

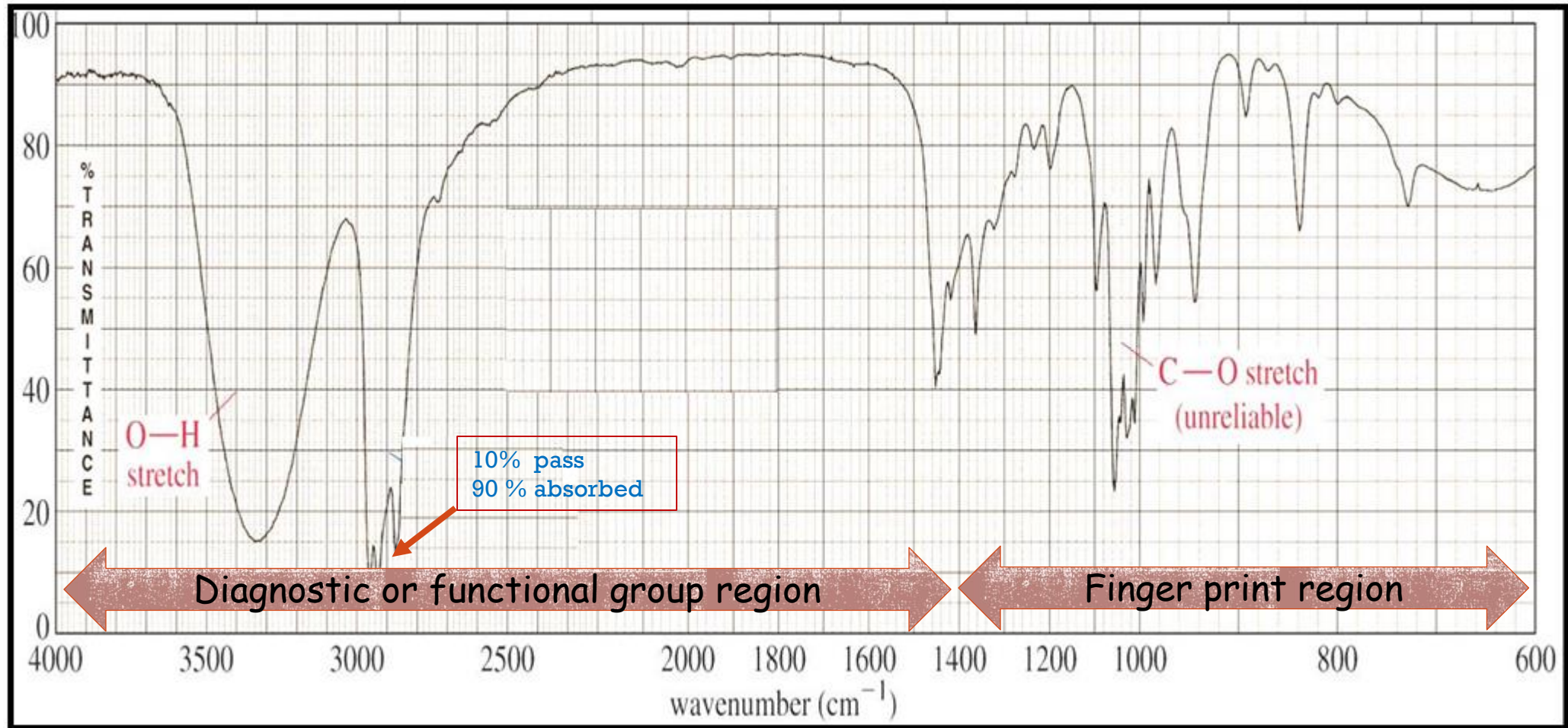
INFRA-RED SPECTROSCOPY

Characteristic Group Vibrations of Organic Molecules

4

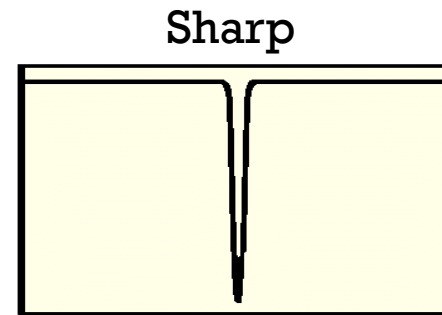
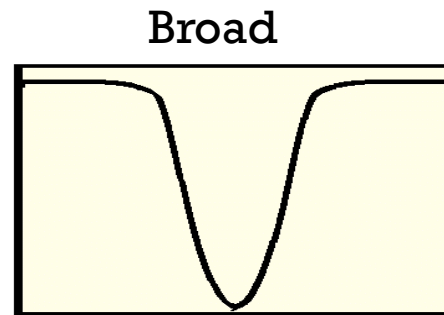
2021-2022

The features of IR spectrum



IR SIGNALS

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

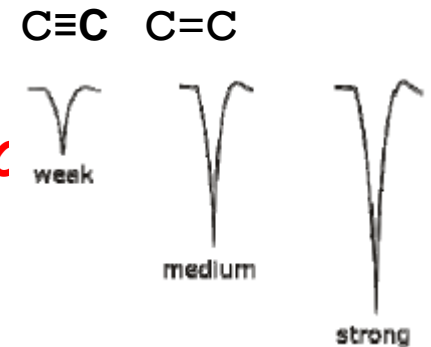


Question: what makes the IR signal broad?

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

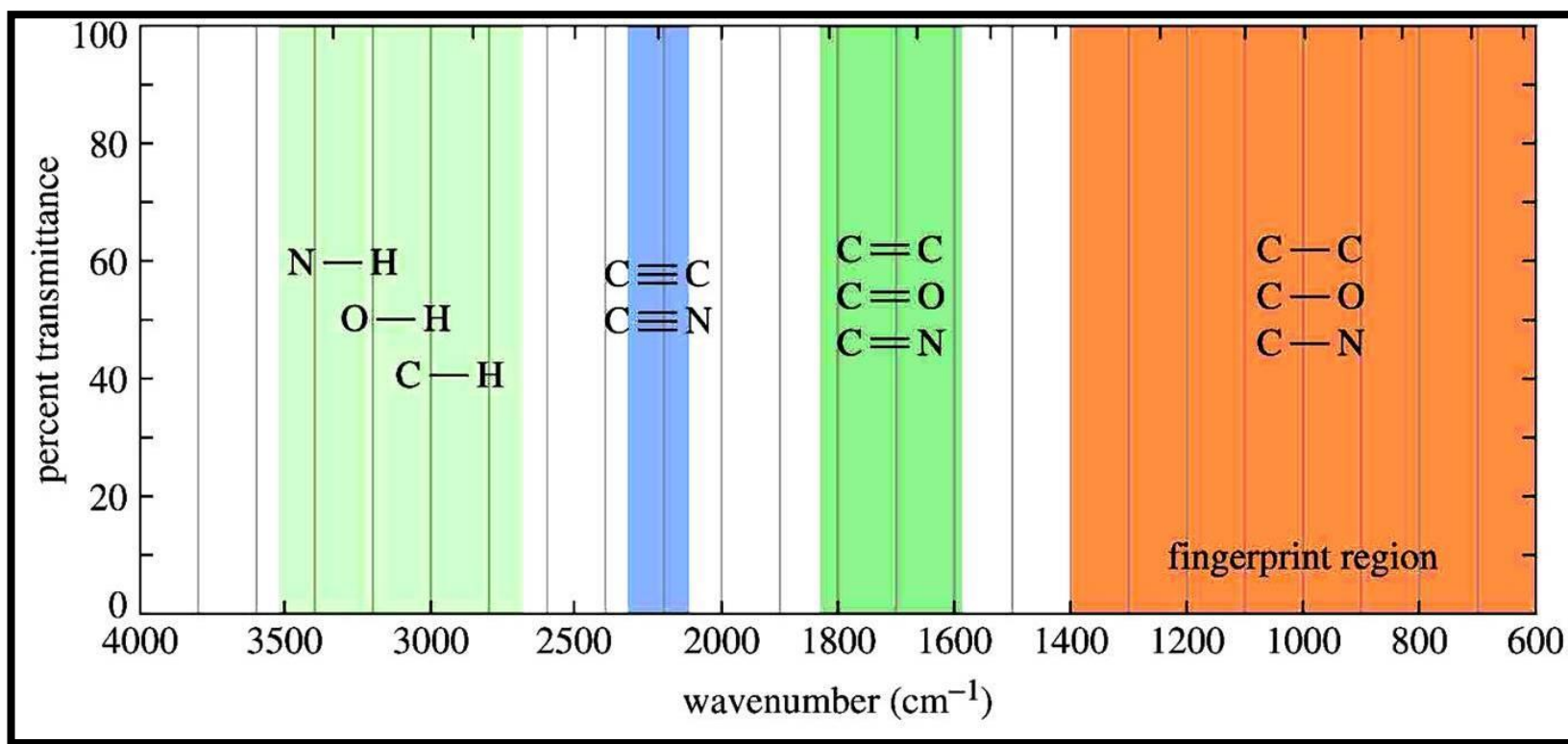
Question: what makes the IR signal sharp?

- A. Non-polar bonds like **C=C** and **C≡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.



