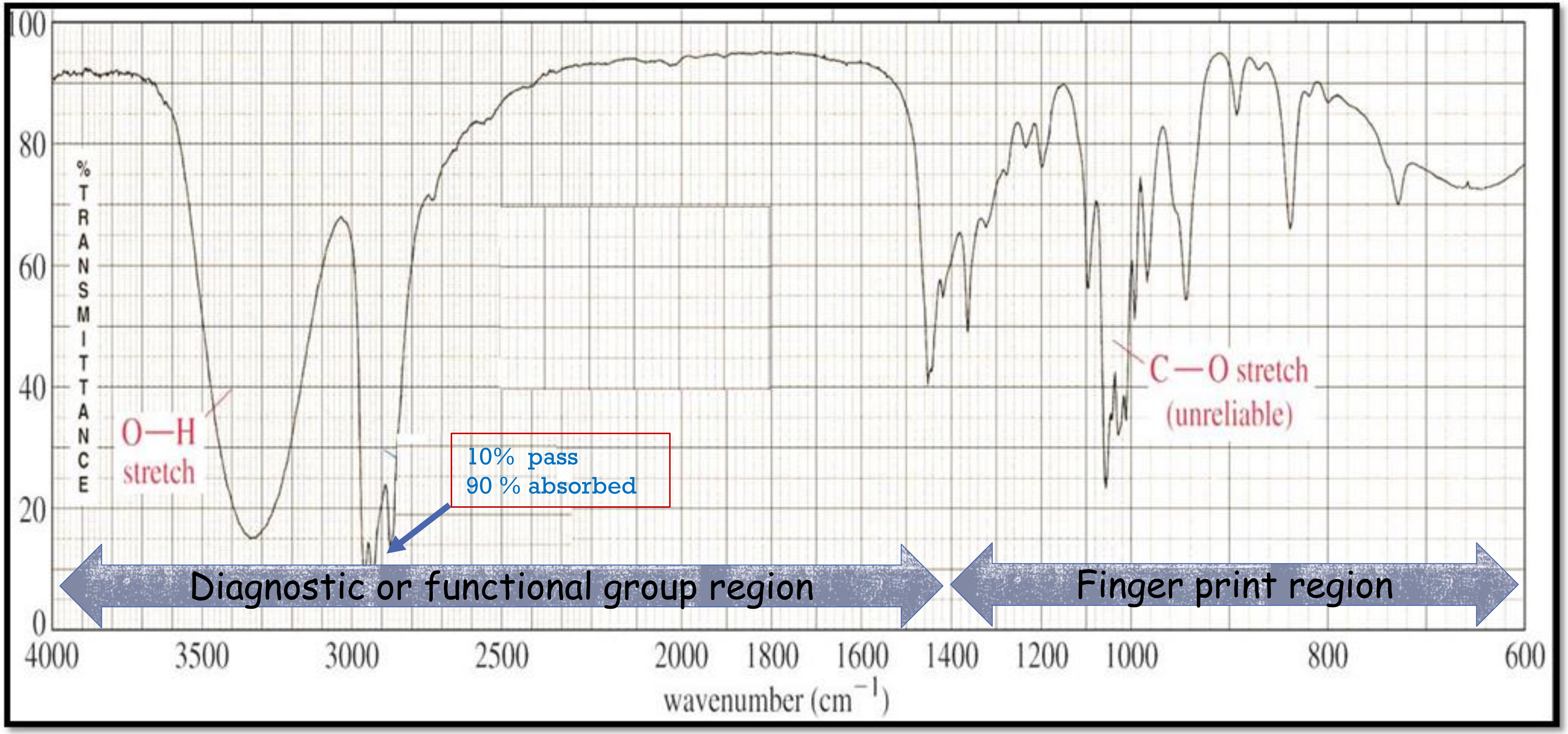
INFRA-RED SPECTROSCOPY

Characteristic Group Vibrations of Organic Molecules

4

2022-2023

The features of IR spectrum



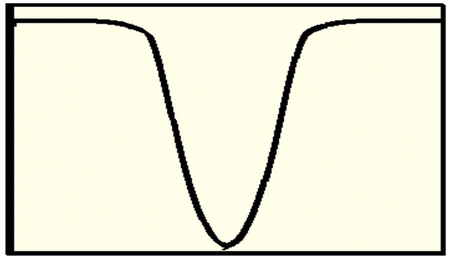
CHARACTERISTIC GROUP ABSORPTIONS OF ORGANIC MOLECULES

- The characteristic group absorptions expressed as **ranges** of absorption bands.
- These values have been assigned following the examination of many compounds in which the groups occur.
- Although the ranges are quite well defined, the precise frequency or wavelength at which a specific group absorbs is dependent on its **environment within the molecule and on its physical state**.

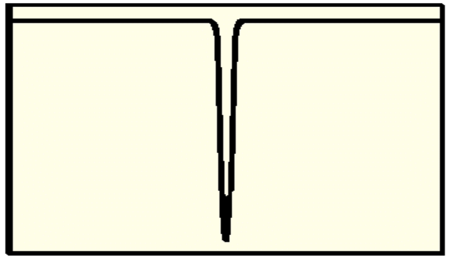
IR SIGNALS

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

Broad



Sharp

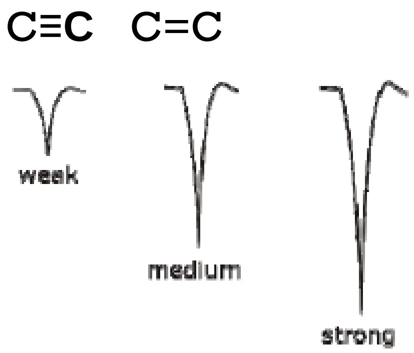


Question: what makes the IR signal broad?

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

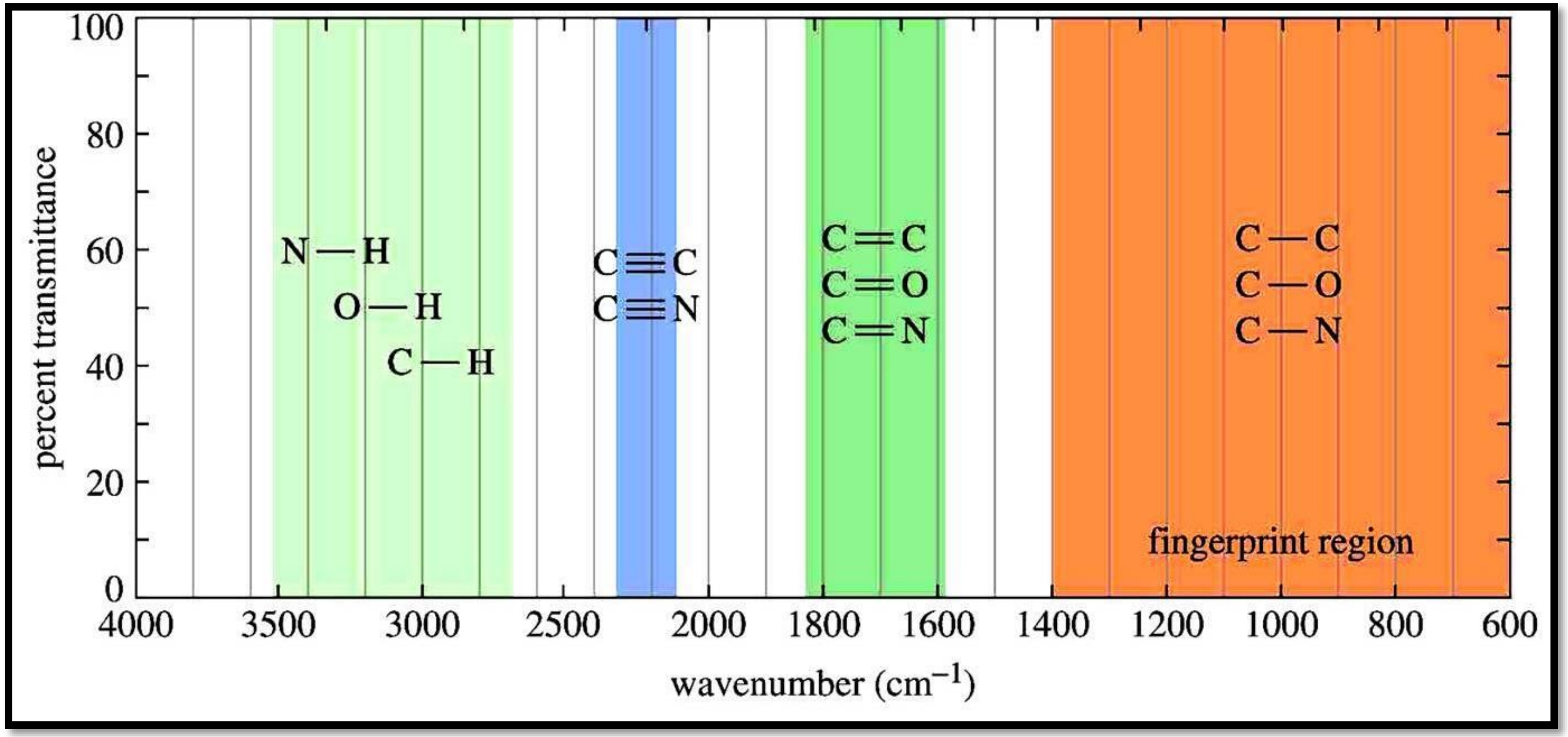
Question: what makes the IR signal sharp?

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.

