COLLEGE OF PHARMACY MUSTANSIRIYAH UNIVERSITY

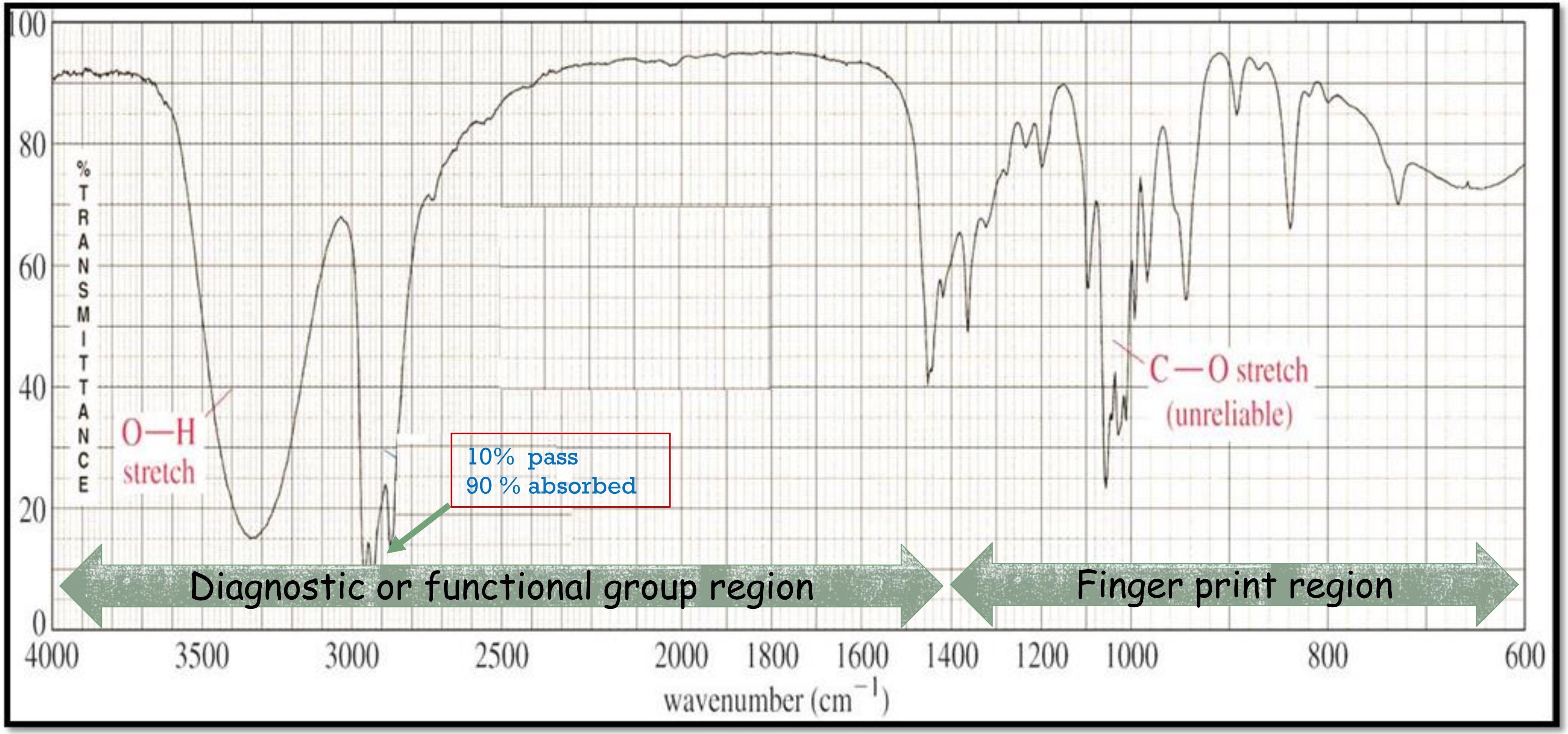
INFRA-RED SPECTROSCOPY

Characteristic Group Vibrations of Organic Molecules

5

2023-2024

The features of IR spectrum



10% pass
90 % absorbed

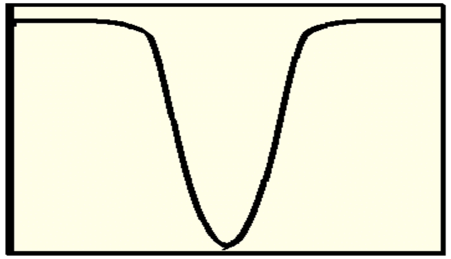
Diagnostic or functional group region

Finger print region

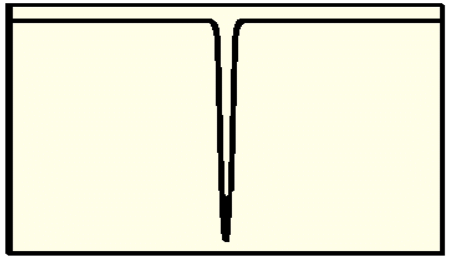
IR SIGNALS

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

Broad



Sharp

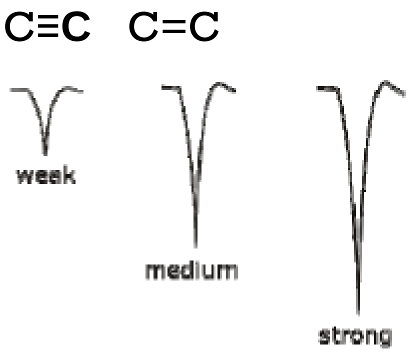


Question: what makes the IR signal broad?

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

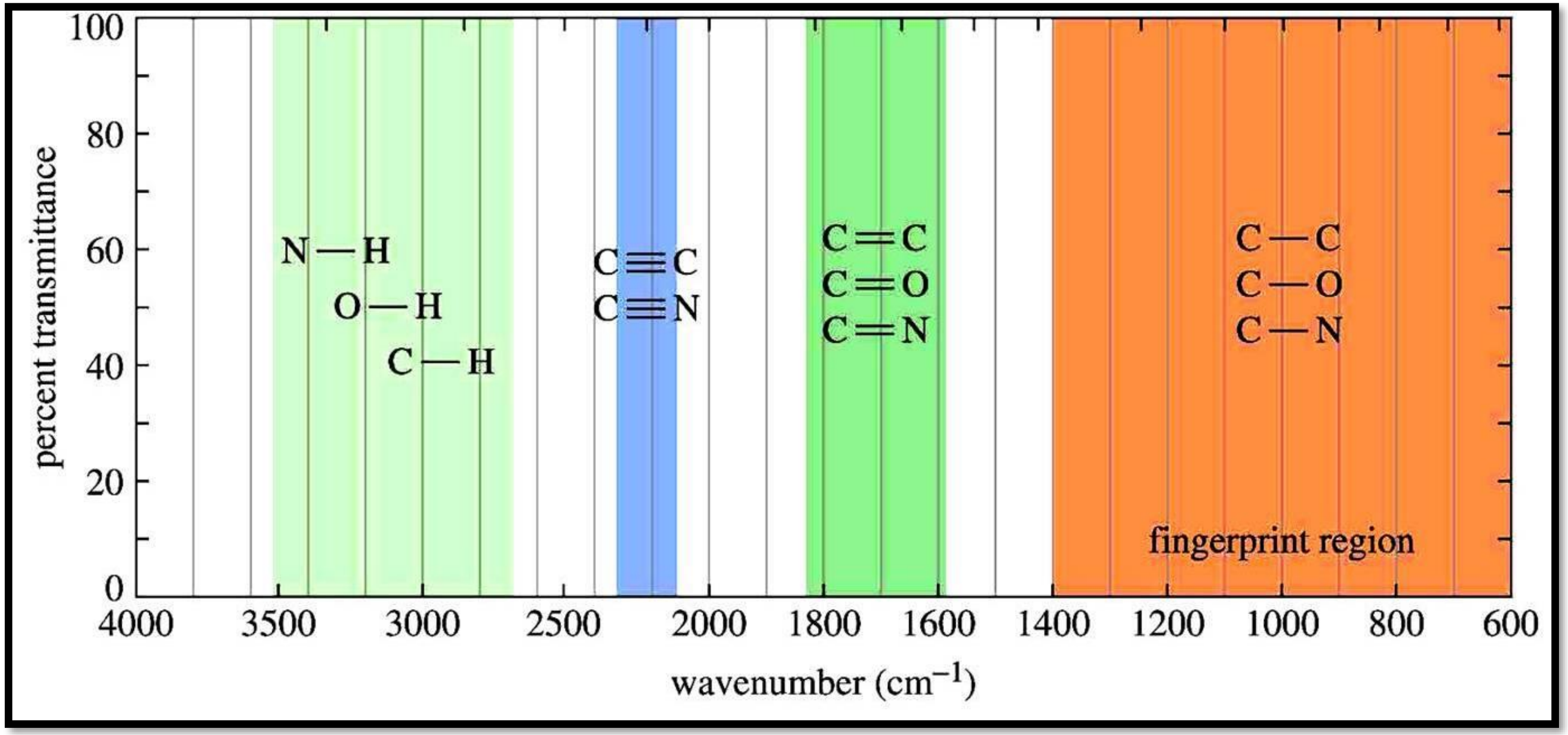
Question: what makes the IR signal sharp?

