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L2

INFRARED SPECTROSCOPY (IR Spectroscopy)

INFRARED SPECTROSCOPY (IR Spectroscopy)

Introduction.

-IR spectroscopy (which is short for infrared spectroscopy) deals with the infrared region of the electromagnetic spectrum. (**light having a longer wavelength and a lower frequency than visible light).** Infrared Spectroscopy generally refers to the analysis of the interaction of a molecule with infrared light.

Spectroscopy provide the information about **molecular structure.**

-The IR spectroscopy concept can generally be analyzed in three ways: by measuring reflection, emission, and absorption. The major use of infrared spectroscopy is to determine the **functional groups** of molecules, relevant to both organic and inorganic chemistry.

- 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.

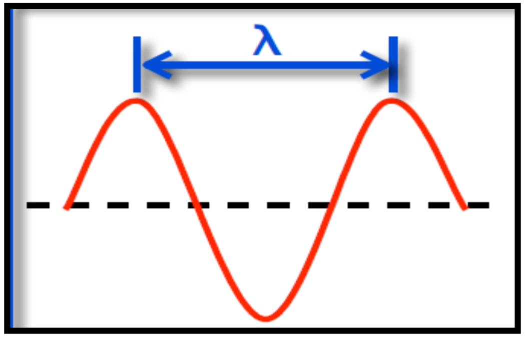
Even a very simple molecule can give an extremely complex spectrum

IR Spectroscopy detects frequencies of infrared light that are absorbed by a molecule.

Molecules tend to absorb these specific frequencies of light since they correspond to the frequency of the vibration of bonds in the molecule.

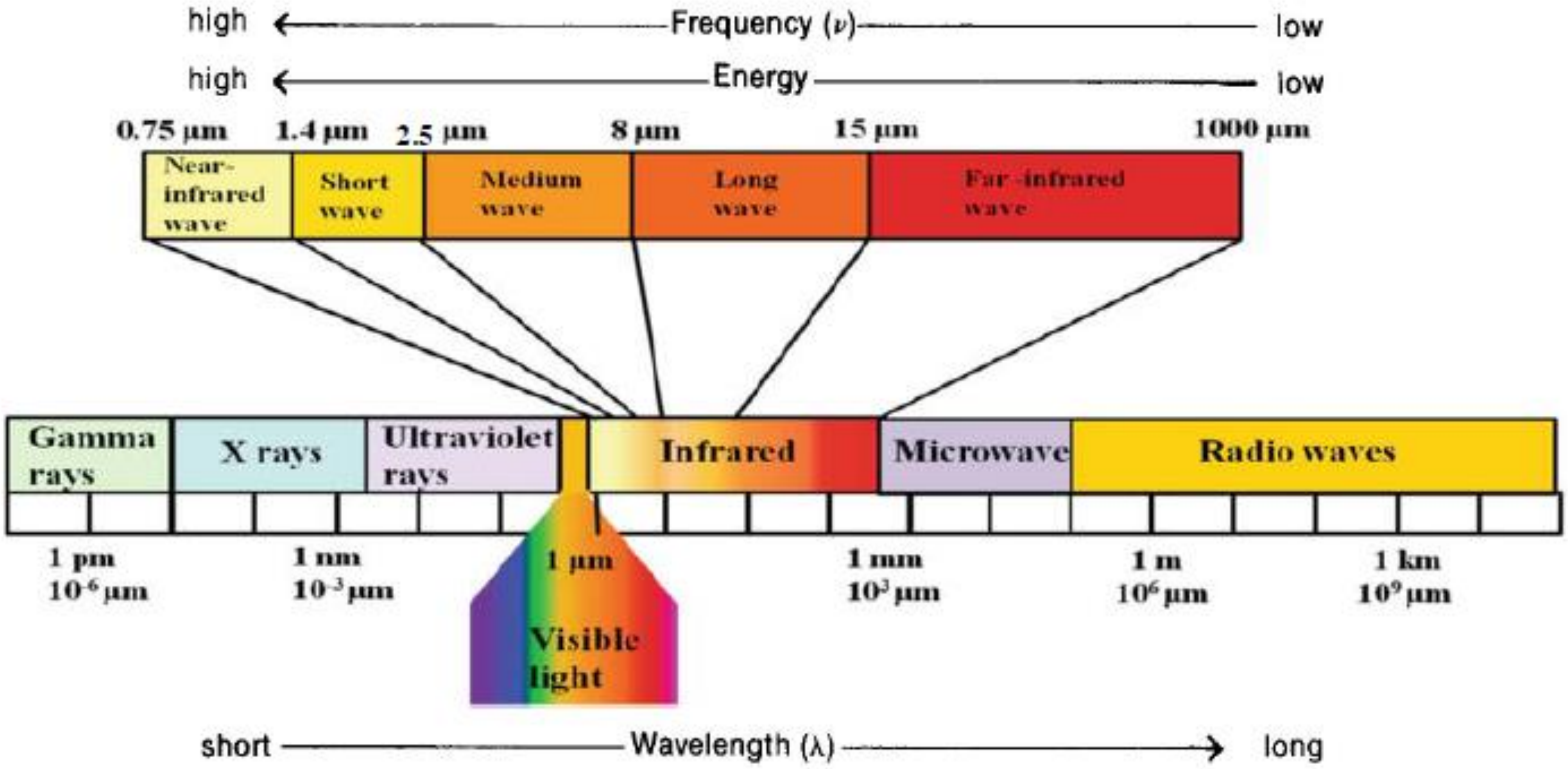
Wavelength & Frequency

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



$$E = h\nu = hc\backslash\,\lambda$$

E = energy (J) of 1 photon
h = Plank's constant (6.63x10–34Js)
c = speed of light (3x108ms^{-1})
ν = frequency (Hz)
λ = wavelength (m)


high
Frequency (ν)
low
high
Energy
low
0.75 µm
1.4 µm
2.5 µm
8 µm
15 µm
1000 µm
Near-infrared wave
Short wave
Medium wave
Long wave
Far-infrared wave
Gamma rays
X rays
Ultraviolet rays
Infrared
Microwave
Radio waves
1 pm
10⁻⁶ µm
1 nm
10⁻³ µm
1 µm
1 mm
10³ µm
1 m
10⁶ µm
1 km
10⁹ µm
Visible light
short
Wavelength (λ)
long

long wavelength = low energy , short wavelength = high energy

.IR frequencies are usually expressed in units of wavenumbers ( ) whose unit is the reciprocal centimeter (cm^{-1}).

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

- **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**.

Regions of the Infrared spectrum .

Three typical spectral regions for IR spectroscopy.

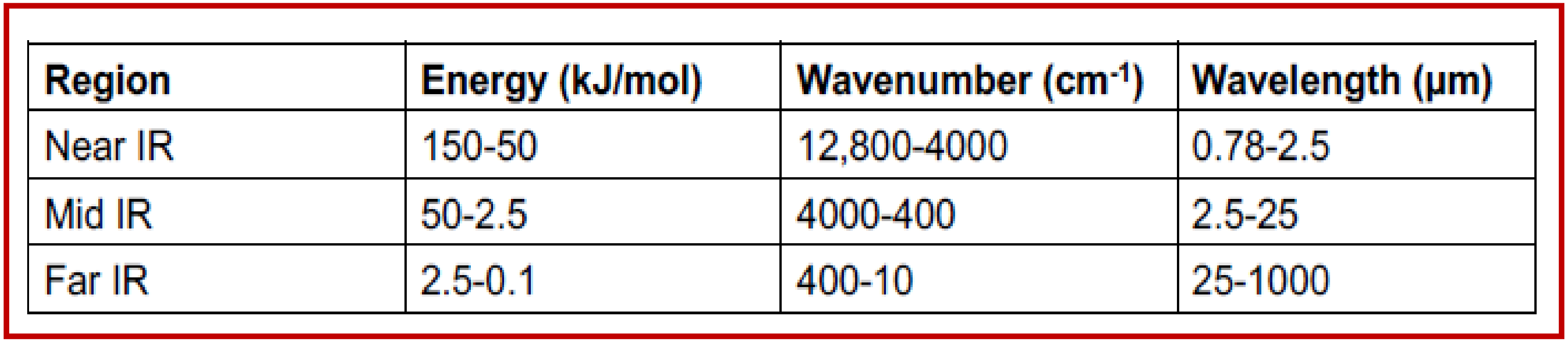
1. **Near-IR**: excites overtones or harmonics of fundamental vibrations (multiple level transition).

   يثير نغمات أو توافقيات الاهتزازات الأساسية (انتقال متعدد المستويات).

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.

   يثير الاهتزازات الأساسية (انتقال مستوى واحد). وهذه المنطقة هي الأكثر استخدامًا في التحليل الطيفي للأشعة تحت الحمراء، لأنها تولد بصمات طيفية توجد فيها معظم الجزيئات العضوية.

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

- **The energy required to excite the bonds belonging to a molecule, and to make them vibrate with more amplitude, occurs in the Infrared region.**
- A bond will only interact with the electromagnetic infrared radiation, however**, if it is polar.**
- The presence of separate areas of partial positive and negative charge in a molecule allows the electric field component of the electromagnetic wave to excite the vibrational energy of the molecule.

The change in the vibrational energy leads to another corresponding change in the dipole moment **of the given molecule.**

The intensity of the absorption depends on the polarity of the bond. Symmetrical non-polar bonds in N≡N and O=O do not absorb radiation, as they cannot interact with an electric field.

Band intensities can be expressed either as **transmittance** (*T*) or **absorbance** (*A*).

- **Transmittance** : T= I/I0 (Intensity of light out/intensity of incident light)
- **Absorbance**: A= log10 (1/T)

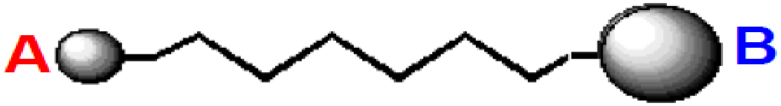
Most of the bands that indicate what **functional group is present are found in the region from 4000 cm^{-1} to 1300 cm^{-1}**. Their bands can be identified and used to determine the functional group of an unknown compound.

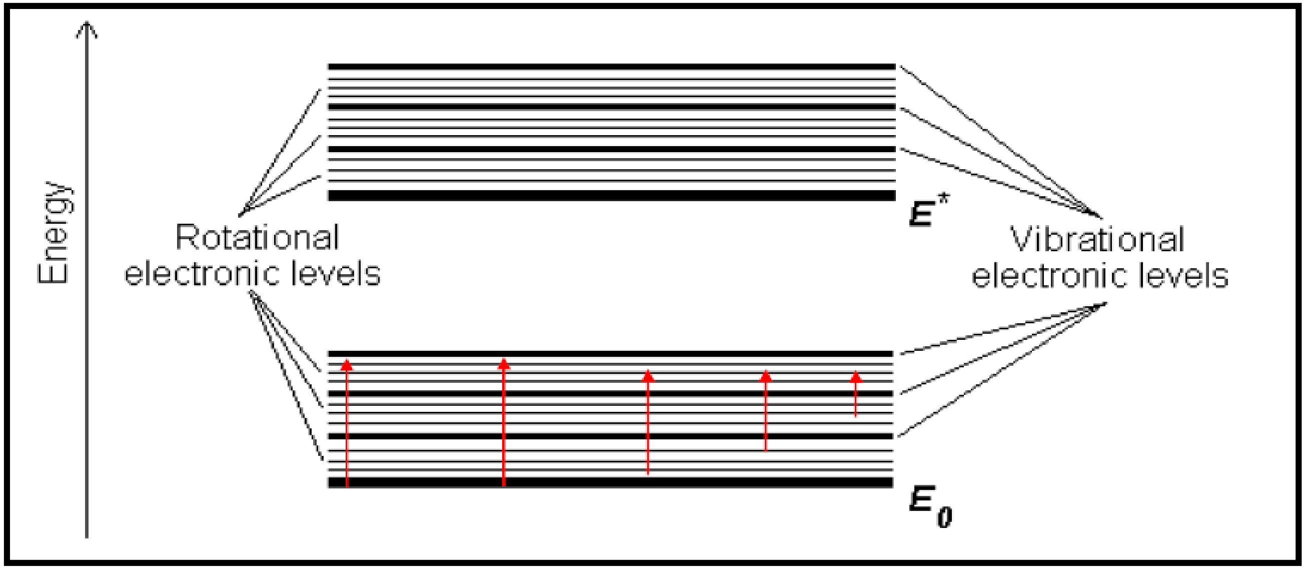
Bands that are unique to each molecule, similar **to a fingerprint, are found in the fingerprint region, from 1300 cm^{-1} to 400 cm^{-1}**. These bands are only used to compare the spectra of one compound to another.

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).




Energy
Rotational electronic levels
Vibrational electronic levels
E^*
E_0

In addition to **rotation** of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms.Consequently, organic compounds will absorb infrared radiation that corresponds in energy to these vibrations.

Absorption in this region implies the occurrence of **vibrational transitions** in the molecule while it remains in its ground state

Identification of organic compounds using Mid IR

Mid IR region is divided into two sub-regions:

- **region of characteristic vibrations of functional groups**

2.5–8 μm (4000–1250 cm-1) contains the characteristic bands of individual bonds and functional groups that correspond mainly to stretching vibrations

- **fingerprint region**

8–25 μm (1250–400 cm-1) contains the bands corresponding mainly to bending Vibrations the spectrum in this region characterizes each molecule as an integral whole

Instrumentation of Infrared (IR) Spectroscopy.

The main parts of the IR spectrometer are as follows:

1- Radiation source .

2- Sample cells and sampling of substances.

3- Monochromators.

4- Detectors .

5- Recorder .

A. IR radiation sources.

IR instruments require a source of radiant energy which emits IR radiation which must be steady, intense enough for detection, and extend over the desired wavelength. Various sources of IR radiations are as follows.

1- Nernst glower

2- Incandescent lamp

3- Mercury arc

4- Tungsten lamp

5- lober source

6- Nichrome wire

B. Sample cells and sampling of substances.

IR spectroscopy has been used for the characterization of solid, liquid, or gas samples.

i. Solid – Various techniques are used for preparing solid samples such as pressed pellet technique, solid run in solution, solid films, mull technique, etc.

ii. Liquid – Samples can be held using a liquid sample cell made of alkali halides. Aqueous solvents cannot be used as they will dissolve alkali halides. Only organic solvents like chloroform can be used.

iii. Gas– Sampling of gas is similar to the sampling of liquids.

C. Monochromators

Various types of monochromators are prism, gratings and filters.

Prisms are made of Potassium bromide, Sodium chloride or Cesium iodide.

Filters are made up of Lithium Fluoride and Diffraction gratings are made up of alkali halides.

D. Detectors.

Detectors are used to measure the intensity of unabsorbed infrared radiation. Detectors like thermocouples, Bolometers, thermisters, Golay cell, and pyro-electric detectors are used.

E. Recorders .

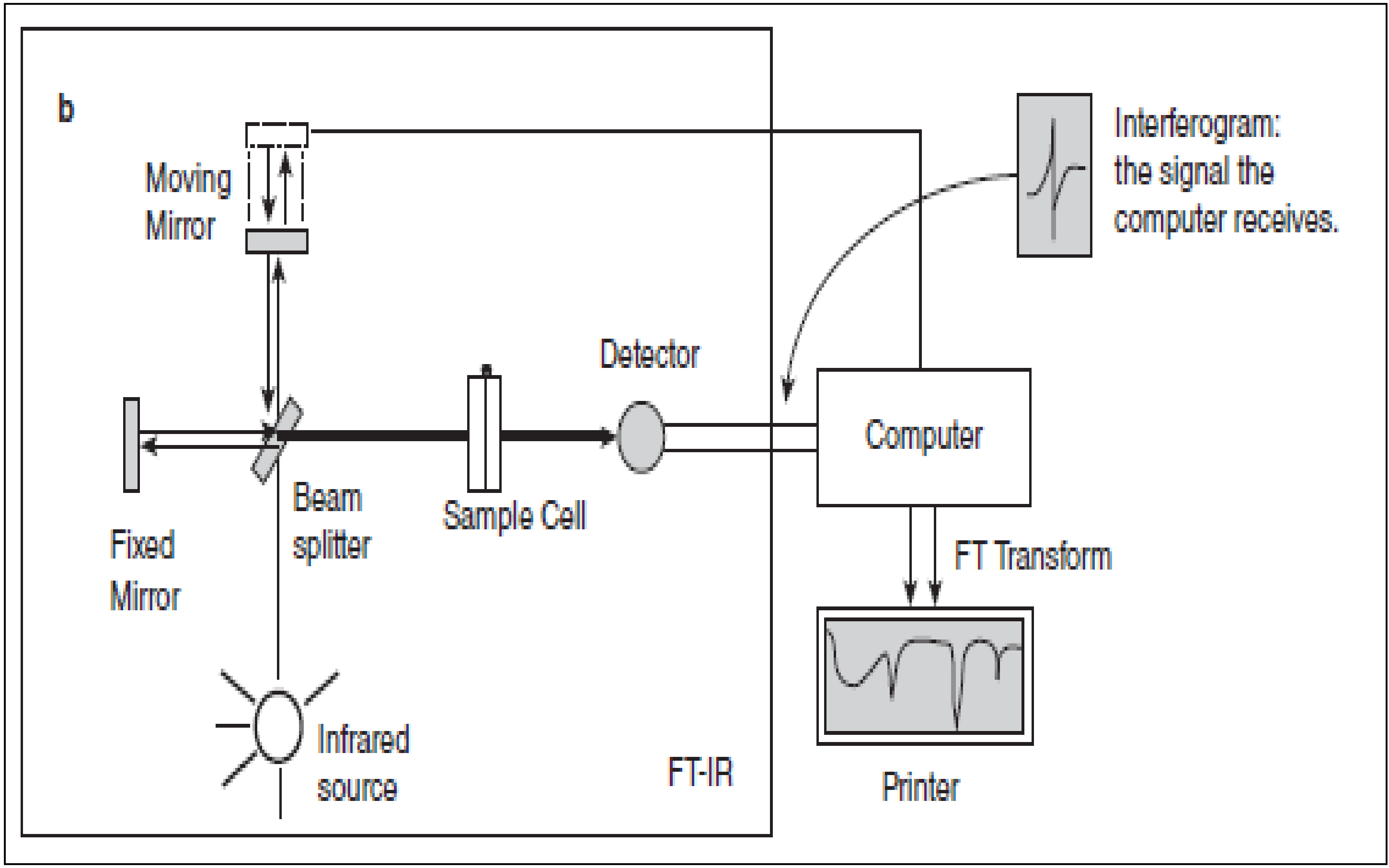
Recorders are used to record the IR spectrum.

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.**

Fourier transform IR spectrometers (FTIR – based on Michelson interferometer)

The beam from source is divided on splitter into two halves; the first is reflected to the fixed mirror, while the second is transmitted to the movable one; the reflected beams are recombined in the splitter again and an interference of waves occurs. For monochromatic radiation, a destructive interference of beams occurs, when $\delta = (n+0,5)\,\lambda$ δ is optical retardation (= two-times the difference between the distance of the fixed mirror to the splitter and the distance of the movable one to the splitter). The constructive interference occurs, when $\delta = \lambda;\ 2\,\lambda; 3\,\lambda; \ldots n\,\lambda$ When polychromatic radiation passes through the interferometer and the sample, the obtained record is an interferogram, which is converted into IR spectrum by Fourier transformation.


b
Moving Mirror
Detector
Interferogram: the signal the computer receives.
Computer
Fixed Mirror
Beam splitter
Sample Cell
FT Transform
Infrared source
FT-IR
Printer

FT-IR Spectrometer

- Uses an interferometer.
- Has better sensitivity.
- Less energy is needed from source.
- Completes a scan in 1-2 seconds.
- Takes several scans and averages them.
- Has a laser beam that keeps the instrument accurately calibrated.

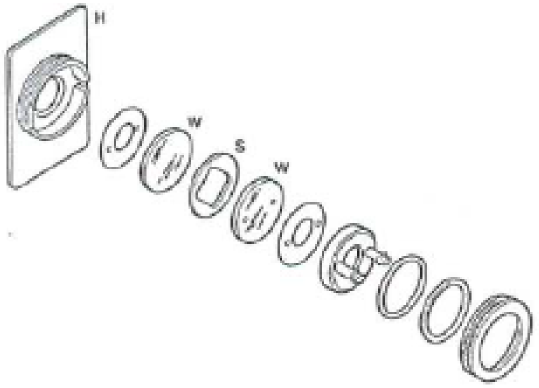
Advantages of FT-IR.

Advantages of FTIR • dispersion elements are not necessary → more energy enters the sample • fast spectrum recording (< 1s) • high resolution (up to 0.01 cm-1)

- **High Speed /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**

Measurement techniques of IR spectroscopy • NaCl, KBr, CaF2, ZnSe, AgCl, TlBr/TlI pro MIR • CsBr, polyethylene (for FIR) • glass, quartz glass (for NIR) Sample types and sample preparation Cells for transmission measurements have windows made of Gaseous samples Cells are firstly evacuated and then filled with a sample; cell path length ranges from 10 cm to 80 m (multiple reflection of the beam inside the cell, outer size of cell is up to 1 m)

Liquid samples



Demountable cell
for liquid samples

For **aqueous solution** it is necessary to use windows made of CaF2 or ZnSe (insoluble in water). The measurement is possible only within the interval of 1400–1000 cm-1, used e.g. for the analysis of sugars in fruit juices based on the measurement of thin films (10–50 m).

Pure liquid samples (e.g. oils) and gels can be measured in a very thin film (1 μm) by transmission technique of by ATR technique

- **FT-IR can be interfaced with chromatographic instrumentation.**

Applications of Infrared (IR) Spectroscopy.

It has been of great significance to scientific researchers in many fields such as:

1- Protein characterization

2-Nanoscale semiconductor analysis

3- Space exploration.

4- Analysis of gaseous, liquid or solid samples.

5- Identification of compounds.

6- Quantitative analysis.

7- Information regarding functional groups of molecules and constitution of molecules 8- can be deduced from IR spectrum

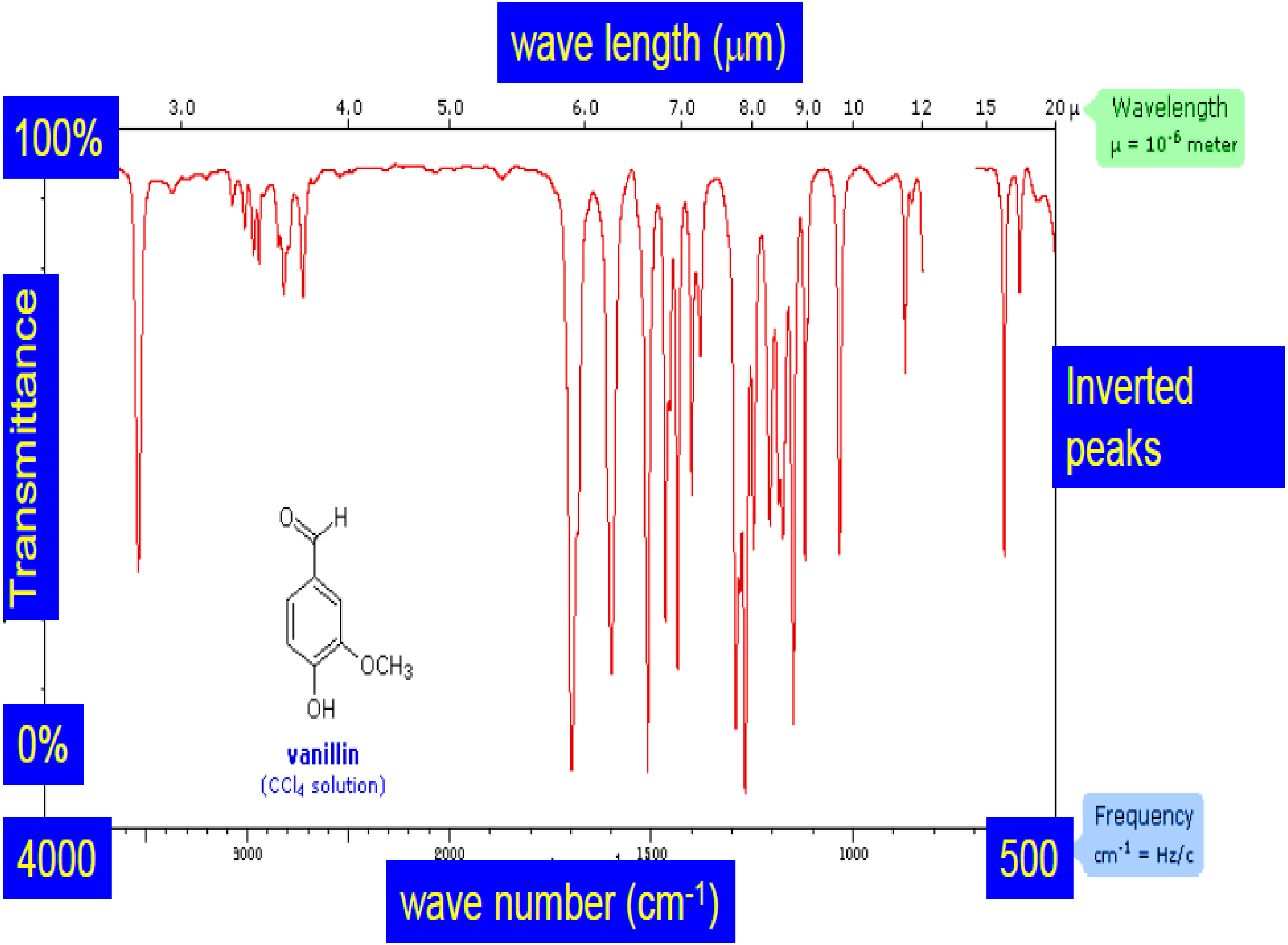
9-To know about interaction among molecules

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).

