Infrared Spectroscopy

تشخيص المركبات بالاشعه تحت الحمراء FT-IR

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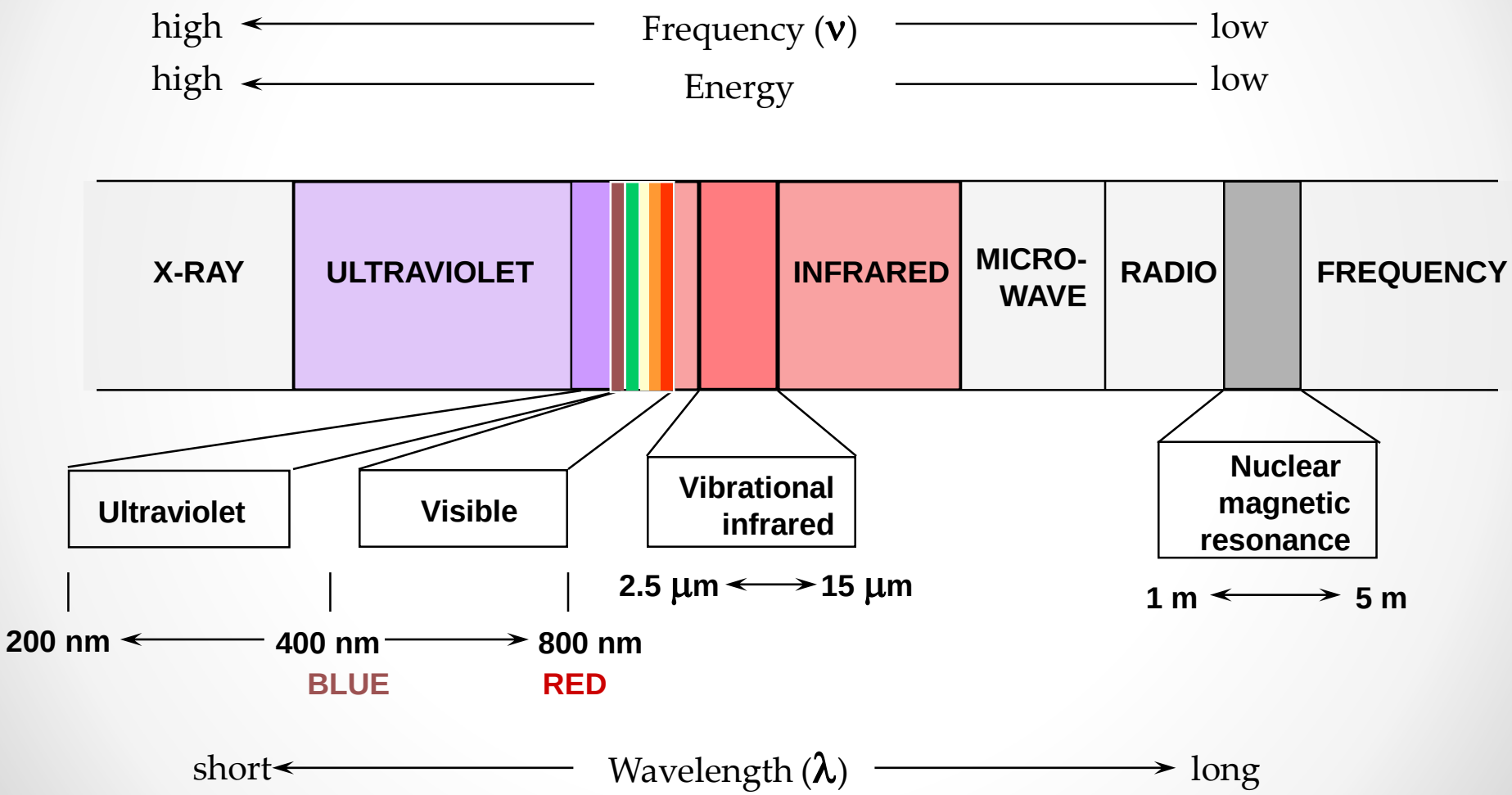
The Electromagnetic Spectrum



- Infrared spectroscopy (IR) measures the bond vibration frequencies in a molecule and is used to determine the functional group.

- The IR region is divided into three regions:

  1. The near IR (12500-4000 cm^{-1}) (overtons region)
  2. The mid IR (4000-200 cm^{-1})
  3. The far IR (200-10 cm^{-1})

- The mid IR region is of greatest practical use to the organic compounds.

The unit used on an IR spectrum is

Wavenumbers $\bar{\nu}$

$$\bar{\nu} = \text{wavenumbers } (cm^{-1}) = \frac{1}{\lambda}$$

wavelength (cm)

ν = frequency = $\bar{\nu}\, C$

C = speed of light
= 3×10^{10} cm/sec

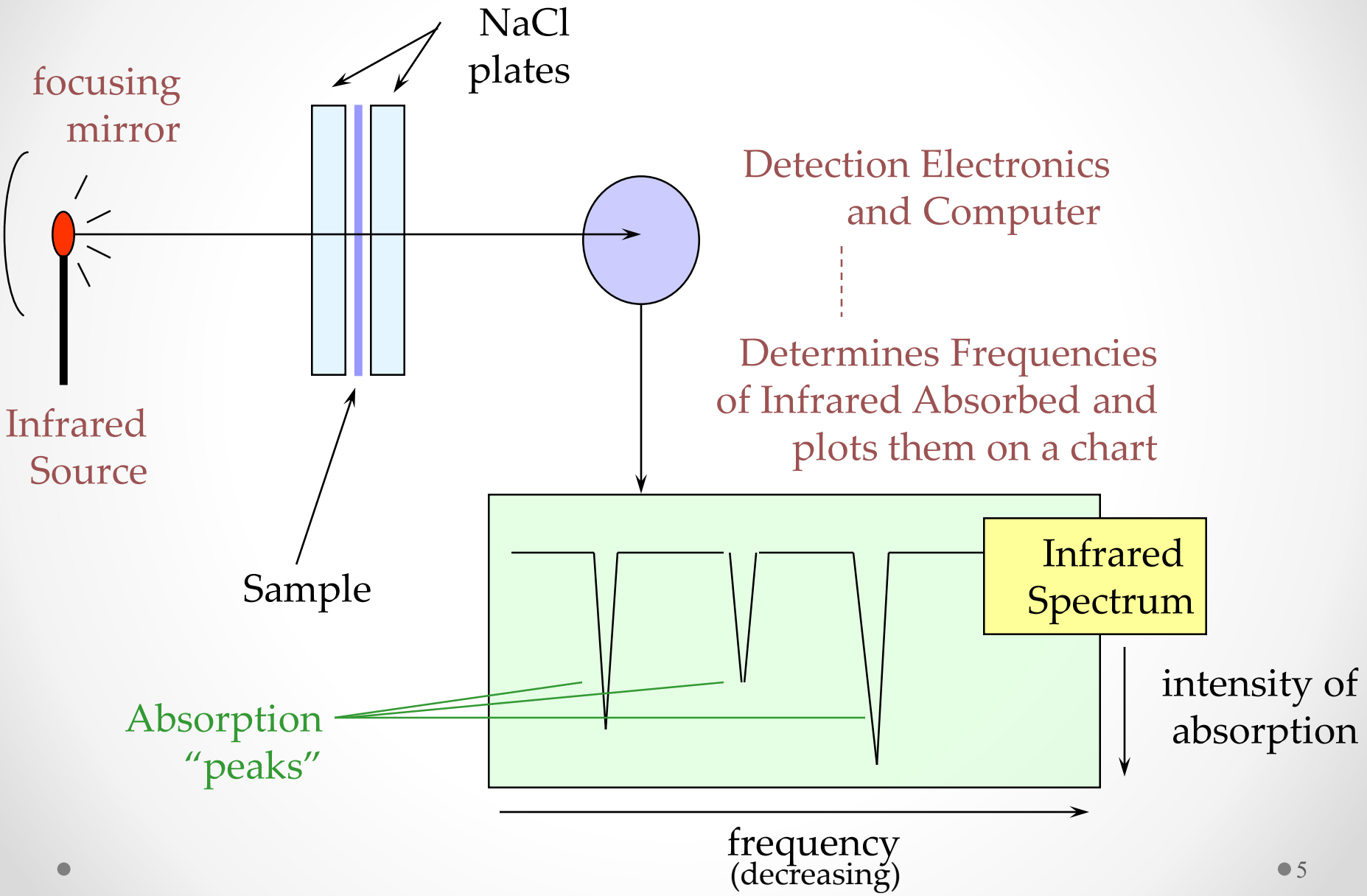
or

$$\nu = \left(\frac{1}{\lambda}\right) C = \frac{C}{\lambda}$$

$$\frac{\text{cm/sec}}{\text{cm}} = \frac{1}{\text{sec}}$$

wavenumbers are directly proportional to frequency

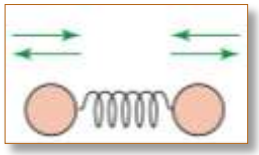
Simplified Infrared Spectrophotometer



Molecular Vibrations

- Molecules are made up of atoms linked by chemical bonds.

