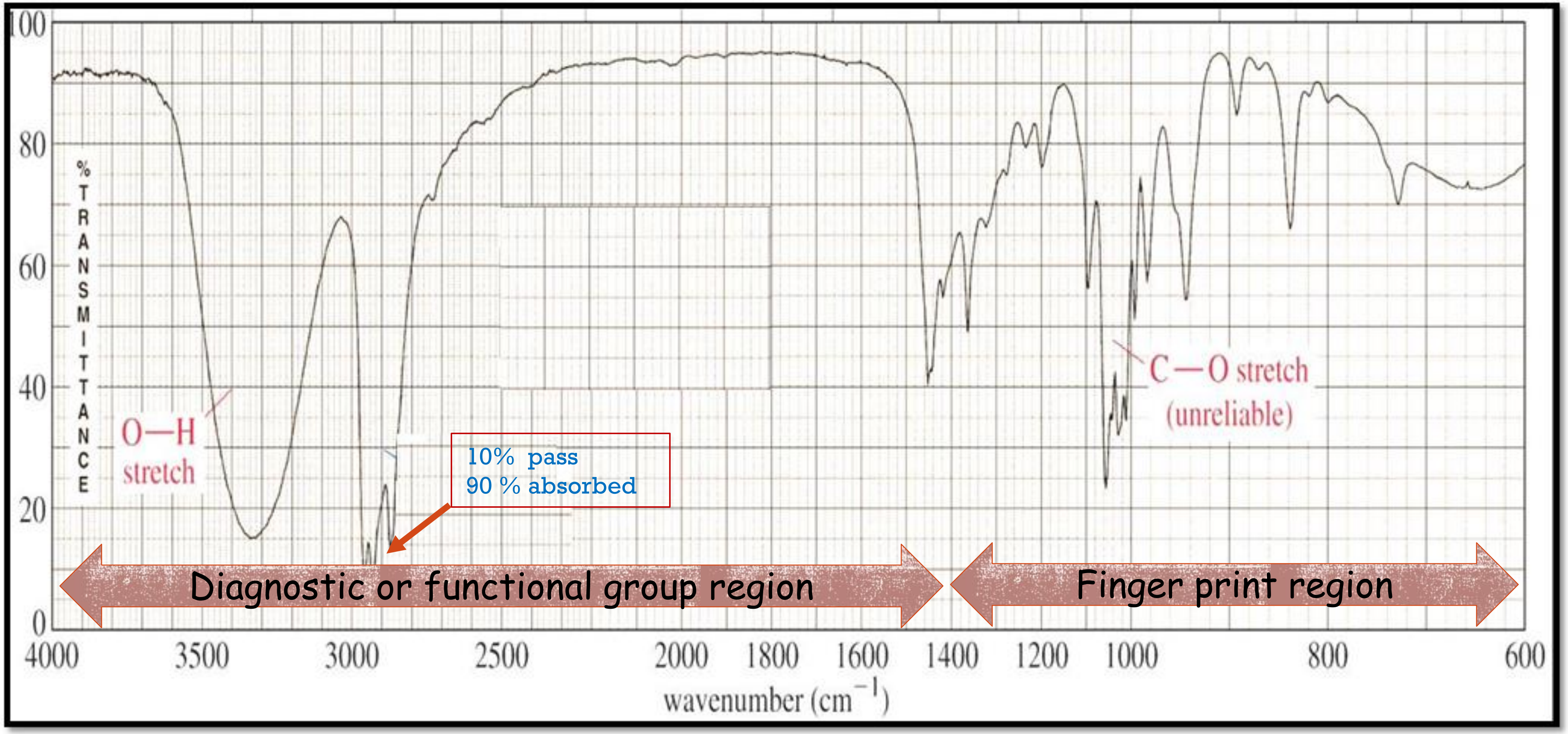
INFRA-RED SPECTROSCOPY

Characteristic Group Vibrations of Organic Molecules

The features of IR spectrum



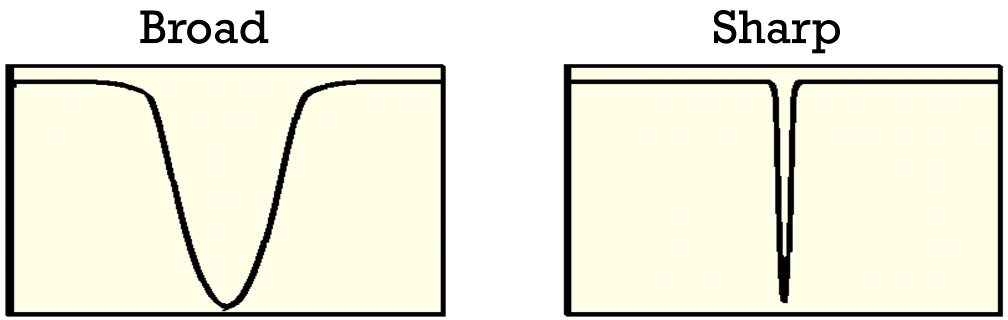
10% pass
90 % absorbed

Diagnostic or functional group region

Finger print region

IR SIGNALS

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

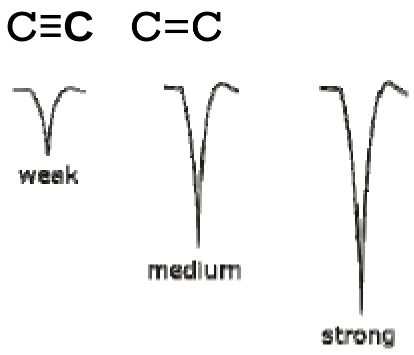


Question: what makes the IR signal broad?

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

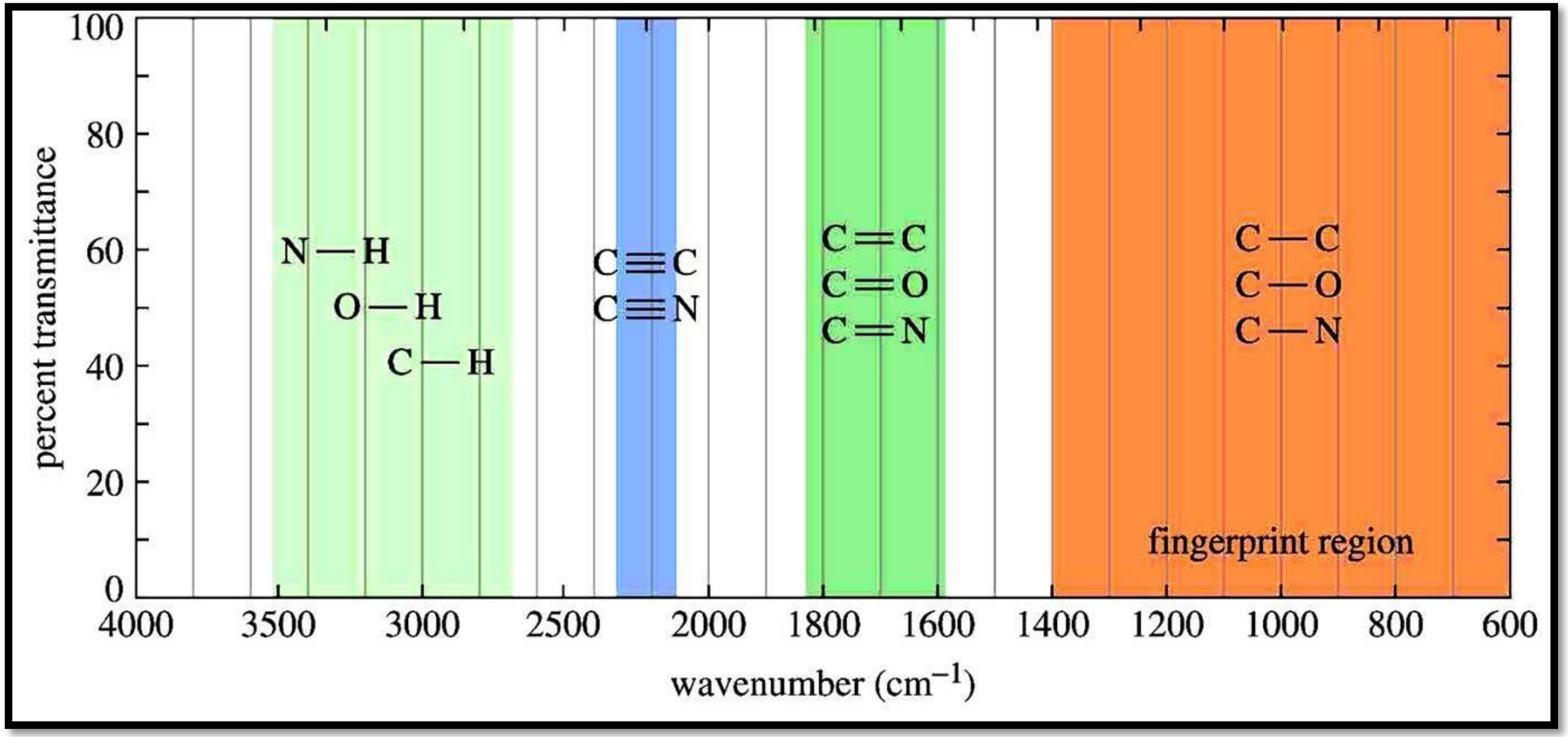
Question: what makes the IR signal sharp?