- Band intensities can be expressed either as **transmittance** (*T*) or **absorbance** (*A*).
- **Transmittance** : T= I/I0 (Intensity of light out/intensity of incident light)
- **Absorbance**: A= log10 (1/T)


wave length (μm)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
15
20 μ
Wavelength
μ = 10⁻⁶ meter
100%
Transmittance
0%
Inverted peaks
O
H
OCH3
OH
vanillin
(CCl4 solution)
4000
3000
2000
1500
1000
500
Frequency
cm⁻¹ = Hz/c
wave number (cm⁻¹)

No two compounds have identical IR spectrum, except enantiomers.

The inverted display of absorption compared with UV-Visible, is characteristic of IR spectra.

Thus a sample that did not absorb at all would record a horizontal line at 100%

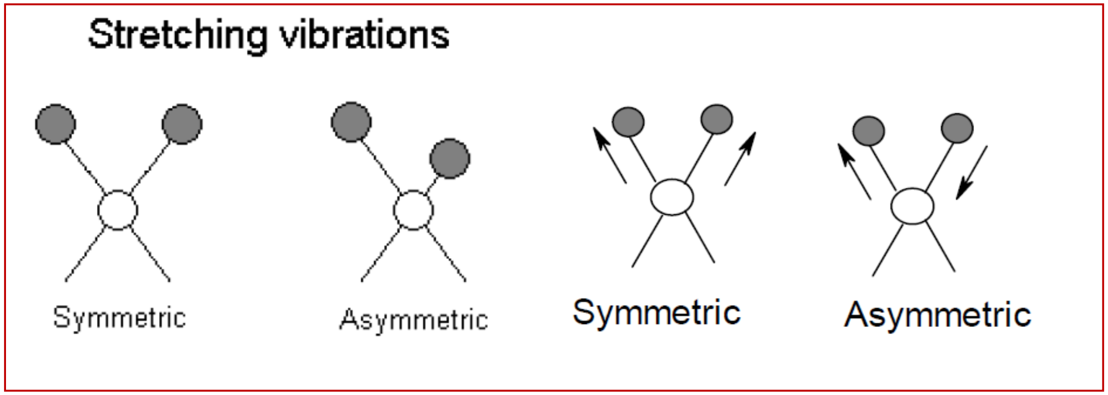
The frequency scale at the bottom of the chart is given in units of reciprocal centimetres (cm^{-1}) rather than Hz, because the numbers are more manageable.

$$\tilde{\nu} = \nu/c$$

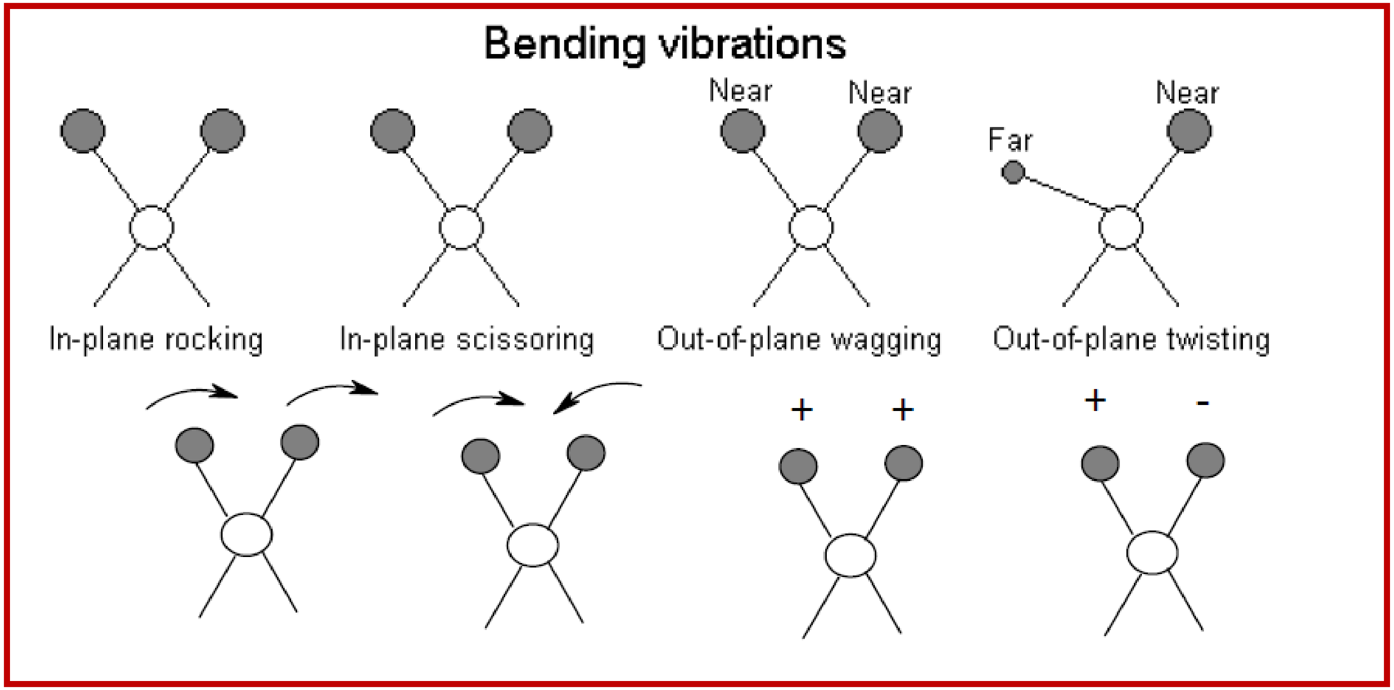
Band intensities are described as **w** (for **weak**), **m** (for **medium**) and **s** (for **strong**).

Types of Molecular Vibration.

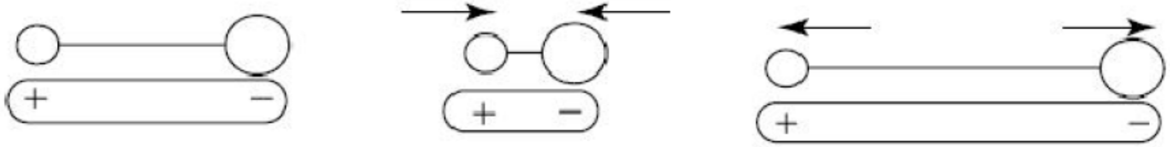
- **Two types** of molecular vibration:
- 1) Stretching:- a rhythmic movement along the bond axis such that the interatomic distance is **increased** or **decreased .**


Stretching vibrations
Symmetric
Asymmetric
Symmetric
Asymmetric

2) Bending:- a change in bond angle between bonds with a common atom or the **movement of a group of atoms** with respect to the remainder of the molecule, with out movement of the atoms in the group with respect to one another.


Bending vibrations
Near
Near
Far
Near
In-plane rocking
In-plane scissoring
Out-of-plane wagging
Out-of-plane twisting
+
+
+
-

Only those vibrations that result in rhythmical change of dipole moment of the molecule are observed in IR.



Homonuclear diatomic molecules such as H_2 or O_2 do not **absorb IR radiation** (they are IR-inactive), since there is no over-all electric (Dipole) moment in the molecule.

O – O

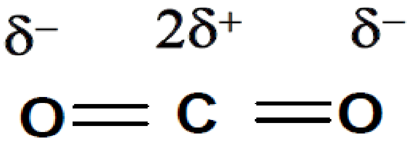
No dipole moment

$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{Cl}}$

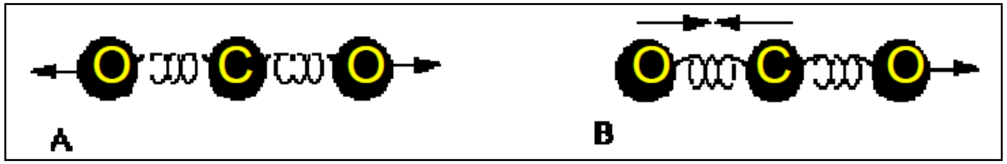
$+\!\!\!\longrightarrow$

HCl, H_2O, NO	Atoms, O_2, H_2, Cl_2
IR active	IR inactive

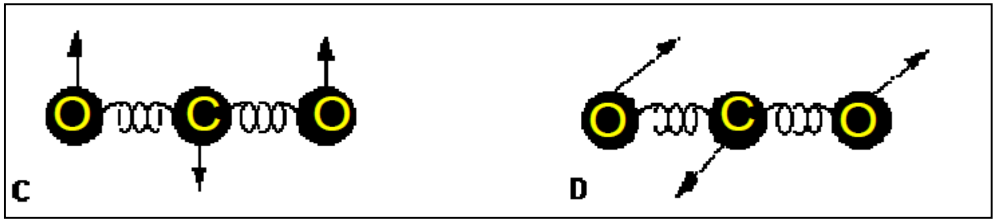
It is not necessary for polyatomic molecules to possess permanent dipole moment in order exhibit IR absorption, provided that some polar bonds are present in the molecule.



$$\overset{\delta^-}{O}=\overset{2\delta^+}{C}=\overset{\delta^-}{O}$$



Symmetrical stretching **Anti-symmetrical stretching**



In plane bending Out of plane bending

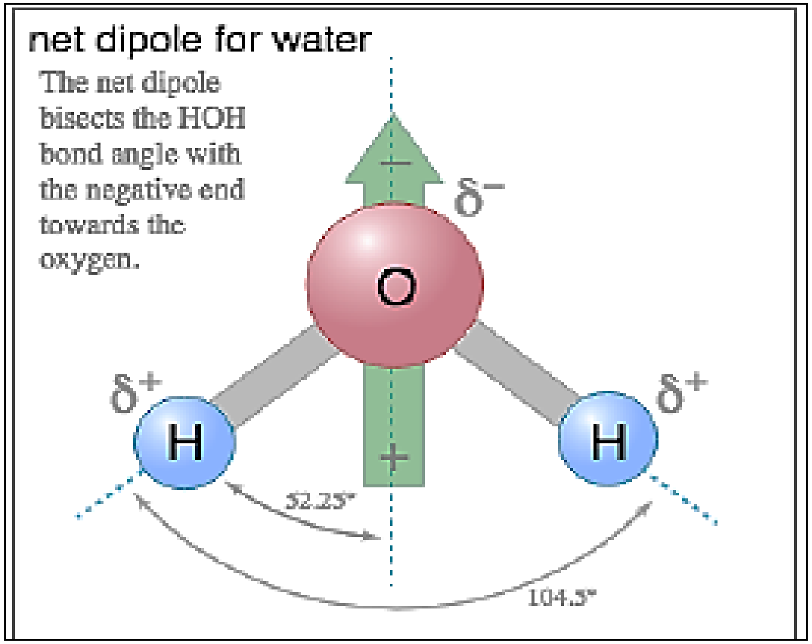
- A is not IR active
- B, C and D are **IR active**
- Its positive and negative electrical centres are no longer coincident,
- A dipole moment is **temporarily induced**.

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.



net dipole for water

The net dipole bisects the HOH bond angle with the negative end towards the oxygen.

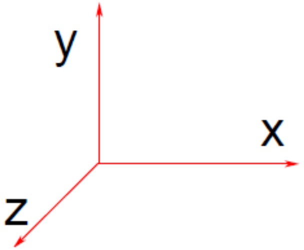
Fundamental Vibrations

- Molecules of n atoms will have 3n degrees of freedom.
- Since its atoms may have its movement resolved along x, y and z **axes**.
- Movement of the whole molecule as a rigid unit
- will take up six of these degrees of freedom,
- three translational and three rotational
- (**two rotational** in the case of linear molecules).
- So, for vibrational motions where atoms move relative to each other, we

have 3n-6 (3n-5 for linear molecules) **fundamental vibrations**

- (vibrations responsible for number of theoretically

expected absorption bands in IR



H_2O

Three atoms (non-linear).

- 3 X 3= **9 degrees of freedom**.
- 3n-6 (fundamental vibrations).
- 9 - 6 = 3 (fundamental vibrations).

CO_2

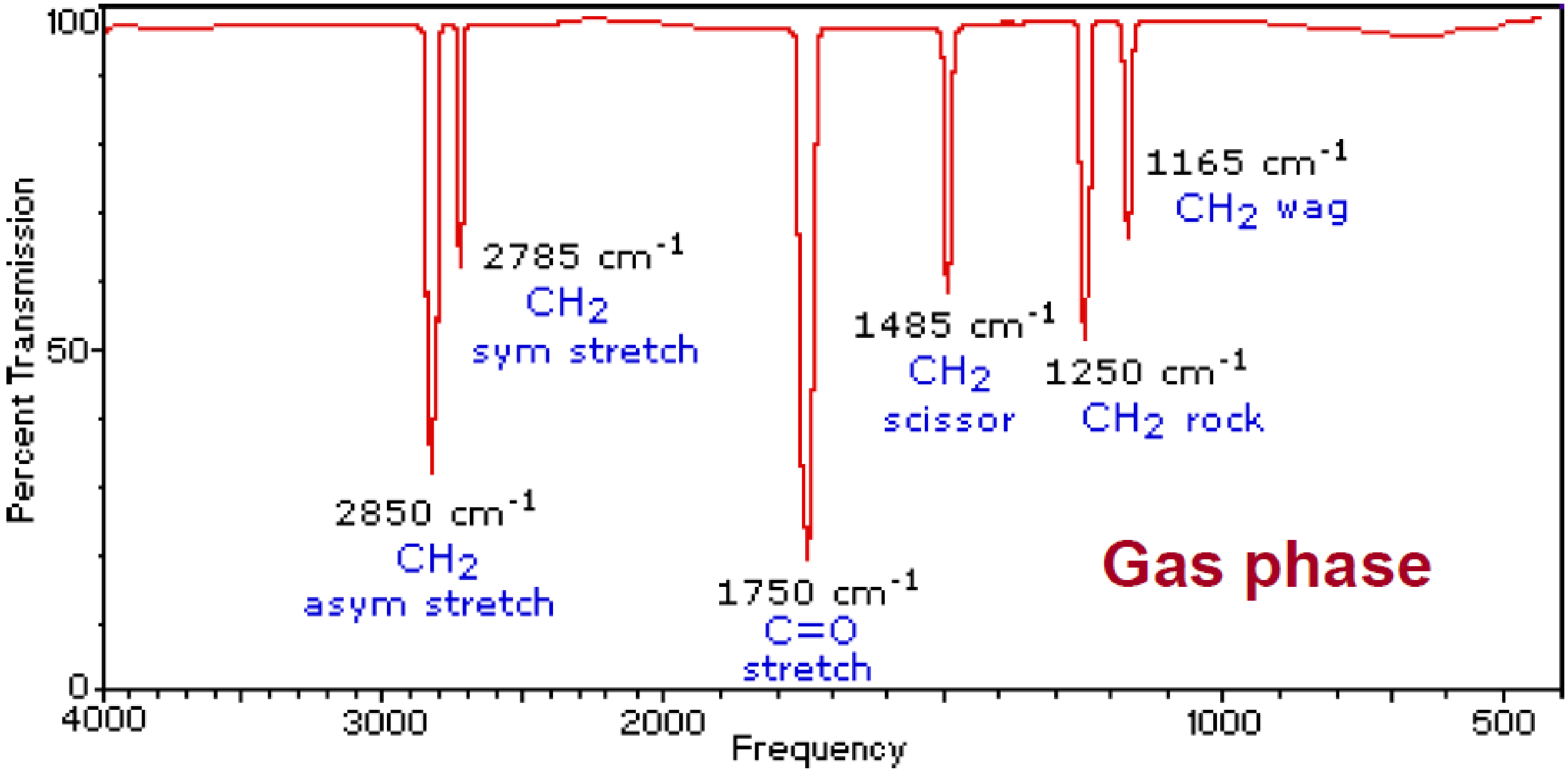
- Three atoms (linear).
- 3 X 3 = **9 degrees of freedom**.
- 3n-5 (fundamental vibrations).
- 9 - 5 = 4 (fundamental vibrations).

Formaldehyde, H2C=O

Four atoms (non-linear).

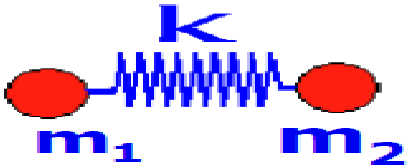
3 X 4= **12 degrees of freedom**.

12 - 6 = 6 (fundamental vibrations



Simple Harmonic Oscillator

1st Approximation, a covalent bond behaves as a weightless spring and obeys Hooke’s Law :- the **restoring force** acting upon it when it is stretched is **proportional** to the **degree of stretching.**



A molecule can be regarded as a collection of balls and springs, where the balls are the atoms and the springs are the chemical bonds.

Hooke’s law

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

μ is the reduced mass

$\bar{\nu}$ **:**wave number of the stretching vibration

k = The force constant (**bond strength**)

m1, m2 = masses of atoms joined by the bond

c = speed of light

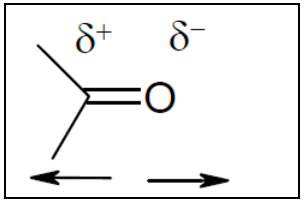
single bond 5 x105 dyne/cm
double bond 10 x105 dyne/cm
triple bond 15 x105 dyne/cm

Band Intensity:

Described as w (for weak), m (for medium) and s (for strong).

- One selection rule that influences the intensity
- is that a change in dipole moment should occur for a vibration to absorb infrared radiation.
- Absorption of **C=O bond** stretching are usually very strong.

because a large change in the dipole moment takes place in that mode



Some General Trends

i) Stretching frequencies are higher than the corresponding **bending frequencies**.

- (It is easier to bend a bond than to stretch or compress it)

ii) Asymetrical stretching frequencies are higher than **symmetrical stretching** frequencies

iii) Bonds to hydrogen have higher stretching frequencies than those to **heavier atoms**.

iv) Triple bonds have higher stretching frequencies than **double bonds**, which in turn have higher frequencies than single nods (except for bonds to hydrogen).

The 1450 to 666 cm^{-1} region is complex.

- It is difficult to assign all the absorption bands. Because of the unique patterns, this region is often called the **fingerprint** region.
- It is characteristic of the molecule as a whole;• useful as **confirmatory evidence** than i**dentification**.

• Absorption bands in the 4000 to 1450 cm^{-1}

region are usually due to stretching vibrations of **diatomic units**, and this is sometimes called:

- The **group frequency** region.
- Useful for **identification of functional groups**.

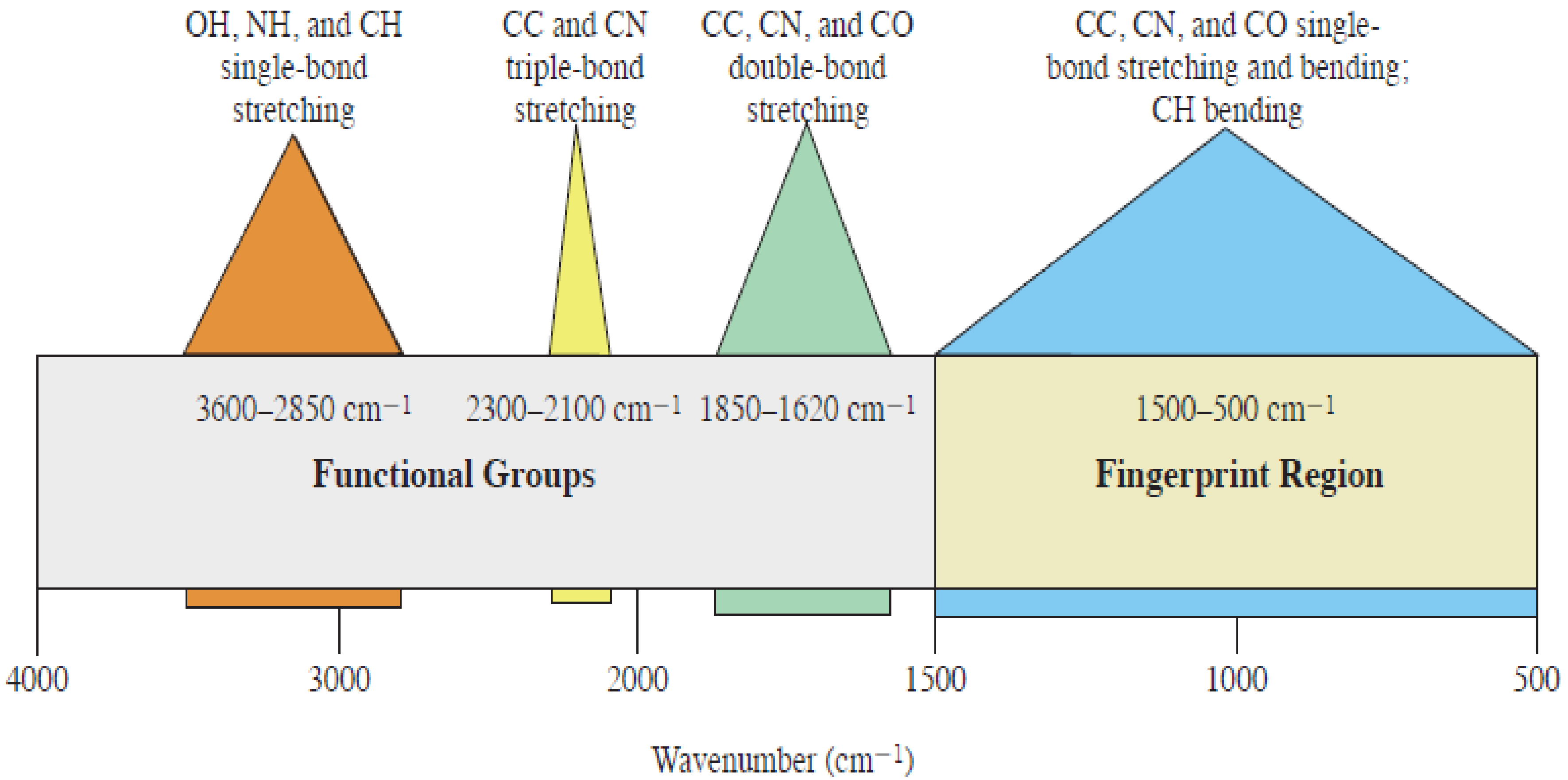
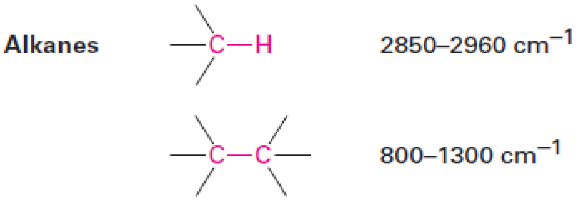

OH, NH, and CH single-bond stretching
CC and CN triple-bond stretching
CC, CN, and CO double-bond stretching
CC, CN, and CO single-bond stretching and bending; CH bending
3600–2850 cm−1
2300–2100 cm−1
1850–1620 cm−1
1500–500 cm−1
Functional Groups
Fingerprint Region
4000
3000
2000
1500
1000
500
Wavenumber (cm−1)

Figure : Structural units are commonly found in specific regions of the infrared spectrum.

