

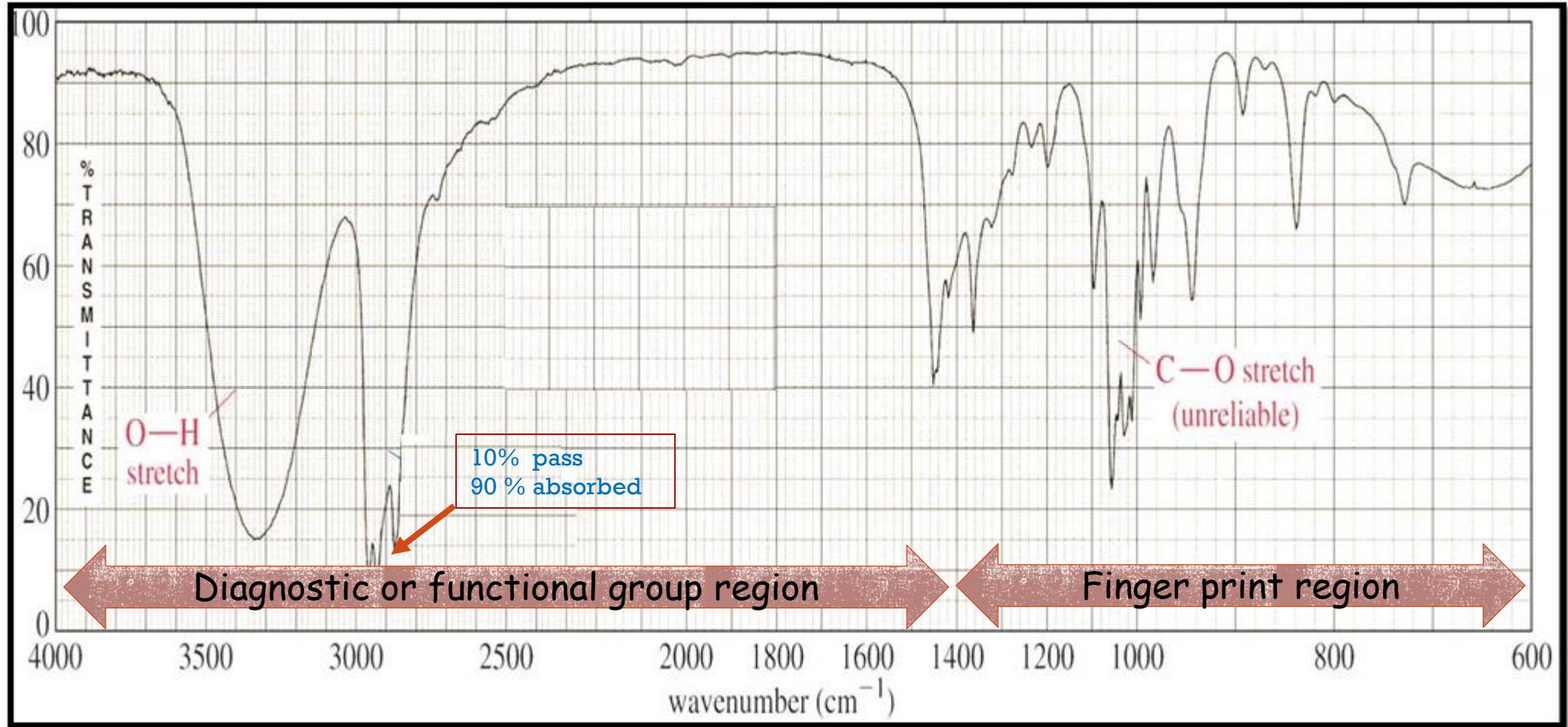
INFRA-RED SPECTROSCOPY

Characteristic Group Vibrations of Organic Molecules

4

2021-2022

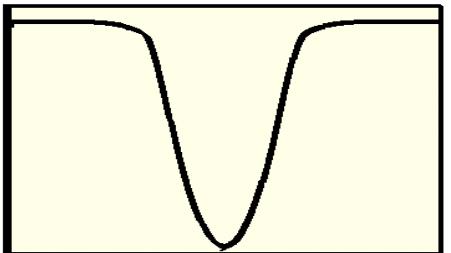
The features of IR spectrum



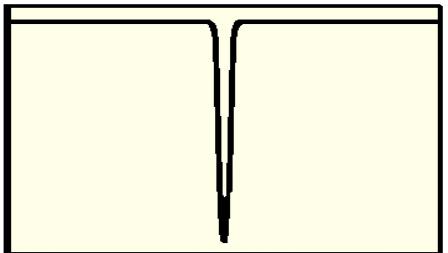
IR SIGNALS

IR signals can be described according to **shape** and **intensity**

Broad



Sharp

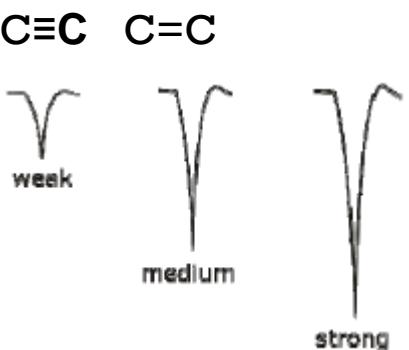


Question: what makes the IR signal broad?

- A. Functional groups that have the ability to form hydrogen bonding, like O-H and N-H
- B. Polar bonds like C=O

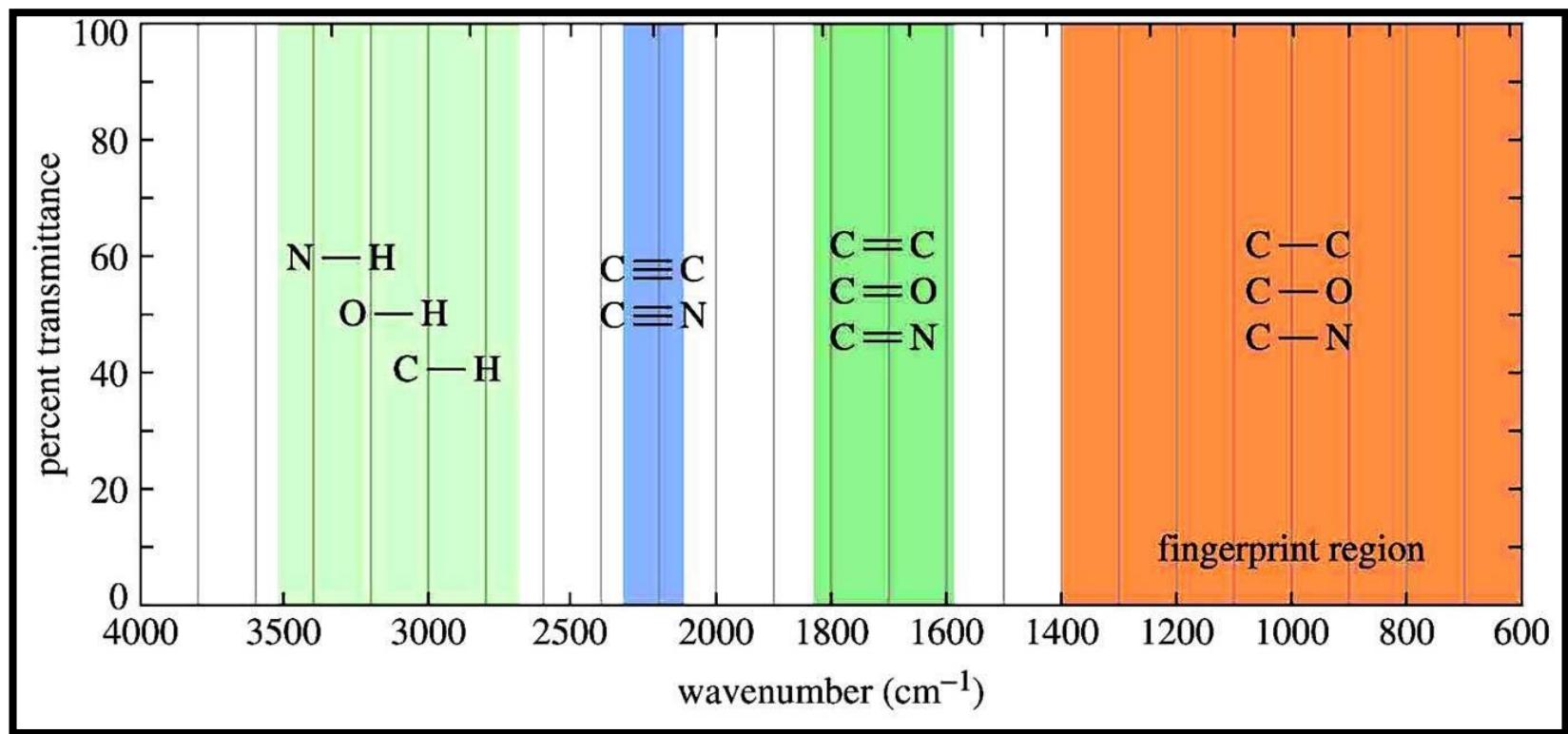
Question: what makes the IR signal sharp?

- A. Non-polar bonds like $C=C$ and $C\equiv C$
- B. It does not have enough dipole moment



IR absorption range

- The typical IR absorption range for covalent bonds is 400 Or 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 $\text{C}\equiv\text{N}$ or a $\text{C}\equiv\text{C}$ bond.