The movement of atoms and chemical bonds like spring and balls (vibration).

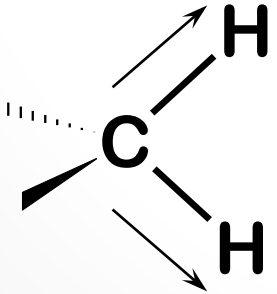


- There are two main vibrational modes :

1- Stretching - change in bond length (higher frequency)

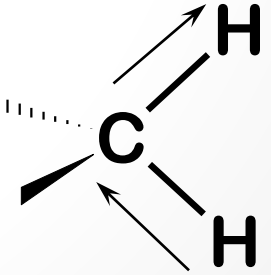
Stretching Types:

in-phase



Symmetric Stretch

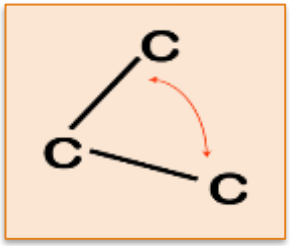
out-of-phase



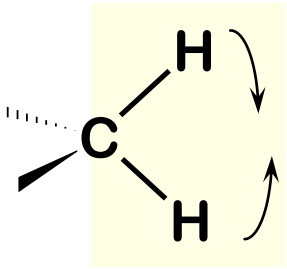
Asymmetric Stretch

2- Bending - change in bond angle (lower frequency)

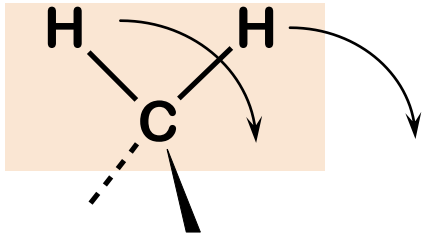
Bending Types:

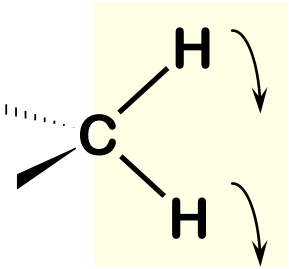


Scissoring

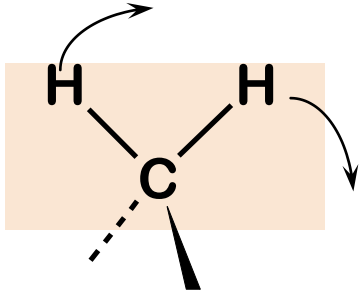


Wagging





Rocking



Twisting

in-plane

out-of-plane

3- Fingerprints

Dipole Moments

Only bonds which have significant dipole moments will absorb infrared radiation.

Factors that influence in determining the locations of the spectrum peaks various

1. Atomic Masses

Frequency decreases with increasing atomic mass.

C-H	>	C-C	>	C-O	>	C-Cl	>	C-Br
3000		1200		1100		750		650

2. Bond Strength

Frequency increases with increasing bond energy.

C≡C	>	C=C	>	C-C
2150		1650		1200

3. The coupling between bonds different groups.

C=O	O=C=O
1800 to 1650	2350

4. stereochemistry effects.

5. Solvents, Temperature and Sample state.

Samples

1. Solid :- KBr disk (1 mg solid sample + 100 mg KBr pressed into a disk)

- Mull (1 mg solid sample suspended in Nujol (heavy liquid hydrocarbon))

2. Liquid : Thin film of liquid between two NaCl plates solution in CCl_4 and put in special NaCl cells.

3. Gas IR spectrum is obtained directly by permitting the sample to expand into an evacuated special cells.

Solvents

1. Must be transparent in the region studied: no single solvent is transparent throughout the entire IR region.

2. Water and alcohols are seldom employed to avoid O-H band of water.

3. Must be chemically inert (does not react with substance or cell holder). CCl_4, CS_2, or $CHCl_3$; may be used but we should consider its IR spectrum.

Describing IR Absorptions

IR absorptions are described by their frequency and appearance.

- *Frequency* (ν) is given in wavenumbers (cm^{-1})
- *Appearance* is qualitative: intensity and shape
- conventional abbreviations:

vs	very strong
s	strong
m	medium
w	weak
br	broad
sh	sharp or shoulder

Index of Hydrogen Deficiency

The index is the sum of the number of ring, the number of double bonds and twice the number of triple bonds.

$$\text{Index} = \text{carbons} - \tfrac{1}{2}\,\text{hydrogens} - \tfrac{1}{2}\,\text{halogens} + \tfrac{1}{2}\,\text{nitrogens} + 1$$

Example:

$$C_6H_{14}$$

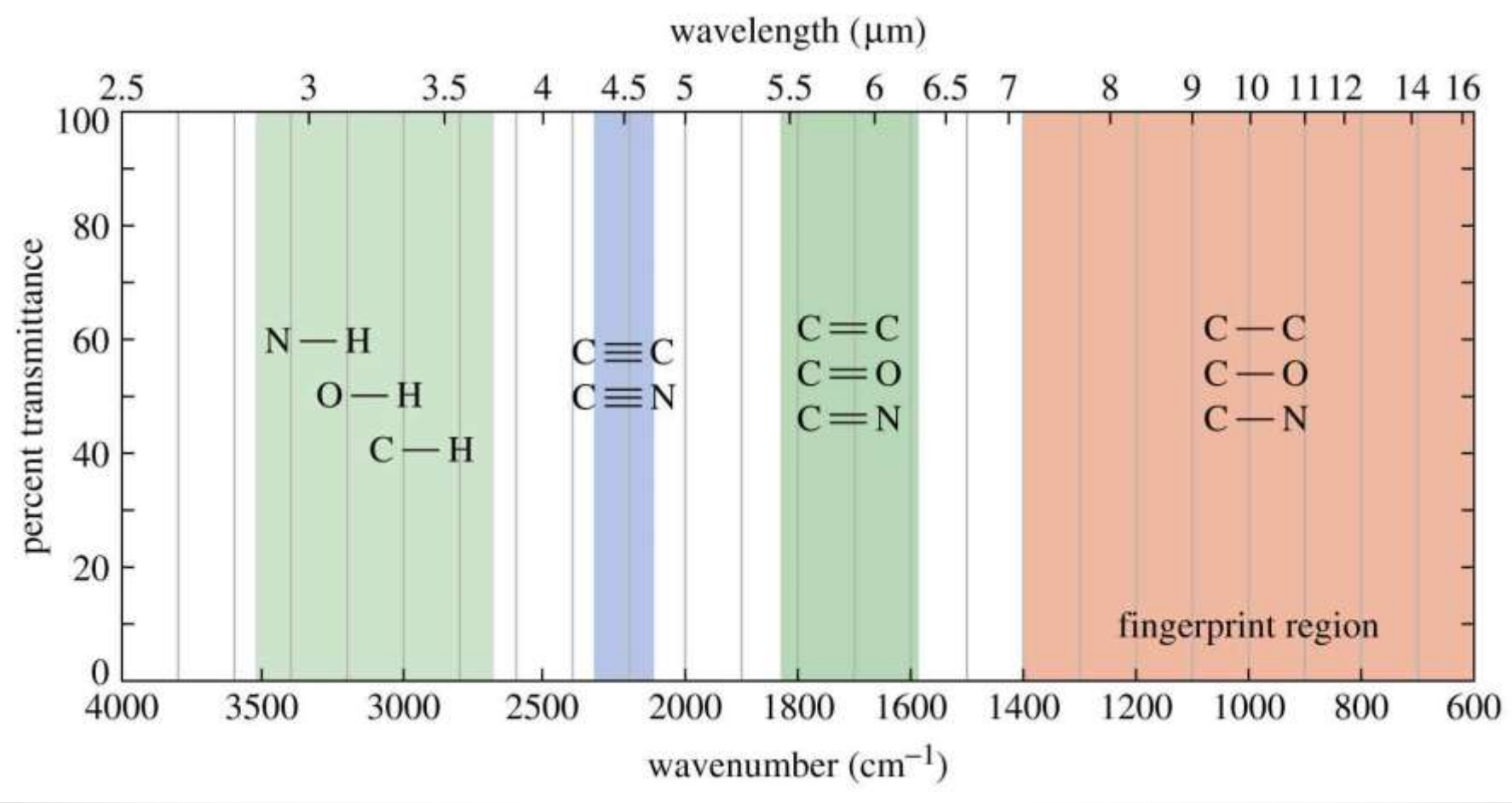
$$\begin{aligned}\text{Index} &= 6 - \tfrac{1}{2}\,(14) - \tfrac{1}{2}\,(0) + \tfrac{1}{2}\,(0) + 1\\ &= 6 - 7 + 0 + 1\\ &= 0\end{aligned}$$