The region below 1500 cm-1 is the fingerprint portion of the IR spectrum. A large number of absorptions due to a variety of C-C, C - O, C -N, and C -X single-bond vibrations occur here.

Characteristic Group Frequencies


Alkanes
C—H
2850–2960 cm−1
C—C
800–1300 cm−1

Alkanes

Two types of bonds (**C-H** and **C-C**) Spectra can be interpreted in terms of **four vibrations:**

1) C-H stretching (2850 to 2960 cm-1)

2) C-H bending

3) C-C stretching (are weak, and appear in the broad region (**800-1300 cm^{-1}**)

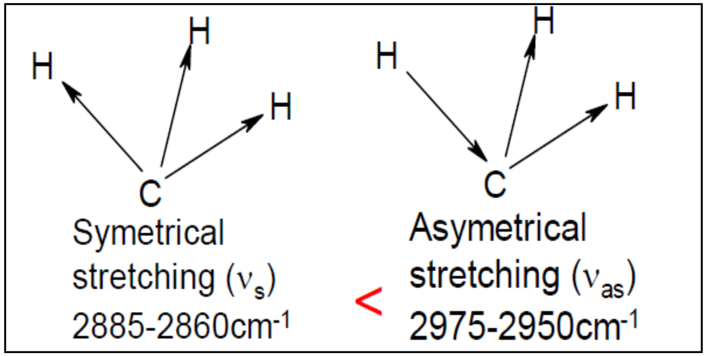
C-C stretching is of **little value** for identification.

4) **C-C bending** (**below 500 cm^{-1}**, do not appear in normal spectra).

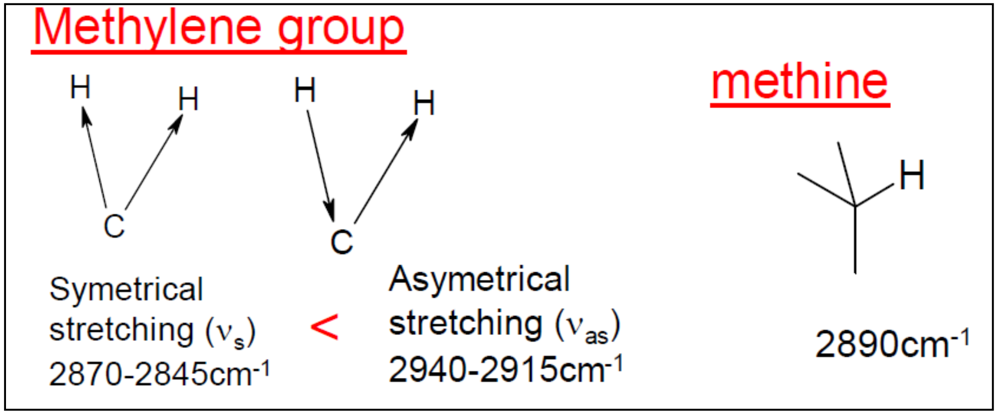
- Thus the **most characteristic** vibrations are those of **C-H stretching** and **C-H bending**.

C-H Stretching Vibration (n)

Methyl group

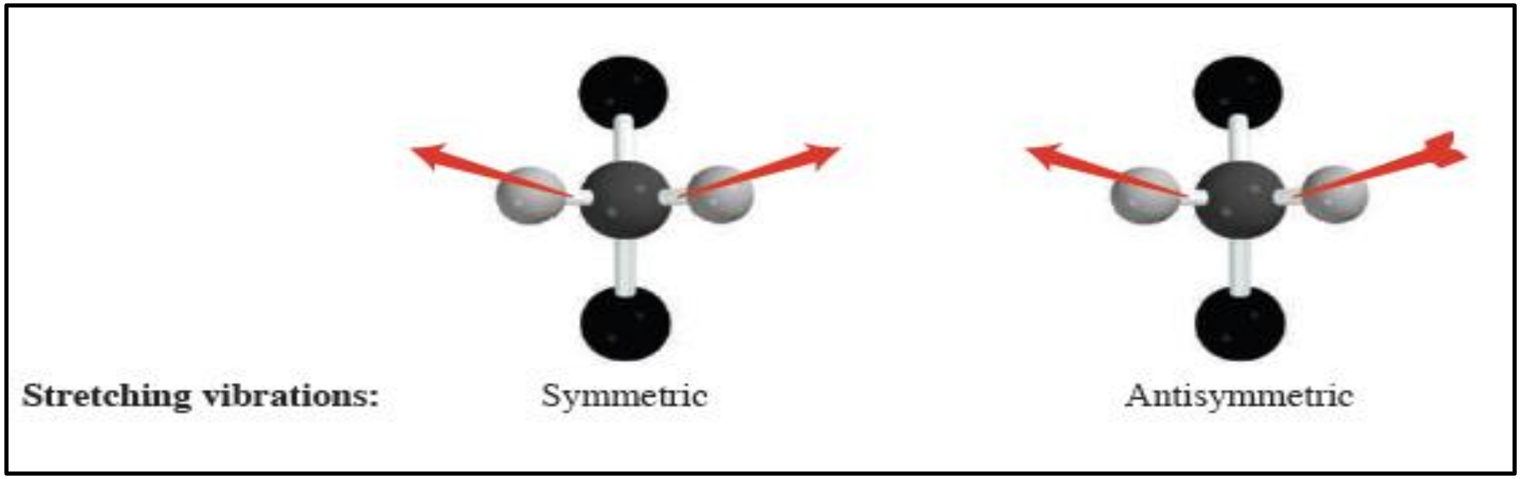


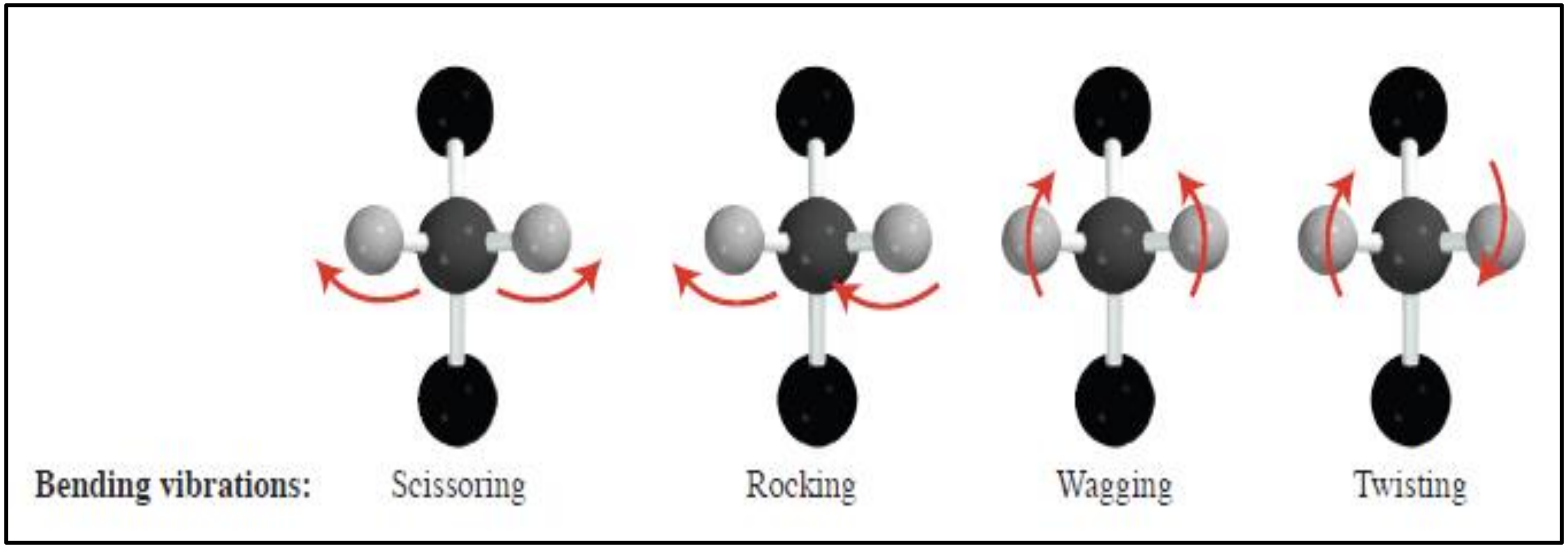
Symetrical stretching (ν_s) 2885-2860cm^{-1} < Asymetrical stretching (ν_{as}) 2975-2950cm^{-1}


Methylene group
H
H
C
H
H
C
methine
H

Symetrical stretching (ν_s) 2870-2845cm^{-1} < Asymetrical stretching (ν_{as}) 2940-2915cm^{-1}

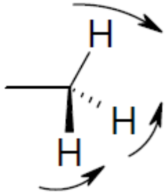
2890cm^{-1}


Stretching vibrations:
Symmetric
Antisymmetric

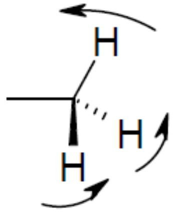

Bending vibrations:
Scissoring
Rocking
Wagging
Twisting

C-H bending vibration.

Methyl group

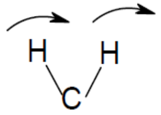


Symetrical bending (δ_s) *ca.* 1375cm^{-1}

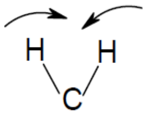


Asymetrical bending (δ_{as}) *ca.* 1450cm^{-1}

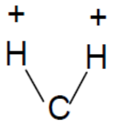
Methylene group



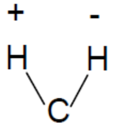
rocking
720-725cm^{-1}



scissoring
1470-1465cm^{-1}

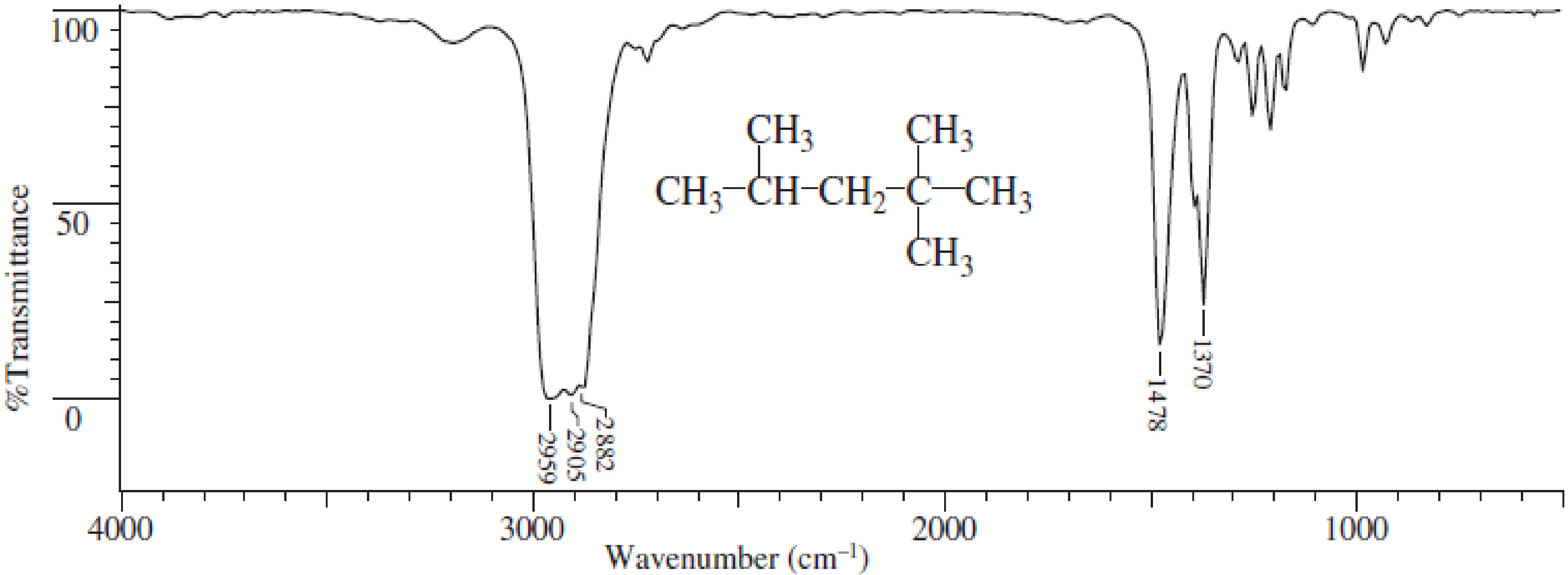


wagging



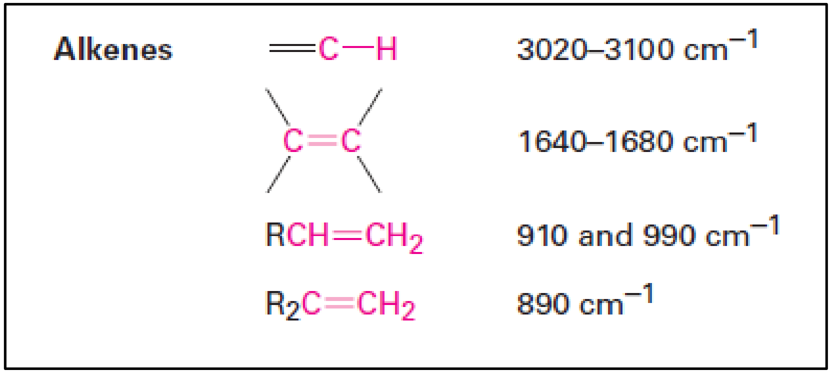
twisting

1390-1350cm^{-1}

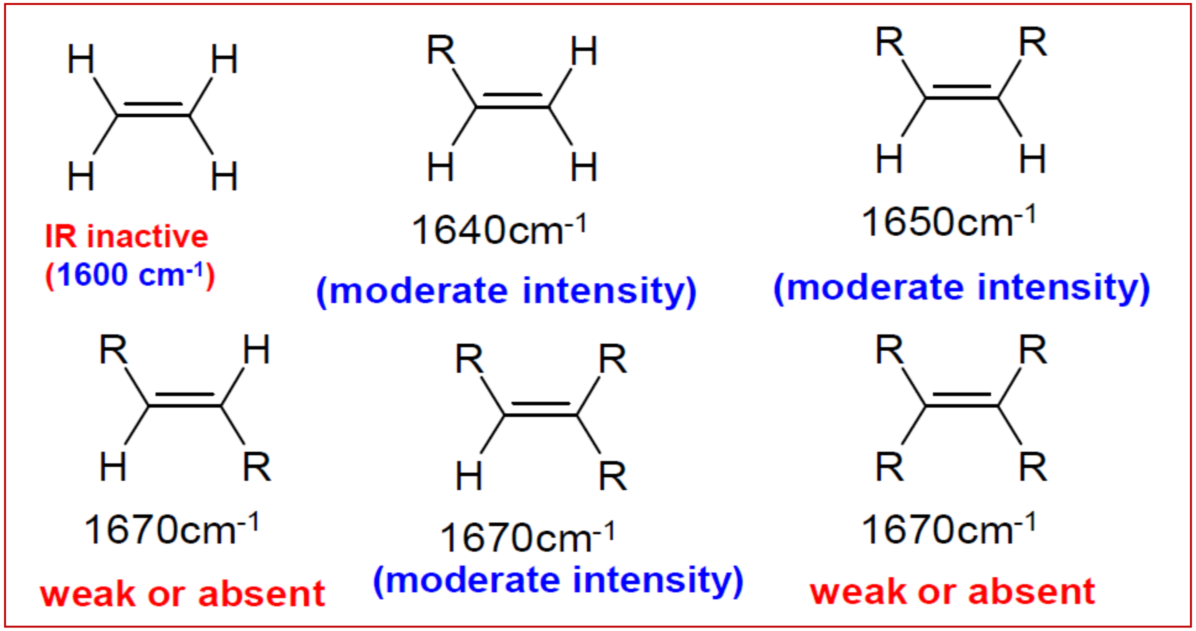


Alkenes.

Alkenes show several characteristic stretching absorptions. Vinylic C –H bonds absorb from 3020 to 3100 cm-1, and alkene C=C bonds usually absorb near 1650 cm-1,



Alkenes		
	$=C-H$	3020–3100 cm^{-1}
	$C=C$	1640–1680 cm^{-1}
	$RCH=CH_2$	910 and 990 cm^{-1}
	$R_2C=CH_2$	890 cm^{-1}



IR inactive
(1600 cm^{-1})

1640cm^{-1}
(moderate intensity)

1650cm^{-1}
(moderate intensity)

1670cm^{-1}
weak or absent

1670cm^{-1}
(moderate intensity)

1670cm^{-1}
weak or absent

More alkyl substitution, shift towards **high frequency,** due to more **coupling interaction** between **C=C** and **C-C** vibrational frequencies .

Alkenes have characteristic C-H out-of-plane bending absorptions in the 700 to 1000 cm-1 range, thereby allowing the substitution pattern on a double bond to be determined **(Figure)**. For example, monosubstituted alkenes such as 1-hexene show strong characteristic bands at 910 and 990 cm21, and 1,1-disubstituted alkenes (R2C = CH2) have an intense band at 890 cm-1

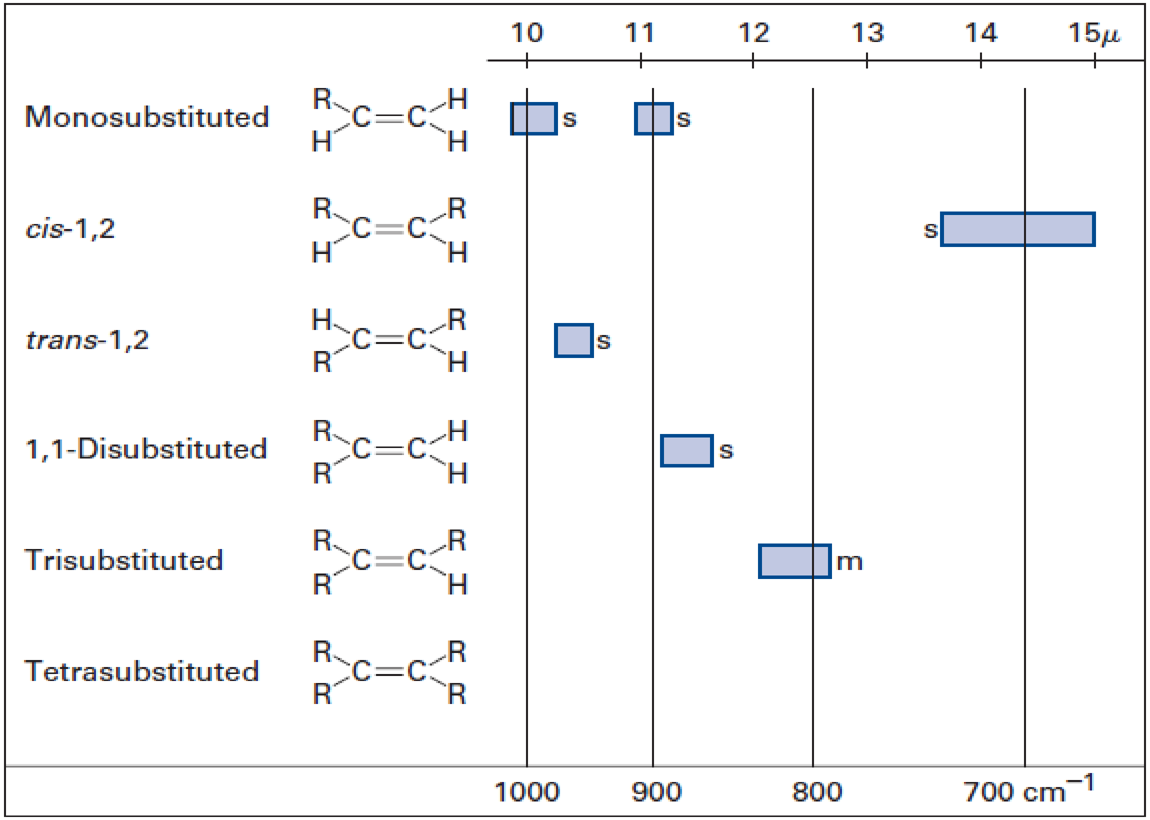
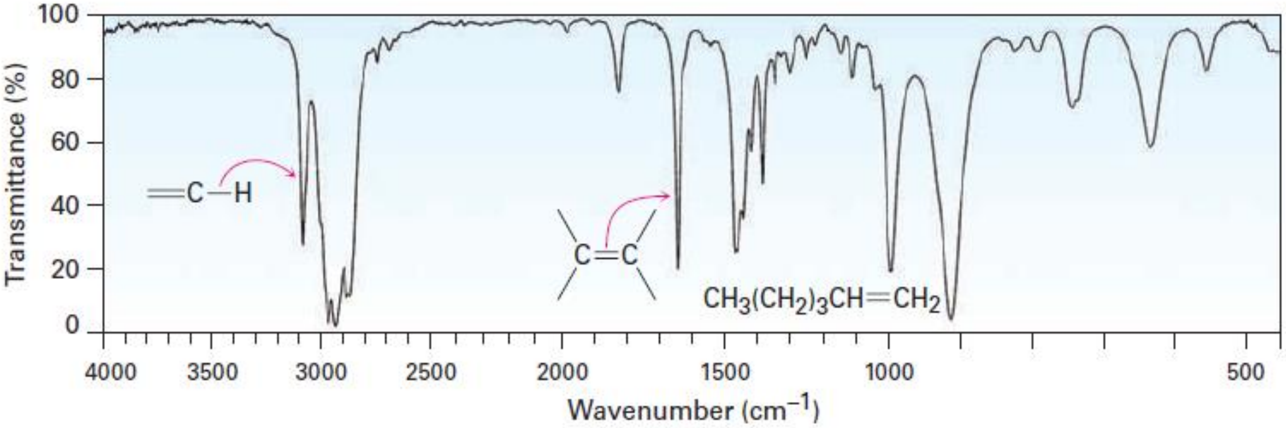
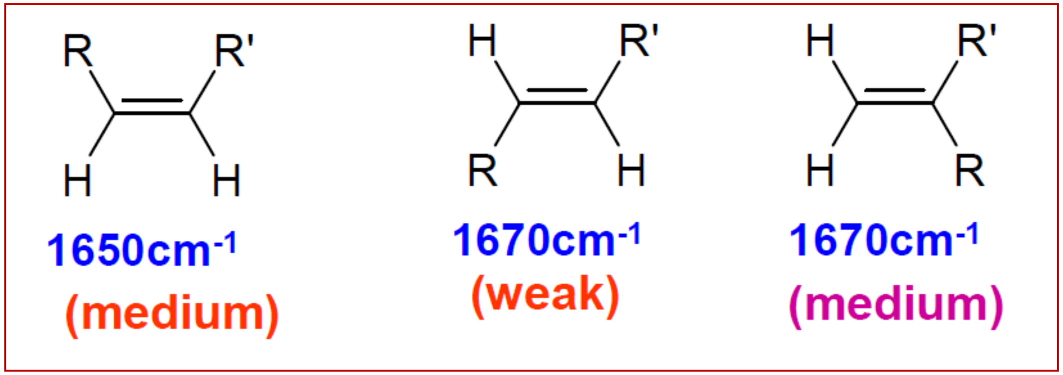


Figure C - H out-of-plane bending vibrations for substituted alkenes.





1650cm^{-1} (medium)

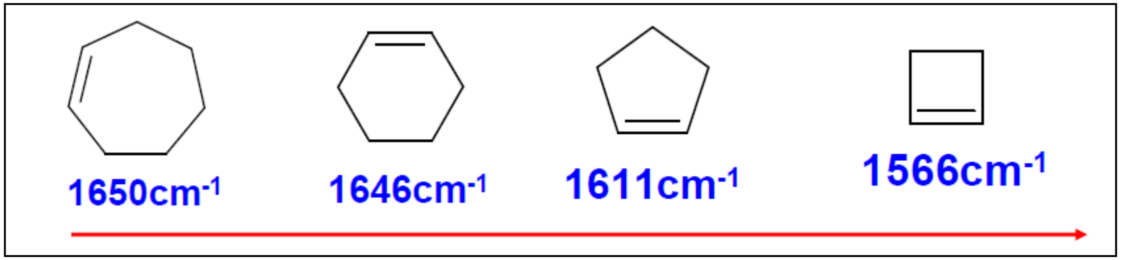
1670cm^{-1} (weak)

1670cm^{-1} (medium)

cis*-**double bonds which lack the symmetry of the ***trans structure absorb more strongly.