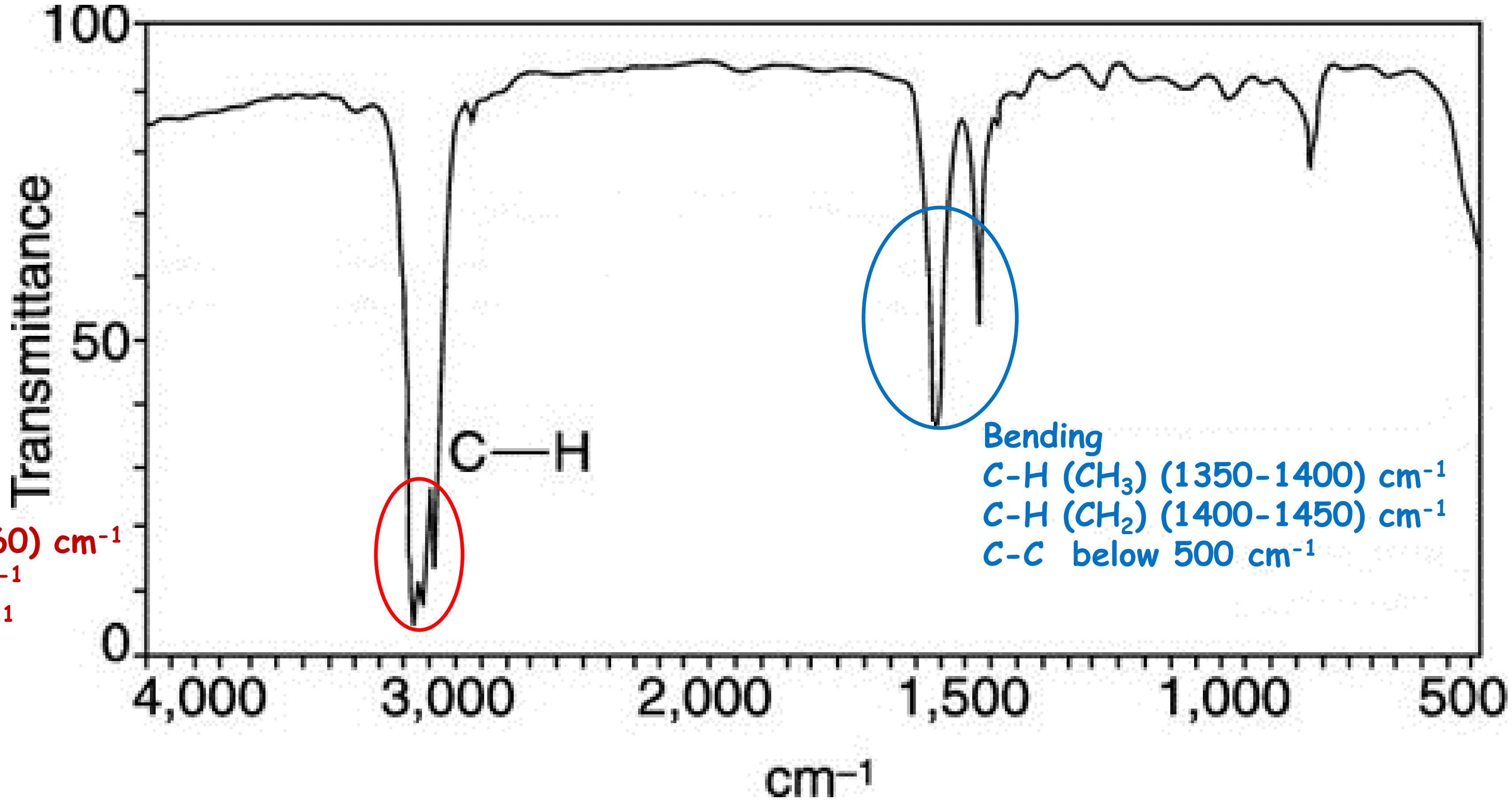


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

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

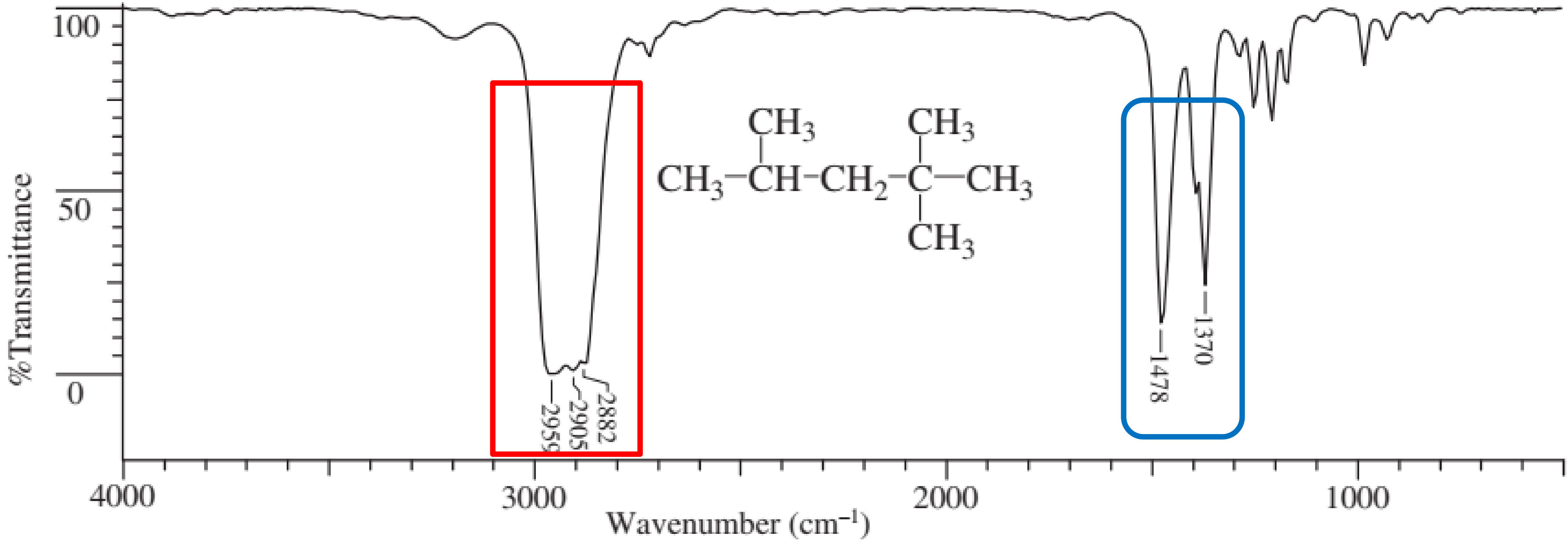
Alkanes:

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}

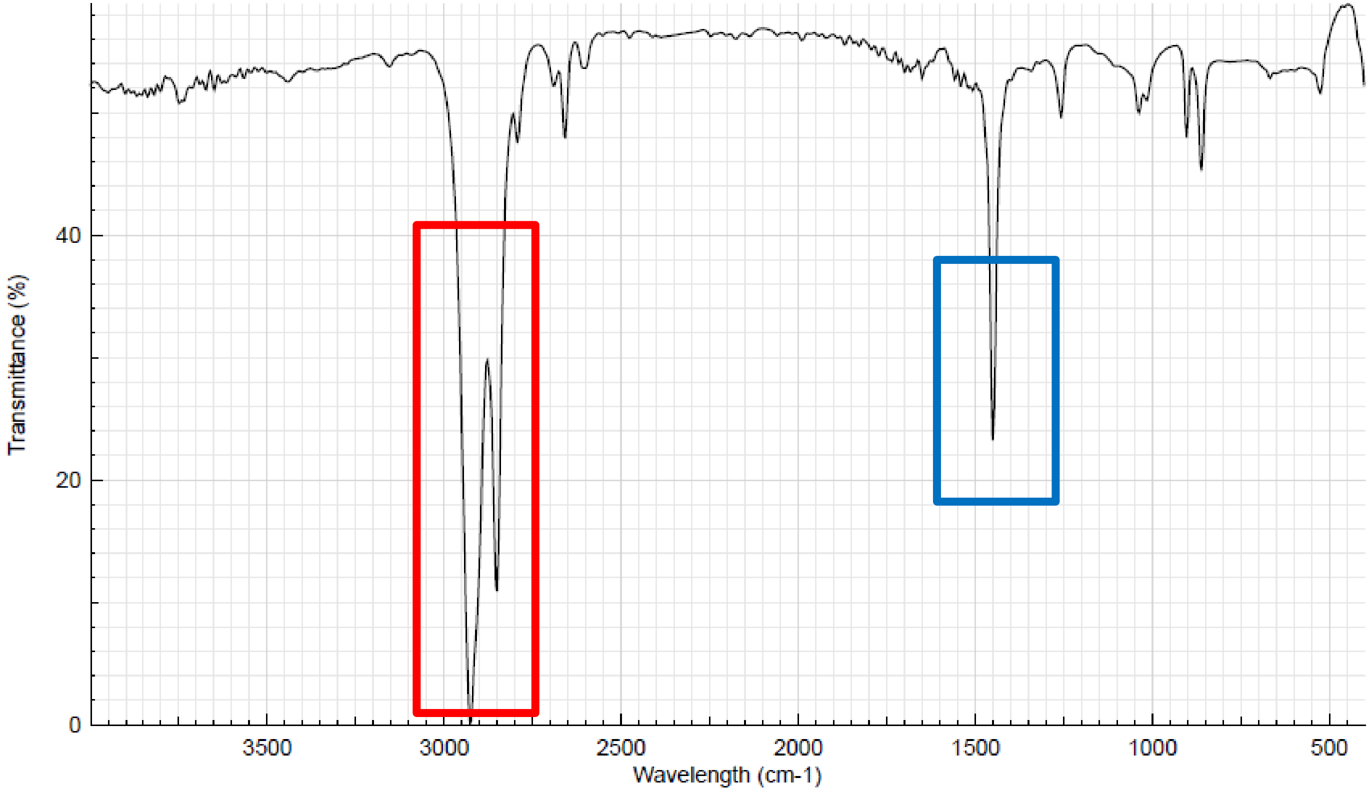
Bending
C-H (CH_3) (1350-1400) cm^{-1}
C-H (CH_2) (1400-1450) cm^{-1}
C-C below 500 cm^{-1}