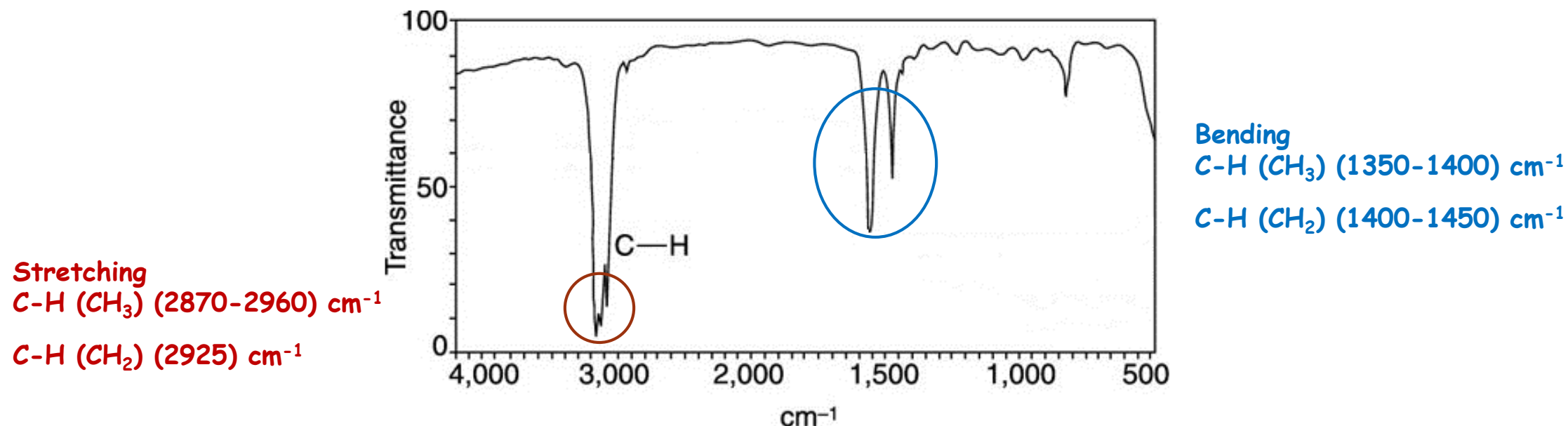
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003



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..



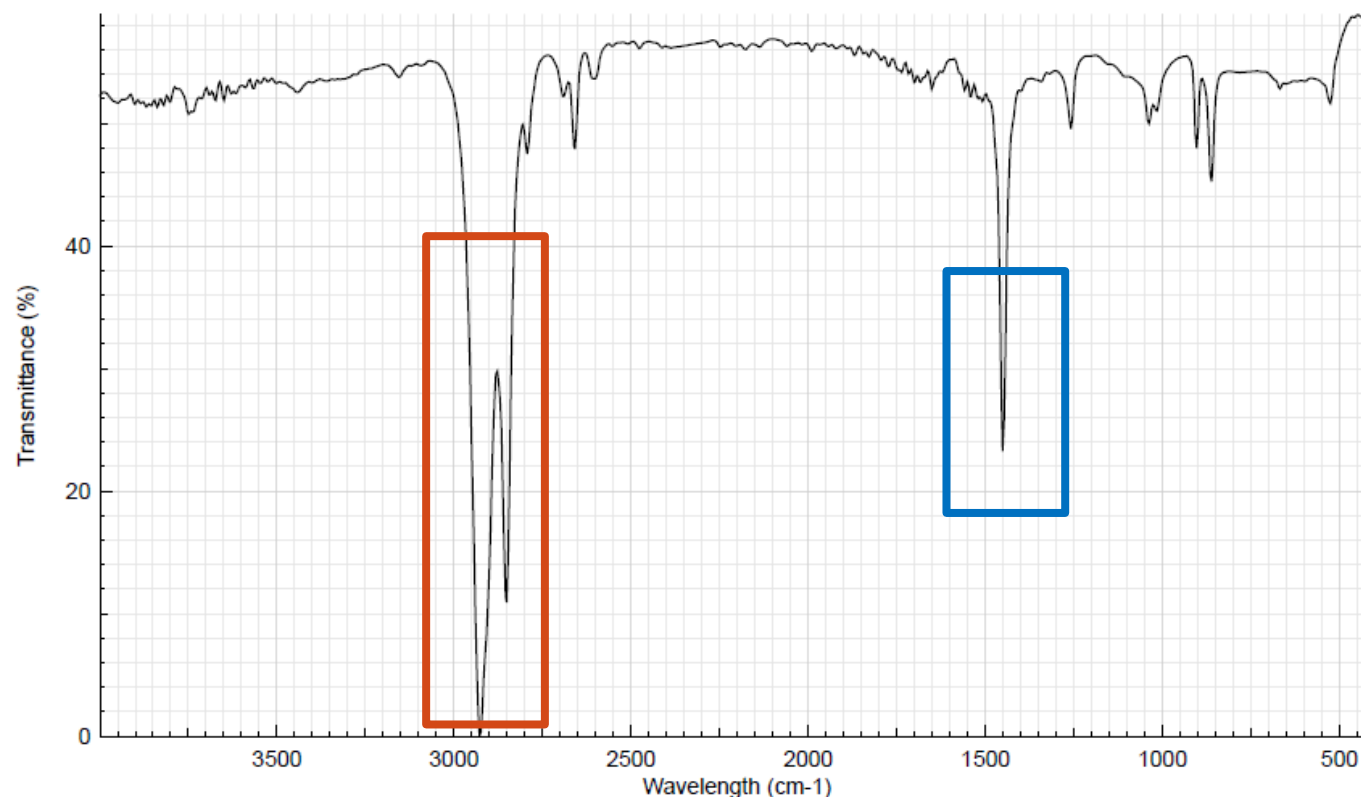
The (**C-C**) bond vibrations appear as weak bands in **1200-800 cm⁻¹** region and are seldom used for structural study. Whereas the (**C-C**) **bending** absorptions occur at **< 500 cm⁻¹** and are usually below the range of IR - instrument.



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 (CH_2) 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 ($2800-3000 \text{ cm}^{-1}$)



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.

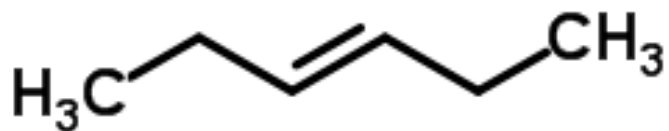
$(C=C)$ stretching $>$ $(C-C)$ stretching
(1680-1620 cm^{-1}) (1200-800 cm^{-1})

- 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



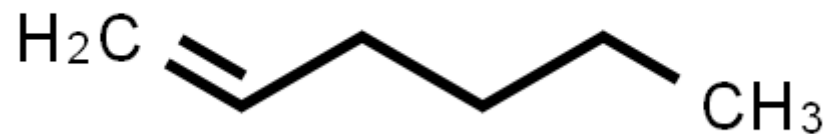
(1620-1680 cm^{-1})



