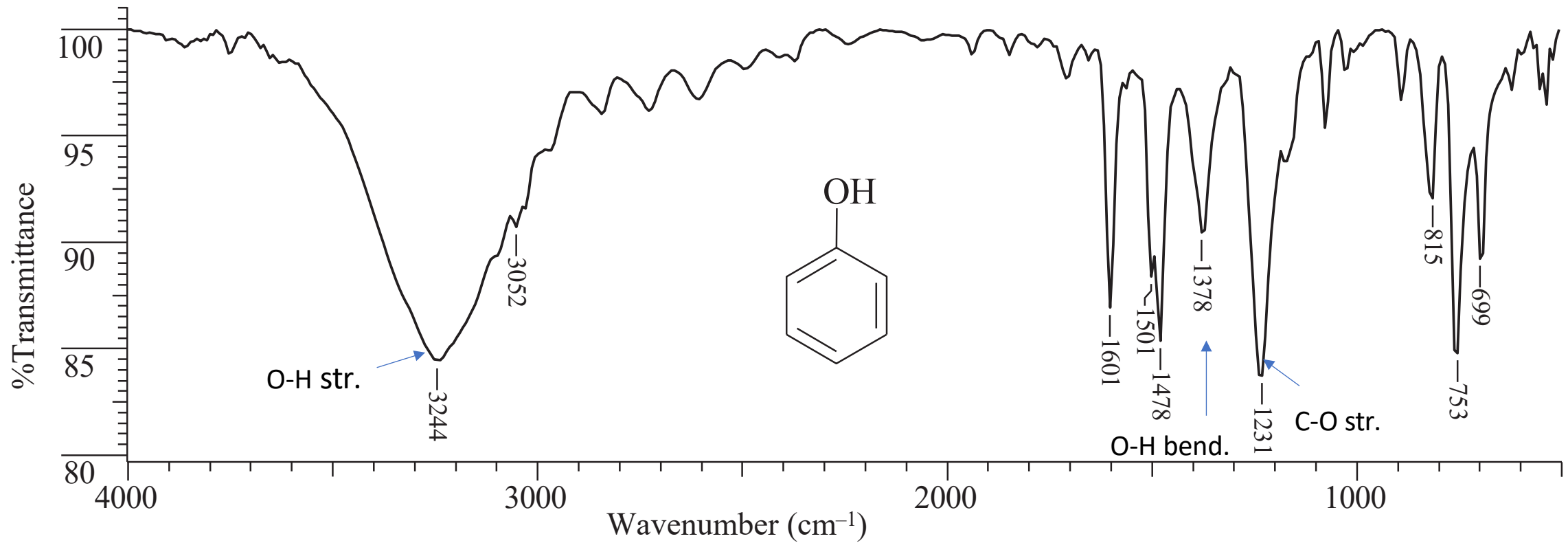
Alcohol



- **Alcohols and Phenols.**
- The characteristic bands observed in the spectra of alcohols and phenols result from **O-H stretching** and **C-O stretching**. These vibrations are **sensitive to hydrogen bonding**.
- **O-H Stretching Vibrations.** The non-hydrogen-bonded or **free hydroxyl group** of alcohols and phenols absorbs strongly in the **3700-3584 cm⁻¹** region.
- Intermolecular hydrogen bonding increases as the concentration of the solution increases, and additional bands start to appear at lower wavenumbers, **3550-3200 cm⁻¹**, at the expense of the free hydroxyl band.
- **C-O Stretching Vibrations.** The C-O stretching vibrations in alcohols and phenols produce a strong band in the **1260-1000 cm⁻¹** region of the spectrum.
- **O-H Bending Vibrations.** The O-H in-plane bending vibration occurs in the general region of **1420-1330 cm⁻¹**.

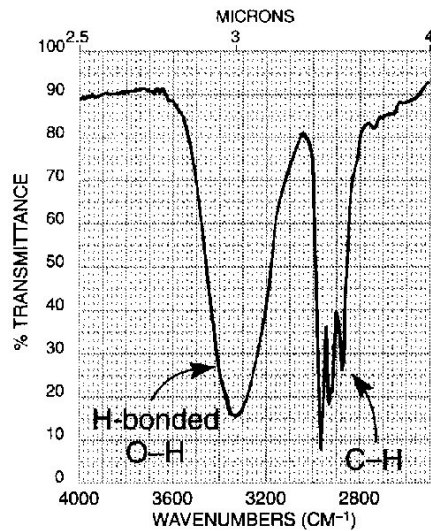


Alcohols and Phenols

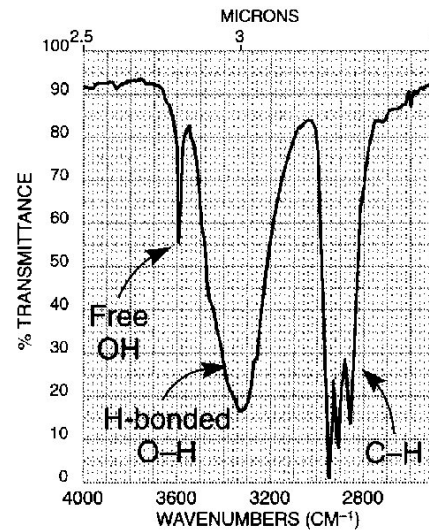




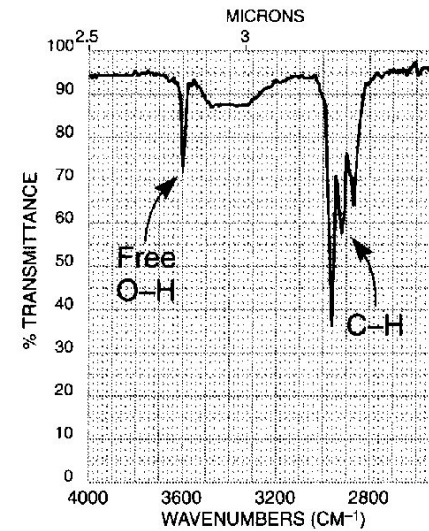
Alcohols and Phenols



(a)



(b)



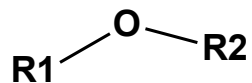
(c)

Compound	C—O Stretch (cm ⁻¹)	O—H Stretch (cm ⁻¹)
Phenols	1220	3610
3° Alcohols (saturated)	1150	3620
2° Alcohols (saturated)	1100	3630
1° Alcohols (saturated)	1050	3640