A. Non-polar bonds like C=C and C≡
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 **C≡N** or a **C≡C** bond.

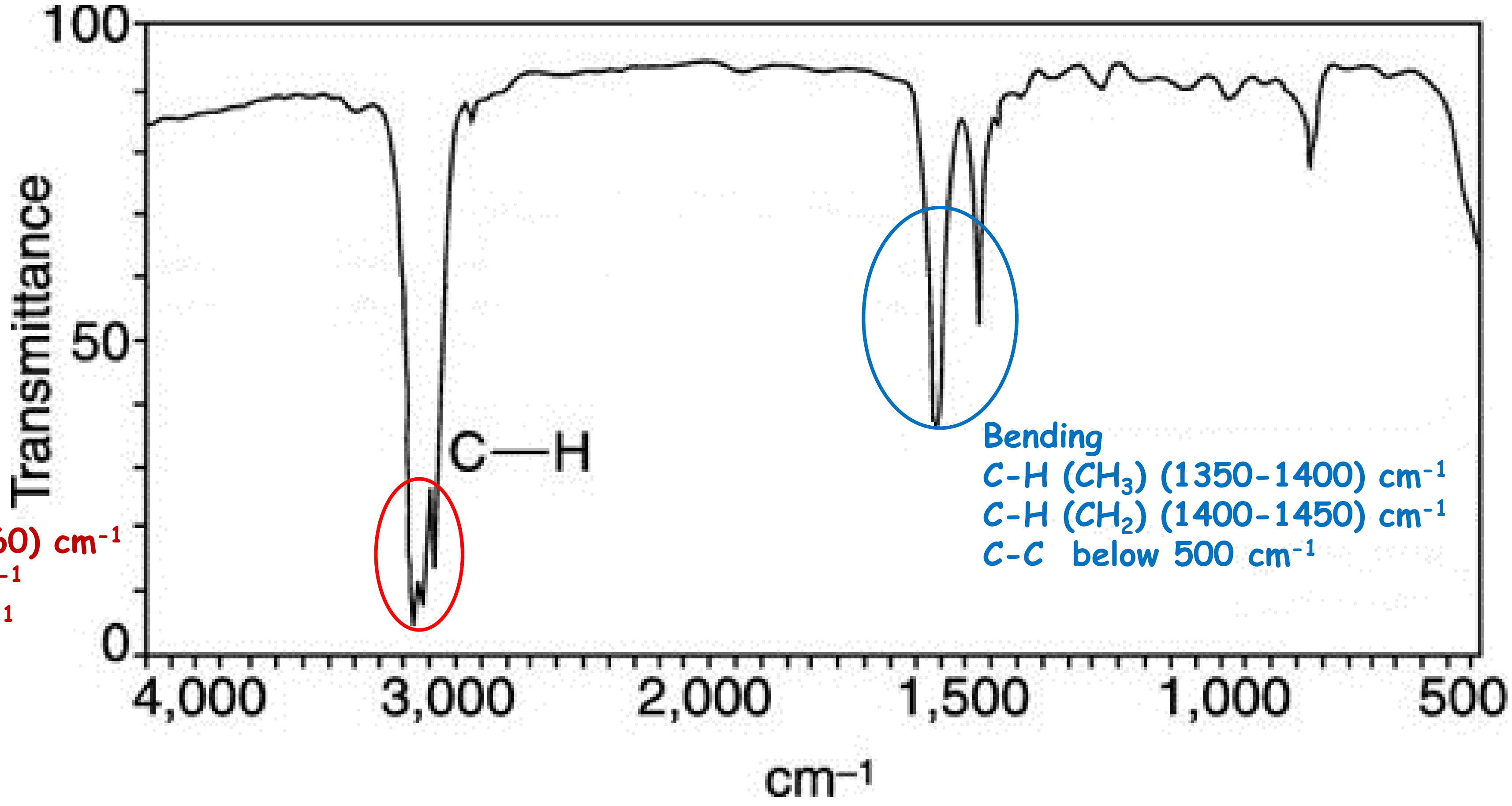


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

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..



Stretching

C-H (CH_3) (2870-2960) cm^{-1}

C-H (CH_2) (2925) cm^{-1}

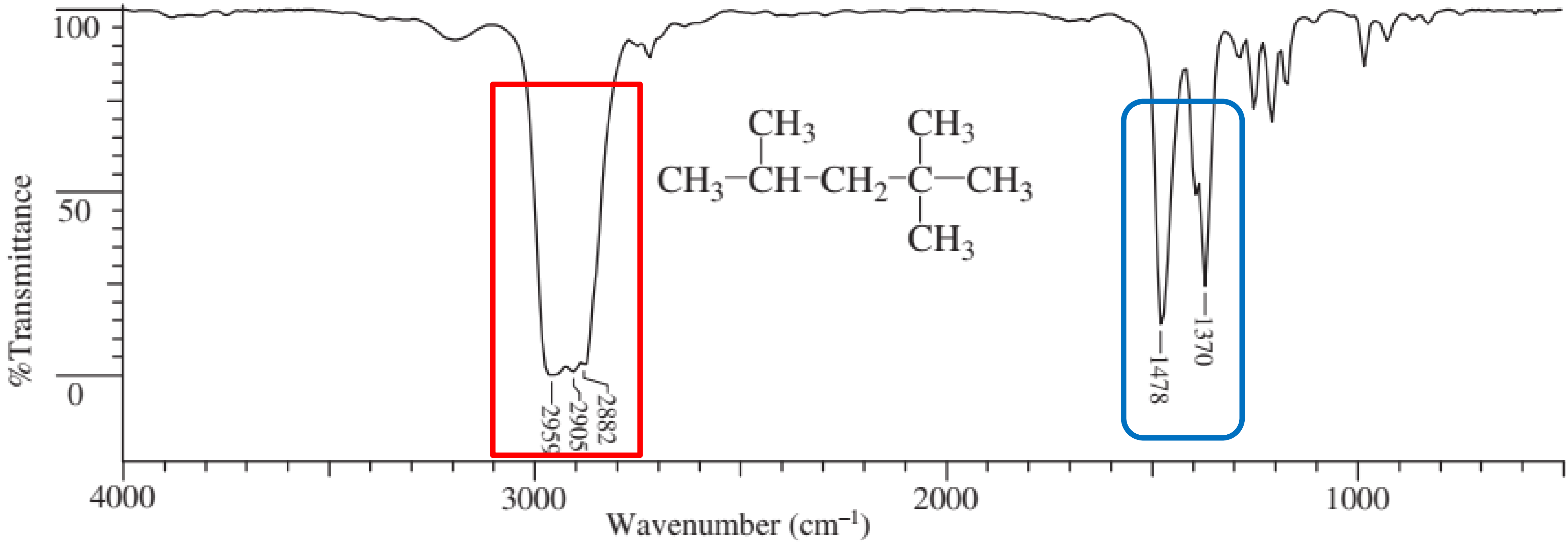
C-C (1200-800) cm^{-1}

Bending

C-H (CH_3) (1350-1400) cm^{-1}

C-H (CH_2) (1400-1450) cm^{-1}

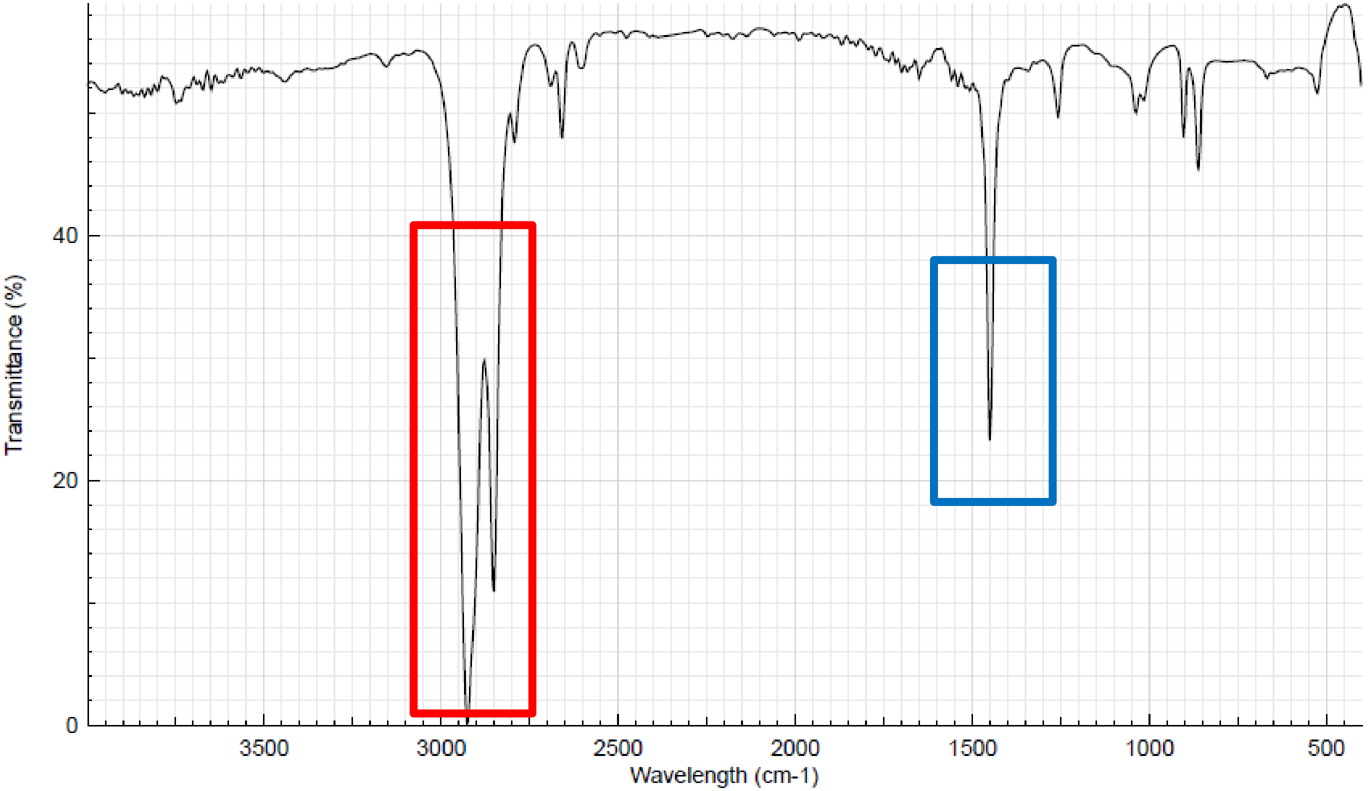
C-C below 500 cm^{-1}


100
50
0
% Transmittance
4000
3000
2000
1000
Wavenumber (cm^{-1})
2959
2905
2882
1478
1370
CH$_3$–CH(CH$_3$)–CH$_2$–C(CH$_3$)$_2$–CH$_3$

Cyclic aliphatic hydrocarbons

The C-H stretching frequencies are the same **(2800 – 3000 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 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.