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 **C≡N** or a **C≡C** bond.

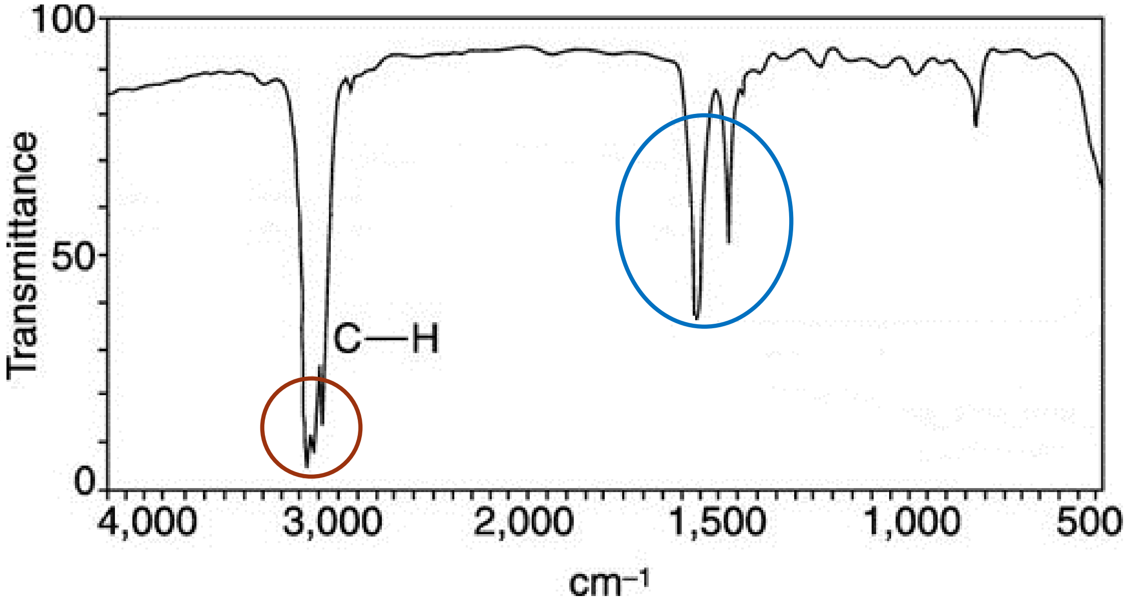


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

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}

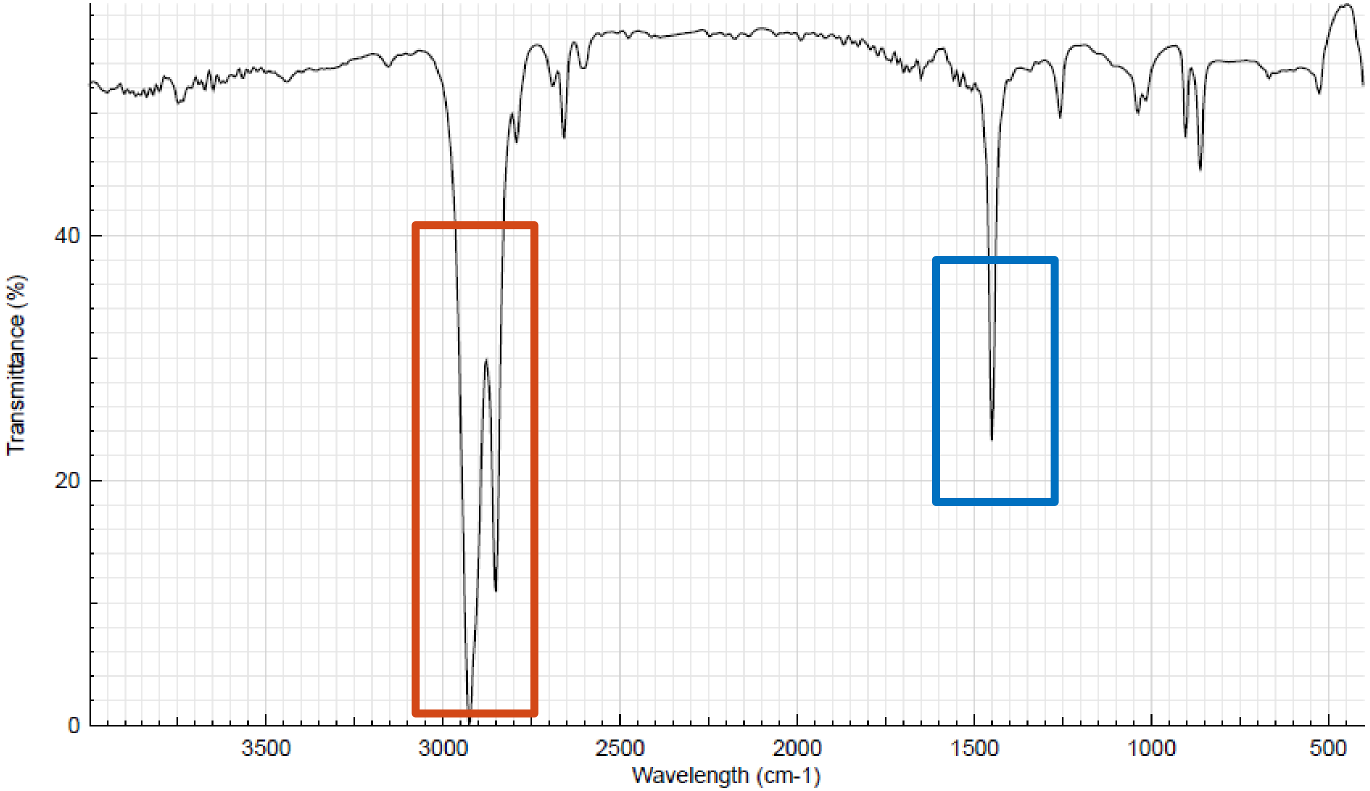
Bending
C-H (CH_3) (1350-1400) cm^{-1}

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

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 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

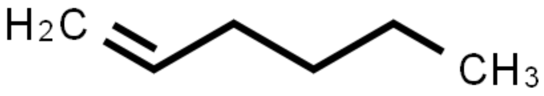
(1680-1620 cm^{-1}) **(1200-800 cm^{-1})**

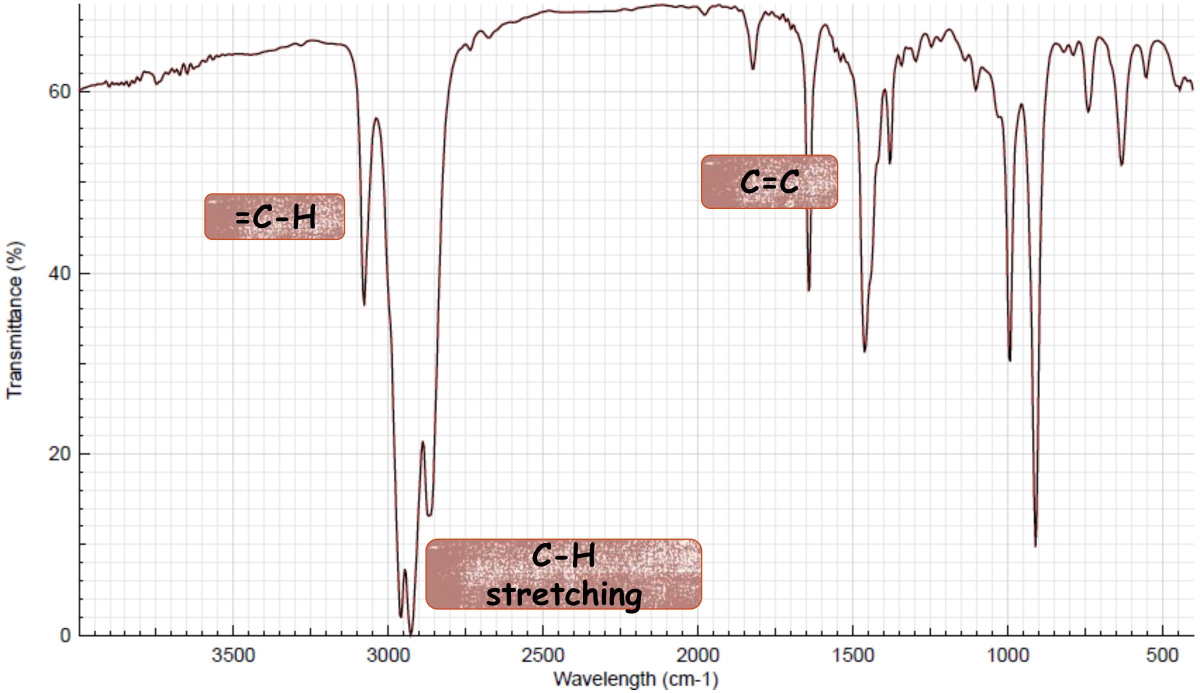
- In completely **symmetrical alkenes**, such as ethylene, tetrachloroethylene etc., **(C=C) stretching** band is absent, *due to lack of change in dipole moment in completely symmetrical molecule*.