100
50
0
% Transmittance
4000
3000
2000
1000
Wavenumber (cm⁻¹)
2959
2905
2882
1478
1370
CH3
CH3
CH3–CH–CH2–C–CH3
CH3

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}

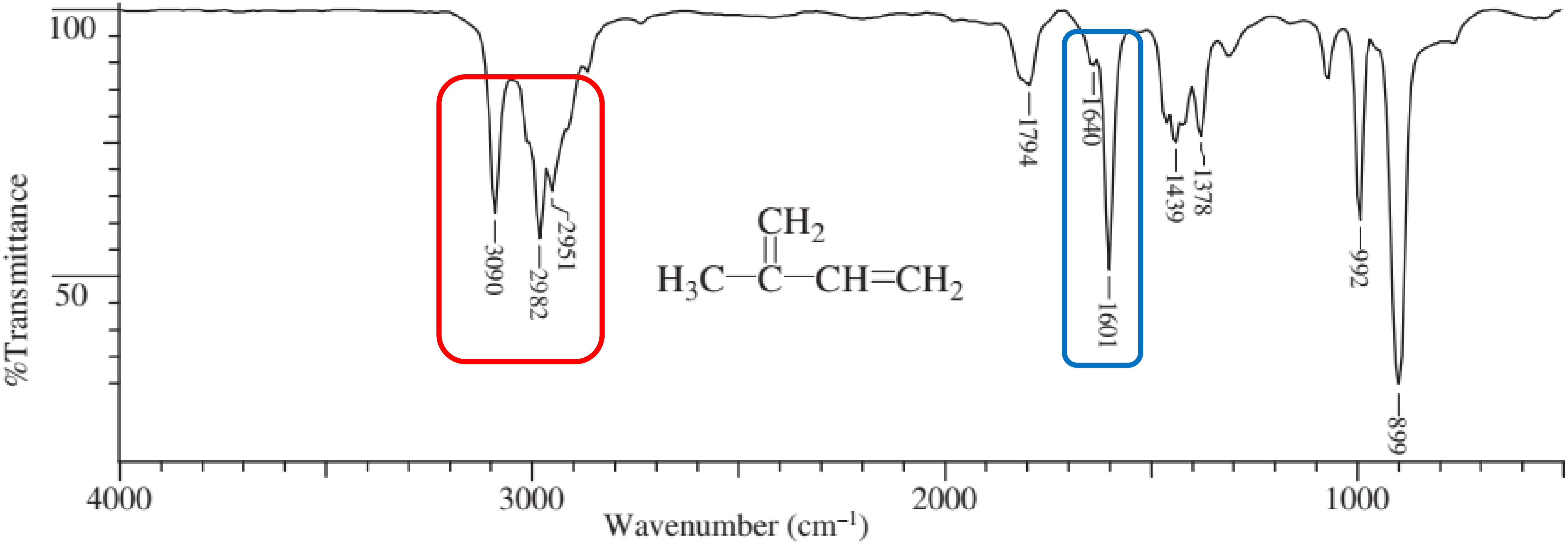
Conjugated C=C (sym) (one band ONLY 1600) cm^{-1}

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.

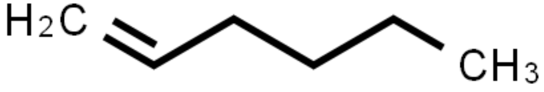
(=C-H) (stretching) above 3000 cm^{-1}

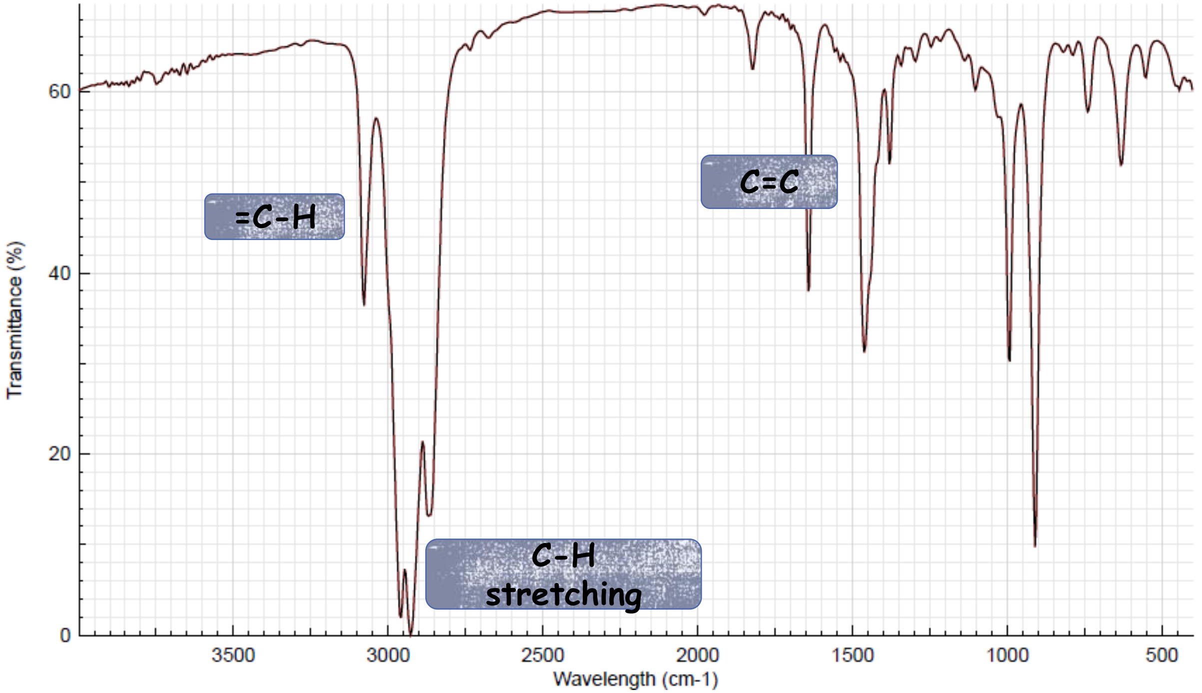
- **Non-symmetrically** substituted double bonds exhibit strong absorption bands. The absorption bands are **more intense for *cis* isomers than for *trans* isomers**; for mono or tri substituted olefins than for di and tetra substituted ones.


100
50
%Transmittance
3090
2982
2951
1794
1640
1601
1439
1378
992
899
4000
3000
2000
1000
Wavenumber (cm^{-1})
CH$_2$
H$_3$C—C—CH=CH$_2$

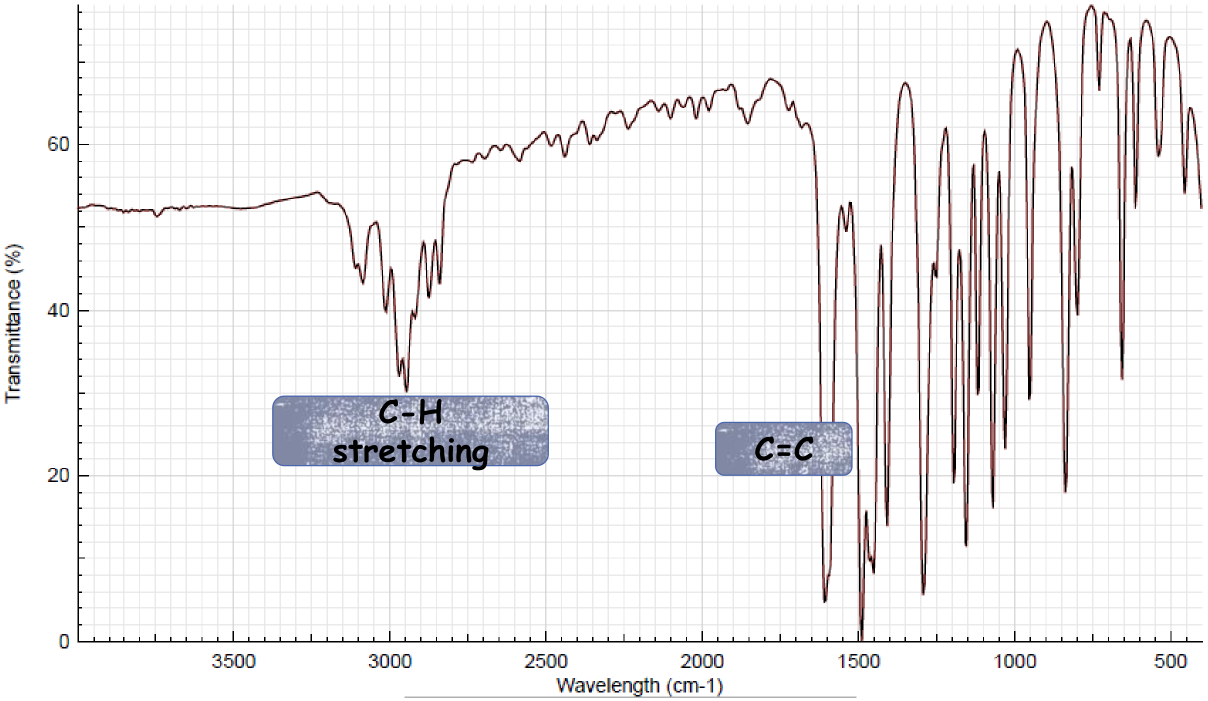
IR SPECTRUM OF ALKENES


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


H$_2$C
CH$_3$


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


H$_3$C
CH$_3$


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**.