$\text{C}=\text{C}$

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

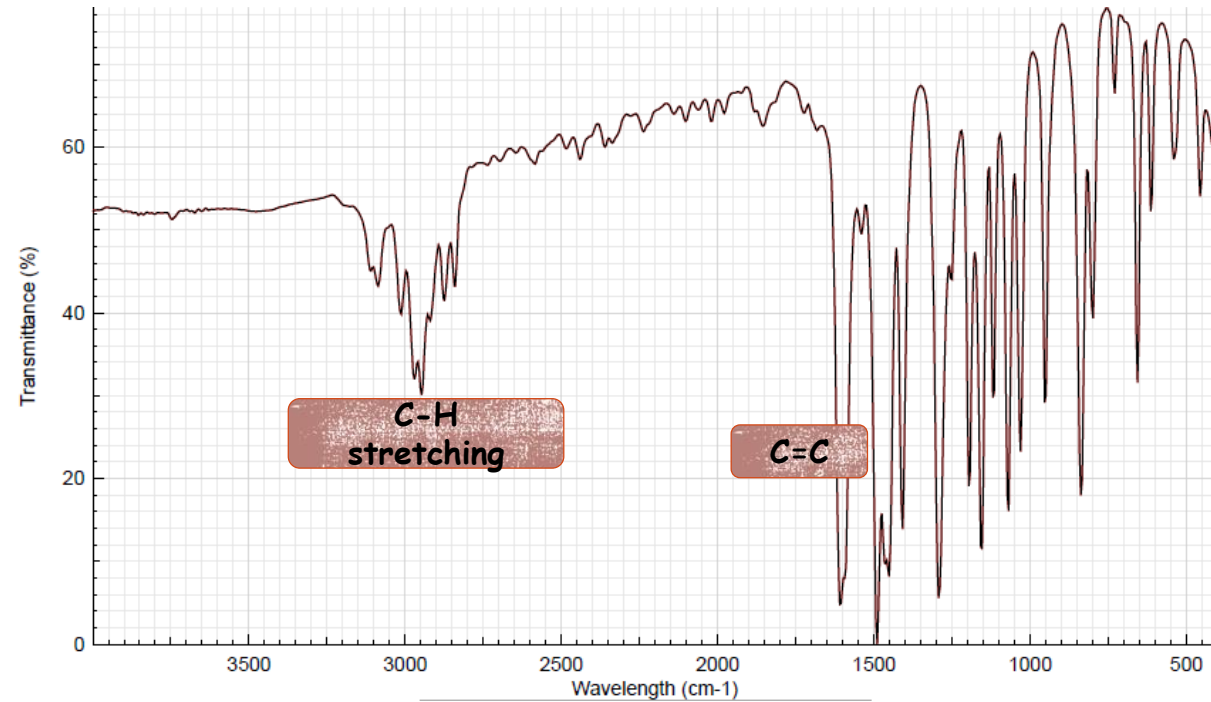
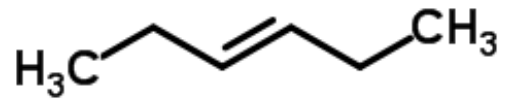
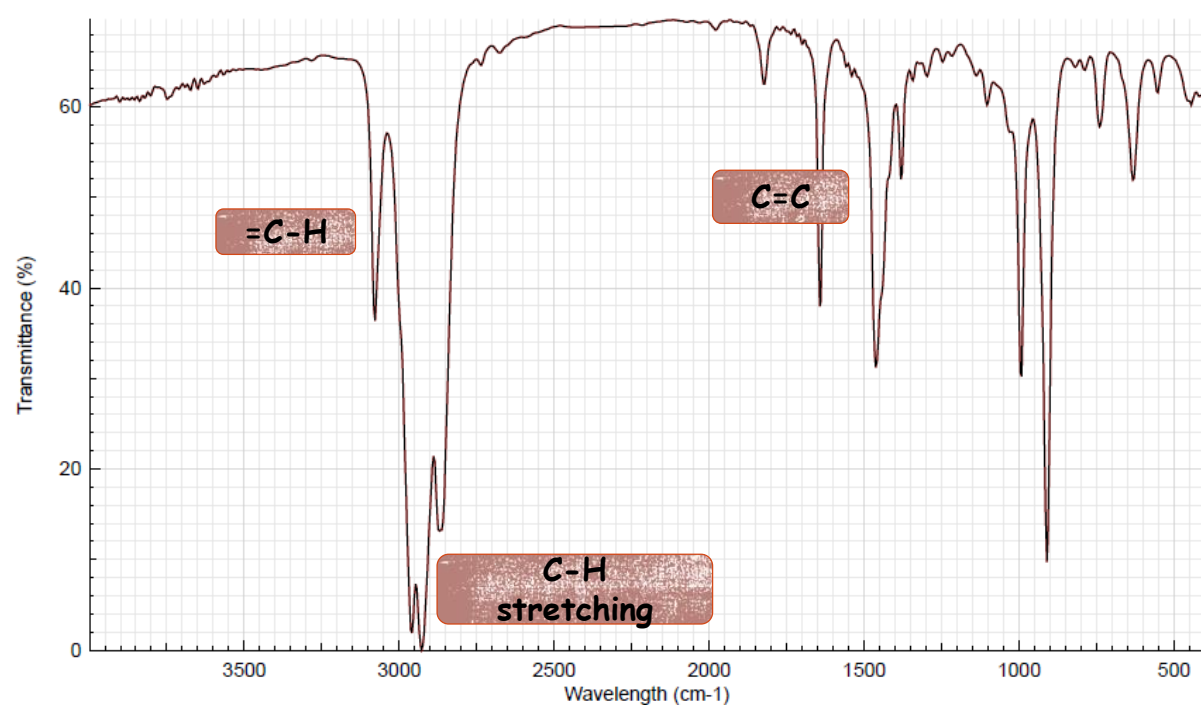
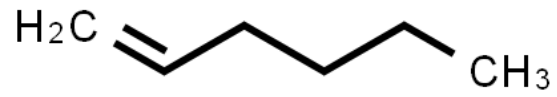
Terminal



(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 ~1600 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 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

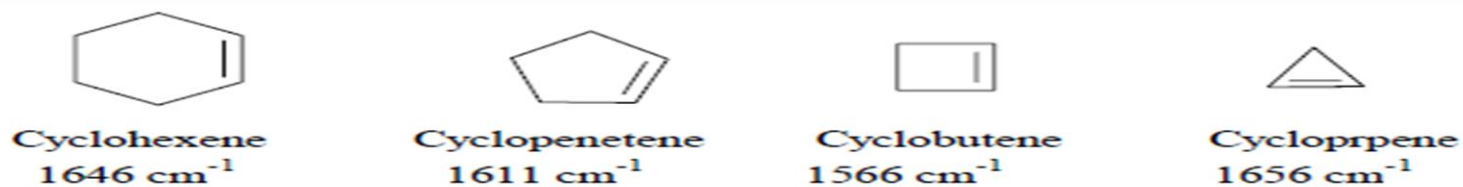
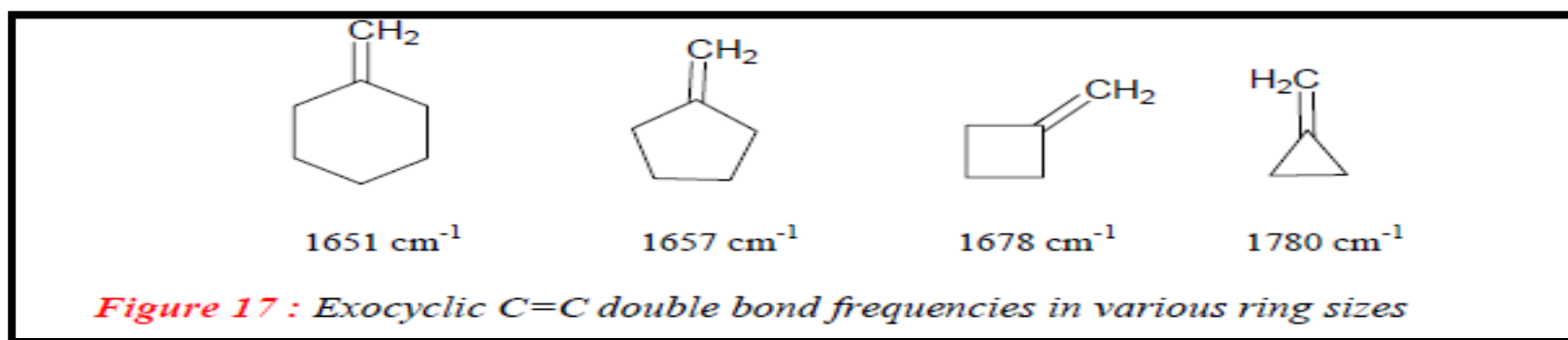


Figure 16 : C=C vibration frequencies of cycloalkenes



- ❖ 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



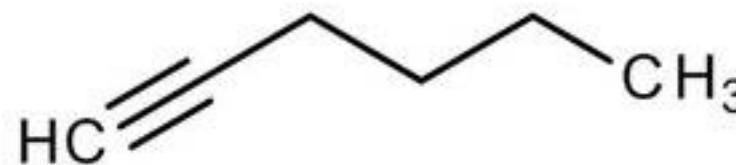
(2000-2200 cm^{-1})