↓ Decrease Increase ↓



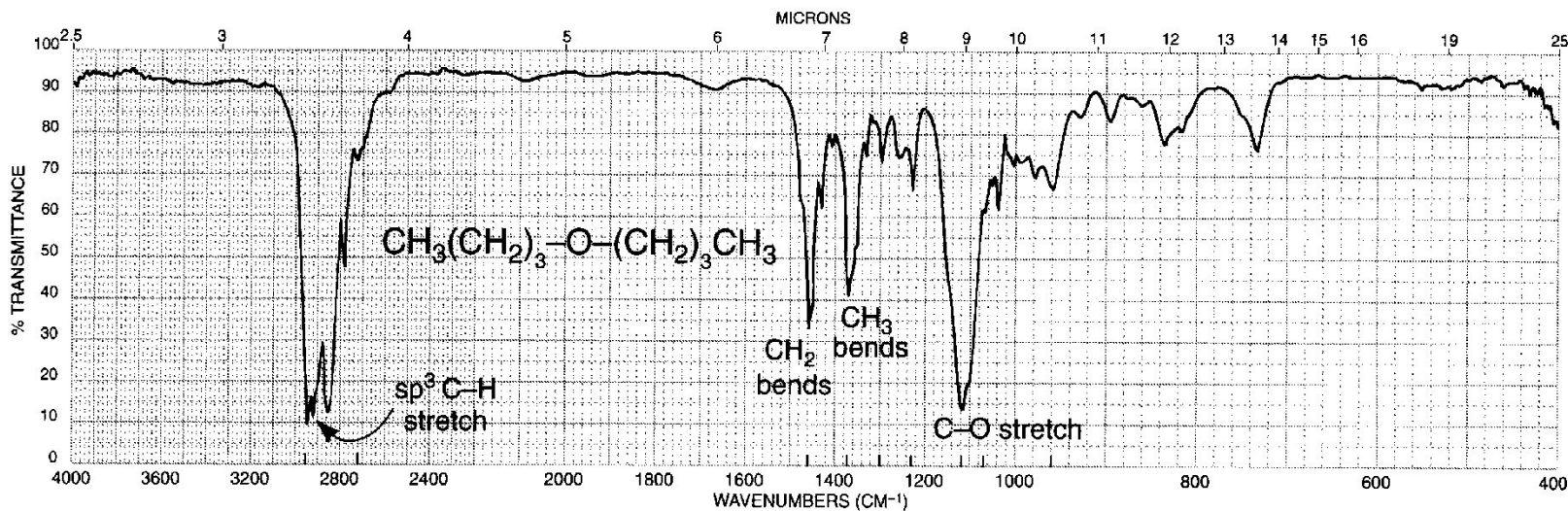
IR for Functional Groups



Ethers

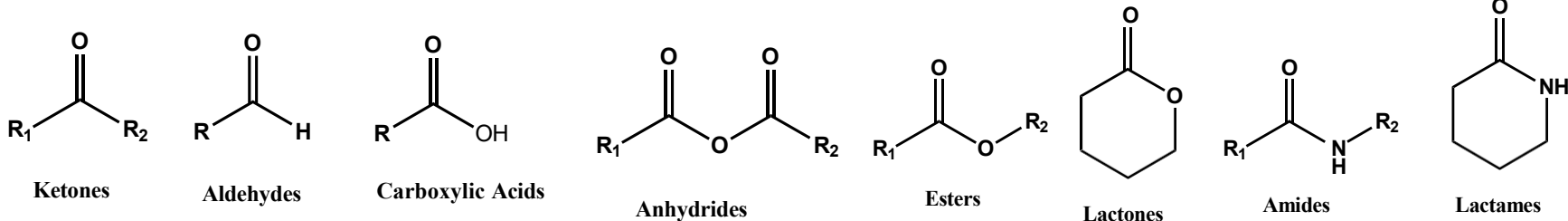
ETHERS

C—O The most prominent band is that due to C—O stretch, $1300\text{--}1000\text{ cm}^{-1}$. Absence of C=O and O—H is required to ensure that C—O stretch is not due to an ester or an alcohol. Phenyl alkyl ethers give two strong bands at about 1250 and 1040 cm^{-1} , while aliphatic ethers give one strong band at about 1120 cm^{-1} .





IR for Functional Groups

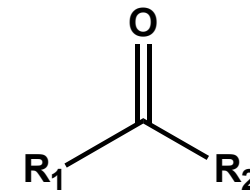


- **Carbonyl Group.**

- ***C=O Stretching Vibrations.*** Ketones, aldehydes, carboxylic acids, carboxylic esters, lactones, acid halides, anhydrides, amides, and lactams absorption band in the region of **1870-1540 cm^{-1}** .
- Its relatively **constant position**, **high intensity**, and **relative freedom from interfering bands** make this one of the **easiest bands to recognize in IR spectra**.
- Within its given range, the position of the C=O stretching band is determined by the following factors:
 - (i) **physical state**,
 - (ii) **electronic and mass effects of neighboring substituents**,
 - (iii) **conjugation**,
 - (iv) **hydrogen bonding** (intermolecular and intramolecular),
 - (v) **ring strain**.



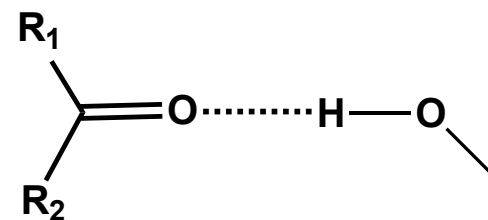
IR for Functional Groups



Ketones

- **Ketones**

- The saturated aliphatic ketone, **1715 cm⁻¹**,
- Conjugation with a **C=C** bond reduces the double-bond character of the **C=O bond**, causing absorption at **lower wavenumbers** of **1685-1666 cm⁻¹** region.
- Intermolecular hydrogen bonding between a ketone and a hydroxylic solvent such as methanol causes a slight decrease in the wavenumber of the carbonyl group. For example, a neat sample of ethyl methyl ketone absorbs at **1715 cm⁻¹**, whereas a 10% solution of the ketone in methanol absorbs at **1706 cm⁻¹**.