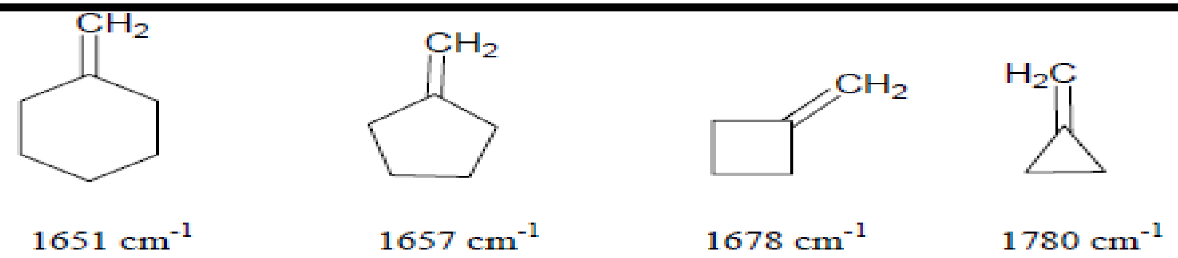
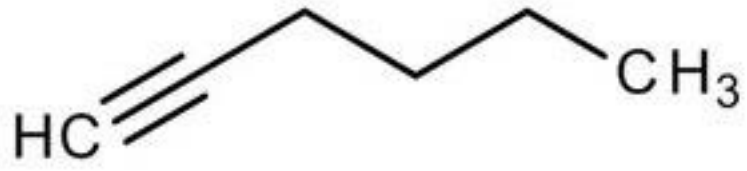


Figure 17 : Exocyclic C=C double bond frequencies in various ring sizes

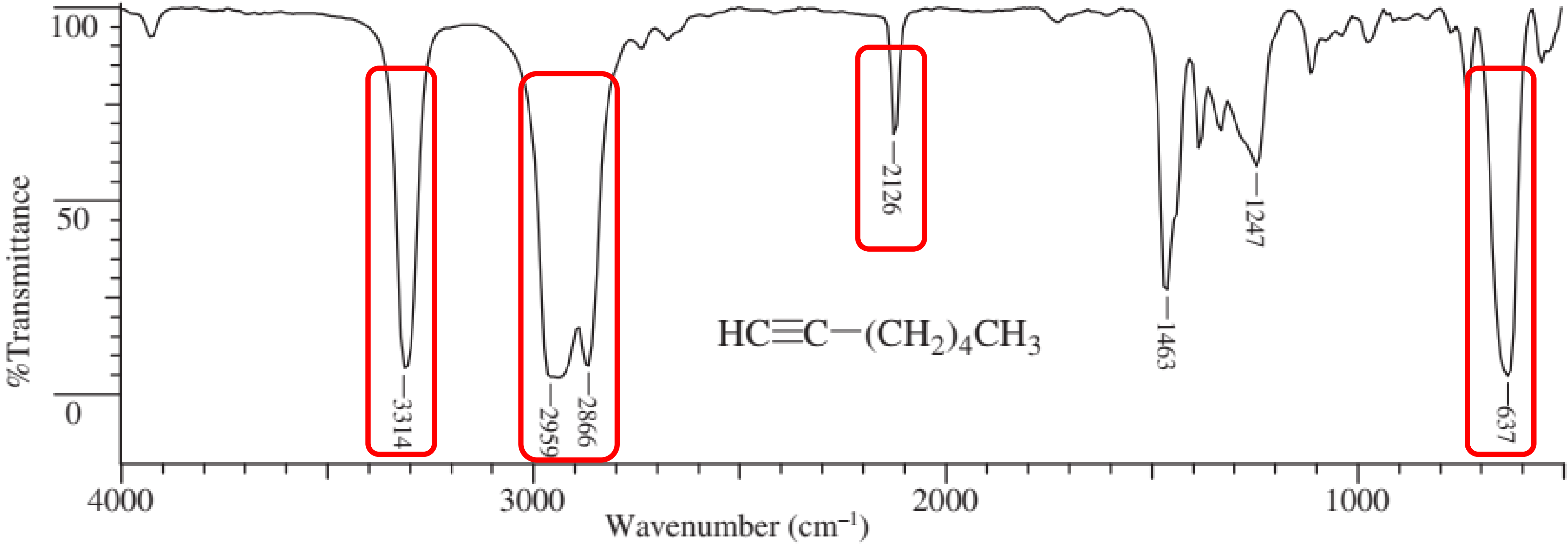
IR SPECTRUM OF ALKYNES



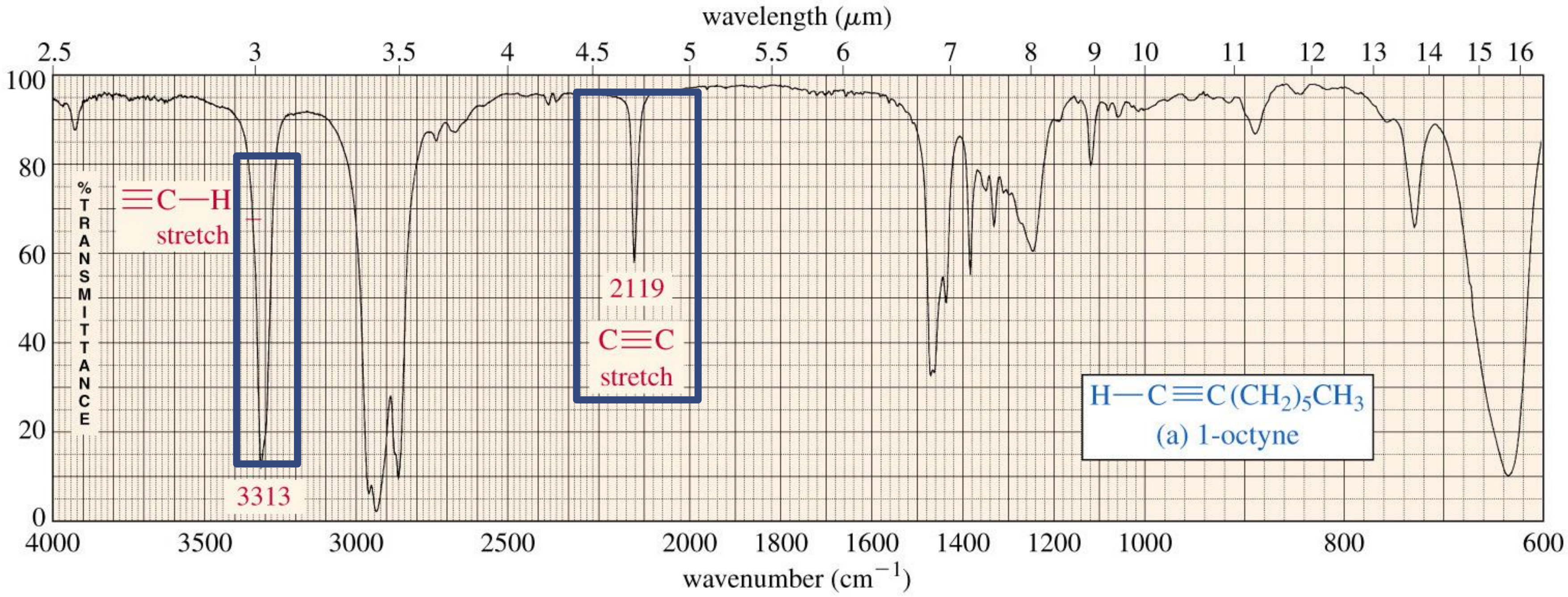
	Internal	**Terminal**
C≡C	**(2260-2000 cm^{-1})**	**(2260-2000 cm^{-1})**
≡C-H	✗	**(3100-3300 cm^{-1})**