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

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

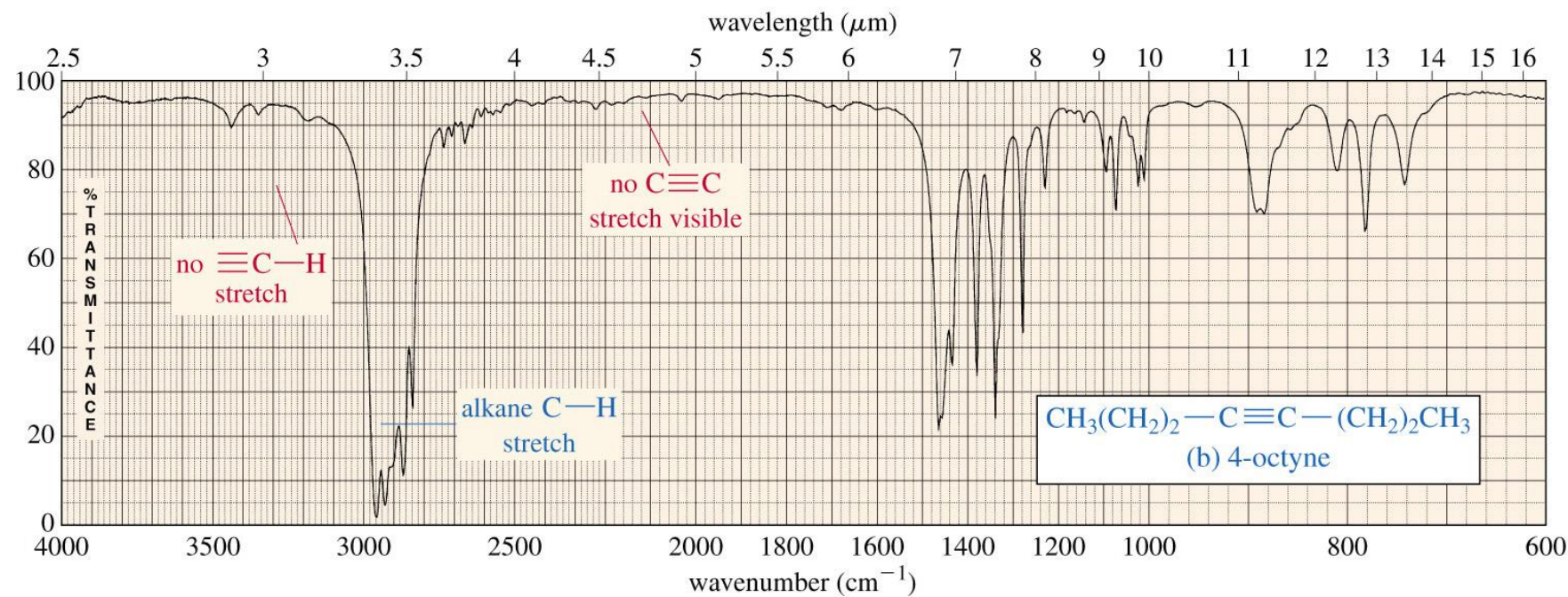
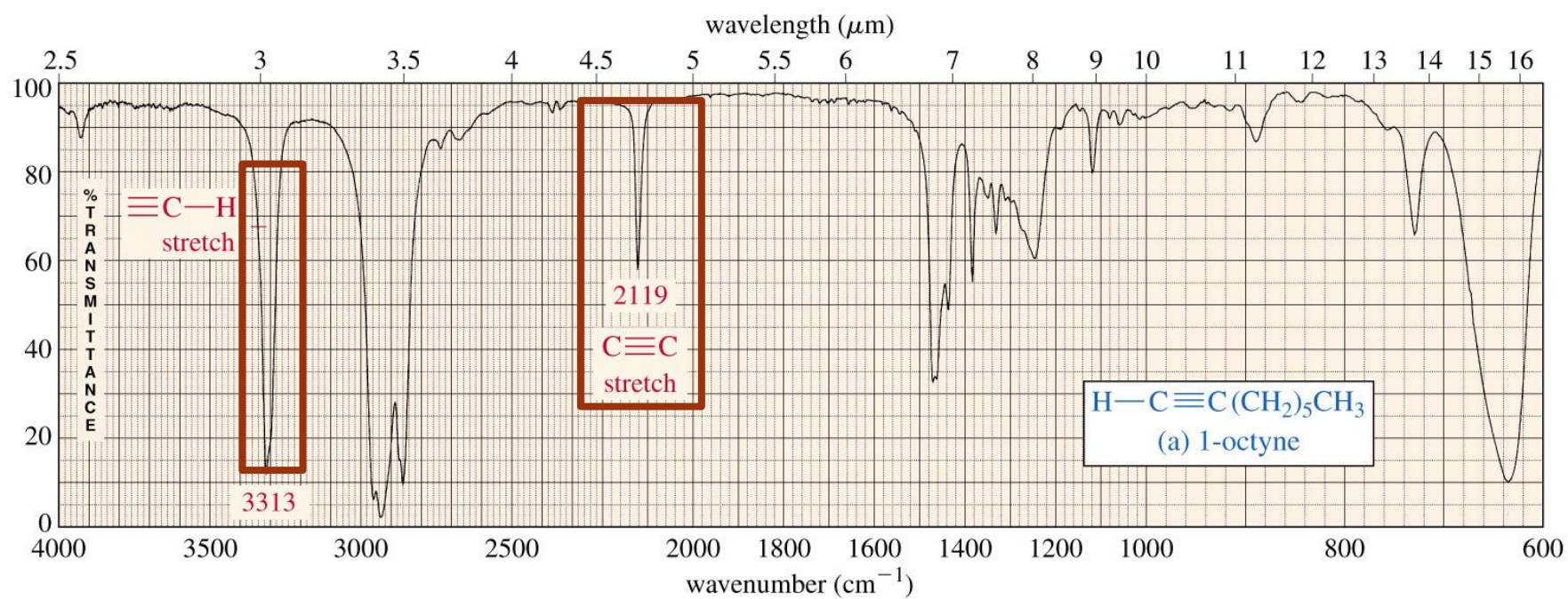
Terminal



(2000-2200 cm^{-1})

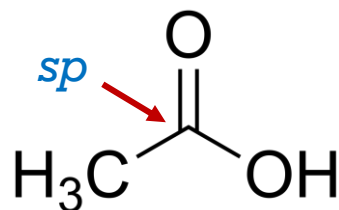
(3100-3300 cm^{-1})





IR SPECTRUM OF CARBOXYLIC ACIDS AND ALCOHOLS

Carboxylic acid



(2500-3300 cm^{-1})

O-H

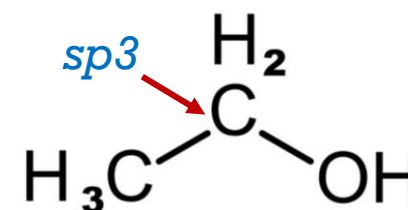
(1700 cm^{-1})

C=O

(1200-1300 cm^{-1})

C-O

Alcohol

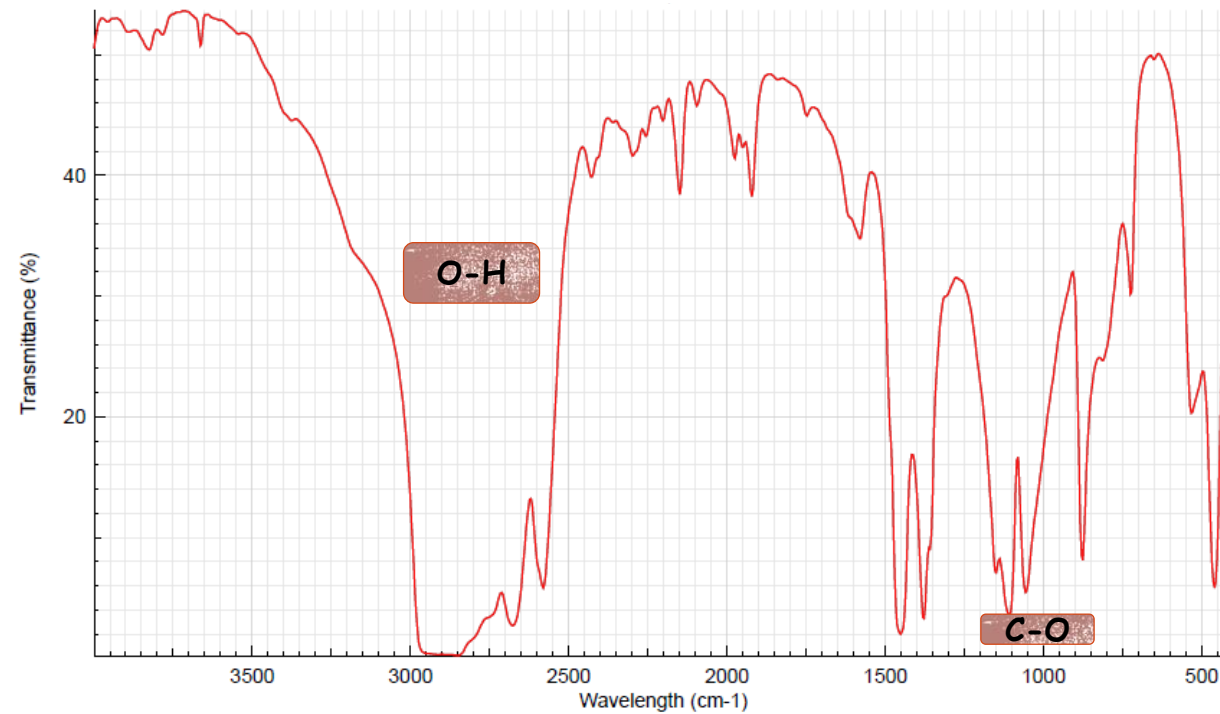
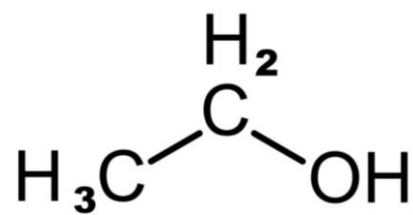
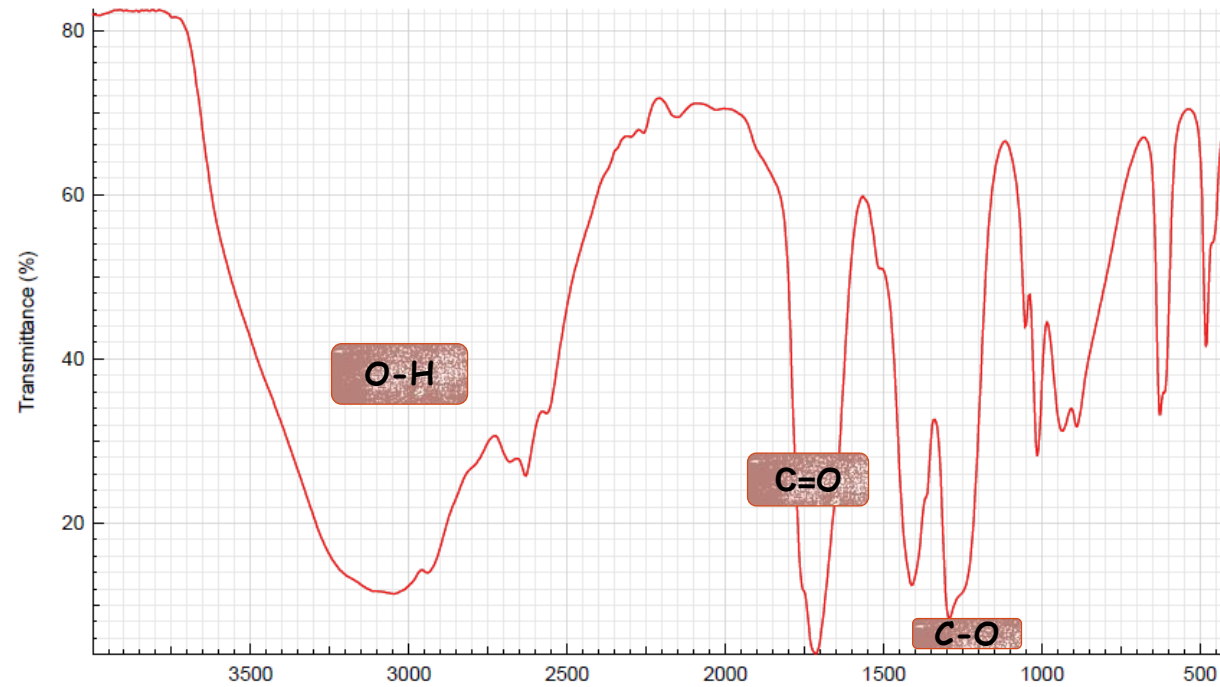
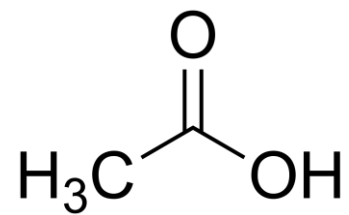


