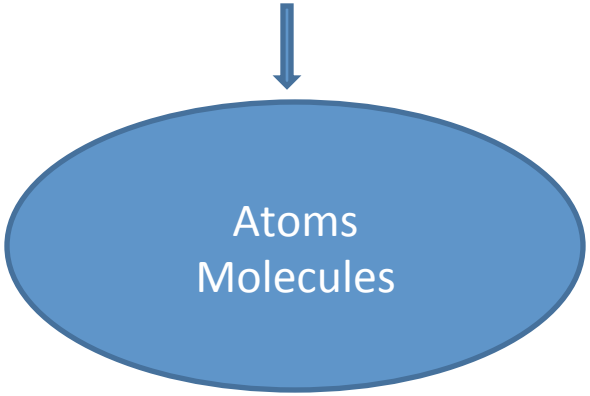
Introduction and Principle of IR Spectrophotometry

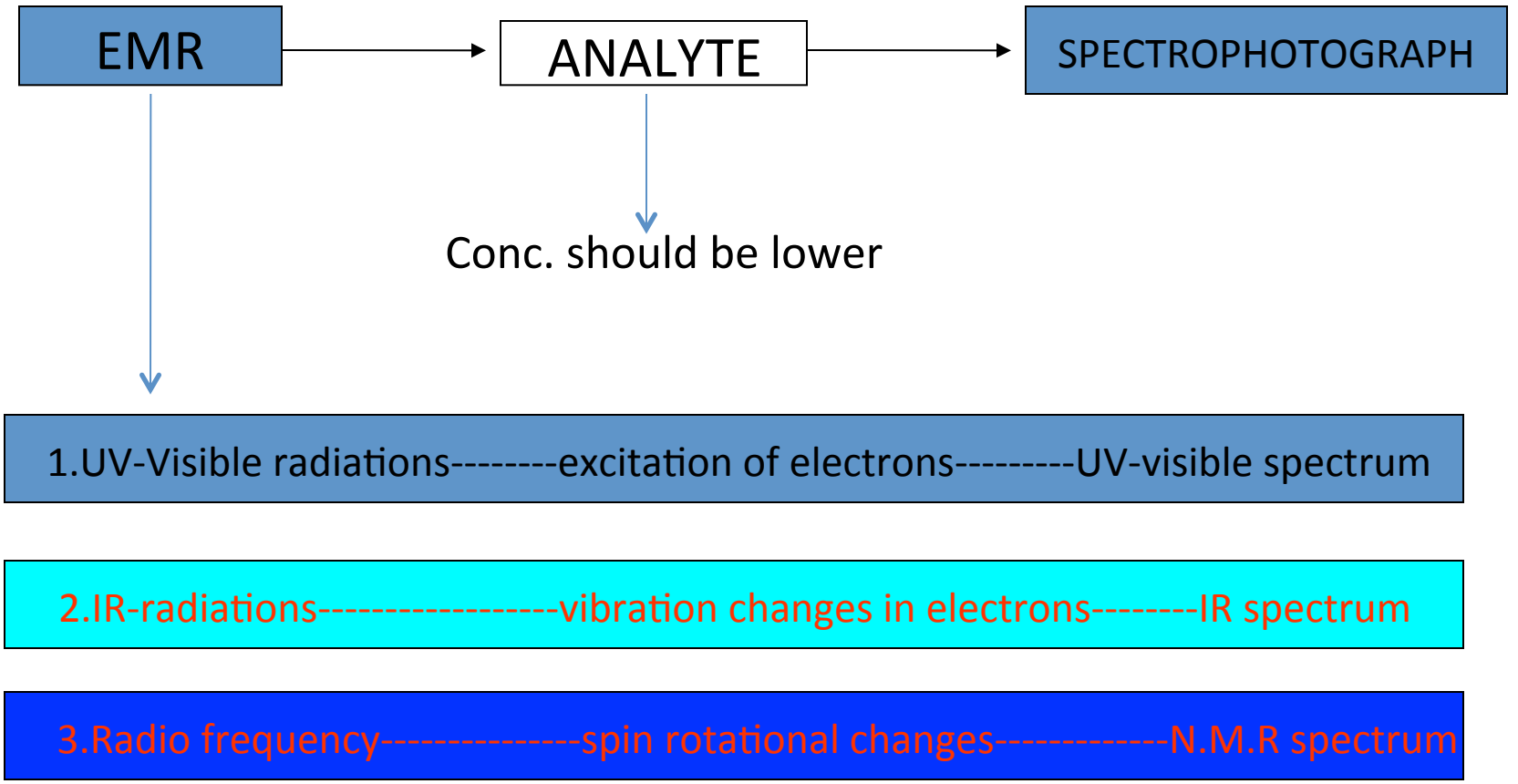
Spectroscopy

- Method of “Seeing the unseeable”

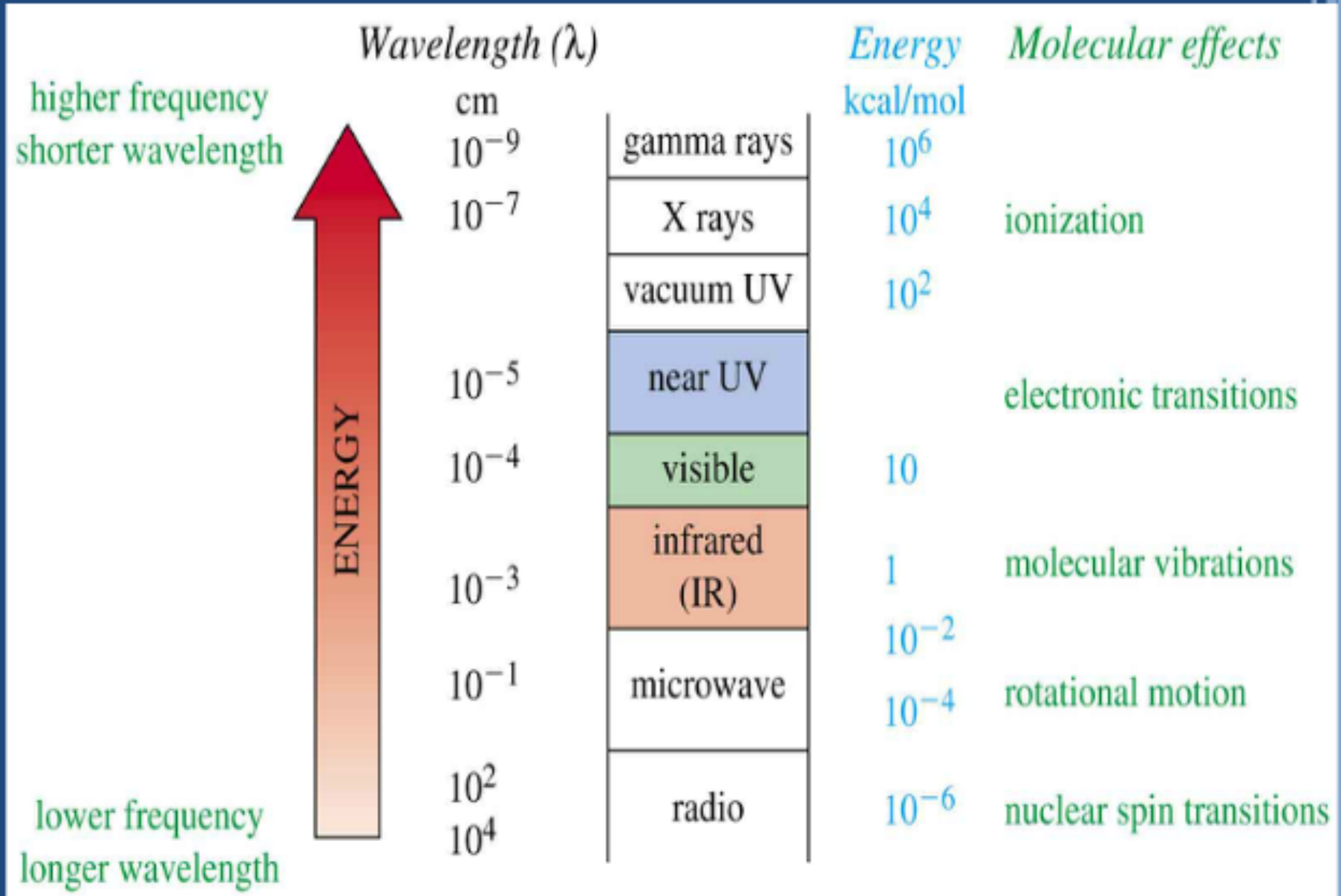


- using electromagnetic radiation to obtain information about atoms and molecules that are too small to see.

Spectroscopy is an instrumentally aided study of the interactions between matter (sample being analyzed) and energy (any portion of the electromagnetic spectrum)



Molecular effects:



IR spectrophotometry

Energy of molecule = Electronic energy+ Vibrational energy + Rotational energy

- IR spectroscopy is concerned with the study of absorption of infrared radiation, which causes vibrational transition in the molecule.

Hence, IR spectroscopy also known as Vibrational spectroscopy.

- IR spectra mainly used in structure elucidation to determine the functional groups.

- IR region: 0.8 µm (800nm) to 1000 µm (1mm)

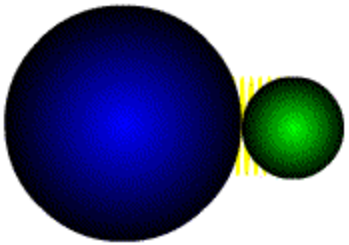
Sub divided into

1. Near IR: 0.8-2.5 µm
2. Middle IR: 2.5-15 µm
3. Far IR: 15-200 µm

Most of the analytical applications are confined to the middle IR region because absorption of organic molecules are high in this region.

Principle of IR spectroscopy

- Molecules are made up of atoms linked by chemical bonds. The movement of atoms and the chemical bonds like spring and balls (vibration).



Vibration of a Diatomic Molecule
Approximates an Oscillating Spring

- This characteristic vibration are called Natural frequency of vibration.

- When energy in the form of infrared radiation is applied then it causes the vibration between the atoms of the molecules and when,

Applied infrared frequency = Natural frequency of vibration

Then, Absorption of IR radiation takes place and a peak is observed.

Different functional groups absorb characteristic frequencies of IR radiation. Hence gives the characteristic peak value.

Therefore, IR spectrum of a chemical substance is a finger print of a molecule for its identification.

A little physics of electromagnetic radiation

- Energy (E) $E = hn = hc/wavelegth$
  - where h is Planck's constant, c is the speed of light, n is frequency or the number of vibrations per second and wavelength.

- Wavenumber (n')- given in cm-1

  Wavenumber= 1/wavelength in cm

  1μ=10-4cm

Energy, frequency, and wavenumber are directly proportional to each other. & wavelength is inversely proportional.

Regions in IR

Regions	Wavelength μ	Wavenumber Cm-1
Near- IR Region	0.8-2.5	12500-4000
Mid- IR Region	2.5-15	4000-667
Far- IR Region	15-200	667-50

Y.R.Sharma,S.Chand; Elementary Organic Spectroscopy, India edition, 2009,Pg. no. 69-70

WHAT IS IR RADIATION

- Natural infrared-

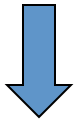
Sunlight, at an effective temperature of 5,780 kelvins, is composed of nearly thermal-spectrum radiation that is slightly more than half infrared.

sunlight provides an irradiance of just over 1 kilowatts per square meter at sea level. Of this energy, 527 watts is infrared radiation, 445 watts is visible light, and 32 watts is ultraviolet radiation.

WWW.Wikipedia.com

Principle of IR spectroscopy

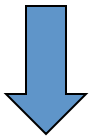
Covalent bond in molecule behave as tiny spring



The atom will not remain in fix motion with respect to each other but the avg. distance remain same So the vibration motion is occured

When internal vibrational energy of molecule matches with energy of externally applied IR, quantized

Molecules is in Resonance absorb IR

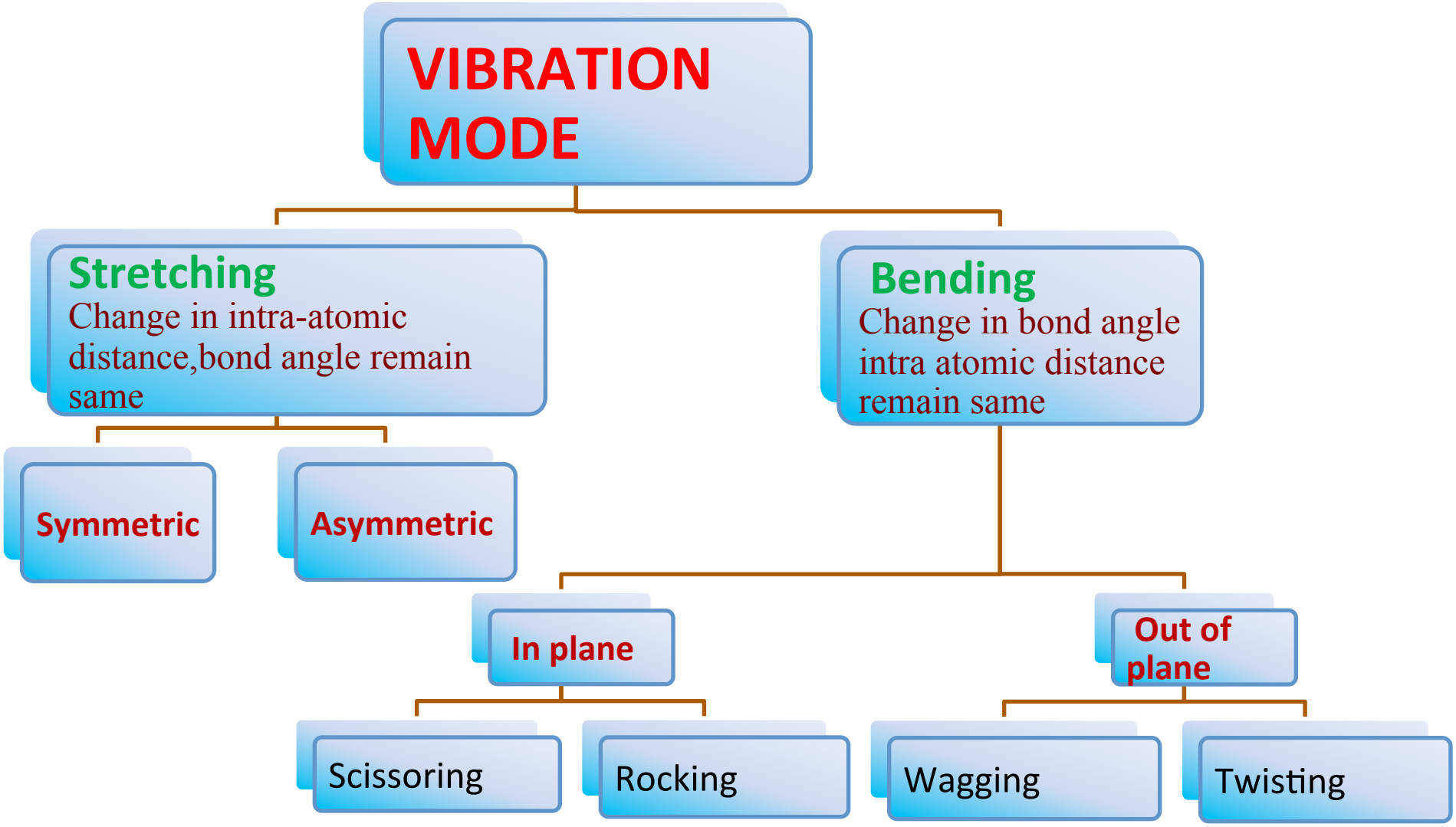


Molecule excited from lower to the higher vibrational level
i.e. Increases the amplitude of vibration

Vibrations

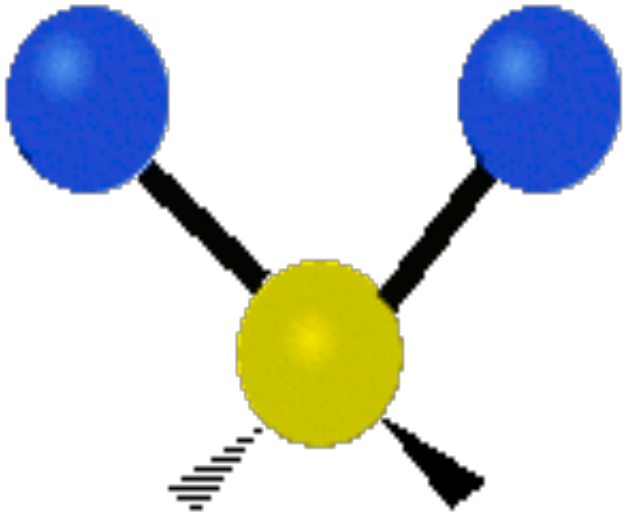
- What is a vibration in a molecule?

  Any change in shape of the molecule- stretching of bonds, bending of bonds, or internal rotation around bonds called vibration.

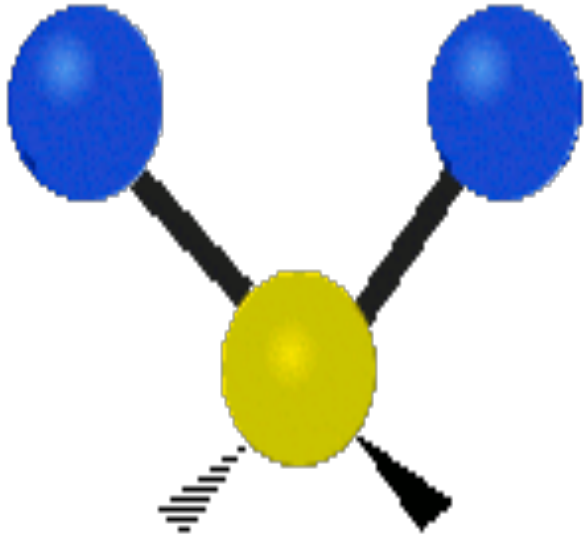

VIBRATION MODE
Stretching
Change in intra-atomic distance,bond angle remain same
Bending
Change in bond angle intra atomic distance remain same
Symmetric
Asymmetric
In plane
Out of plane
Scissoring
Rocking
Wagging
Twisting

Stretching vibration

Symmetric Stretching

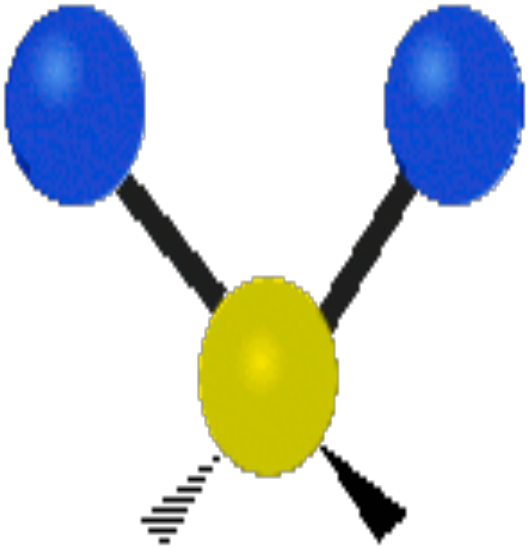


Asymmetric Stretching

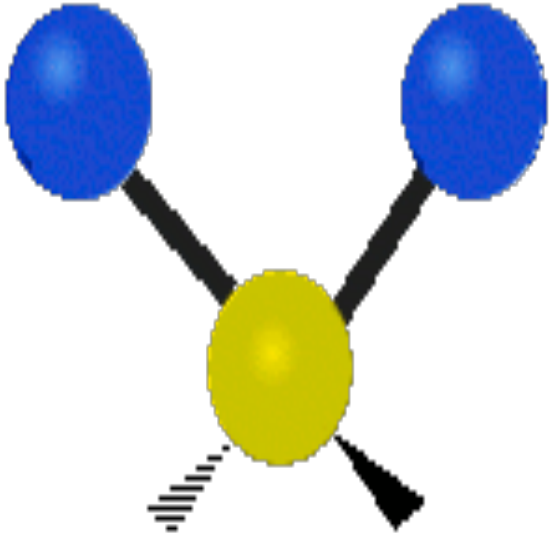


Bending vibration (in plane)

Scissoring

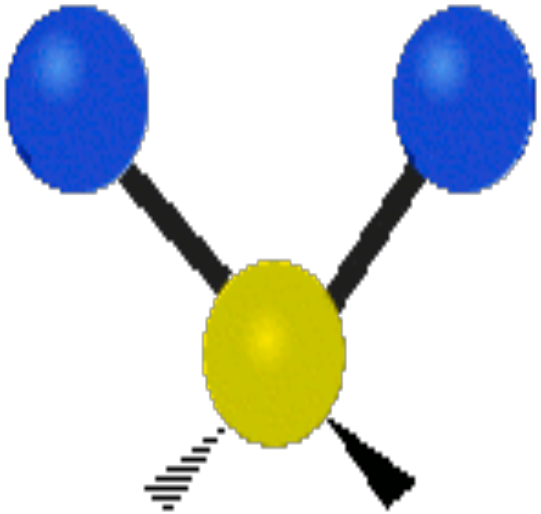


Rocking

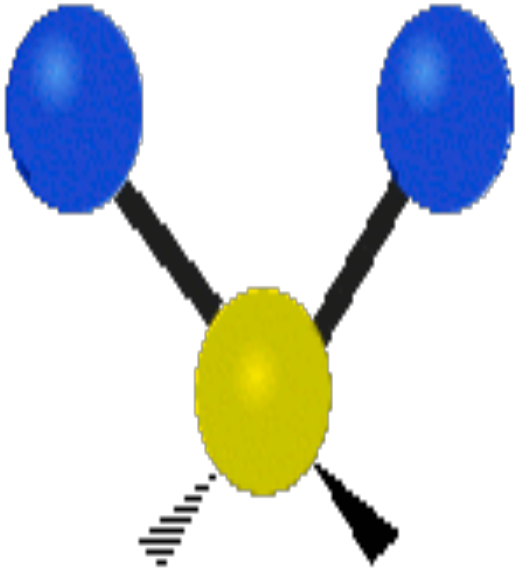


Bending vibration (out of plane)

Twisting



Wagging



What is mean by IR Active Compounds??

- If the vibration transition in molecule is capable of change in dipole moment so the molecule is Said to be IR active

- Asymmetrical stretching/bending and internal rotation change the dipole moment of a molecule. Asymmetrical stretching/bending are IR active.
- Eg- C=0,N-H,O-H etc.

What is mean by IR Inactive Compounds??

If the vibration transition in molecule is not produce change in dipole moment so the molecule is Said to be IR inactive

So the symmetric compound is inactive in IR

Eg. C=C, H_2, N_2, Cl_2

- All the functional groups are asymmetric so they are detected by IR

Requirements of IR Radiation

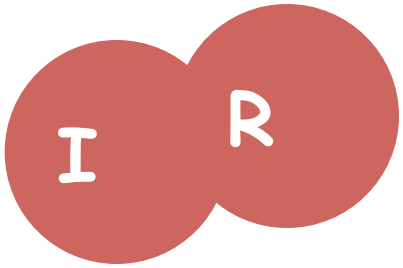
Correct wavelength of radiation-

Natural frequency of vibration of molecule= frequency of the incident radiation.

Eg- HCL natural frequency=2890cm-1

HCL absorbed in frequency=2890cm-1

Molecule vibrates at an increase amplitude.



Change in Dipole moment-

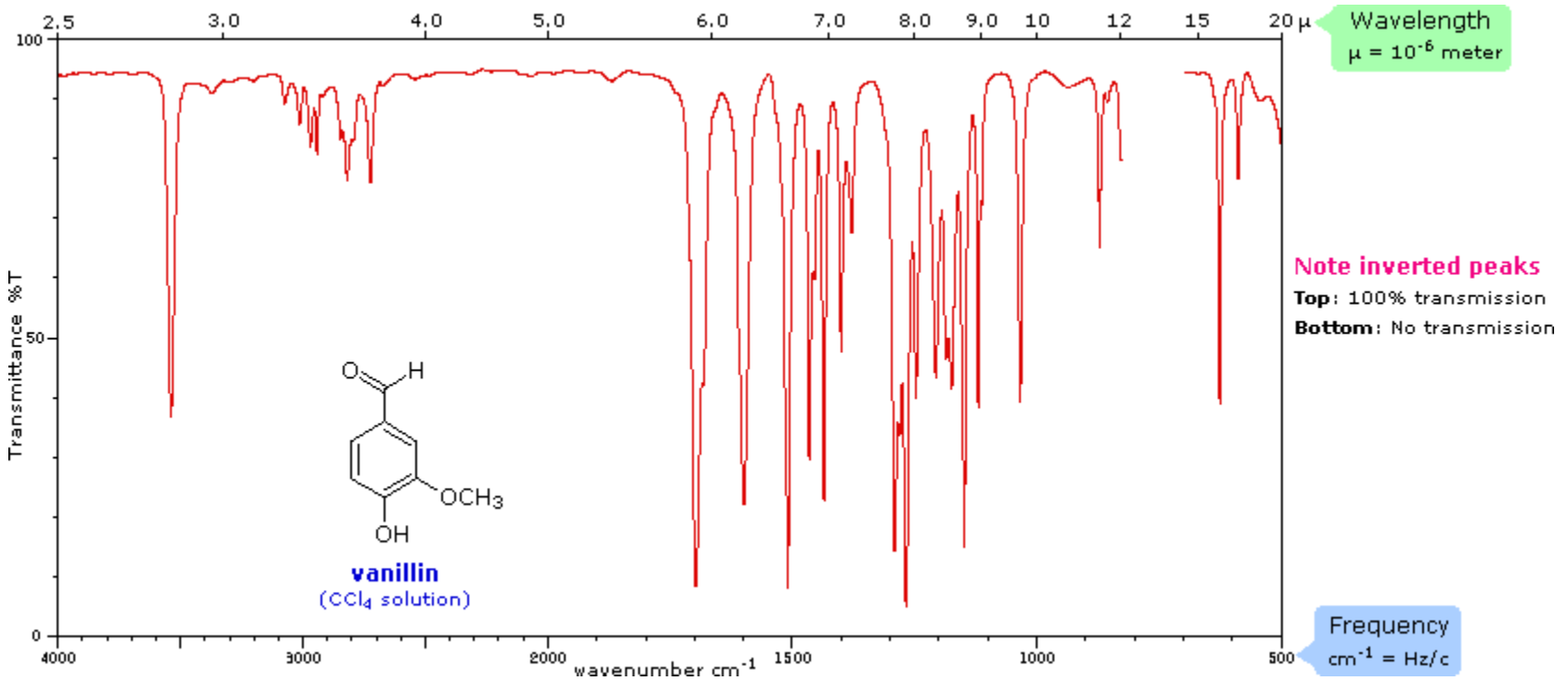
There is slight positive & negative charge on its component atoms & changing the distance between charged atom called change in dipole moment.