IR Absorption Regions

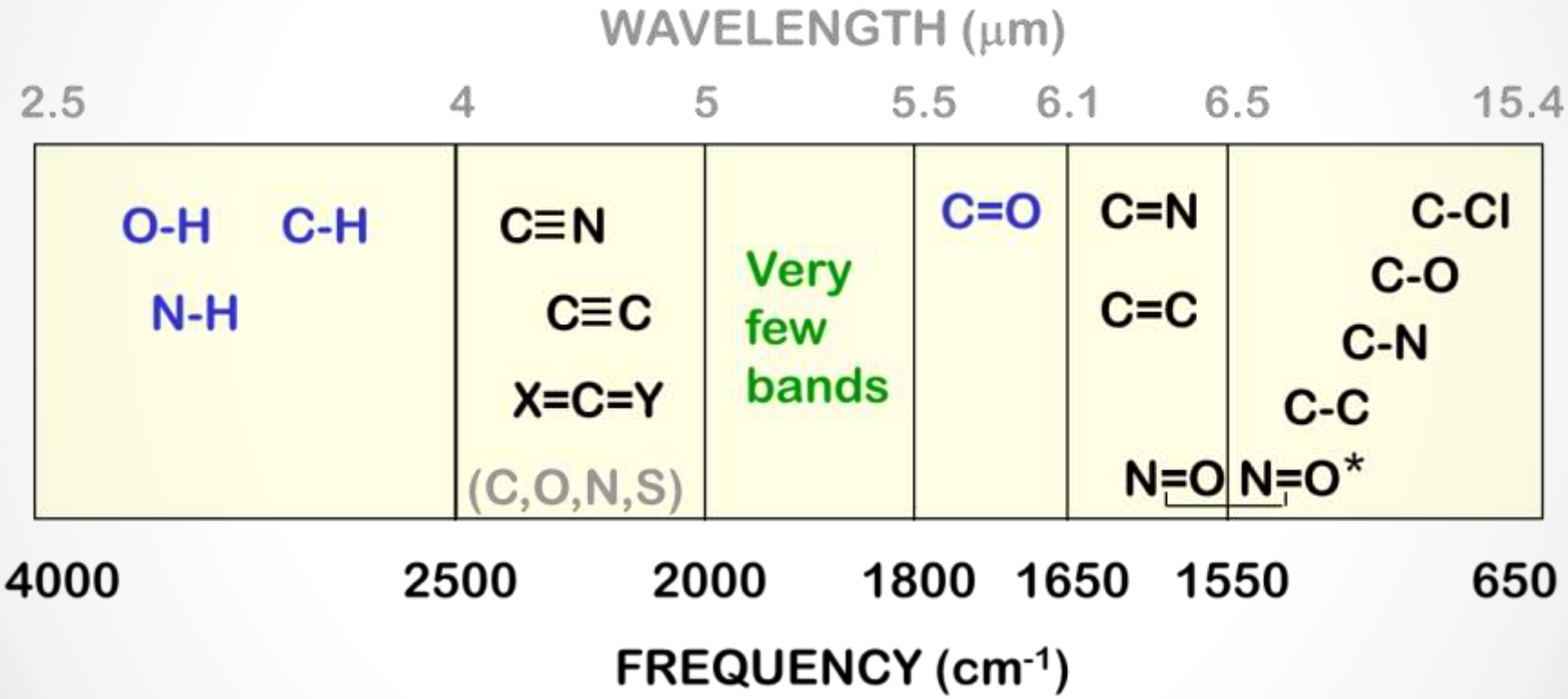
In general, the IR spectrum can be split into four regions for interpretation:

- 4000 – 2500 cm^{-1}: Absorption of single bonds formed by hydrogen and other elements e.g. O–H, N–H, C–H
- 2500 – 2000 cm^{-1}: Absorption of triple bonds e.g. C≡C, C≡N
- 2000 – 1500 cm^{-1}: Absorption of double bonds e.g. C=C, C=O
- 1500 – 400 cm^{-1}: This region often consists of many different, complicated bands, called the fingerprint region. It is rarely used for identification of particular functional groups.

Summary of IR Absorptions



Typical IR Absorption Regions



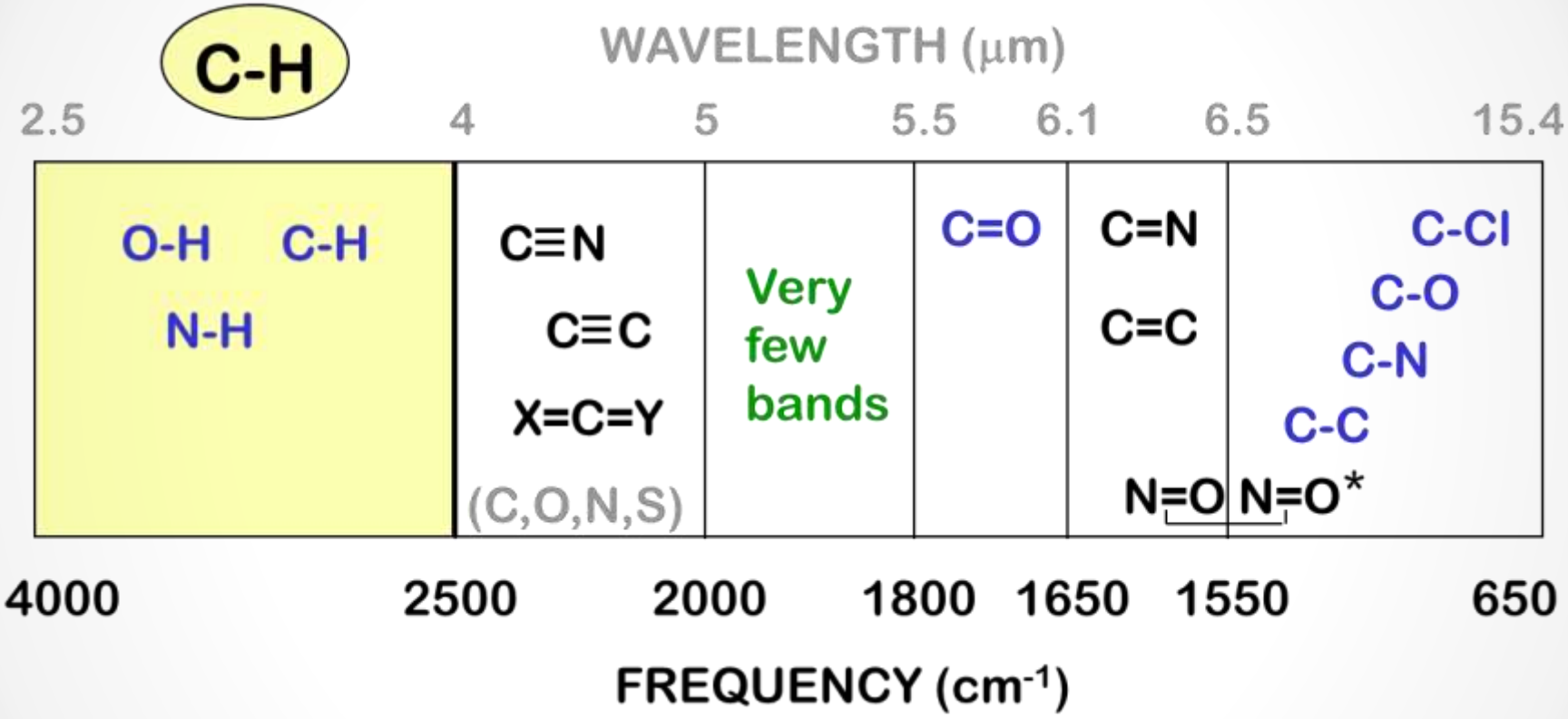
Base Values
(+/-10 cm^{-1})