(3200-3500 cm^{-1})



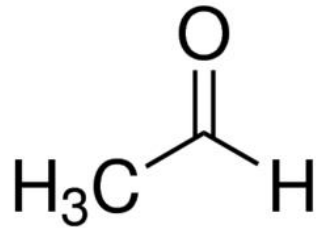
(1000-1150 cm^{-1})





IR SPECTRUM OF ALDEHYDES AND KETONES

Aldehyde



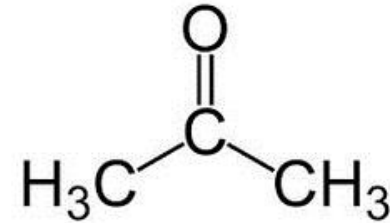
(1700 cm⁻¹)

C=O

(2700 and 2800 cm⁻¹)

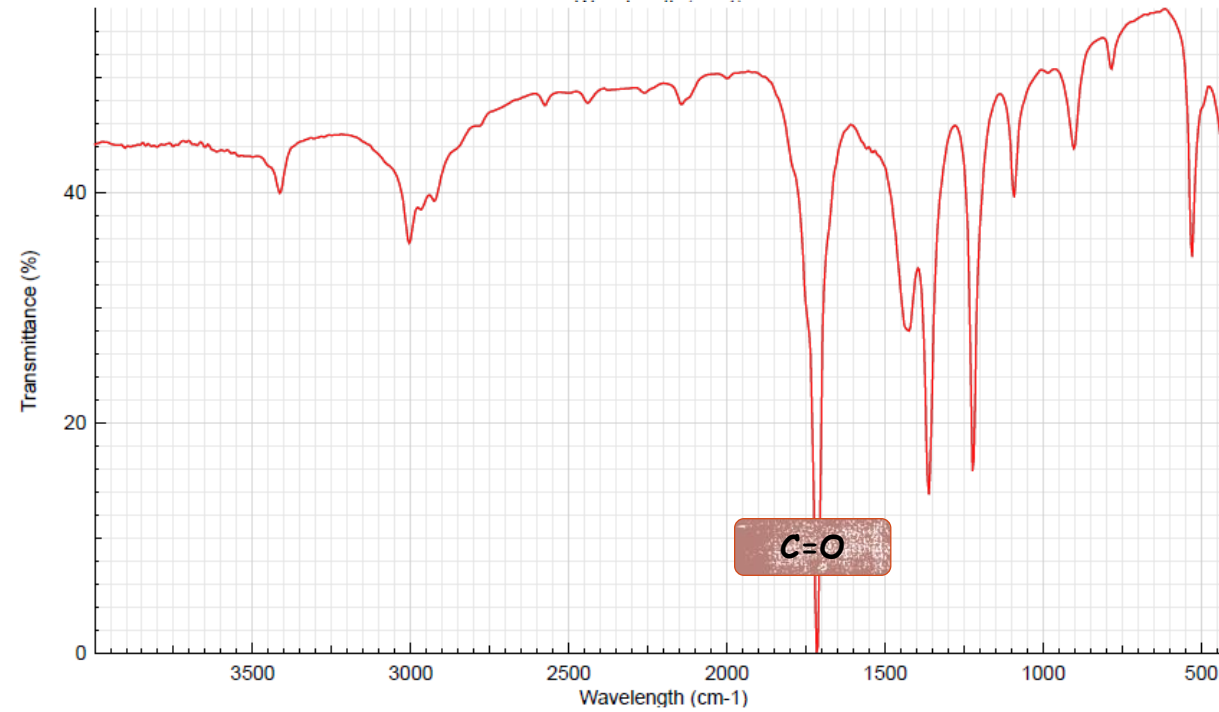
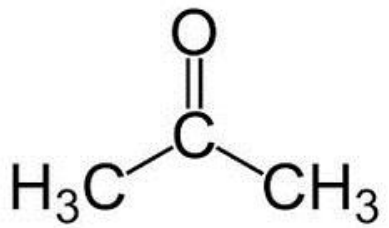
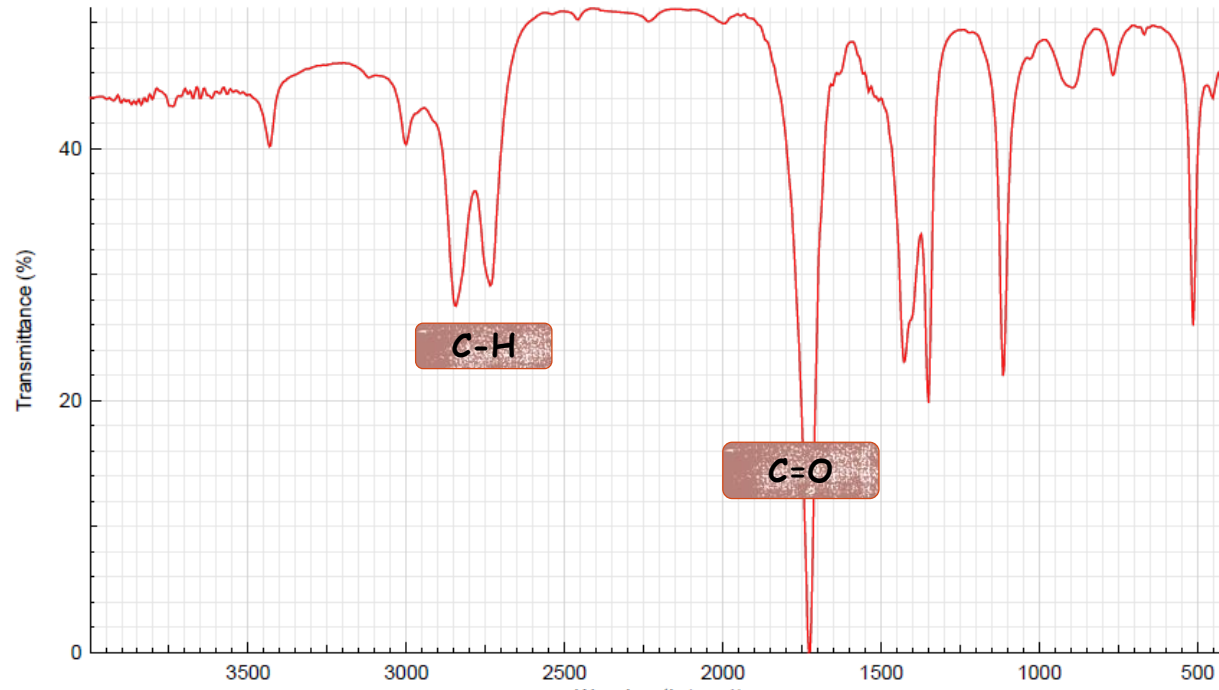
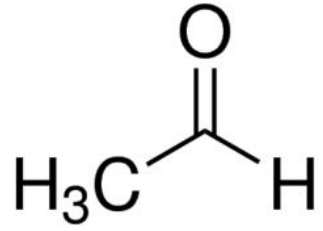
C-H

Ketone



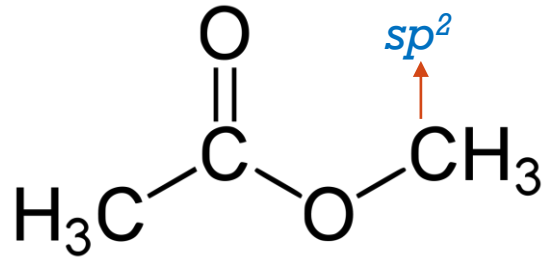
(1700 cm⁻¹)





IR SPECTRUM OF ESTERS AND ETHERS

Ester



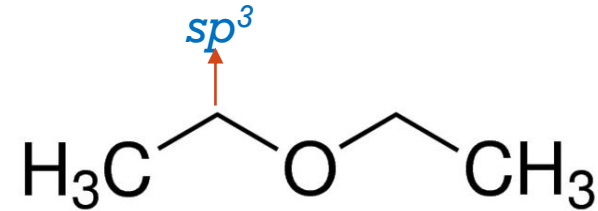
(1200-1300 cm^{-1})

(1735 cm^{-1})