(C=C) stretching > (C-C) stretching

(1680-1620 cm^{-1}) (1200-800 cm^{-1})

Non-conjugated C=C (1660-1640) cm^{-1}

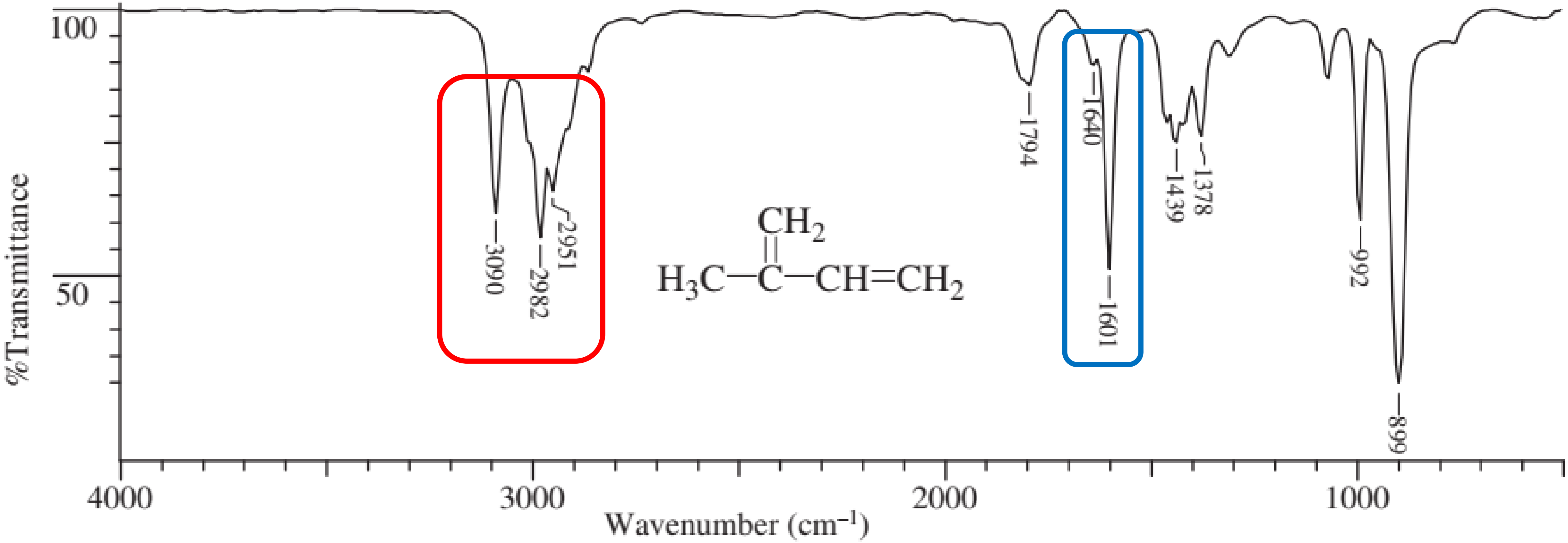
Conjugated C=C (sym) (one band ONLY 1600) cm^{-1}

Conjugated C=C (asym) (1650 & 1600) 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.

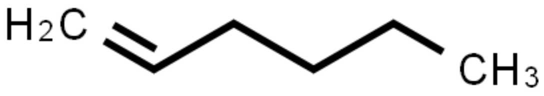
(=C-H) (stretching) above 3000 cm^{-1}

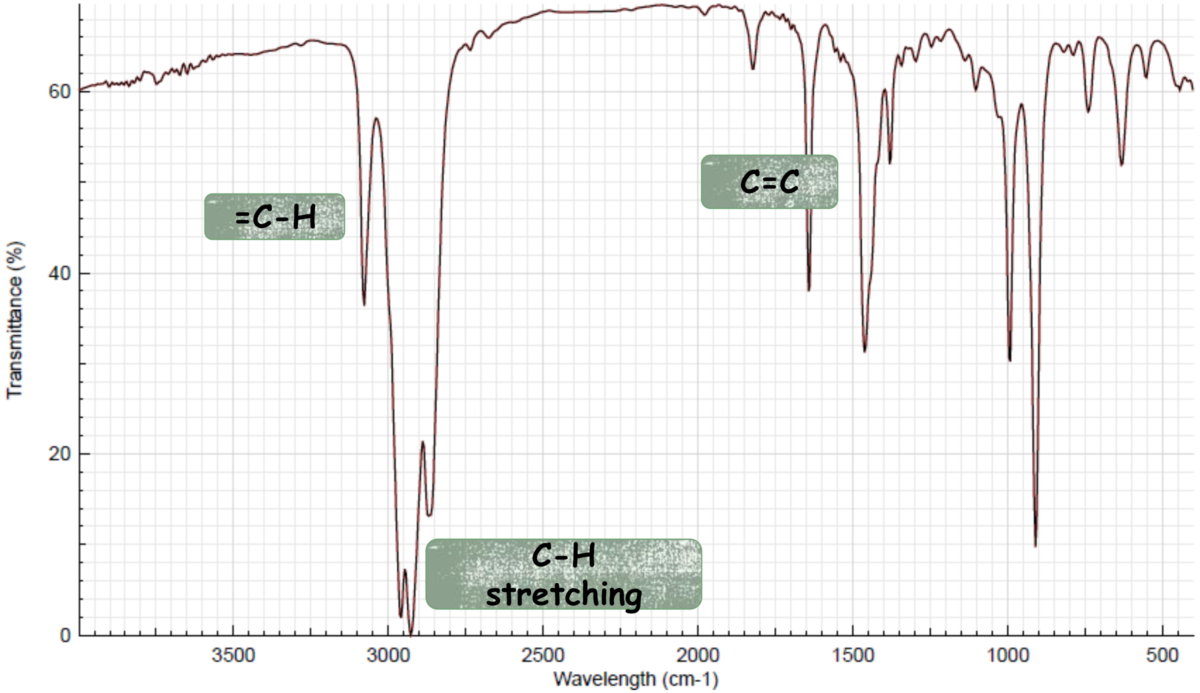
- **Non-symmetrically** substituted double bonds exhibit strong absorption bands. The absorption bands are **more intense for *cis* isomers than for *trans* isomers**; for mono or tri substituted olefins than for di and tetra substituted ones.


100
50
%Transmittance
3090
2982
2951
1794
1640
1601
1439
1378
992
899
4000
3000
2000
1000
Wavenumber (cm⁻¹)
CH2
H3C—C—CH=CH2

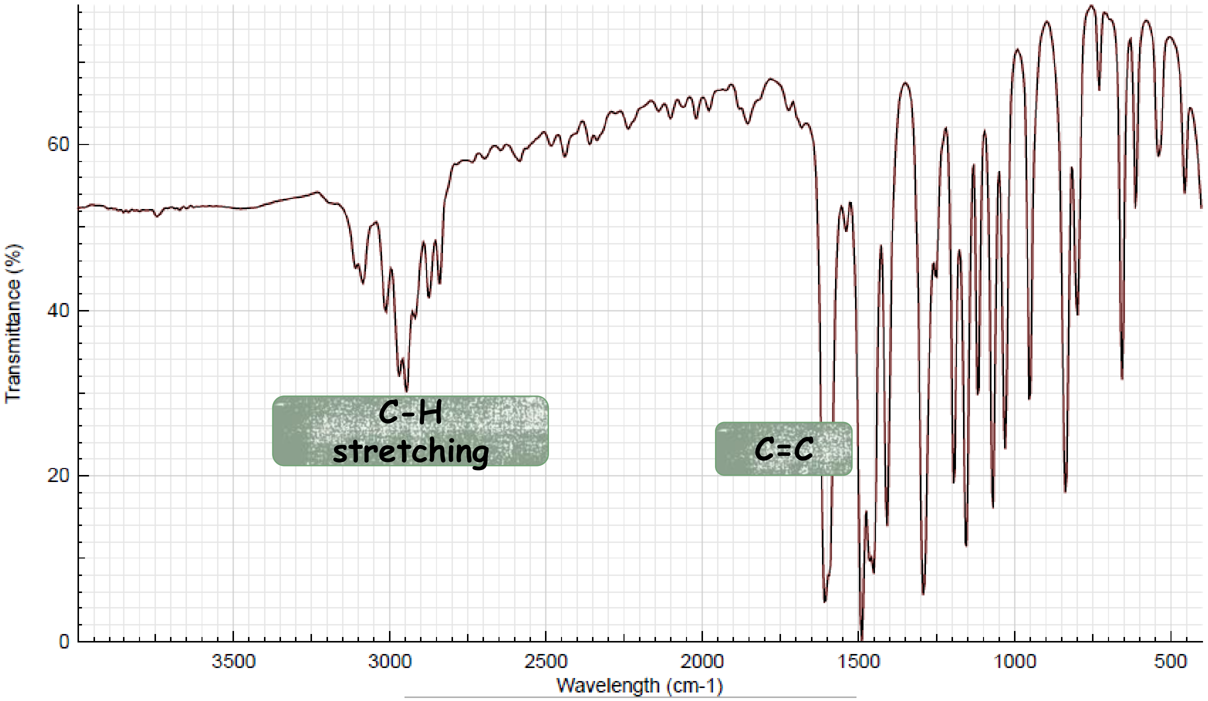
IR SPECTRUM OF ALKENES

Internal		Terminal
(1620-1680 cm^{-1})	C=C	(1620-1680 cm^{-1})
✗	=C-H	(3000-3100 cm^{-1})


H_2C
CH_3


=C-H
C=C
C-H stretching
Transmittance (%)
0
20
40
60
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)


H_3C
CH_3


C-H stretching
C=C
Transmittance (%)
0
20
40
60
3500
3000
2500
2000
1500
1000
500
Wavelength (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**.