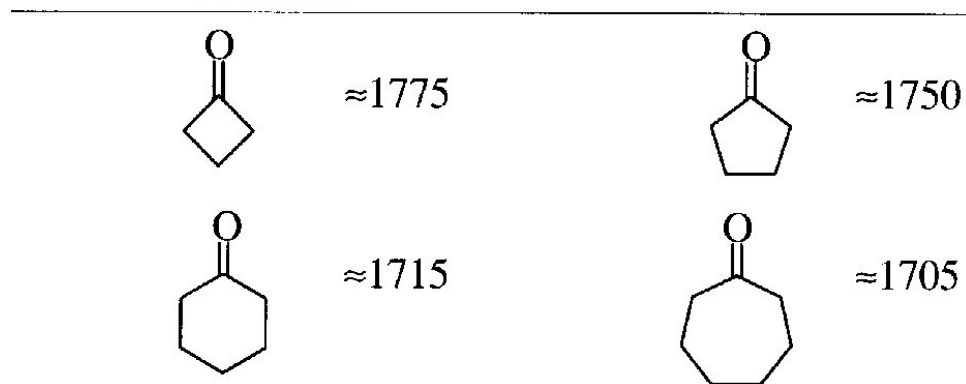




IR for Functional Groups



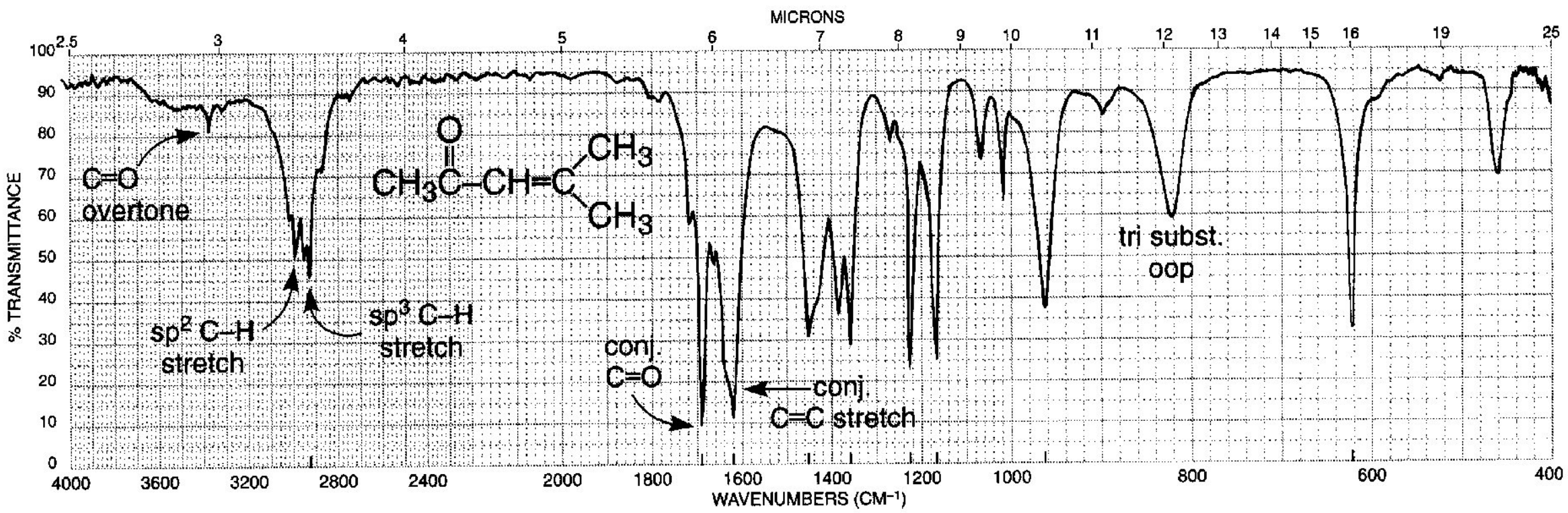
- **Ketones**
- Conjugation with a **C=C** bond reduces the double-bond character of the **C=O bond**, causing absorption at **lower wavenumbers** of **1685-1666 cm⁻¹** region.
- In acyclic ketones and in ketones with a six-membered ring, the angle is near **120°**.
- In **strained rings** in which the angle is **<120°**, interaction with C-C bond stretching **increases the energy required to produce C=O stretching and thus increases the stretching frequency.**



- C-C(O)-C bending appears at **1300-1100 cm⁻¹**

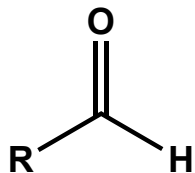


Ketone





IR for Functional Groups

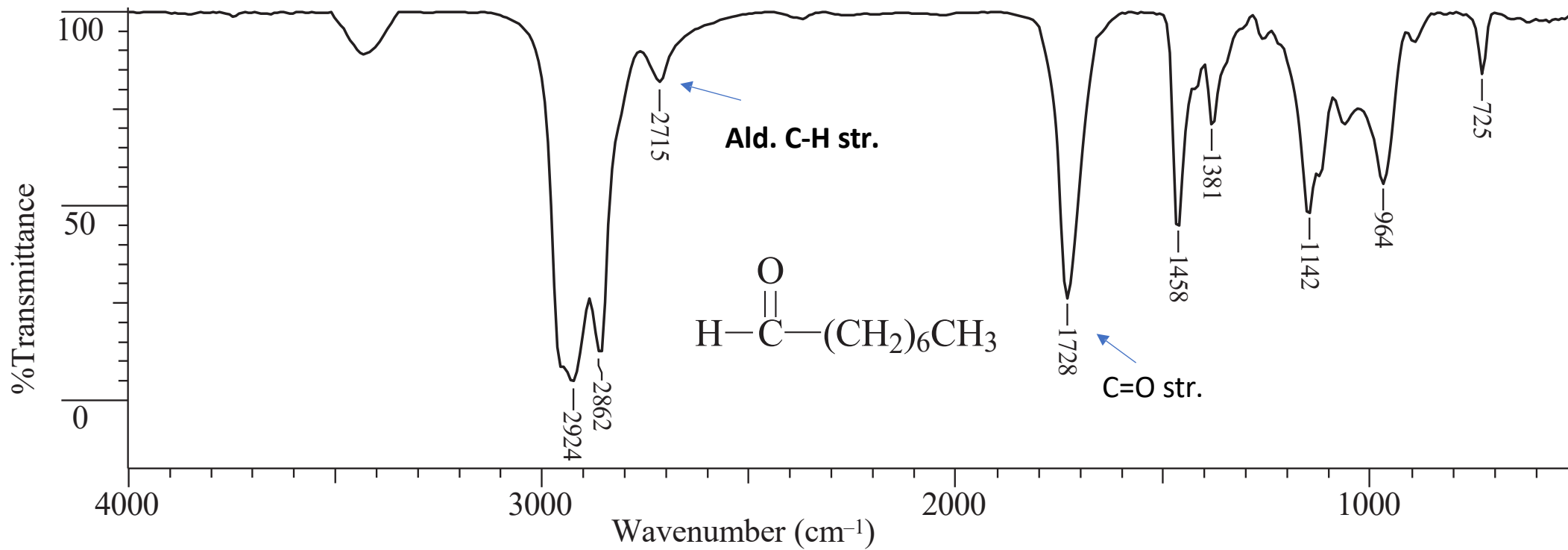


Aldehydes

- **Aldehyde**
- ***C=O Stretching Vibrations***. The carbonyl groups of aldehydes absorb at **slightly higher frequencies than those of the corresponding methyl ketones**.
- Aliphatic aldehydes absorb near **1740-1720 cm^{-1}** .
- ***C-H Stretching Vibrations***. The majority of aldehydes show aldehydic C-H stretching absorption in the **2830-2700 cm^{-1}** region.