Internal double bonds absorb more weakly , than **terminal double bonds,** because of *pseudo*-symmetry

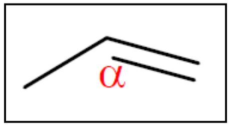
Cycloalkenes



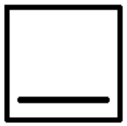
1650cm^{-1} 1646cm^{-1} 1611cm^{-1} 1566cm^{-1}

Decreasing bond angle Decreasing order of C=C stretching frequency

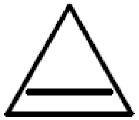
The C=C stretching vibration is **coupled** with **C-C stretching vibration** of the adjacent bonds. Coupling is dependent on bond angle α



As the angle (α) becomes smaller the coupling interaction becomes less until it is minimum at 90° (the attached C-C bond is orthogonal to C=C bond) In cyclopropene,



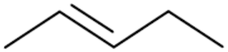
$1566\,cm^{-1}$



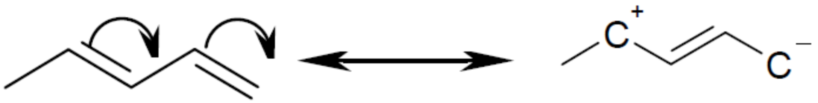
$1641\,cm^{-1}$

In cyclopropene , interaction becomes again appreciable ($1641cm^{-1}$) .The C=C vibration is **strongly coupled** to the attached C-C single bond vibration .

Effect of Conjugation



$1670cm^{-1}$



$1630cm^{-1}$

Conjugation of a double bond provides a **single bond character** through resonance, which lowers force constant K, thus a **lower frequency** of vibration .

Alkynes

Contains $C\equiv C$ group

Three characteristic bands are present 1- $C\equiv C$ stretching

2100 to 2260 cm-1

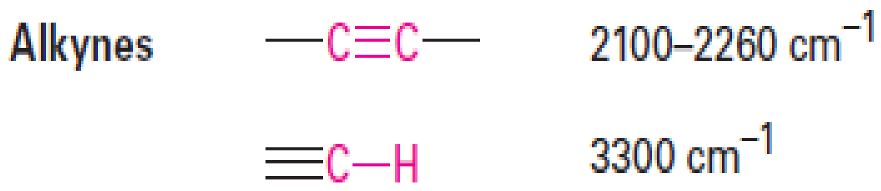
In symmetrical substituted alkynes $R-C\equiv C-R$ stretching vibration is **not observed**

Even in non-symmetrical substituted alkynes $R-C\equiv C-R$ stretching vibration is **very weak,** due to ***psudo*-symmetry** Only in **mono-substituted** alkynes this is observed

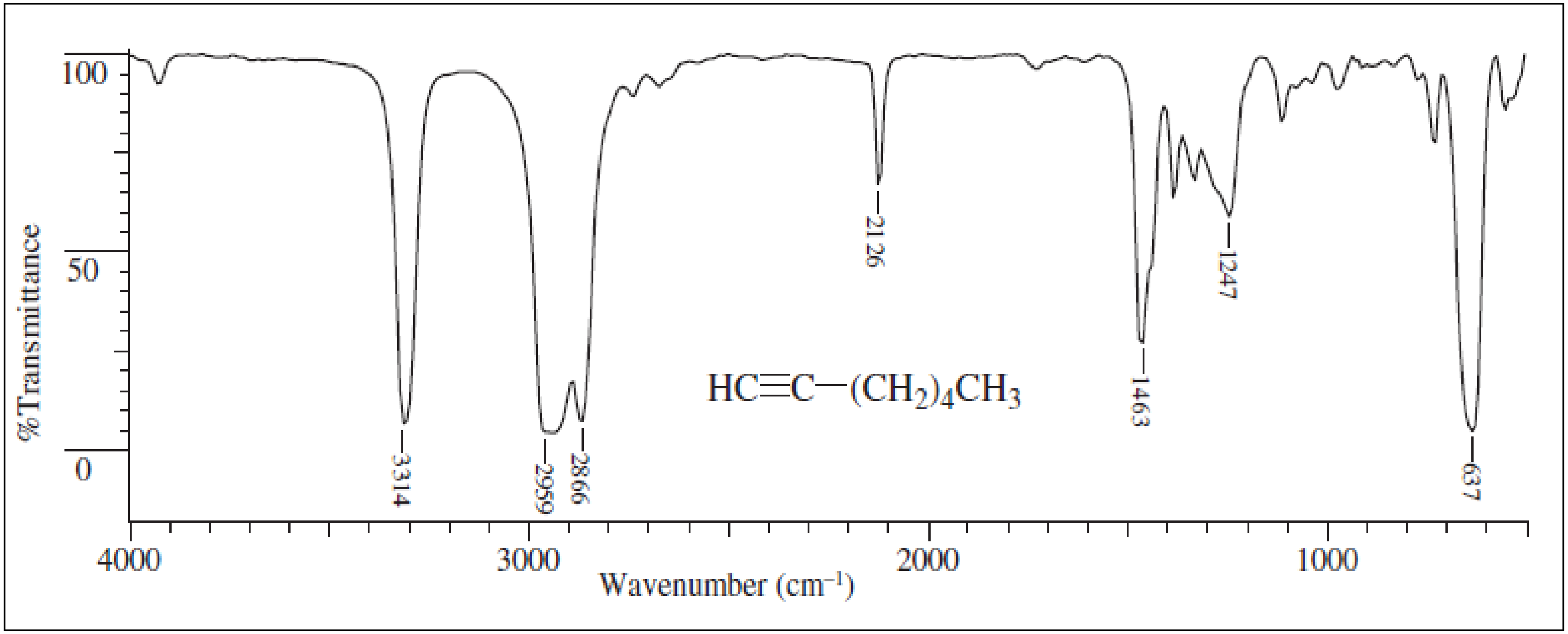
2) C-H stretching $C\equiv C-H$ **(3250-3300 cm^{-1})**

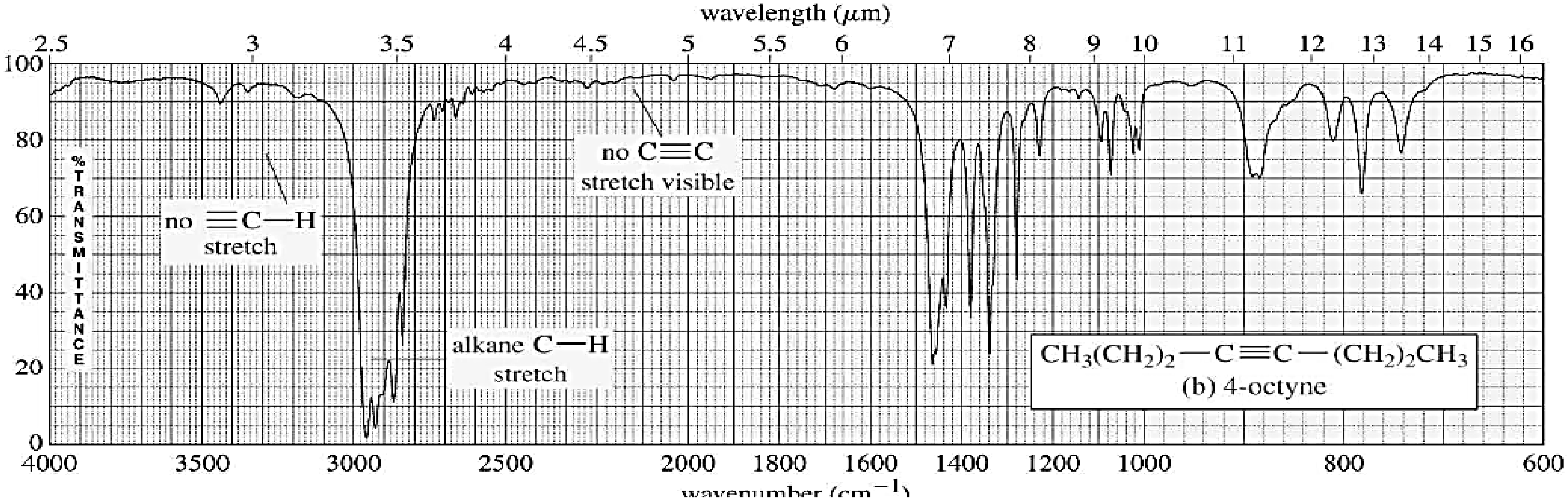
Narrower than hydrogen-bonded O-H and N-H bands which occurring in the same region.

3) C-H bending $C\equiv C-H$ **(600-700 cm^{-1})** Observed in mono-substituted acetylenes (Strong band).



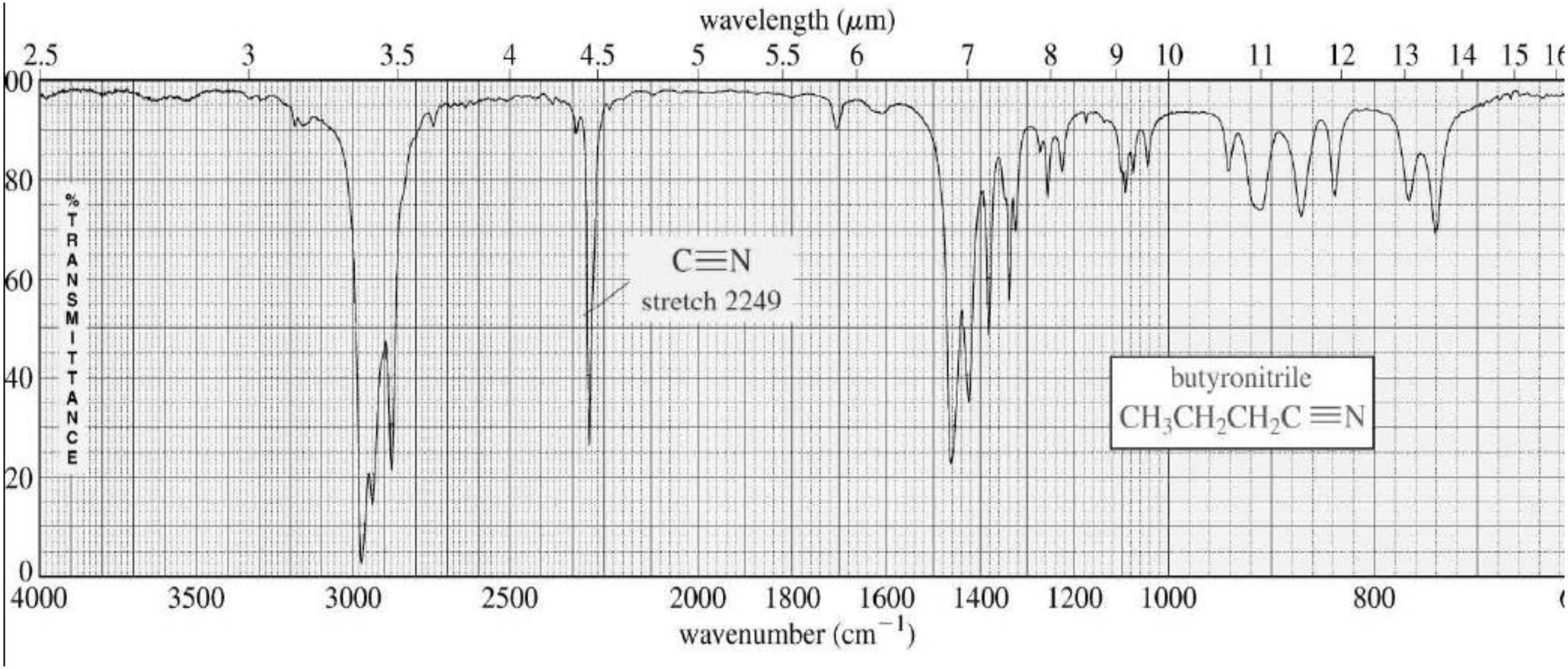
Alkynes	$-C\equiv C-$	2100–2260 cm^{-1}
	$\equiv C-H$	3300 cm^{-1}


100
50
0
% Transmittance
3314
2959
2866
2126
1463
1247
637
HC≡C—(CH2)4CH3
4000
3000
2000
1000
Wavenumber (cm−1)


wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
no ≡C—H stretch
no C≡C stretch visible
alkane C—H stretch
CH3(CH2)2—C≡C—(CH2)2CH3
(b) 4-octyne
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm−1)

Nitriles (cyano group)

- The spectra of nitriles ($-C\equiv N$) are characterized by weak-to-medium absorption in the triple bond stretching region of the spectrum. Aliphatic nitriles absorb at 2240- **2280 cm^{-1}**.
- Conjugation, such as occurs in aromatic nitriles, reduces the wavenumber of absorption to **2240- 2222 cm^{-1}** and enhances the intensity.



Why do different functional groups absorb where they do? As noted previously, a good analogy is that of two weights (atoms) connected by a spring (a bond). This type of system is a harmonic oscillator. In a harmonic oscillator, when a bond vibrates, its energy of vibration is continually and periodically changing from kinetic to potential energy and back again. The total amount of energy is proportional to the frequency of the vibration,

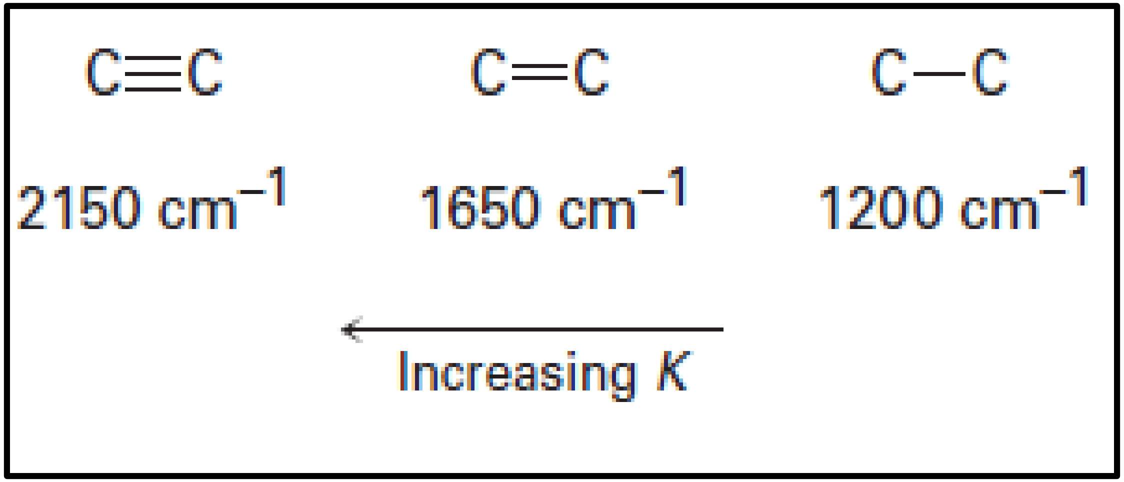
$$E_{\mathrm{osc}} \propto h\nu_{\mathrm{osc}}$$

The vibrational frequency of a harmonic oscillator is inversely proportional to the reduced mass of the oscillator, *m*, and is directly proportional to the stiffness (strength) of the spring, *K*. The natural frequency of vibration of a bond is given by the equation

$$\boxed{\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}}$$

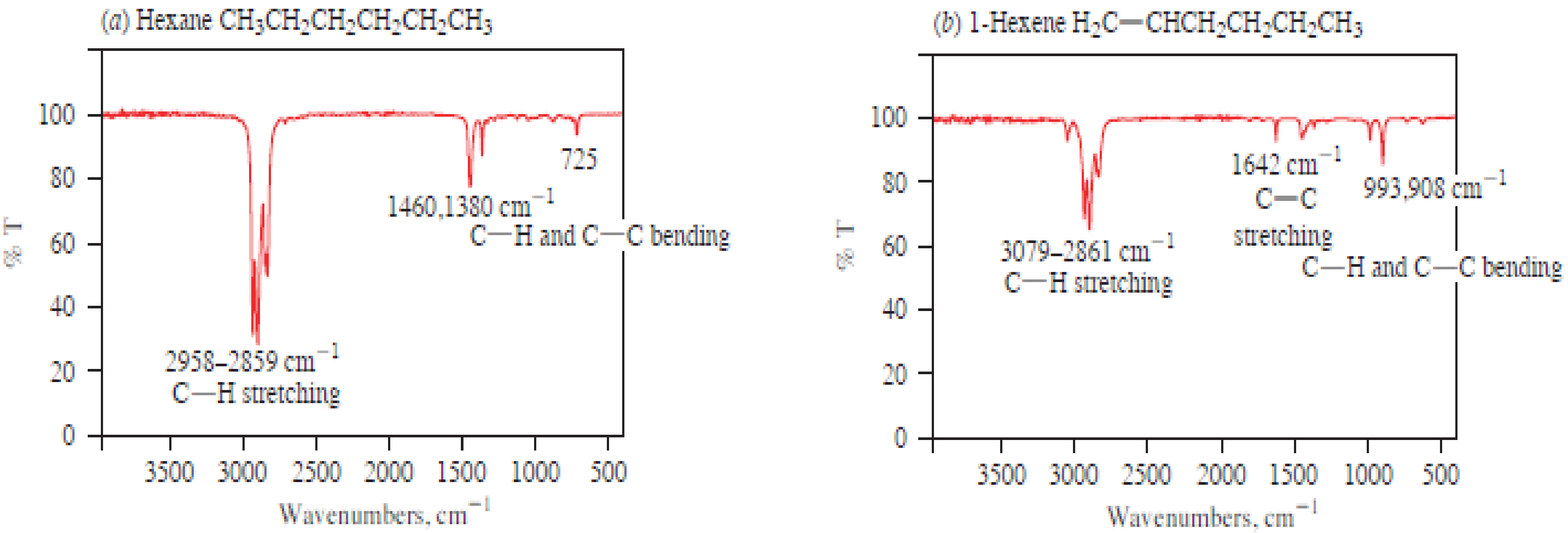
Springs connecting small weights vibrate faster than springs connecting large weights. Short, strong bonds vibrate at a higher energy and higher frequency than do long, weak bonds, just as a short, strong spring vibrates faster than a long, weak spring.

Thus, triple bonds absorb at a higher frequency than double bonds, which in turn absorb at a higher frequency than single bonds. In addition, C-H, O - H, and N -H bonds vibrate at a higher frequency than bonds between heavier C, O, and N atoms.



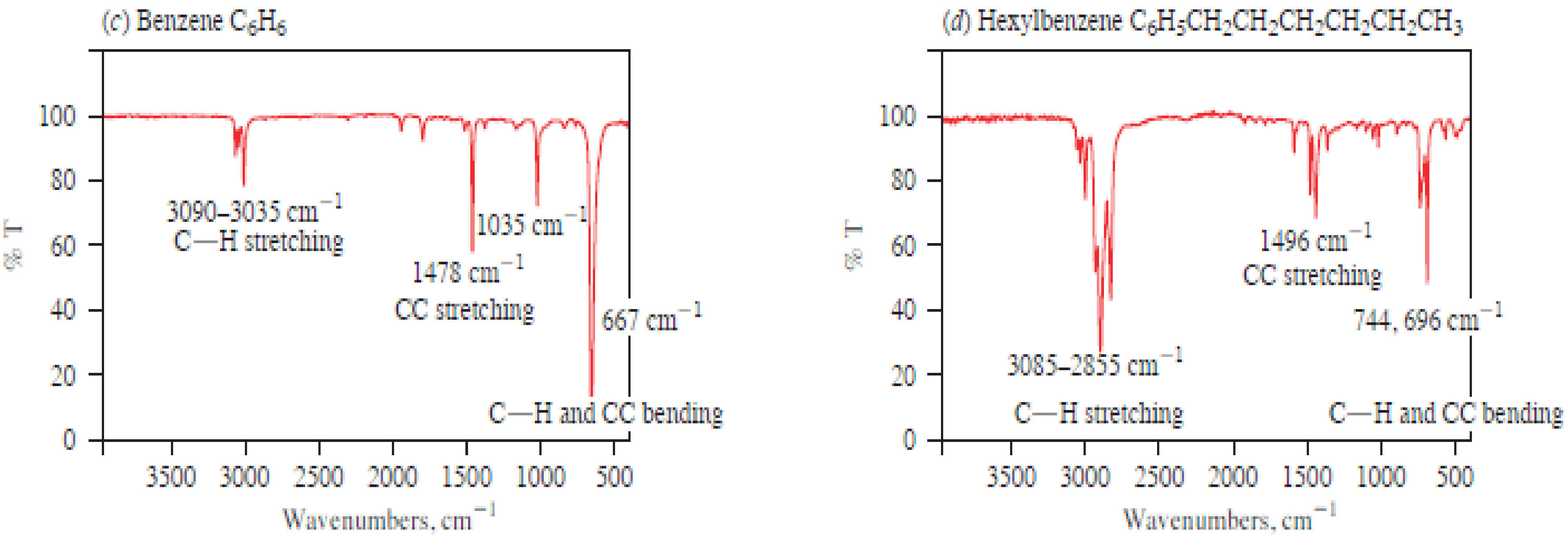
$C\equiv C$	$C=C$	$C-C$
$2150\ cm^{-1}$	$1650\ cm^{-1}$	$1200\ cm^{-1}$

$\longleftarrow$ Increasing K



(*a*) Hexane $CH_3CH_2CH_2CH_2CH_2CH_3$

(*b*) 1-Hexene $H_2C{=}CHCH_2CH_2CH_2CH_3$



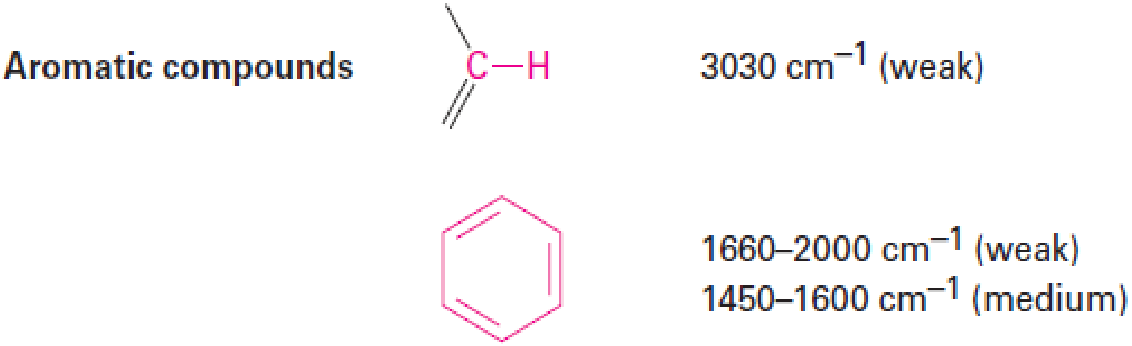
(*c*) Benzene C_6H_6

(*d*) Hexylbenzene $C_6H_5CH_2CH_2CH_2CH_2CH_2CH_3$

Aromatic Compounds

Aromatic compounds, such as benzene, have a weak C - H stretching absorption at 3000 - 3100 cm-1, just to the left of a typical saturated C - H band. In addition, they have a series of weak absorptions in the 1660 to 2000 cm-1 range and a series of medium-intensity absorptions in the 1450 to 1600 cm-1 region C=C .