When these charge atom vibrates, they shows change in dipole moment, & molecule absorb IR radiation.

Gurdeep R. Chatwal, Sham K.Anand; Instrumental Methods Of Chemical Analysis, Enlarge edition 2002,Pg. no. 2.31-2.32

Practically IR Spectra

- ✓ IR Spectra recorded as % transmittance of radiation Vs frequency or wave number cm-1
- ✓ 100% transmittance mean no absorption means no peak



Criteria for a compound to absorb IR radiation

1. Correct wavelength of radiation
2. Change in dipole moment

1. Correct wavelength of radiation:

A molecule to absorb IR radiation, the natural frequency of vibrations of some part of a molecule is the same as the frequency of incident radiation.

2. Change in dipole moment

- A molecule can only absorb IR radiation when its absorption cause a change in its electric dipole
- A molecule is said to have an electric dipole when there is a slight positive and a slight negative charge on its component of atoms.

Molecular vibrations

There are 2 types of vibrations:

1. Stretching vibrations
2. Bending vibrations

3. Stretching vibrations:

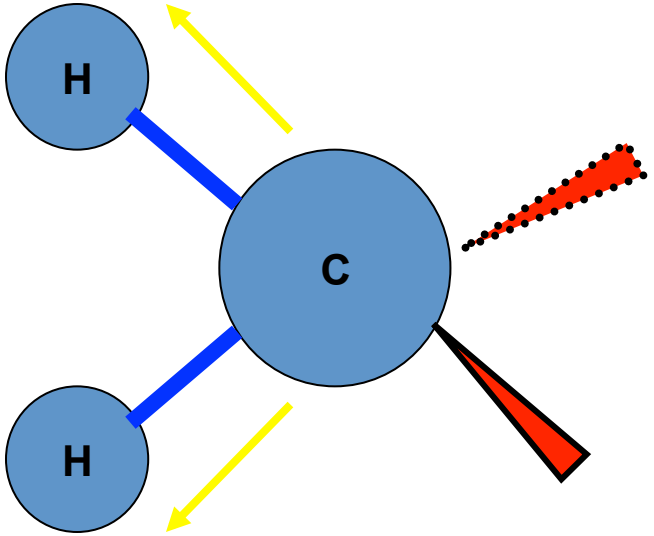
- Vibration or oscillation along the line of bond
- Change in bond length
- Occurs at higher energy: 4000-1250 cm^{-1}
- 2 types:

a) Symmetrical stretching

b) Asymmetrical stretching

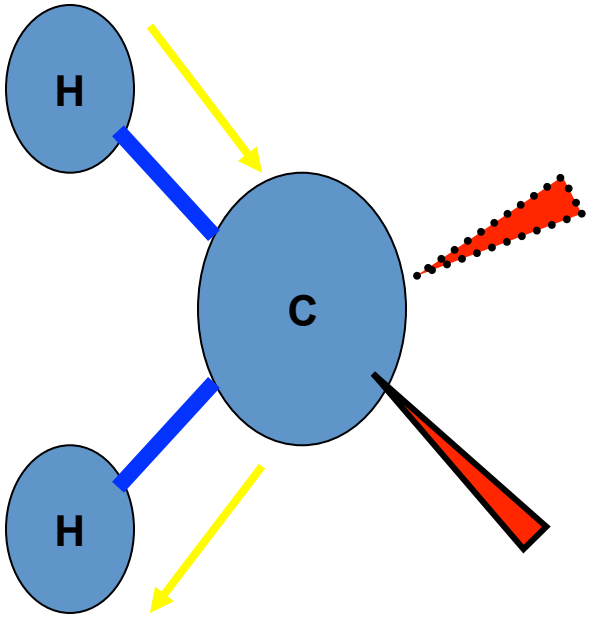
a) Symmetrical stretching:

2 bonds increase or decrease in length simultaneously.



b) Asymmetrical stretching

- in this, one bond length is increased and other is decreased.



2. Bending vibrations

- Vibration or oscillation not along the line of bond
- These are also called as deformations
- In this, bond angle is altered
- Occurs at low energy: 1400-666 cm^{-1}
- 2 types:

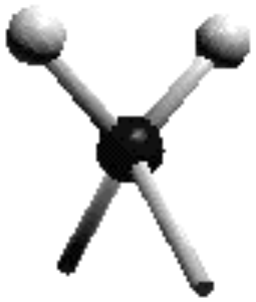
a) In plane bending: scissoring, rocking

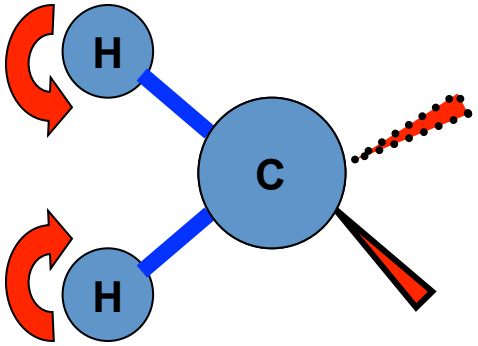
b) Out plane bending: wagging, twisting

a) In plane bending

i. Scissoring:

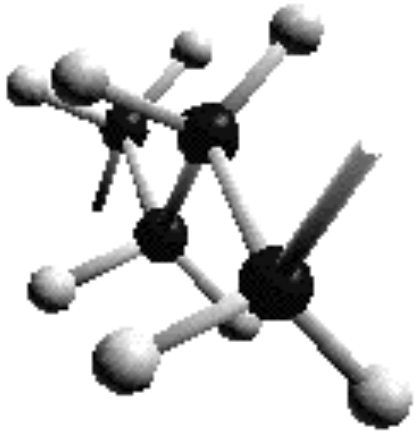
- This is an in plane blending
- 2 atoms approach each other
- Bond angles are decrease

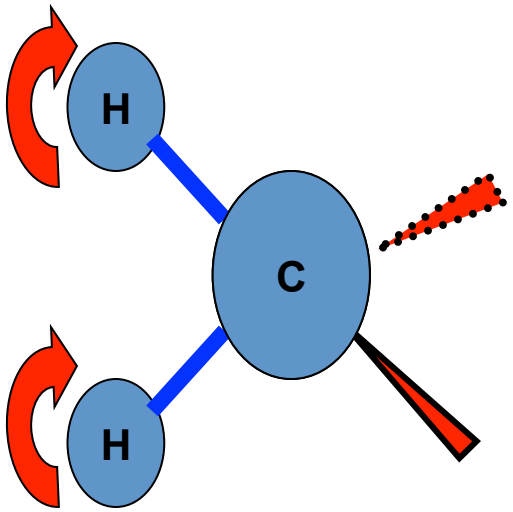




ii. Rocking:

- Movement of atoms take place in the same direction.

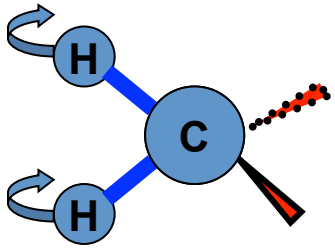




b) Out plane bending

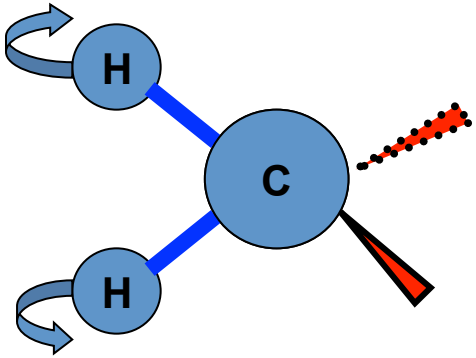
i. Wagging:

- 2 atoms move to one side of the plane. They move up and down the plane.



ii. Twisting:

- One atom moves above the plane and another atom moves below the plane.

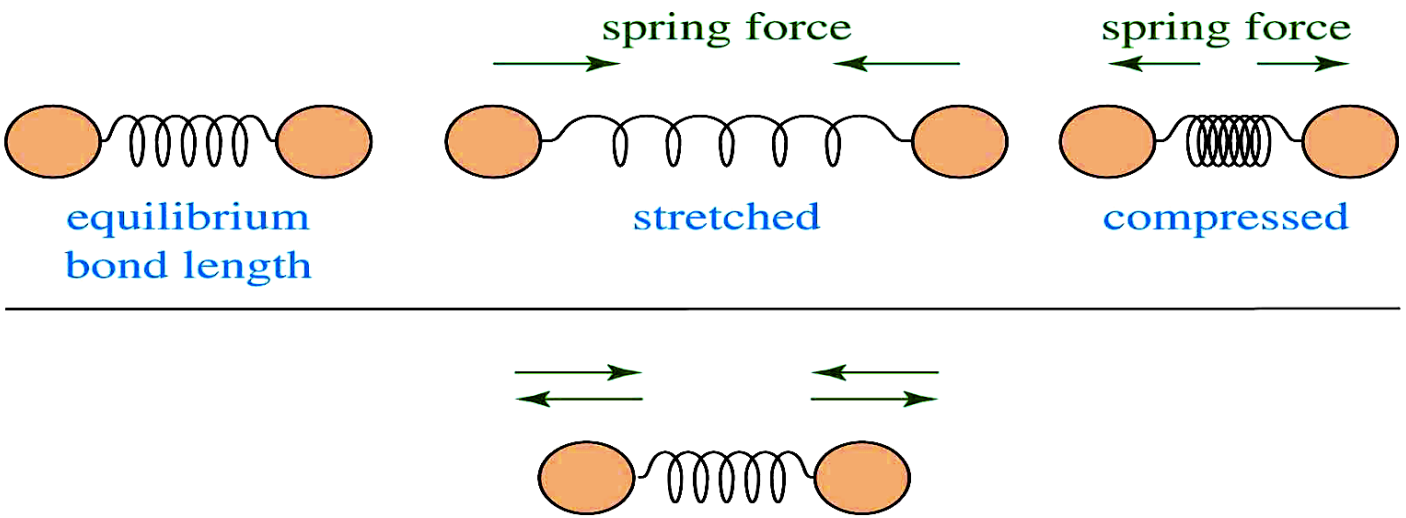


VIBRATIONAL MODES

- Infrared radiation induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two atoms.

- Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.

Specific bonds respond to (absorb) **specific** frequencies



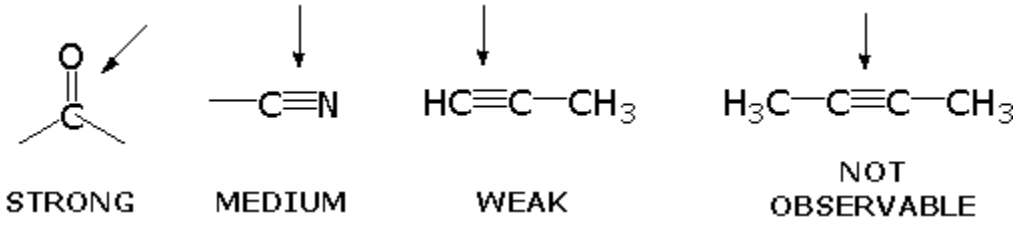
Types of IR Absorptions

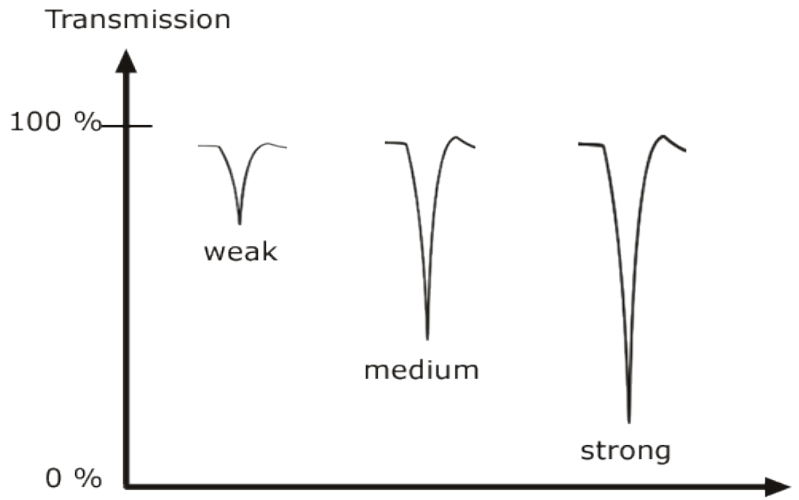
IR absorption occurs from the stretching and bending of the covalent bonds in molecules To be accompanied by IR absorption a stretch or bend must change the dipole moment of the molecule Molecules with symmetric bonds such as N_2, O_2, or F_2 do not absorb in the infrared since bond stretching does not change the dipole moment of the molecule

INFRARED ACTIVE BONDS

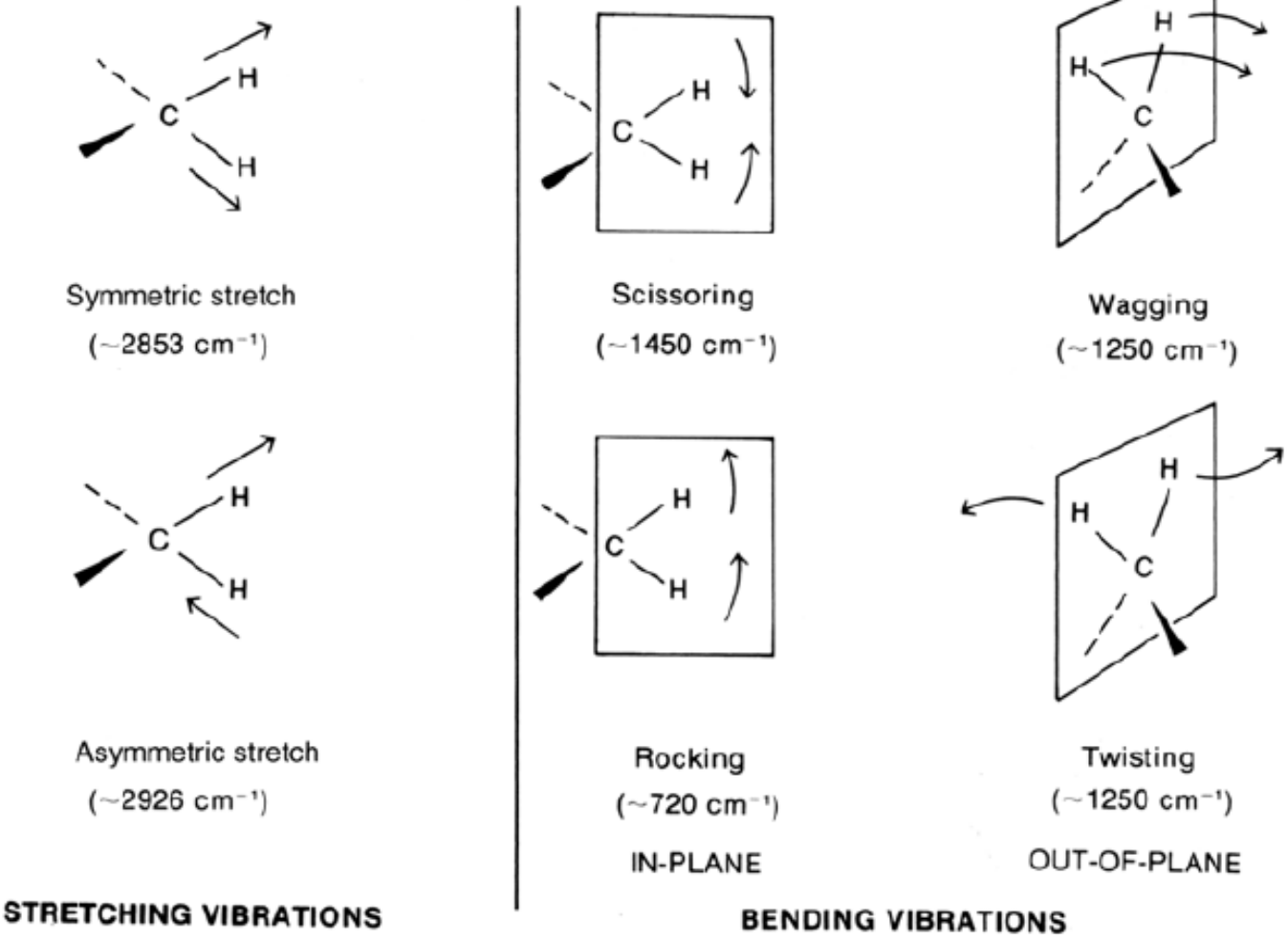
Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active**.

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.





The two primary modes of vibration are *stretching* and *bending* Stretching modes are typically of higher energy than bending modes Stretching modes are often divided into two a symmetric and asymmetric stretch; the asymmetric stretch is usually of higher energy



- Stretching frequencies are higher than bending frequencies
  (it is easier to bend a bond than stretching or compressing them)
- Bond involving Hydrogen are higher in freq. than with heavier atoms
- **The energy of the stretch <u>decreases</u> as the mass of the atoms is <u>increased</u>**
- Triple bond have higher freq than double bond which has higher frequency than single bond **$sp > sp^2 > sp^3$**

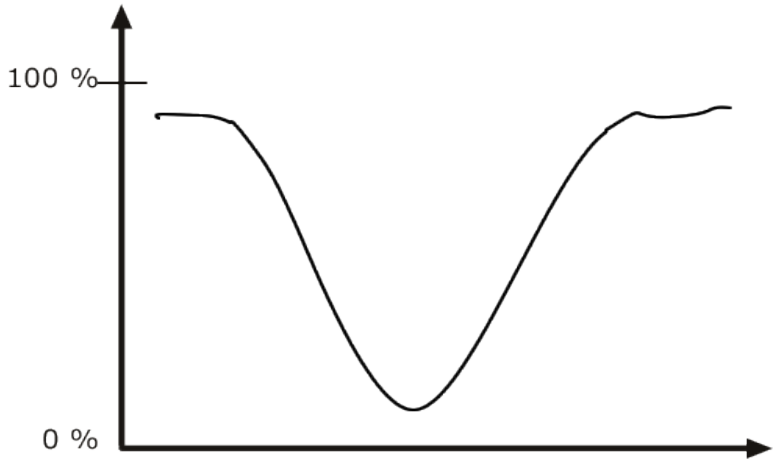
C-H	3000 cm^{-1}
C-C	1200 cm^{-1}
C-O	1100 cm^{-1}
C-Cl	750 cm^{-1}
C-I	500 cm^{-1}

C-H sp	3300 cm^{-1}
C-H sp^2	3100 cm^{-1}
C-H sp^3	2900 cm^{-1}

Infrared Band Shapes

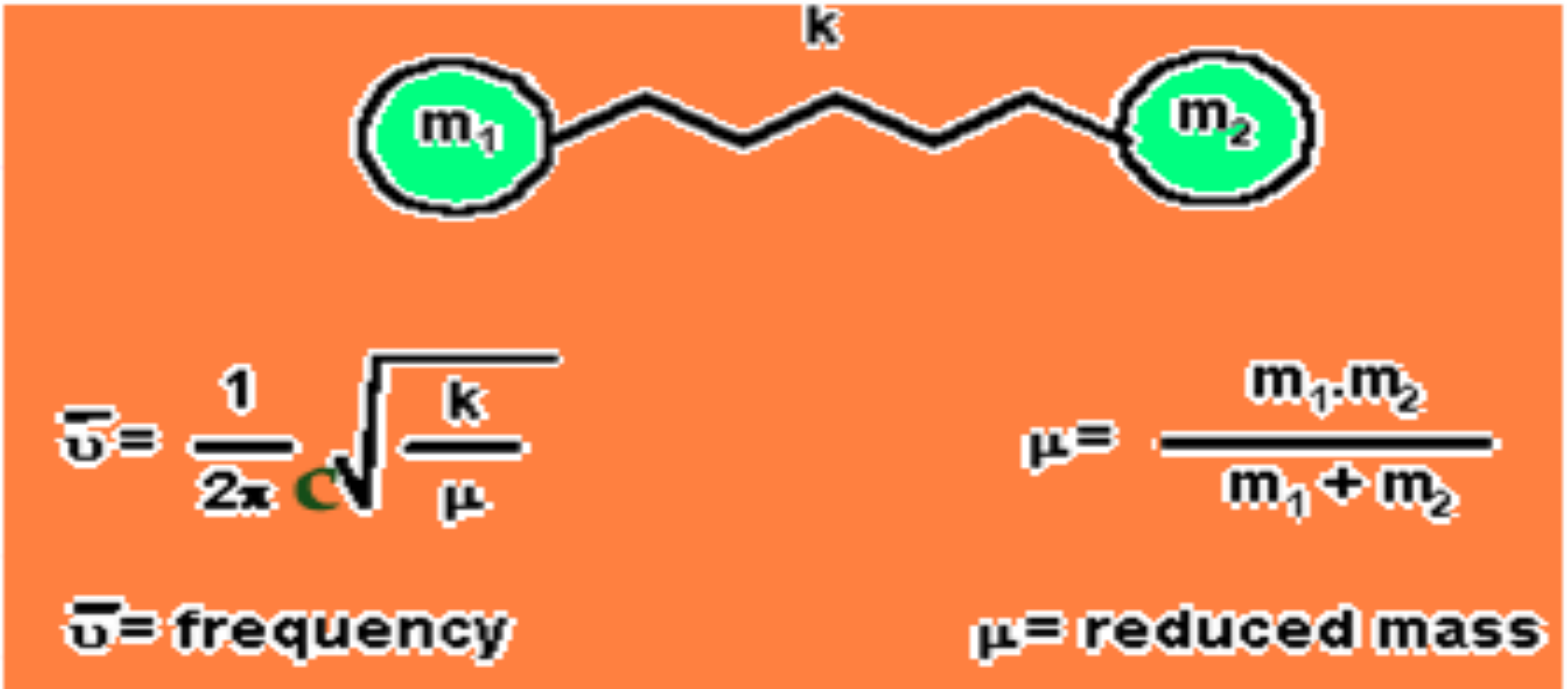
Infrared band shapes come in various forms. Two of the most common are **narrow** and **broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



Vibrational Frequency

- The value of stretching vibrational frequency of bond can be calculated by using Hooke's law.
- Hooke's law states that the vibrational frequency of a bond is directly proportional to the bond strength and inversely proportional to the masses at the ends of the bond.



Vibrational frequency or wave number depend upon following:

1. BOND STRENGTH

The frequency of vibration will be directly proportional to

strength of bond (K).