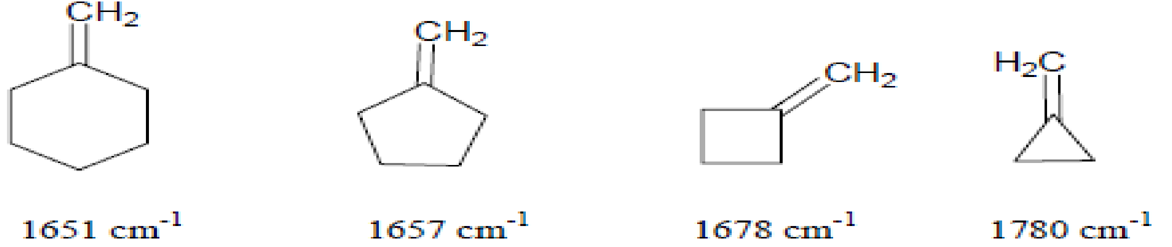
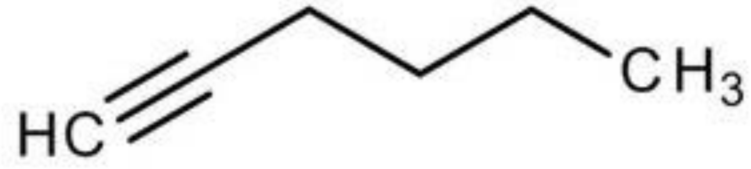


Figure 17 : Exocyclic C=C double bond frequencies in various ring sizes

IR SPECTRUM OF ALKYNES

Internal

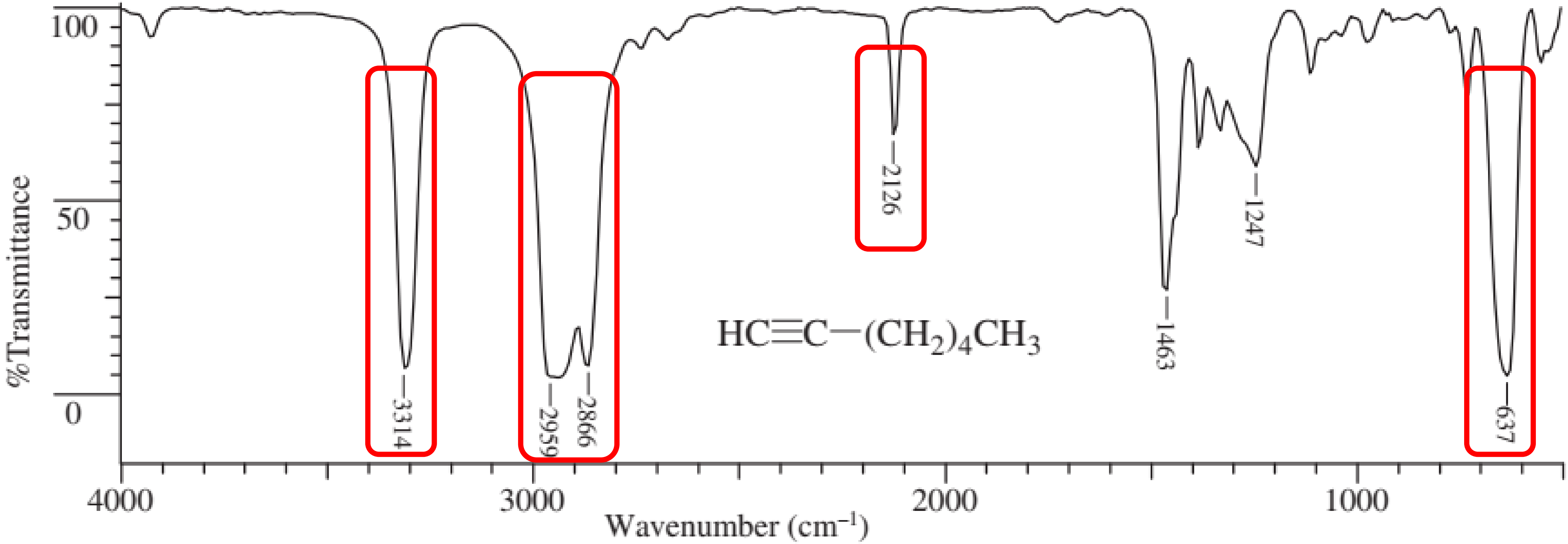
Terminal

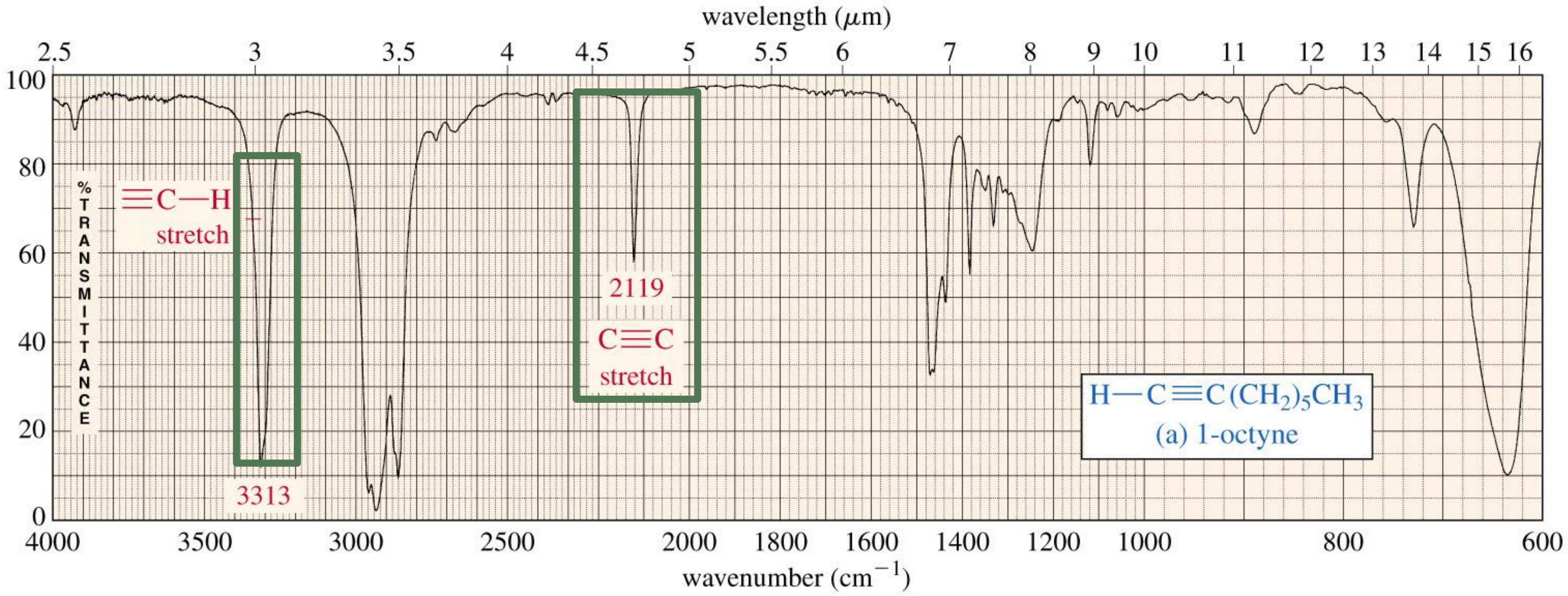


	Internal	Terminal
C≡C	**(2260-2000 cm^{-1})**	**(2260-2000 cm^{-1})**
≡C-H	✗	**(3100-3300 cm^{-1})**

When the substituents are similar in mass, or produce similar inductive and resonance effects, the band may be so weak as to be unobserved in the IR spectrum.