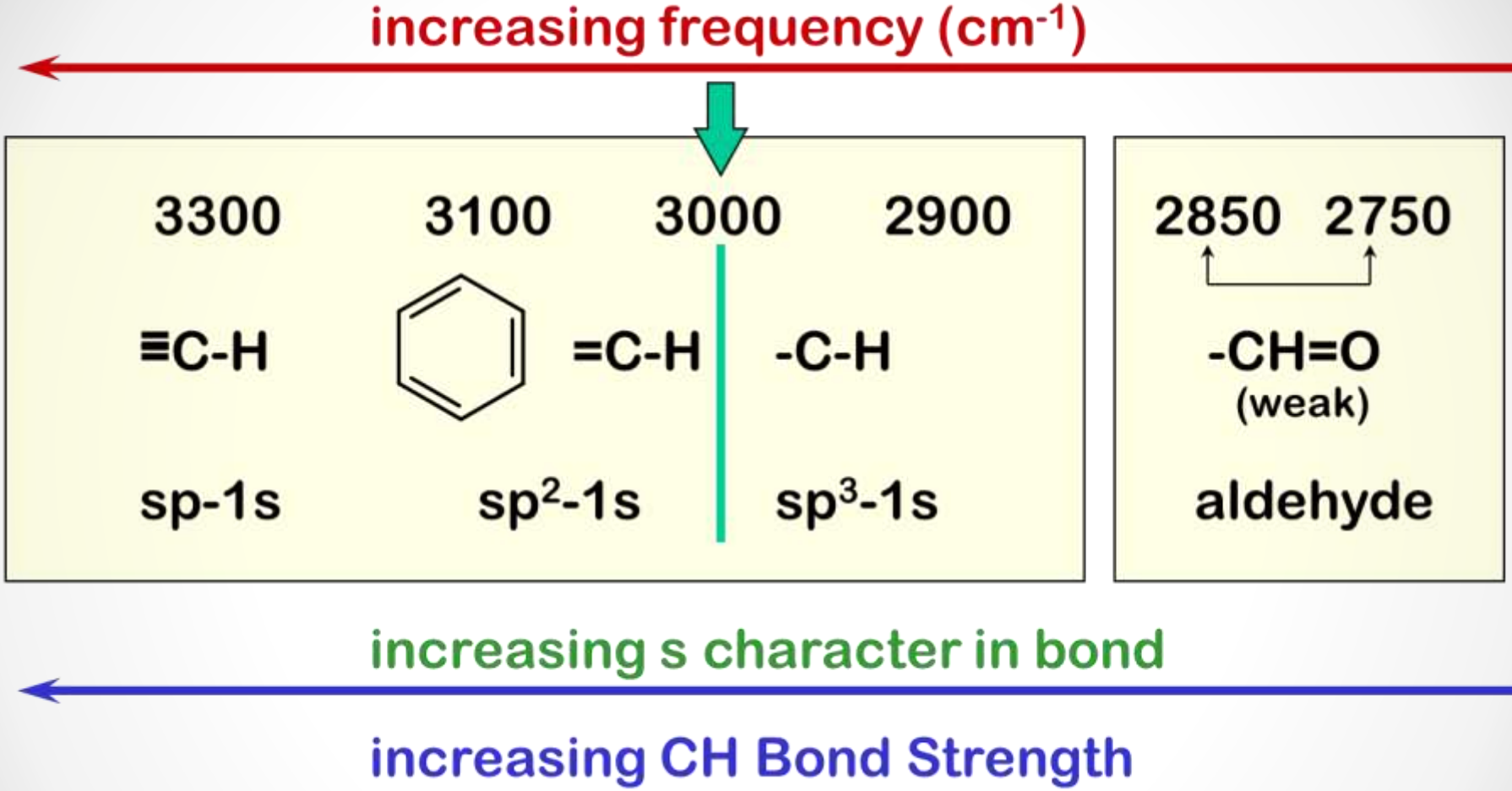
O-H	3600
N-H	3400
C-H	3000
C≡N	2250
C≡C	2150
C=O	1715
C=C	1650
C–O	~1100