E.g.- Stretching vibration of triple bond will appear at high frequency than that of either a double or single bond

	C≡C	C=C	C-C
Frequency=	2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

2. MASS : Vibrational frequency is inversely proportional to the masses at the ends of the bond.

C-H	C-C	C-O	C-Cl	C-Br	C-I	
3000	1200	1100	750	600	500	Cm^{-1}

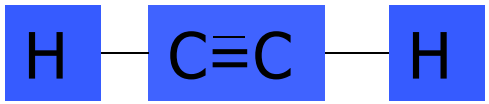
3. Hybridization:

- Hybridization affects the bond strength or force constant(K).
- Bonds are stronger in order :

SP > SP^2 > sp^3

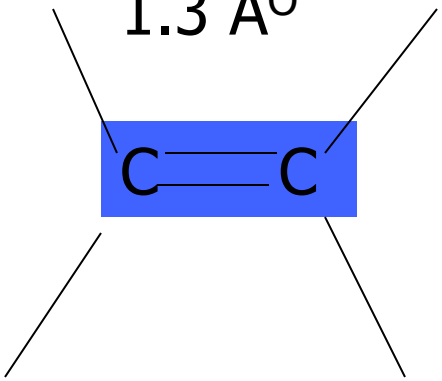
3300 CM^{-1}

1.20 A^O



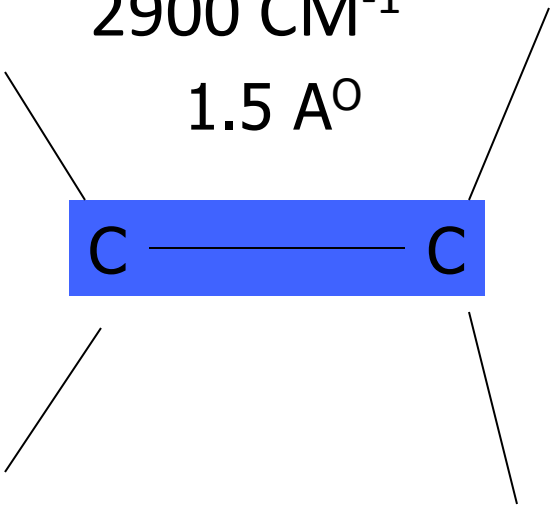
3100 CM^{-1}

1.3 A^O



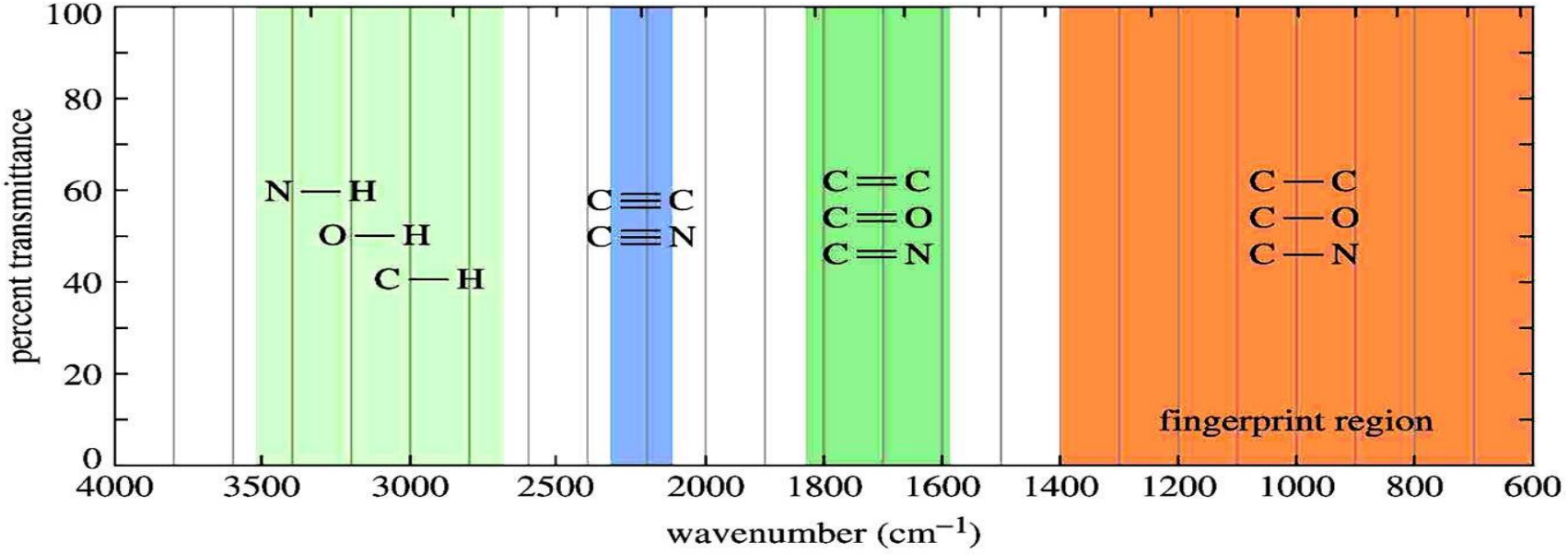
2900 CM^{-1}

1.5 A^O



IR Absorption Range

The typical IR absorption range for covalent bonds is **600 - 4000 cm^{-1}**. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around 2200-2400 cm^{-1} would indicate the possible presence of a C-N or a C-C triple bond.



Important IR Peaks

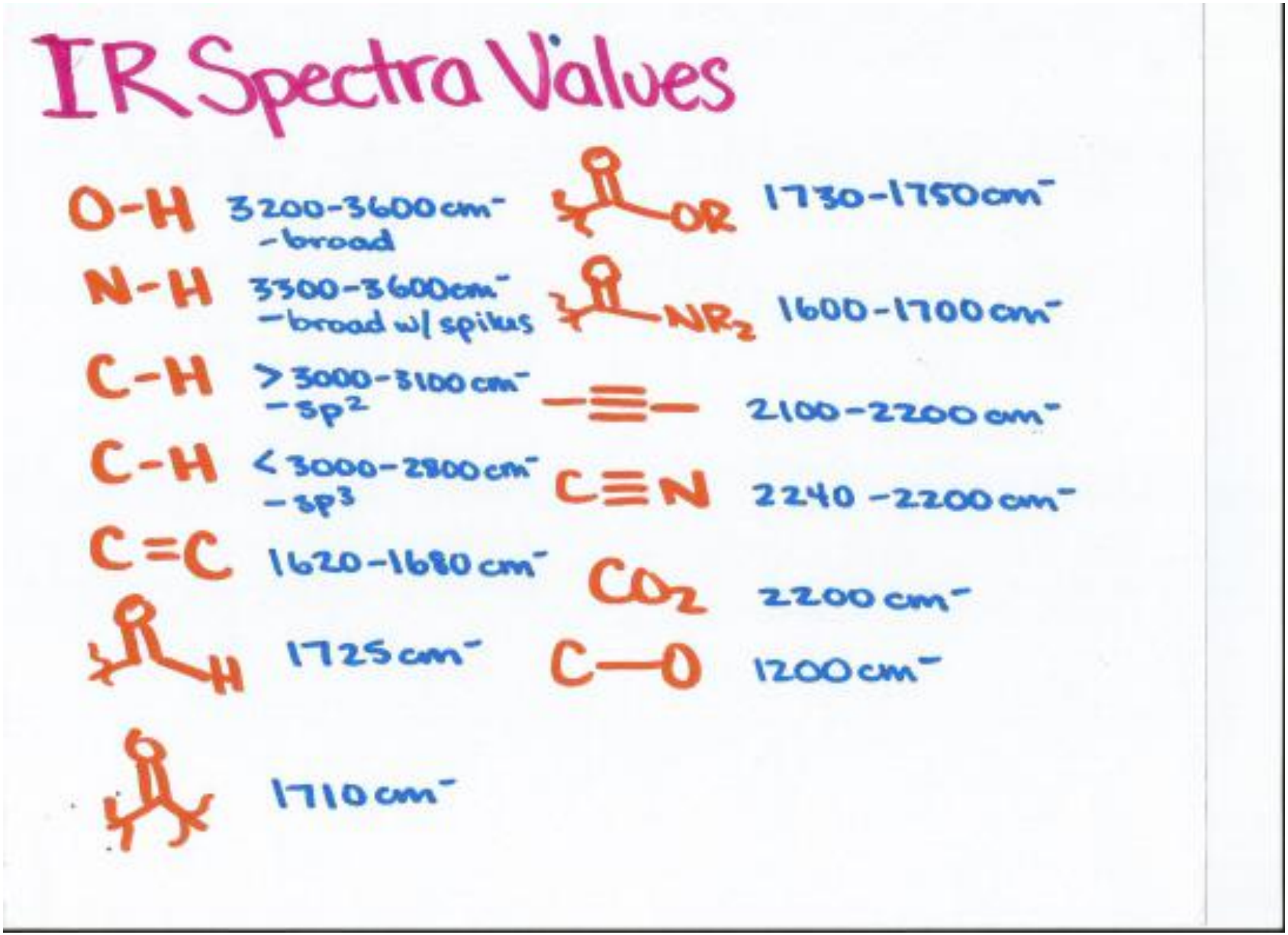
IR Absorptions of Common Functional Groups		
Functional Group	***Absorption Location (cm^{-1})***	***Absorption Intensity***
Alkane (C–H)	2,850–2,975	Medium to strong
Alcohol (O–H)	3,400–3,700	Strong, broad
Alkene (C=C) (C=C–H)	1,640–1,680 3,020–3,100	Weak to medium Medium
Alkyne (C≡C) (C≡C–H)	 2,100–2,250 3,300	 Medium Strong
Nitrile (C≡N)	2,200–2,250	Medium
Aromatics	1,650–2,000	Weak
Amines (N–H)	3,300–3,350	Medium
Carbonyls (C=O) Aldehyde (CHO) Ketone (RCOR) Ester (RCOOR) Acid (RCOOH)	 1,720–1,740 1,715 1,735–1,750 1,700–1,725	Strong

Important IR Peaks

Functional Group	*Characteristic Absorption(s)* (cm^{-1})
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)

s=strong, m=medium, w=weak, v=variable.

Important IR Peaks



1) Absorptions of Alkanes

C-H stretch occurs at 3000 – 2840 cm^{-1}

CH_2 bending modes at 1465 cm^{-1}

CH_3 bending absorption at 1375 cm^{-1}

CH_2 (four or more CH_2 groups) rocking at 720 cm^{-1}

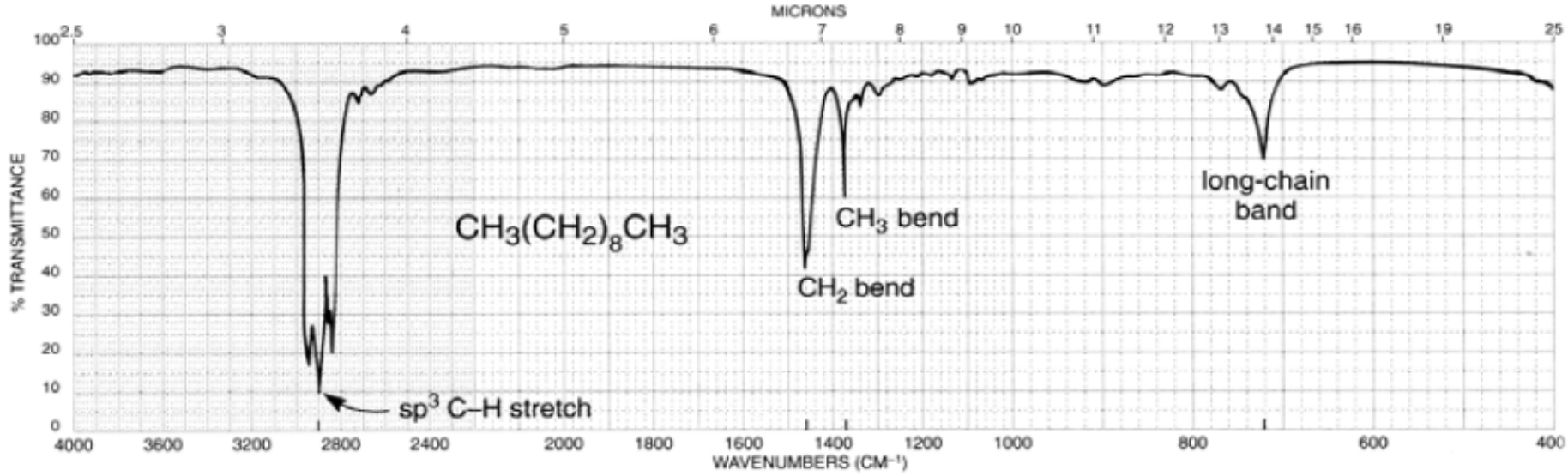


FIGURE 2.7 The infrared spectrum of decane (neat liquid, KBr plates).

2) Absorptions in Alkenes

- C-H stretch occurs in region of 3095 – 3010 cm^{-1}
- C=C stretch occurs in region of 1680 – 1620 cm^{-1}
- C-H out of plane bending (oop) absorbs at 1000 – 650 cm^{-1}

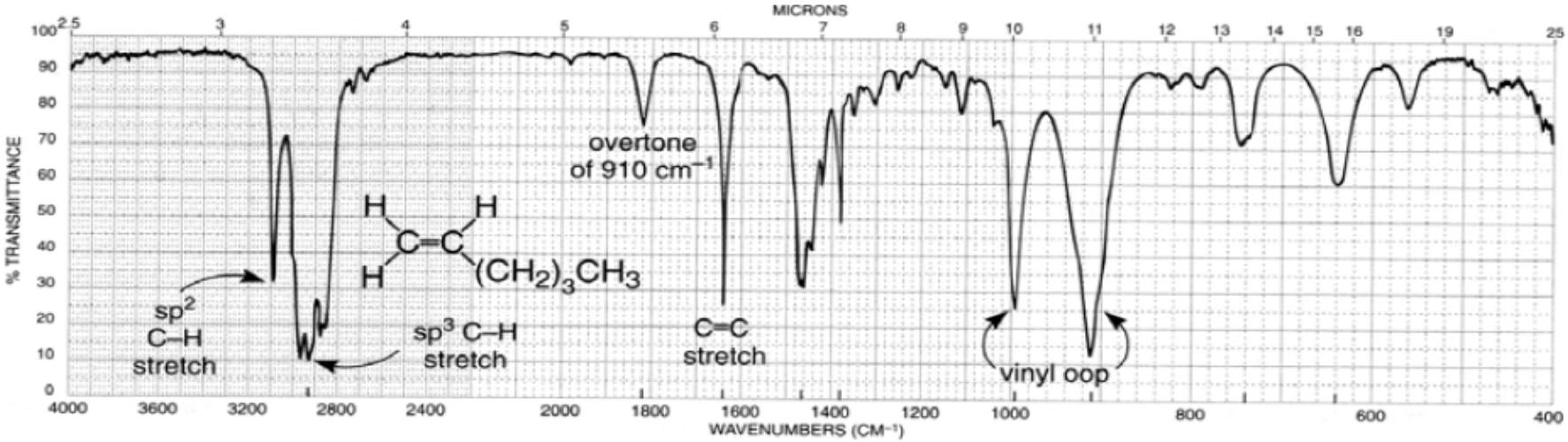


FIGURE 2.10 The infrared spectrum of 1-hexene (neat liquid, KBr plates).

2) Absorptions in Alkenes

C-H stretch occurs in region of 3095 – 3010 cm^{-1}

(note higher wavenumber relative to alkanes)

C=C stretch occurs in region of 1670 – 1640 cm^{-1}

Can be used to determine type of substitution:

Symmetrically substituted does not absorb at all

A cis isomer absorbs more strongly than a trans isomer

(cis is less symmetrical than trans)

Simple monosubstituted absorbs at 1640 cm^{-1}

Simple 1,1-disubstituted absorbs at 1650 cm^{-1}

2) Absorptions in Alkenes

C-H out of plane bending (oop) absorbs at 1000 – 650 cm^{-1}

Often very strong absorptions

Can be used to determine type of substitution:

Monosubstituted gives two peaks near 990 and 910 cm^{-1}

1,2-disubstituted (cis) gives one strong band near 700 cm^{-1}

1,2-disubstitued (trans) gives on band near 970 cm^{-1}

1,1-disubstituted gives one strong band near 890 cm^{-1}

A trisubstituted double bond absorbs near 815 cm^{-1}

A tetrasubstituted double bond does not absorb at all

2) Absorptions in Alkenes

A monosubstituted alkene gives two strong peaks near 990 and 910 cm^{-1}

2) Absorptions in Alkenes

A cis 1,2-disibstiuted alkene gives one strong band near 700 cm^{-1}

Note that the C=C stretch is much less intense than for the mono substituted example

2) Absorptions in Alkenes

The strength of the C=C stretch can serve to differentiate between cis and trans isomers

The cis isomer – more intense C=C stretch Note the single large peak at 700 cm^{-1} (indicates cis isomer)

2) Absorptions in Alkenes

The trans isomer – less intense C=C stretch Note the band near 970 cm^{-1} (indicates trans isomer)

3) Absorptions in Alkynes

- **C-H stretching frequency is approximately 3300 cm^{-1}**

(still higher than for alkanes or alkenes)

- **C-C stretch occurs at approximately 2100-2260 cm^{-1}**

(but not observed if alkyne is symmetric)

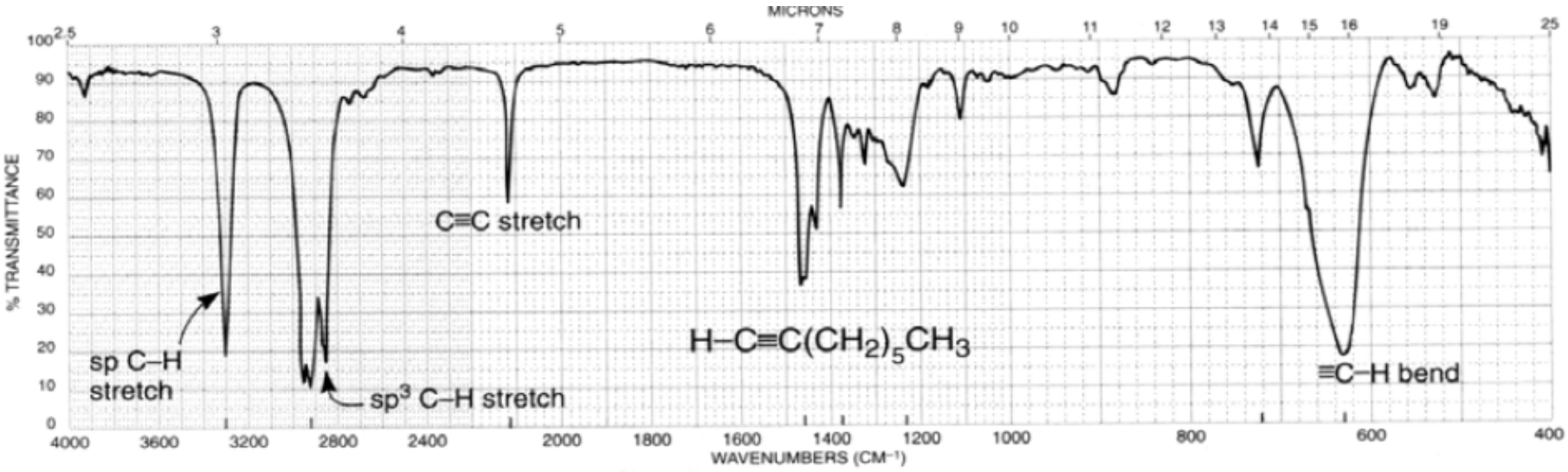


FIGURE 2.14 The infrared spectrum of 1-octyne (neat liquid, KBr plates).

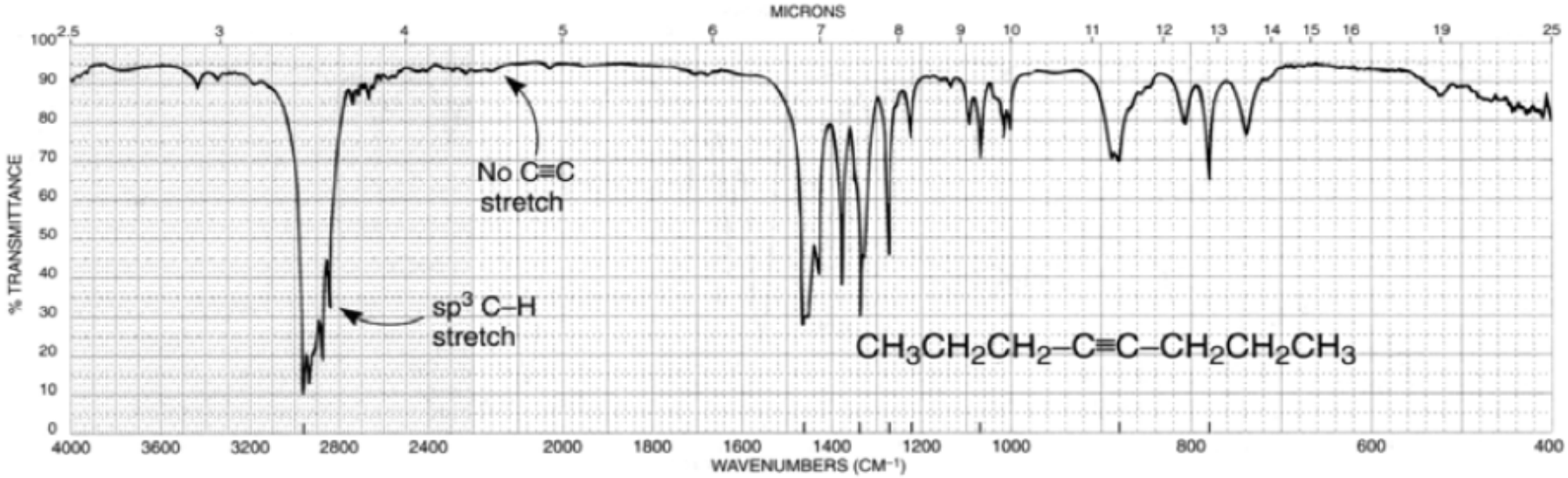


FIGURE 2.15 The infrared spectrum of 4-octyne (neat liquid, KBr plates).

4) Absorptions in Aromatic Compounds

- C-H stretch occurs between 3050 and 3010 cm^{-1}
- C=C stretching often occurs in pairs at 1600 cm-1 and 1475 cm^{-1}
- Overtone and combination bands occur between 2000 and 1667 cm-1

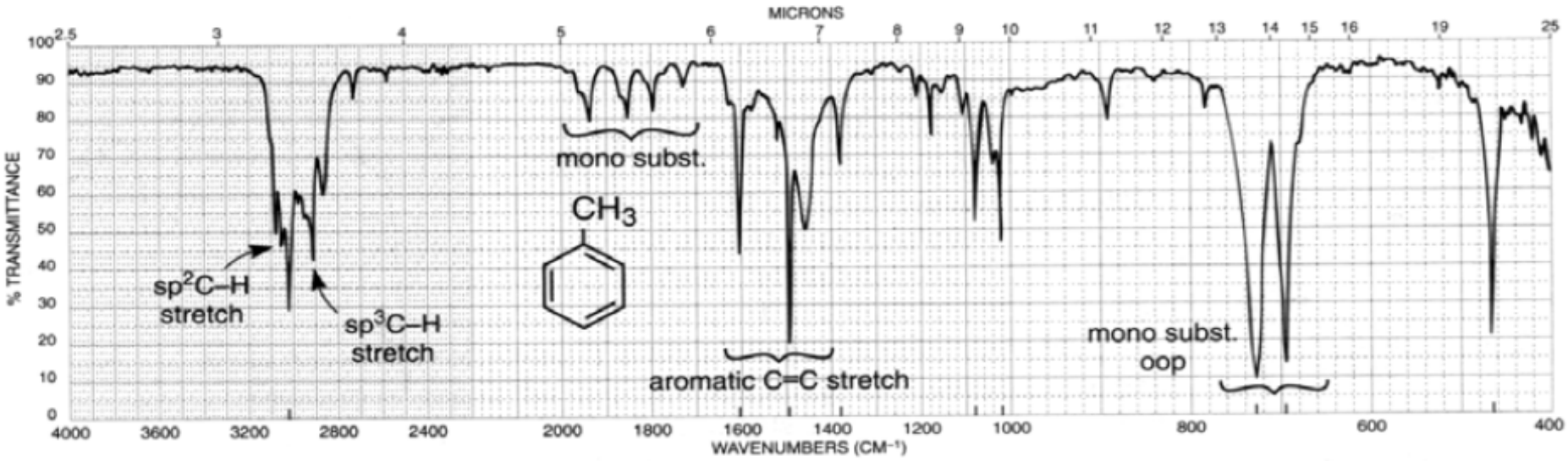


FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

Monosubstituted rings give strong absorptions at 690 cm^{-1} and 750 cm^{-1} (second may be masked by hydrocarbon solvent)

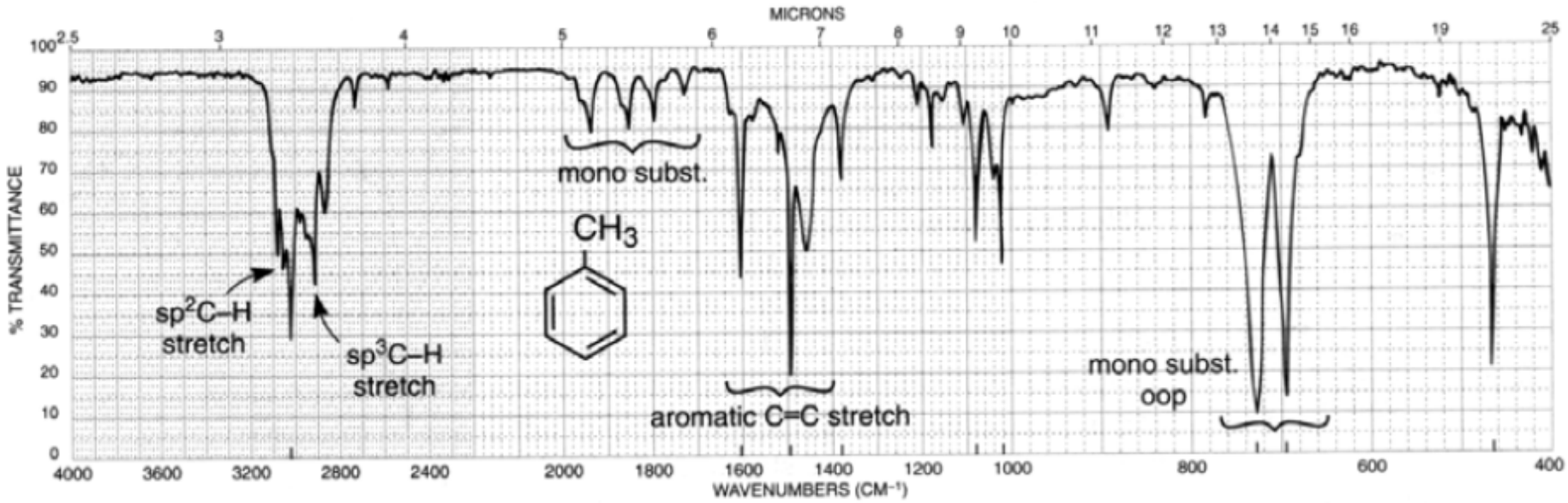


FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

***Ortho* substituted rings** give one strong band at 750 cm^{-1}

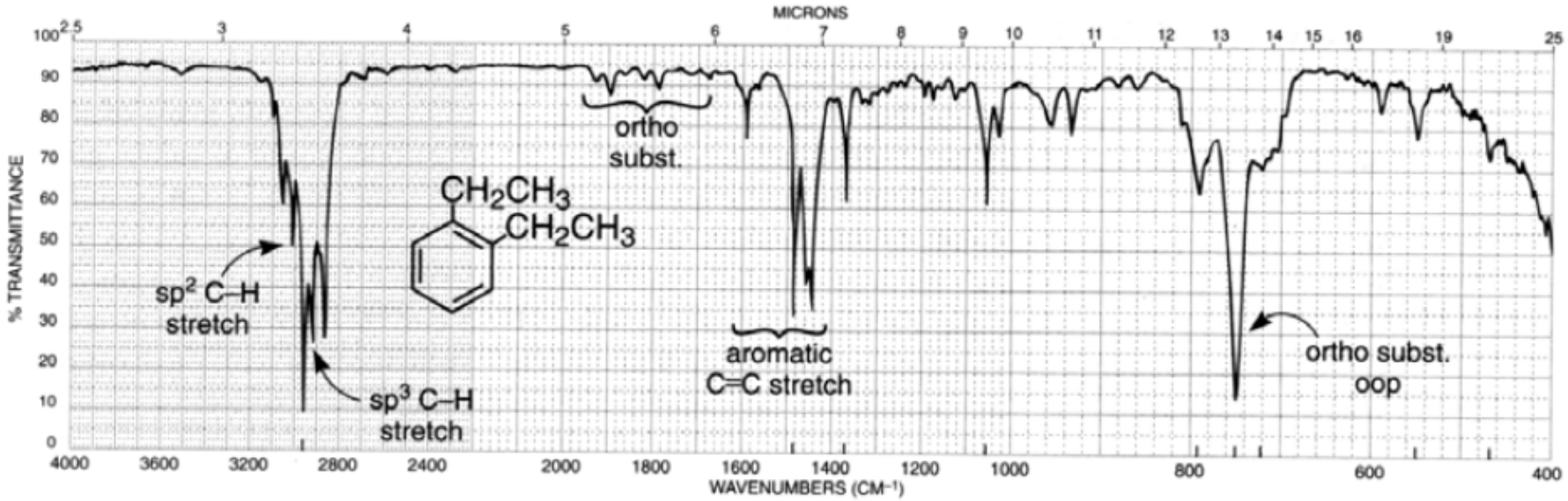


FIGURE 2.24 The infrared spectrum of *ortho*-diethylbenzene (neat liquid, KBr plates).