- **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.

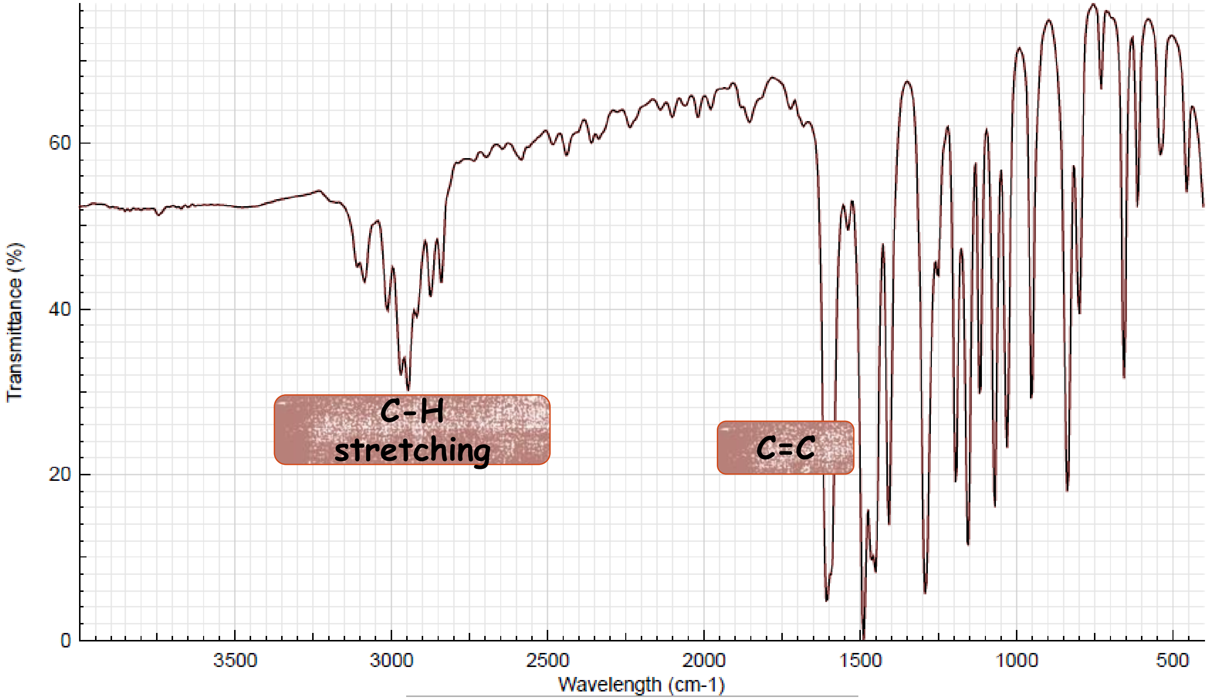
IR SPECTRUM OF ALKENES

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


H2C
CH3


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


H3C
CH3


C-H stretching
C=C
Transmittance (%)
60
40
20
0
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**.

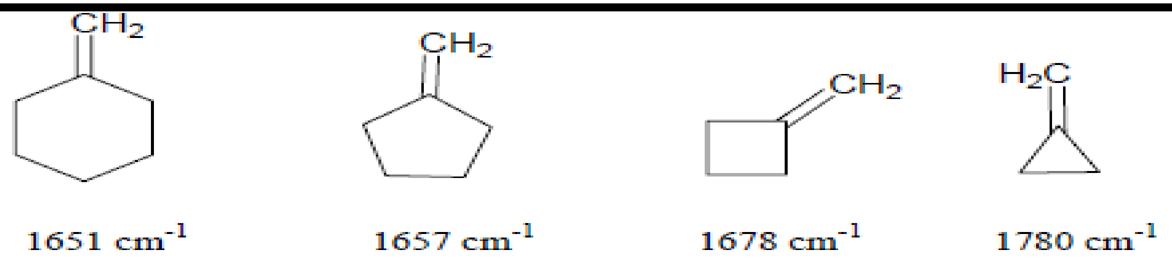
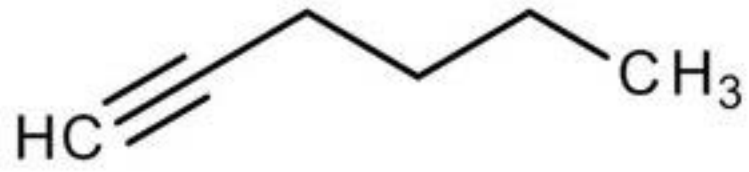
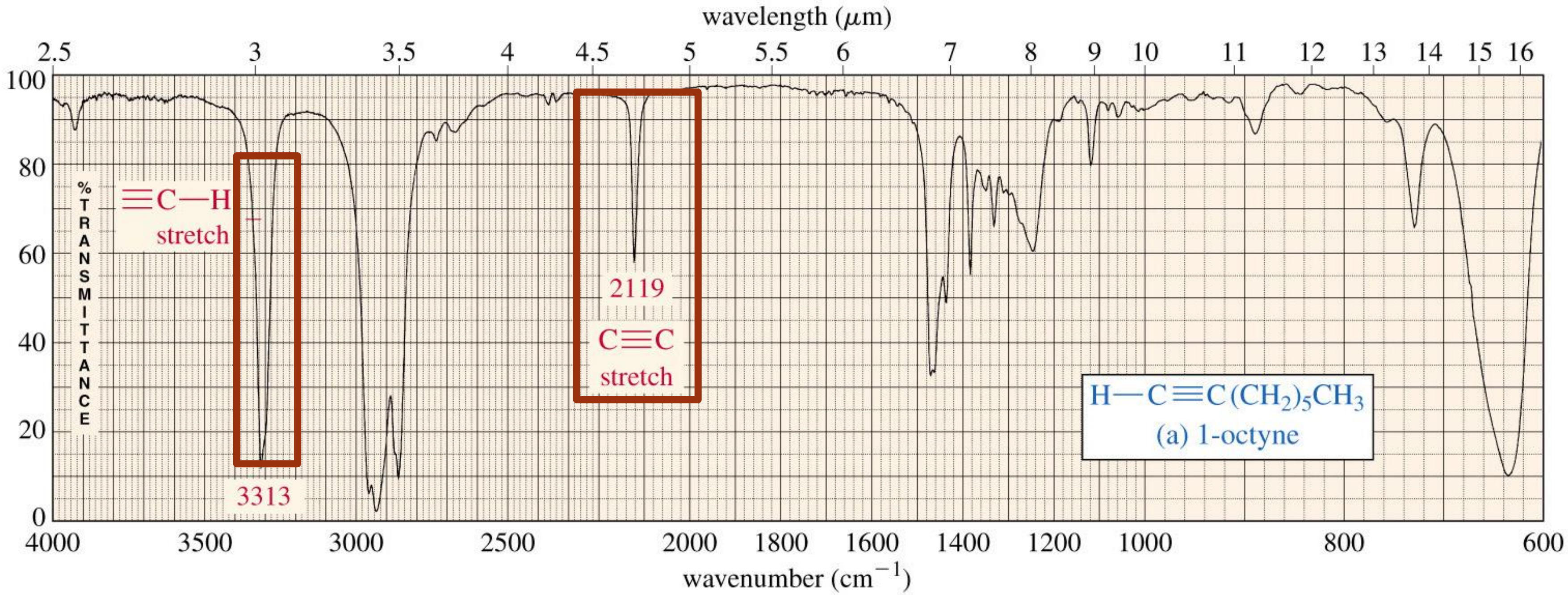