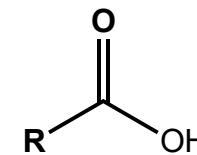


Aldehydes



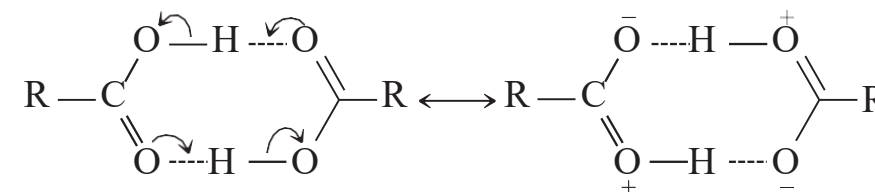


IR for Functional Groups



Carboxylic Acids

- **Carboxylic Acids**
- Free hydroxyl stretching vibration (near 3520 cm^{-1}) is observed only in very dilute solution in nonpolar solvents or in the vapor phase.
- Carboxylic acid dimers display very broad, intense O-H stretching absorptions in the region of **$3300\text{-}2500\text{ cm}^{-1}$** . The band is usually centered near **3000 cm^{-1}** .



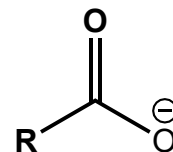
- **C=O Stretching Vibrations.** The C=O stretching bands of acids are considerably **more intense** than ketonic C=O stretching bands and it absorbs at **$1730\text{-}1700\text{ cm}^{-1}$** .



IR for Functional Groups



- **Carboxylic Acids**
- ***C=O Stretching and O-H Bending Vibrations.*** Two bands arising from C=O stretching and O-H bending appear in the spectra of carboxylic acids near **1320-1210 cm⁻¹** and **1440-1395 cm⁻¹**, respectively.

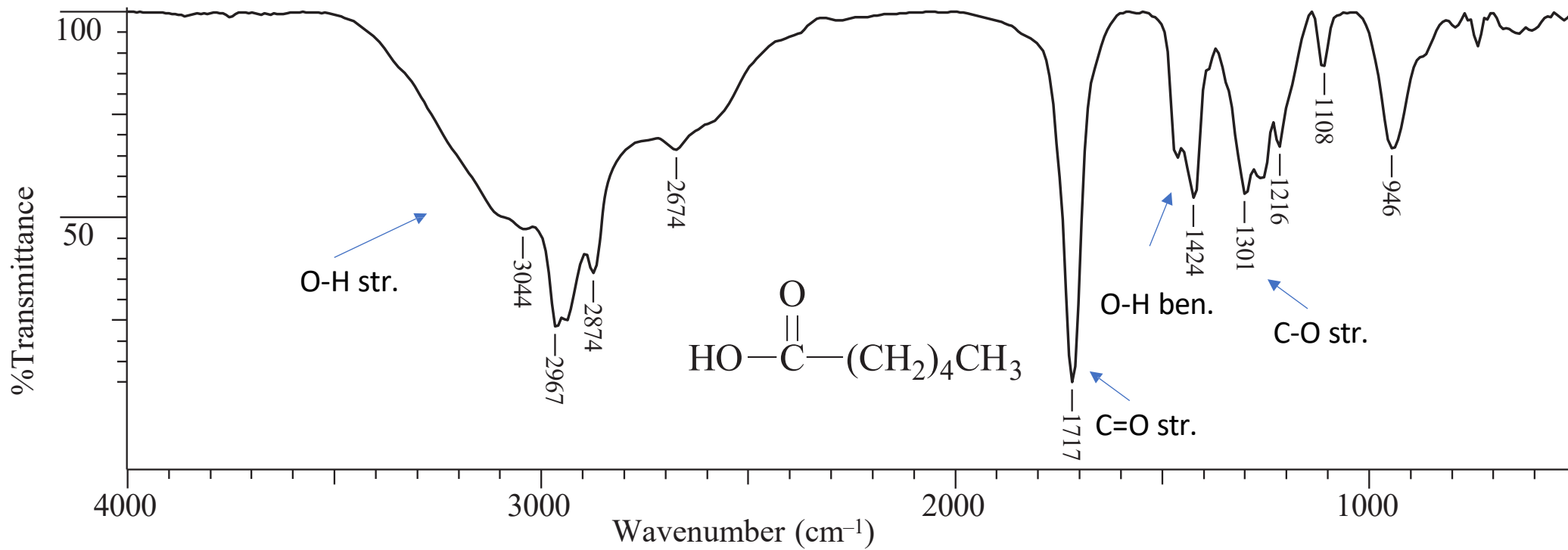


Carboxylate

- **Carboxylate Anion**
- The carboxylate anion has two strongly coupled C=O bonds with bond strengths intermediate between C=O and C-O.
- The carboxylate ion gives rise to **two bands: a strong asymmetrical stretching band near 1650-1550 cm⁻¹** and **a weaker symmetrical stretching band near 1400 cm⁻¹**.
- The O-H stretching band disappears.