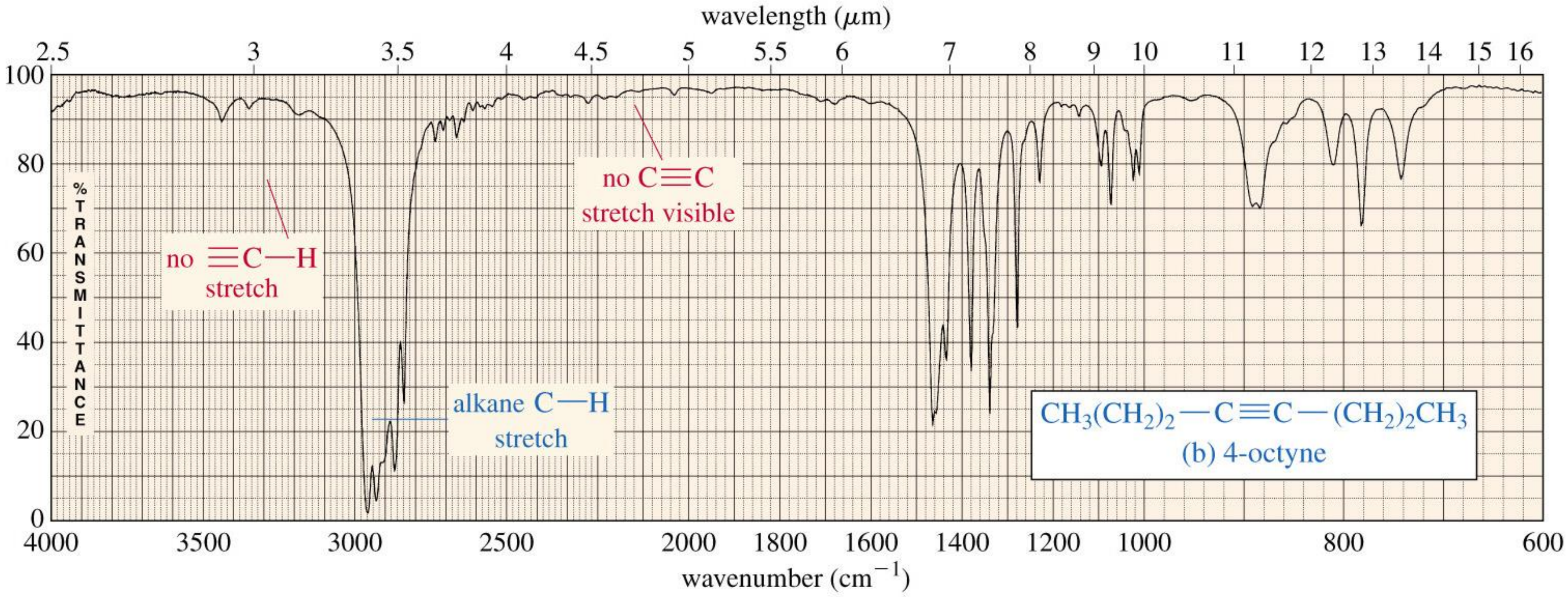
When the substituents are similar in mass, or produce similar inductive and resonance effects, the band may be so weak as to be unobserved in the IR spectrum.

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≡C—(CH$_2$)$_4$CH$_3$
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
≡C—H stretch
3313
2119
C≡C stretch
H—C≡C(CH$_2$)$_5$CH$_3$
(a) 1-octyne
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

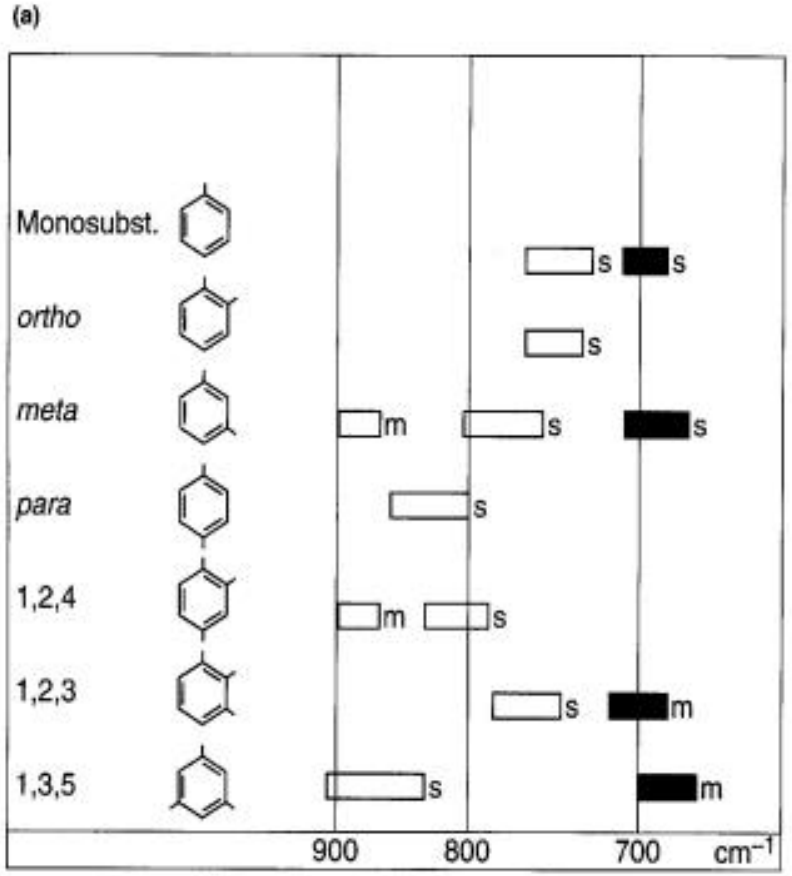

wavelength (μm)
2.5
3
3.5
4
4.5
5
5.5
6
7
8
9
10
11
12
13
14
15
16
100
80
60
40
20
0
% TRANSMITTANCE
no ≡C—H stretch
no C≡C stretch visible
alkane C—H stretch
CH$_3$(CH$_2$)$_2$—C≡C—(CH$_2$)$_2$CH$_3$
(b) 4-octyne
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
wavenumber (cm^{-1})

IR for Functional Groups

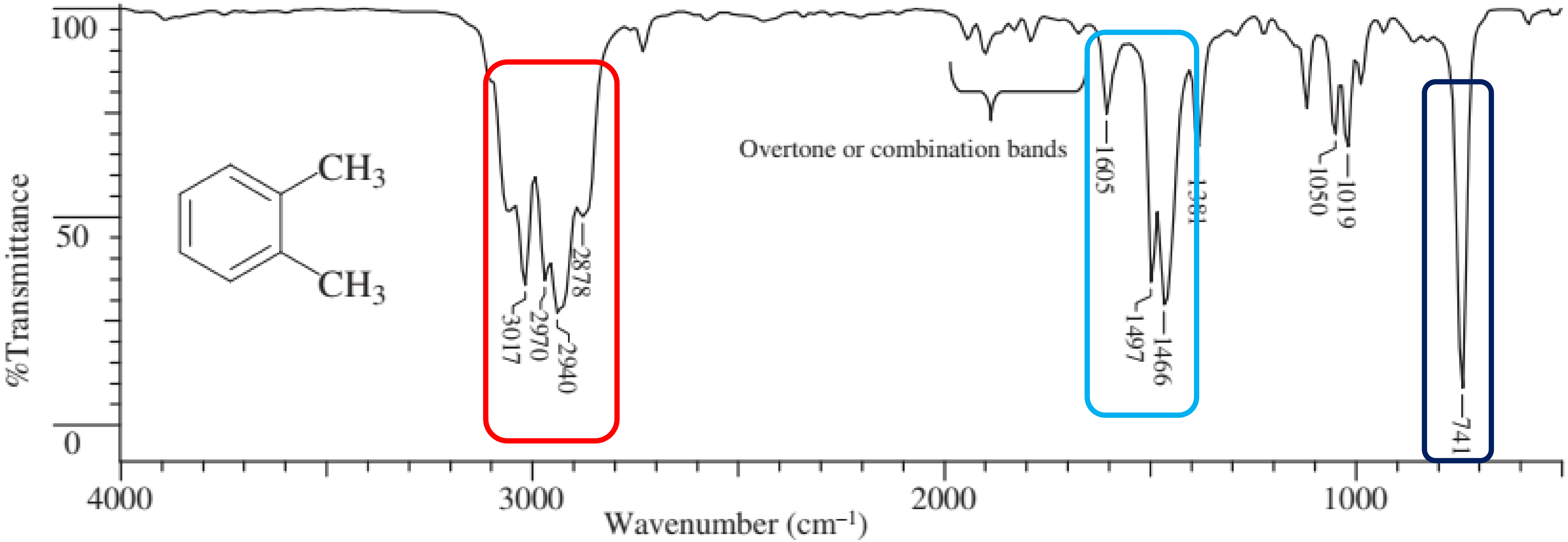
- **Aromatic Hydrocarbons**
- The most prominent and most informative bands in the spectra of aromatic compounds occur in the **low-frequency range** from **900 cm^{-1} to 675 cm^{-1}**.
- Skeletal vibrations, involving **carbon–carbon stretching** within the ring (aromatic C=C), absorb in the **1600 cm^{-1} to 1585 cm^{-1}** and **1500 cm^{-1} to 1400 cm^{-1}** regions.
- **Aromatic C—H** stretching bands occur between **3100 cm^{-1} and 3000 cm^{-1}**.
- Weak combination and overtone bands appear in the **2000 cm^{-1}** to **1650 cm^{-1}** region.
- ***Out-of-Plane C—H Bending Vibrations.*** The in-phase, out-of-plane bending. The bands are frequently intense and appear at **900 cm^{-1} to 675 cm^{-1}**.