C-O

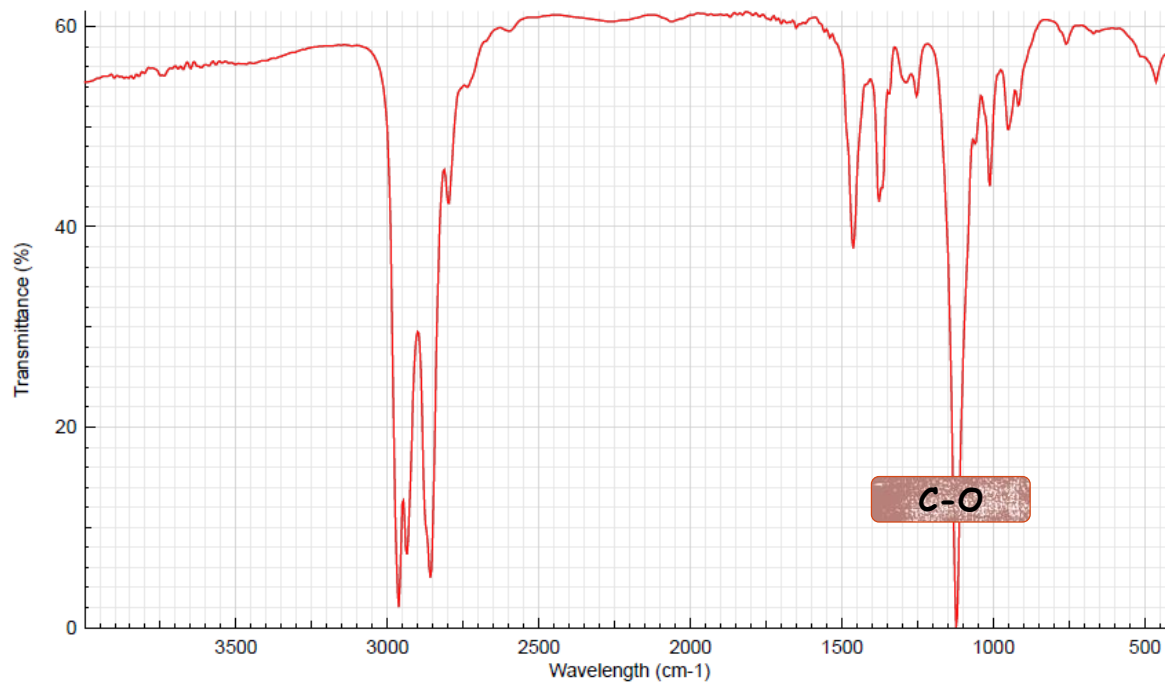
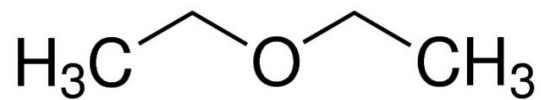
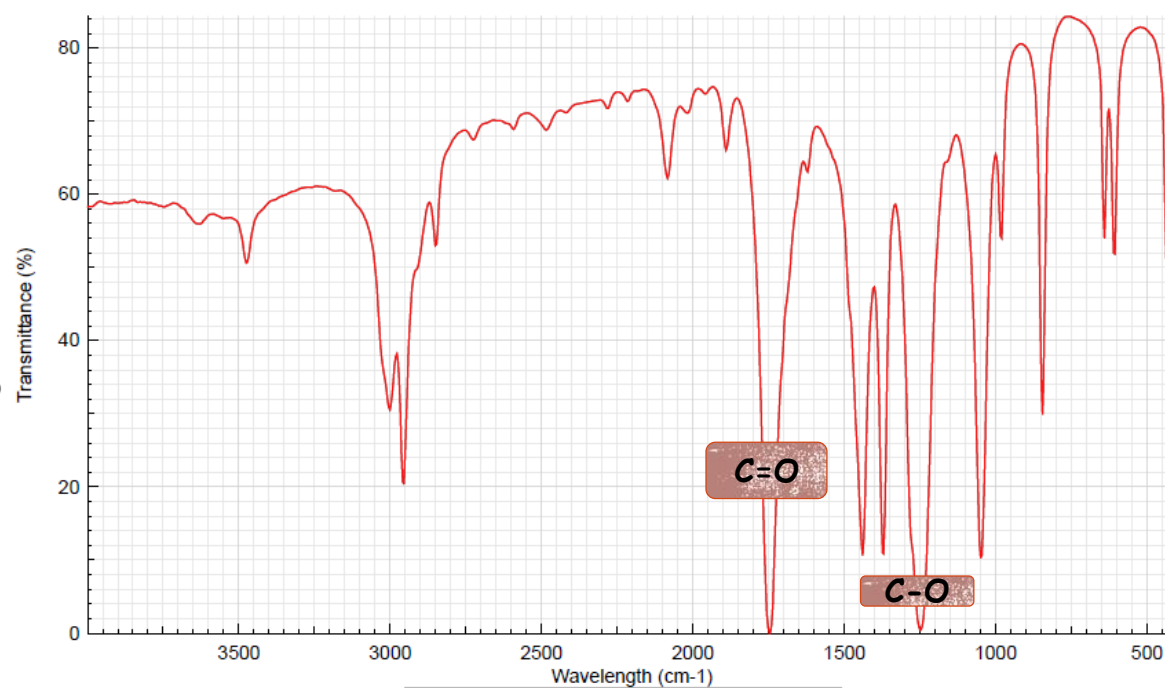
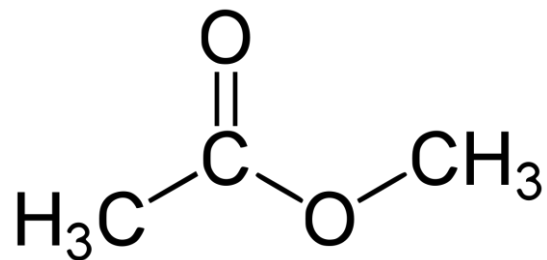
C=O

Ether



(1000-1150 cm^{-1})





IR SPECTRUM OF AMINE

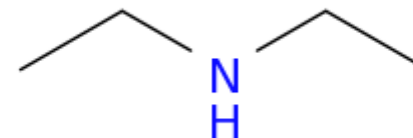
1° amine



TWO peaks

(N-H) (3300-3500 cm^{-1})

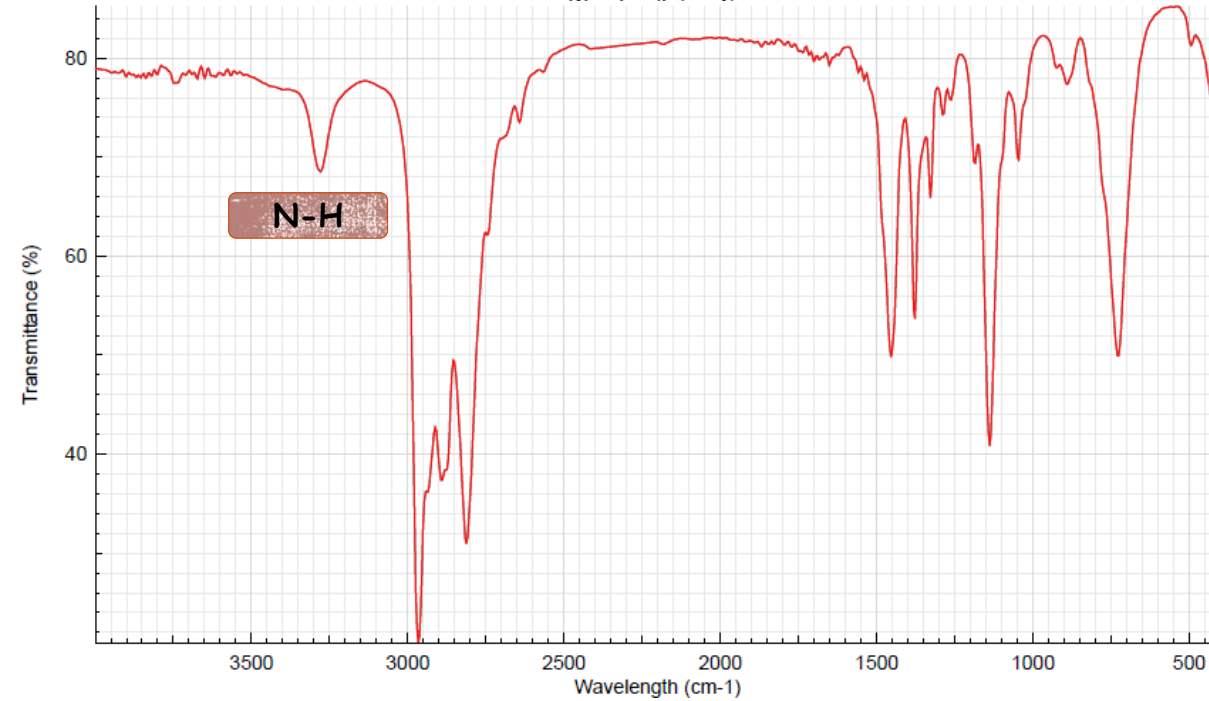
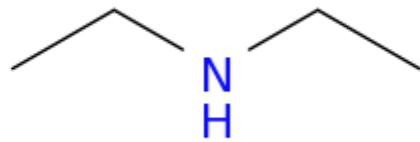
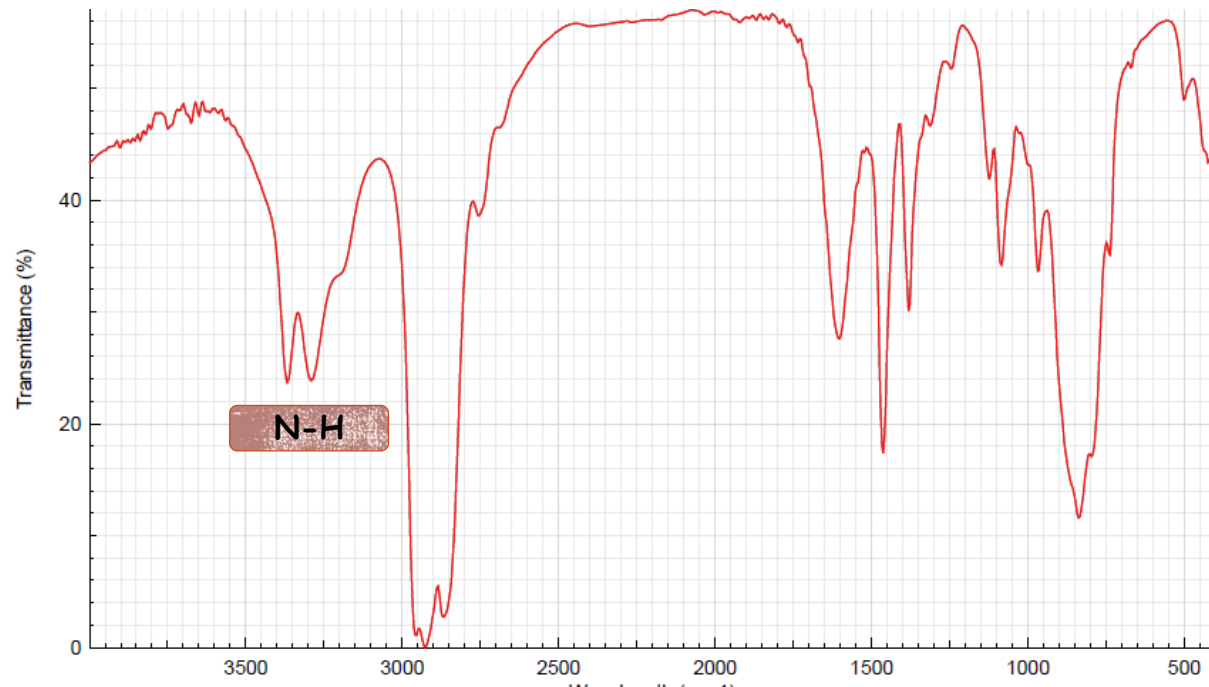
2° amine