large range

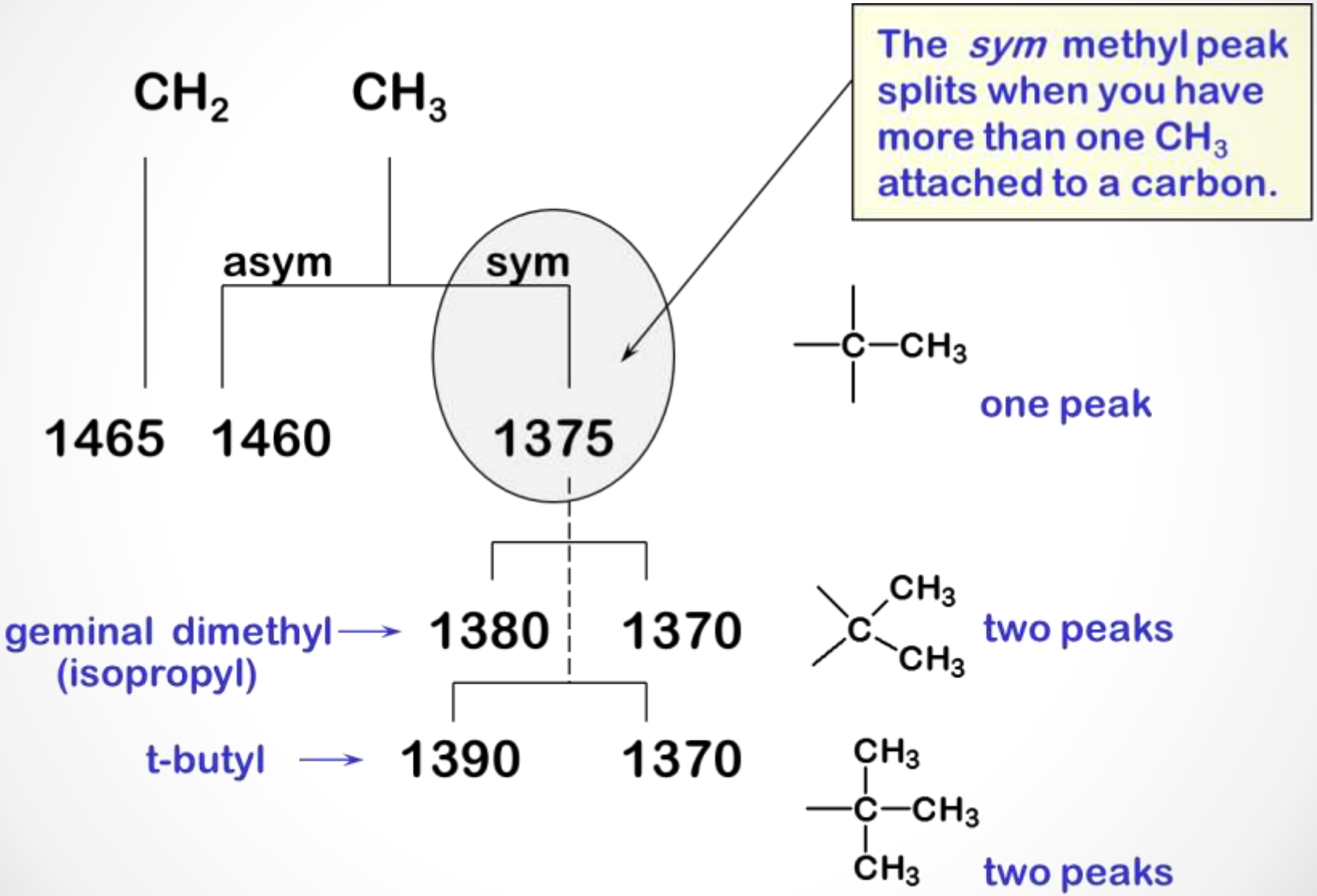
The C-H Stretching Region

Base Value = 3000 cm^{-1}



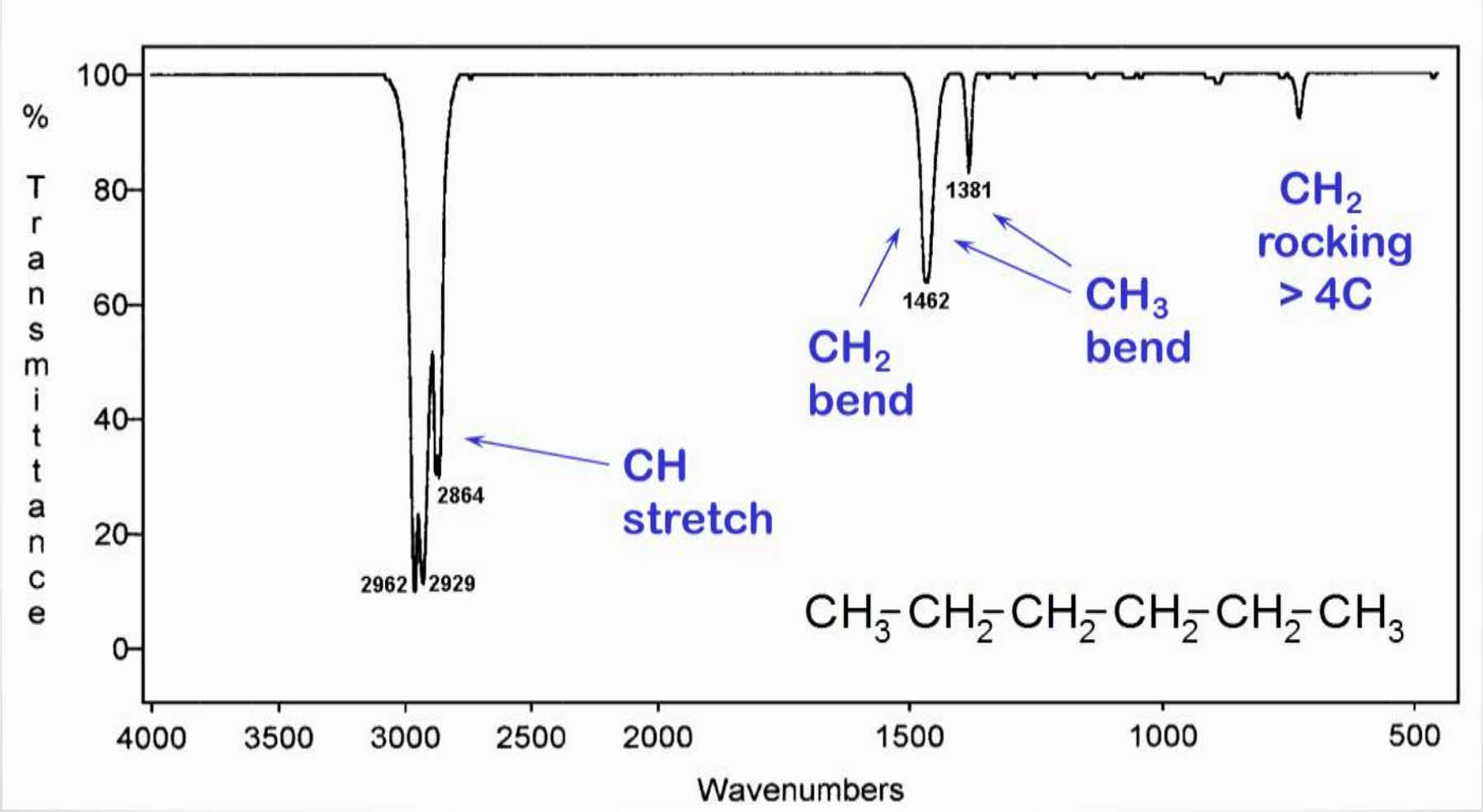

increasing frequency (cm-1)
3300
3100
3000
2900
2850
2750
≡C-H
=C-H
-C-H
-CH=O
(weak)
sp-1s
sp2-1s
sp3-1s
aldehyde
increasing s character in bond
increasing CH Bond Strength