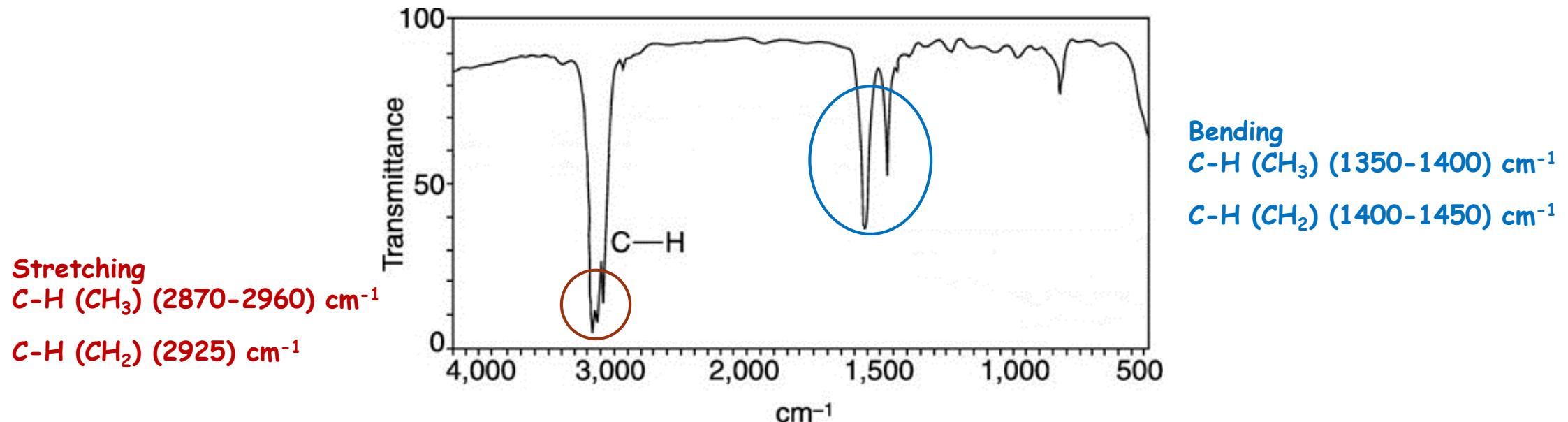


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

Hydrocarbons C-H and C-C stretching and bending vibrations

Alkanes:

In simple hydrocarbons, only two types of atoms C and H and only two types of bonds (C-C) and (C-H) are present..



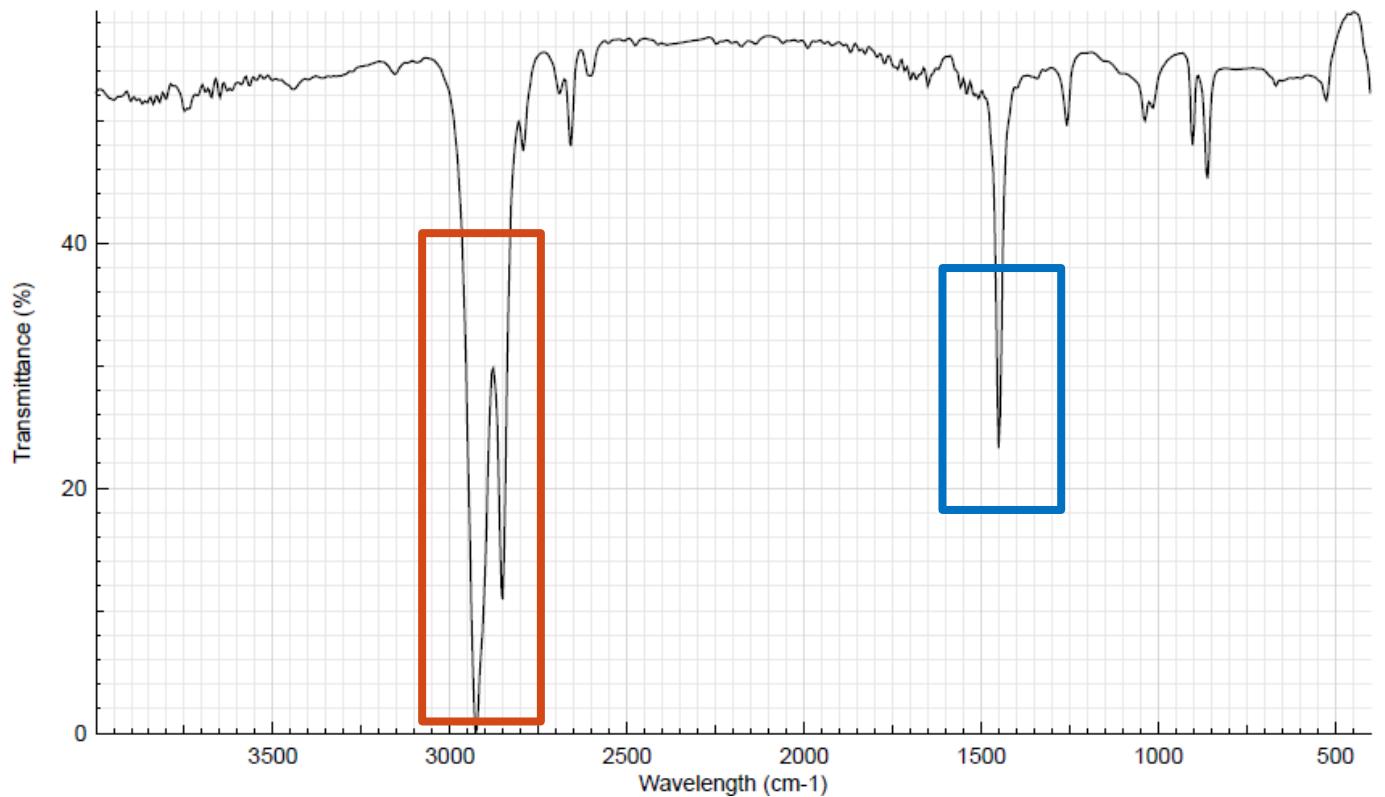
The (C-C) bond vibrations appear as weak bands in $1200-800 \text{ cm}^{-1}$ region and are seldom used for structural study. Whereas the (C-C) bending absorptions occur at $< 500 \text{ cm}^{-1}$ and are usually below the range of IR - instrument.



Cyclic aliphatic hydrocarbons

The C-H stretching frequencies are the same ($2800 - 3000 \text{ cm}^{-1}$) as in the case of acyclic compounds, if the ring is unstrained. However, methylene (CH₂) scissoring bands shift slightly to smaller wavenumber (1470 cm^{-1} in hexane and 1448 cm^{-1} in cyclohexane). In satirically strained cyclic compounds, the C-H stretching normally occurs at slightly higher wavenumber e.g. $3080 - 3040 \text{ cm}^{-1}$ in cyclopropane.

Stretching
C-H ($2800-3000$) cm^{-1}



Bending
C-H (1448) cm^{-1}

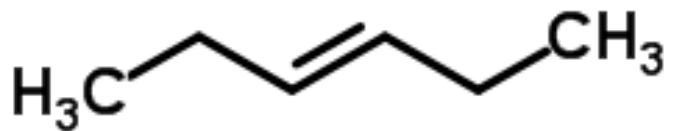
Alkenes:

- The $(C=C)$ bond has a higher force constant than a $(C-C)$ bond and in a non-conjugated olefin.

- In completely symmetrical alkenes, such as ethylene, tetrachloroethylene etc., ($C=C$) **stretching** band is absent, due to lack of change in dipole moment in completely symmetrical molecule.
- Non-symmetrically substituted double bonds exhibit strong absorption bands. The absorption bands are **more intense for *cis* isomers than for *trans* isomers**; for mono or tri substituted olefins than for di and tetra substituted ones.

IR SPECTRUM OF ALKENES

Internal



(1620-1680 cm^{-1})