These latter absorptions are due to complex molecular motions of the entire ring. The C - H out-of-plane bending region for benzene derivatives, between 650 to 1000 cm-1, gives valuable information about the ring's substitution pattern, as it does for the substitution pattern of alkenes



Aromatic compounds	C—H	3030 cm^{-1} (weak)
		1660–2000 cm^{-1} (weak) 1450–1600 cm^{-1} (medium)

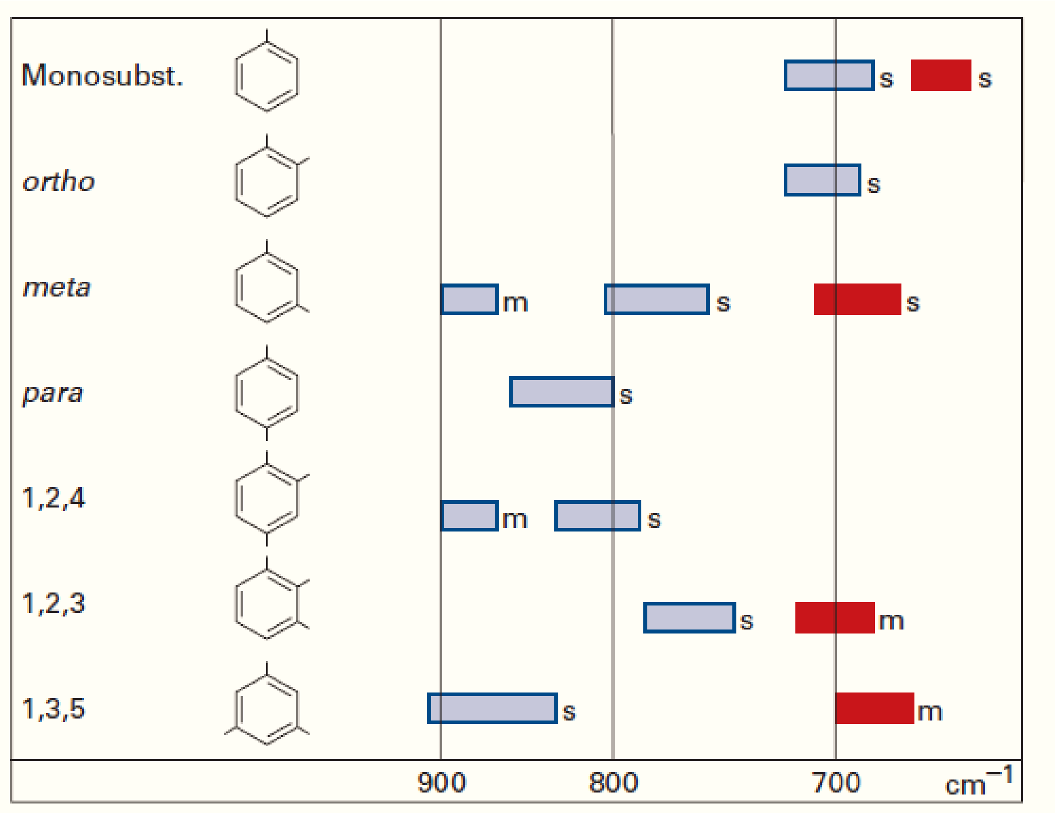
Bands of the out-of-plane bending in substituted benzene.

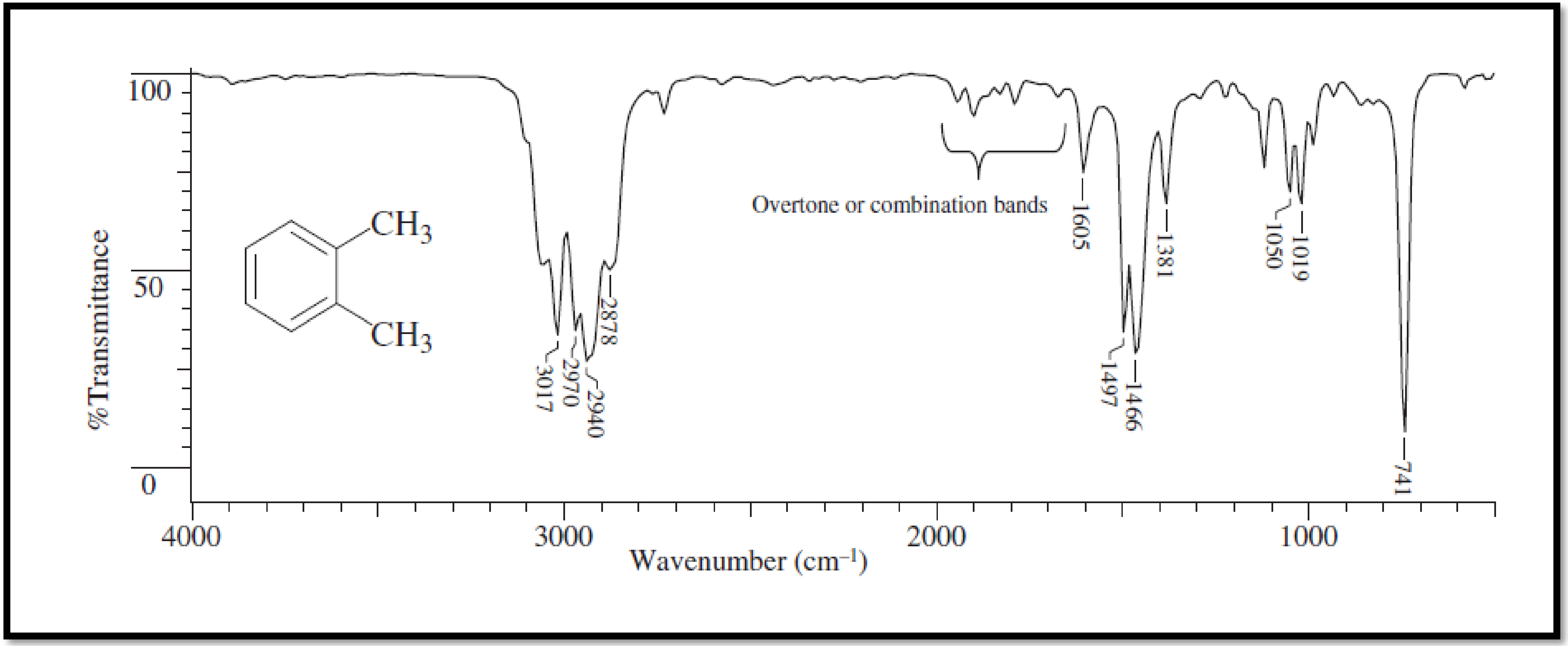
The =C-H oops bands are usually intense

- **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**
- 800-850 cm^{-1} (st)
- **Combination and overtones**
- mono, di, tri, tetra, penta or hexsubstitutes



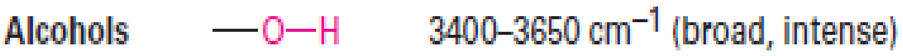


100
50
0
%Transmittance
CH$_3$
CH$_3$
3017
2970
2940
2878
Overtone or combination bands
1605
1497
1466
1381
1050
1019
741
4000
3000
2000
1000
Wavenumber (cm^{-1})

Alcohols and Phenols

- Characteristic bands due to O-H and C-O stretching.

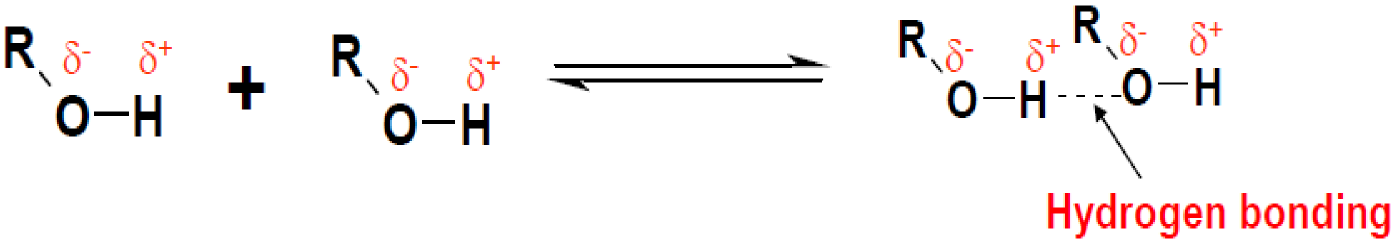
O-H stretching



Alcohols —O—H 3400–3650 cm^{-1} (broad, intense)

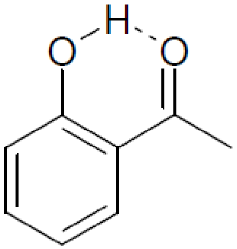
- Effected by **hydrogen bonding .**
- Free' hydroxyl groups absorb between 3585- 3650 cm^{-1} (**strong and sharp**).
- 'Free' OH bands are only observed in the vapor phase or very dilute solution of **non-polar** solvents (eg. CCl4).
- Intermolecular H-bonding increases as the **concentration** of the solution increases or when the sample is analyzed neat.
- This lowers frequency of absorption to 3200-3550cm^{-1}.

Reason:



- The stronger the hydrogen-bonding
- The longer the O-H bond (more polarized).
- The lower the **force constant .**
- The lower the **vibrational frequency .**
- The broader the band (**H-bonding is not uniform throughout the sample**) and
- The more intense (due to **increased polarization** of the O-H bond) the absorption band.

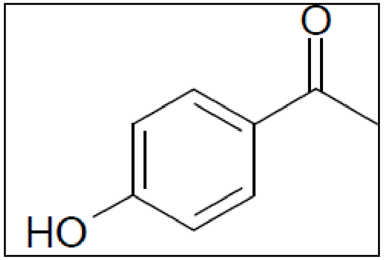
Can IR spectroscopy distinguish these isomers?

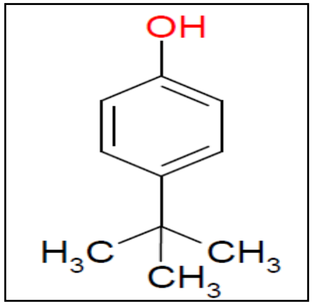


Intramolecular H-bonding occurs in *O*-Hydroxyacetophenone

at **3077 cm-1 (lower frequency) (independent of concentration)**

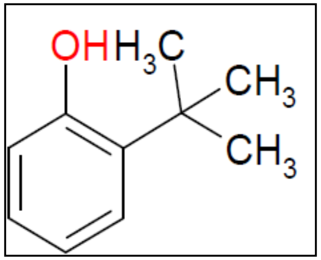
free' hydroxyl peak at **3600 cm^{-1}** (**Sharp**) in **dilute solution of CCl$_4$. intermolecular** H-bonded peak at **3100 cm-^{1}** (**broad**) when run **neat sample (high concentration**




OH
H3C
CH3
CH3

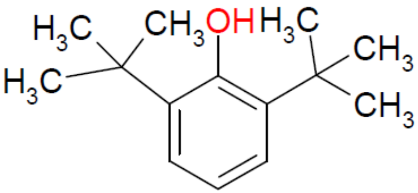
3105cm^{-1}

H-bonded OH


OH
H3C
CH3
CH3

3105cm^{-1} - 3643cm^{-1}

Partly H-bonded OH


H3C
H3C
CH3
OH
H3C
CH3
CH3

3643cm^{-1}

No H-bonding

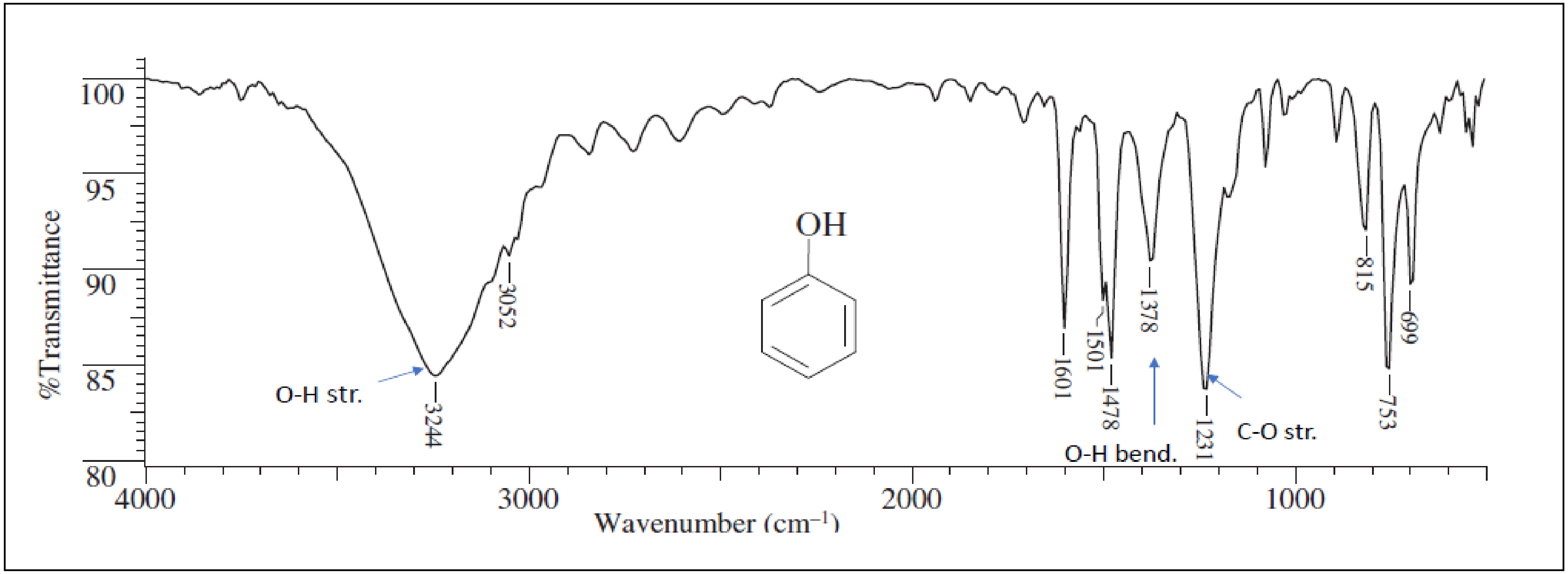
Why the difference in absorption position?

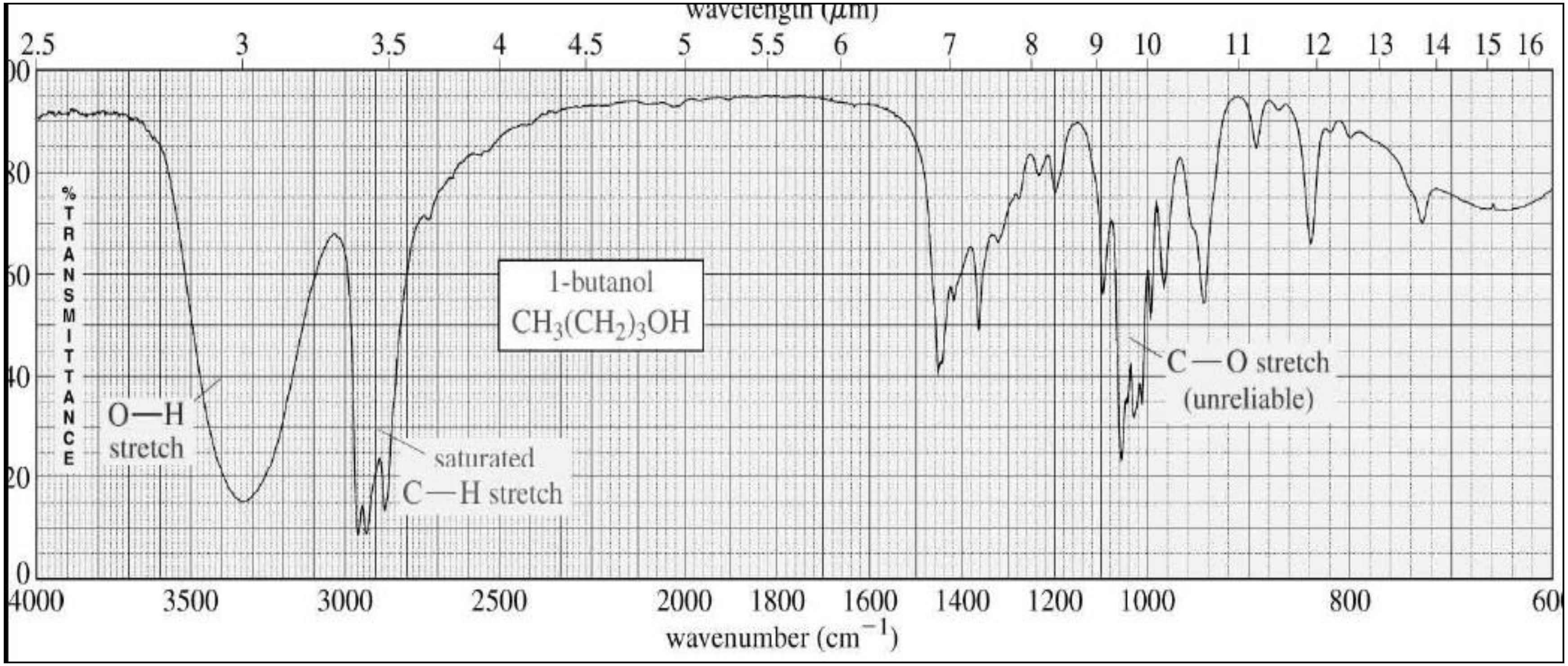
2,6-di-*t*-butylphenol in which steric hindrance **prevents hydrogen-bonding**, No **H-bonded** hydroxyl band is observed, not even in spectra of **neat samples .**

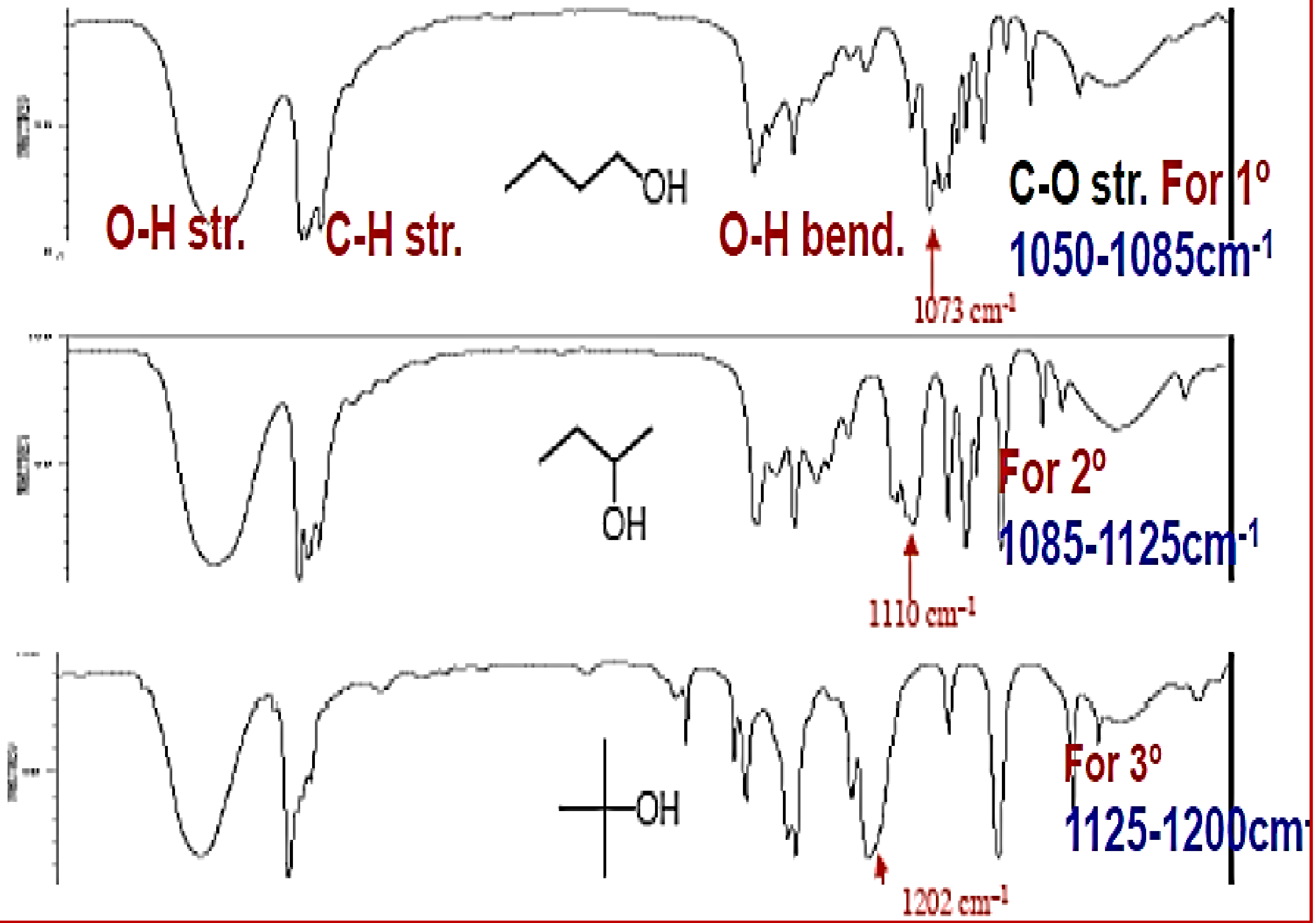
- **C-O stretching** appear at 1300-1000 cm^{-1}.
- **O-H bending** also occurs but such bands

couple with other vibrations and produce

complex bands in the fingerprint region (1420- 1330 cm^{-1}).


100
95
90
85
80
%Transmittance
OH
O-H str.
3244
3052
1601
1501
1478
1378
1231
815
753
699
O-H bend.
C-O str.
4000
3000
2000
1000
Wavenumber (cm^{-1})


wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
00
80
60
40
20
0
% TRANSMITTANCE
1-butanol
CH$_3$(CH$_2$)$_3$OH
O—H stretch
saturated C—H stretch
C—O stretch (unreliable)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
60
wavenumber (cm^{-1})


O-H str.
C-H str.
OH
O-H bend.
C-O str. For 1°
1050-1085cm-1
1073 cm-1
OH
For 2°
1085-1125cm-1
1110 cm-1
OH
For 3°
1125-1200cm
1202 cm-1

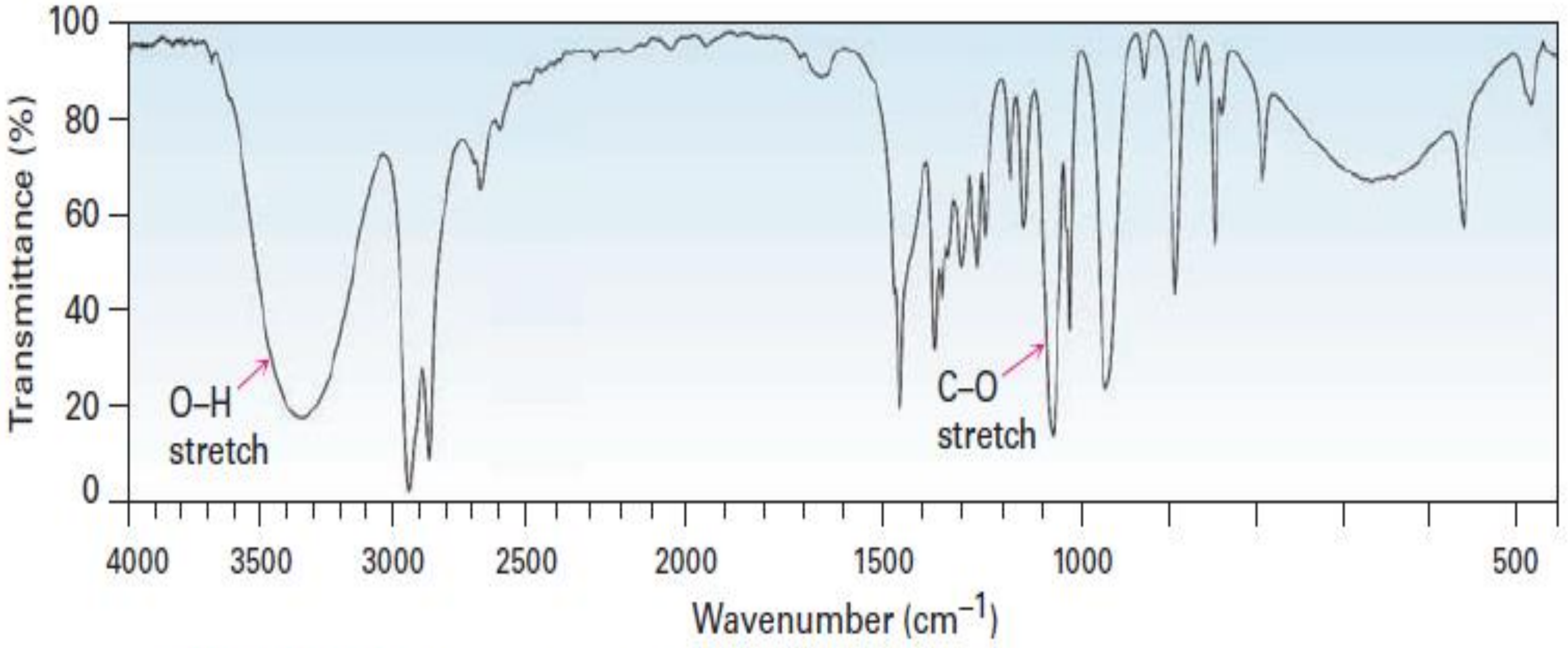
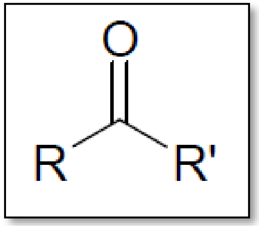


FIGURE 12-24 IR spectrum of cyclohexanol.