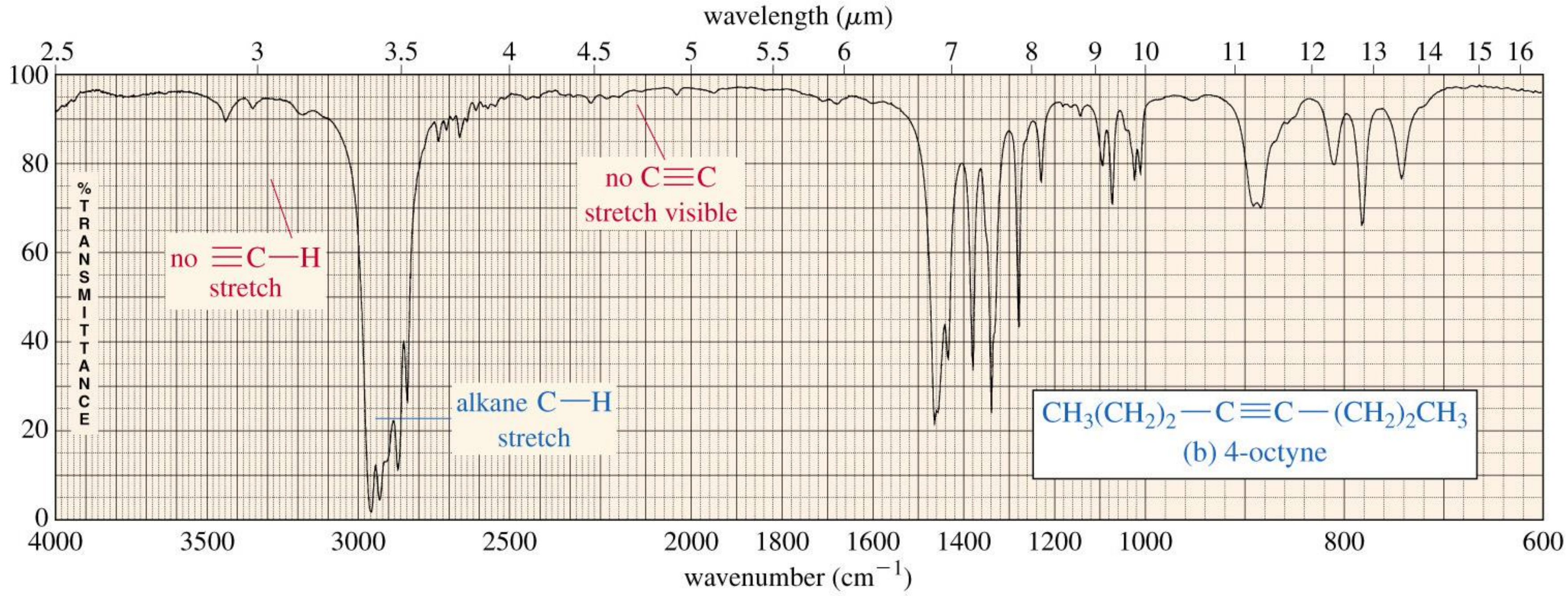
The ≡C-H bending of alkynes or monosubstituted alkynes leads to **strong, broad** absorption in the **(700-610) cm^{-1}** region


100
50
0
% Transmittance
3314
2959
2866
2126
1463
1247
637
$HC\equiv C-(CH_2)_4CH_3$
4000
3000
2000
1000
Wavenumber (cm^{-1})



H—C≡C(CH$_2$)$_5$CH$_3$

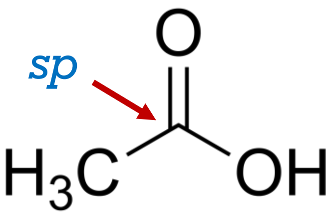
(a) 1-octyne

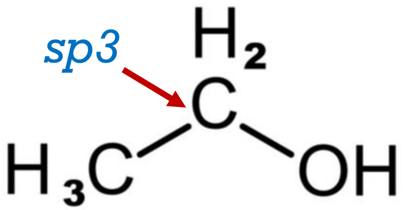


CH$_3$(CH$_2$)$_2$—C≡C—(CH$_2$)$_2$CH$_3$

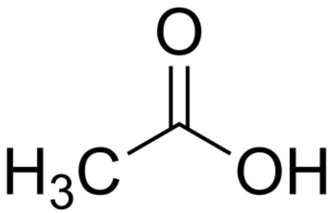
(b) 4-octyne

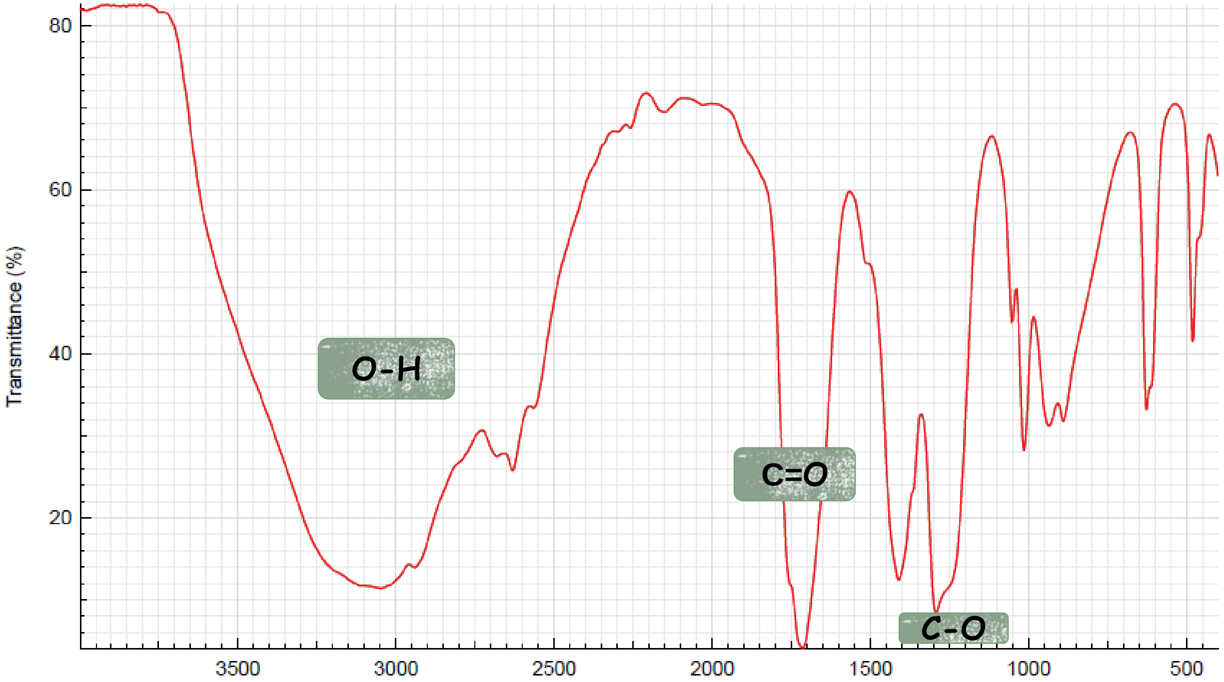
IR SPECTRUM OF CARBOXYLIC ACIDS AND ALCOHOLS

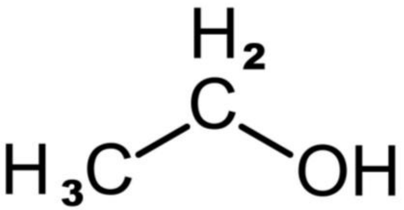


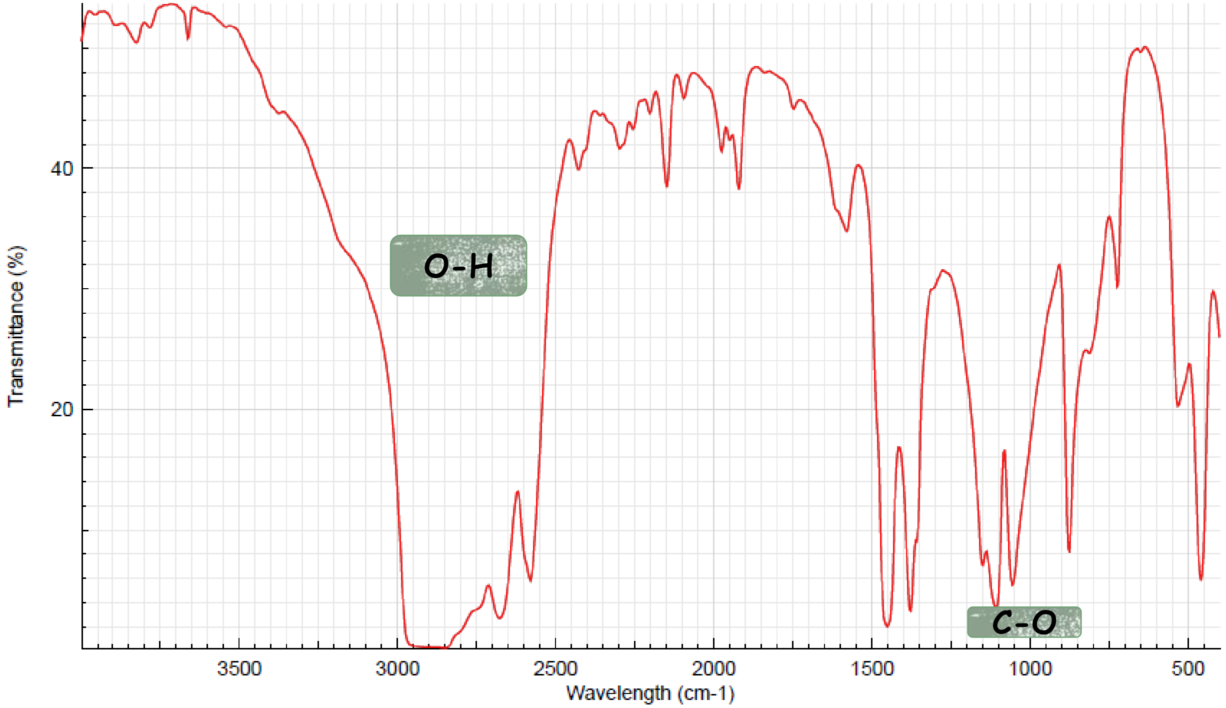


Carboxylic acid		Alcohol
(2500-3300 cm^{-1})	O-H	(3200-3500 cm^{-1})
(1700 cm^{-1})	C=O	✗
(1200-1300 cm^{-1})	C-O	(1000-1150 cm^{-1})


O
H3C
OH

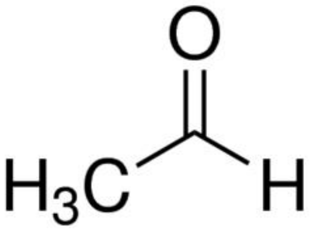

80
60
40
20
Transmittance (%)
O-H
C=O
C-O
3500
3000
2500
2000
1500
1000
500


H2
C
H3C
OH

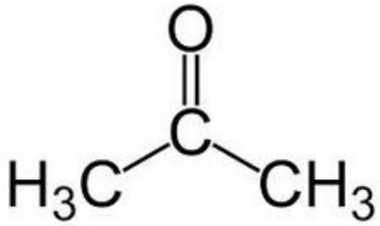

40
20
Transmittance (%)
O-H
C-O
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