IR for Functional Groups

- 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



Note/ The aim of this slide is to show students that different phenyl substitution leads to different IR absorption at area 900-675 cm^{-1}


100
50
0
%Transmittance
CH3
CH3
Overtone or combination bands
3017
2970
2940
2878
1605
1497
1466
1381
1050
1019
741
4000
3000
2000
1000
Wavenumber (cm⁻¹)

Important Rules

Stronger bonds vibrate at a higher frequency than weaker bonds

$HC{\equiv}CH$ — 2150 cm-1

$H_2C{=}CH_2$ — 1650 cm-1

$H_3C{-}CH_3$ — 1200 cm-1

Bending modes occur at lower frequencies than stretching

stretch

$C{-}H$

3000 cm-1

bend

$C{-}H$

1400 cm-1

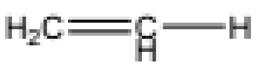
Hybridization changes the force constant (values are for the C-H stretch)

sp

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

3300 cm-1

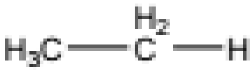
sp^2



$H_2C{=}\underset{H}{C}{-}H$

3100 cm-1

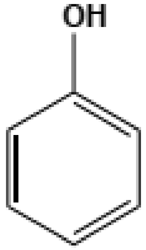
sp^3



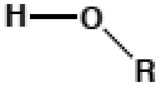
$H_3C{-}\overset{H_2}{C}{-}H$

2900 cm-1

IR for Functional Groups

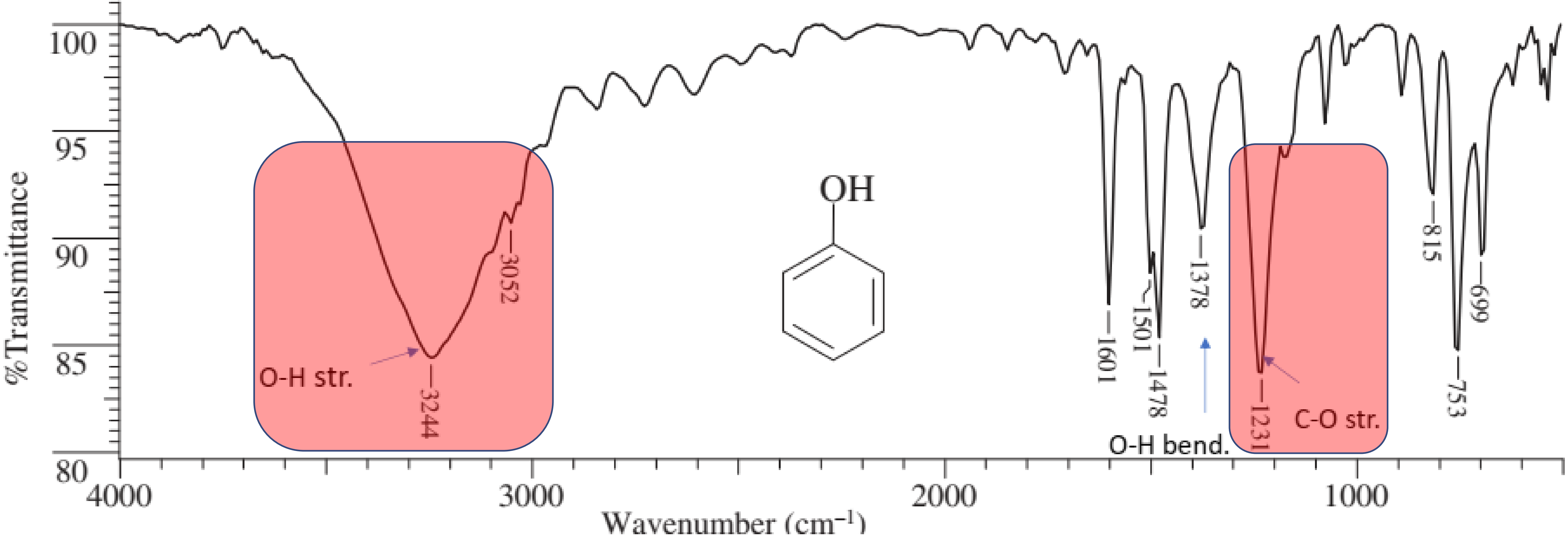


Phenol

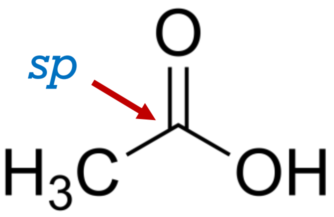


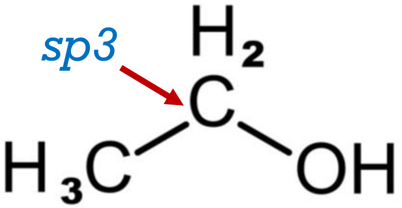
Alcohol

- **Alcohols and Phenols.**
- The characteristic bands observed in the spectra of alcohols and phenols result from **O—H** stretching and **C—O stretching**. These vibrations are **sensitive to hydrogen bonding**.
- ***O—H Stretching Vibrations***. The non-hydrogen- bonded or **free hydroxyl group** of alcohols and phenols absorbs strongly in the **3700-3584 cm^{-1}** region.
- Intermolecular hydrogen bonding increases as the concentration of the solution increases, and additional bands start to appear at lower wavenumbers, **3550-3200 cm^{-1}**, at the expense of the free hydroxyl band.
- ***C—O Stretching Vibrations***. The C—O stretching vibrations in alcohols and phenols produce a strong band in the **1260–1000 cm^{-1}** region of the spectrum.
- ***O—H Bending Vibrations.*** The O—H in-plane bending vibration occurs in the general region of **1420-1330 cm^{-1}**.

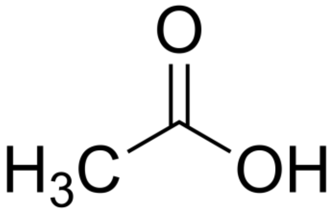

100
95
90
85
80
%Transmittance
4000
3000
2000
1000
Wavenumber (cm⁻¹)
3244
3052
O-H str.
OH
1601
1501
1478
1378
O-H bend.
1231
C-O str.
815
753
699

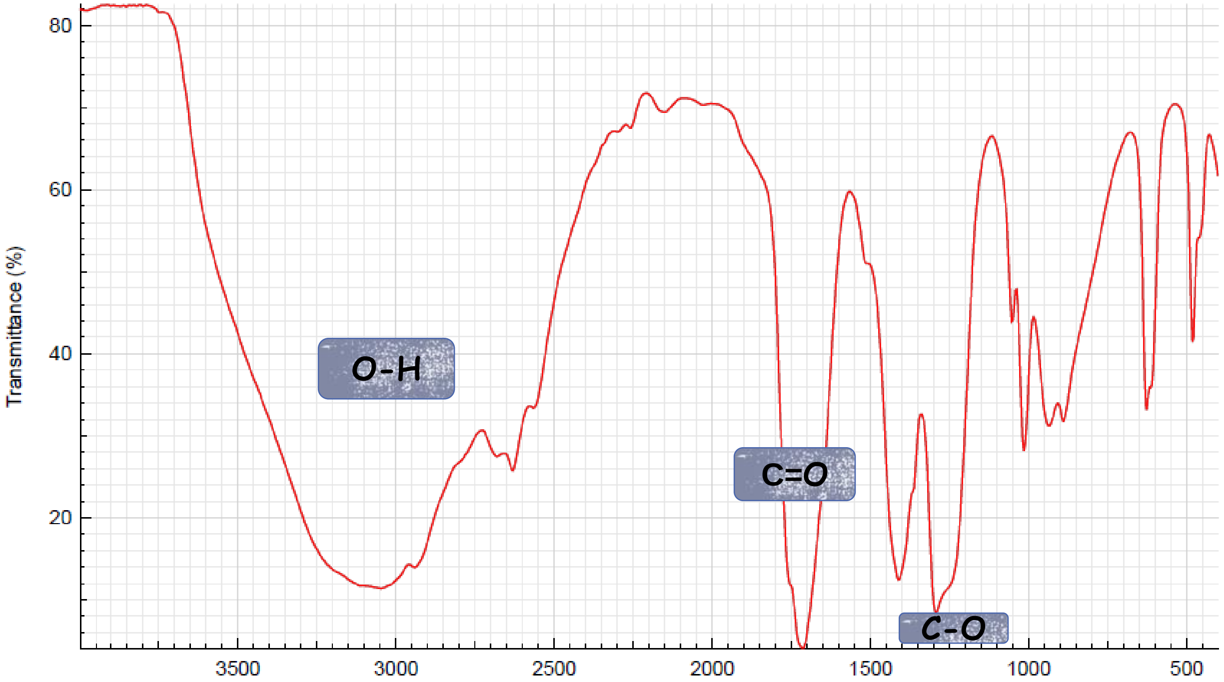
IR SPECTRUM OF CARBOXYLIC ACIDS AND ALCOHOLS

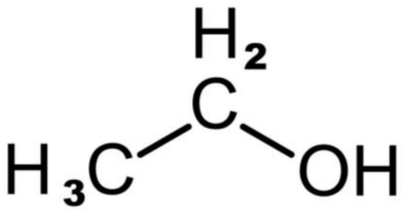


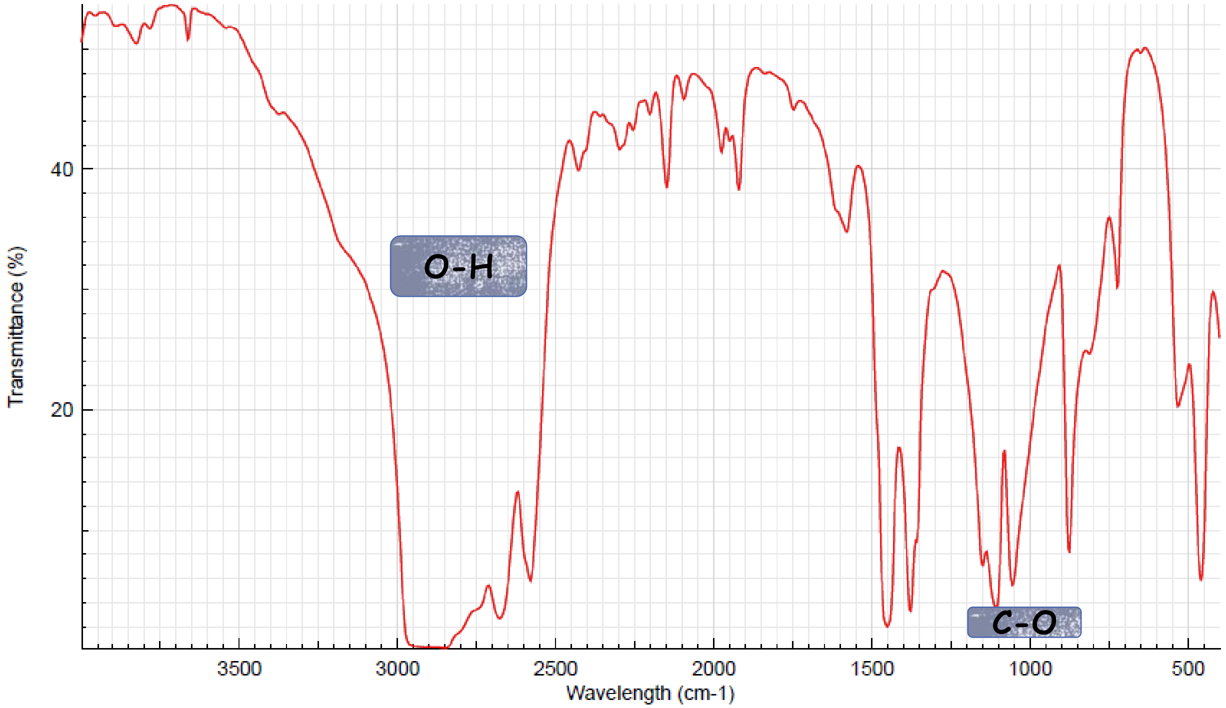


Carboxylic acid		Alcohol
(2500-3300 cm^{-1})	O-H	(3200-3500 cm^{-1})
(1700 cm^{-1})	C=O	✗
(1200-1300 cm^{-1})	C-O	(1000-1150 cm^{-1})