***Meta* substituted** rings gives bands at 690 cm^{-1}, 780 cm^{-1}, and sometimes a third band of medium intensity at 880 cm^{-1}

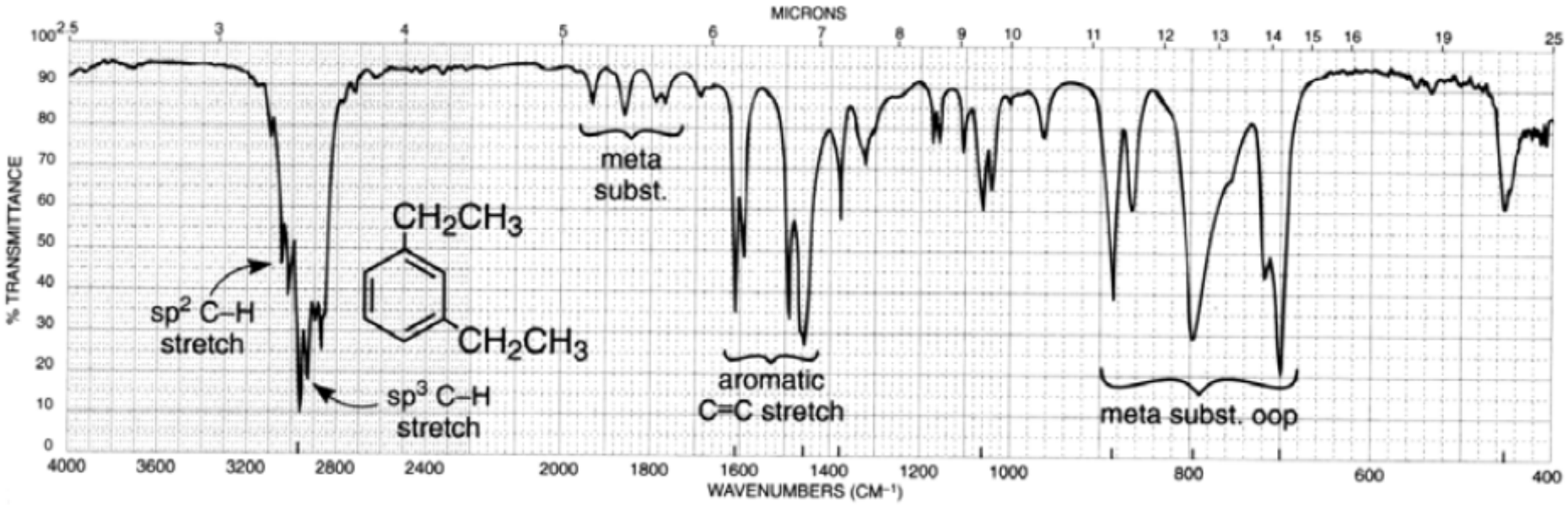


FIGURE 2.25 The infrared spectrum of *meta*-diethylbenzene (neat liquid, KBr plates).

Para substituted rings give one band from **800 to 850** cm^{-1}

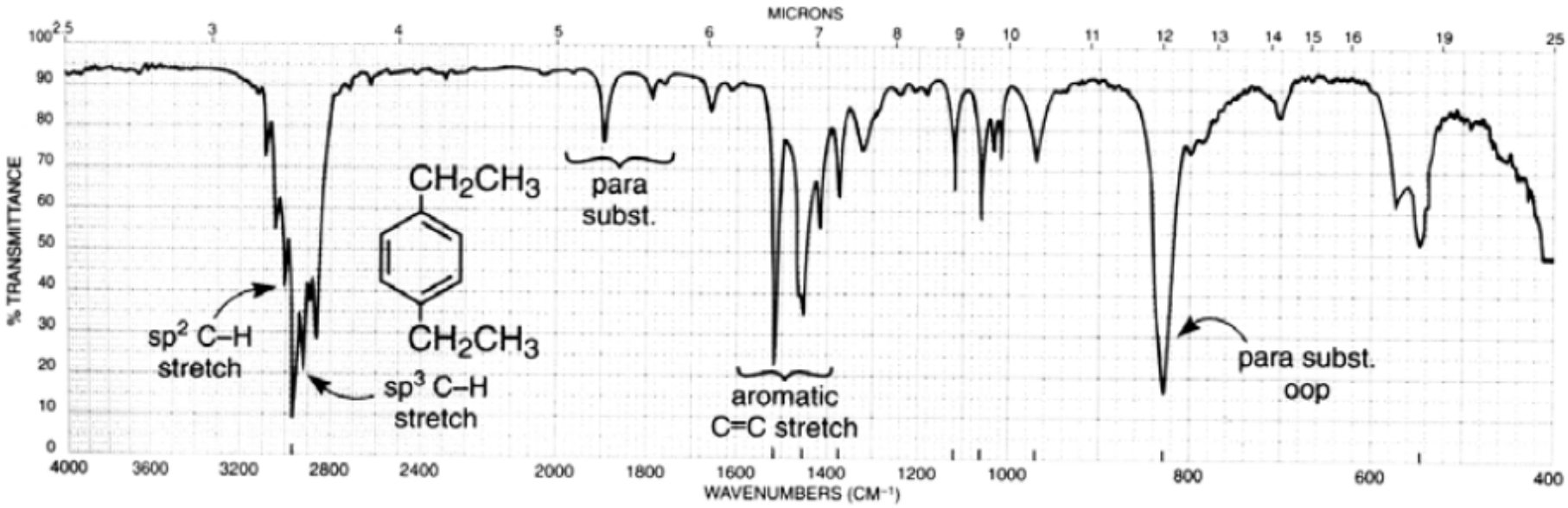


FIGURE 2.26 The infrared spectrum of *para*-diethylbenzene (neat liquid, KBr plates).

5) Alcohols and Phenols

- **Hydrogen-bonded O-H stretching occurs as a very broad and intense peak at 3400-3300 cm-1**
- **C-O stretching occurs in range 1260 – 1000 cm^{-1}**

The position of the C-O stretch can be used to determine the type of alcohol
Phenols – 1220 cm^{-1}
Tertiary alcohols – 1150 cm^{-1}
Secondary alcohols – 1100 cm^{-1}
Primary alcohols – 1050 cm^{-1}

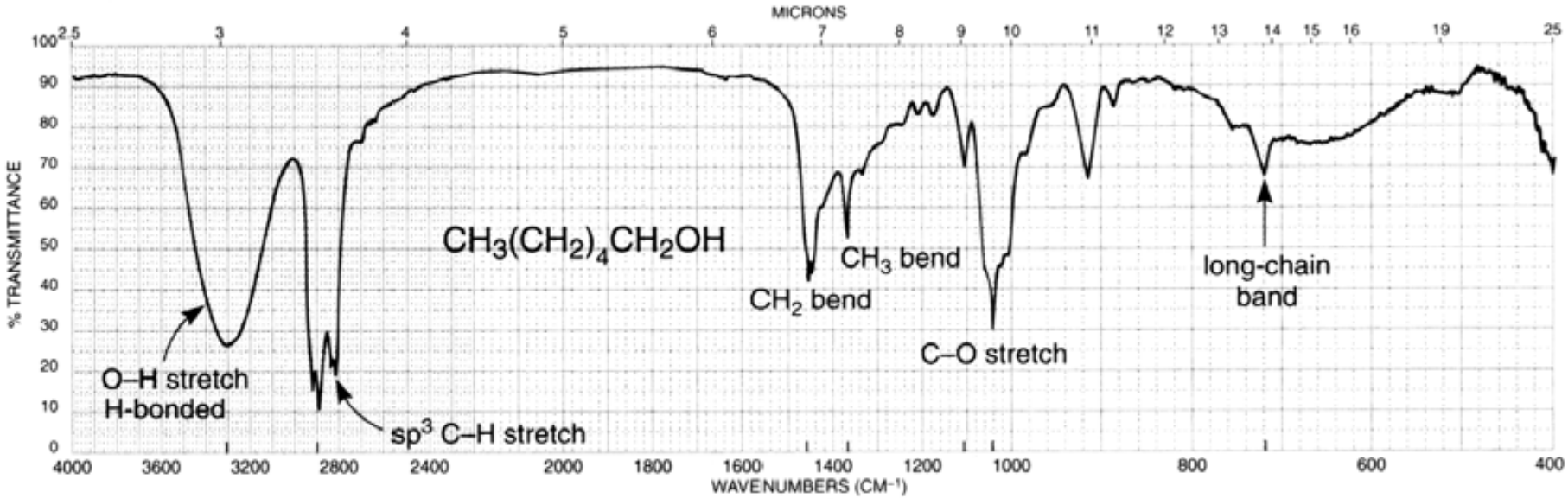


FIGURE 2.29 The infrared spectrum of 1-hexanol (neat liquid, KBr plates).

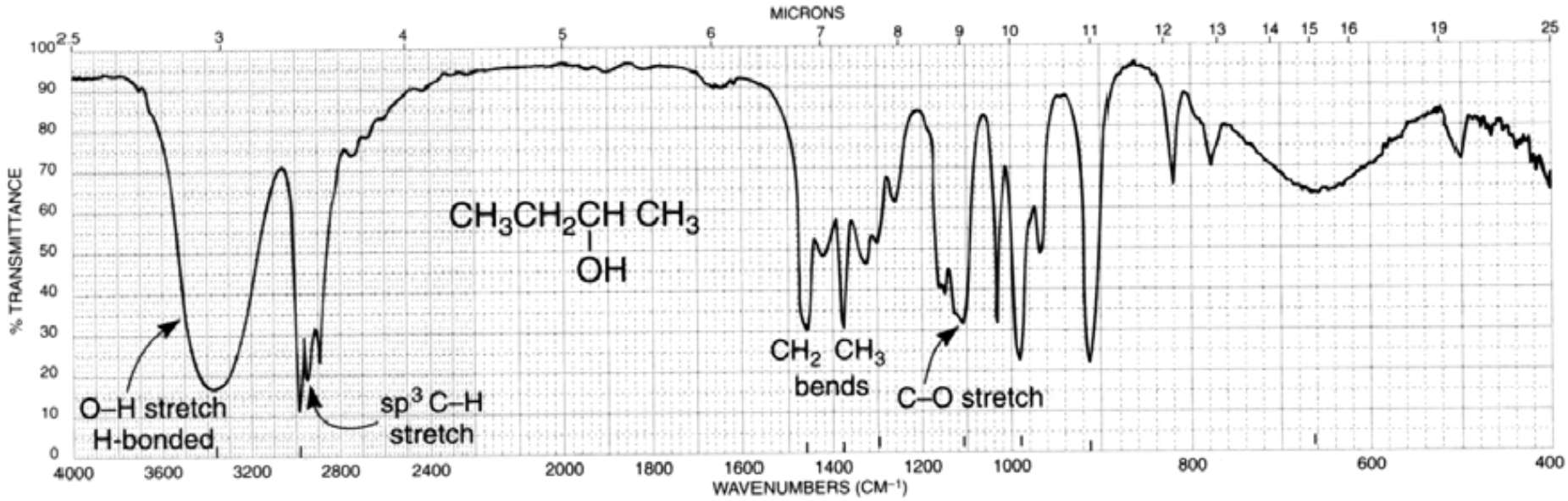


FIGURE 2.30 The infrared spectrum of 2-butanol (neat liquid, KBr plates).

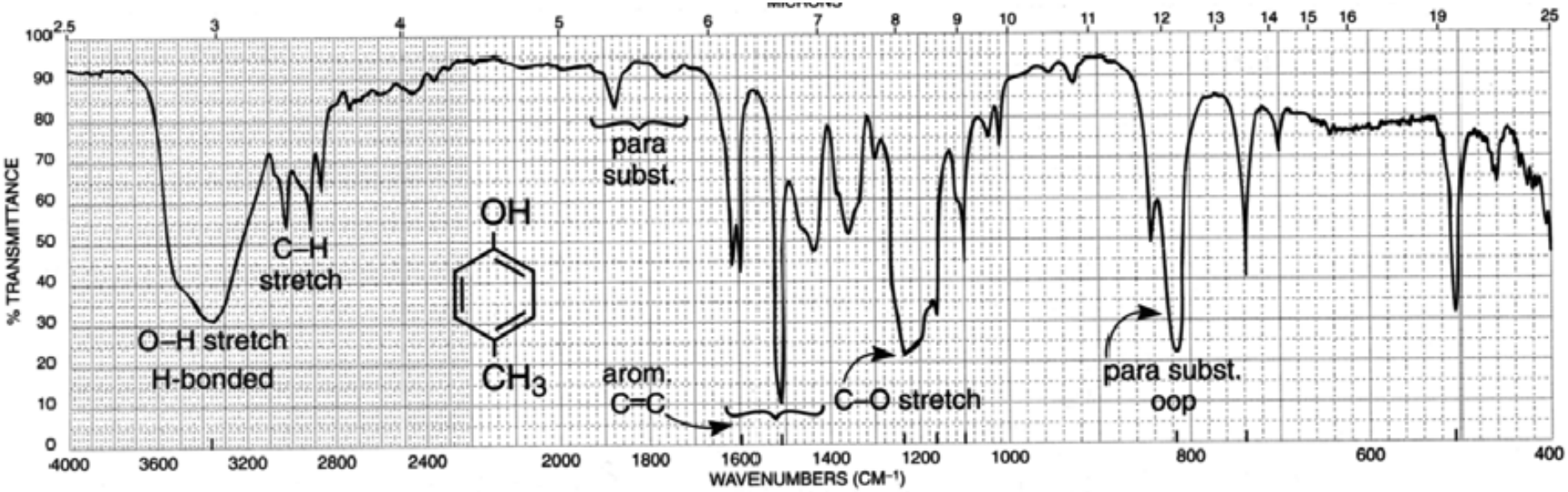


FIGURE 2.31 The infrared spectrum of *para*-cresol (neat liquid, KBr plates).

6) Aldehydes

Contains a C=O stretch at:

1740 – 1725 cm^{-1} for normal aliphatic aldehyde

1700 – 1680 cm^{-1} for conjugation with double bond

1700 – 1660 cm^{-1} for conjugation with phenyl group

The (CO)-H stretch occurs as a pair of weak bands at 2860 – 2800 cm^{-1} and 2760 – 2700 cm^{-1}; the higher-frequency bands are often masked by alkane C-H absorptions

Above band can help to differentiate between aldehydes and ketones as these both have a carbonyl group

1740 – 1725 cm^{-1} for normal aliphatic aldehyde

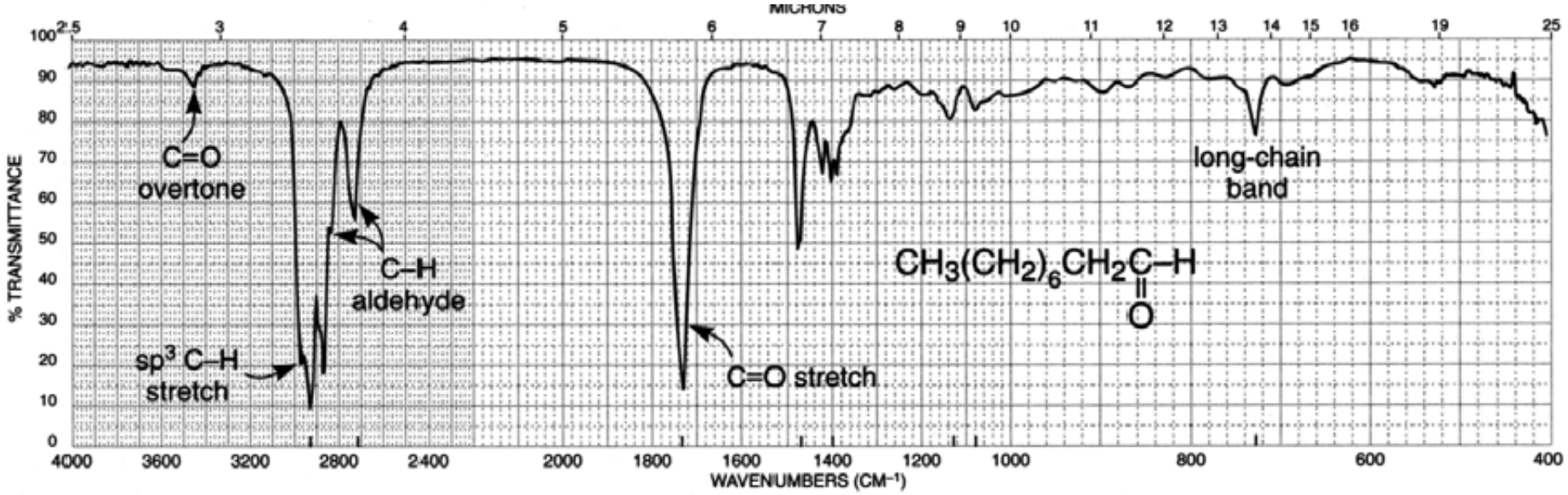


FIGURE 2.36 The infrared spectrum of nonanal (neat liquid, KBr plates).

1700 – 1680 cm^{-1} for conjugation with double bond

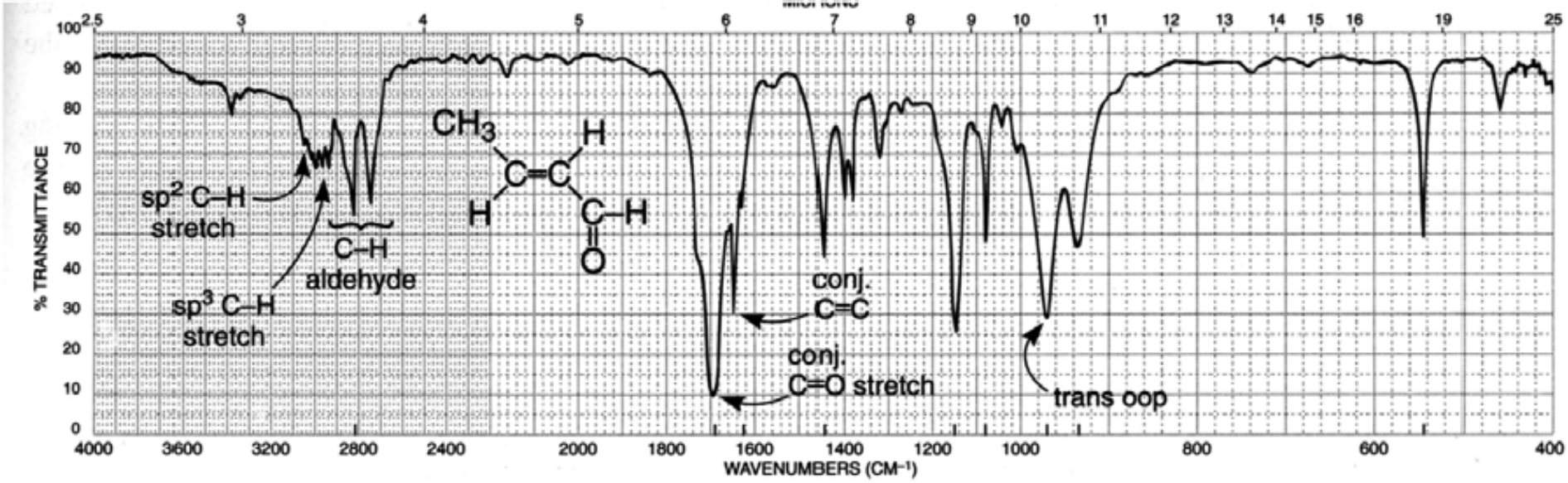


FIGURE 2.37 The infrared spectrum of crotonaldehyde (neat liquid, KBr plates).

1700 – 1660 cm^{-1} for conjugation with phenyl group

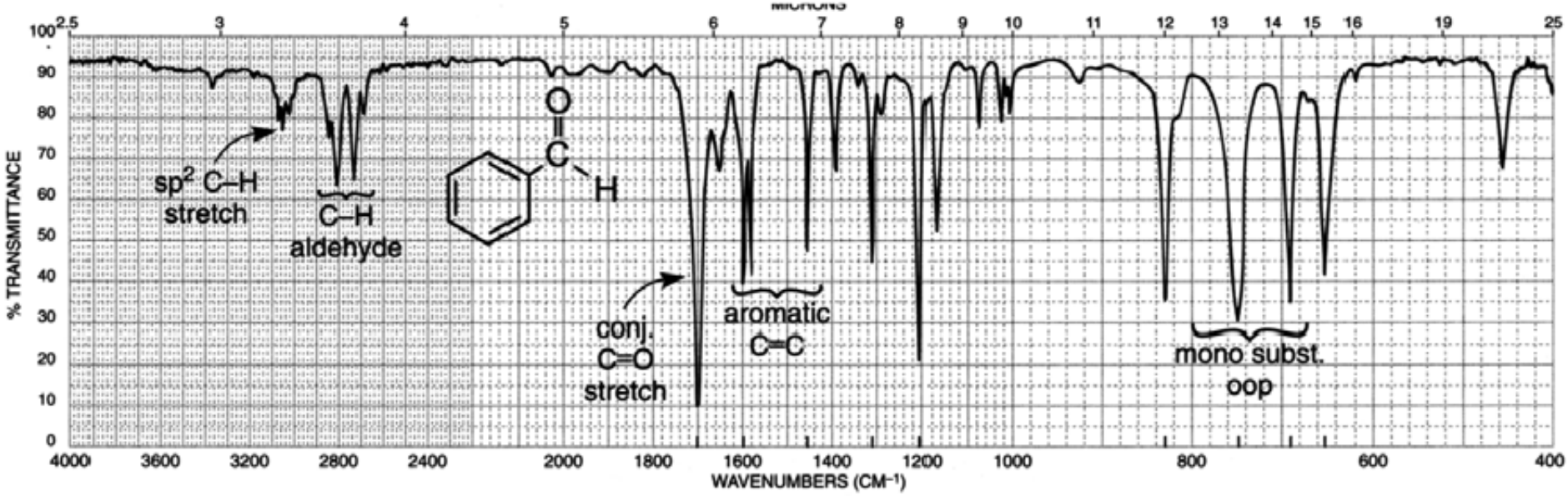
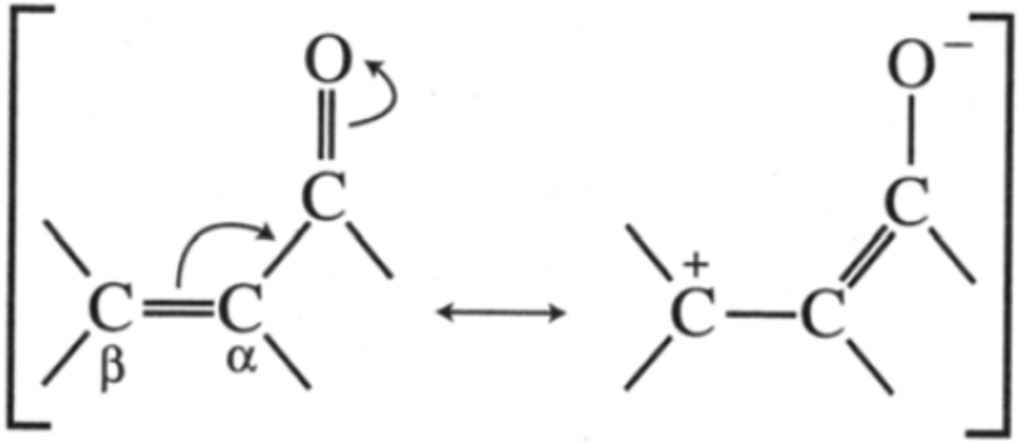


FIGURE 2.38 The infrared spectrum of benzaldehyde (neat liquid, KBr plates).