IR SPECTRUM OF ALDEHYDES AND KETONES

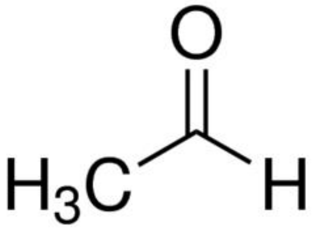
Aldehyde

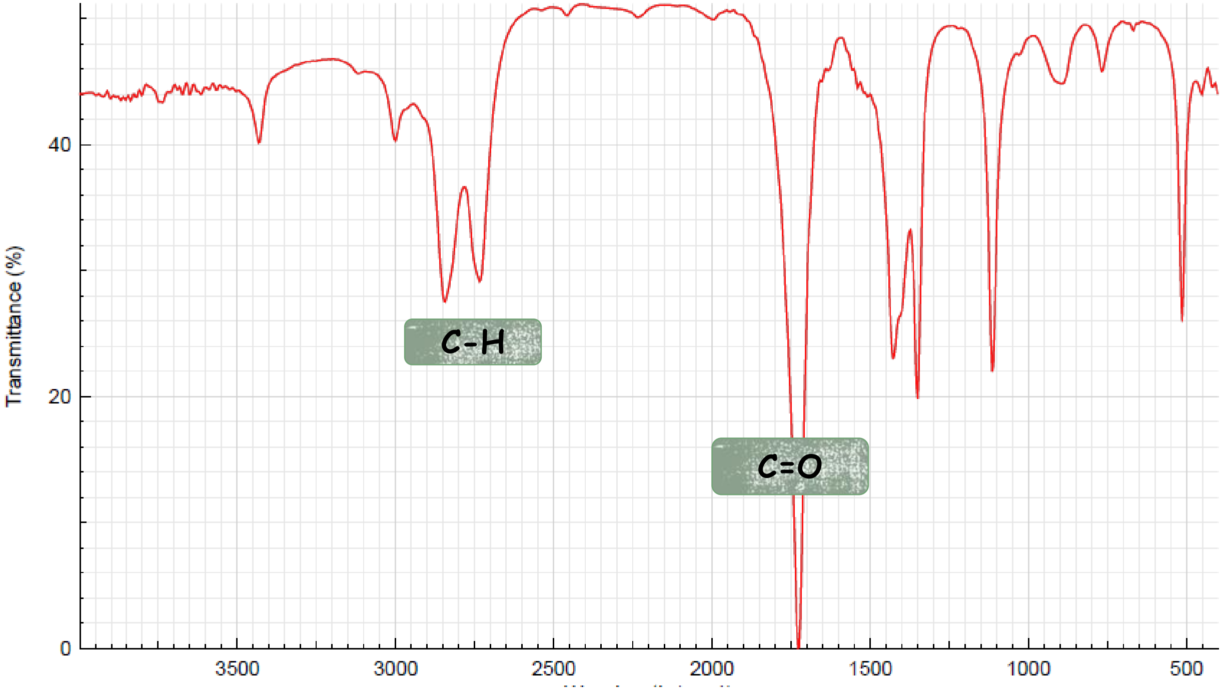


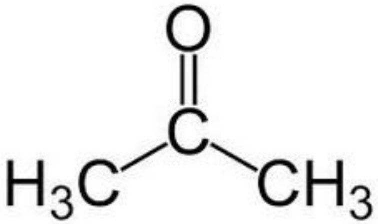
Ketone



(more than 1700 cm^{-1})	C=O	(1715 cm^{-1})
(2830 and 2700 cm^{-1})	C-H	✗


O
H3C
H

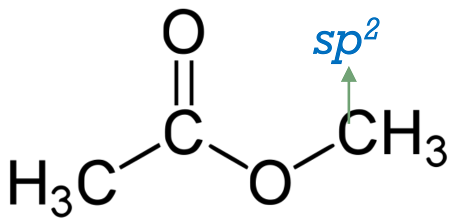

Transmittance (%)
0
20
40
3500
3000
2500
2000
1500
1000
500
C-H
C=O


O
C
H3C
CH3

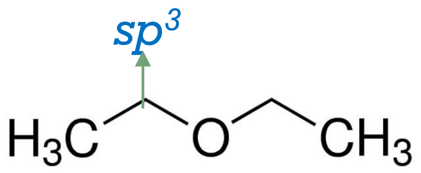

Transmittance (%)
0
20
40
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C=O