The C-H Bending Region



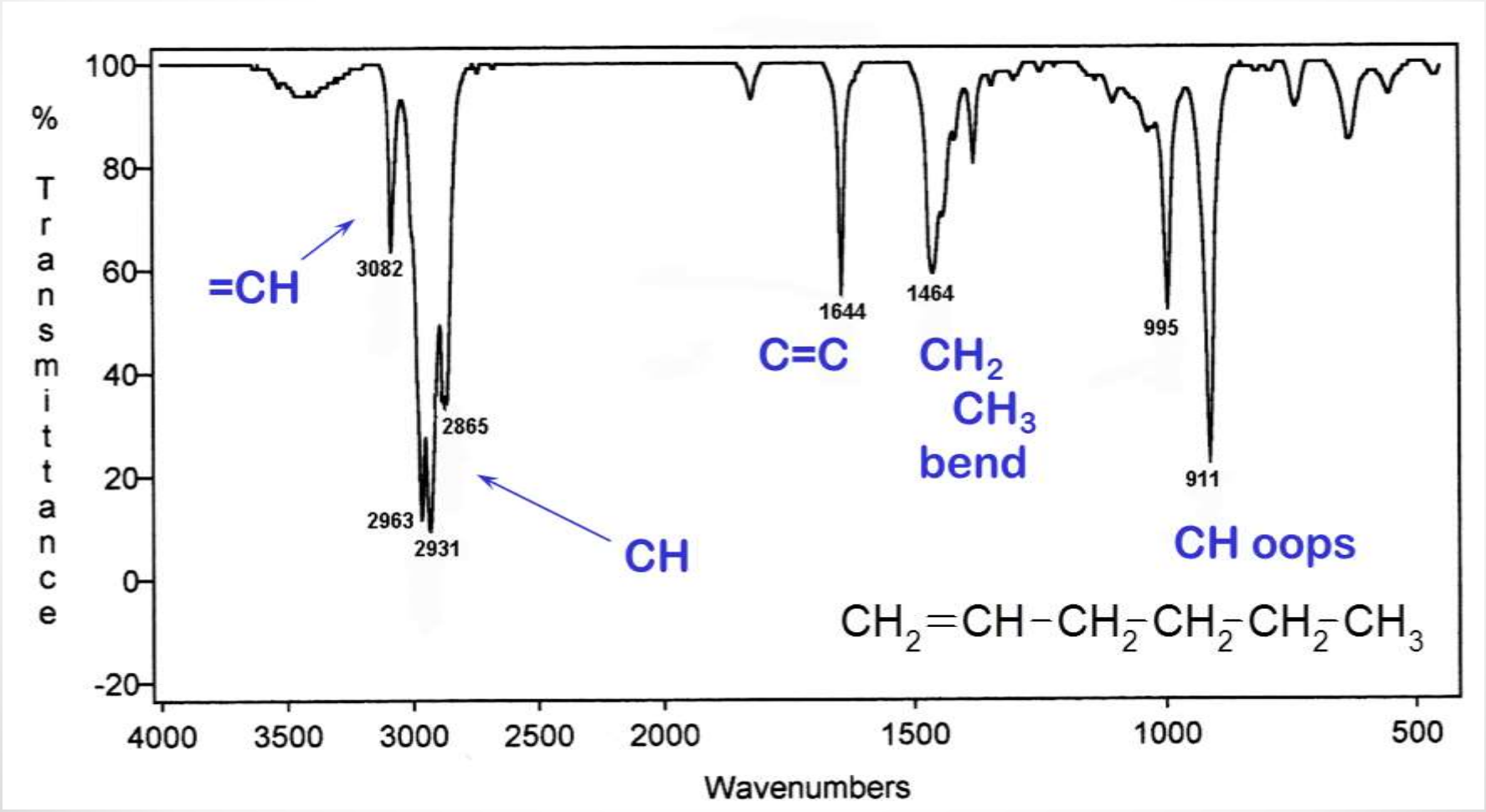
Alkane

Hexane



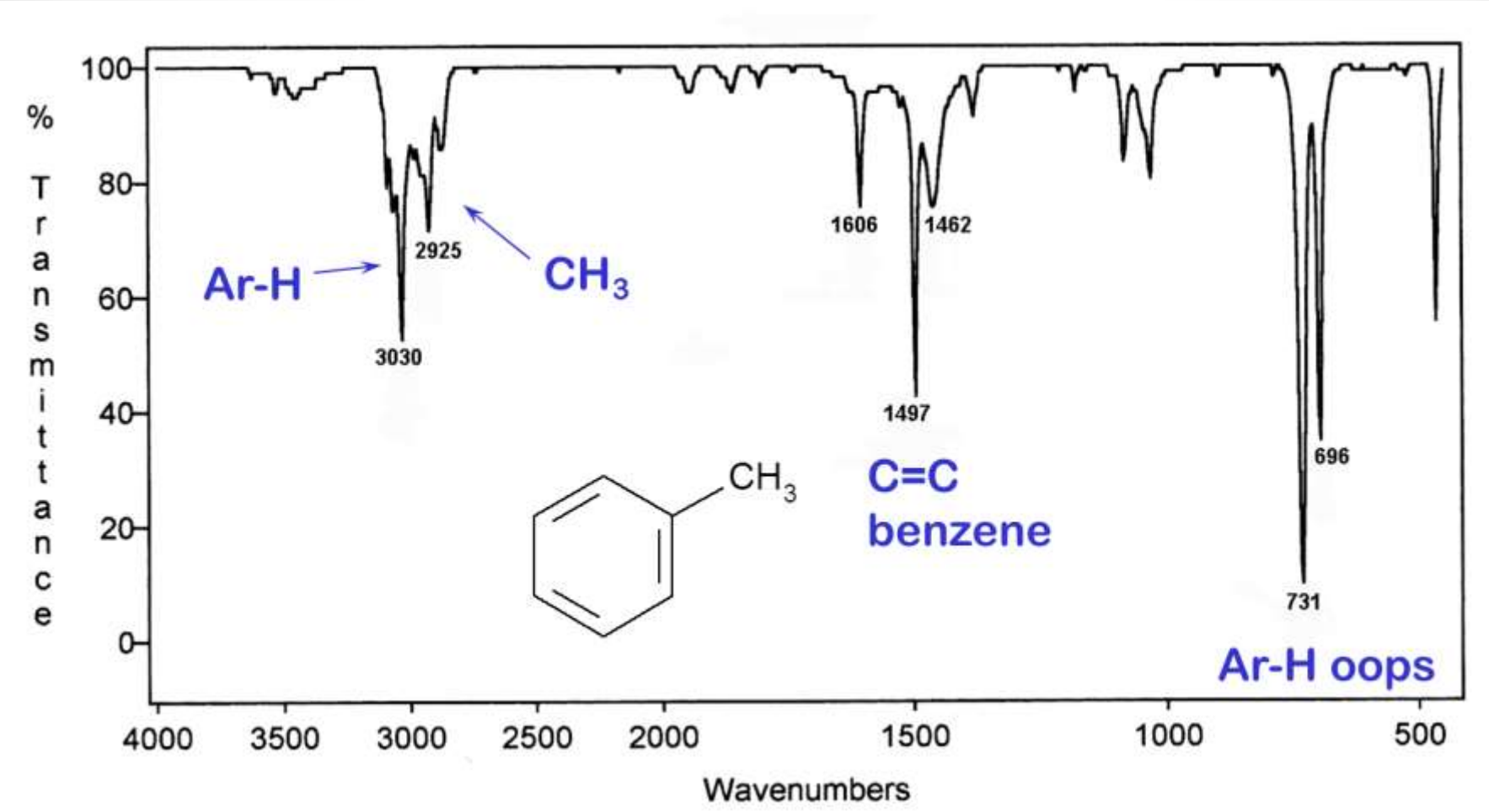
Alkene

1-Hexene



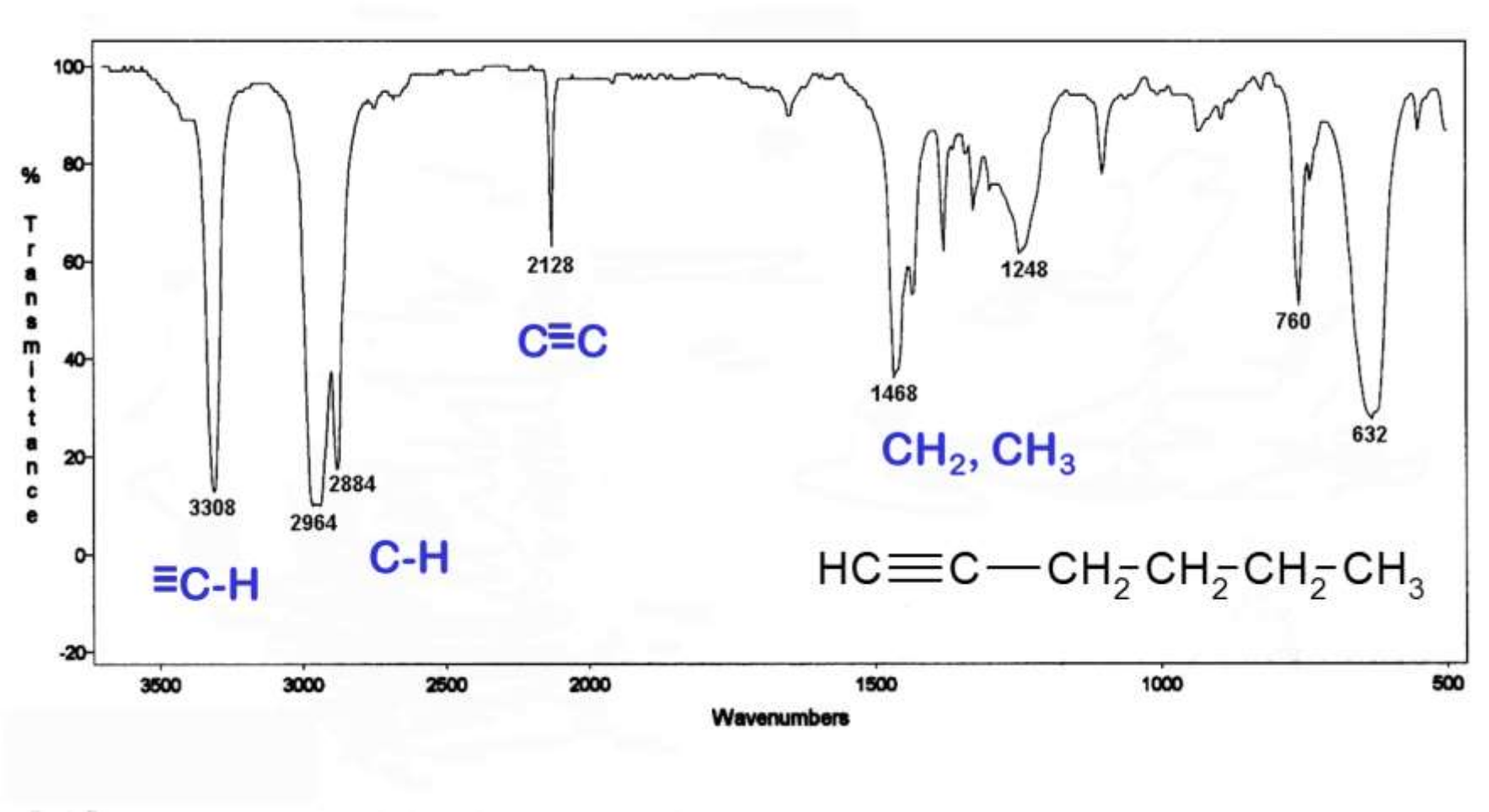
Aromatic

Toluene