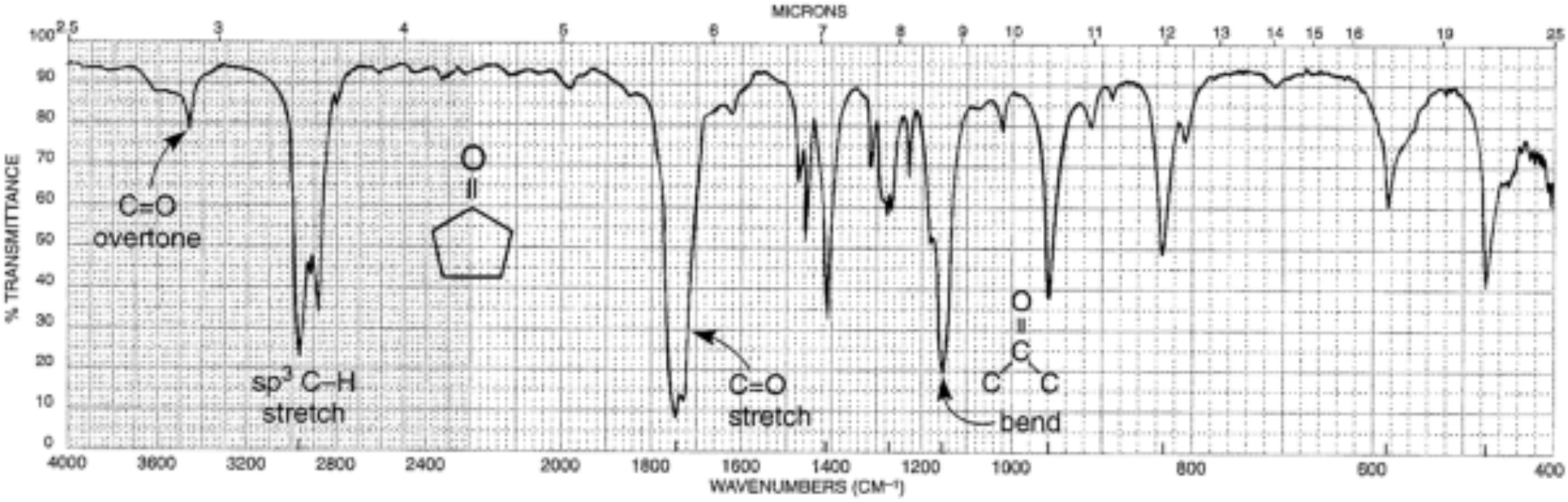
Conjugation decreases the C-O bond order and therefore decreases the stretching frequency



7) Ketones

Contains a C=O stretch at:
1720 – 1708 cm^{-1} for normal aliphatic **Ketones**

(slightly lower frequency than for aldehydes)


MICRONS
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
19
25
% TRANSMITTANCE
100
90
80
70
60
50
40
30
20
10
0
C=O
overtone
sp3 C–H
stretch
O
C=O
stretch
O
C
C
C
bend
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS (CM–1)

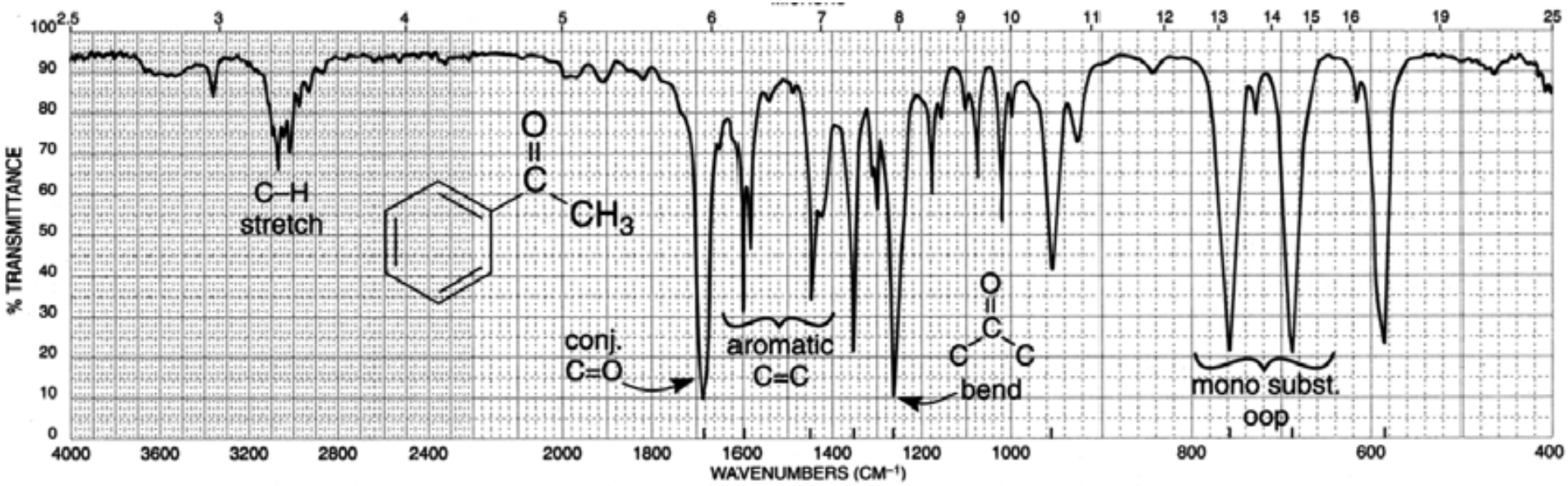
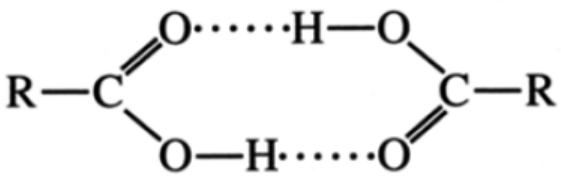


FIGURE 2.40 The infrared spectrum of acetophenone (neat liquid, KBr plates).

8) Carboxylic Acids

Carboxylic acids occur as hydrogen-bonded dimers unless in dilute solution



C=O stretch occurs in the following regions:

- 1730 – 1700 cm-1 for simple aliphatic acids in dimeric form Occurs at lower frequencies if conjugated with an alkene or aromatic
- O-H stretch occurs as a very broad peak at 3400 to 2400 cm^{-1}, may partially obscure C-H stretching bands
- C-O stretch of medium intensity observed at 1320 –1210 cm^{-1}

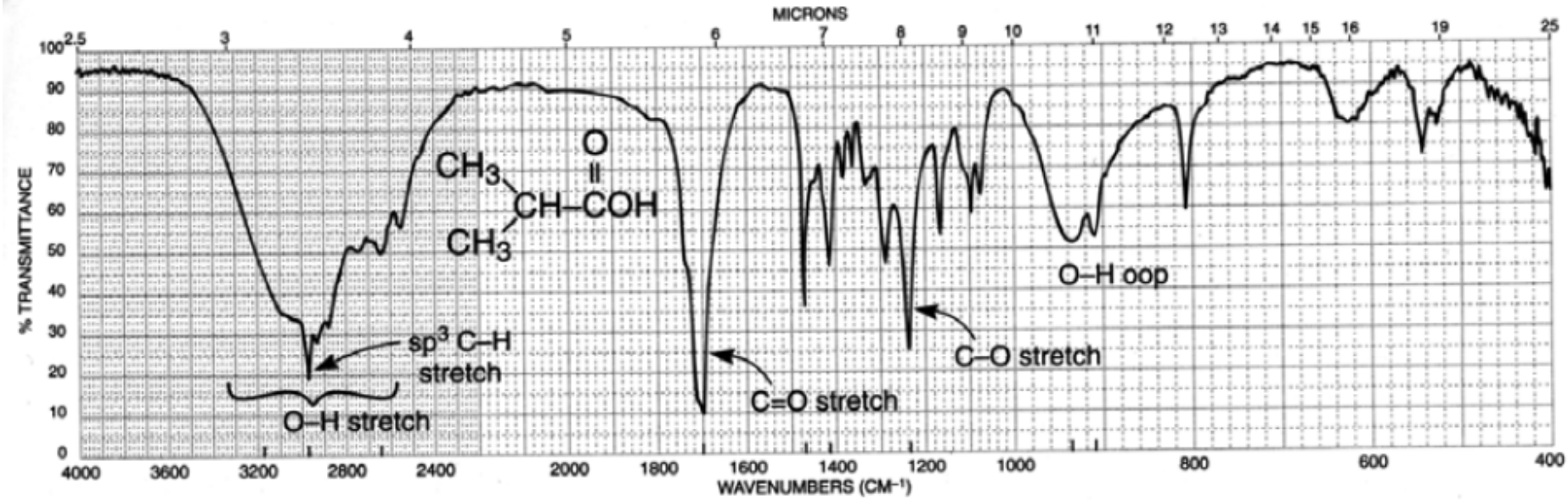


FIGURE 2.45 The infrared spectrum of isobutyric acid (neat liquid, KBr plates).

9) Esters

C=O stretch occurs at:

- 1750 – 1735 cm^{-1} for normal aliphatic esters

(example – ethyl butyrate, 1738 cm^{-1})

- 1740 – 1750 cm^{-1} if carbonyl carbon conjugated with an alkene

(example – methyl methacrylate, 1725 cm^{-1})

- 1740 – 1715 cm^{-1} if carbonyl carbon conjugated with aromatic

(example – methyl benzoate, 1724 cm^{-1})

- 1765 – 1762 cm^{-1} if oxygen atom conjugated with alkene or aromatic

(note that this is a shift to higher frequency)

(example – phenyl acetate, 1765 cm^{-1})

(example – vinyl acetate, 1762 cm^{-1})

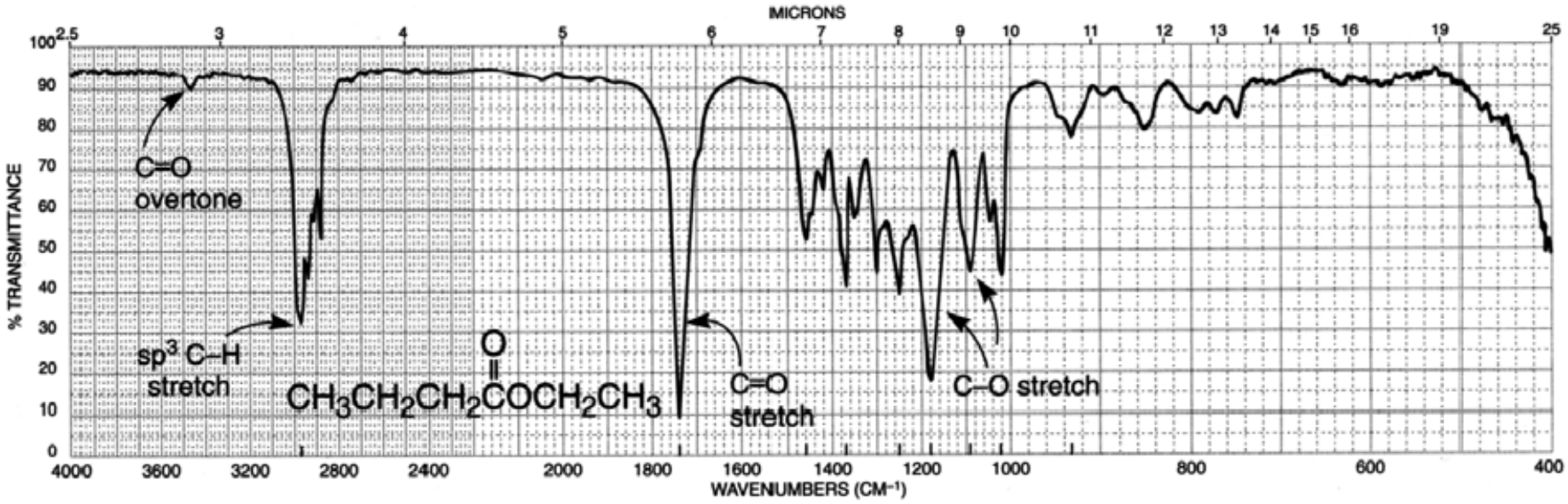


FIGURE 2.47 The infrared spectrum of ethyl butyrate (neat liquid, KBr plates).

- 1740 – 1750 cm^{-1} if carbonyl carbon conjugated with an alkene

(example – methyl methacrylate, 1725 cm^{-1})

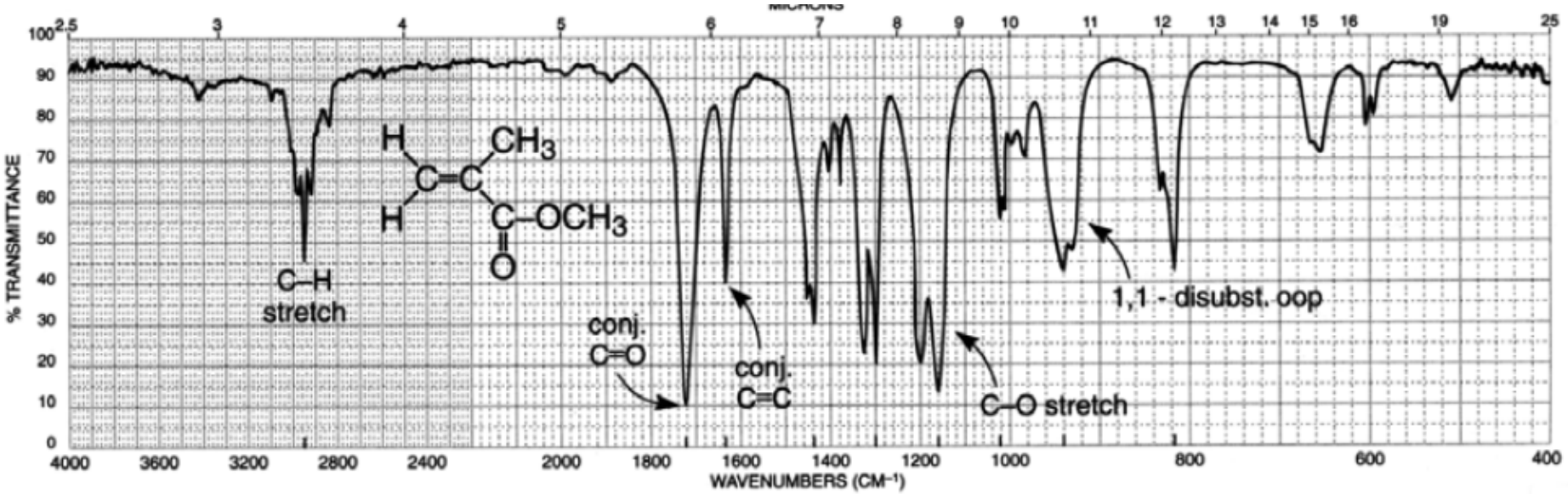


FIGURE 2.48 The infrared spectrum of methyl methacrylate (neat liquid, KBr plates).

- 1740 – 1715 cm^{-1} if carbonyl carbon conjugated with aromatic

(example – methyl benzoate, 1724 cm^{-1})

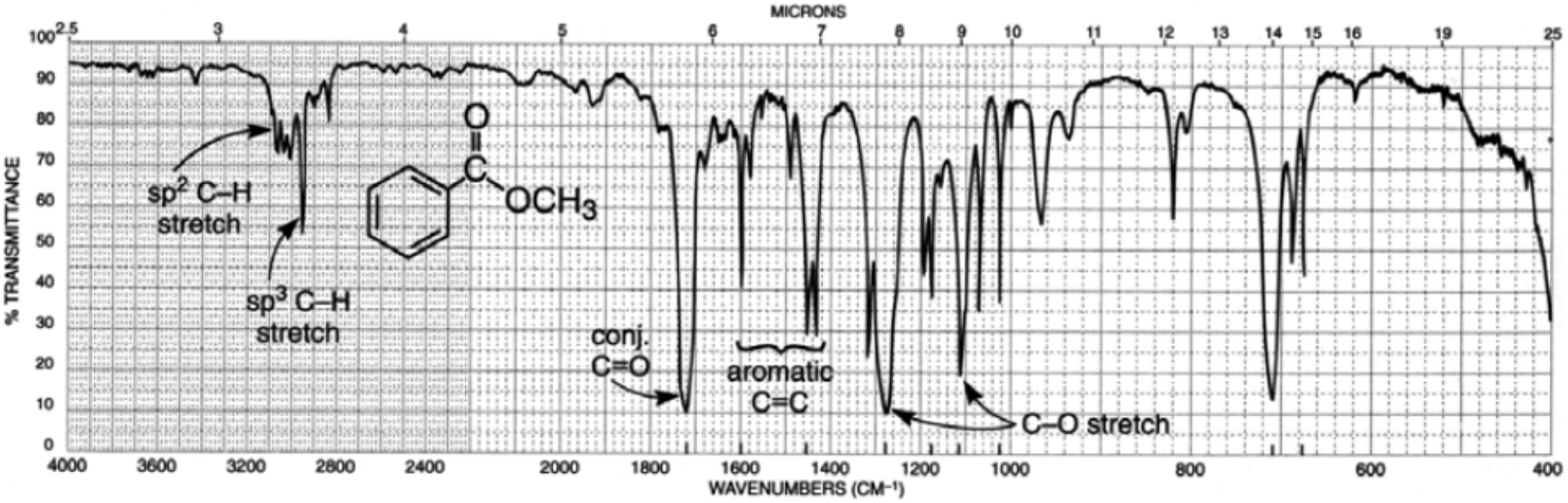


FIGURE 2.50 The infrared spectrum of methyl benzoate (neat liquid, KBr plates).

- 1765 – 1762 cm^{-1} if oxygen atom conjugated with alkene or aromatic (note that this is a shift to higher frequency)

(example – vinyl acetate, 1762 cm^{-1})

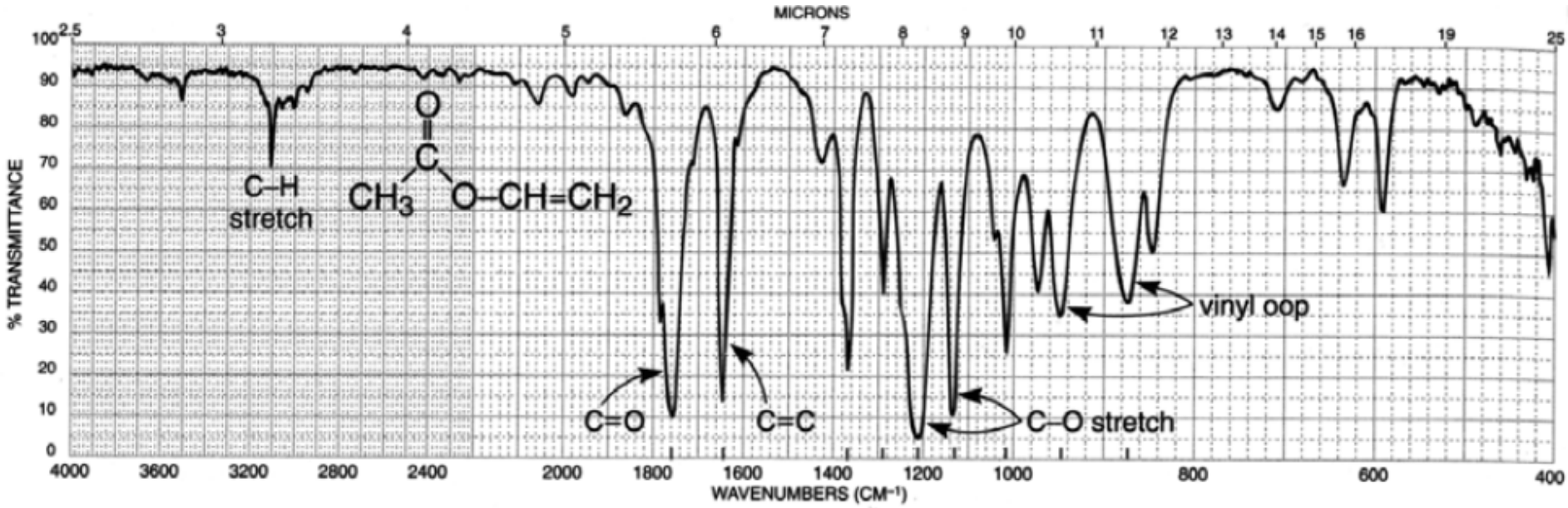


FIGURE 2.49 The infrared spectrum of vinyl acetate (neat liquid, KBr plates).

10) Amines

N-H stretch occurs at 3500 –3300 cm^{-1}

- **Primary amines** – two bands
- **Secondary amines** – one band; weak for aliphatic amines but stronger for aromatic
- **Tertiary amines** have no absorption in this region (no N-H bonds)

N-H out of plane bending occurs at 800 cm^{-1}

Butylamine – primary amine

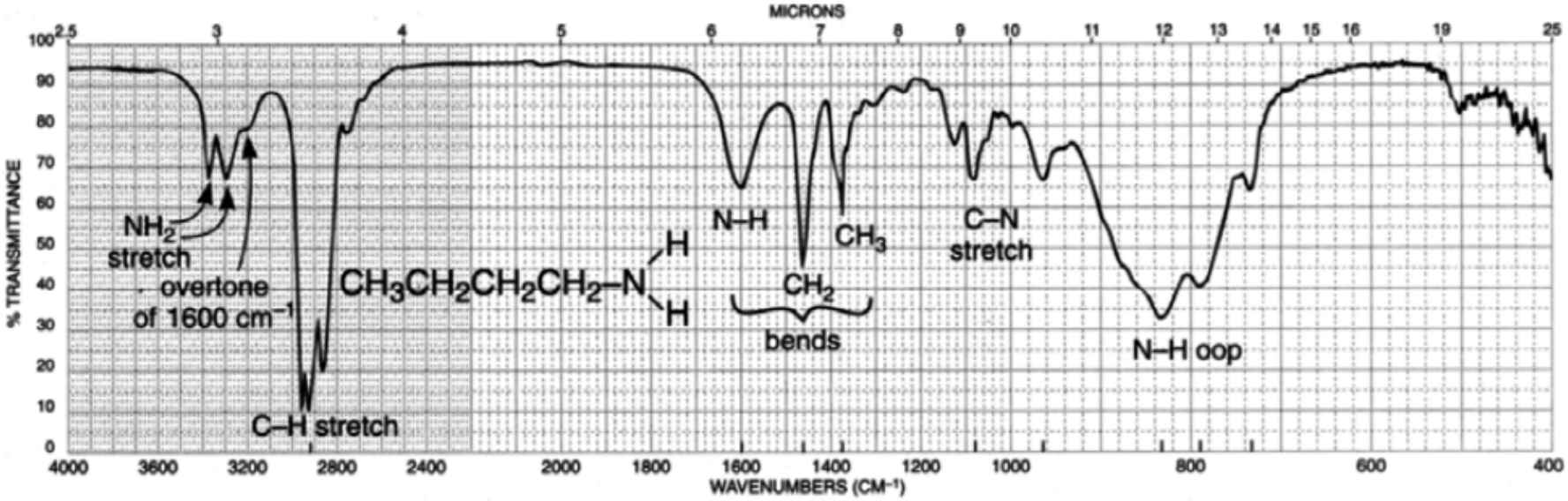


FIGURE 2.58 The infrared spectrum of butylamine (neat liquid, KBr plates).

Dibutyl amine – secondary amine

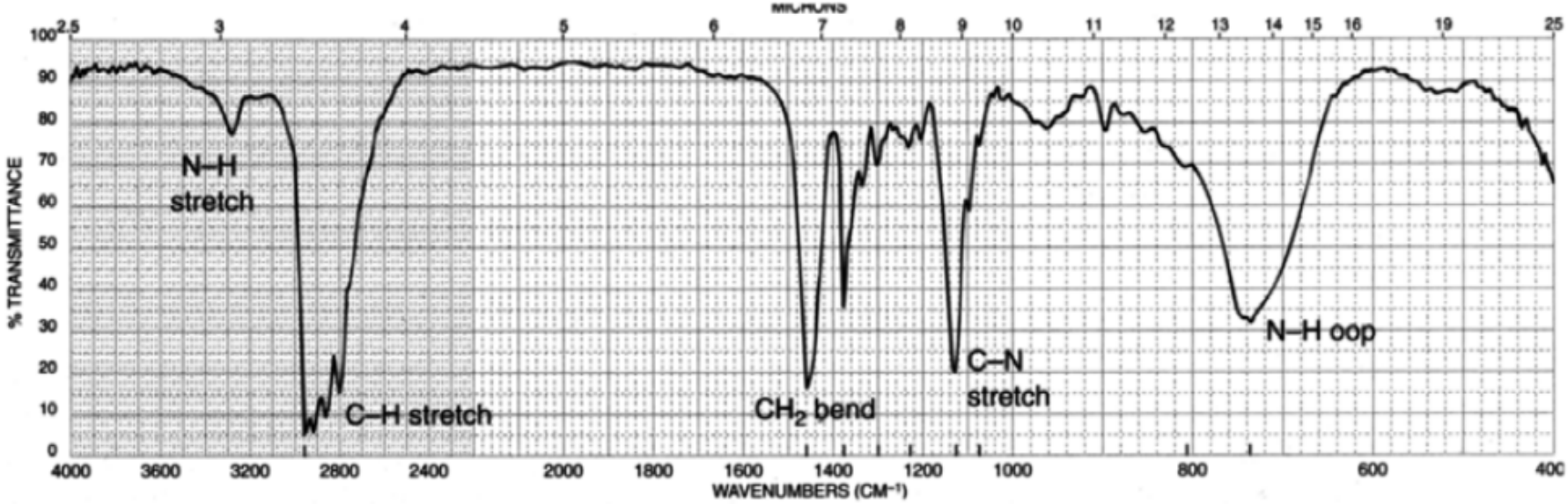
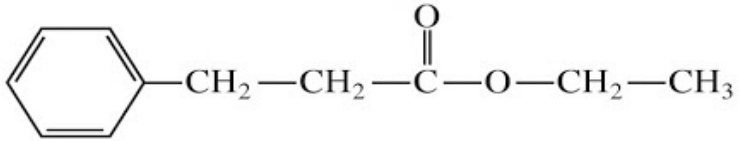


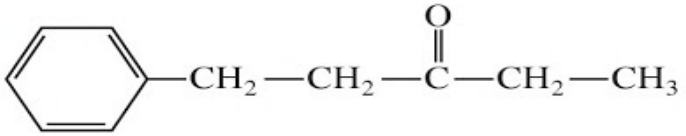
FIGURE 2.59 The infrared spectrum of dibutylamine (neat liquid, KBr plates).