ONE peak

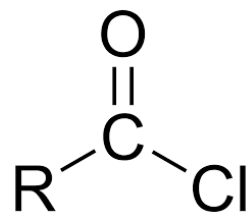
□ **NOTE:** N-H signal in amines is broad BUT it is not broader than O-H signal in alcohols





IR SPECTRUM OF ACID CHLORIDE AND ANHYDRIDE

Acid chloride



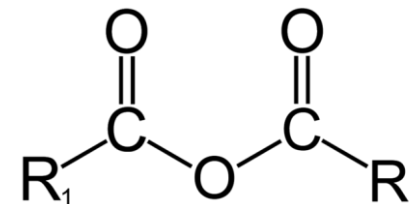
(1790-1810 cm^{-1})



C=O

C-O

Anhydride

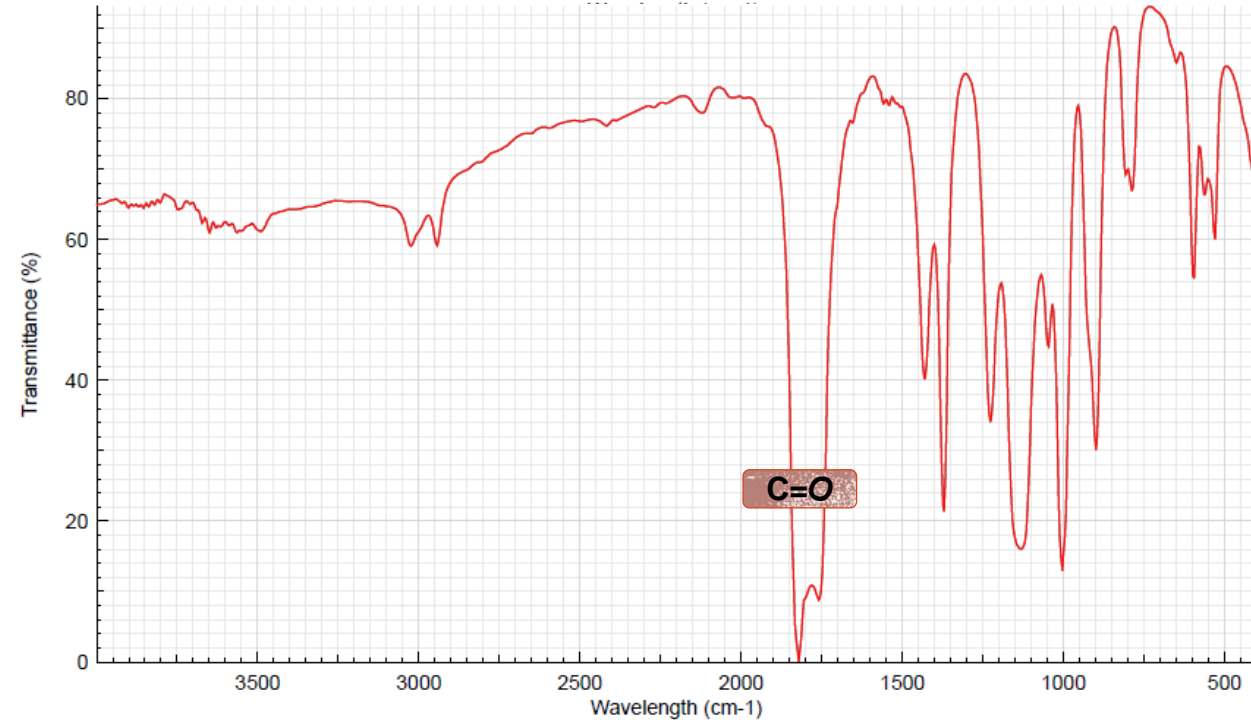
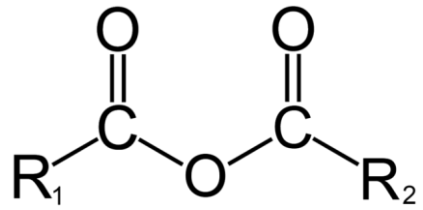
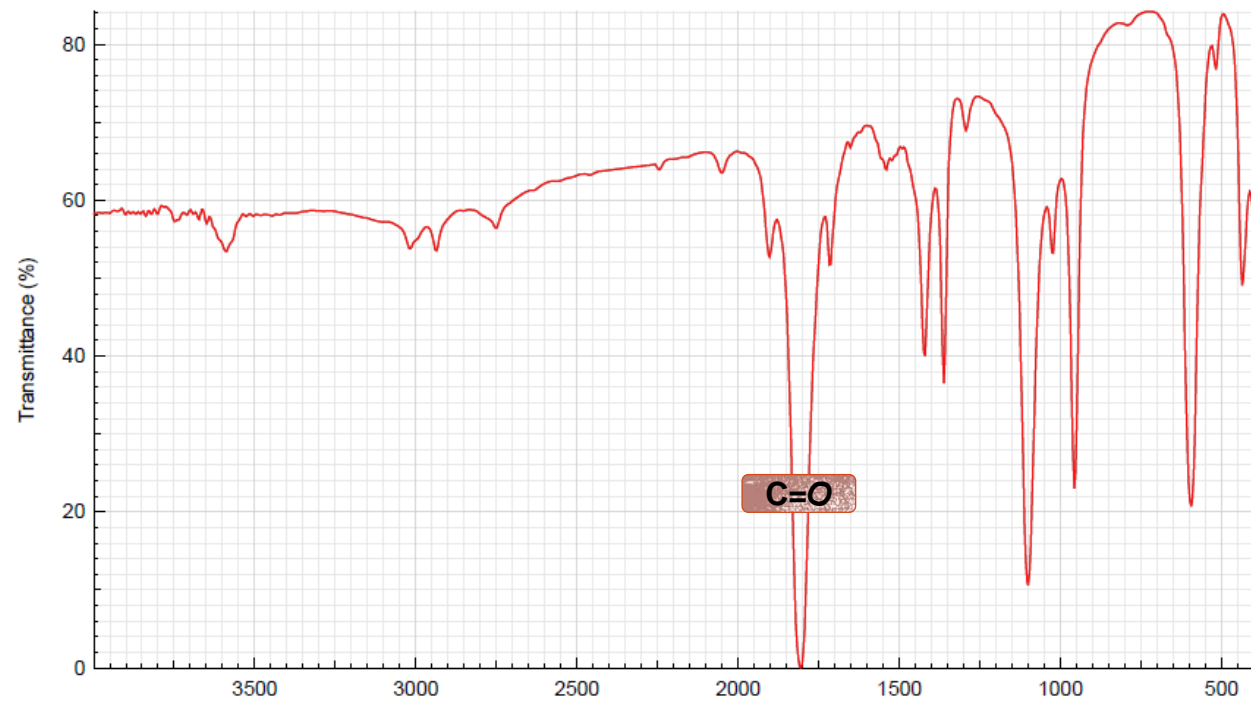
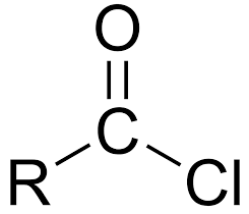


(1750-1800 cm^{-1})

(900-1300 cm^{-1})

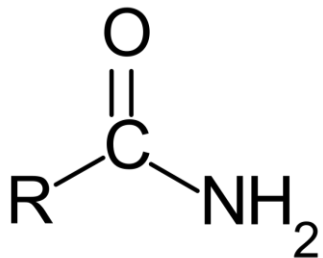
- ❑ In case of **acid chlorides**, the (C=O) stretching frequencies appear at 1810-1790 cm^{-1} which is attributed to high electronegativity of chlorine
- ❑ In case of **anhydrides of conjugated carboxylic acids**, the frequencies due to these bands are shifted to 1775 and 1720 cm^{-1} .