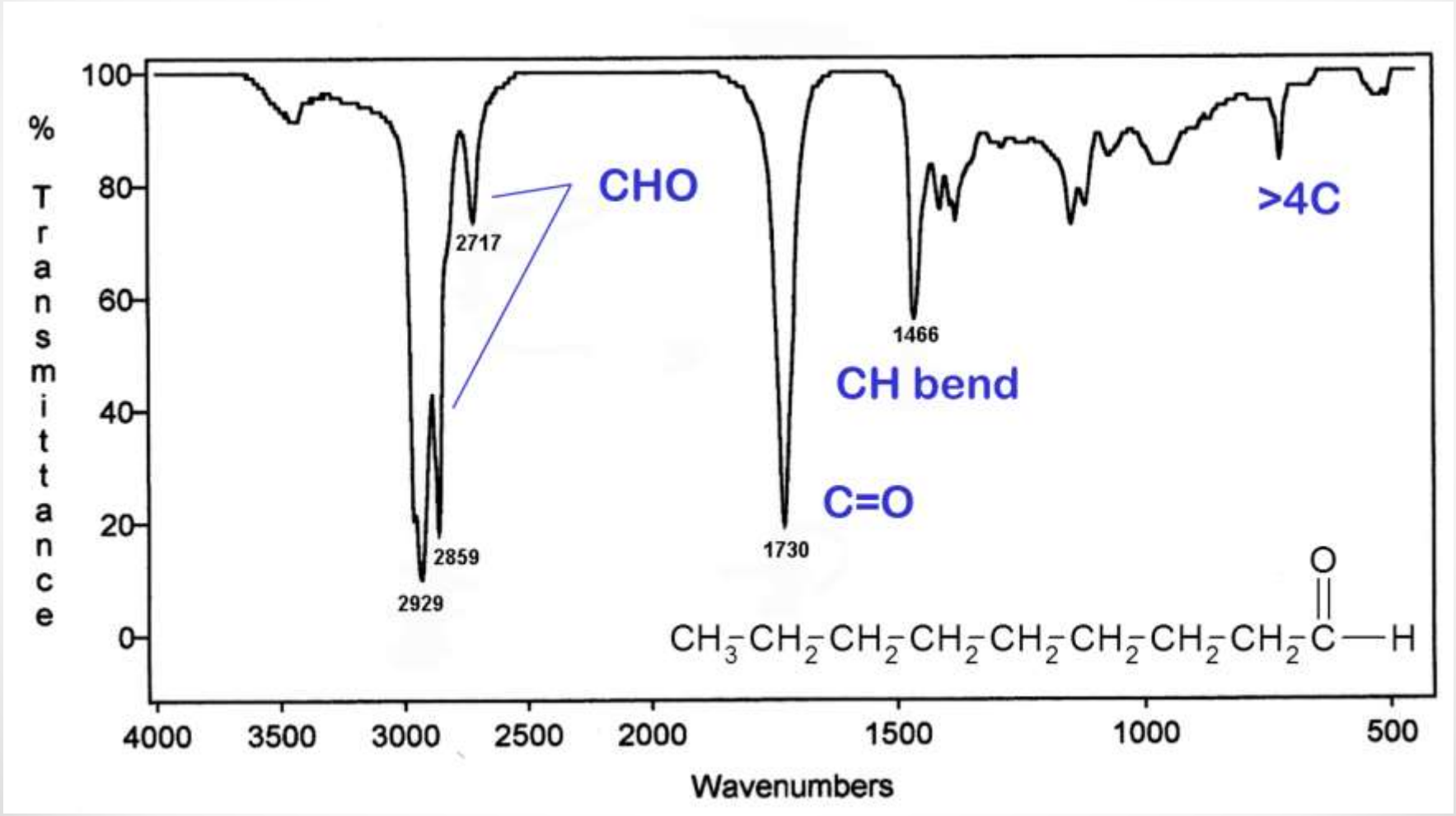
Alkyne

1-Hexyne

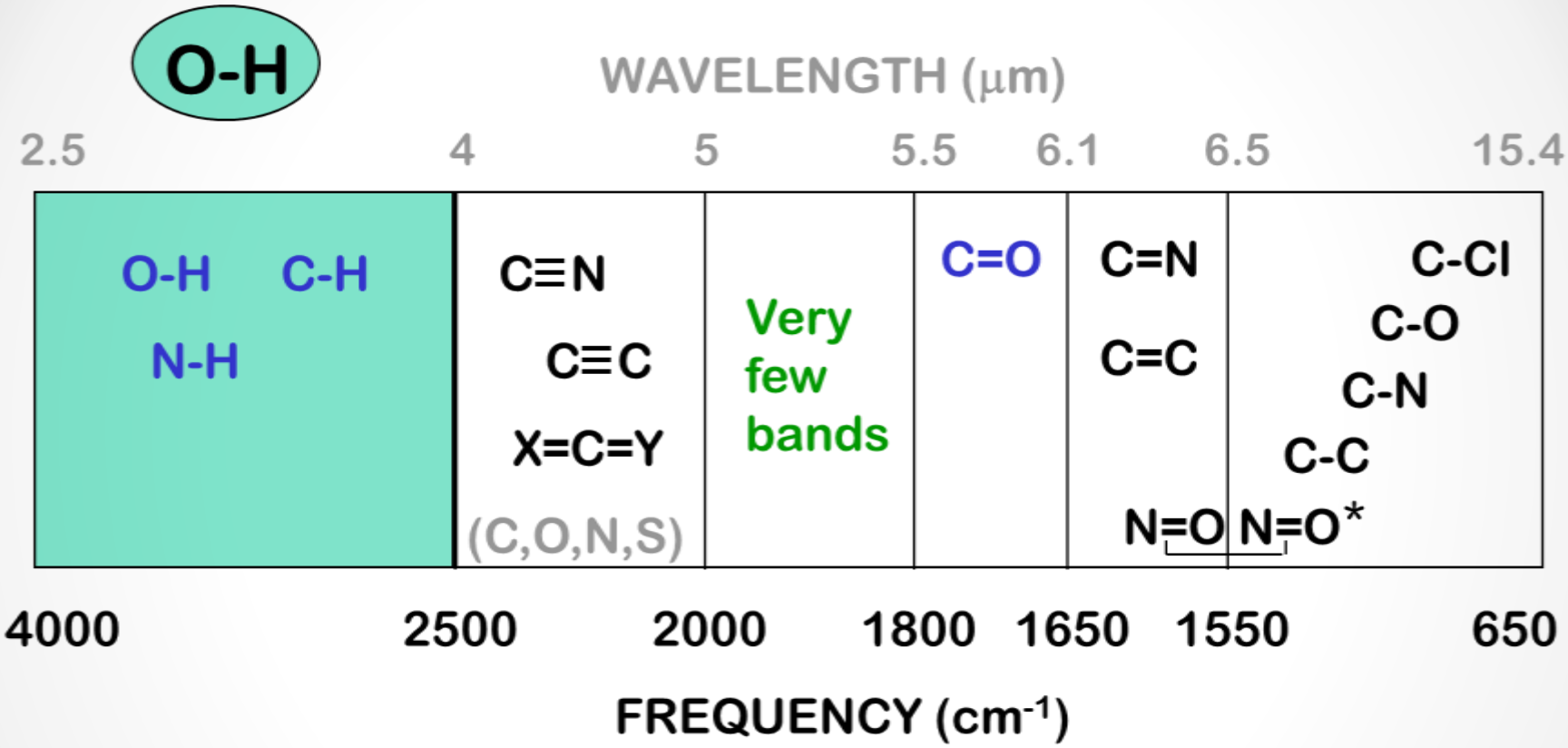


Aldehyde

Nonanal

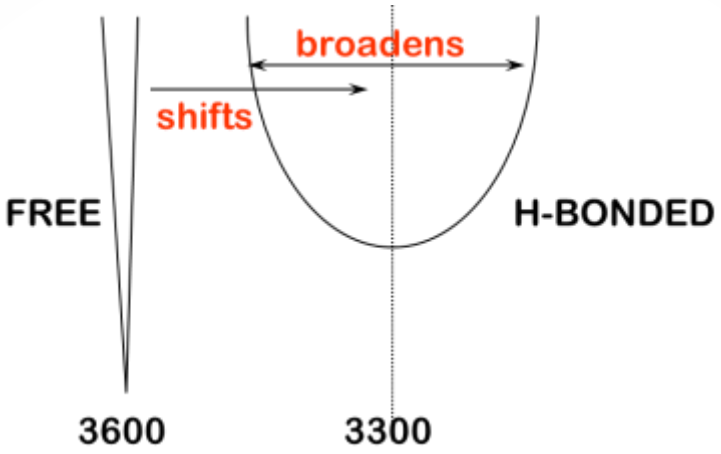


The O-H Stretching Region

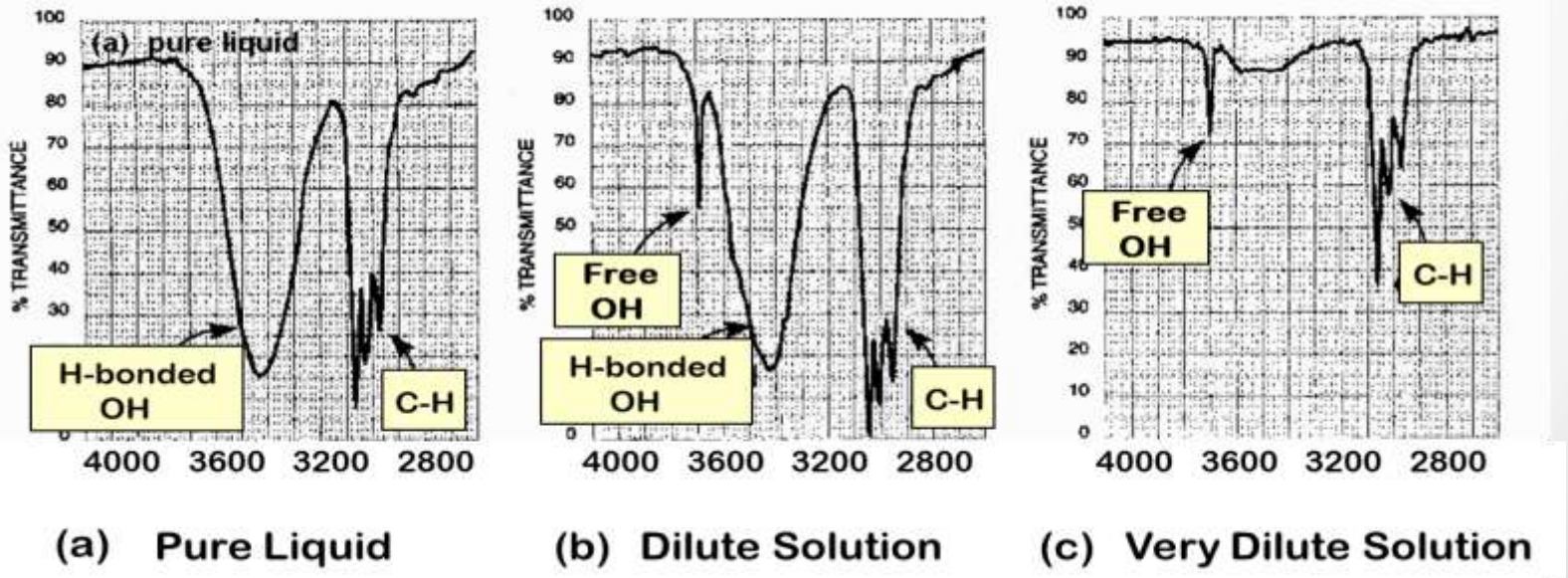