In each part, choose the structure that best fits the infrared spectrum shown.

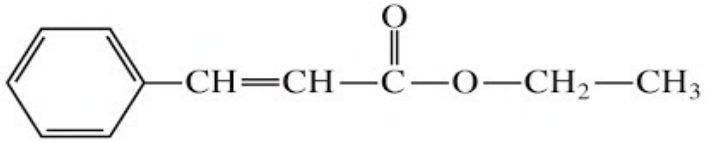
*(a)



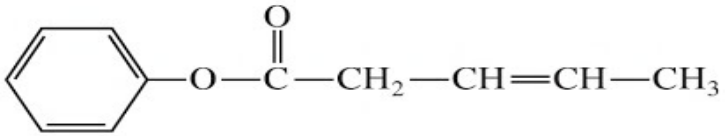
A



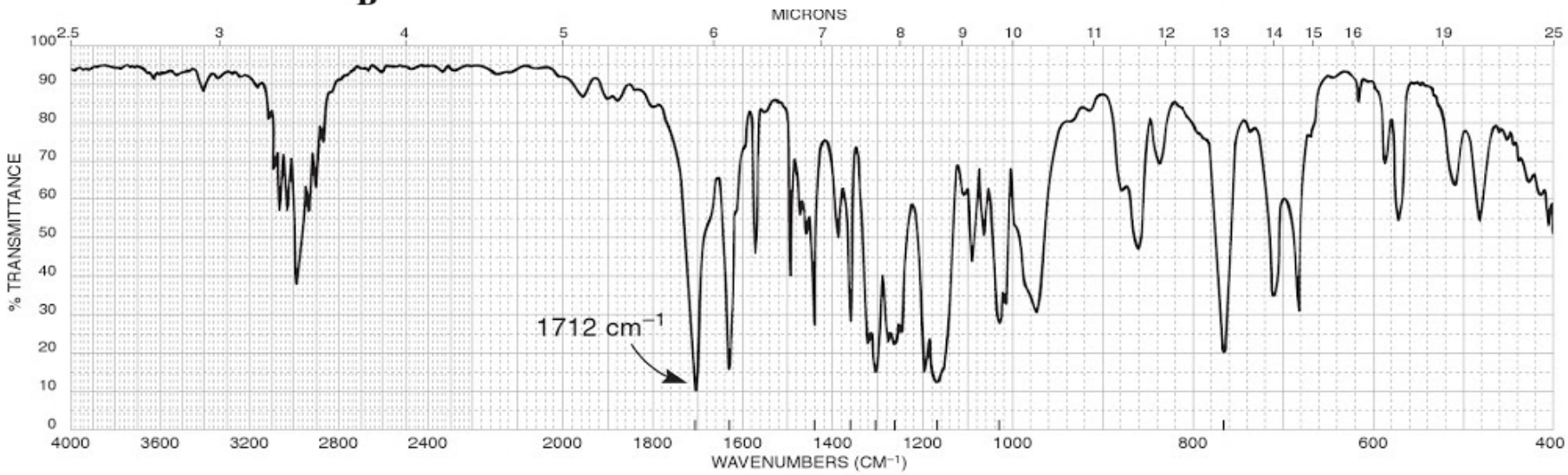
C



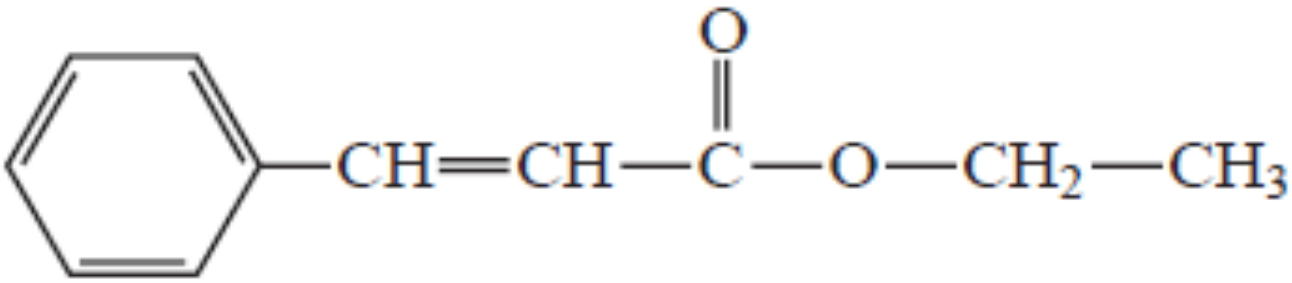
B



D

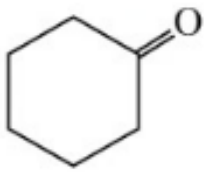


(a) Structure B (ethyl cinnamate)

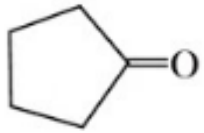


B

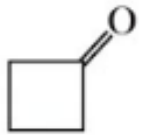
*(b)



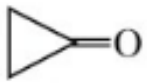
A



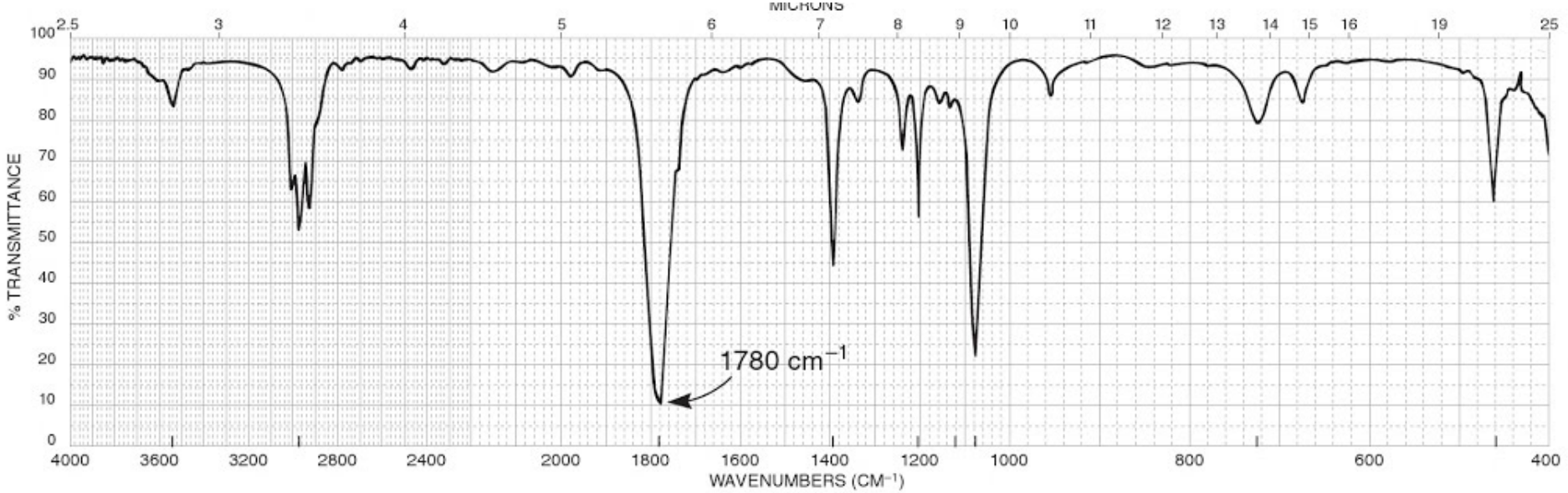
B



C



D


MICRONS
2.5
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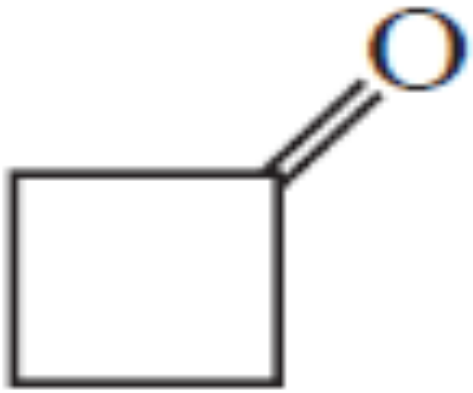
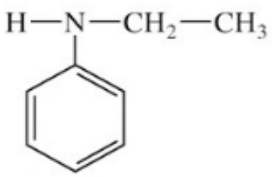
11
12
13
14
15
16
19
25
100
90
80
70
60
50
40
30
20
10
0
% TRANSMITTANCE
1780 cm⁻¹
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS (CM⁻¹)

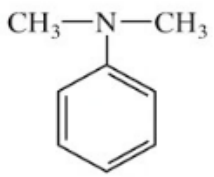
(b) Structure C (cyclobutanone)



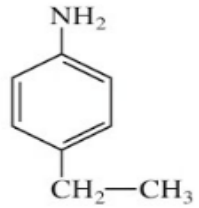
C

*(c) 

A



B



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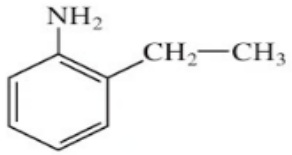
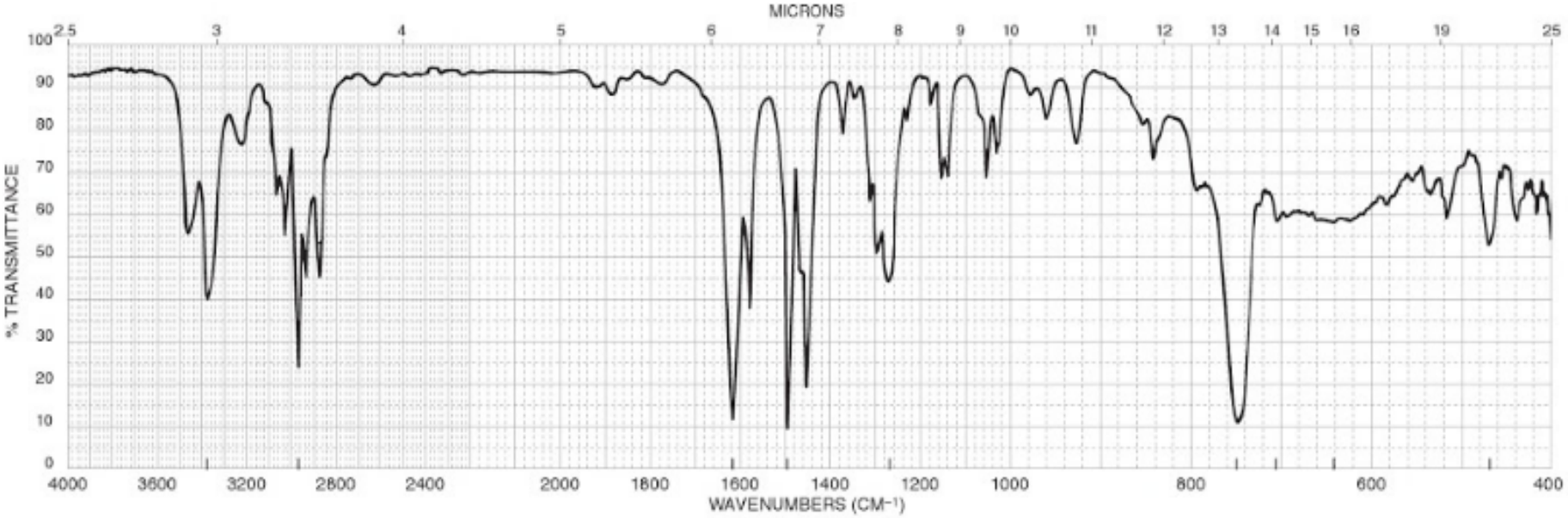


D


MICRONS
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% TRANSMITTANCE
4000
3600
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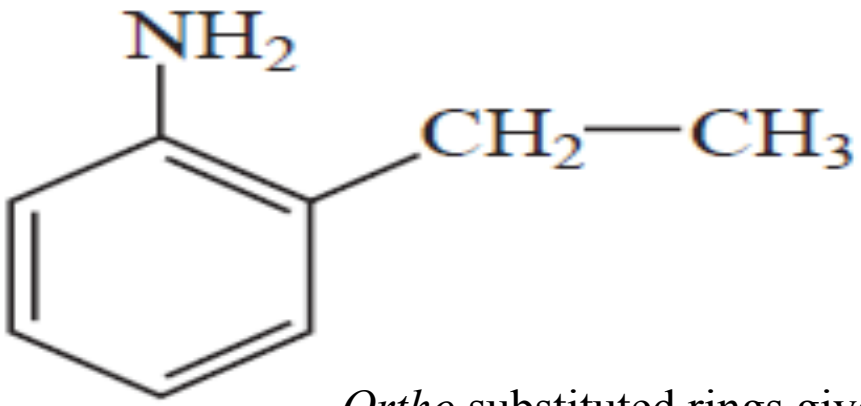
WAVENUMBERS (CM⁻¹)

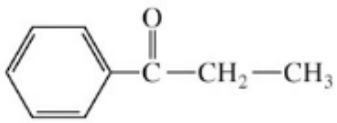
(c) Structure D (2-ethylaniline)



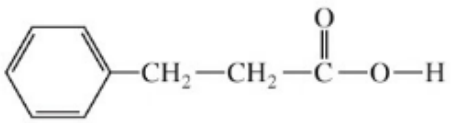
Ortho substituted rings give one strong band at 750 cm^{-1}

D

*(d)



A



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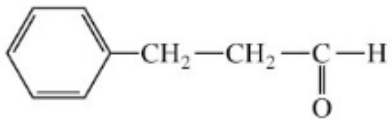

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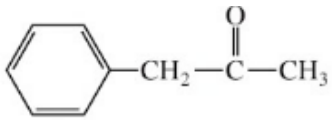
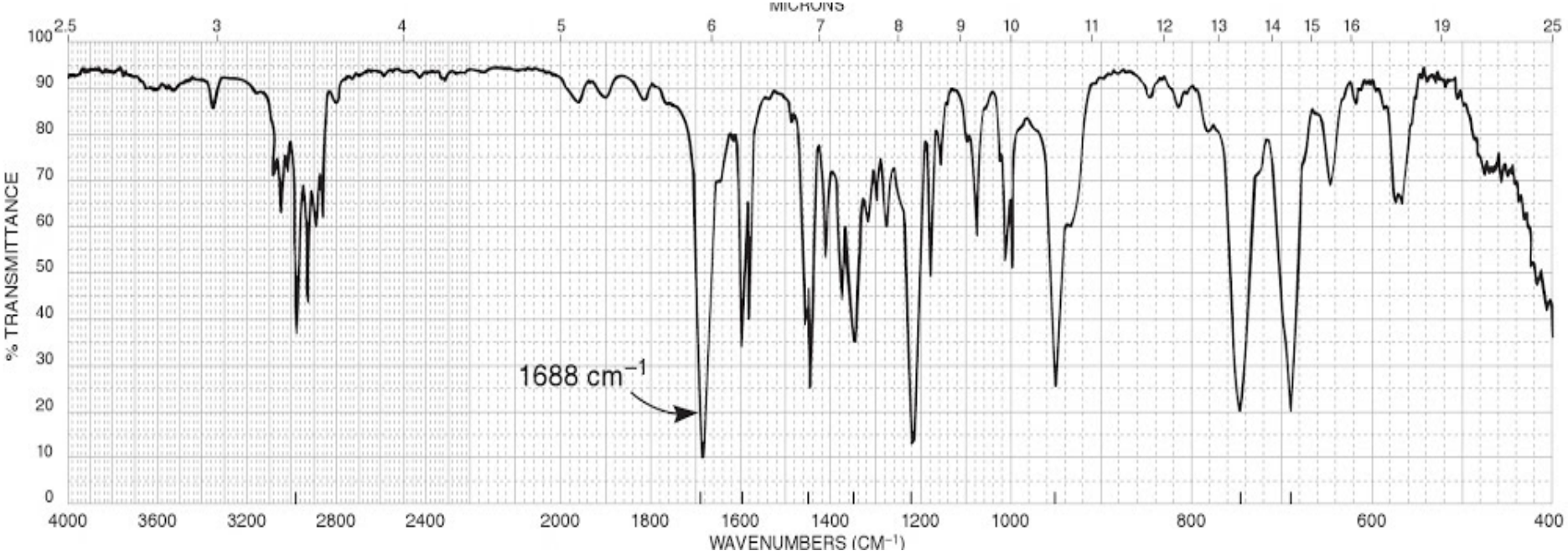


D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% TRANSMITTANCE
1688 cm−1
4000
3600
3200
2800
2400
2000
1800
1600
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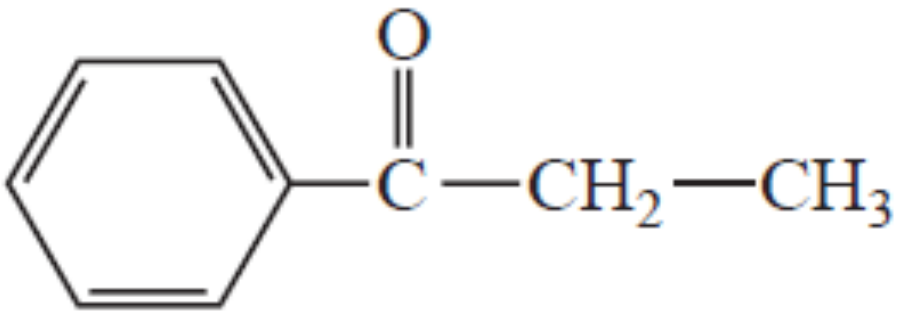
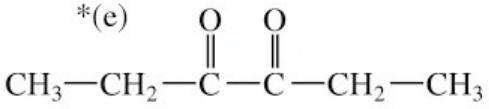
WAVENUMBERS (CM−1)

(d) Structure A (propiophenone)

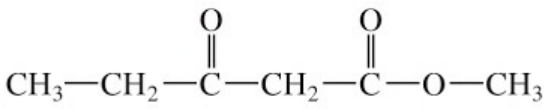


A

*(e)



A



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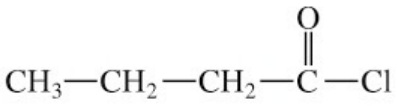
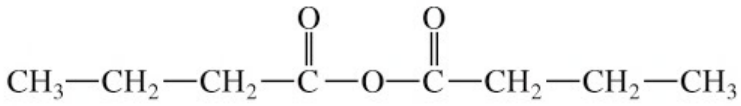
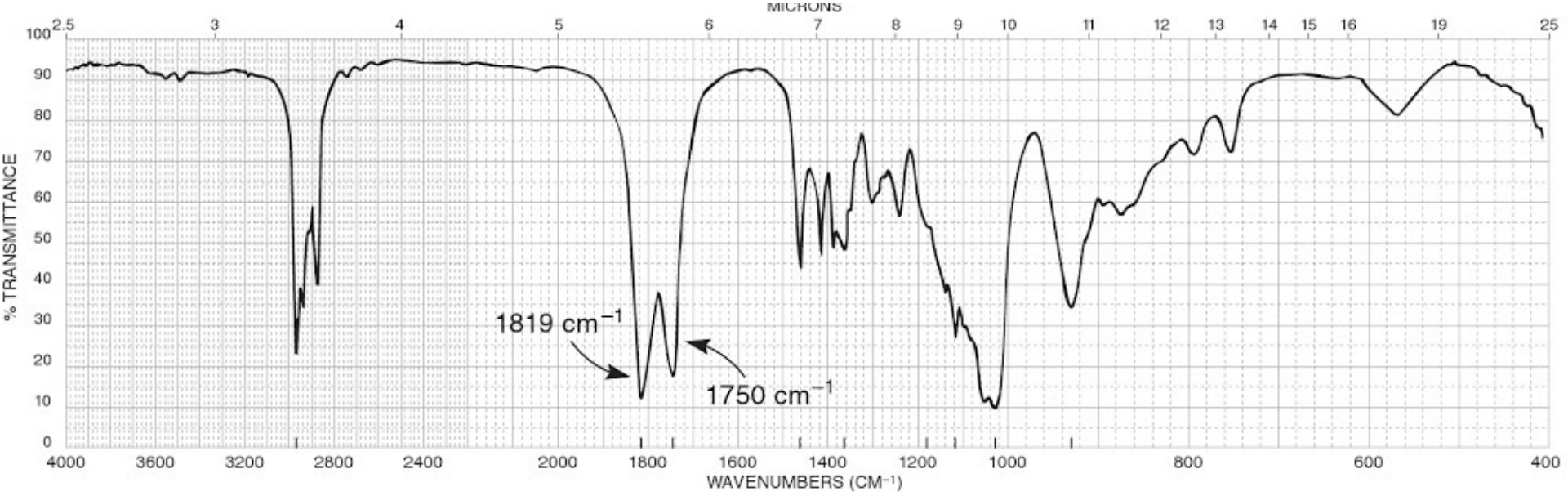


C



D


MICRONS
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% TRANSMITTANCE
1819 cm−1
1750 cm−1
4000
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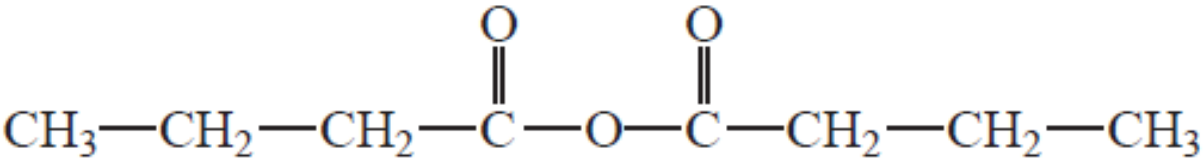
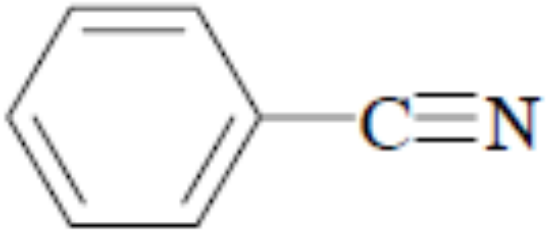
WAVENUMBERS (CM−1)

(e) Structure D (butanoic anhydride)

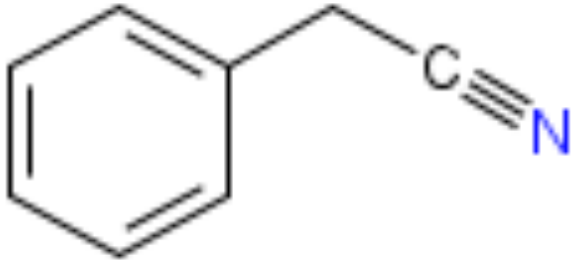


D

Either benzonitrile or phenylacetonitrile shows a band of medium intensity at 2940 cm-1: the other compound shows nothing in the range 3000-2500 cm-1, explain.

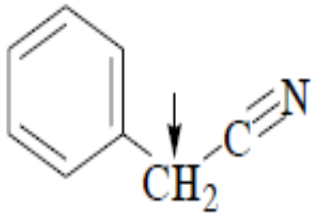


benzonitrile

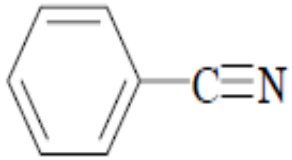


Phenylacetonitrile

Since the indicated carbon of phenylacetonitrile is sp^3 hybridized, it is reasonable for this compound to show C–H stretching at less than 3000 cm^{-1} (2960-2940 cm^{-1}). Where as benzonitrile has only aromatic C–H stretching which is typically between 3100 - 3000 cm^{-1}



phenylacetonitrile



benzonitrile

Factor affecting vibrational frequency

1. Coupling interaction.
2. Fermi resonance.
3. Hydrogen bonding.
4. Electronic displacement effects.

1. Coupling interaction

- It is expected that there is a stretching absorption frequency for an isolated C-H bond. But in case of Methylene(-CH2-) group, two absorption occurs which corresponds to symmetric & asymmetric vibrations.
- Asymmetric vibration always takes place at high wave number compared with symmetric vibration.
- These are knows as coupled vibrations because vibration occurs at different frequencies than that required for an isolated C-H stretching.