$C=C$

$=C-H$

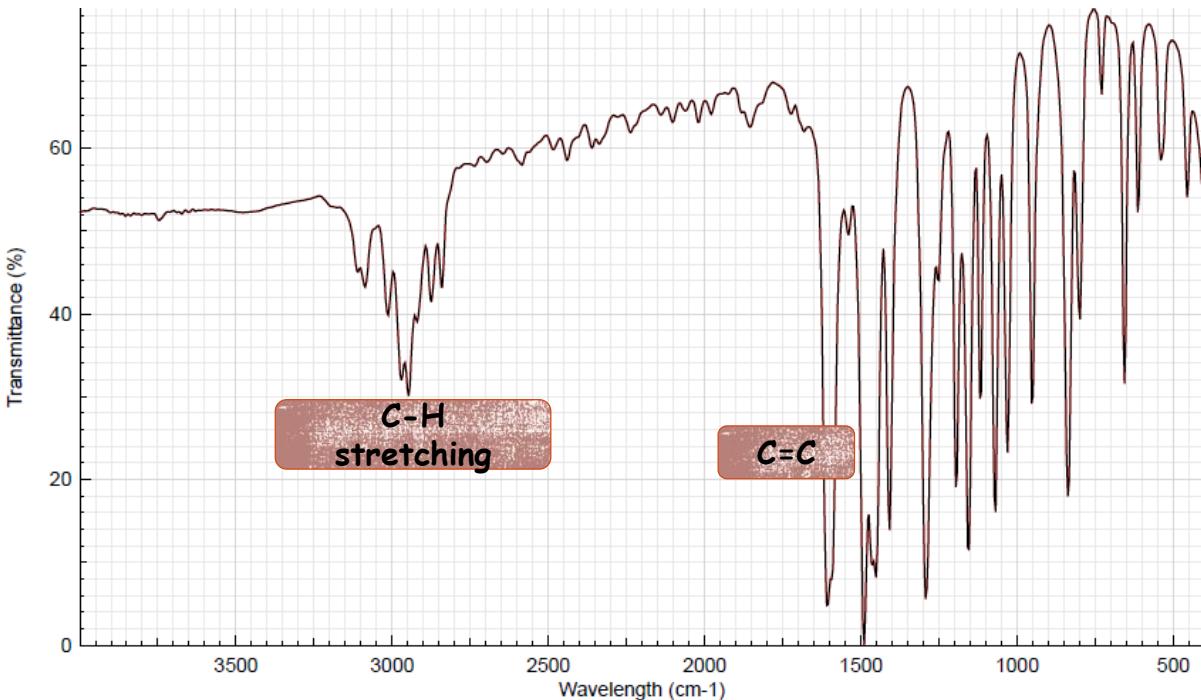
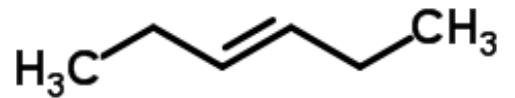
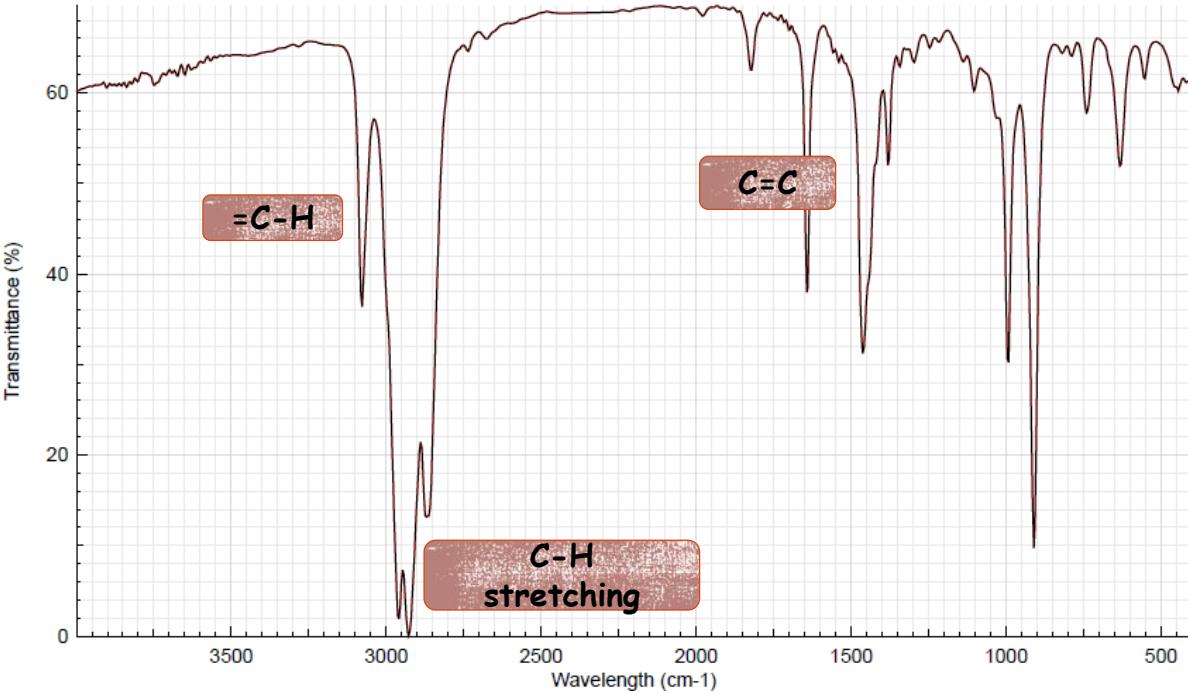
Terminal



(1620-1680 cm^{-1})

(3000-3100 cm^{-1})





- ❖ In case of olefins, conjugated with an aromatic ring, the (C=C) stretching appears at 1625 cm^{-1} (s) and an additional band at $\sim 1600\text{ cm}^{-1}$ is observed due to aromatic double bond.
- ❖ In compounds containing both olefinic and alkyl C-H bonds, the bands above 3000 cm^{-1} are generally attributed to aromatic or aliphatic (C-H) stretching, whereas between $3000-2840\text{ cm}^{-1}$ are generally assigned to the alkyl C-H stretching.
- ❖ The absorption frequency of a (C=C) bond in a cyclic ring is very sensitive to ring size. The absorption frequency decreases as the internal angle decreases and is lowest in cyclobutene (90° angle). The frequency increases again for cyclopropane

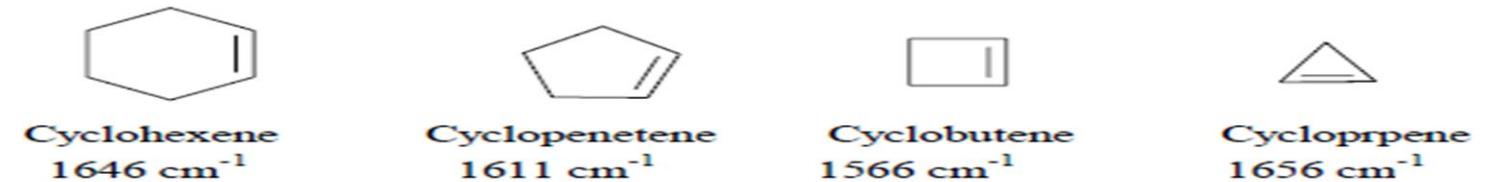
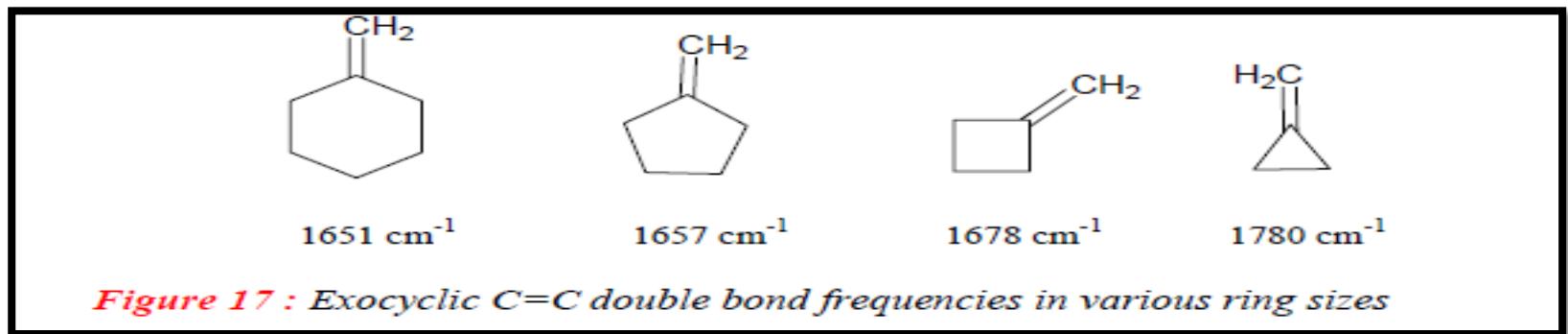


Figure 16 : C=C vibration frequencies of cycloalkenes

❖ The exocyclic (C=C) bonds exhibit an *increase in frequency with decrease in ring size*. The exocyclic double bond on six-membered ring absorbs at **1651 cm⁻¹** and it is shifted to **1780 cm⁻¹** in case of exocyclic (C=C) bond on cyclopropane.



IR SPECTRUM OF ALKYNES

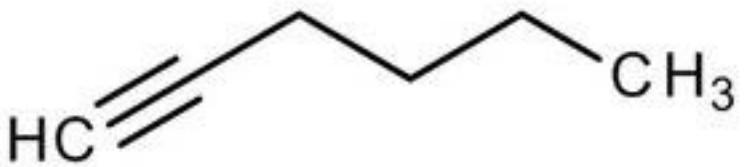
Internal



(2000-2200 cm^{-1})