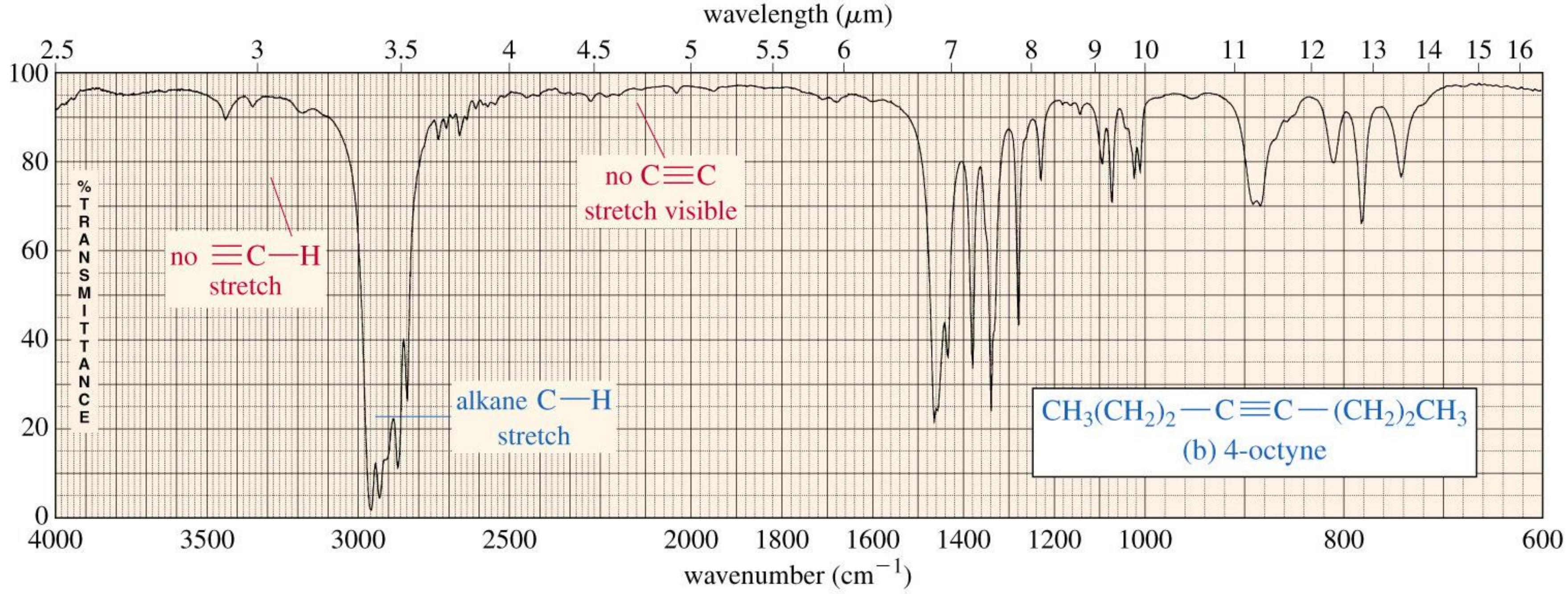
Figure 17 : Exocyclic C=C double bond frequencies in various ring sizes

IR SPECTRUM OF ALKYNES



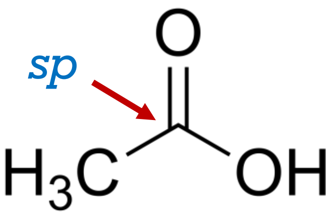
Internal		**Terminal**
(2000-2200 cm^{-1})	C≡C	(2000-2200 cm^{-1})
✗	≡C-H	(3100-3300 cm^{-1})


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
$\equiv$C—H stretch
3313
2119
C$\equiv$C stretch
H—C$\equiv$C(CH$_2$)$_5$CH$_3$
(a) 1-octyne
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

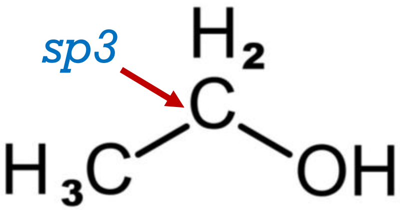

wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
no $\equiv$C—H stretch
no C$\equiv$C stretch visible
alkane C—H stretch
CH$_3$(CH$_2$)$_2$—C$\equiv$C—(CH$_2$)$_2$CH$_3$
(b) 4-octyne
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

IR SPECTRUM OF CARBOXYLIC ACIDS AND ALCOHOLS

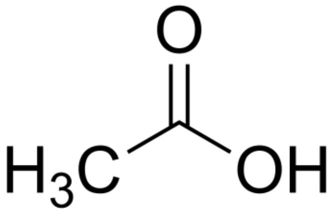
Carboxylic acid

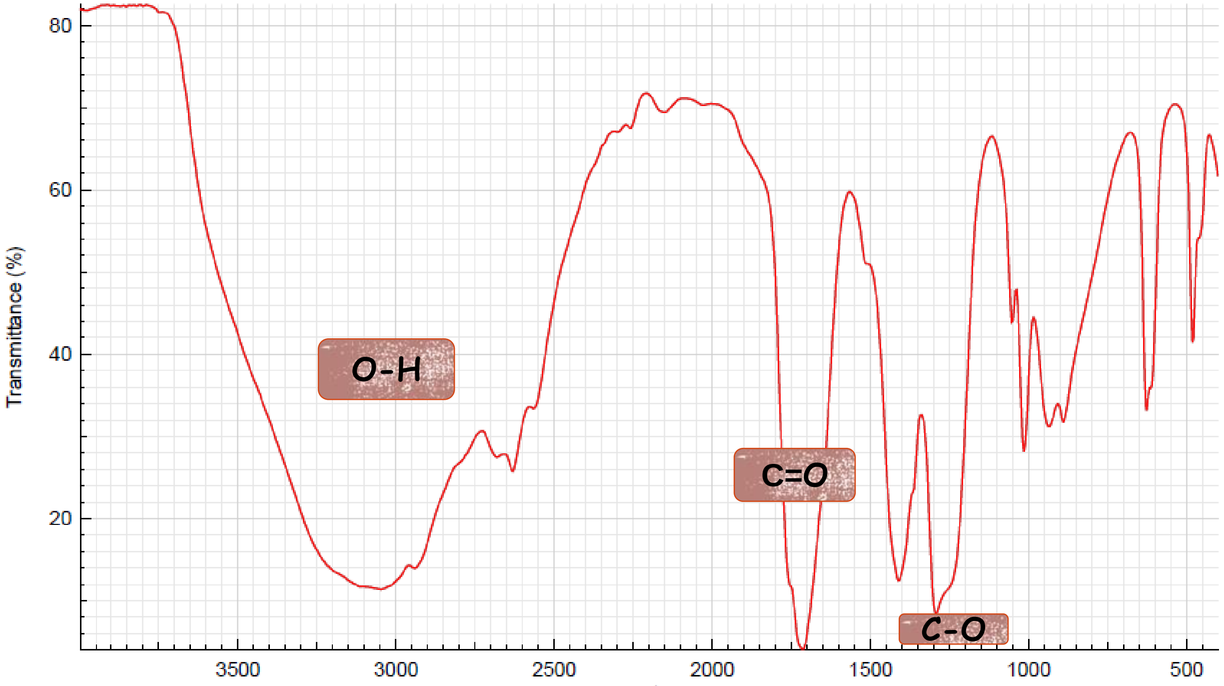


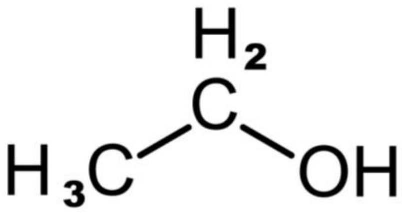
Alcohol

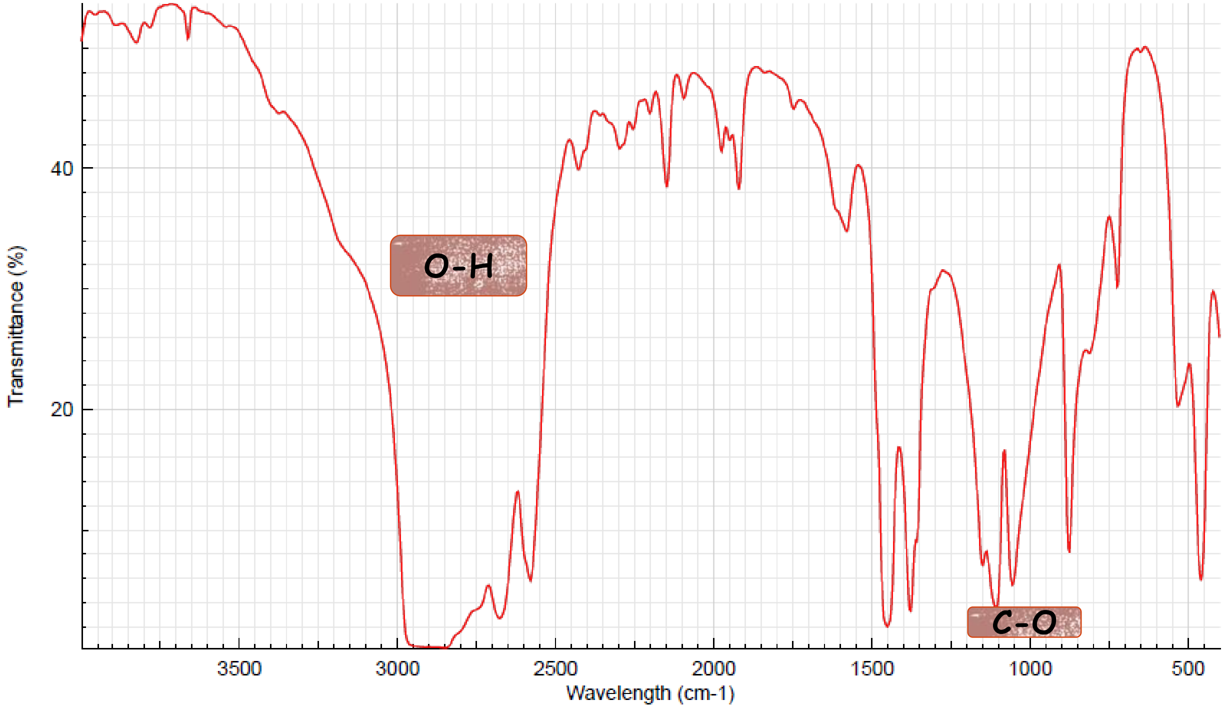


($2500-3300\ cm^{-1}$)	O-H	($3200-3500\ cm^{-1}$)
($1700\ cm^{-1}$)	C=O	✗
($1200-1300\ cm^{-1}$)	C-O	($1000-1150\ cm^{-1}$)