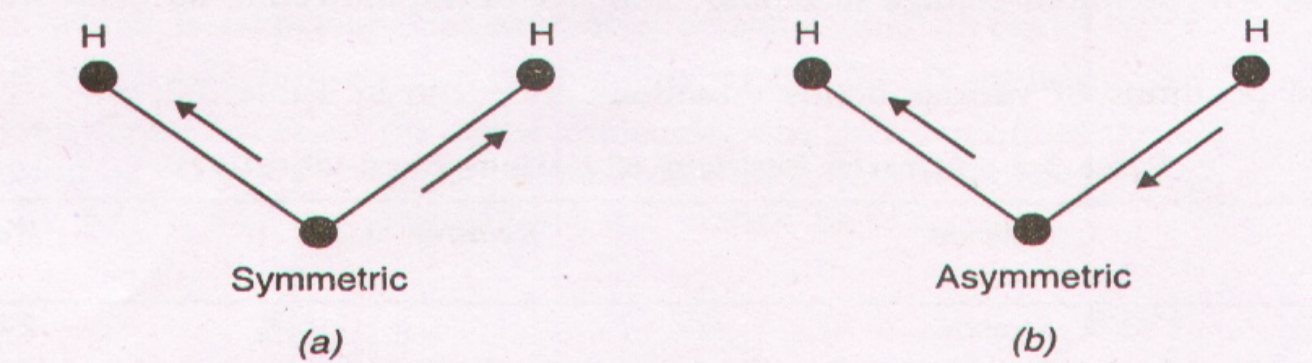
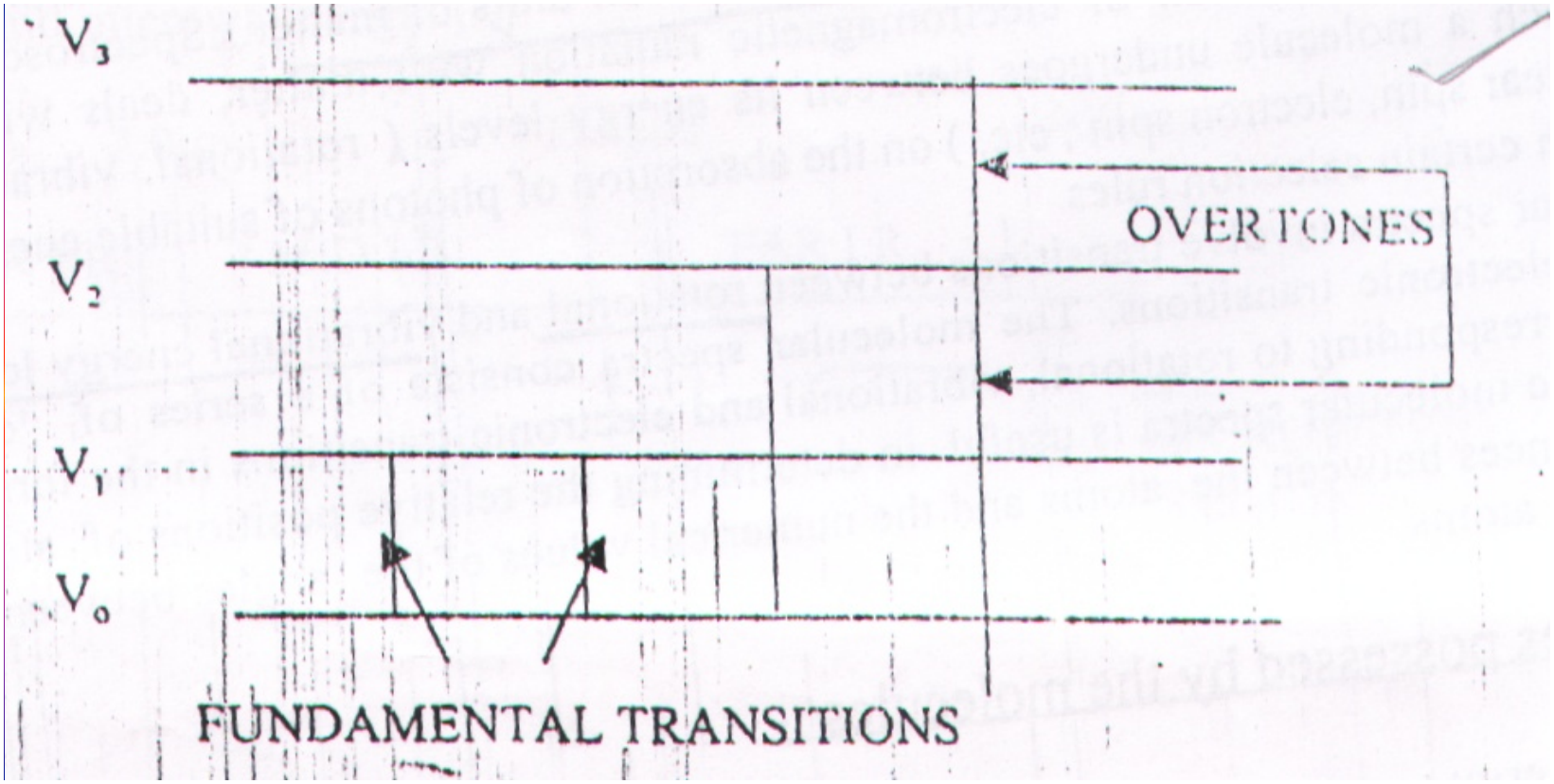


Fig. 3.25 : Stretching vibrations in methylene group.

2. Fermi resonance

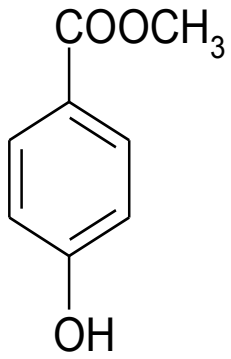
- It occurs when a fundamental vibration couples with an overtone or combination band.
- When an overtone or a combination of band has the same frequency to a fundamental, two bands appear close together.



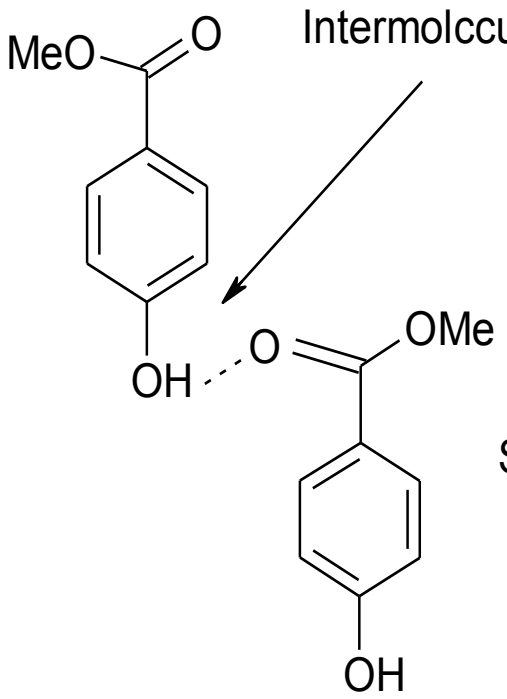
- The effect is greatest when the frequencies match, and the two bands are referred to as a *Fermi doublet*.
- When two bonds share a common atom as in the case of a linear tri-atomic molecule CO_2, consisting of two CO bonds (O=C=O), two fundamental stretching vibrations: symmetric and asymmetric takes place.
- As the symmetric stretching vibration produces no change in the dipole movement of the molecules, it is inactive in the IR spectra.
- In the asymmetric vibration, one oxygen approach the carbon atom as other may be away. Asymmetric stretching vibration appears in the IR region 2330 cm-1

3. Hydrogen bonding

- Hydrogen bonding gives rise to downward frequency shifts.
- Stronger the bonding, greater the absorption shift towards lower wave number from normal value.
- Generally, intermolecular hydrogen bonds are sharp and well defined.
- Intermolecular hydrogen bonds are concentration dependent. On dilution, intensities of such bands decreases and finally disappears.

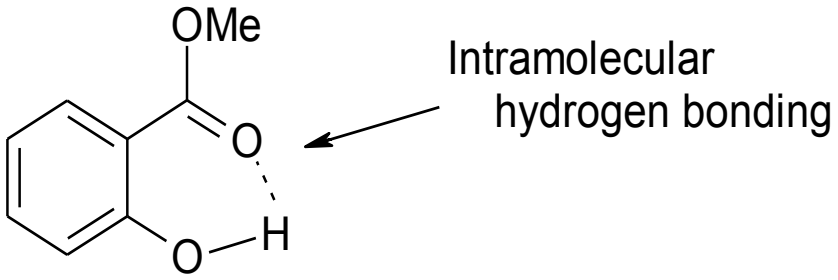


P- hydroxy methyl benzoate



Stretching 1710cm-1

Stretching 1740-1780 cm-1



Stretching 1680 cm-1

4. Electronic Displacement Effect

- The frequency shifts from normal position of absorption occur because of electronic effects which include: Inductive effect, mesomeric effect, configuration effect or field effect .
- Under the influence of these effects, the force constant (K) or the bond strength changes and its absorption frequency shifts from the normal value.
- The introduction of alkyl group in an alpha- position of C=O group exerts inductive effect which results in shortening or strengthening of the bond. Consequently the force constant increases and so the frequency or the wave number of absorption also increases.

- Inductive effects are divided into two parts:

+ve inductive effect	-ve inductive effect
Eletron deficient	Electron rich
e.g Alkyl group	e.g Cl, Br, I, OH
Bond length ↑	Bond length ↓
K ↓	K ↑
Frequency ↓	Frequency ↑

- Mesomeric effect works along with inductive effect. In some cases, inductive effect dominates mesomeric effect and vice versa.
- Configuration decreases the wavenumber of absorption. Oxygen atom of esters is more electronegative than nitrogen atom of amide. Hence, one pair of electron pair of nitrogen atom of amides participate more in conjugation thereby decreasing the absorption frequency of C=O group of amide.

Compound	Wave Number (cm-1)
Benzamide	1663
Phenylacetate	1730

REGIONS OF IR SPECTRUM

IR spectra is divided into 2 regions.

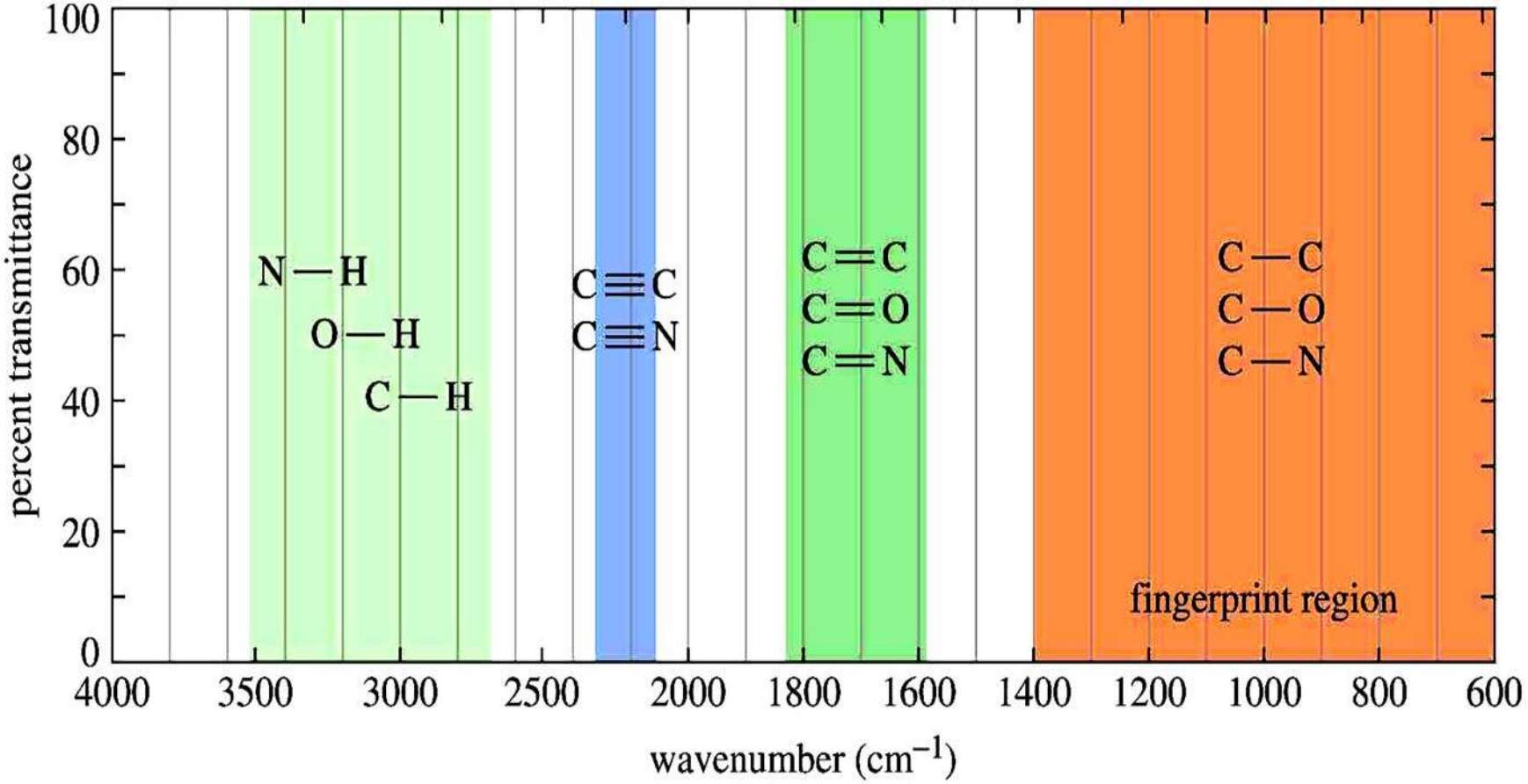
1. Region 4000- 1500 cm-1

- It consists of absorption bands of vibrational states of various types of bonds present in the molecule.
- The important groups accounted for include NH, OH, C=O, C=C, C=N, etc.
- The presence of aromatic nucleus (2000-1670 cm-1) and hydrogen bonding O-H, N-H, etc are also encountered in this region.

➢The graph shows the regions of the spectrum where the

following types of bonds normally absorb.

For example, a sharp band around 2200-2400 cm^{-1} would



2. Fingerprint region

- This region accounts for many absorption bands characteristic of functional group. Since numbers of sharp bands of varying intensities are encountered, close examination is needed.
- This region is useful for the identification of compounds since no two compounds can have identical IR spectra under identical conditions.
- Regions present below 1500 cm-1 shows absorption bands due to bending vibrations and stretching vibrations of C-C, C-O and C-N bonds.
- Regions less than 1250 cm-1 consists of complex vibrational and rotational spectra of the complete molecule.

Fingerprint region is further divided into three regions.

i. Region 1500- 1350 cm^{-1}

- The presence of double peaks near 1380 cm-1 and 1365 cm-1 indicates presence of tertiary butyl group in the compound.

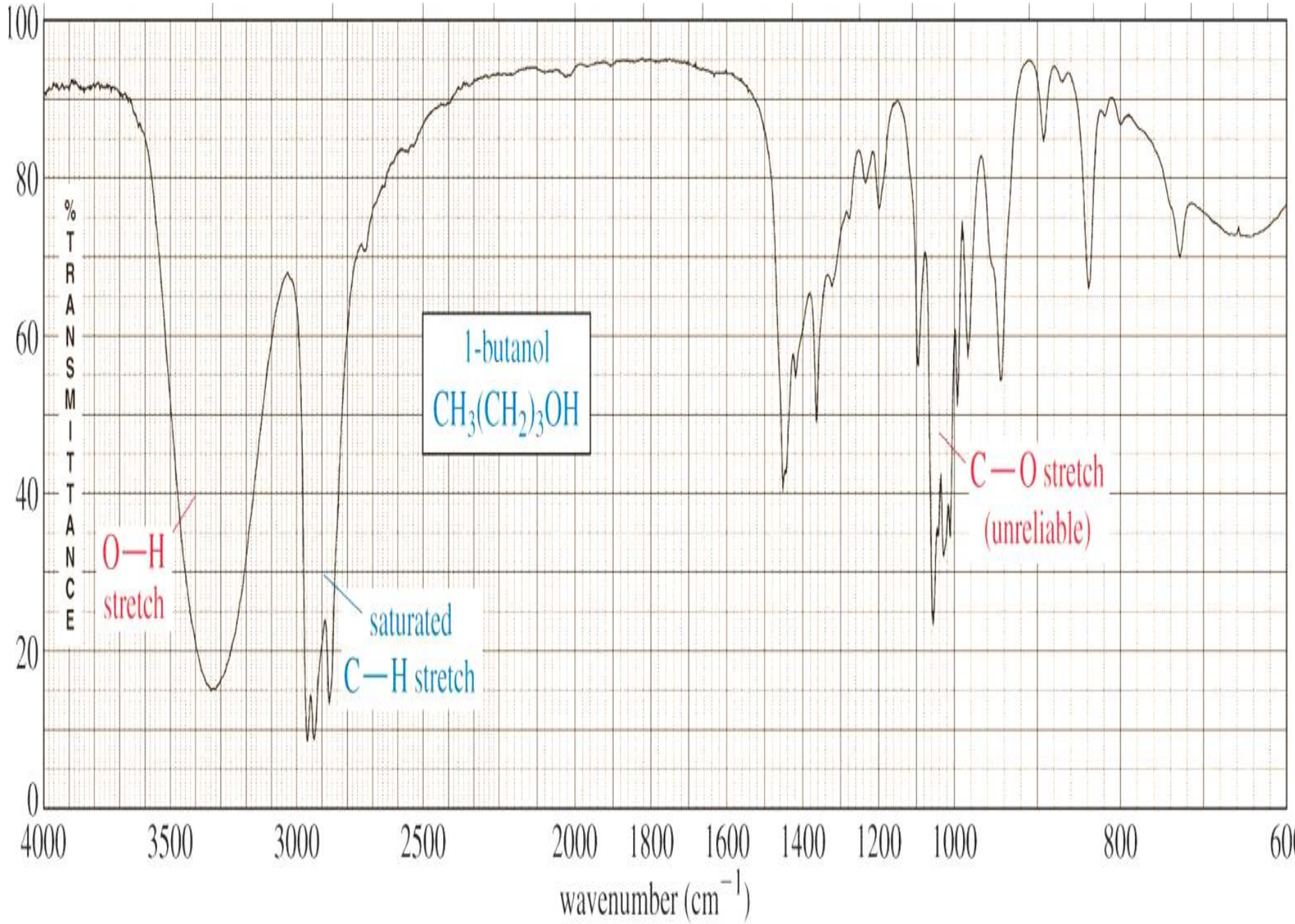
ii. Regions 1350-1000 cm^{-1}

- Characteristic strong bands due to C-O stretching are present.

Compound	IR region
Ethers	1150- 1070 cm^{-1}
Primary alcohols	1350- 1260 cm^{-1} and Near 1050 cm^{-1}
Esters	1380- 1050 cm^{-1}
Phenols	Near 1200 cm^{-1}

iii. Less than 1000 cm^{-1}

- Absorption band in the region 750- 700 cm^{-1} indicates the presence of mono substituted benzenes.
- Geometrical isomers of olefins can be distinguished in the region 970 – 700 cm^{-1}.
- Cis- isomer shows strong intensity absorption band at 700 cm-1 and trans- isomer at 970-960 cm^{-1}.


100
80
60
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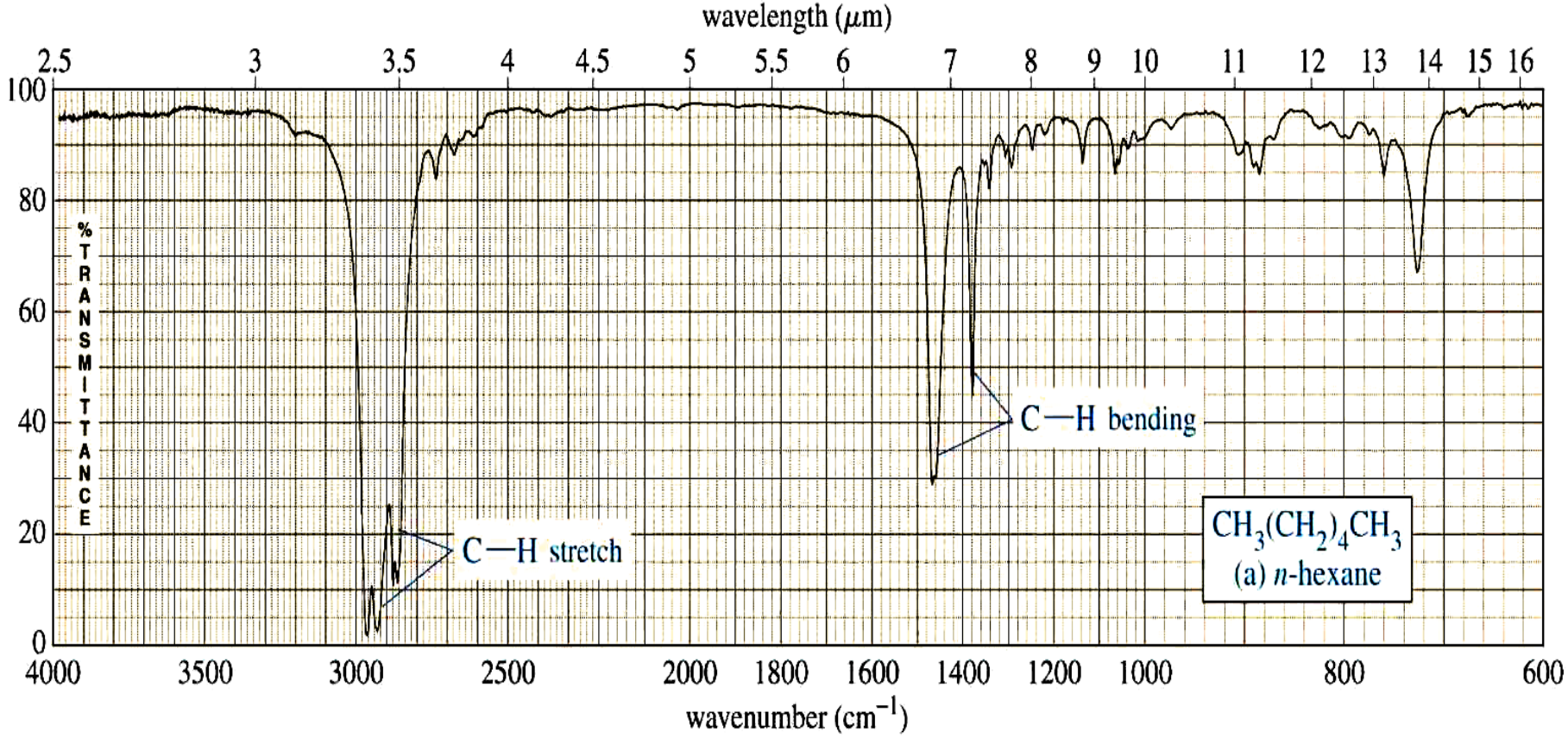
0
% TRANSMITTANCE
1-butanol
$CH_3(CH_2)_3OH$
O—H
stretch
saturated
C—H stretch
C—O stretch
(unreliable)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

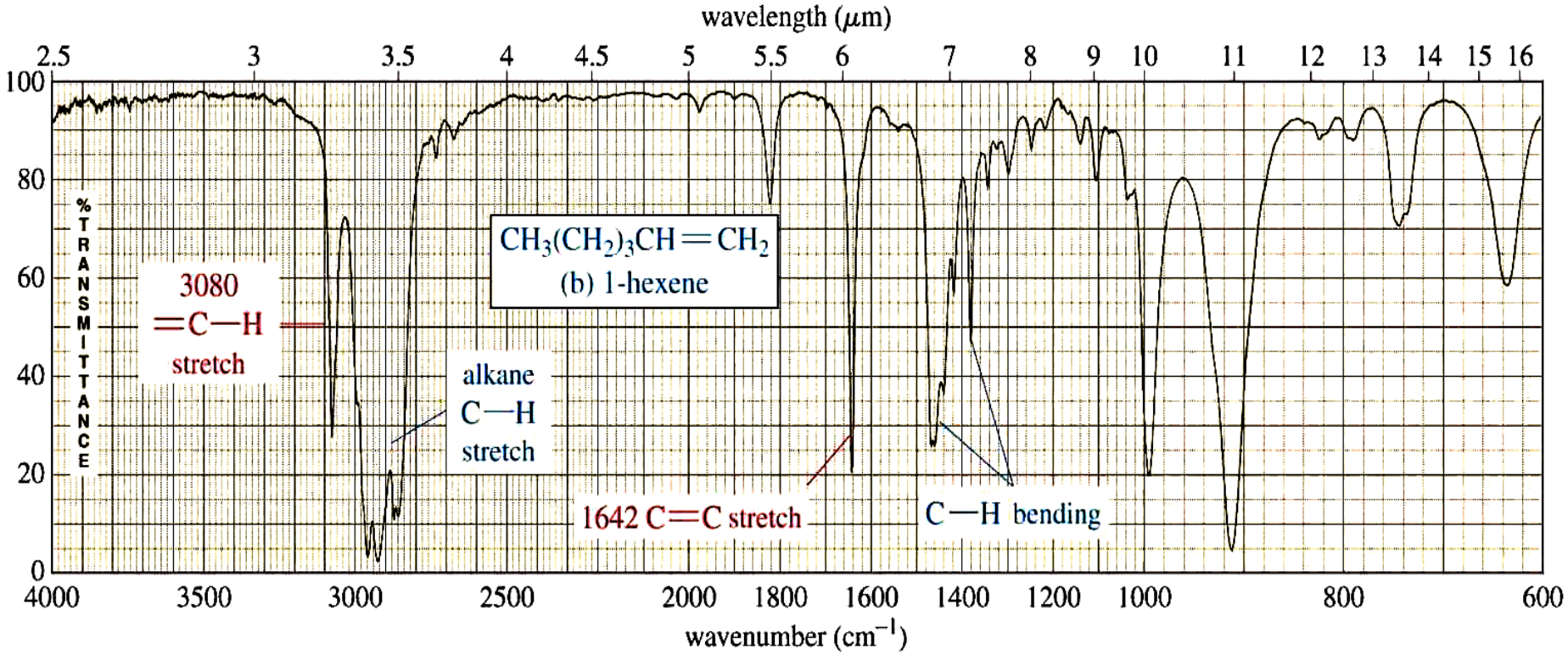
IR SPECTRUM OF ALKANES

Alkanes have no functional groups. Their IR spectrum displays only C-C and C-H bond vibrations. Of these, the most useful are the **C-H bands**, which appear around **3000 cm^{-1}** due to C-H stretching vibrations.