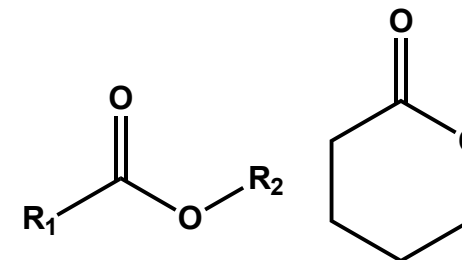


Carboxylic Acids



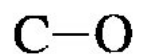
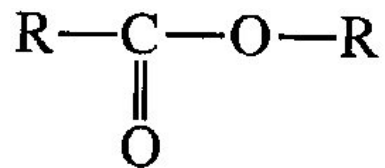


Esters and Lactones



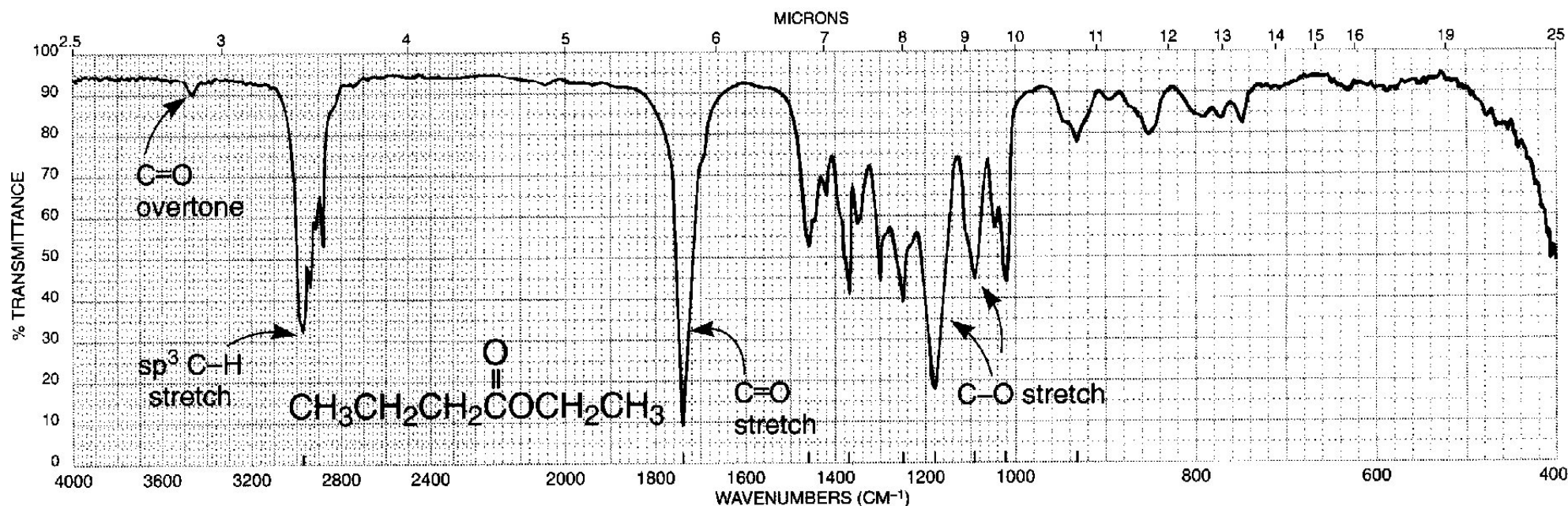
Esters

Lactones



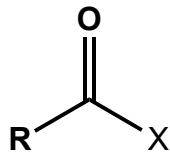
C=O stretch appears in range $1750-1735 \text{ cm}^{-1}$ for normal aliphatic esters.

Stretch in two or more bands, one stronger and broader than the other, occurs in the range $1300-1000 \text{ cm}^{-1}$.





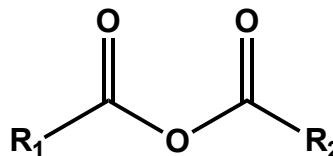
IR for Functional Groups



Acid Halide

- **Acid Halides**

- Acid halides show strong absorption in the **C=O stretching region**. Unconjugated acid chlorides absorb in the **1815-1785 cm⁻¹** region.



Anhydrides

- **Carboxylic Acid Anhydrides**

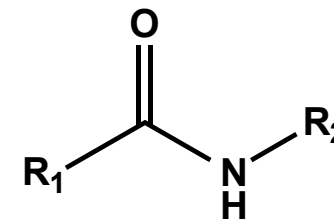
- **C=O Stretching Vibrations.** Anhydrides display two stretching bands in the carbonyl region. The two bands result from asymmetrical and symmetrical C=O stretching modes. Saturated acyclic anhydrides absorb near **1818-1750 cm⁻¹**.
- **C-O Stretching Vibrations.** Other strong bands appear in the spectra of anhydrides as a result of stretching vibrations near **1300-900 cm⁻¹**.



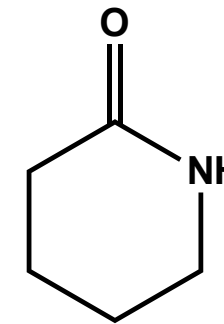
IR for Functional Groups



- **Amides and Lactams**



Amides



Lactames

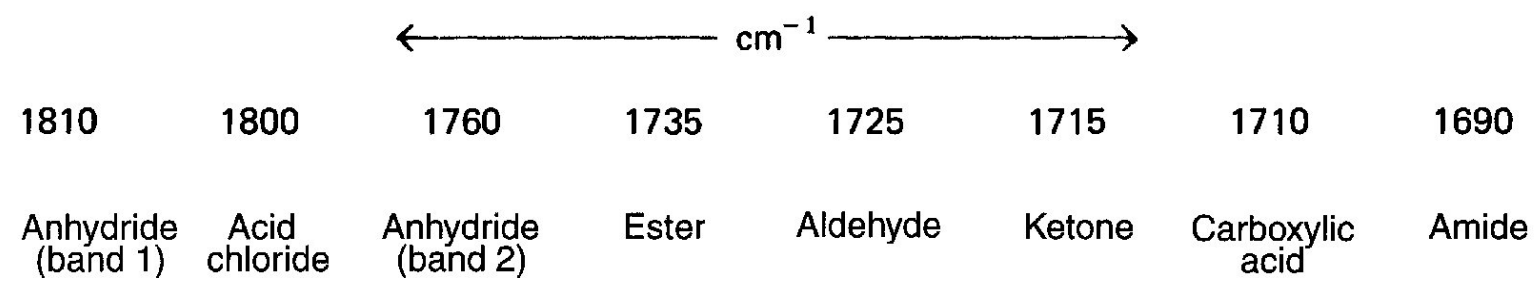
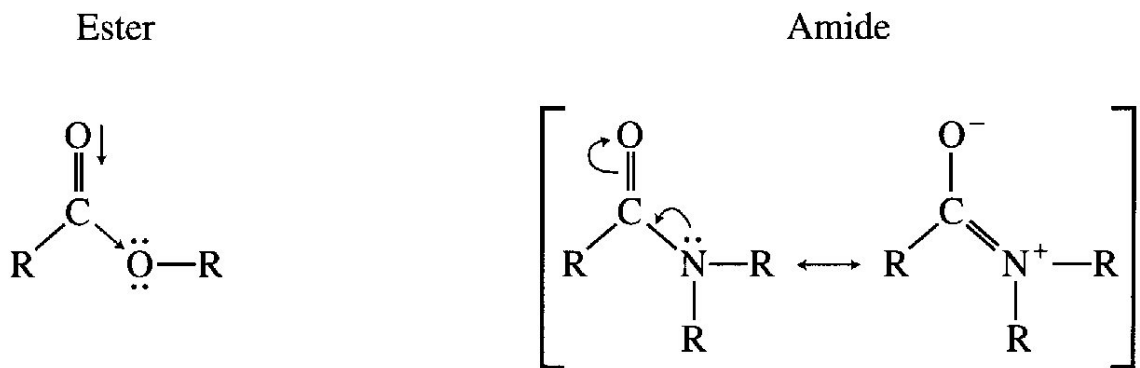
- ***C=O Stretching Vibrations (Amide I Band)***. The C=O absorption of amides occurs at lower frequencies than “normal” carbonyl absorption at **1680-1630 cm⁻¹** due to the resonance effect.
- The **N-H stretching** is observed in the range of **3350–3180 cm⁻¹**,
- ***N-H Bending Vibrations (Amide II Band)***. All primary amides show a sharp absorption band in dilute solution (amide II band) resulting from N-H bending at a somewhat lower frequency than the C=O band at **1620-1590 cm⁻¹**, and normally is separated from the amide I band.