O
H3C
OH

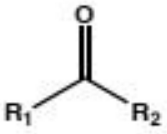

80
60
40
20
Transmittance (%)
O-H
C=O
C-O
3500
3000
2500
2000
1500
1000
500


H2
C
H3C
OH

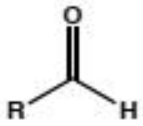

40
20
Transmittance (%)
O-H
C-O
3500
3000
2500
2000
1500
1000
500
Wavelength (cm-1)

IR for Functional Groups

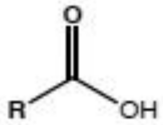
- **Carbonyl Group.**



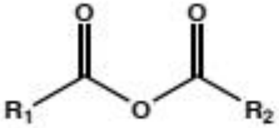
Ketones



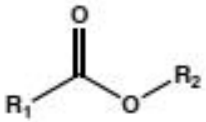
Aldehydes



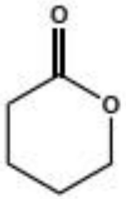
Carboxylic Acids



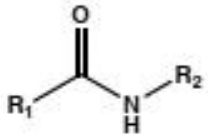
Anhydrides



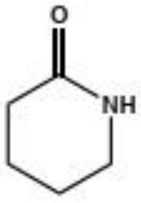
Esters



Lactones



Amides

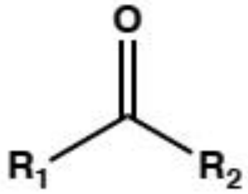


Lactames

- ***C=O Stretching Vibrations.*** Ketones, aldehydes, carboxylic acids, carboxylic esters, lactones, acid halides, anhydrides, amides, and lactams absorption band in the region of **1870-1540 cm^{-1}**.
- Its relatively **constant position**, **high intensity**, and **relative freedom from interfering bands** make this one of the **easiest bands to recognize in IR spectra**.
- Within its given range, the position of the C=O stretching band is determined by the following factors:

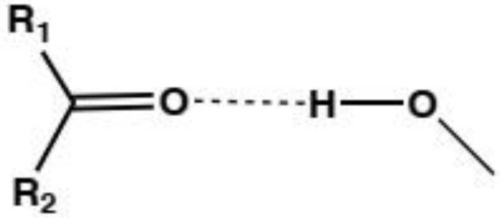
  (i) **physical state**,
- (ii) **electronic and mass effects of neighboring substituents**,
- (iii) **conjugation**,
- (iv) **hydrogen bonding** (intermolecular and intramolecular),
- (v) **ring strain.**

IR for Functional Groups

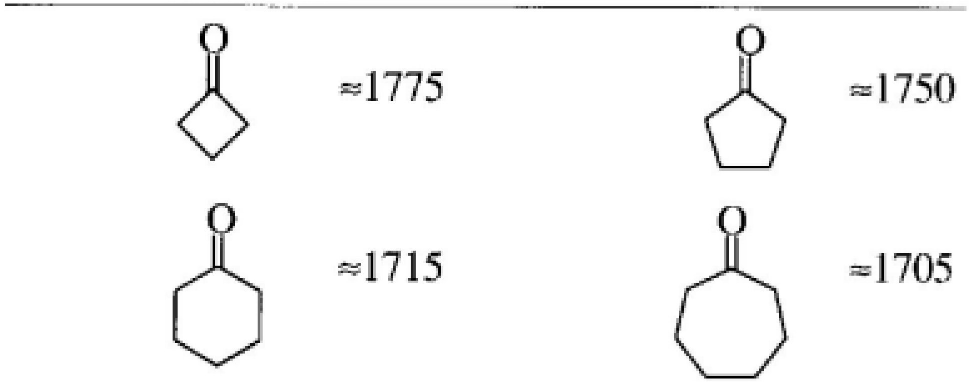


Ketones

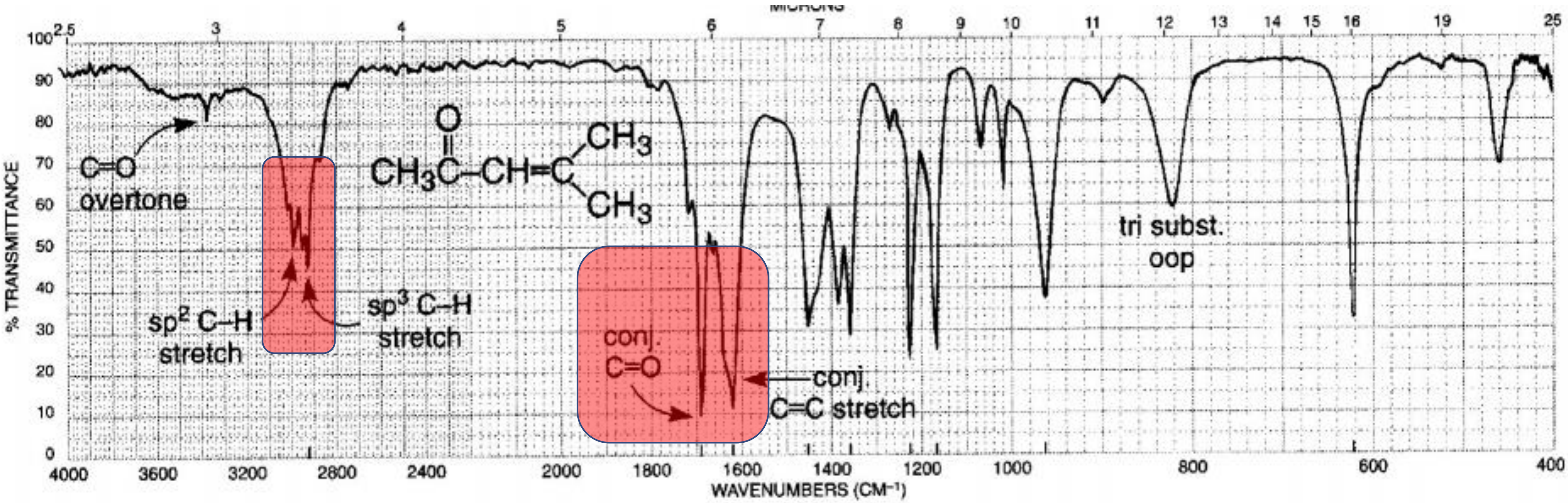
- **Ketones**
- The saturated aliphatic ketone, **1715 cm^{-1}**,
- Conjugation with a **C=C** bond reduces the double-bond character of the **C=O bond**, causing absorption at **lower wavenumbers** of **1685-1666 cm^{-1}** region.
- Intermolecular hydrogen bonding between a ketone and a hydroxylic solvent such as methanol causes a slight decrease in the wavenumber of the carbonyl group. For example, a neat sample of ethyl methyl ketone absorbs at **1715 cm^{-1}**, whereas a 10% solution of the ketone in methanol absorbs at **1706 cm^{-1}**.



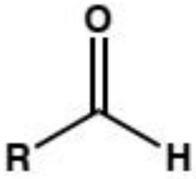
- In acyclic ketones and in ketones with a six-membered ring, the angle is near **120**°.
- In **strained rings** in which the angle is **<120**°, interaction with C—C bond stretching **increases the energy required to produce C=O stretching and thus increases the stretching frequency.**