Terminal



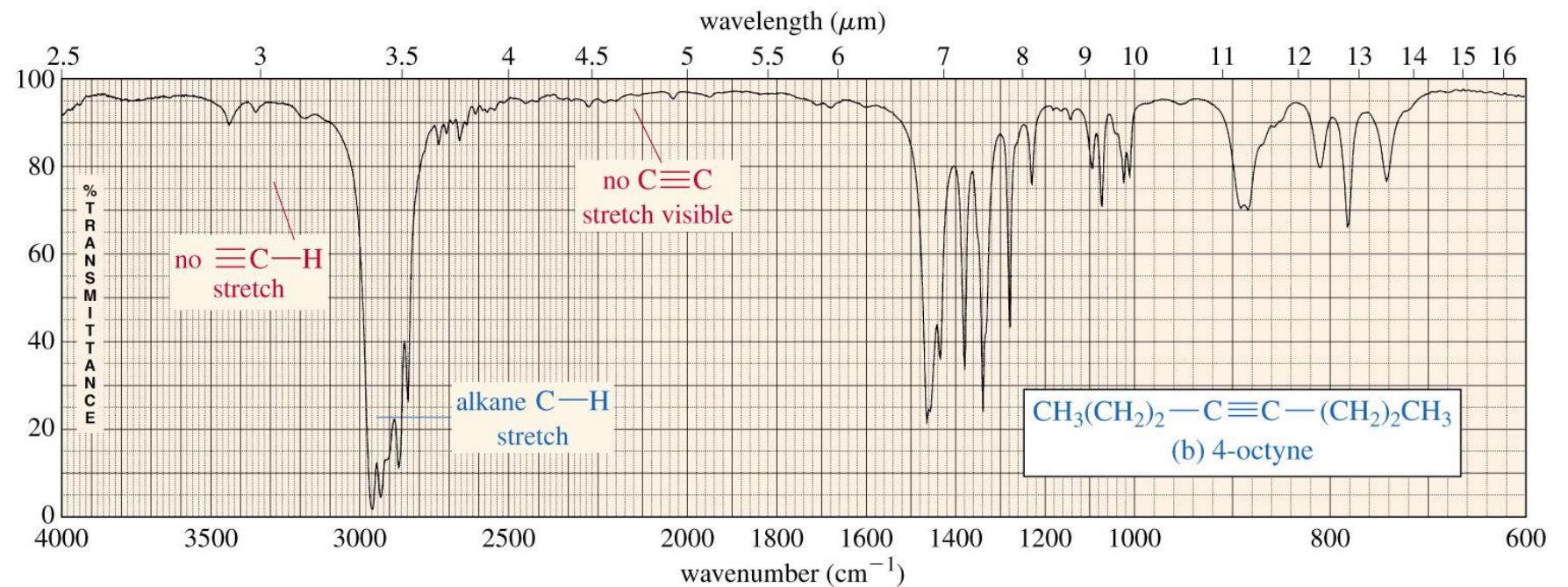
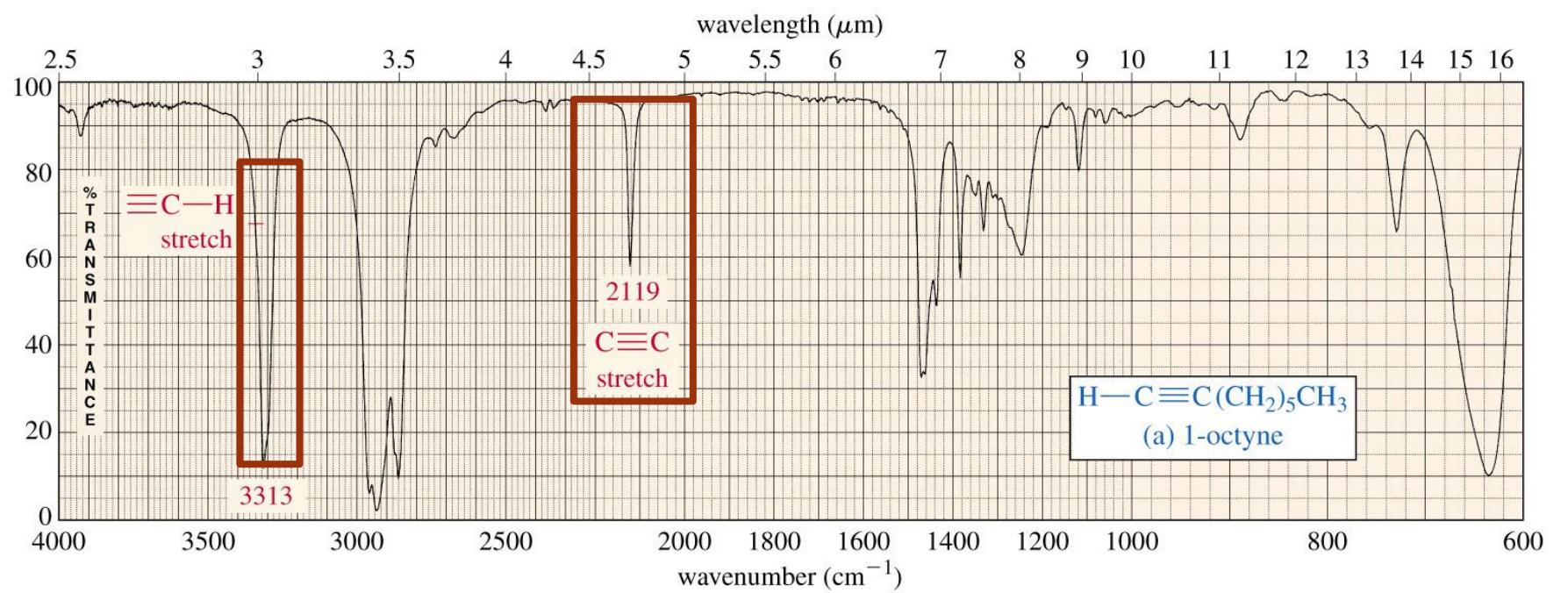
(2000-2200 cm^{-1})

$\text{C}\equiv\text{C}$

$\equiv\text{C}-\text{H}$

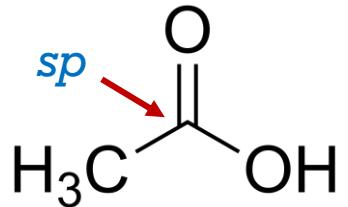
(3100-3300 cm^{-1})





IR SPECTRUM OF CARBOXYLIC ACIDS AND ALCOHOLS

Carboxylic acid



(2500-3300 cm^{-1})

O-H

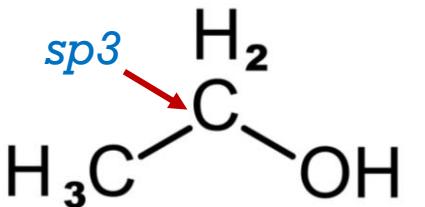
(1700 cm^{-1})

C=O

(1200-1300 cm^{-1})

C-O

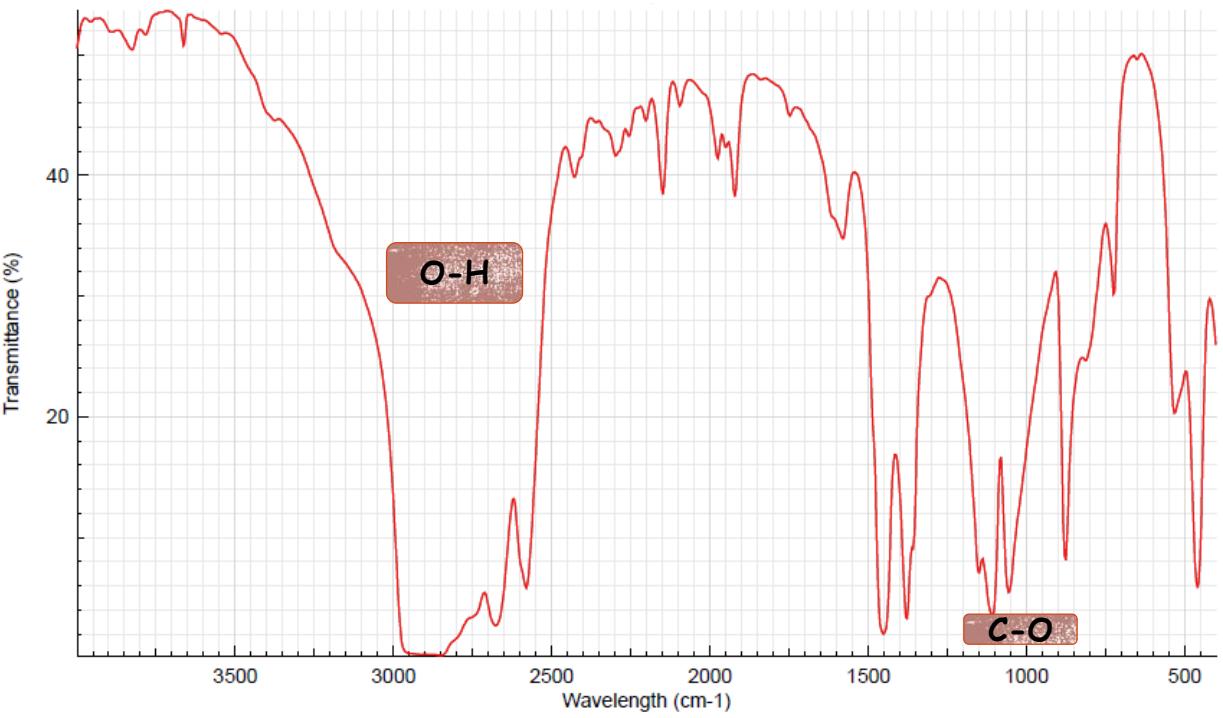
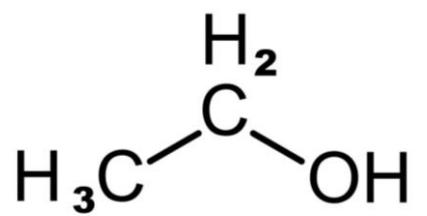
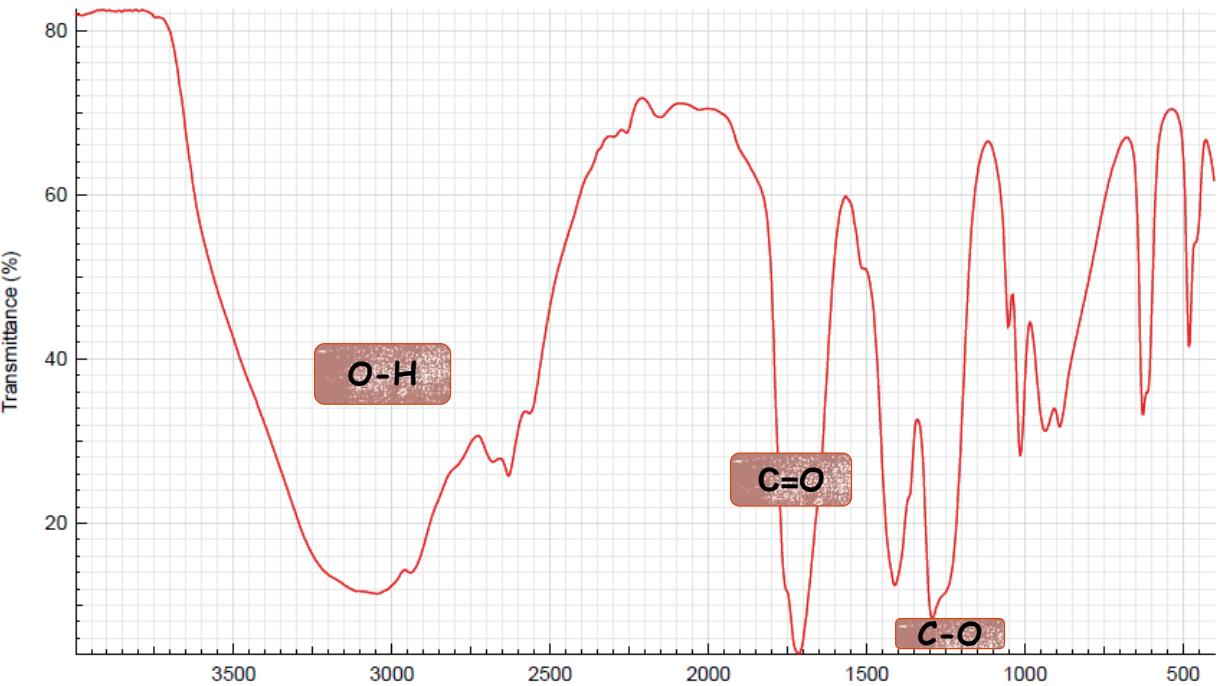
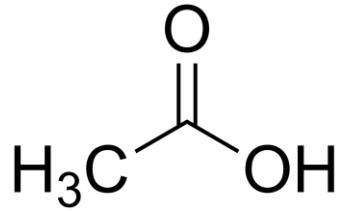
Alcohol