Carbonyl Compounds .

Carbonyl functional groups are the easiest to identify of all IR absorptions because of their sharp, intense peak in the range 1670 to 1780 cm-1. Most important, the exact position of absorption within this range can often be used to identify the exact kind of carbonyl functional group—aldehyde, ketone, ester, and so forth. The principles of resonance, inductive electronic effects, and hydrogen bonding help us explain and understand the different frequencies at which different carbonyl groups absorb IR radiation.

- Neat sample of saturated aliphatic ketone, 1715 cm^{-1} as '**normal**'.



Aliphatic ketone (1715 cm^{-1})

Change in the environment of the carbonyl can either lower or raise the absorption frequency .

Factors affecting position of C=O absorption .

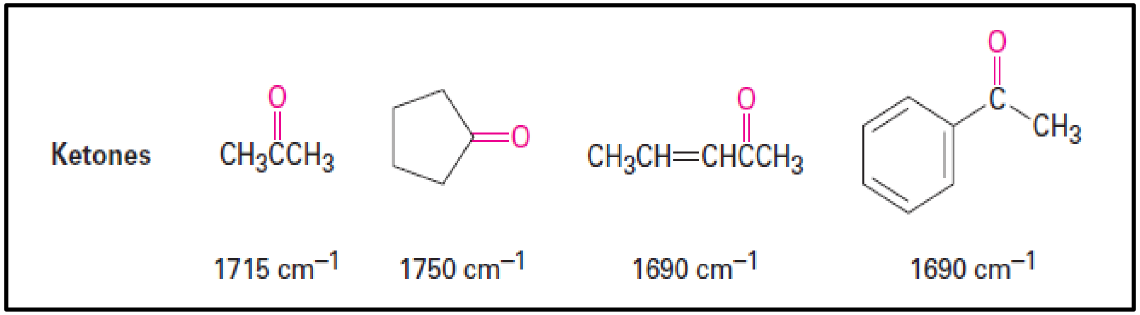
1) The physical state of measurement (solid, neat, dilute solution, conc. solution).

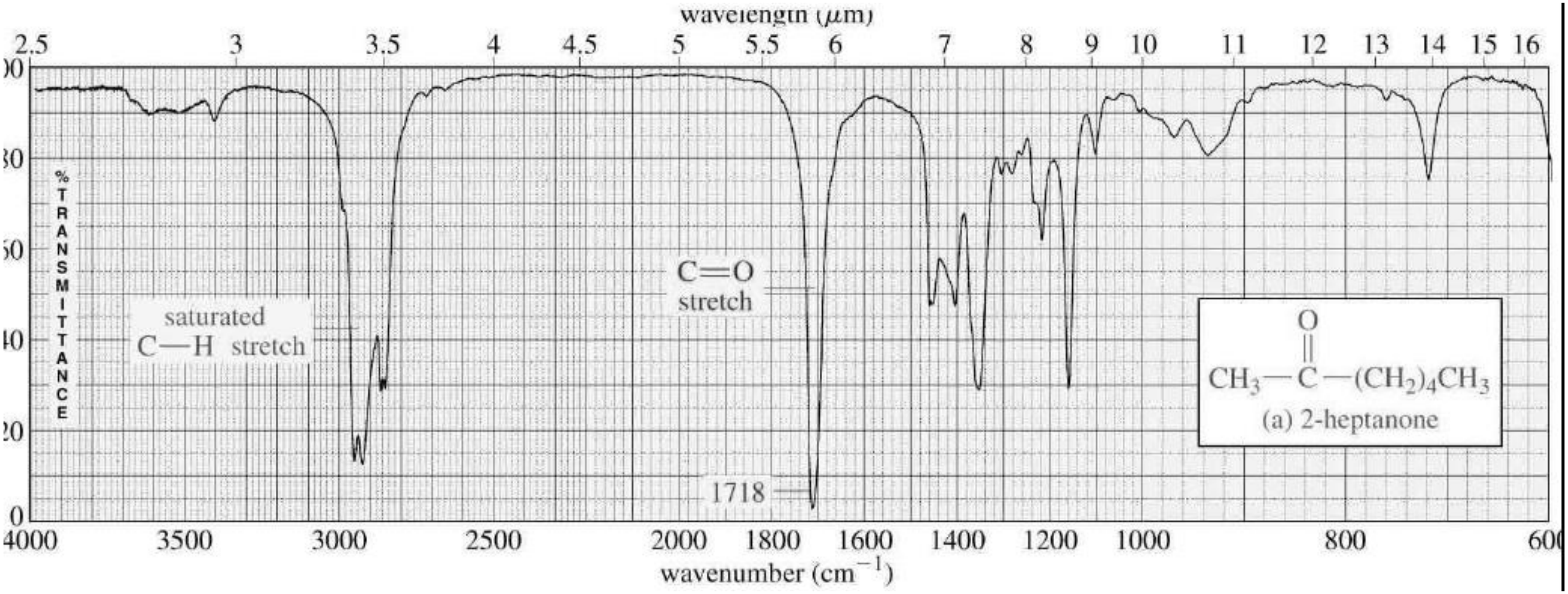
2) Electronic effect of substituents.

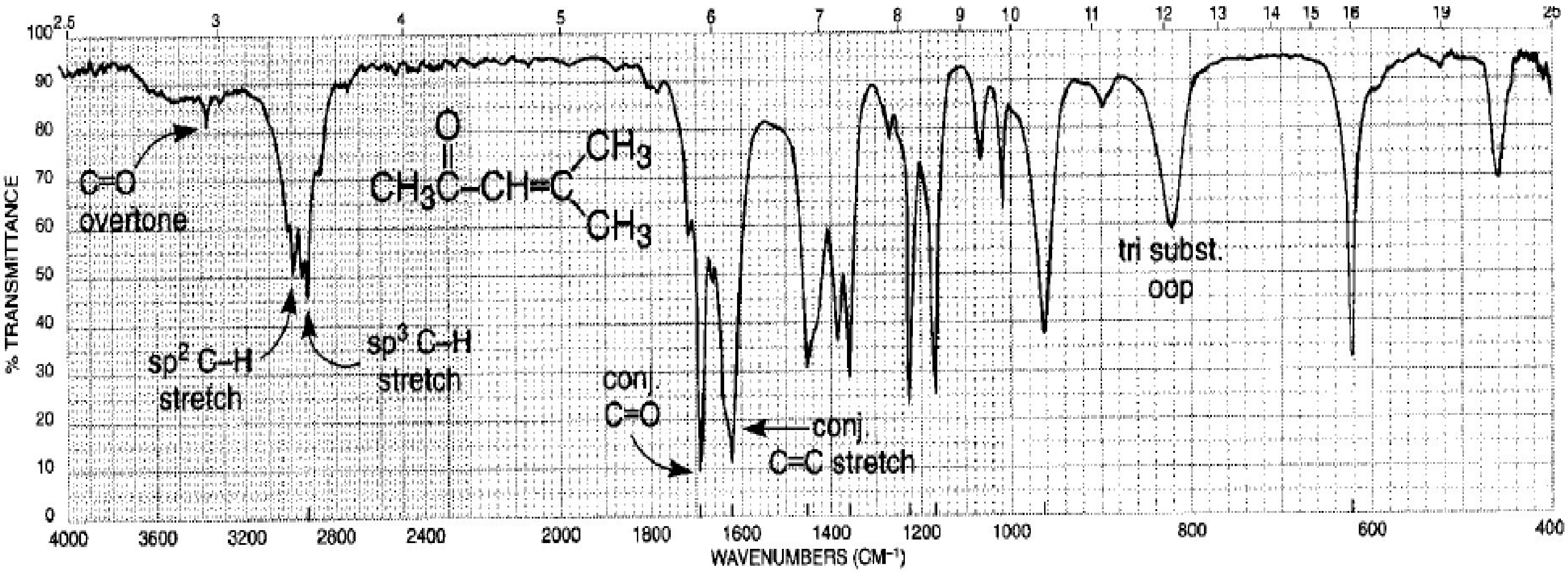
3) Conjugation.

4) Hydrogen bonding;

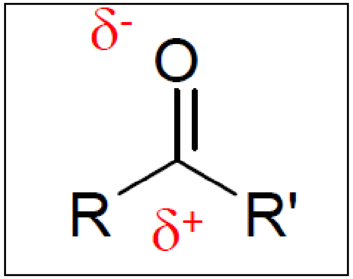
5) Ring strain.




wavelength (μm)
2.5 3 3.5 4 4.5 5 5.5 6 7 8 9 10 11 12 13 14 15 16
% TRANSMITTANCE
00 80 60 40 20 0
saturated
C—H stretch
C=O
stretch
1718
O
CH3—C—(CH2)4CH3
(a) 2-heptanone
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600
wavenumber (cm−1)


100 2.5 3 4 5 6 7 8 9 10 11 12 13 14 15 16 19 25
% TRANSMITTANCE
90 80 70 60 50 40 30 20 10 0
C=O
overtone
O
CH3C–CH=C
CH3
CH3
sp2 C–H
stretch
sp3 C–H
stretch
conj.
C=O
conj.
C=C stretch
tri subst.
oop
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400
WAVENUMBERS (CM−1)

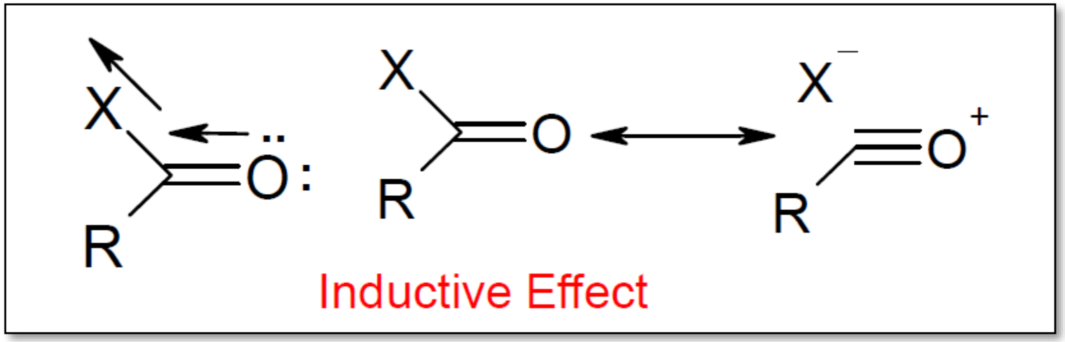
1) Physical State .



- Non-polar solvents increase absorption frequency.
- Polar solvents decrease absorption frequency.
- Due to **solvent-carbonyl** interaction.
- Overall range of solvent effect does not exceed 25 cm^{-1}.

2) Electronic Effect of Substituents .

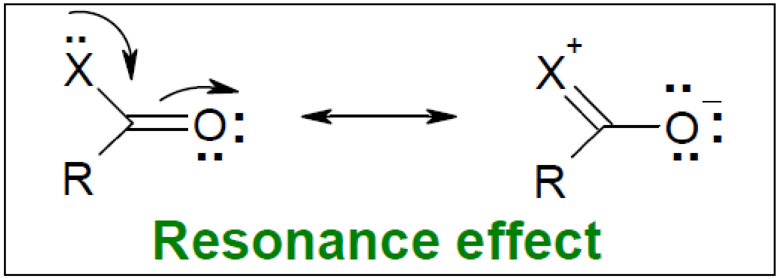
- Replacement of an alkyl group of a saturated aliphatic ketone by heteroatom (X) shifts the carbonyl absorption.
- The direction of the shift depends on whether inductive effect or resonance effect **predominates**.

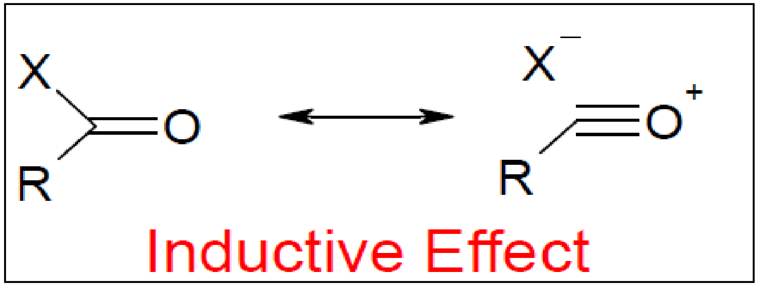


Inductive effect reduces the length of the C=O bond increases its force constant .- the frequency of absorption will **increase.**

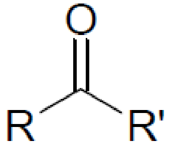
Resonance effect increases the length of the C=O bond - reduces its force constant.

- the frequency of absorption will **decrease**.


X
R
O
X+
R
O−
Resonance effect


X
R
O
X−
R
O+
Inductive Effect

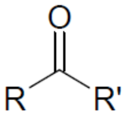
Substituent effects predominantly inductive



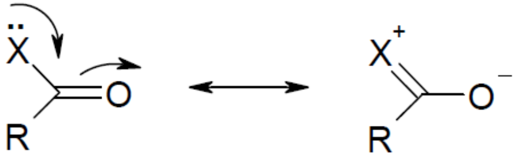
aliphatic ketone,
1715 cm^{-1}

X	C=O absorption (cm^{-1})
F	1869
Cl	1815-1785
Br	1812
OH	1760
OR	1750-1735

Substituent effects predominantly resonance

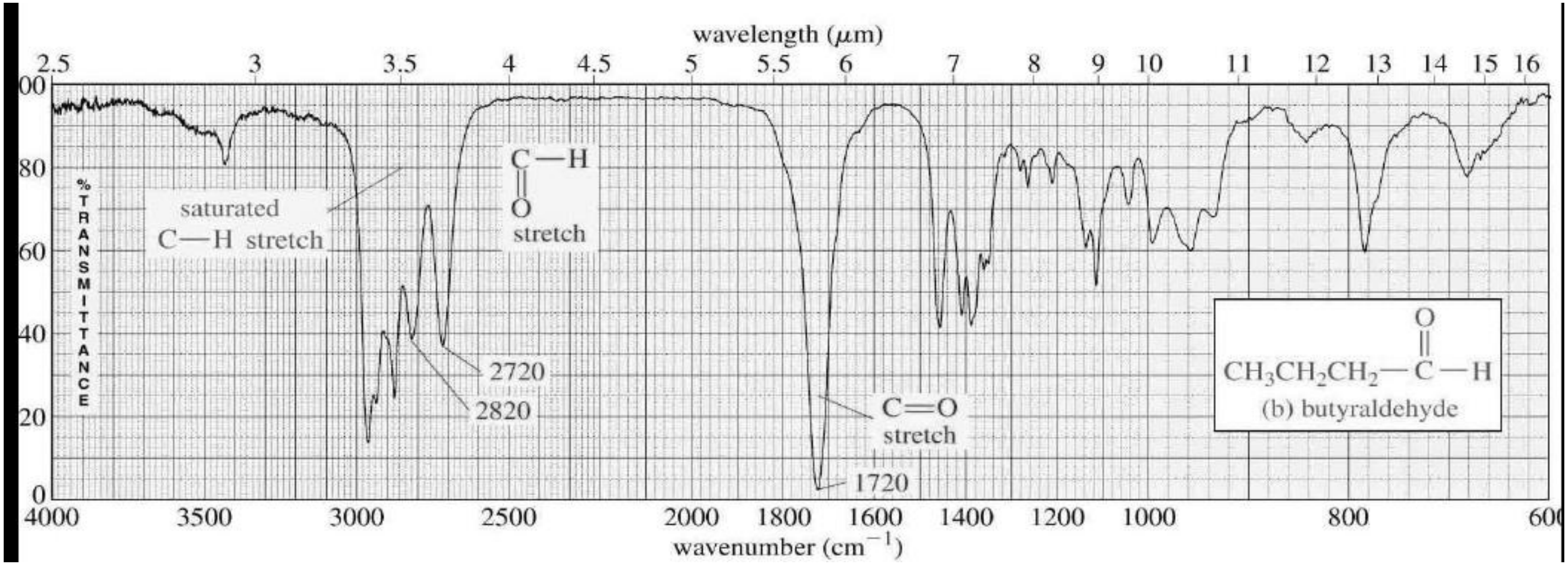


aliphatic ketone,
1715 cm^{-1}



Resonance effect

X	C=O absorption (cm^{-1})
NH_2	1695-1650
SR	1710-1690

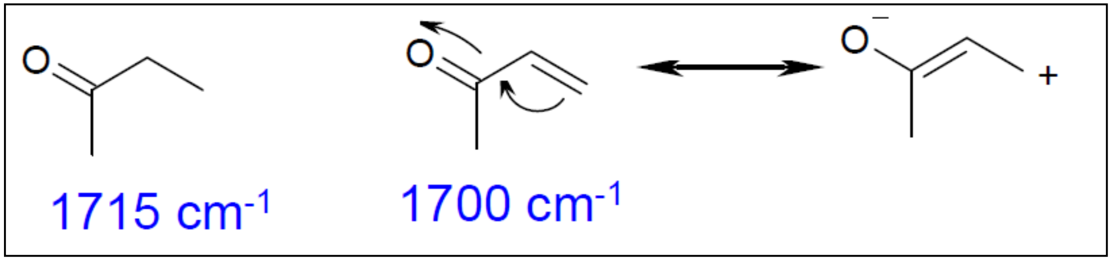


Acetone (CH_3COCH_3) and 2-propen-1-ol ($H_2C{=}CHCH_2OH$) are isomers. How could you distinguish them by IR spectroscopy?

Solution

Acetone has a strong C=O absorption at 1715 cm1, while 2-propen-1-ol has an OH absorption at 3500 cm1 and a C=C absorption at 1660 cm 1.

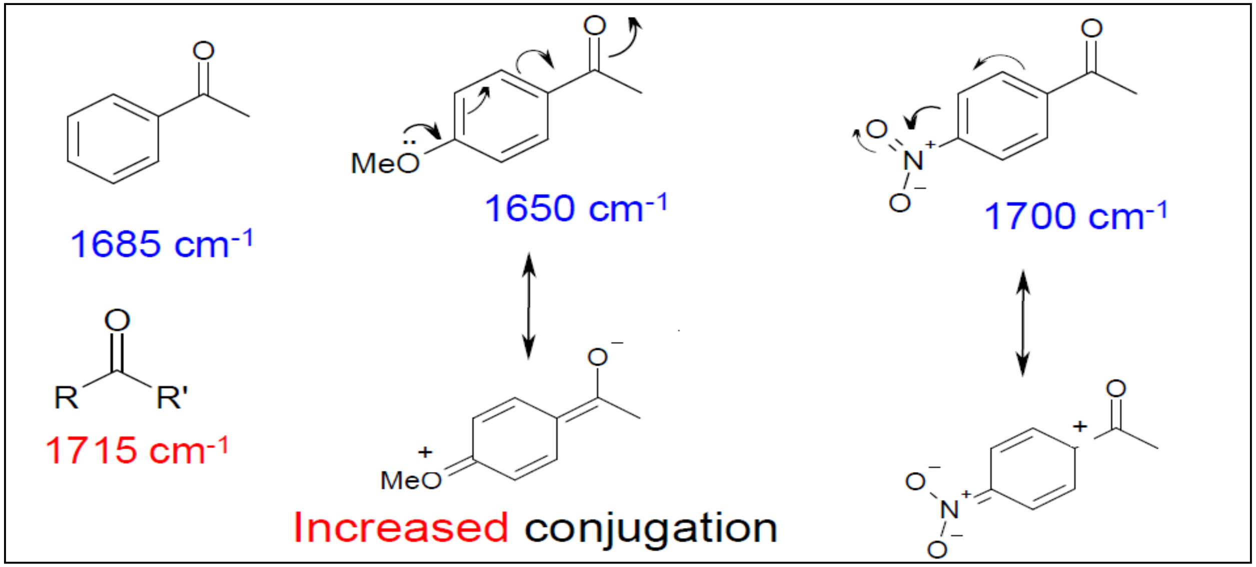
3) Conjugation .



O
1715 cm-1
O
1700 cm-1
O
−
+

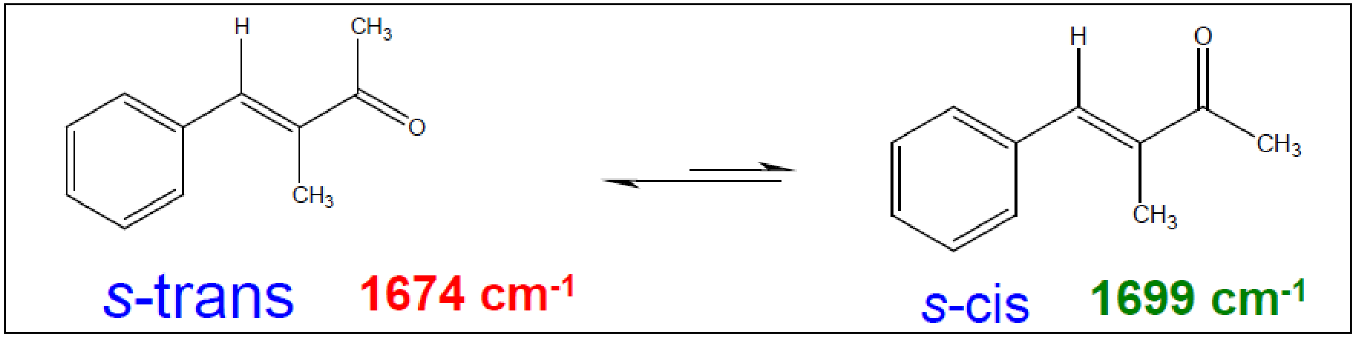
Conjugation lowers the stretching frequency of carbonyl by 15-40 cm^{-1}. This is because the carbonyl **bond order** (double bond character) is reduced and hence the **force constant falls** (reduces).

Increased conjugation with carbonyl group **Lowers frequency ,** Decreased conjugation with carbonyl group Increases frequency .



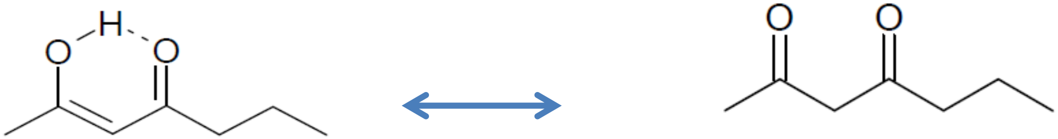
O
1685 cm-1
O
R
R'
1715 cm-1
O
MeO
1650 cm-1
O
−
+
MeO
O
O
N
+
O
−
1700 cm-1
O
+
O
−
N
+
O
−
Increased conjugation

(E)-3-Methyl-4-phenylbut-3-en-2-one , Shows two C=O bands at **1674** and **1699 cm^{-1}** . **Why?**


H
CH3
O
CH3
H
O
CH3
CH3
s-trans
1674 cm-1
s-cis
1699 cm-1

Steric effects in s-cis reduces co-planarity of the conjugated system and reduces the effect of conjugation

How can you distinguish the two isomers using IR?