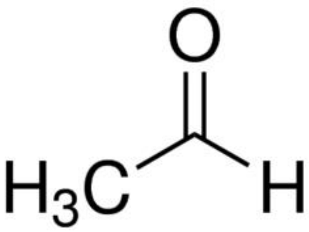

O
H3C
OH

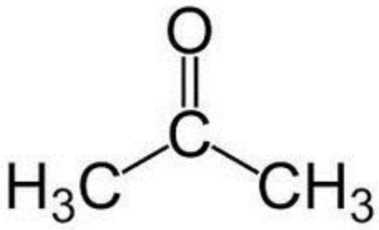

80
60
40
20
Transmittance (%)
O-H
C=O
C-O
3500
3000
2500
2000
1500
1000
500


H2
C
H3C
OH

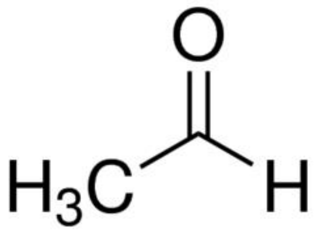

40
20
Transmittance (%)
O-H
C-O
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

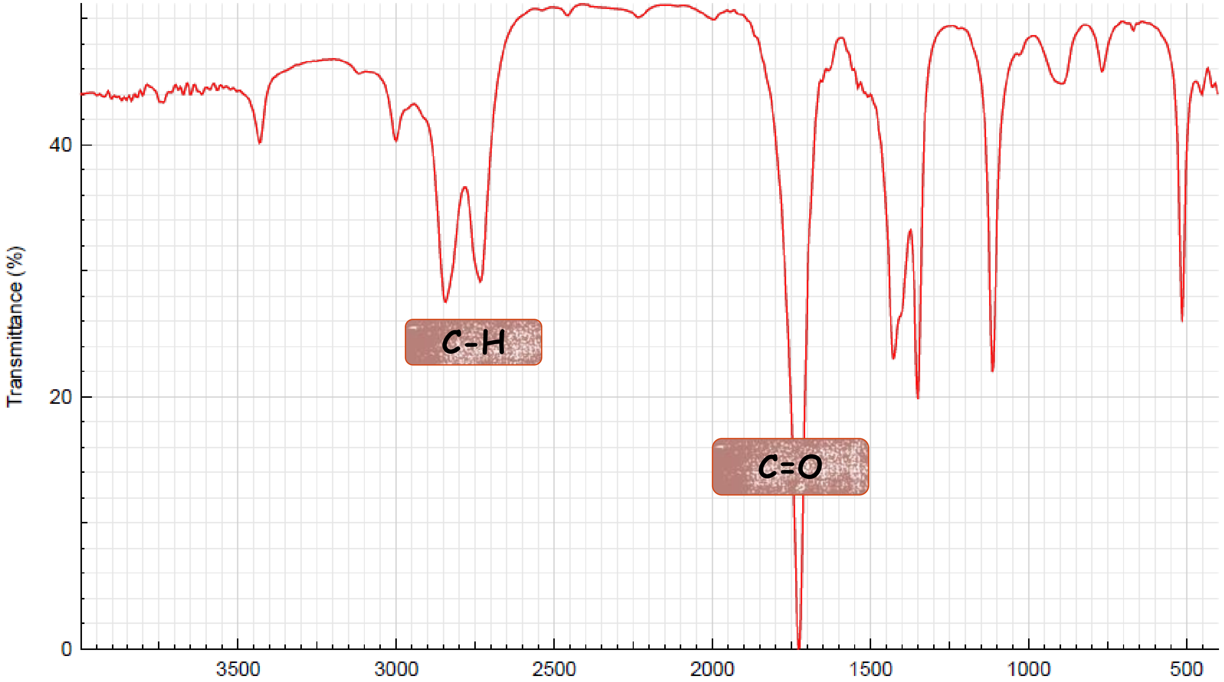
IR SPECTRUM OF ALDEHYDES AND KETONES

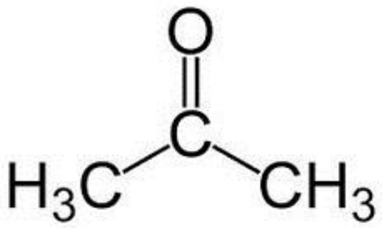


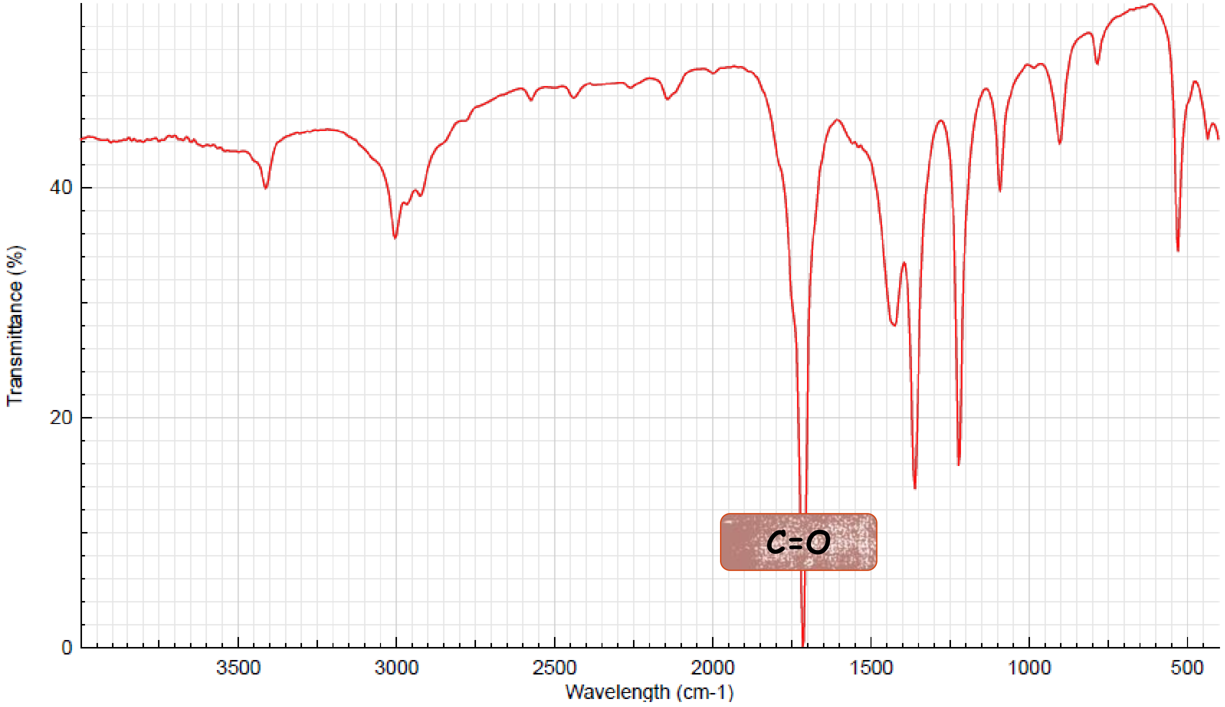


Aldehyde		Ketone
(1700 cm^{-1})	C=O	(1700 cm^{-1})
(2700 and 2800 cm^{-1})	C-H	✗


O
H_3C
H

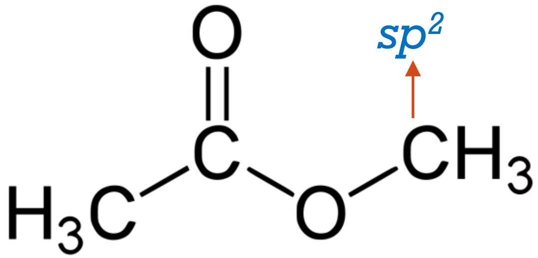

Transmittance (%)
40
20
0
3500
3000
2500
2000
1500
1000
500
C-H
C=O


O
C
H_3C
CH_3

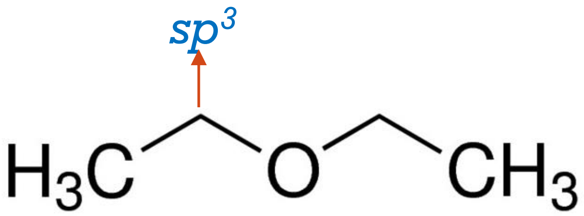