Ester vs Amide



More electron withdrawing element (higher frequency) see ester
Resonance (lower frequency) see amide





IR for Functional Groups



- **Amines**

- **N-H Stretching Vibrations.**

- Primary amines, display **two weak** absorption bands: one at **3400-3300 cm⁻¹** and the other at **3330-3250 cm⁻¹**.

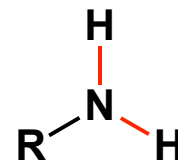
- **Aromatic primary amines** absorb at slightly **higher wavenumbers** than aliphatic primary amines.

- Secondary amines show a **single weak** band in the **3350-3310 cm⁻¹** region.

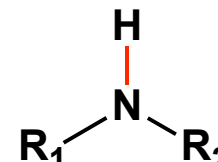
- These bands are shifted to **longer wavelengths** by **hydrogen bonding**. The associated N-H bands are **weaker** and frequently **sharper** than the corresponding O-H bands.

- In the primary and secondary amines, a **shoulder** appears on the **low-frequency side** of the **N-H stretching band**, arising from the **overtone** of the NH bending band intensified by **Fermi resonance**.

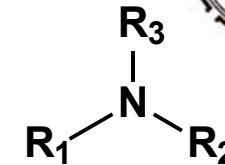
- **Tertiary amines** **do not** absorb in this region.



primary amine



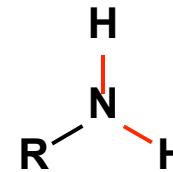
secondary amine



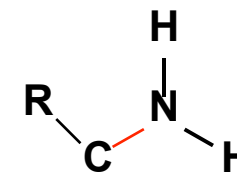
tertiary amine



IR for Functional Groups



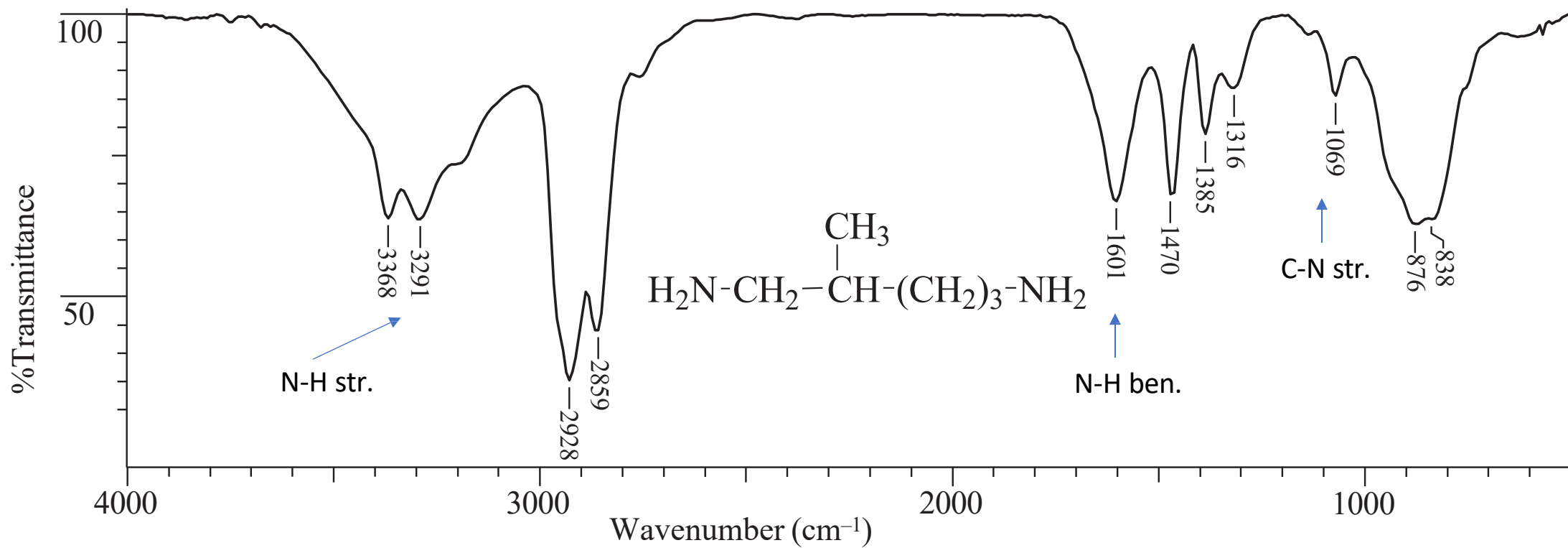
- **Amines**
- **$N-H$ Bending Vibrations.** The $N-H$ bending (scissoring) vibration of primary amines is observed in the **$1650-1580\text{ cm}^{-1}$** region of the spectrum.
- **$C-N$ Stretching Vibrations.** Medium absorption bands for the unconjugated $C-N$ linkage in primary, secondary, and tertiary aliphatic amines appear in the region of **$1250-1020\text{ cm}^{-1}$** .



- Aromatic amines display strong $C-N$ stretching absorption in the **$1342-1266\text{ cm}^{-1}$** region. It is higher than the corresponding absorption of aliphatic amines because the force constant of the $C-N$ bond is increased by resonance with the ring.