(3200-3500 cm^{-1})

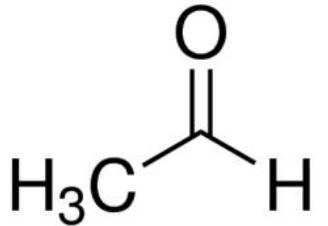


(1000-1150 cm^{-1})



IR SPECTRUM OF ALDEHYDES AND KETONES

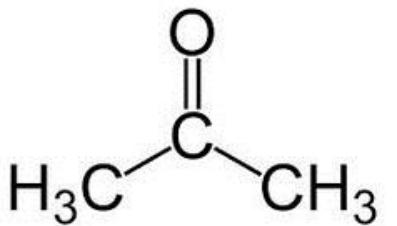
Aldehyde



(1700 cm^{-1})

C=O

Ketone

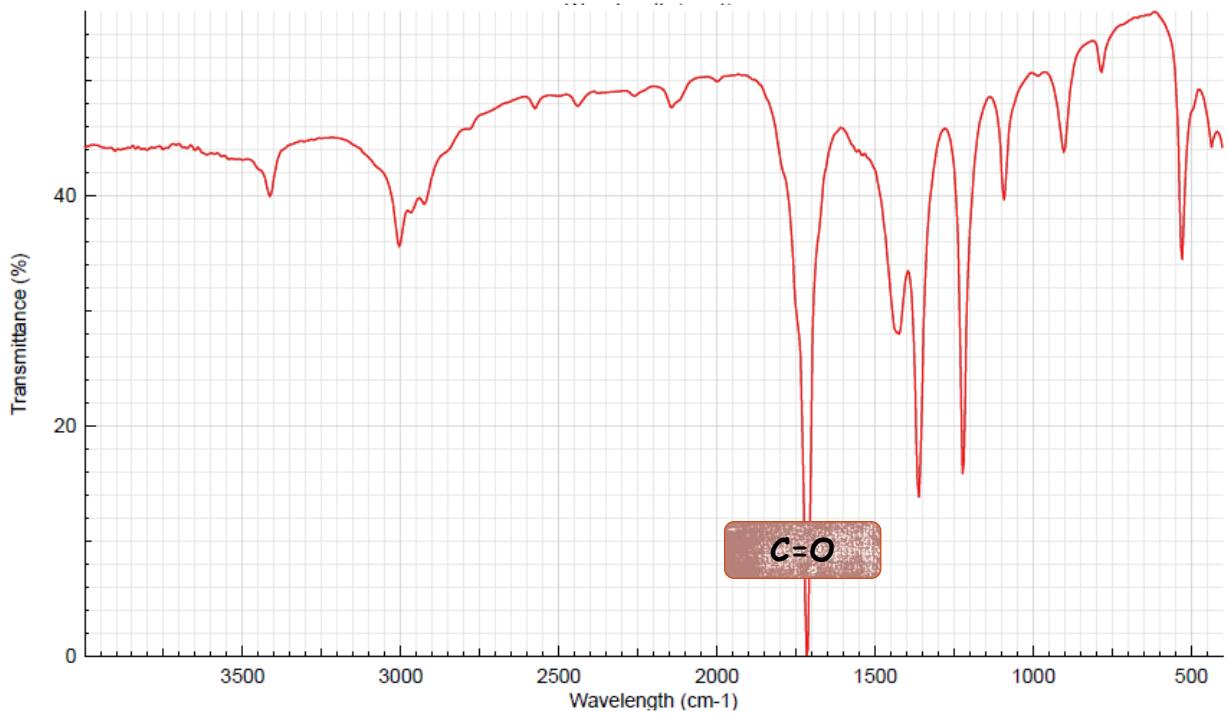
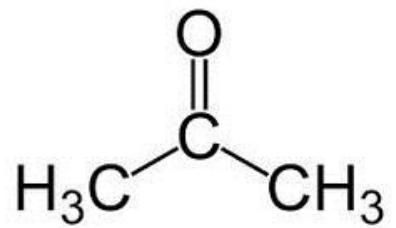
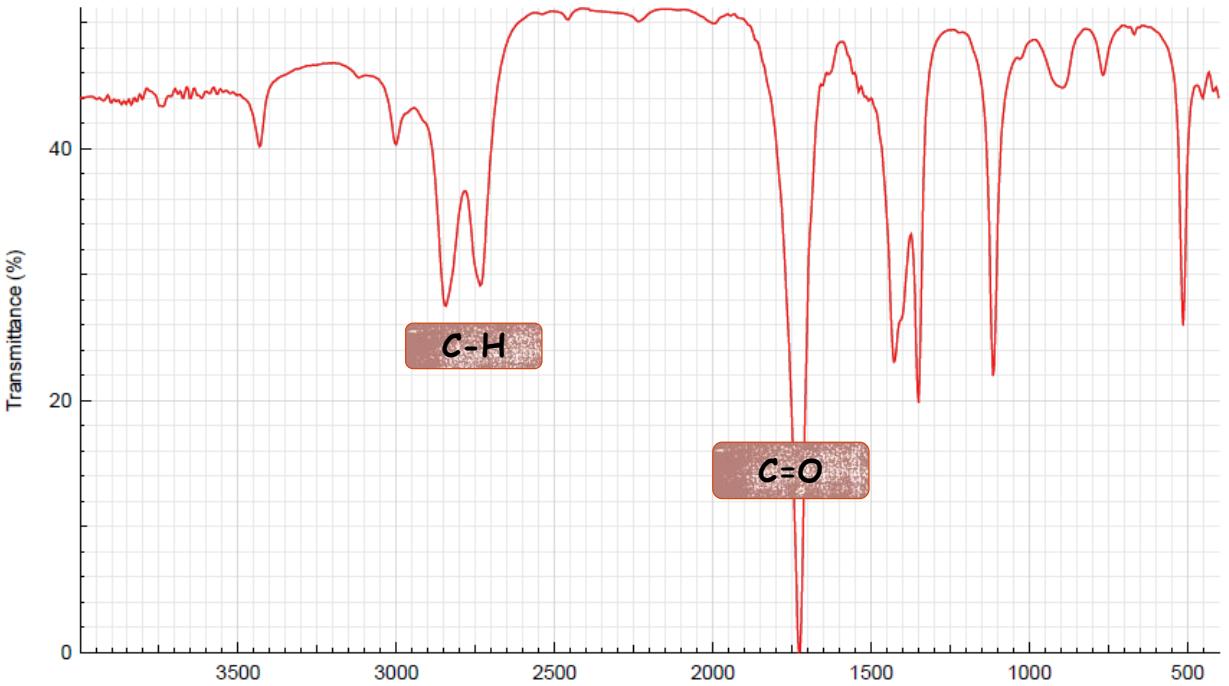
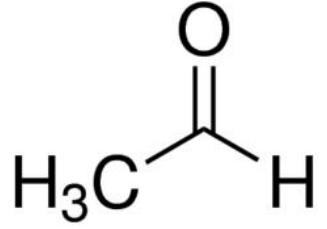


(1700 cm^{-1})