Transmittance (%)
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C=O

IR SPECTRUM OF ESTERS AND ETHERS

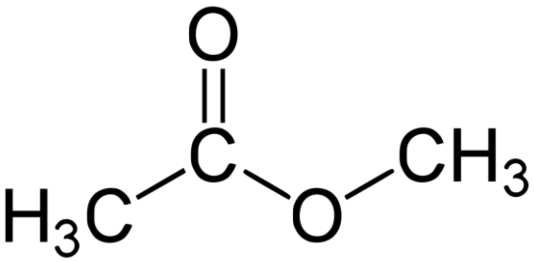
Ester

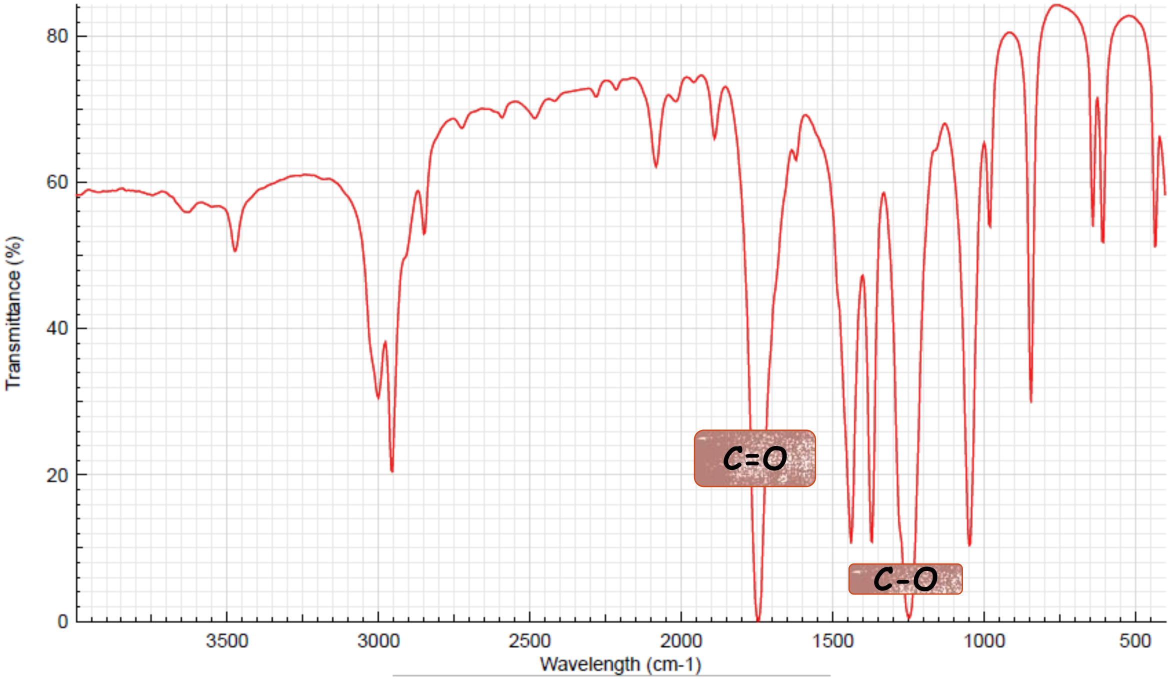


Ether

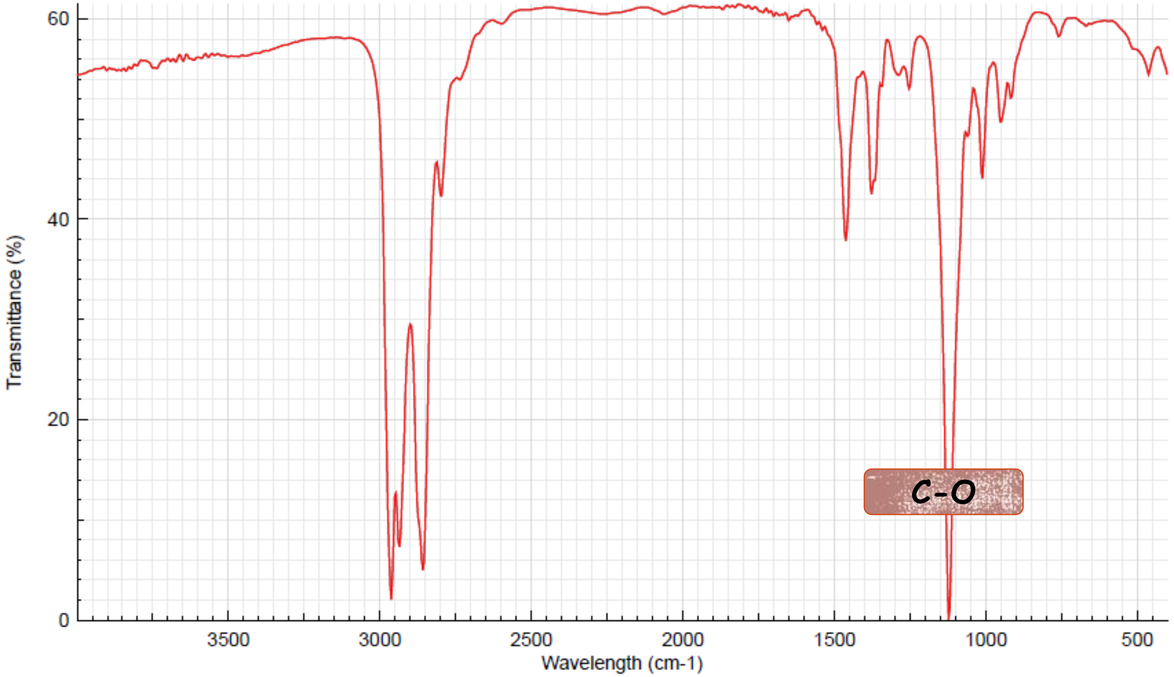


(1200-1300 cm^{-1})	C-O	(1000-1150 cm^{-1})
(1735 cm^{-1})	C=O	✗


O
C
H3C
O
CH3


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


H3C
O
CH3


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

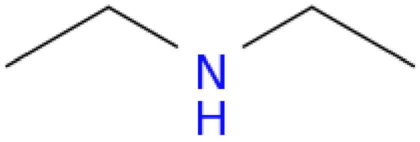
IR SPECTRUM OF AMINE

1° amine

TWO peaks

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

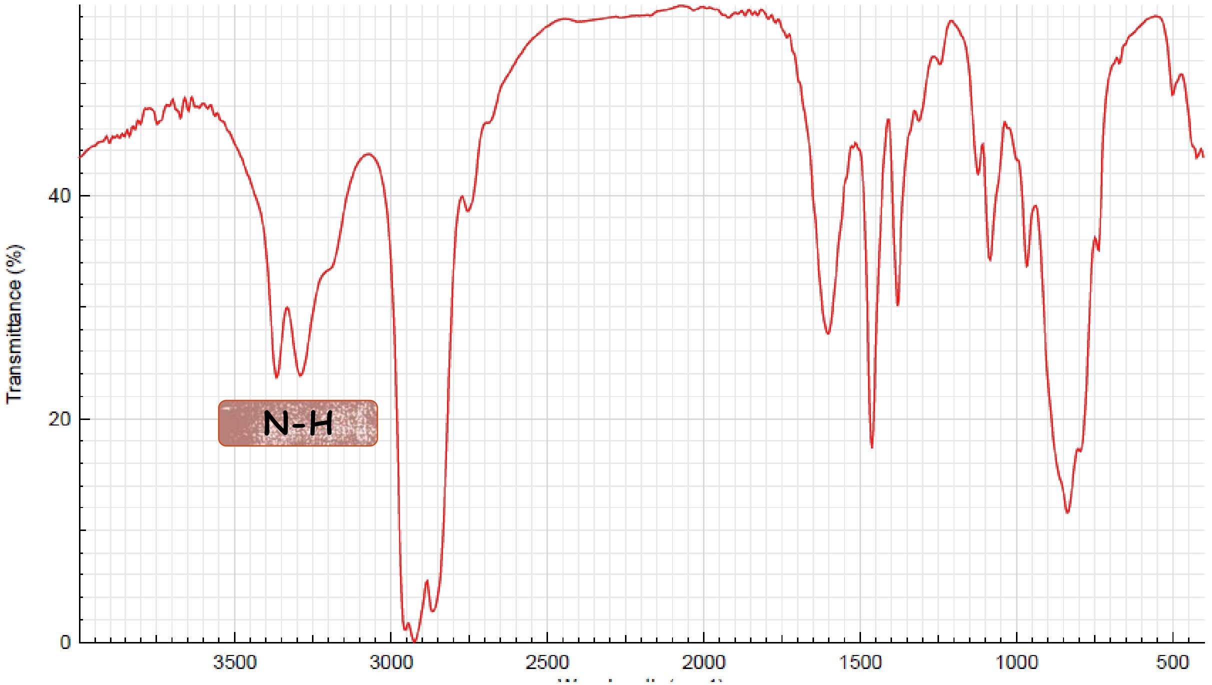
2° amine

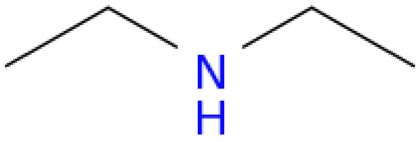


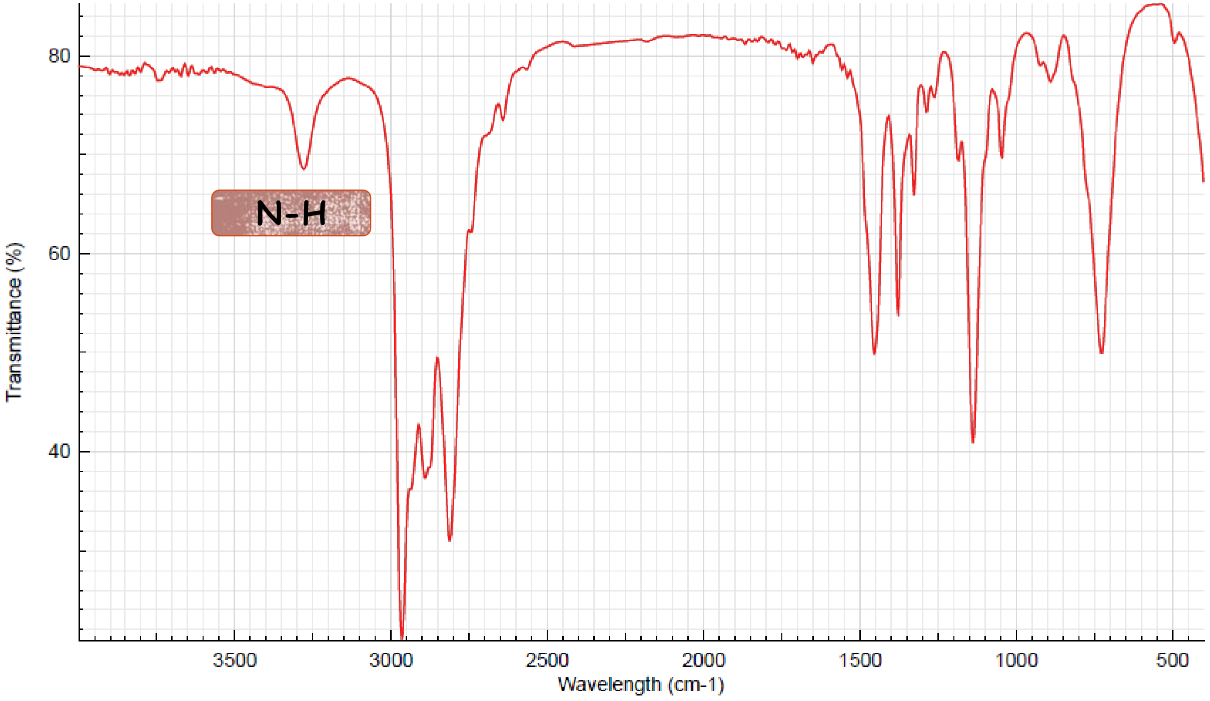