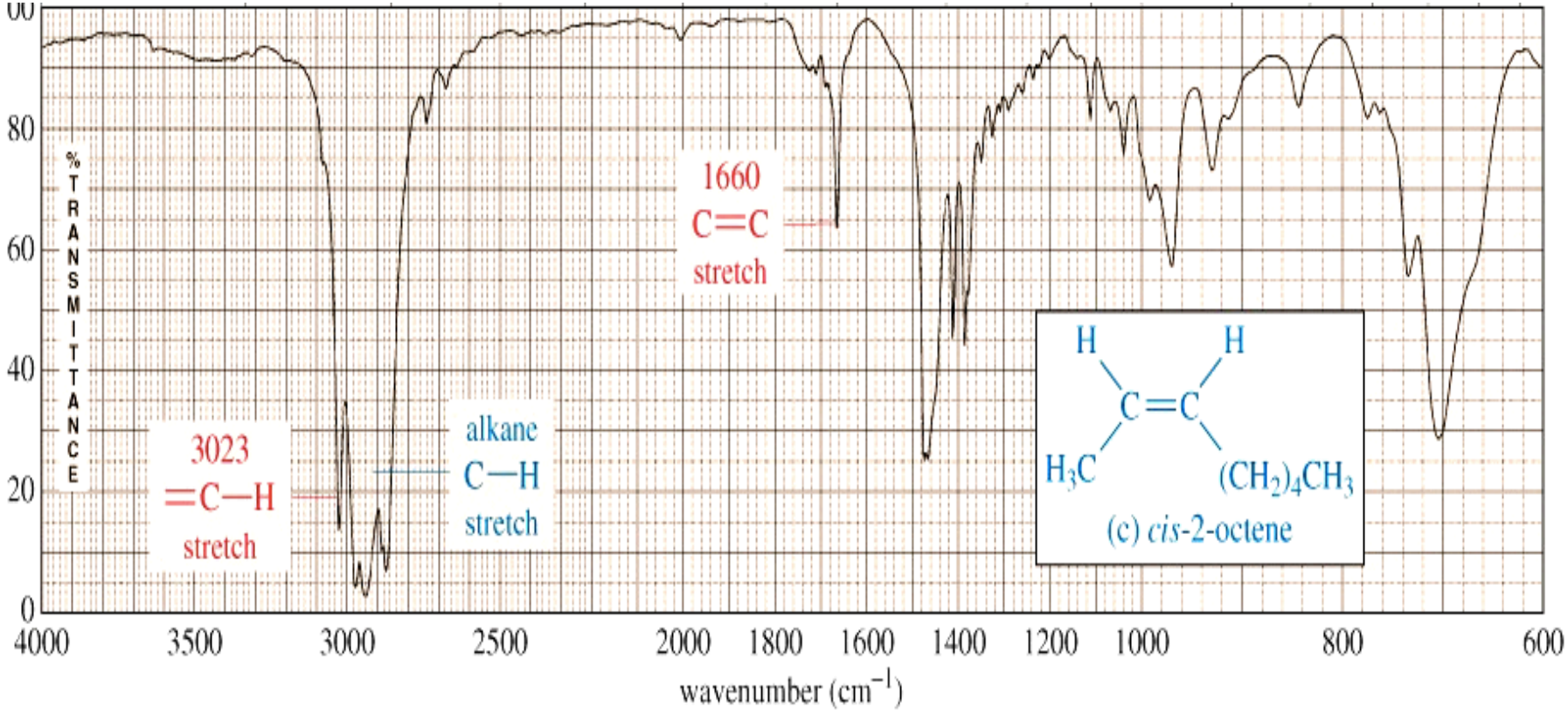
IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm^{-1}**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm^{-1}** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm^{-1}.



IR SPECTRUM OF ALKENES

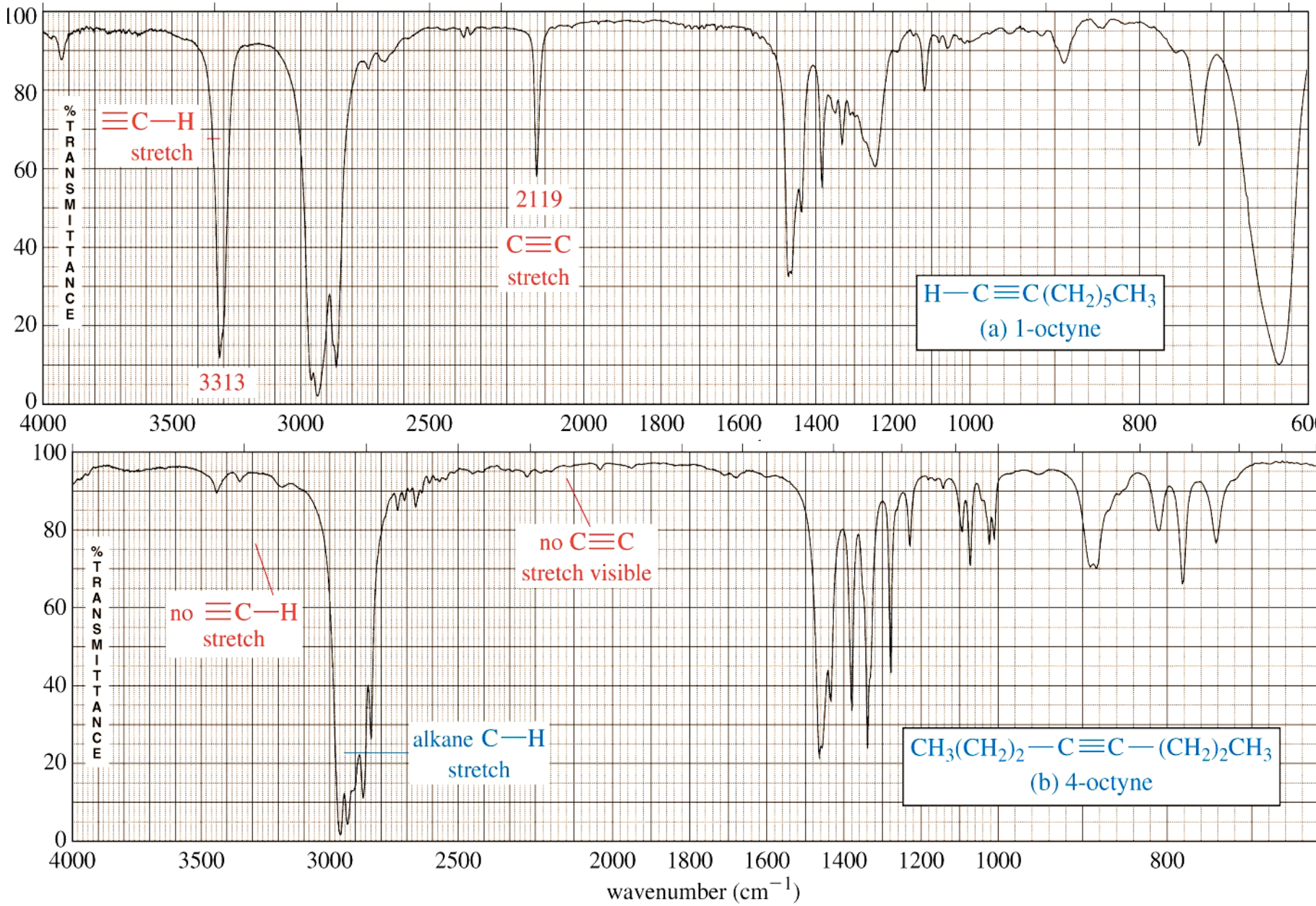
This spectrum shows that the band appearing around **3080 cm^{-1}** can be obscured by the broader bands appearing around 3000 cm^{-1}.



IR SPECTRUM OF ALKYNES

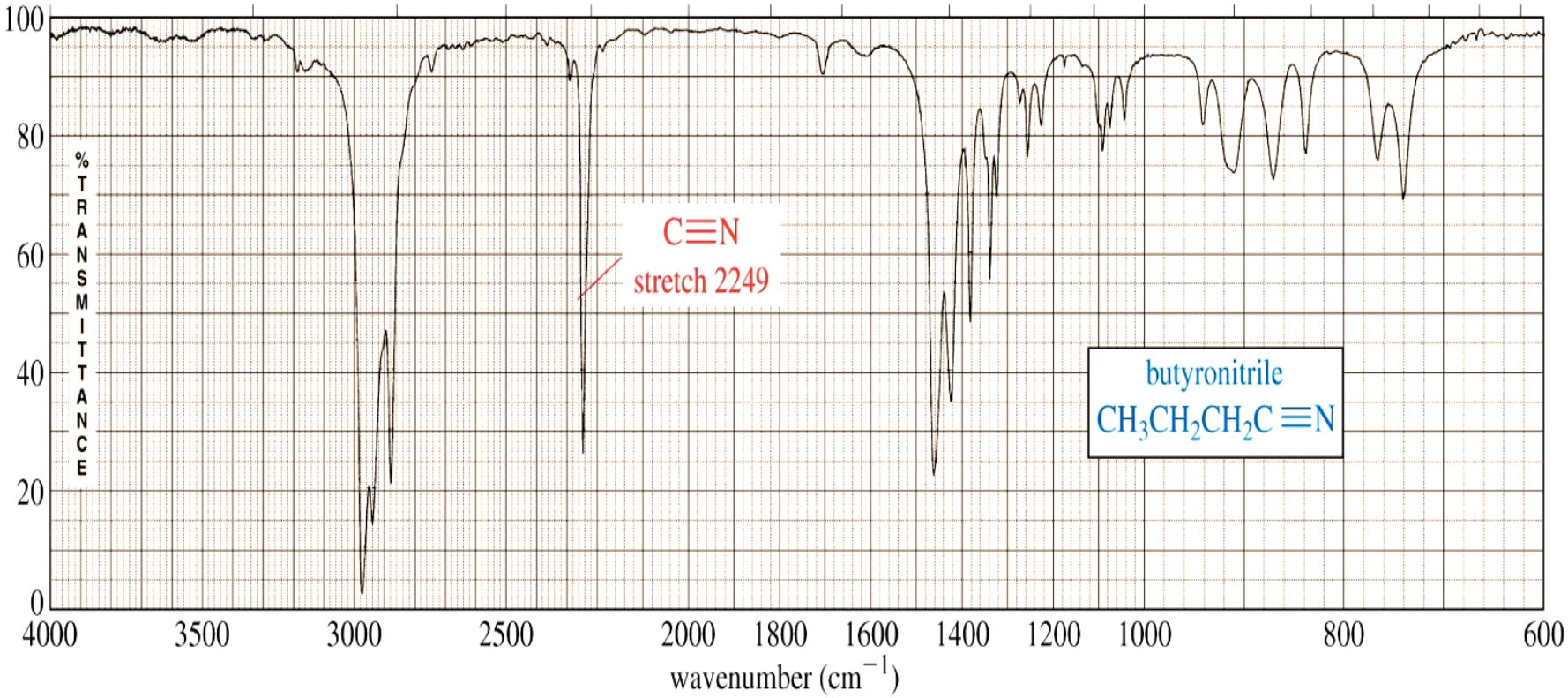
- The most prominent band in alkynes corresponds to the **carbon-carbon triple bond**. It shows as a sharp, weak band at about **2100 cm^{-1}**. The reason it's weak is because the triple bond is not very polar. In some cases, such as in highly symmetrical alkynes, it may not show at all due to the low polarity of the triple bond associated with those alkynes.
- Terminal alkynes, i.e. those where the triple bond is at the end of a carbon chain, have C-H bonds involving the *sp* carbon. Therefore they may also show a sharp, weak band at about **3300 cm^{-1}** corresponding to the C-H stretch.
- Internal alkynes, i.e. those where the triple bond is in the middle of a carbon chain, do not have C-H bonds to the *sp* carbon and therefore lack the aforementioned band.

IR SPECTRUM OF ALKYNES



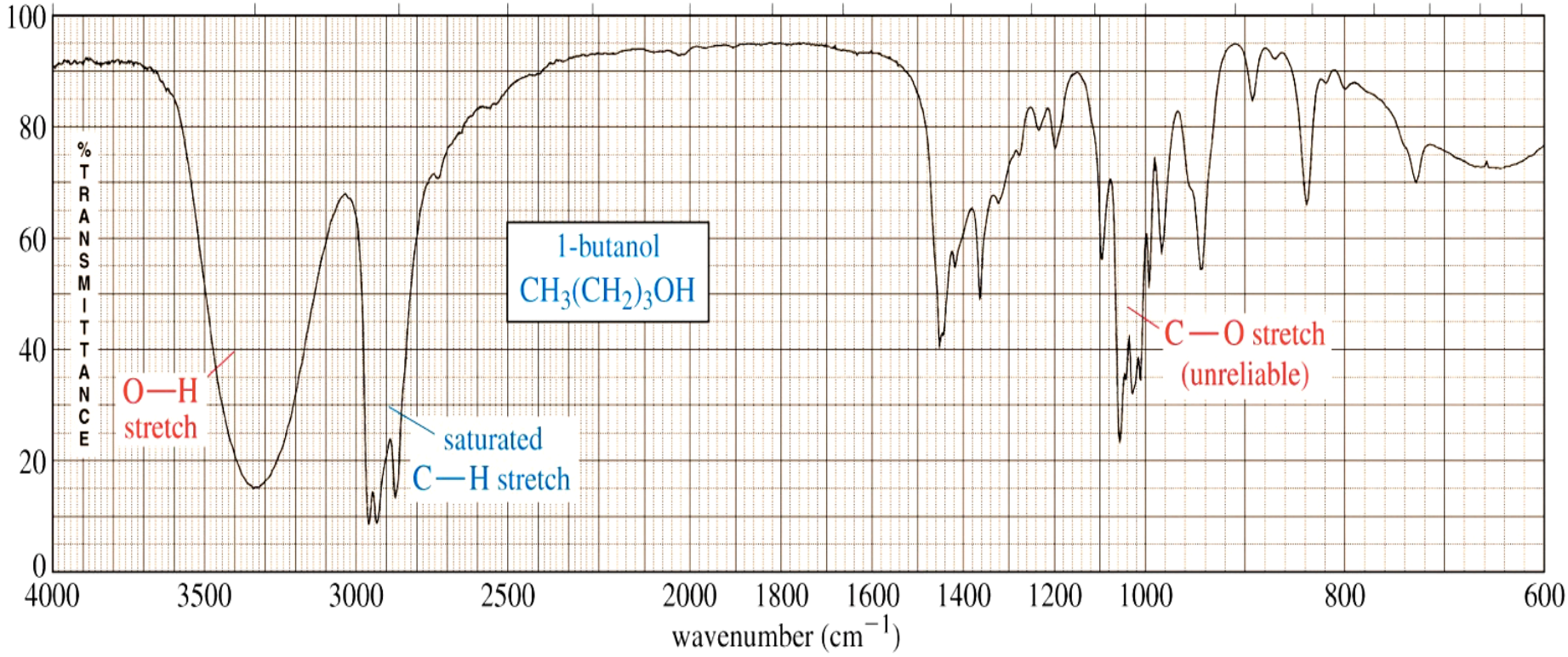
IR SPECTRUM OF A NITRILE

In a manner very similar to alkynes, nitriles show a prominent band around **2250 cm^{-1}** caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne C-C triple bond, but because the CN triple bond is more polar, this band is stronger than in alkynes.



IR SPECTRUM OF AN ALCOHOL

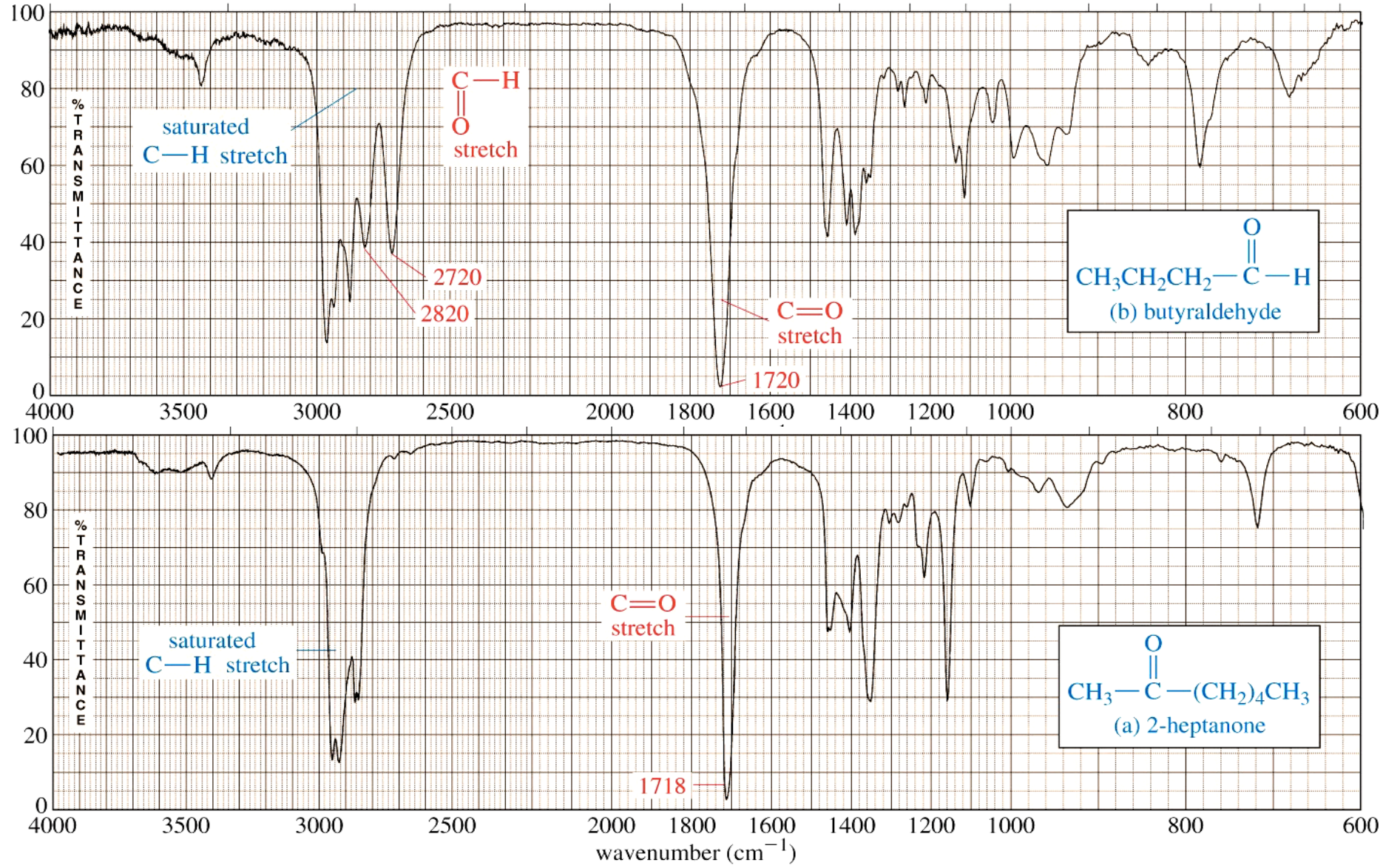
The most prominent band in alcohols is due to the **O-H bond**, and it appears as a strong, broad band covering the range of about **3000 - 3700 cm^{-1}**. The sheer size and broad shape of the band dominate the IR spectrum.



IR SPECTRUM OF ALDEHYDES AND KETONES

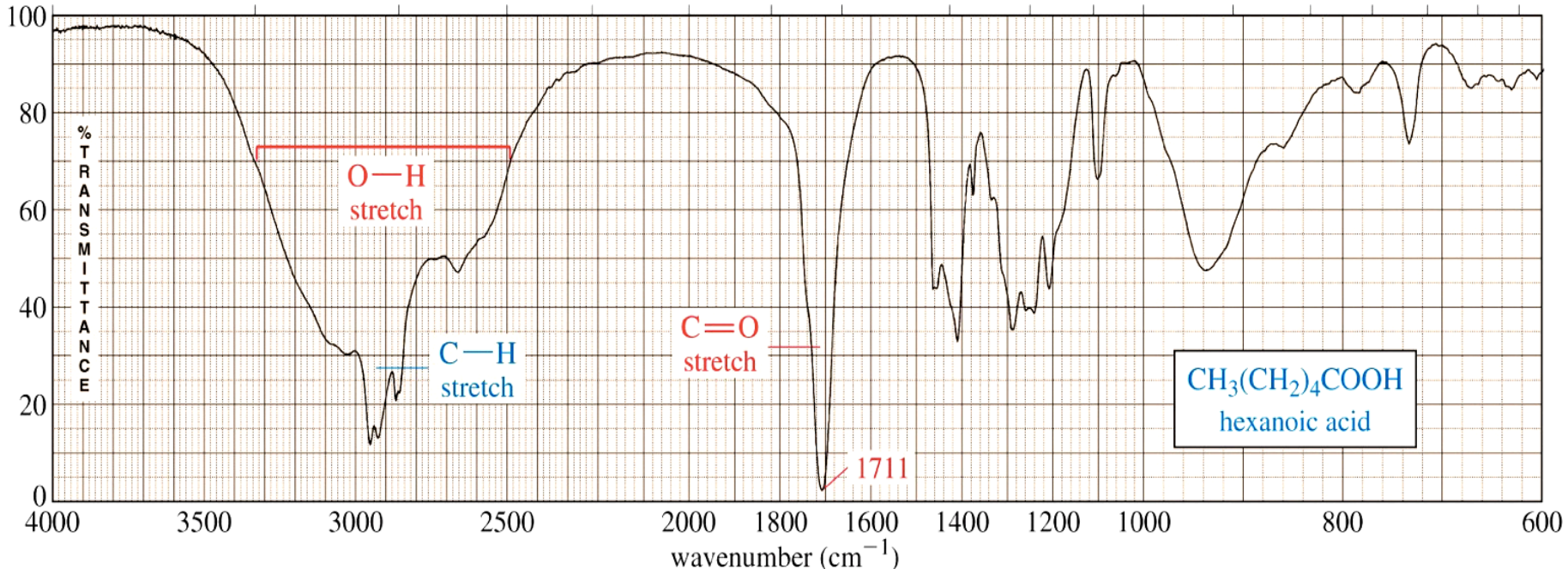
- In aldehydes, **C=O functional group** is at the end of a carbon chain, whereas in ketones it's in the middle of the chain. As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons.
- Aldehydes and ketones show a strong, prominent, stake-shaped band around **1710 - 1720 cm^{-1}**. This band is due to the **highly polar C=O bond.**
- Because aldehydes also contain a C-H bond to the sp^2 carbon of the C=O bond, they also show a pair of medium strength bands positioned about **2700** and **2800 cm^{-1}**. These bands are missing in the spectrum of a ketone because the sp^2 carbon of the ketone lacks the C-H bond.

IR SPECTRUM OF ALDEHYDES AND KETONES



IR SPECTRUM OF A CARBOXYLIC ACID

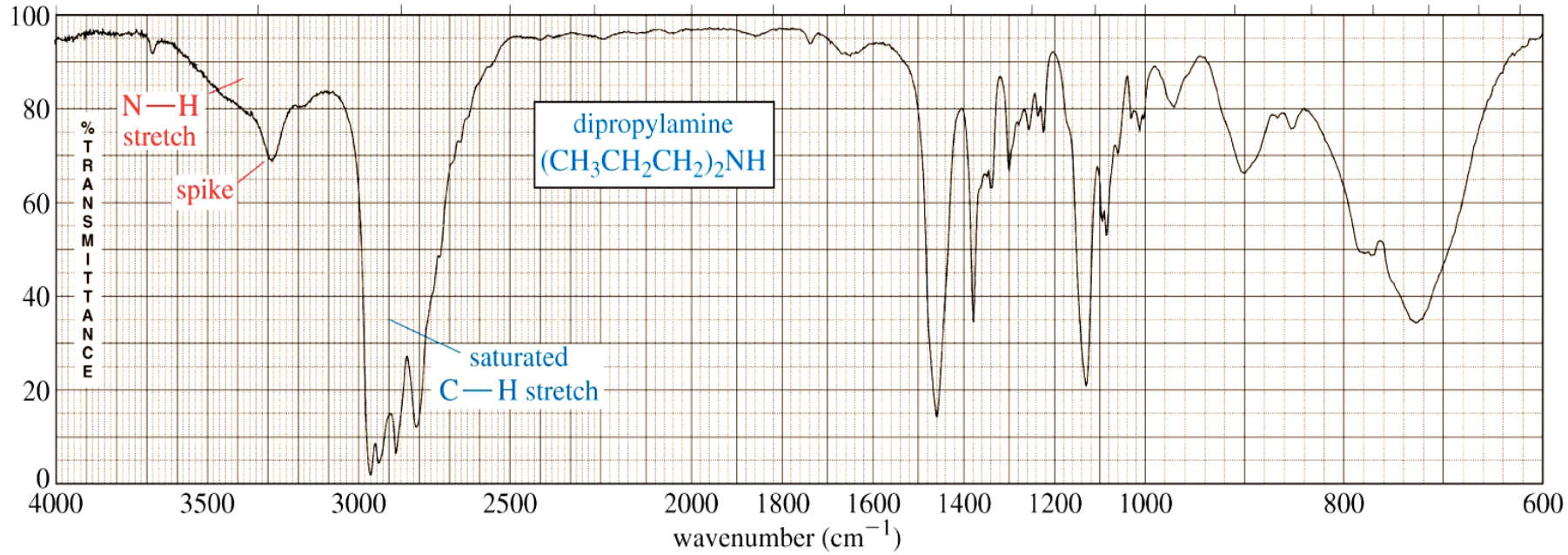
A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm^{-1}** for the O-H stretch and also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** corresponding to the C=O stretch.



IR SPECTRA OF AMINES

➢The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a weak to medium, somewhat broad band. This band is positioned in the range of about **3200 - 3600 cm^{-1}**.

➢Primary amines have two N-H bonds, therefore they typically show two spikes. Secondary amines have only one N-H bond. Finally, tertiary amines have no N-H bonds, and therefore this band is absent from the IR spectrum altogether. The spectrum below shows a secondary amine.



IR SPECTRUM OF AMIDES

The amide functional group combines the features of amines and ketones because it has both the **N-H bond** and the **C=O bond**. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between **3100** and **3500 cm^{-1}** for the N-H stretch. At the same time they also show the stake-shaped band around **1710 cm^{-1}** for the C=O stretch. As with amines, primary amides show two spikes, whereas secondary amides show only one spike.