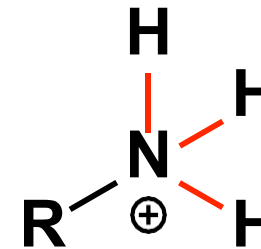


Amines





IR for Functional Groups



amine salt

- **Amine Salts**
- **$N-H$ Stretching Vibrations.** The ammonium ion gives a strong, broad absorption in the **3300-3030 cm^{-1}** region because of $N-H$ stretching vibrations. There is also a band in the **2000-1709 cm^{-1}** region.
- **$N-H$ Bending Vibrations.** The ammonium ion displays a strong, broad bending band near **1429 cm^{-1}** .

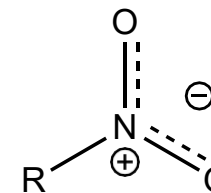


IR for Functional Groups



- **Nitriles (cyano group) —C≡N**
- The spectra of nitriles (—C≡N) are characterized by weak-to-medium absorption in the triple-bond stretching region of the spectrum. Aliphatic nitriles absorb at **2260-2240 cm⁻¹**.
- Conjugation, such as occurs in aromatic nitriles, reduces the wavenumber of absorption to **2240-2222 cm⁻¹** and enhances the intensity.

- **Nitro compounds**, show absorption caused by **asymmetrical** and **symmetrical** stretching of the **NO₂ group**.



nitro

- Asymmetrical absorption results in a strong band in the **1661-1499 cm⁻¹** region; while the symmetrical absorption occurs in the region between **1389-1259 cm⁻¹**.
- Conjugation lowers the wavenumbers of both bands.



Organic Sulfur Compounds



- ***S-H Stretching Vibrations: Mercaptans.*** Aliphatic mercaptans and thiophenols show S-H stretching absorption in the range of **2600-2550 cm⁻¹**.
- The **S-H stretching** band is characteristically **weak** and may go **undetected** in the spectra of dilute solutions. However, since few other groups show absorption in this region, it is useful in detecting S-H groups.
- ***C=S Stretching Vibration***
- The **C=S group** is **less polar** than the **C=O group** and has a weaker bond. So, the **band is not intense**, and it **falls at lower frequencies** at a region of **1250-1020 cm⁻¹**.



IR for Functional Groups



- **Compounds Containing Sulfur-Oxygen Bonds**
- ***S=O Stretching Vibrations.***
- **Sulfoxides** show strong absorption in the **1070-1030 cm^{-1}** region. This absorption occurs at **1050 cm^{-1}** for DMSO.
- The hydrogen bonding shifting the absorption to slightly lower frequencies.
- **Sulfones** Spectra of sulfones show strong absorption bands at **1350-1300 cm^{-1}** and **1160-1120 cm^{-1}** . These bands arise from asymmetric and symmetric SO_2 stretching, respectively.
- **Sulfonamides** absorb strongly at **1370-1335 cm^{-1}** and **1170-1155 cm^{-1}** .
- Primary sulfonamides show strong N-H stretching bands at **3390-3330 cm^{-1}** and **3300-3247 cm^{-1}** in while secondary sulfonamides absorb near **3265 cm^{-1}** .



IR for Functional Groups



- **Organic Halogen Compounds**
- The strong absorption of halogenated hydrocarbons arises from the stretching vibrations of the **carbon–halogen bond**.
- Fluoro- compounds in **1400-1000 cm^{-1}** region.
- Aliphatic C–Cl absorption is observed in the broad region between **850-550 cm^{-1}** .
- Brominated compounds absorb in the **690-515 cm^{-1}** region.
- Iodo- compounds in the **600-500 cm^{-1}** region.
- A strong CH_2 wagging band is observed for the CH_2X (X = Cl, Br, and I) group in the **1300-1150 cm^{-1}** .



IR for Functional Groups



- **Phosphorus Compounds**
- *P-H, P-C, and P=O Vibrations.*
- The P-H bond has **stretching vibrations** in the region of **2350-2440 cm^{-1}** and **bending vibrations** at **1120-950 cm^{-1}** .
- The stretching vibrations of P-C bonds in aliphatic phosphine oxides appear in the range of **650-750 cm^{-1}** .
- In the phosphoryl group (P=O), unlike for C=O, the oxygen atom bonds with the phosphorus in a highly polar bond that is frequently designated as a (P⁺-O⁻) group. The phosphoryl stretching absorption occurs at a range of **1310-1150 cm^{-1}** .



IR Interpretation



- **Requirements for good interpretation**

1. The spectrum must be **adequately resolved** and of **adequate intensity**.
2. The sample should have a **reasonable purity**.
3. The spectrometer should be **calibrated** so that the bands are observed at their proper frequencies or wavelengths. Proper calibration can be made with reliable standards, such as **polystyrene** film.
4. The method of sample handling must be specified.



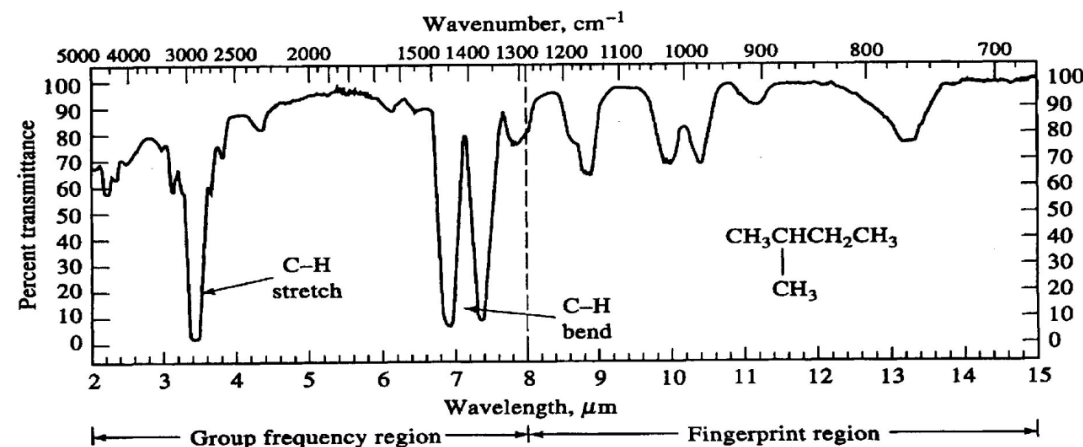
IR Interpretation



- IR spectra can be qualitatively split into two regions.
 - Functional group region **4000-1300 cm⁻¹**
 - Fingerprint region **1300-400 cm⁻¹**
- First take a qualitative look to identify functional groups.
- Concentrate on major functional groups that are diagnostic.