ONE peak

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


NH2

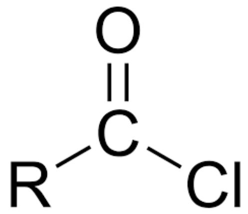

N-H
Transmittance (%)
0
20
40
3500
3000
2500
2000
1500
1000
500


N
H

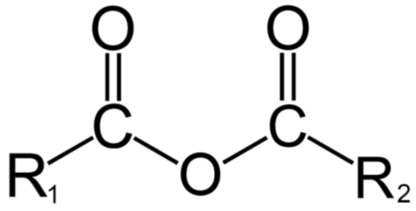

N-H
Transmittance (%)
40
60
80
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

IR SPECTRUM OF ACID CHLORIDE AND ANHYDRIDE

Acid chloride

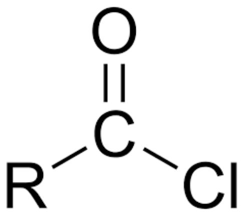


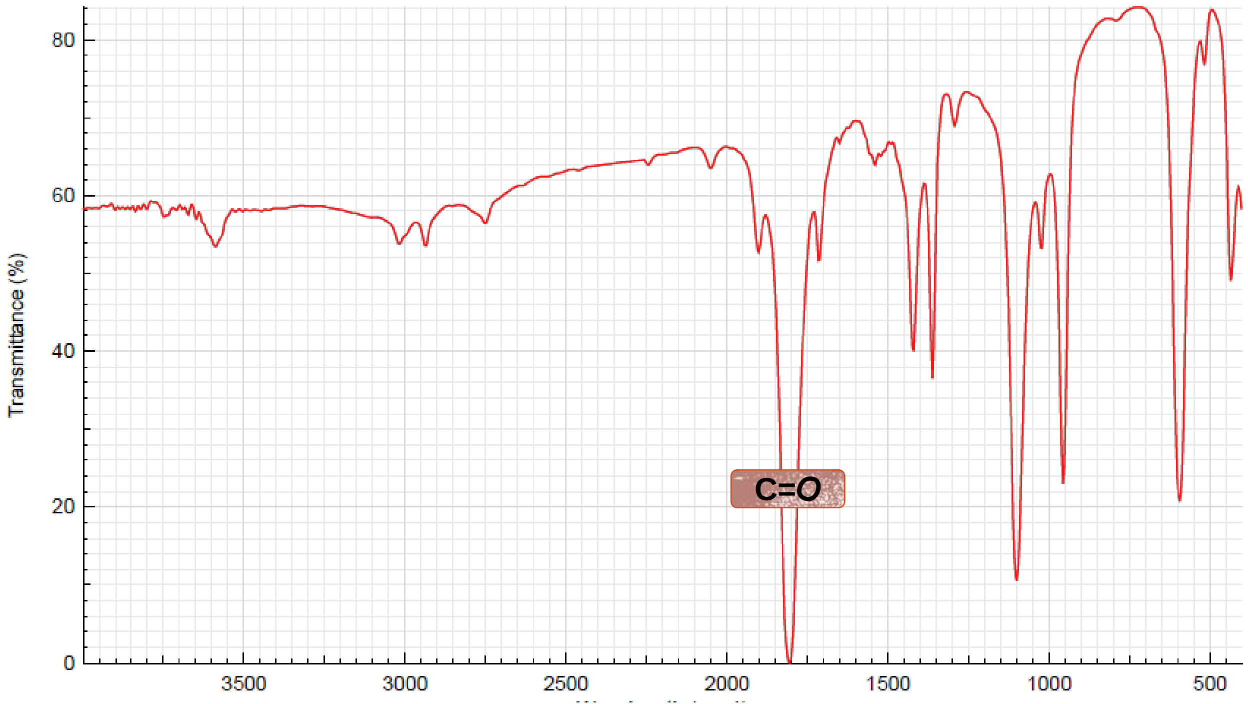
Anhydride

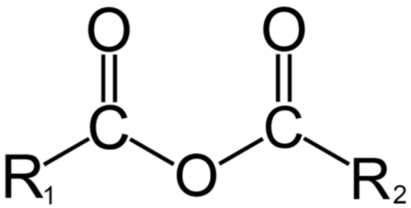


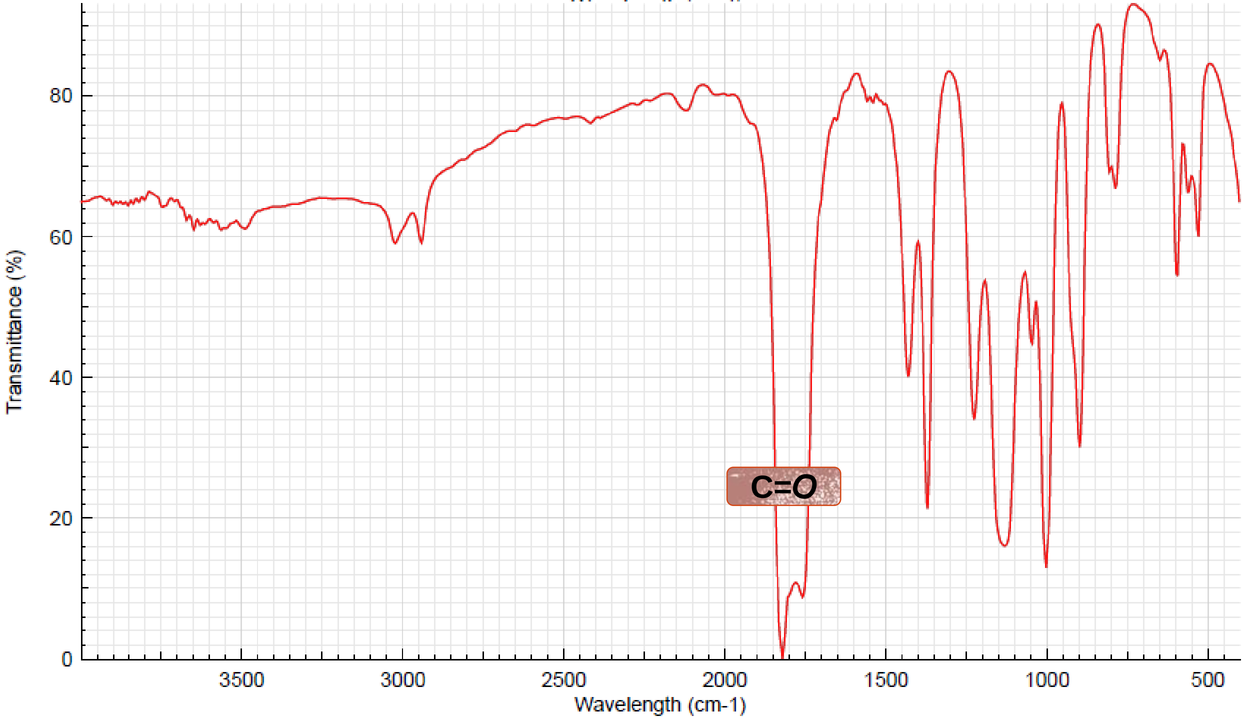
	Acid chloride	Anhydride
C=O	(1790-1810 cm^{-1})	(1750-1800 cm^{-1})
C-O	✗	(900-1300 cm^{-1})

- ❑ 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}.