IR SPECTRUM OF ESTERS AND ETHERS

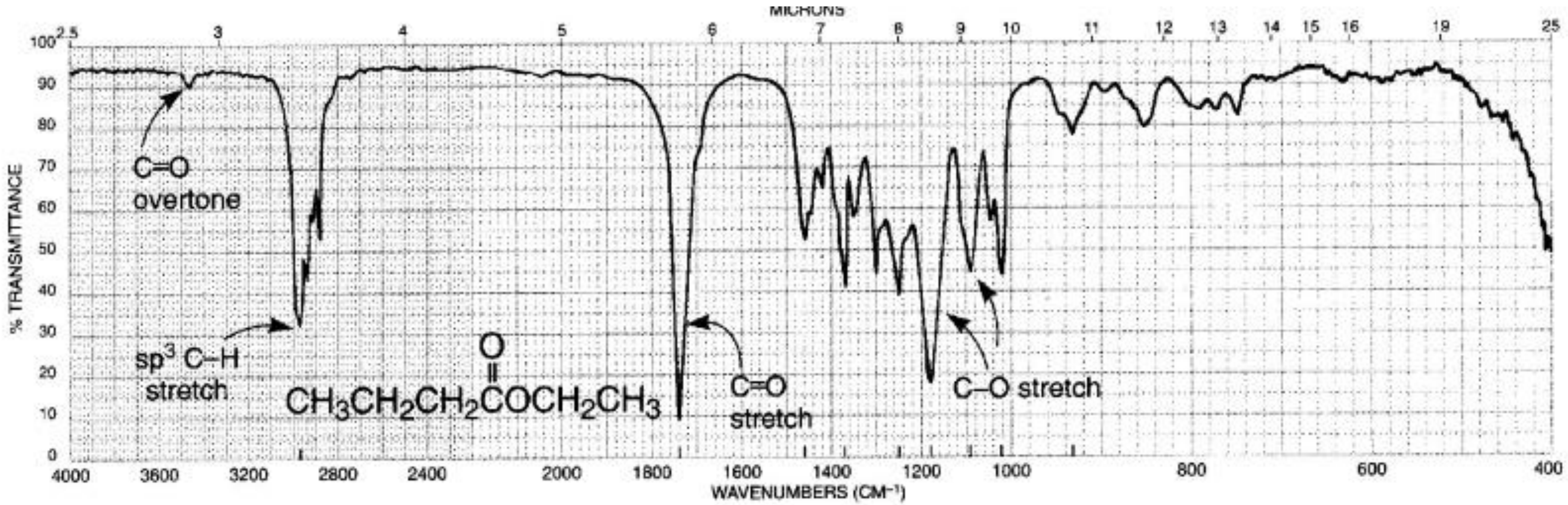
Ester

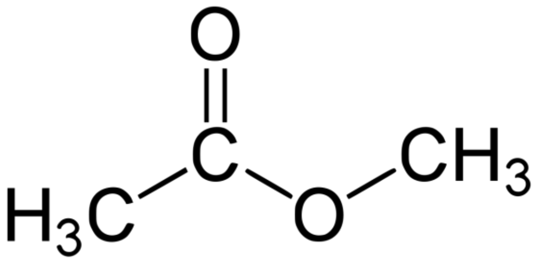


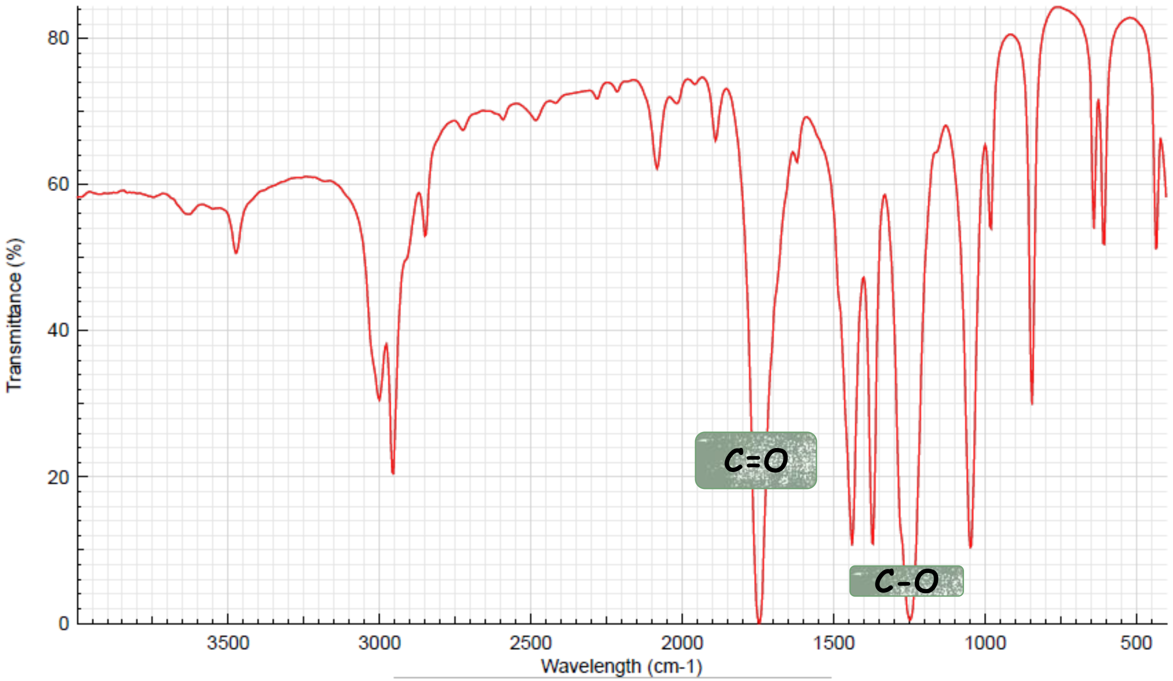
Ether



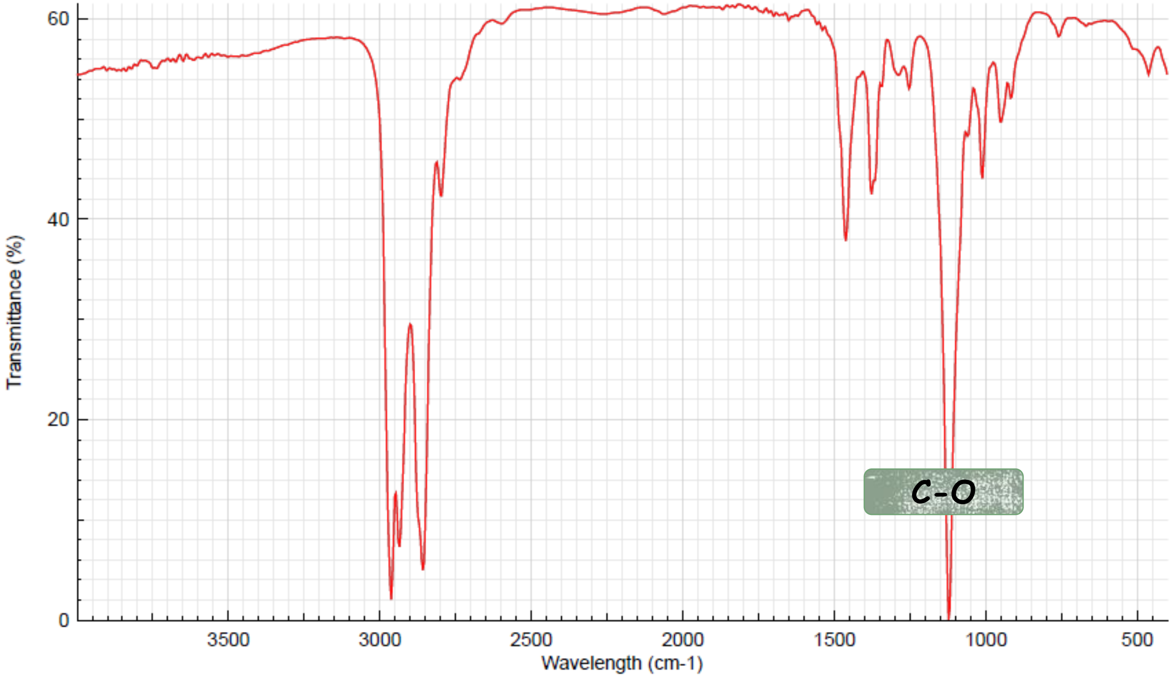
Ester		Ether
(1000-1300 cm^{-1}) two bands	C-O	(1000-1150 cm^{-1})
(1735-1750 cm^{-1})	C=O	✗



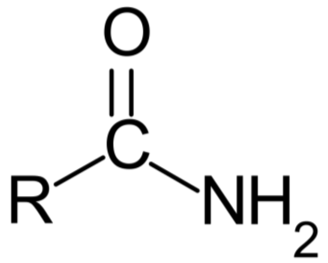

O
H_3C
C
O
CH_3

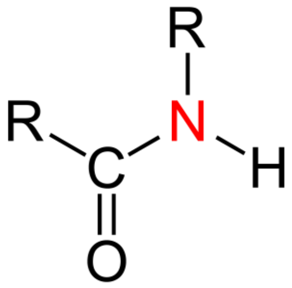

Transmittance (%)
80
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C=O
C-O


H_3C
O
CH_3


Transmittance (%)
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C-O

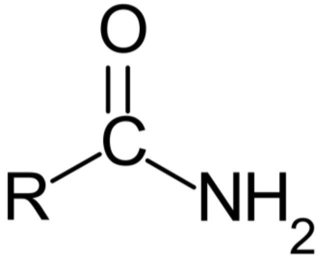
IR SPECTRUM OF AMIDES

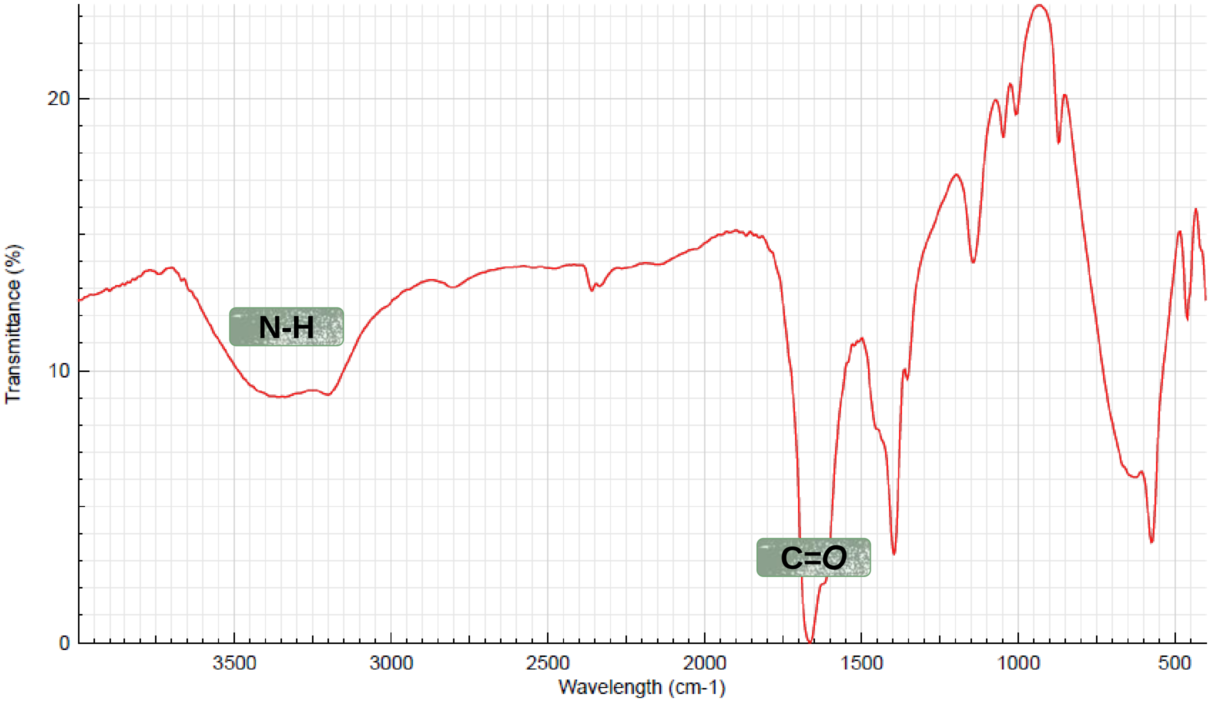


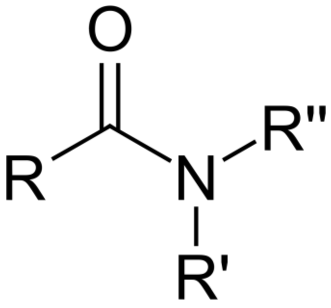


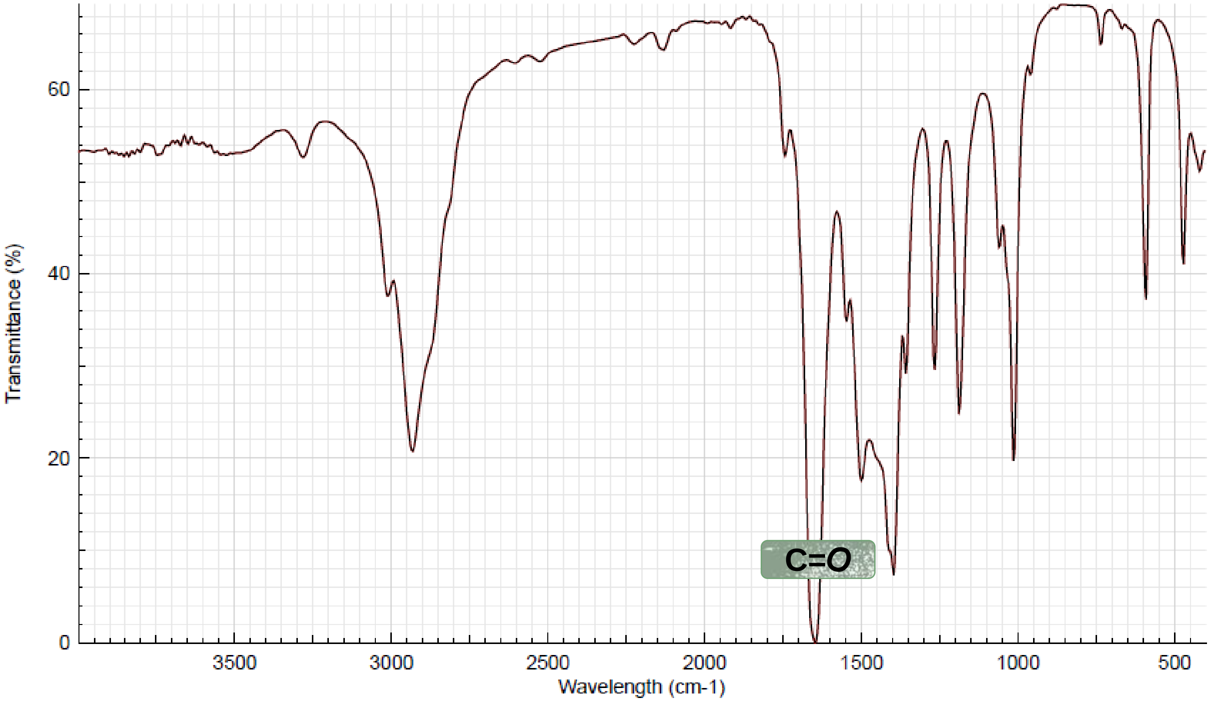
1° amide		2° amide
(1630-1680 cm^{-1})	C=O	(1630-1680 cm^{-1})
(3350 and 3180 cm^{-1})	(N-H) stretching	~ (3300 cm^{-1})