C=O	1800-1650 cm ⁻¹
-NH ₂	3400-3300 cm ⁻¹
phenyl	900-700 cm ⁻¹
-NO ₂	1550 and 1350 cm ⁻¹

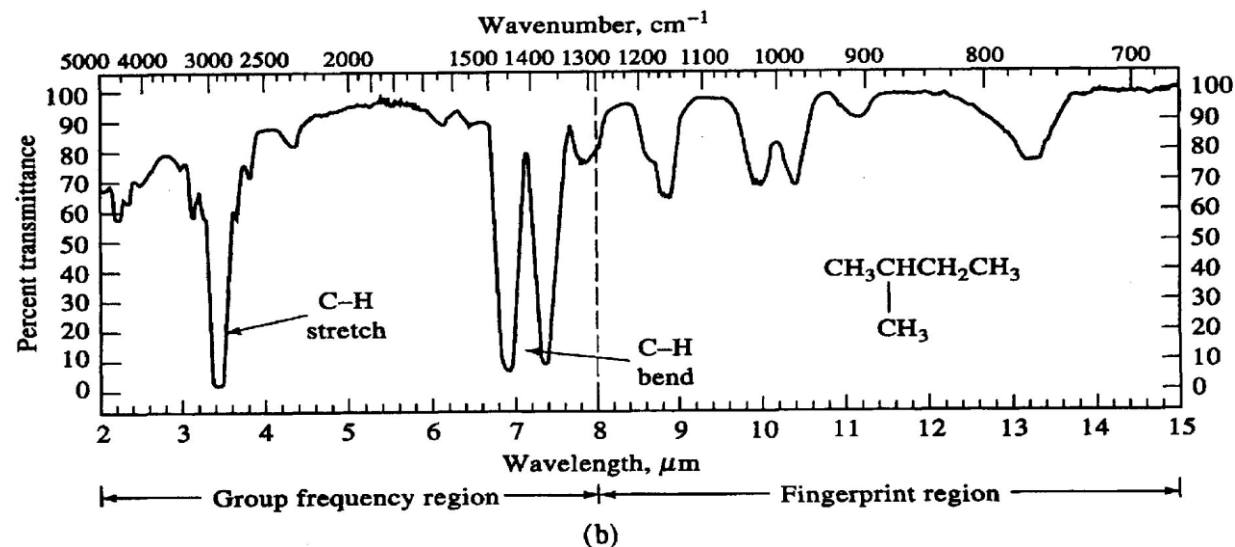


(b)



IR Interpretation

- The fingerprint region ($1300\text{-}400\text{ cm}^{-1}$) involves several low intensity and overlapped bands.
- Therefore, **hard to achieve peak-by-peak interpretation** in the fingerprint area.
- However, the **complexity** of fingerprint area makes **no two compounds** having the same absorption behavior at this region.
- Sample identification can be carried out by comparing the fingerprint of unknown sample to the authentic sample absorption to determine the sample identity.



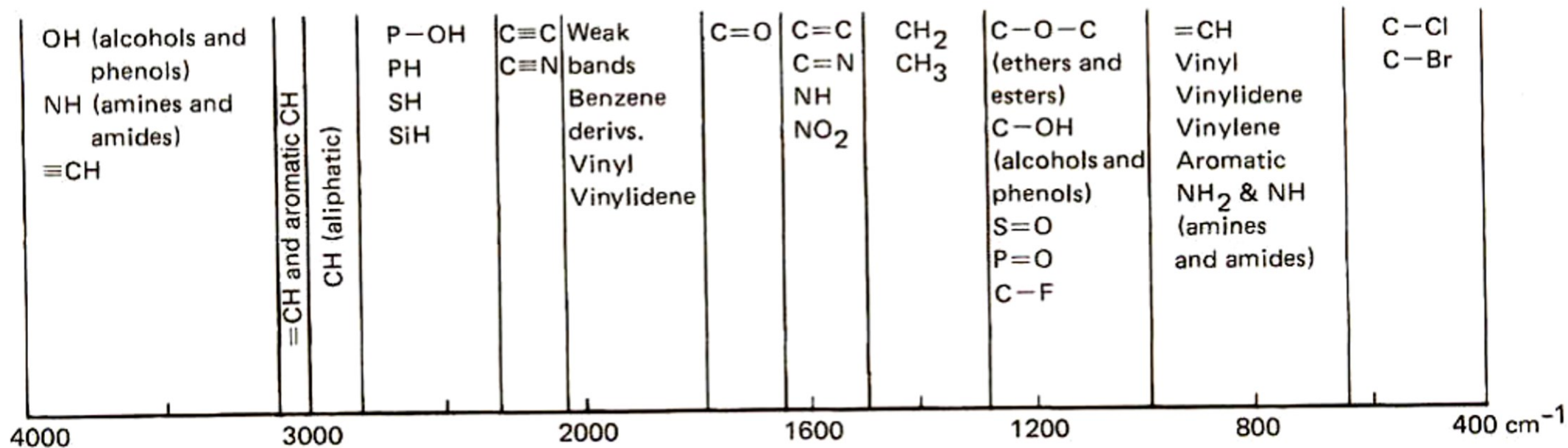


The Applications of IR Spectroscopy



A- Identification of functional group and structure elucidation

- The functional group can be determined according to **corresponding peaks**.
- Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed.





The Applications of IR Spectroscopy



B- Identification of chemical substances

- IR spectroscopy is used to establish whether a given sample is identical with another or not.
- This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two compounds will produce identical spectra is almost zero.
- If two compounds have identical IR spectra, then both are samples of the same substance.



The Applications of IR Spectroscopy



C- The analysis of pharmaceutical substances

- The pharmaceutical substances can be identified and critically examined by IR spectroscopy.
- The latest versions of British Pharmacopoeia (BP) and United States Pharmacopoeia (USP) contain the complete IR-spectrum of such pure pharmaceutical substances that are essentially included in the respective *official compendium*.
- These authentic IR-spectra are profusely used in many well-equipped Quality Assurance Laboratories in checking the purity of commercially available drugs before employing them in various formulations.



The Applications of IR Spectroscopy



D- The determination of drug-excipient interactions pharmaceutical dosage forms

- IR is the commonly used for the screening of drug-excipient compatibility.
- IR provides rapid analysis, quick and easy detection of incompatibilities due to spectral shifts and the detection of interaction byproducts.