- C—(C=O)—C bending appears at **1300-1100 cm^{-1}**

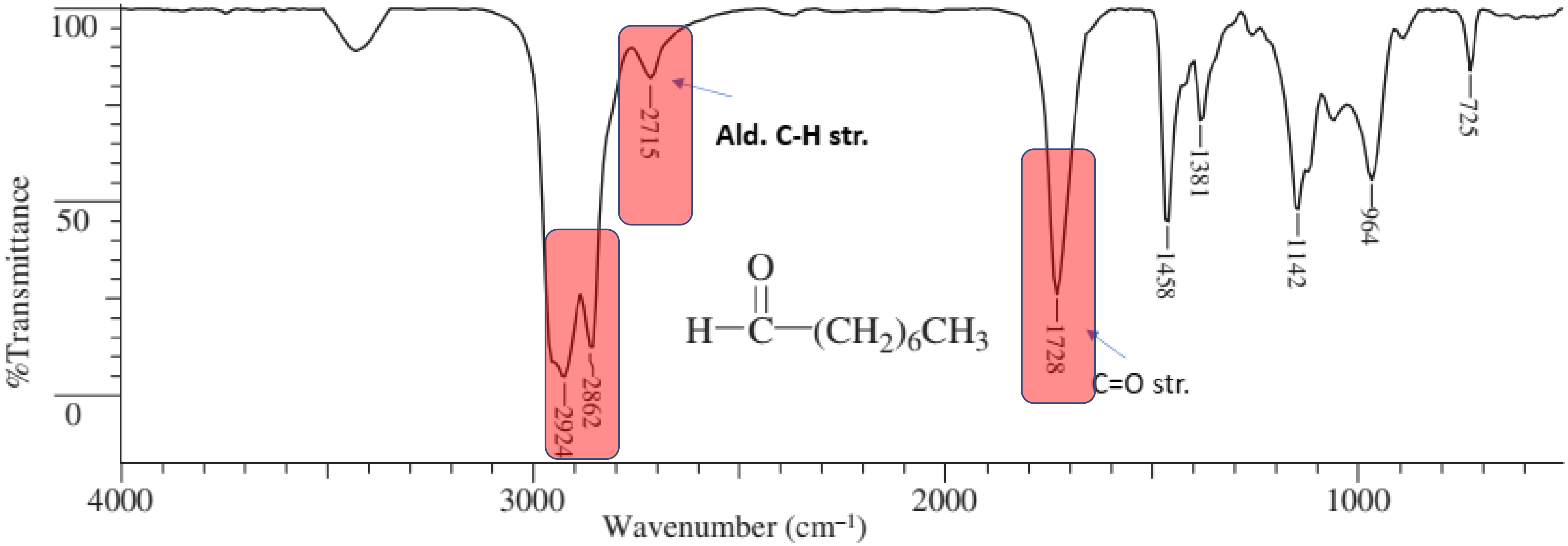

MICRONS
2.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
19
25
100
90
80
70
60
50
40
30
20
10
0
% TRANSMITTANCE
C=O
overtone
sp^2 C–H
stretch
sp^3 C–H
stretch
$CH_3C(=O)–CH=C(CH_3)_2$
conj.
C=O
conj.
C=C stretch
tri subst.
oop
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS (CM^{-1})

IR for Functional Groups



Aldehydes

- **Aldehyde**
- ***C=O Stretching Vibrations.*** The carbonyl groups of aldehydes absorb at **slightly higher frequencies than those of the corresponding methyl ketones**.
- Aliphatic aldehydes absorb near **1740-1720 cm^{-1}**.
- ***C—H Stretching Vibrations.*** The majority of aldehydes show aldehydic C—H stretching absorption in the **2830-2700 cm^{-1}** region.



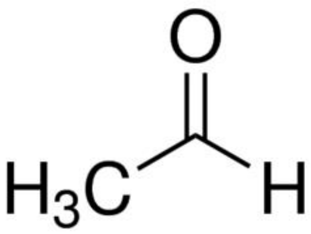
Ald. C-H str.

C=O str.

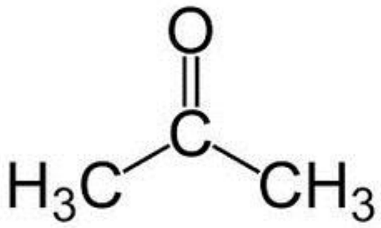
$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_6CH_3}$$

IR SPECTRUM OF ALDEHYDES AND KETONES

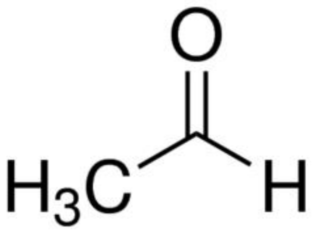
Aldehyde

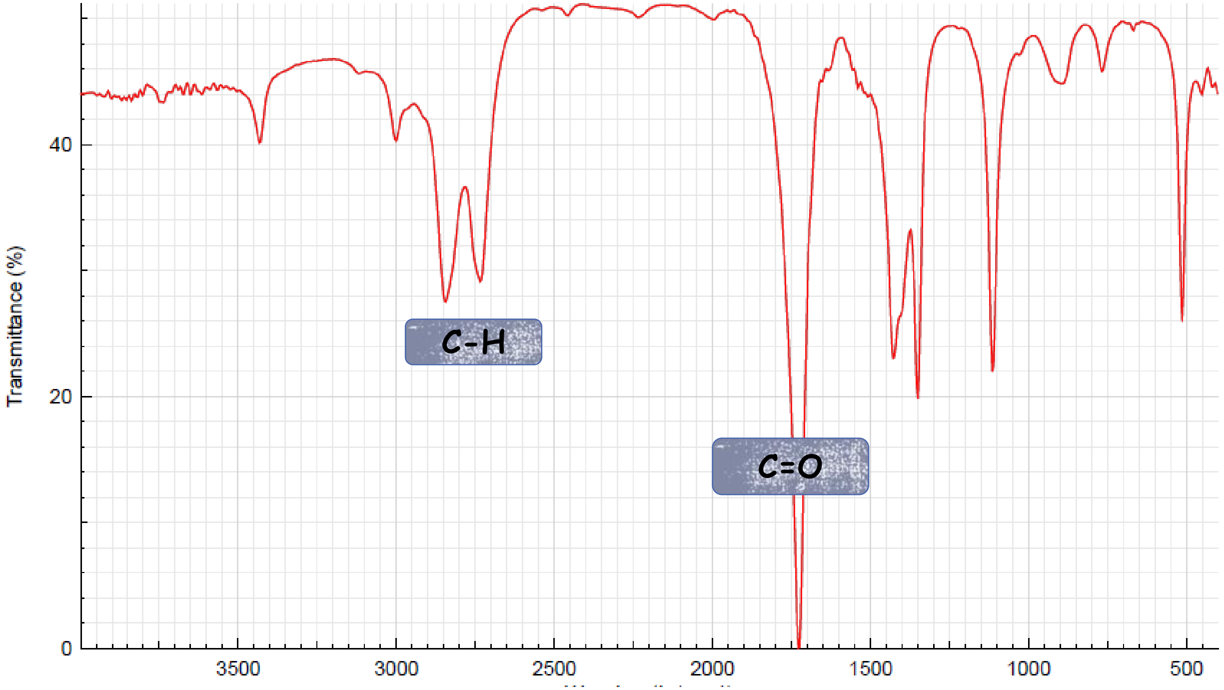


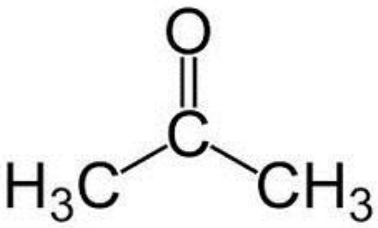
Ketone

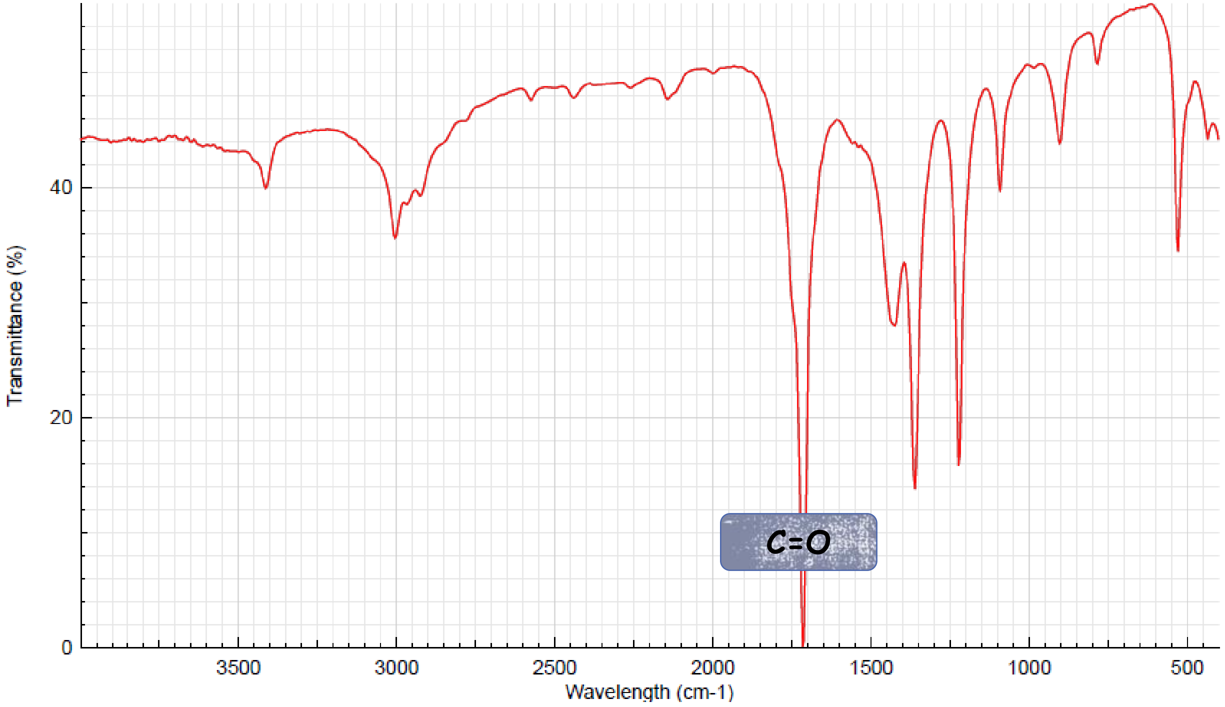


(more than 1700 cm^{-1})	C=O	(1715 cm^{-1})
(2830 and 2700 cm^{-1})	C-H	✗


O
H3C
H


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


O
C
H3C
CH3


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