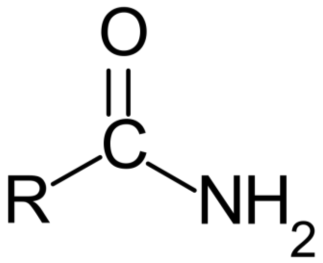
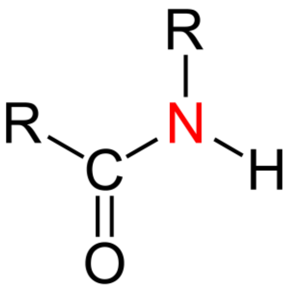

O
C
R
Cl


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

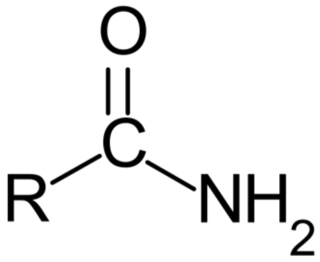

O
O
C
C
R1
O
R2

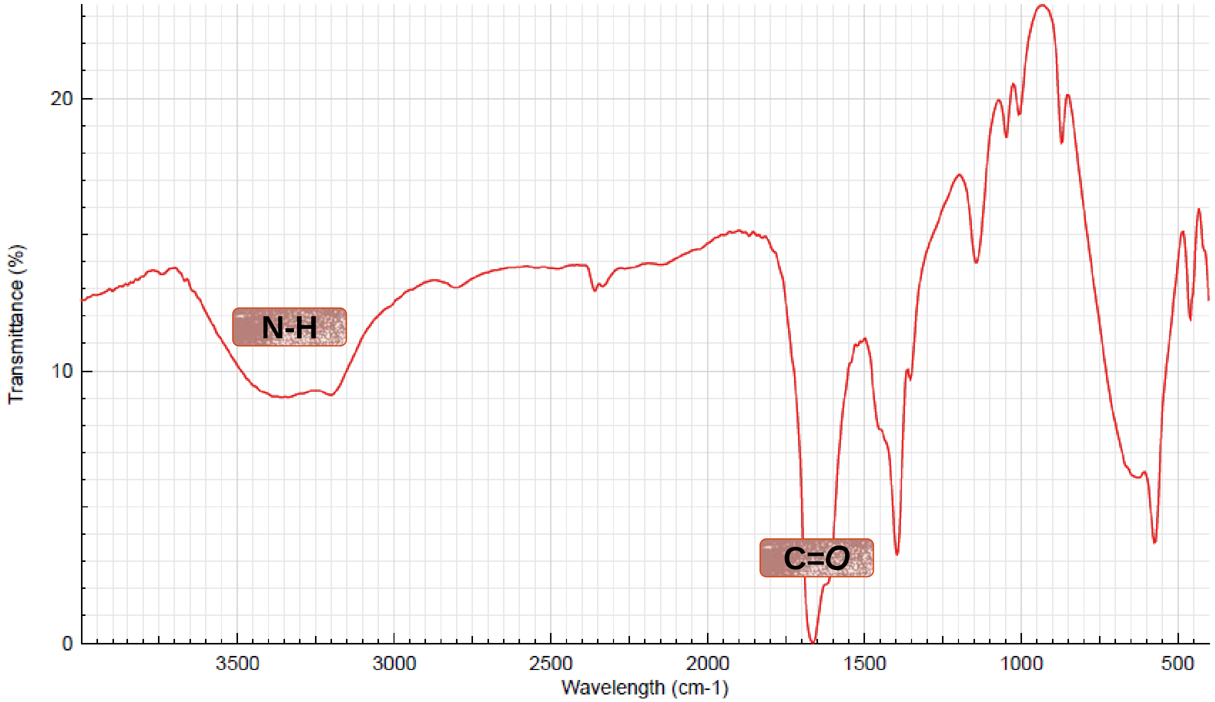

Transmittance (%)
80
60
40
20
0
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)
C=O

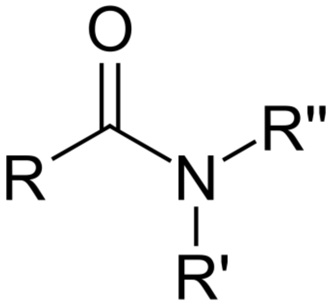
IR SPECTRUM OF AMIDES

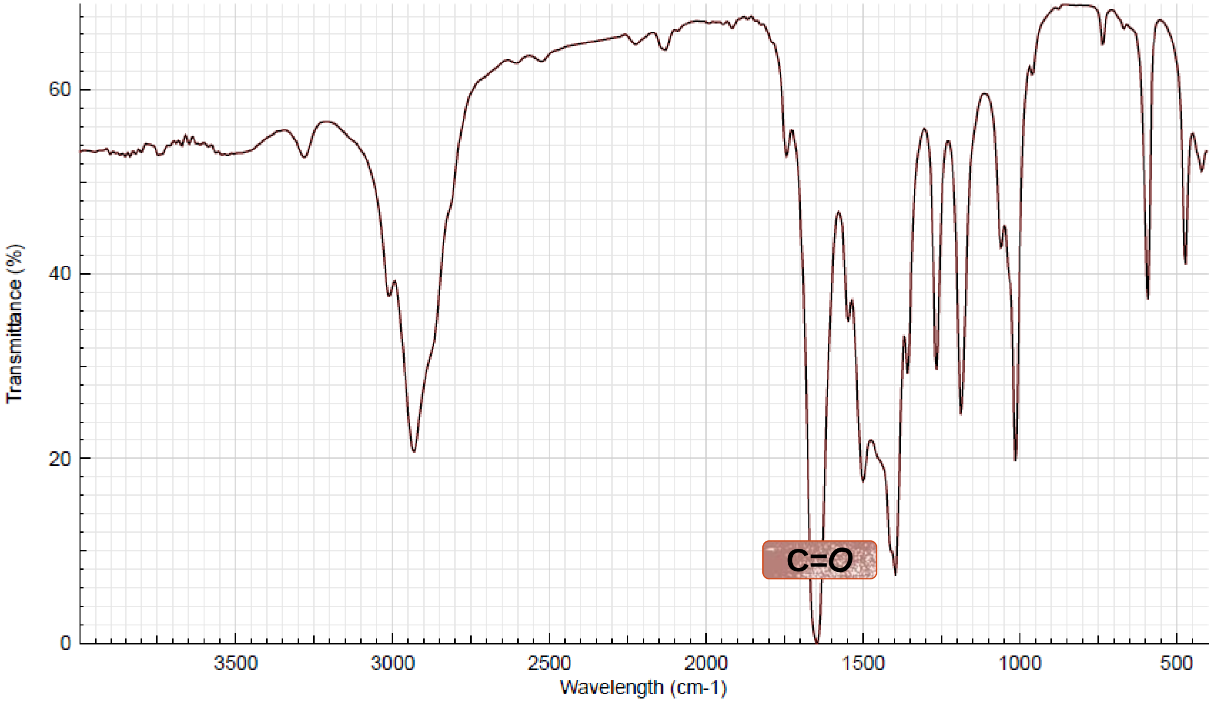
1° amide		2° amide
		
(1650-1690 cm^{-1})	C=O	(1650-1690 cm^{-1})
(3550 and 3180 cm^{-1})	(N-H) stretching	~ (3300 cm^{-1})

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

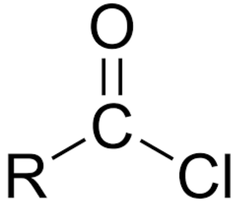
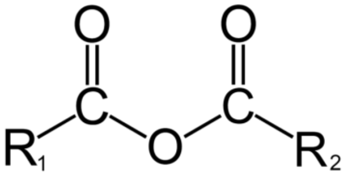
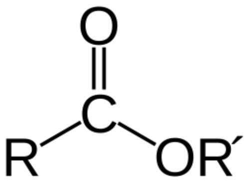
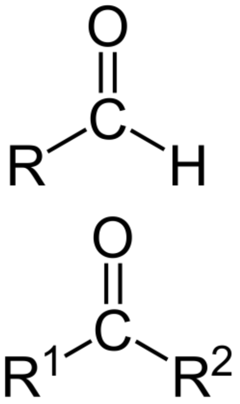
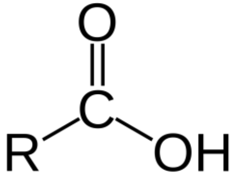
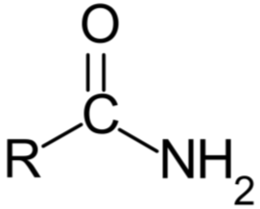

O
C
R
NH2


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


O
R
N
R''
R'


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

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

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