$(2700 \text{ and } 2800 \text{ cm}^{-1})$

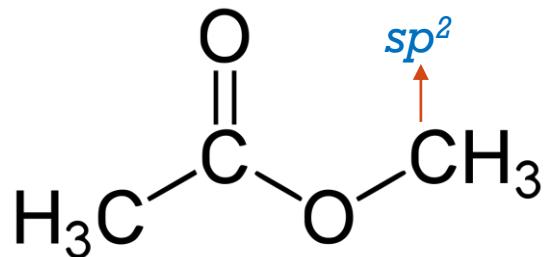
C-H





IR SPECTRUM OF ESTERS AND ETHERS

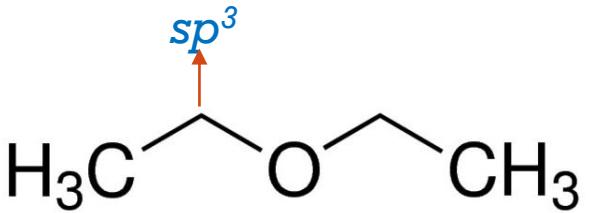
Ester



(1200-1300 cm^{-1})

C-O

Ether

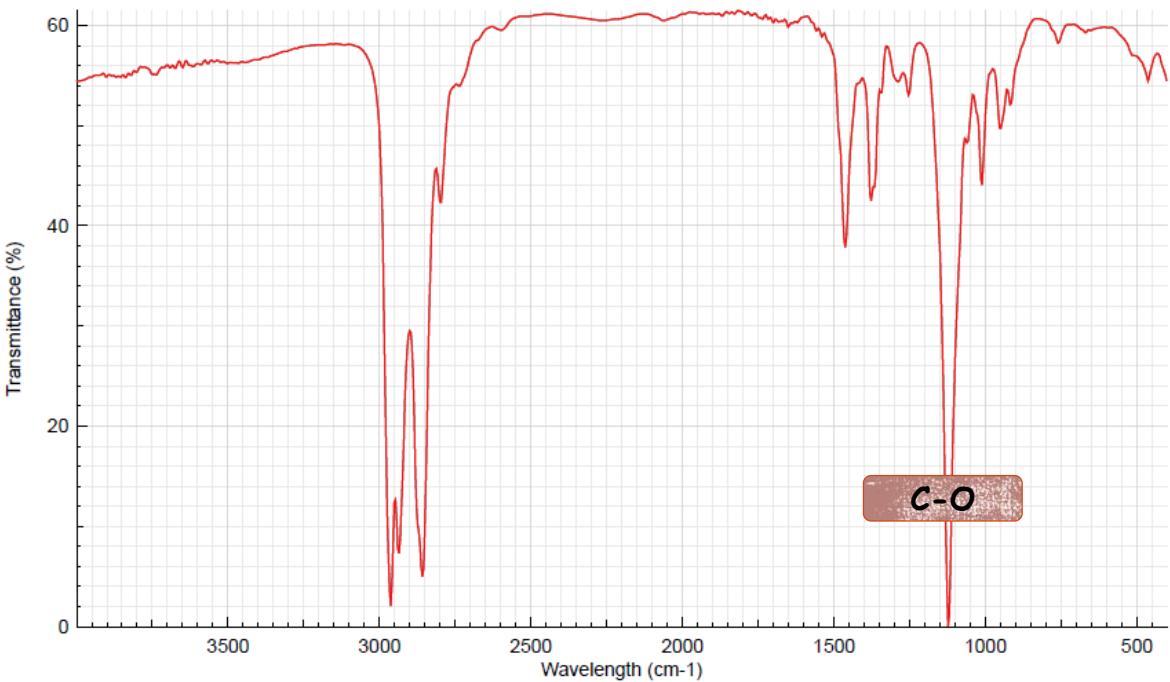
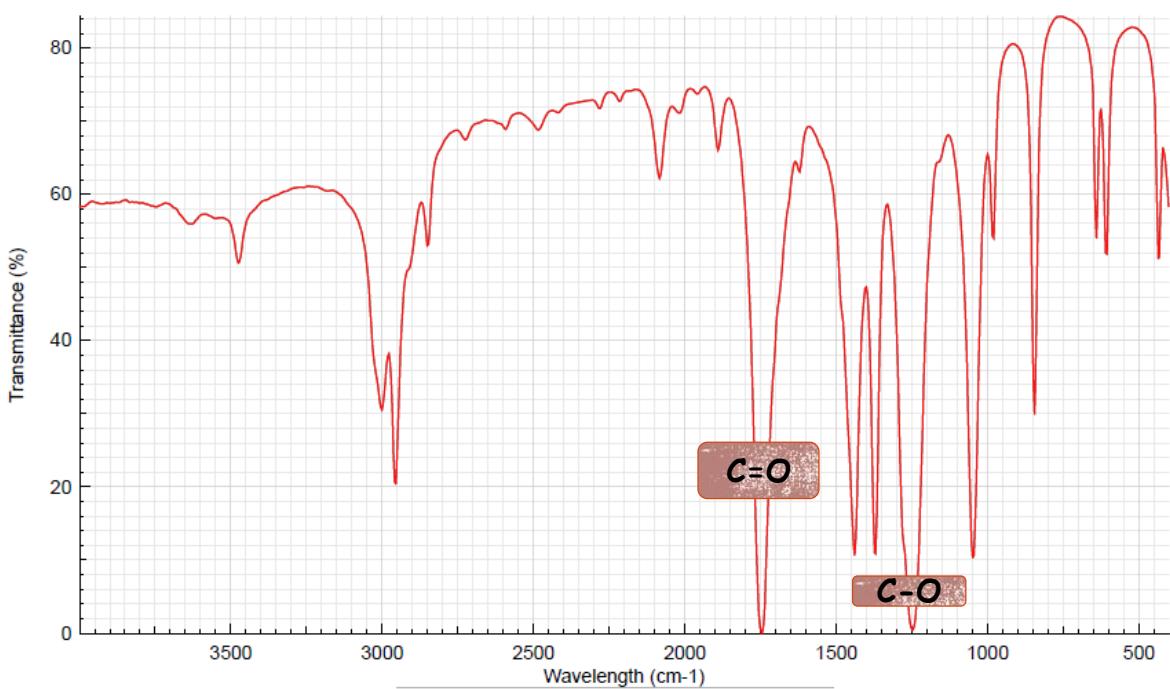
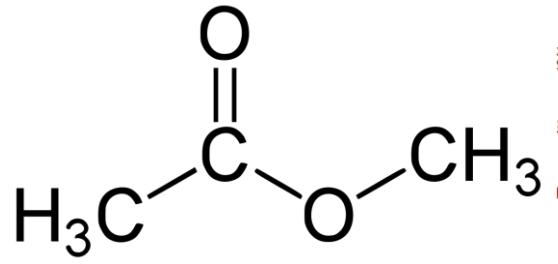


(1000-1150 cm^{-1})

C=O

(1735 cm^{-1})