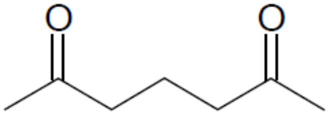


64%

1613 cm^{-1}

Heptane-2,4-dione

36% 1725 cm^{-1}

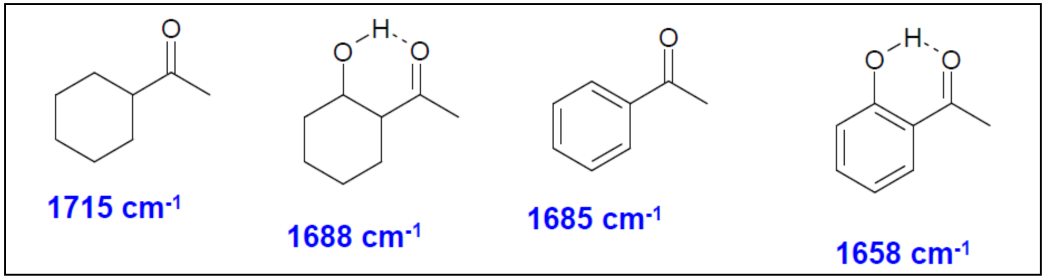


Heptane-2,6-dione

1715 cm^{-1}

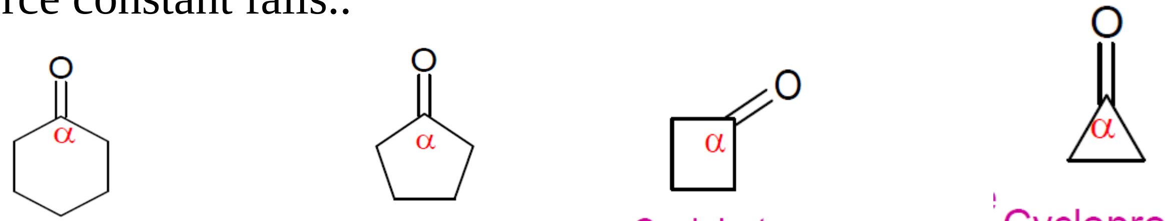
3077 cm-1 for O-H stretching (H-bonded)

4) Hydrogen Bonding


O
1715 cm^{-1}
O
H
O
1688 cm^{-1}
O
1685 cm^{-1}
O
H
O
1658 cm^{-1}

H-bonding reduces C=O stretching frequency. This is because the carbonyl bond order is reduced and the force constant falls..

5) Ring Strain


O
α
O
α
O
α
O
α

Cyclohexanone	Cyclopentanone	Cyclobutanone	Cyclopropanone
1715 cm^{-1}	1751 cm^{-1}	1775 cm^{-1}	1815 cm^{-1}

The bond angle (α) influences the absorption frequency of C=O.

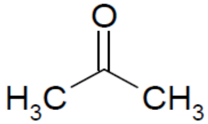
In non-cyclic ketones and in **cyclohexanone** $\alpha = 120^\circ$

In strained rings in which $\alpha < 120^\circ$

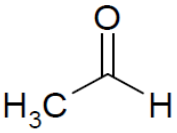
The **energy** of C=O stretching increases, Hence stretching frequency is increased.

Aldehydes .

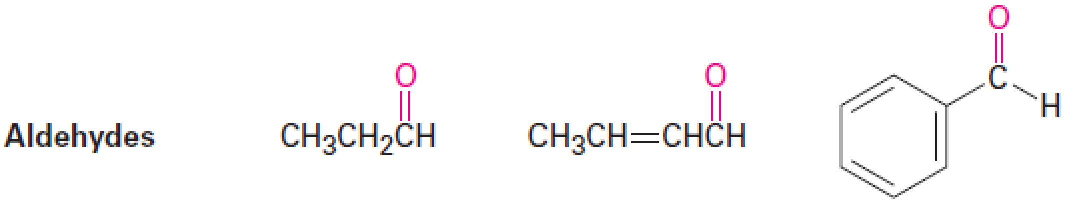
C=O stretching vibrations of aldehydes absorb at slightly higher frequencies than that of ketones. Hyperconjugation (which reduces vibrational frequency) is **higher in ketones** than in aldehydes



1715 cm^{-1}

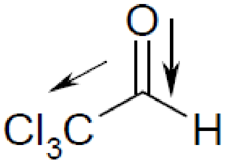


1730 cm^{-1}

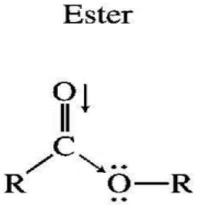

Aldehydes
CH_3CH_2CH
$CH_3CH{=}CHCH$
O
C
H

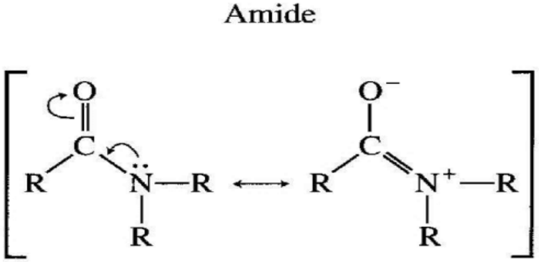
1730 cm^{-1} 1705 cm^{-1} 1705 cm^{-1}

Electronegative substituents on **Alph -carbon** increases the frequency of carbonyl absorption

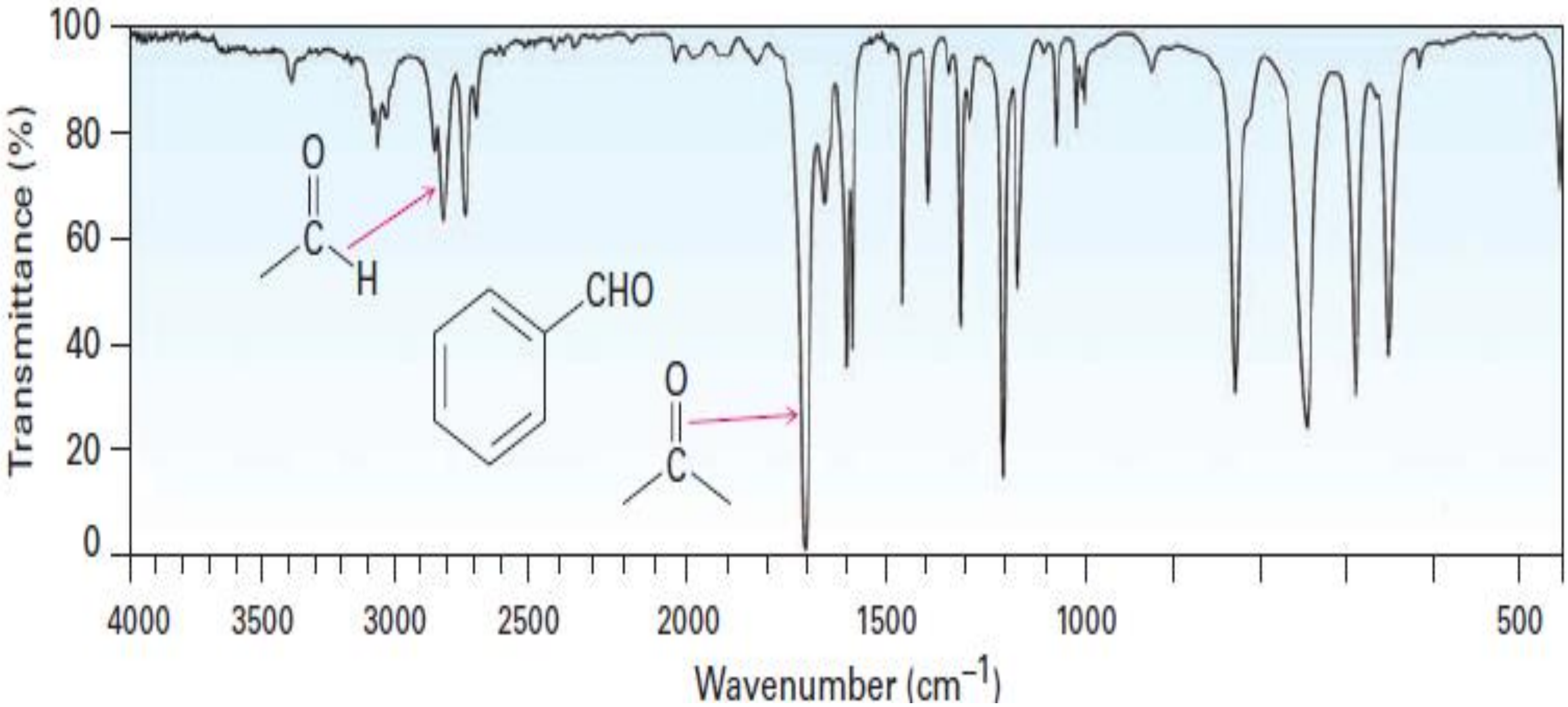


1768 cm^{-1}


Ester
O
C
R
Ö—R


Amide
O
C
R
N—R
R
O⁻
C
R
N⁺—R
R

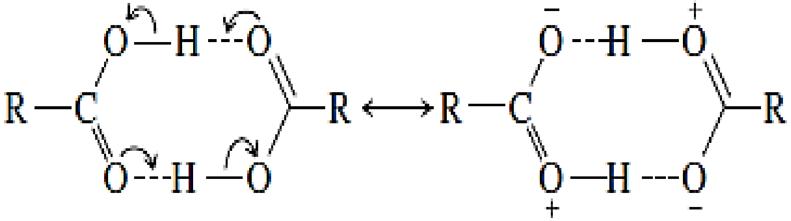
C- H Stretching Vibrations. The majority of aldehydes show aldehydic C-H stretching absorption in the 2700-2800 cm^{-1} region , 2800-2900


100
80
60
40
20
0
Transmittance (%)
O
C
H
CHO
O
C
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

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 **3300-2500 cm^{-1}** . The band is usually centered near **3000 cm^{-1}.**



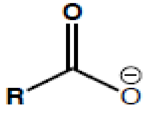
C=O *Stretching Vibrations.* The C=O stretching bands of acids are considerably **more intense** than ketonic C=O stretching bands and it absorbs at **1730-1700 cm^{-1}**.

- **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.

- ***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 .

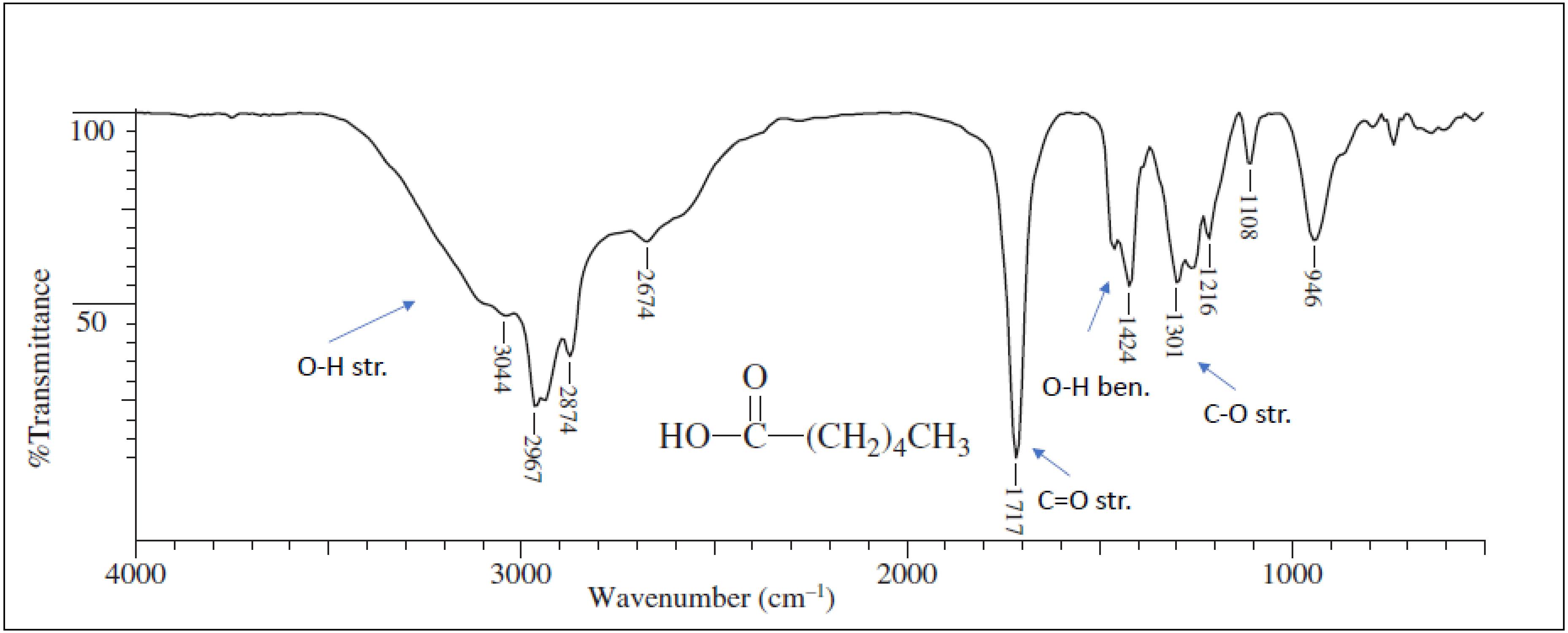
Carboxylate Anion

- The carboxylate anion has two strongly coupled C=O bonds with bond strengths intermediate between C=O and C-O.

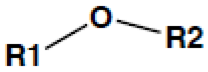


Carboxylate

- 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.

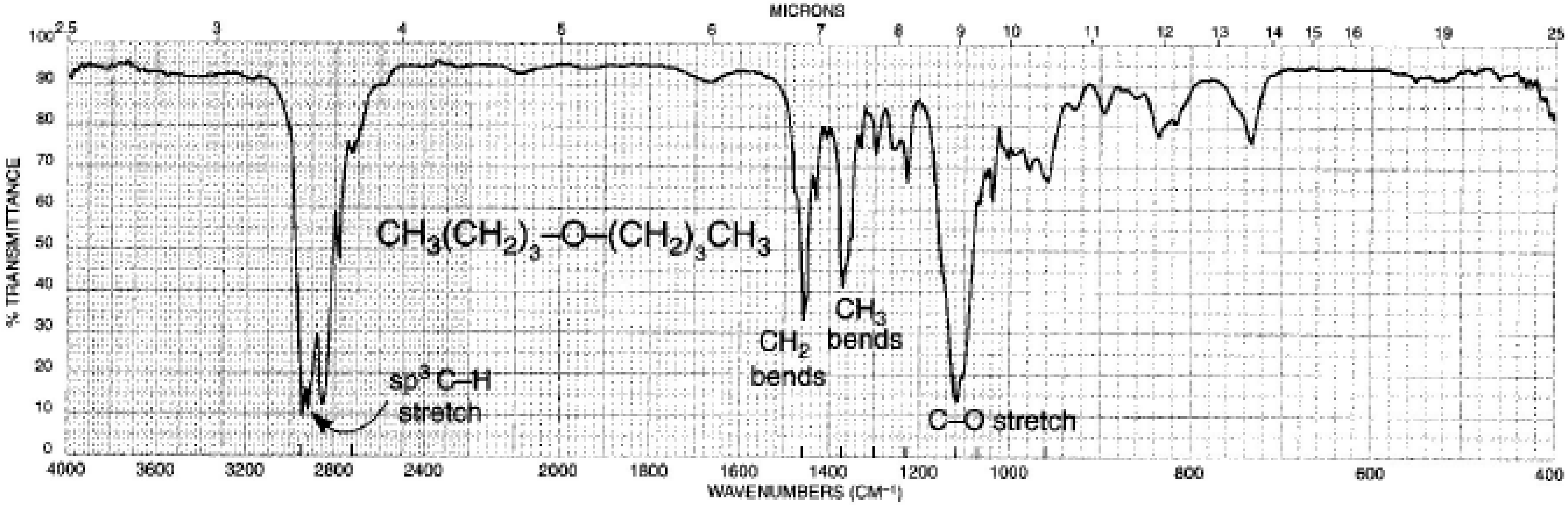

100
50
%Transmittance
O-H str.
3044
2967
2874
2674
HO—C(=O)—(CH2)4CH3
1717
C=O str.
1424
O-H ben.
1301
1216
C-O str.
1108
946
4000
3000
2000
1000
Wavenumber (cm−1)

ETHERS

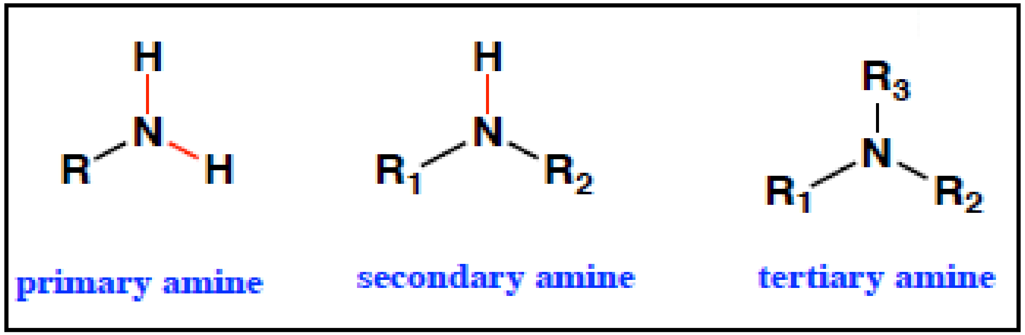


Ethers

The most prominent band is that due to C−O stretch, 1300–1000 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}.



Amines



- **N-H Stretching Vibrations.**

- Primary amines, display **two weak** absorption bands: one at 3300 to 3500 **cm^{-1}** range and the other at **3250- 3330 cm^{-1}**. • **Aromatic primary amines** absorb at slightly **higher wavenumbers than aliphatic primary amines**. Primary amines exhibit two absorbance's one for the symmetric stretching mode and one for the asymmetric mode

- Secondary amines show a **single weak** band in the **3310-3350 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 N-H bending band intensified by **Fermi resonance**.

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

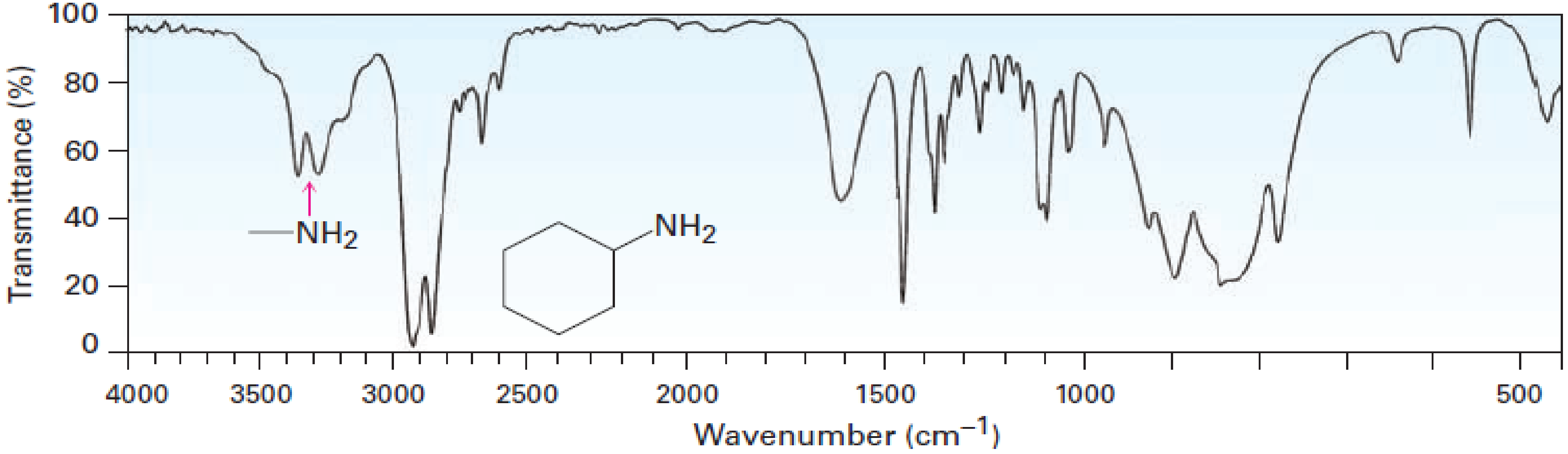
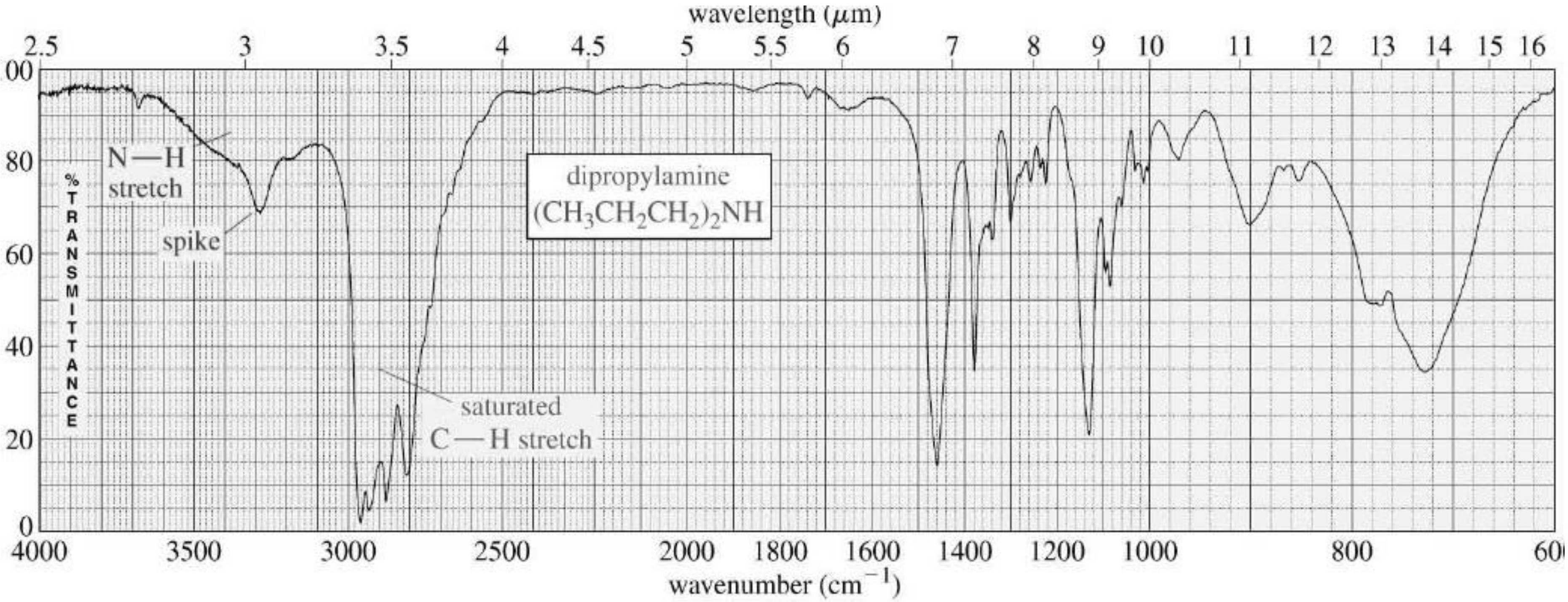
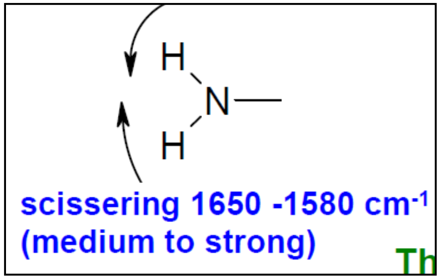
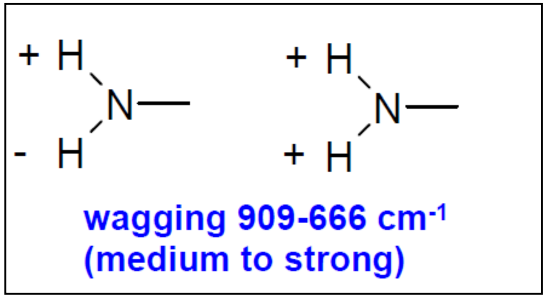


FIGURE 12-25 IR spectrum of cyclohexylamine.



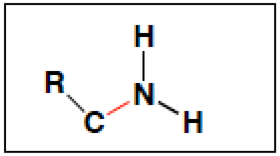
N-H Bending Vibrations. The N-H bending (scissoring) vibration of primary amines is observed in the **1650-1580 cm^{-1}** region of the spectrum.


H
N
H
scissering 1650 -1580 cm^{-1}
(medium to strong)
Th


+ H
N
- H
+ H
N
+ H
wagging 909-666 cm^{-1}
(medium to strong)

The position is affected by H-bonding

- ***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 cm^{-1}**.



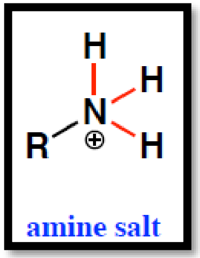
- Aromatic amines display strong C-N stretching absorption in the **1342-1266 cm^{-1}** region. It is higher than the corresponding absorption of aliphatic amines because the force constant of the C-N bond is increased by resonance with the ring.

Amine Salts .

- ***N-H Stretching Vibrations.*** The ammonium ion gives a strong, broad absorption in the **3030- 3300 cm^{-1}** region because of N-H stretching vibrations.