IR SPECTRUM OF AMIDES

1° amide



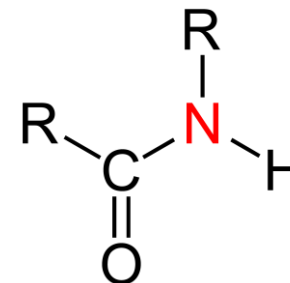
(1650-1690 cm^{-1})

C=O

(3550 and 3180 cm^{-1})

(N-H) stretching

2° amide

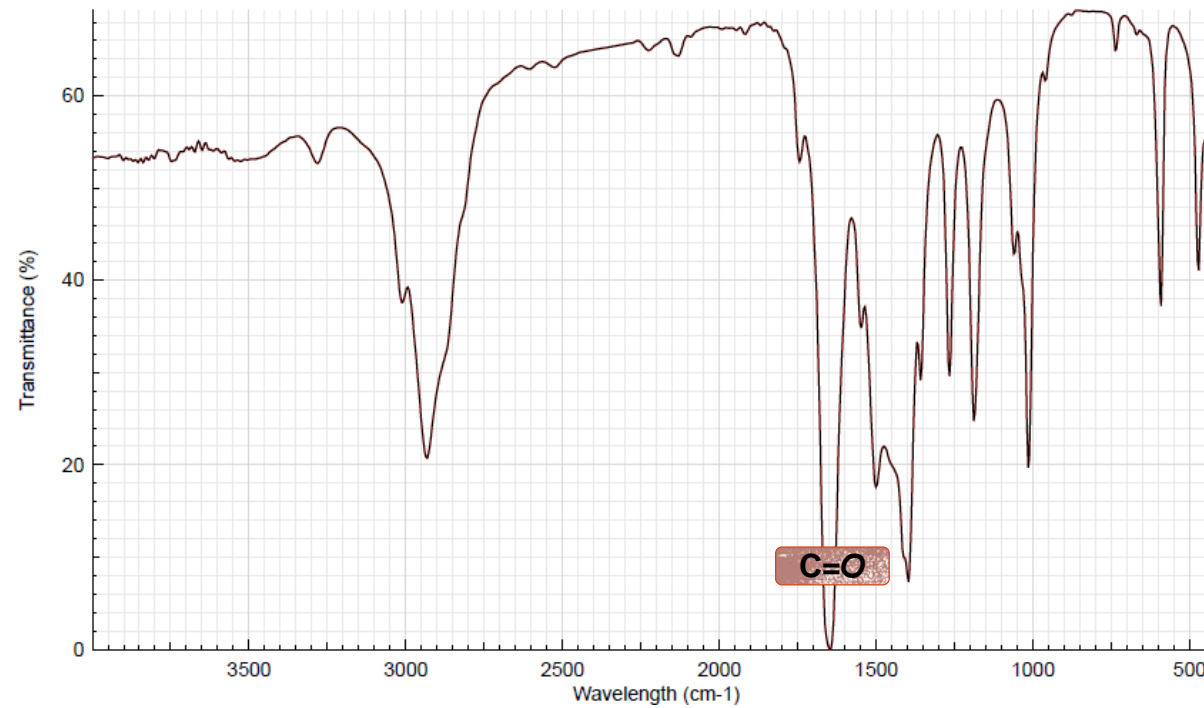
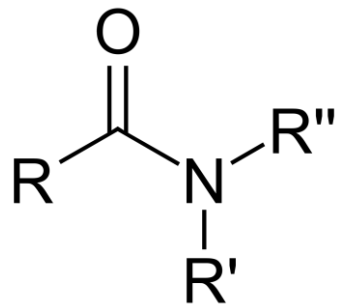
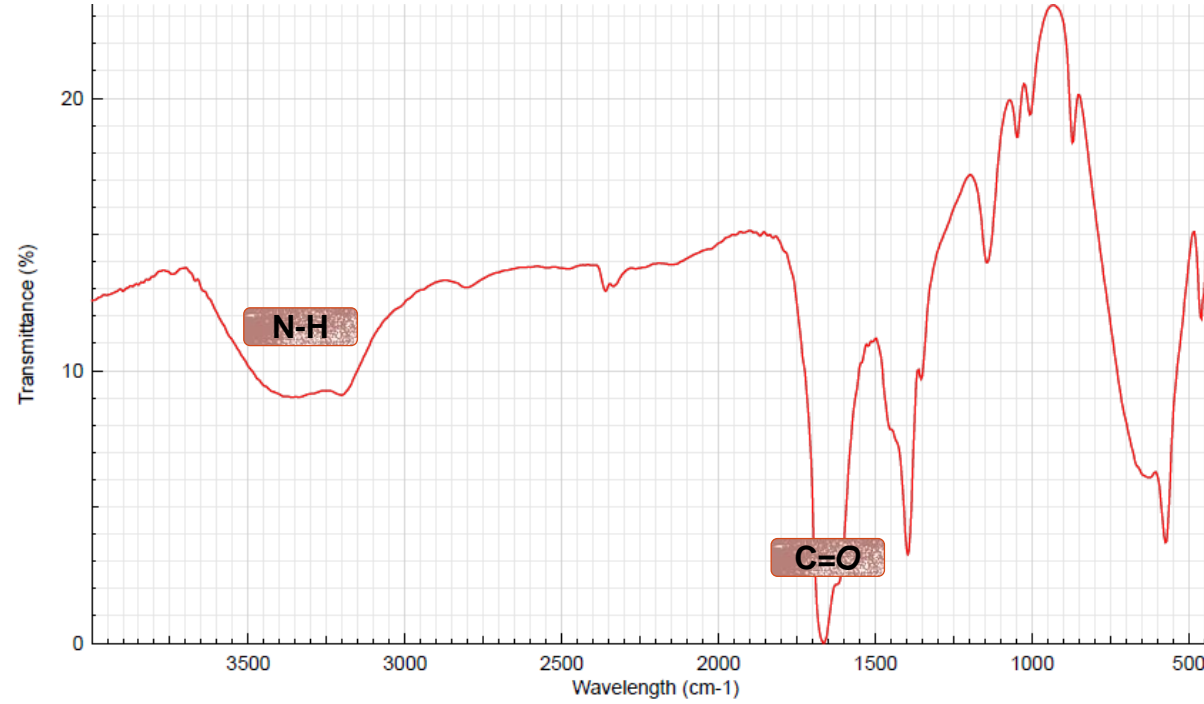
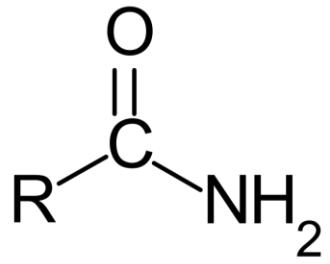


(1650-1690 cm^{-1})

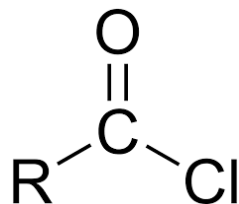
~ (3300 cm^{-1})

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

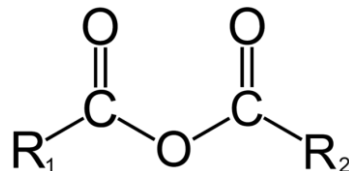




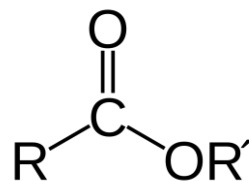
(C=O) stretching values (in cm^{-1}) of carbonyl compounds



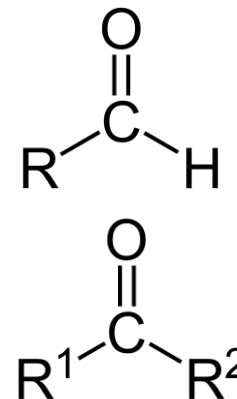
1800



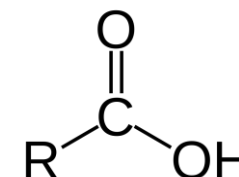
1750-1800



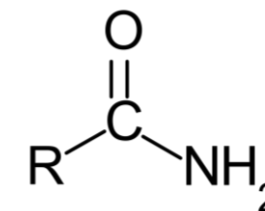
1730- 1750



1710-1750



1700-1725



1650-1690