IR SPECTRUM OF AMINE

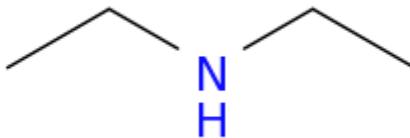
1° amine



TWO peaks

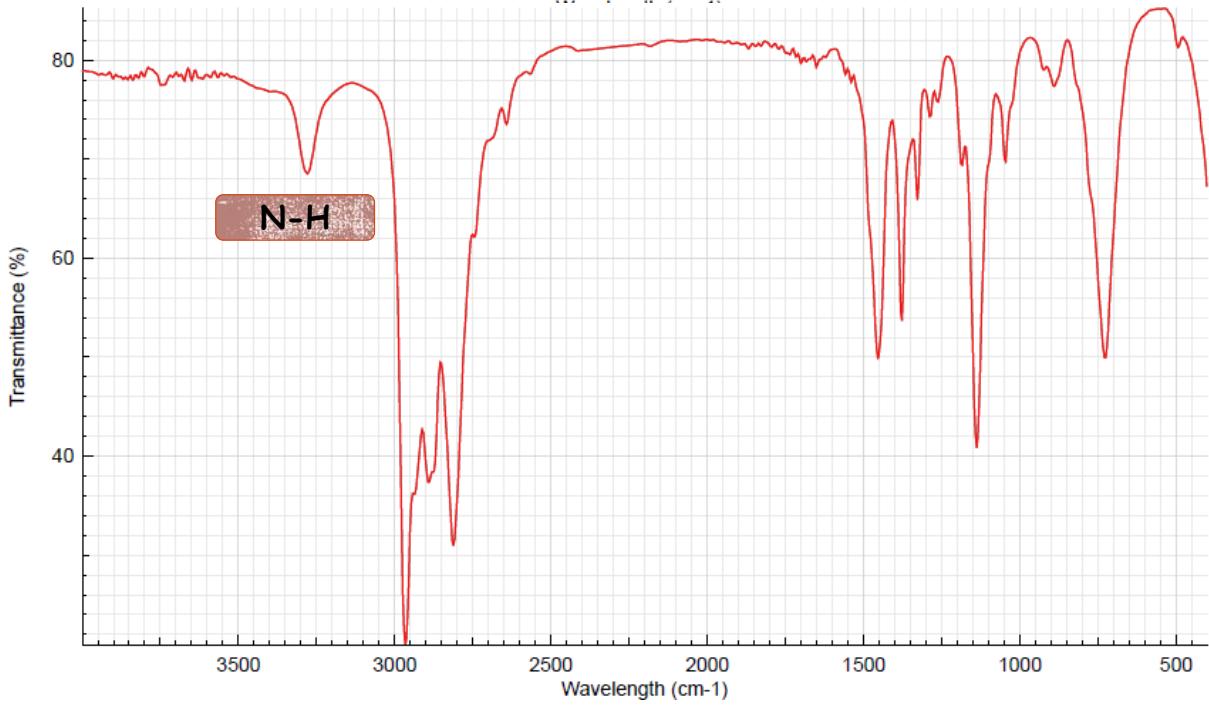
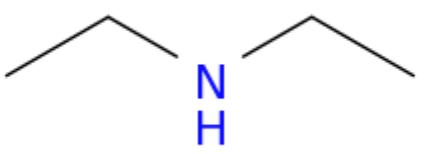
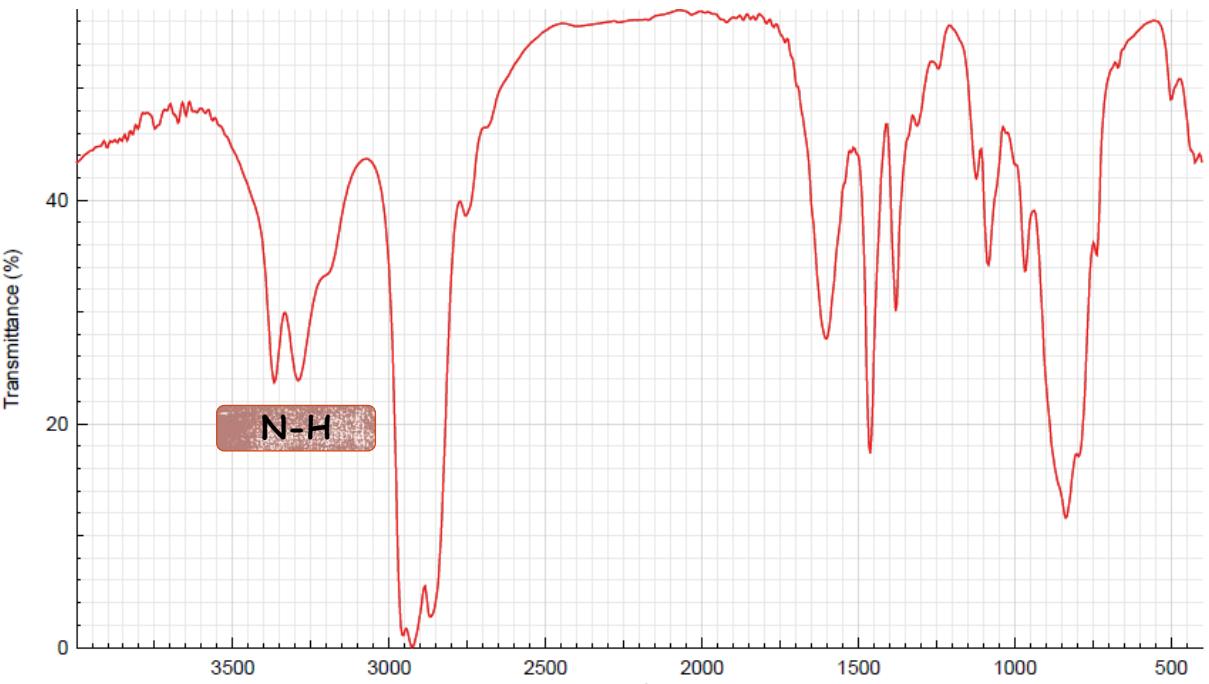
(N-H) (3300-3500 cm⁻¹)

2° amine



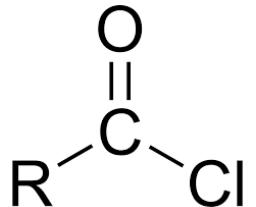
ONE peak

- NOTE: N-H signal in amines is broad BUT it is not broader than O-H signal in alcohols



IR SPECTRUM OF ACID CHLORIDE AND ANHYDRIDE

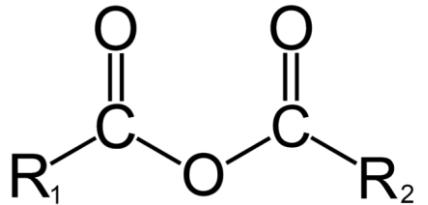
Acid chloride



(1790-1810 cm^{-1})



Anhydride



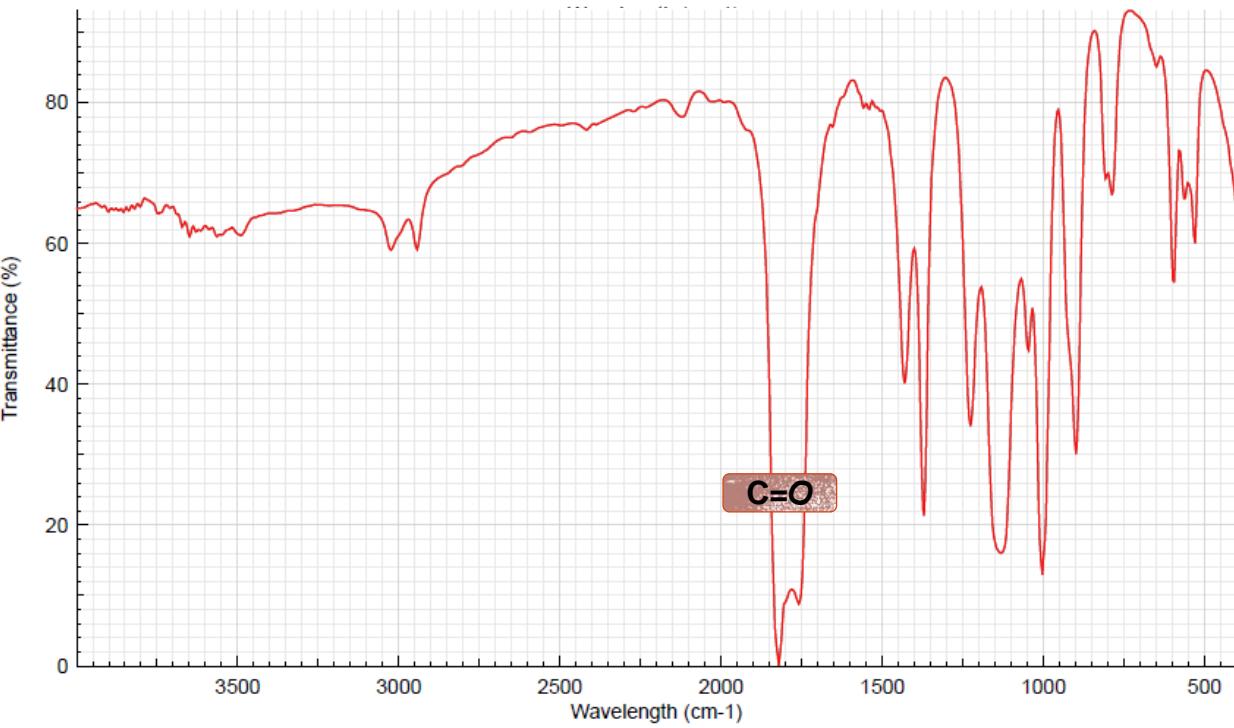
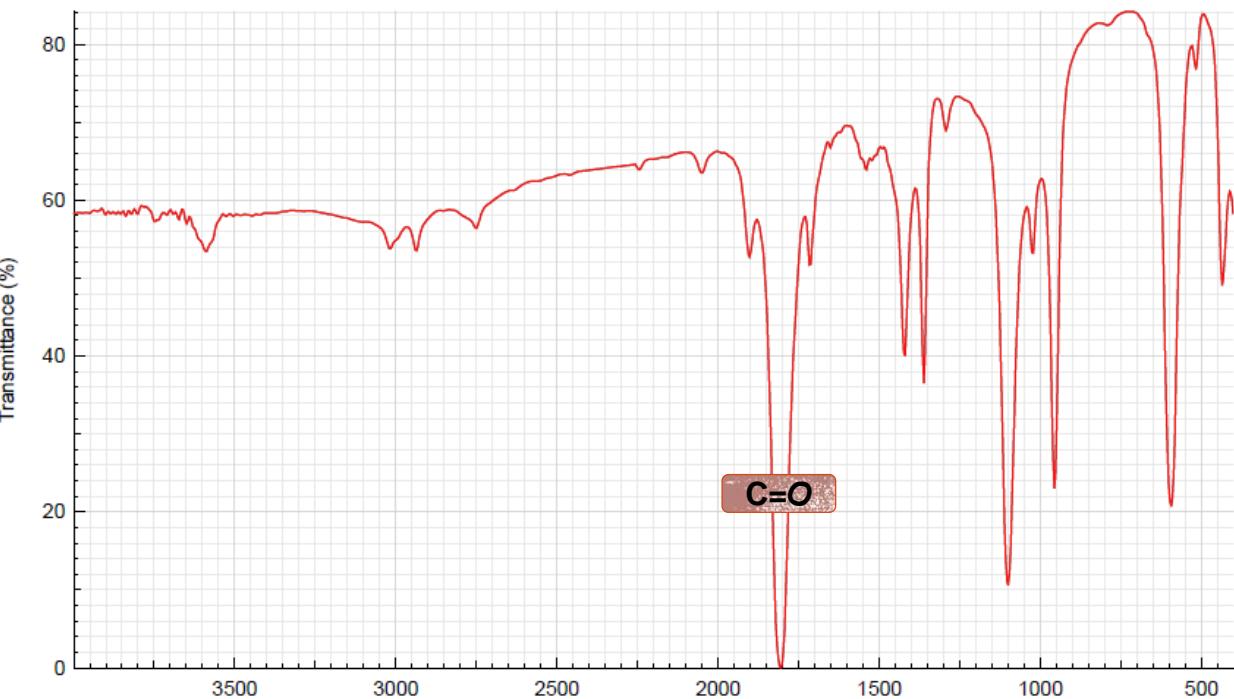
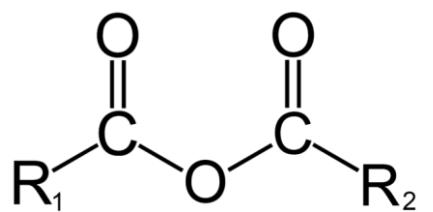
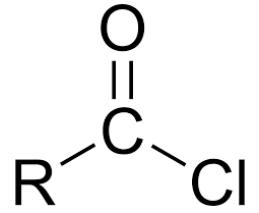
(1750-1800 cm^{-1})

C-O

(900-1300 cm^{-1})

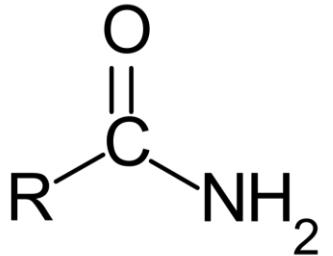
- In case of **acid chlorides**, the **(C=O)** stretching frequencies appear at 1810-1790 cm^{-1} which is attributed to high electronegativity of chlorine
- In case of **anhydrides of conjugated carboxylic acids**, the frequencies due to these bands are shifted to 1775 and 1720 cm^{-1} .