There is also a band in the 1709 - 2000-cm^{-1} region.

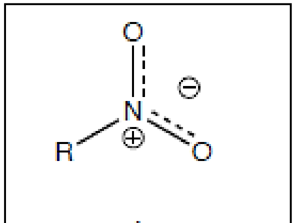
- ***N-H Bending Vibrations.*** The ammonium ion displays a strong, broad bending band near **1429 cm^{-1}**.



amine salt

Nitro compounds, show absorption caused by **asymmetrical** and **symmetrical** stretching of the **NO$_2$ group**. • 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.

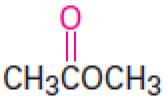


nitro

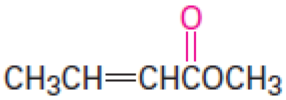
Esters and Lactones.

Saturated esters absorb at 1735 cm-1. In addition to the C-O absorbance, esters also have two strong absorbances in the 1300 to 1000 cm-1 range from the C=O portion of the functional group. Like the other carbonyl functional groups, esters next to either an aromatic ring or a double bond absorb at 1715 cm-1 , 20 to 30 cm-1 lower than a saturated ester.

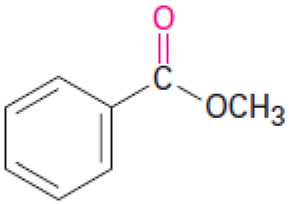
Esters


$CH_3\overset{O}{\overset{\|}{C}}OCH_3$

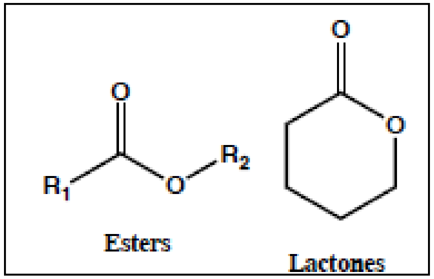
$1735\ cm^{-1}$


$CH_3CH{=}CH\overset{O}{\overset{\|}{C}}OCH_3$

$1715\ cm^{-1}$

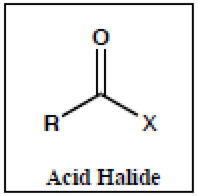


$1715\ cm^{-1}$



Acid Halides

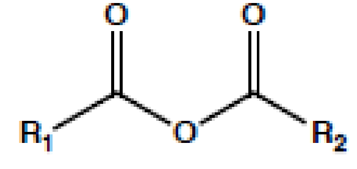
- Acid halides show strong absorption in the **C=O stretching region**. Unconjugated acid chlorides absorb in the **1815-1785 cm^{-1}** region.



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}**.

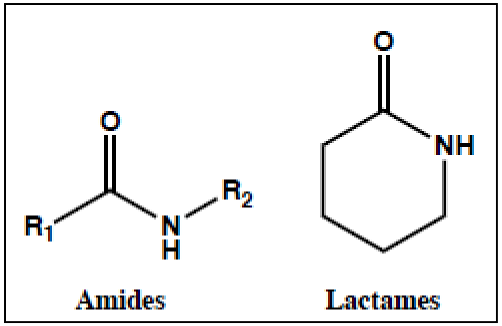
- ***C-O Stretching Vibrations.*** Other strong bands appear in the spectra of anhydrides as a result of stretching vibrations near **1300-900 cm^{-1}**.



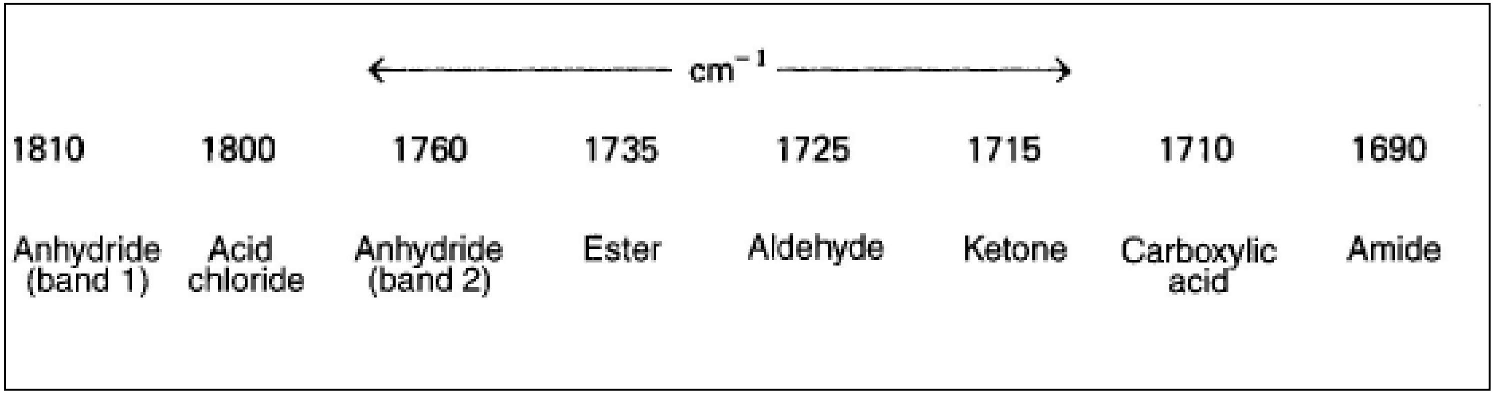
Anhydrides

Amides and Lactams .

- ***C=O Stretching Vibrations (Amide I Band).*** The C=O absorption of amides occurs at lower frequencies than “normal” carbonyl absorption at **1630-1680 cm^{-1}** due to the resonance effect.
- The ***N-H* stretching** is observed in the range of 3180- 3350–**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 1590 - 1620 cm^{-1}, and normally is separated from the amide I band.



Amides Lactames



← cm^{-1} →

1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

Organic Sulfur Compounds

S-H Stretching Vibrations*: *Mercaptans. Aliphatic mercaptans and thiophenols show S-H stretching absorption in the range of 2550- **2600 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 1020 **-1250-cm^{-1}**.

Compounds Containing Sulfur=Oxygen Bonds • *S=O Stretching Vibrations.*

- **Sulfoxides** show strong absorption in the **1030-1070 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 **1300-1350 cm^{-1}** and **1120-1160 cm^{-1}.**

These bands arise from asymmetric and symmetric SO_2 stretching, respectively.

- **Sulfonamides** absorb strongly at **1335-1370 cm^{-1}** and **1155-1170 cm^{-1}**.
- Primary sulfonamides show strong N-H stretching bands at 3330-3390 **cm^{-1}** and **3247- 3300 cm^{-1}** in while secondary sulfonamides absorb near **3265 cm^{-1}**.

Organic Halogen Compounds

- The strong absorption of halogenated hydrocarbons arises from the stretching vibrations of the **carbon–halogen bond**.
- Fluoro- compounds in **1000-1400 cm^{-1}** region.
- Aliphatic C-Cl absorption is observed in the broad region between **550- 850 cm^{-1}**.

- Brominated compounds absorb in the 515 - 690-cm^{-1} region.
- Iodo- compounds in the **500-600 cm^{-1}** region.
- A strong CH_2 wagging band is observed for the CH_2X (X = Cl, Br, and I) group in the **1150- 1300 cm^{-1}**.

- **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}**.

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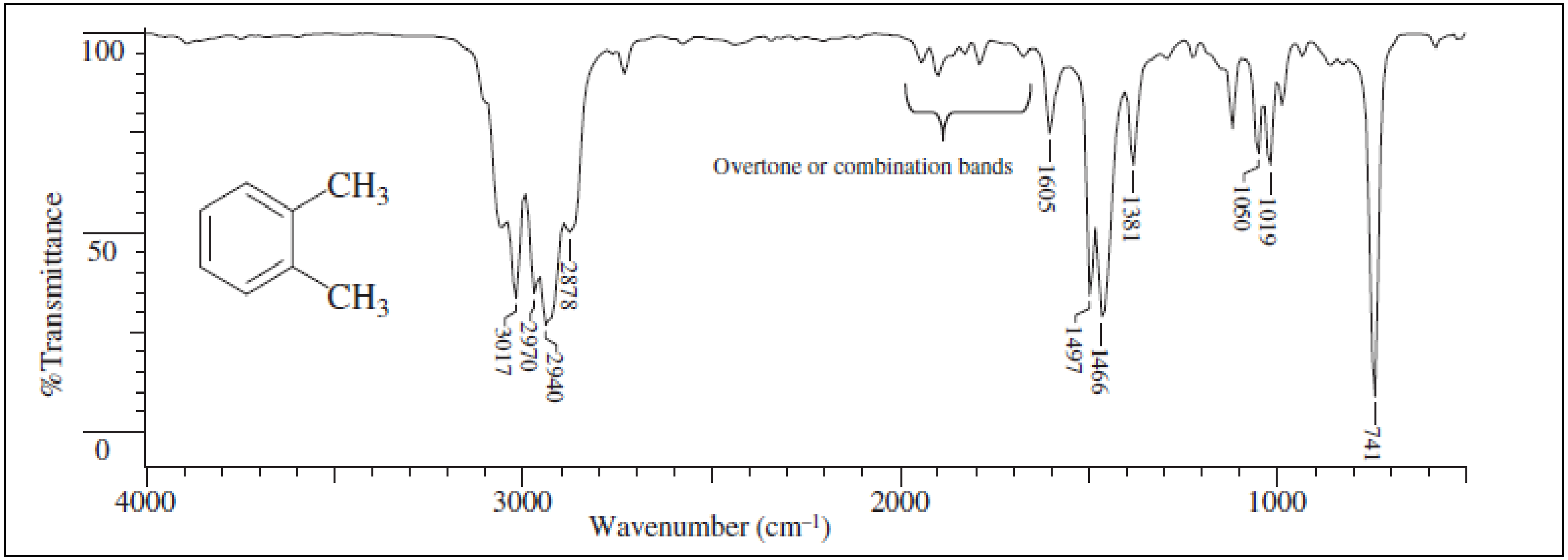
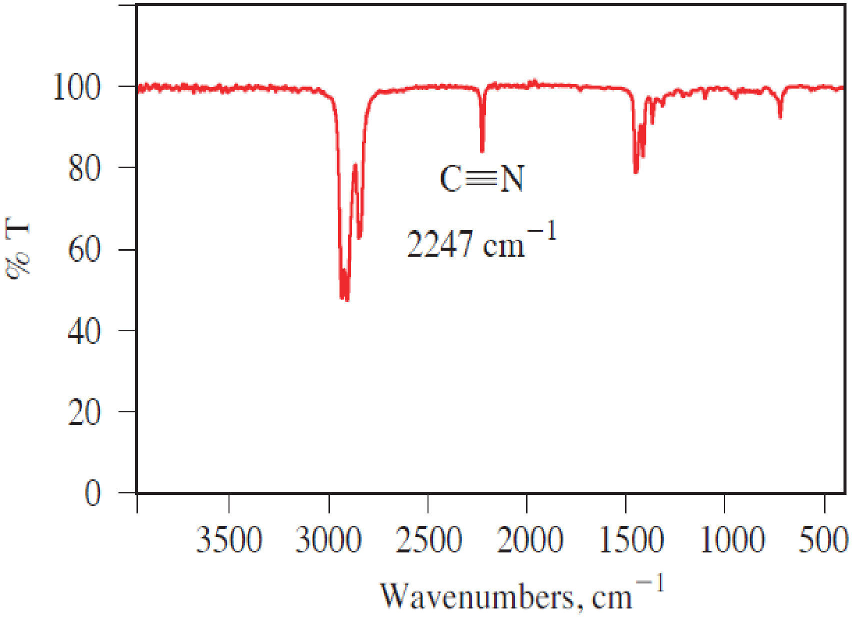
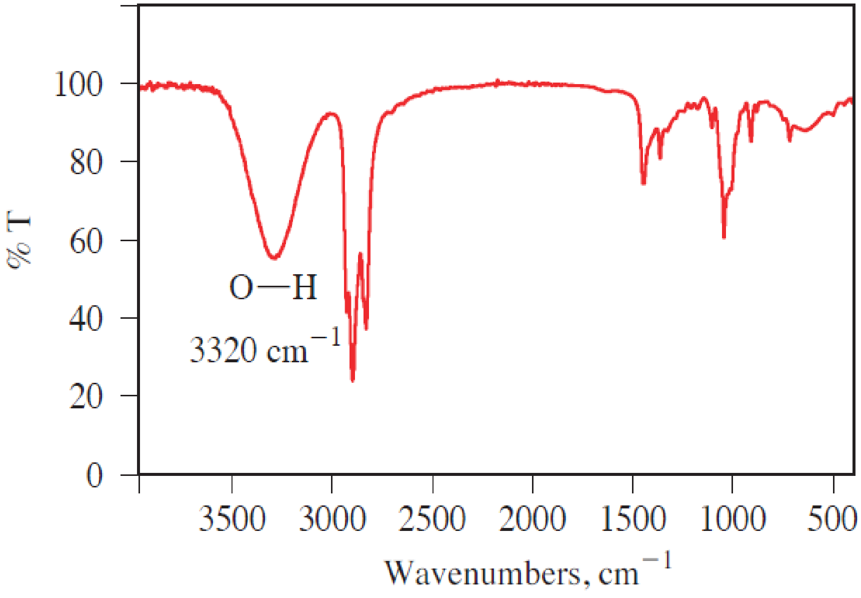


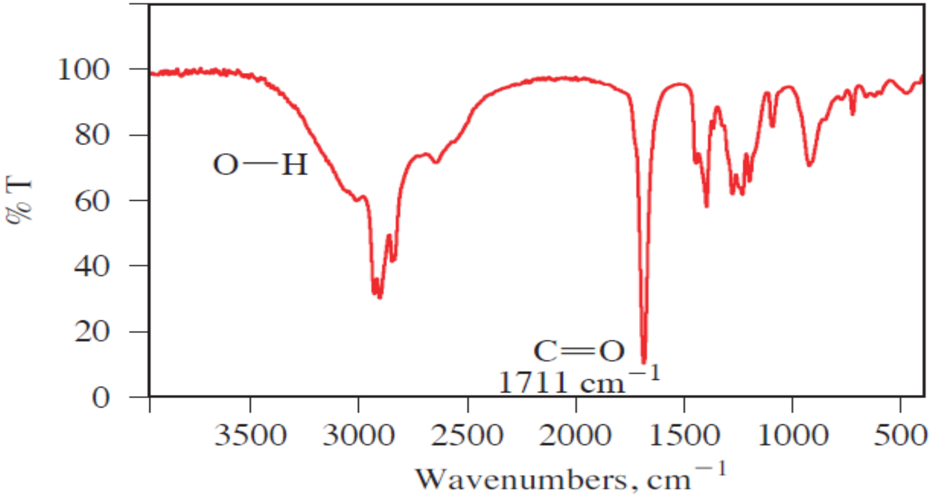
Hexanenitrile: $CH_3(CH_2)_4C{\equiv}N$



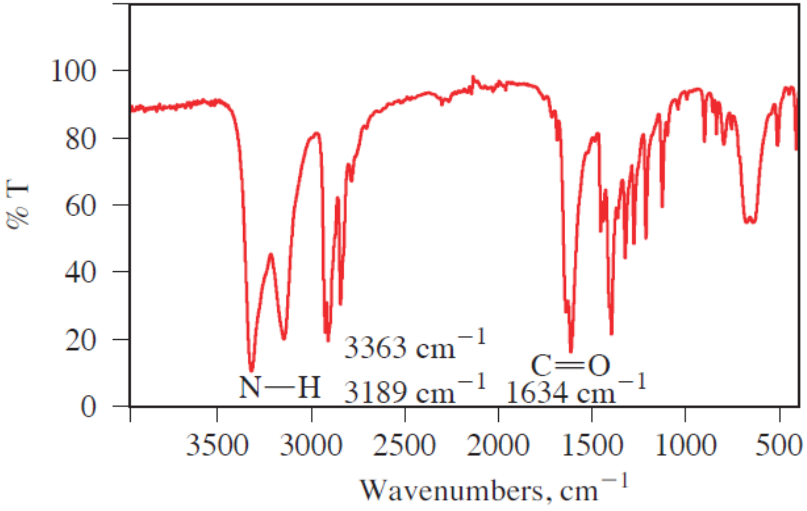
1-Hexanol: $CH_3(CH_2)_4CH_2OH$

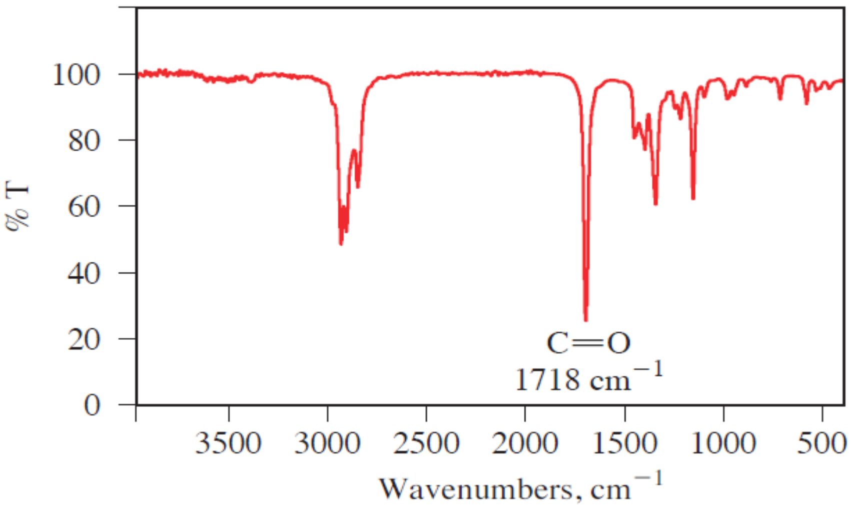


Hexanoic acid: $CH_3(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}}OH$

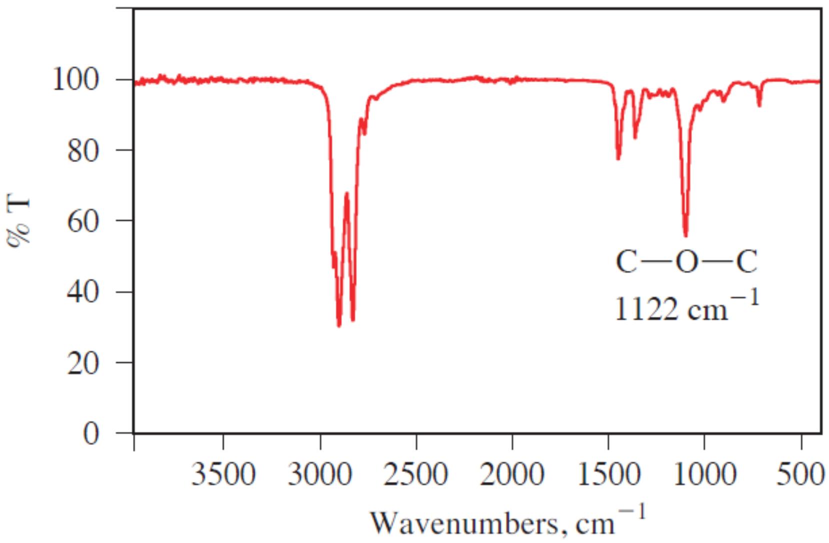


Hexanamide: $CH_3(CH_2)_4\overset{\displaystyle O}{\overset{\|}{C}}NH_2$

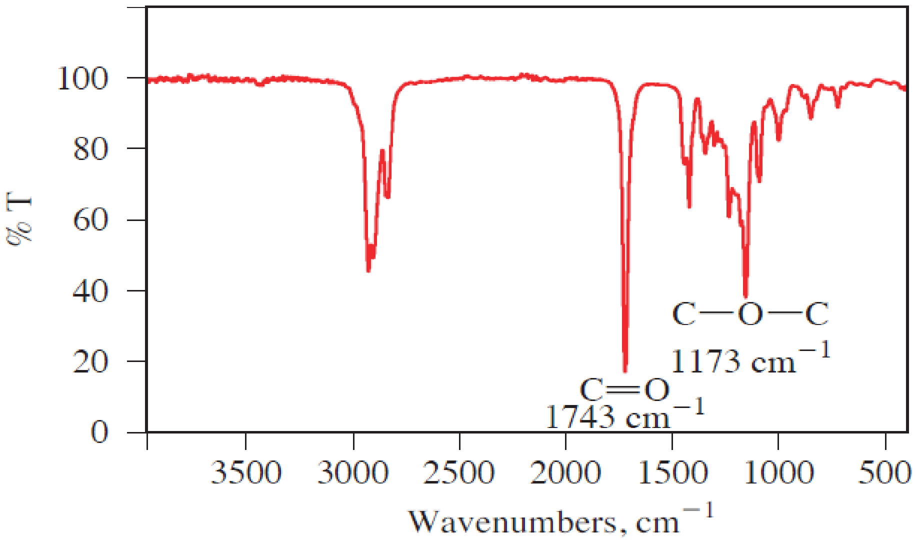




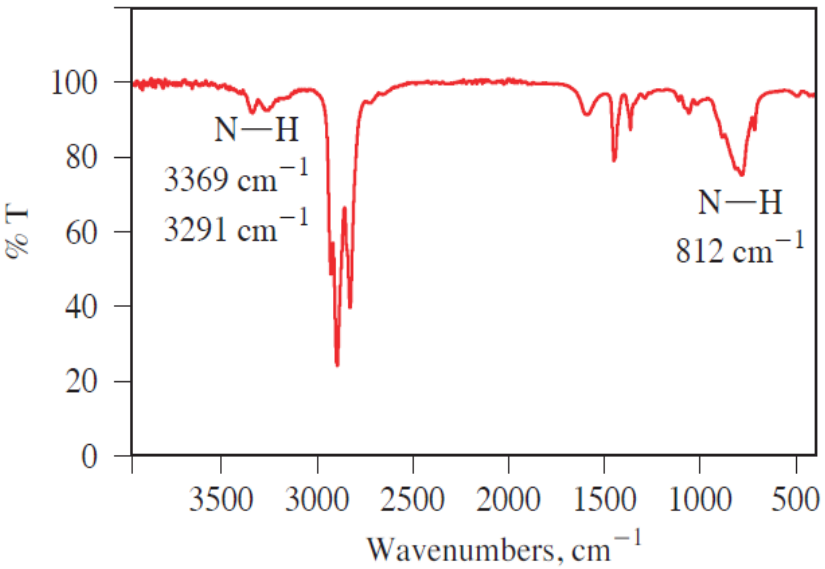
2-Hexanone: $CH_3\overset{\overset{O}{\|}}{C}(CH_2)_3CH_3$



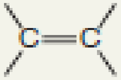
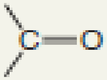
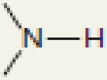
Dihexyl ether: $[CH_3(CH_2)_4CH_2]_2O$



Methyl hexanoate: $CH_3(CH_2)_4\overset{\overset{O}{\|}}{C}OCH_3$



Hexylamine: $CH_3(CH_2)_4CH_2NH_2$

Structural unit	**Frequency, cm^{-1}**	**Structural unit**	**Frequency, cm^{-1}**
		Stretching vibrations	
Single bonds		**Double bonds**	
—O—H (alcohols)	3200–3600	 	1620–1680
—O—H (carboxylic acids)	2500–3600		
	3350–3500		
sp C—H	3310–3320	Aldehydes and ketones	1710–1750
sp^2 C—H	3000–3100	Carboxylic acids	1700–1725
sp^3 C—H	2850–2950	Acid anhydrides	1800–1850 and 1740–1790
sp^2 C—O	1200	Acyl halides	1770–1815
sp^3 C—O	1025–1200	Esters	1730–1750
		Amides	1680–1700
		Triple bonds	
		$-\mathrm{C}\equiv\mathrm{C}-$	2100–2200
		$-\mathrm{C}\equiv\mathrm{N}$	2240–2280
		Bending vibrations of diagnostic value	
Alkenes:		***Substituted derivatives of benzene:***	
$\mathrm{RCH{=}CH_2}$	910, 990	Monosubstituted	730–770 and 690–710
$\mathrm{R_2C{=}CH_2}$	890	Ortho-disubstituted	735–770
cis-$\mathrm{RCH{=}CHR'}$	665–730	Meta-disubstituted	750–810 and 680–730
trans-$\mathrm{RCH{=}CHR'}$	960–980	Para-disubstituted	790–840
$\mathrm{R_2C{=}CHR'}$	790–840		