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


O
C
R
NH2

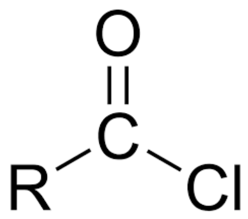

N-H
C=O
Transmittance (%)
20
10
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)


O
R
N
R''
R'

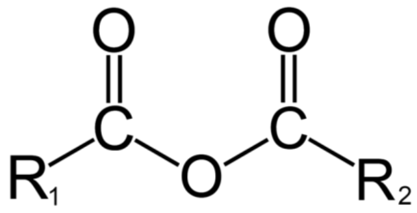

C=O
Transmittance (%)
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

IR SPECTRUM OF ACID CHLORIDE AND ANHYDRIDE

Acid chloride

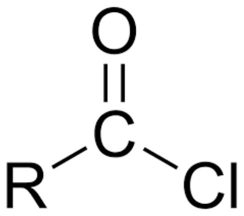


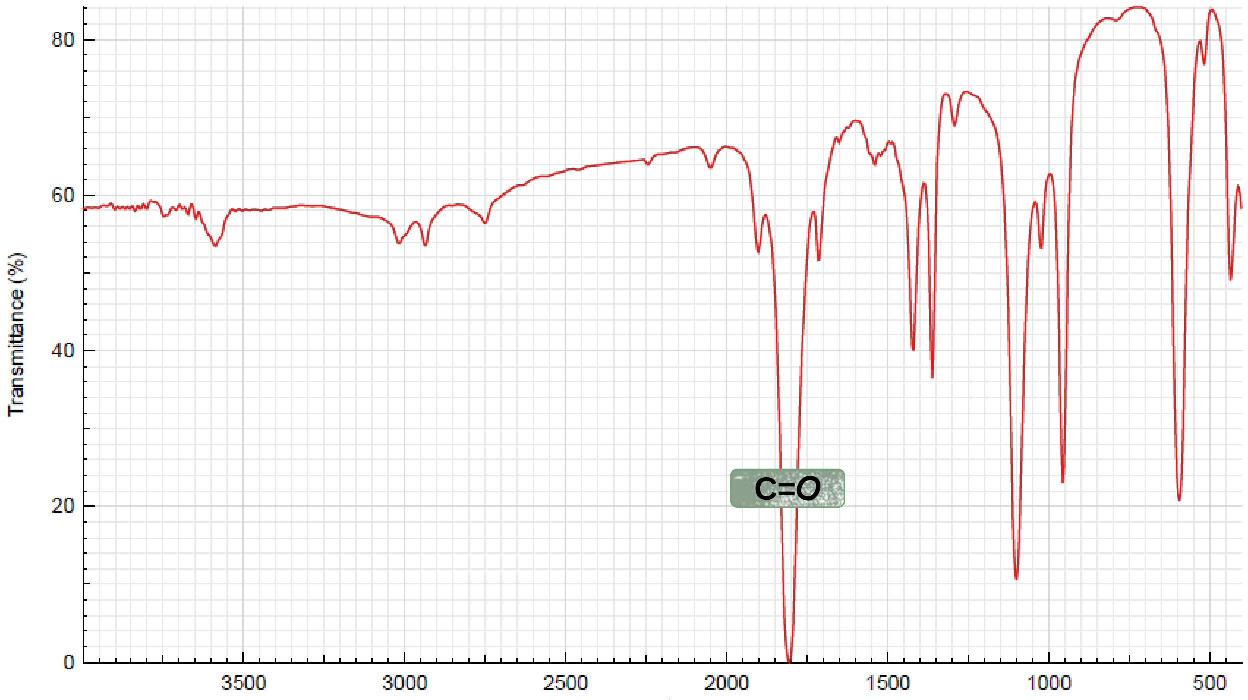
Anhydride

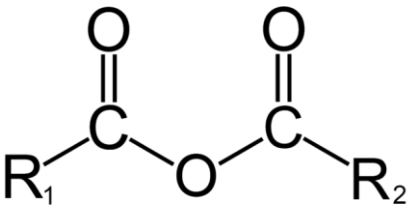


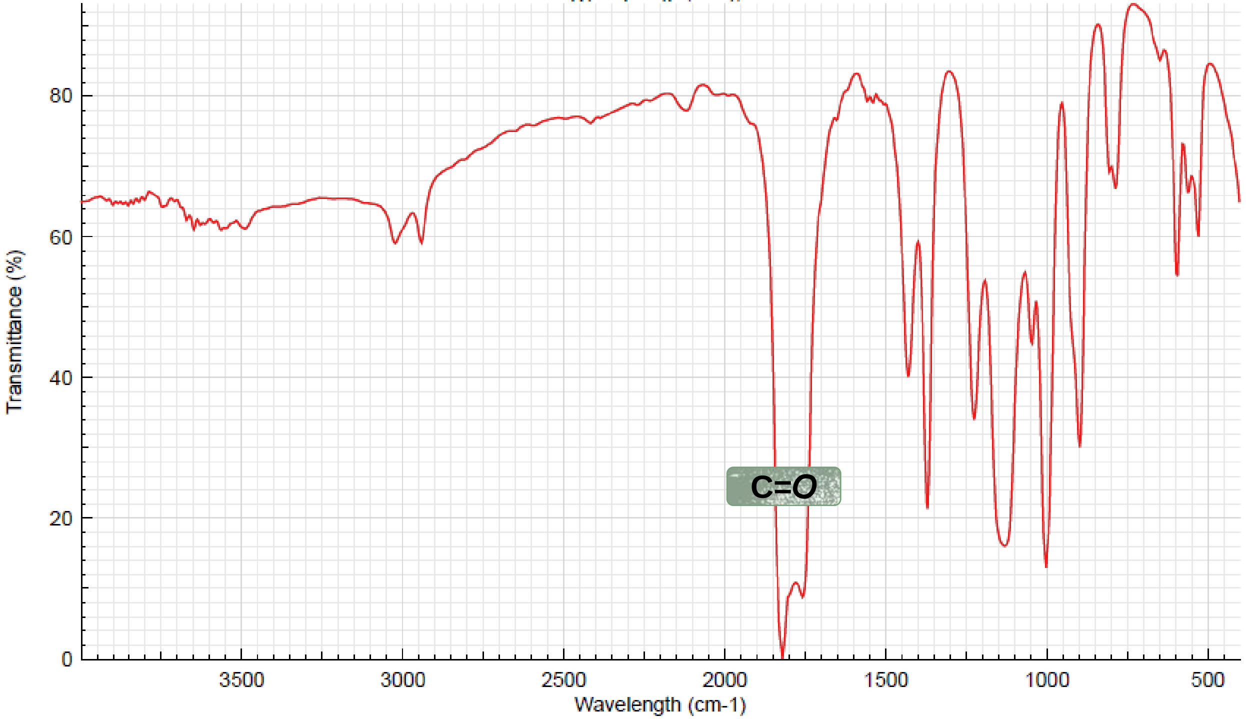
Acid chloride		Anhydride
(1790-1810 cm^{-1})	C=O	(1750-1800 cm^{-1})
✗	C-O	(900-1300 cm^{-1})

- ❑ 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}.

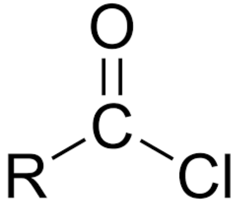
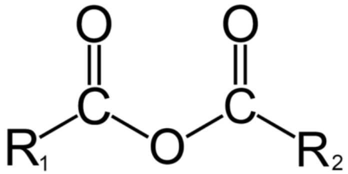
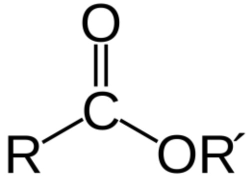
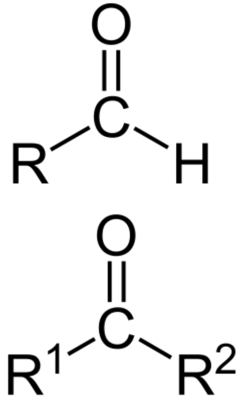
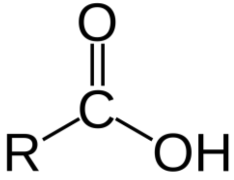
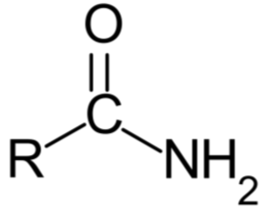

O
C
R
Cl


80
60
40
20
0
Transmittance (%)
3500
3000
2500
2000
1500
1000
500
C=O


O
O
C
C
R1
O
R2


80
60
40
20
0
Transmittance (%)
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C=O

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

					
1800	**1750-1800**	**1730- 1750**	**1710-1750**	**1700-1725**	**1650-1690**