IR SPECTRUM OF AMIDES

1° amide



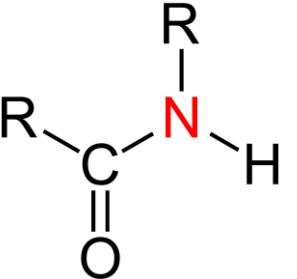
(1650-1690 cm^{-1})

(3550 and 3180 cm^{-1})



(N-H) stretching

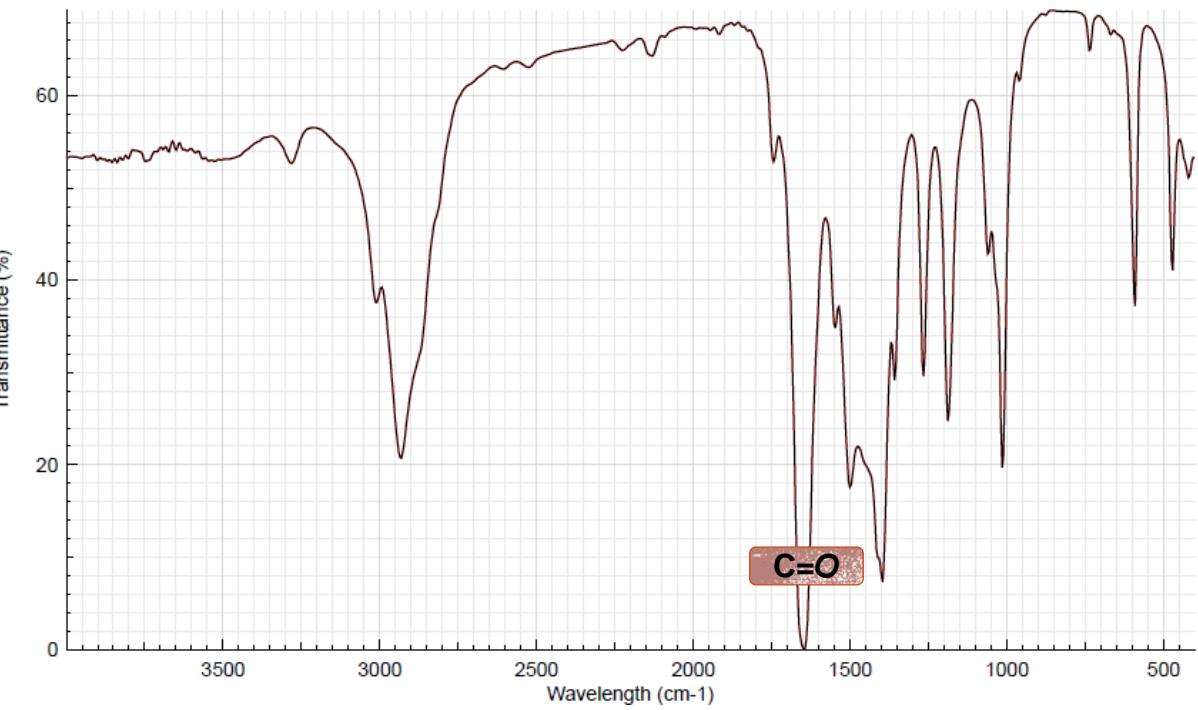
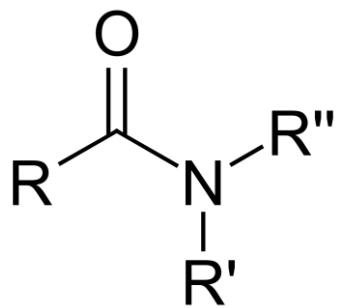
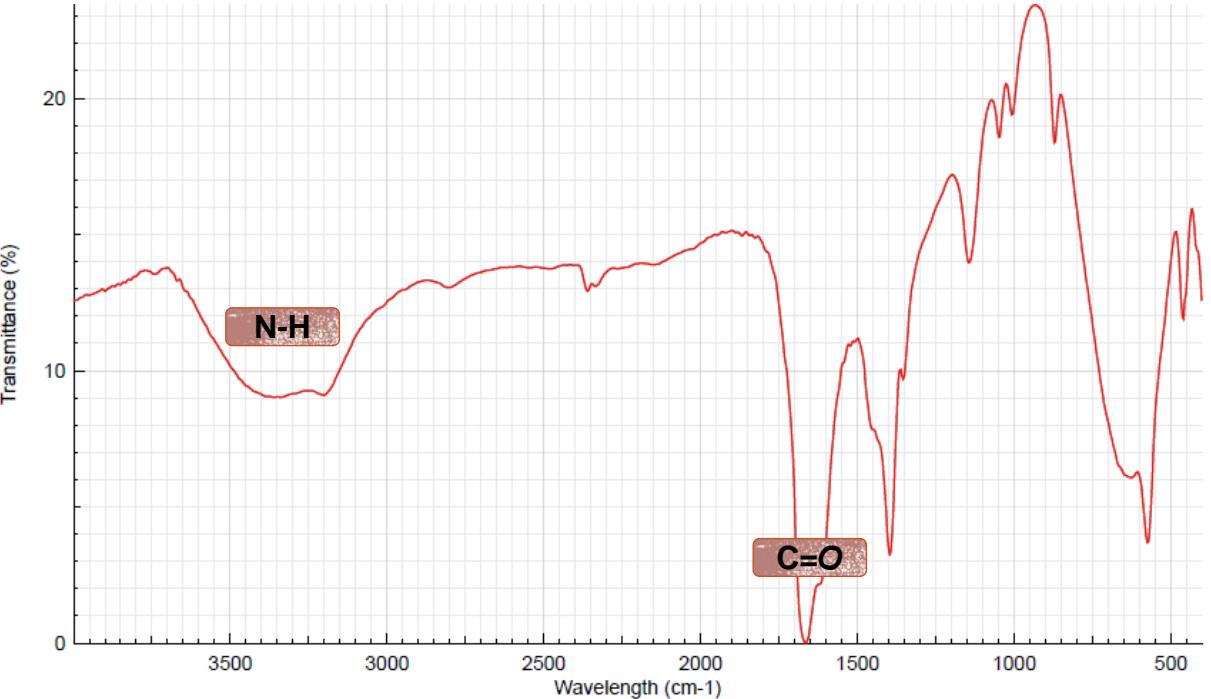
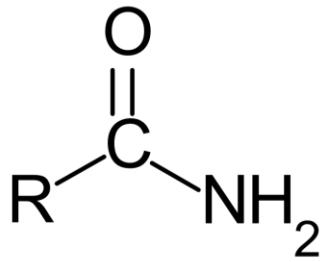
2° amide



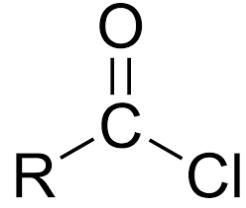
(1650-1690 cm^{-1})

\sim (3300 cm^{-1})

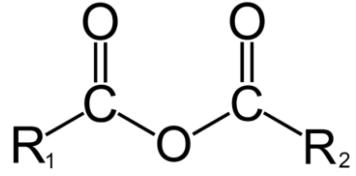
In 3° amide, there is no (N-H) stretching



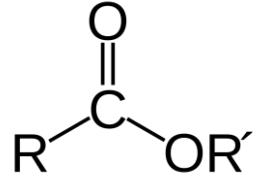
$(C=O)$ stretching values (in cm^{-1}) of carbonyl compounds



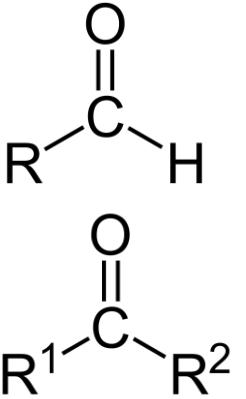
1800



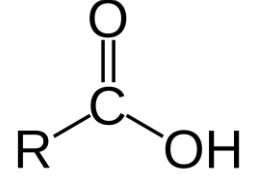
1750-1800



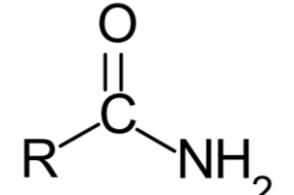
1730- 1750



1710-1750



1700-1725



1650-1690