- O-H 3600 cm^{-1} (alcohol, free)
- O-H 3300 cm^{-1} (alcohols & acids, H-bonding)

Effect of Hydrogen-Bonding on O-H Stretching



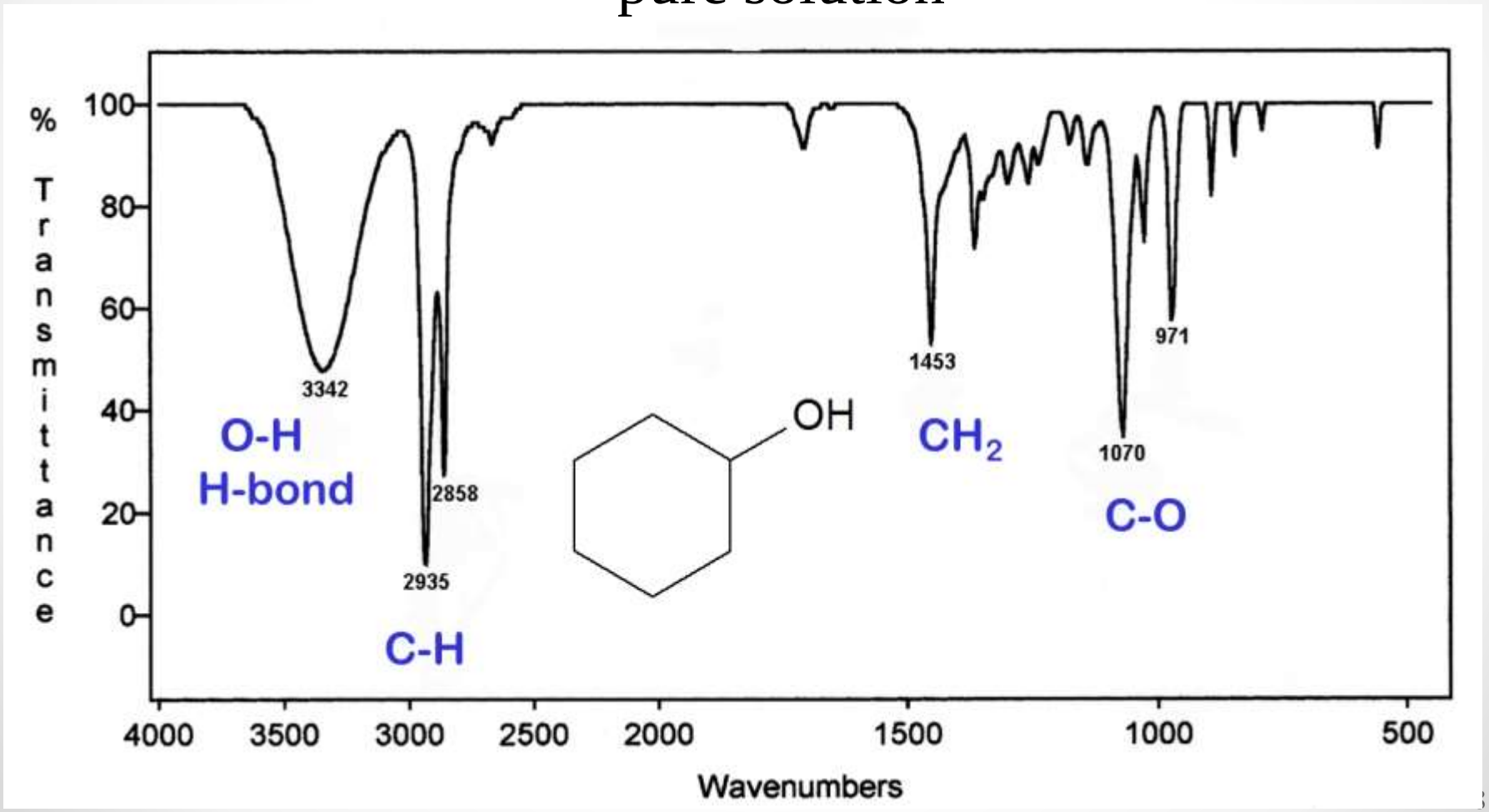
1-Butanol



Alcohol

Cyclohexanol

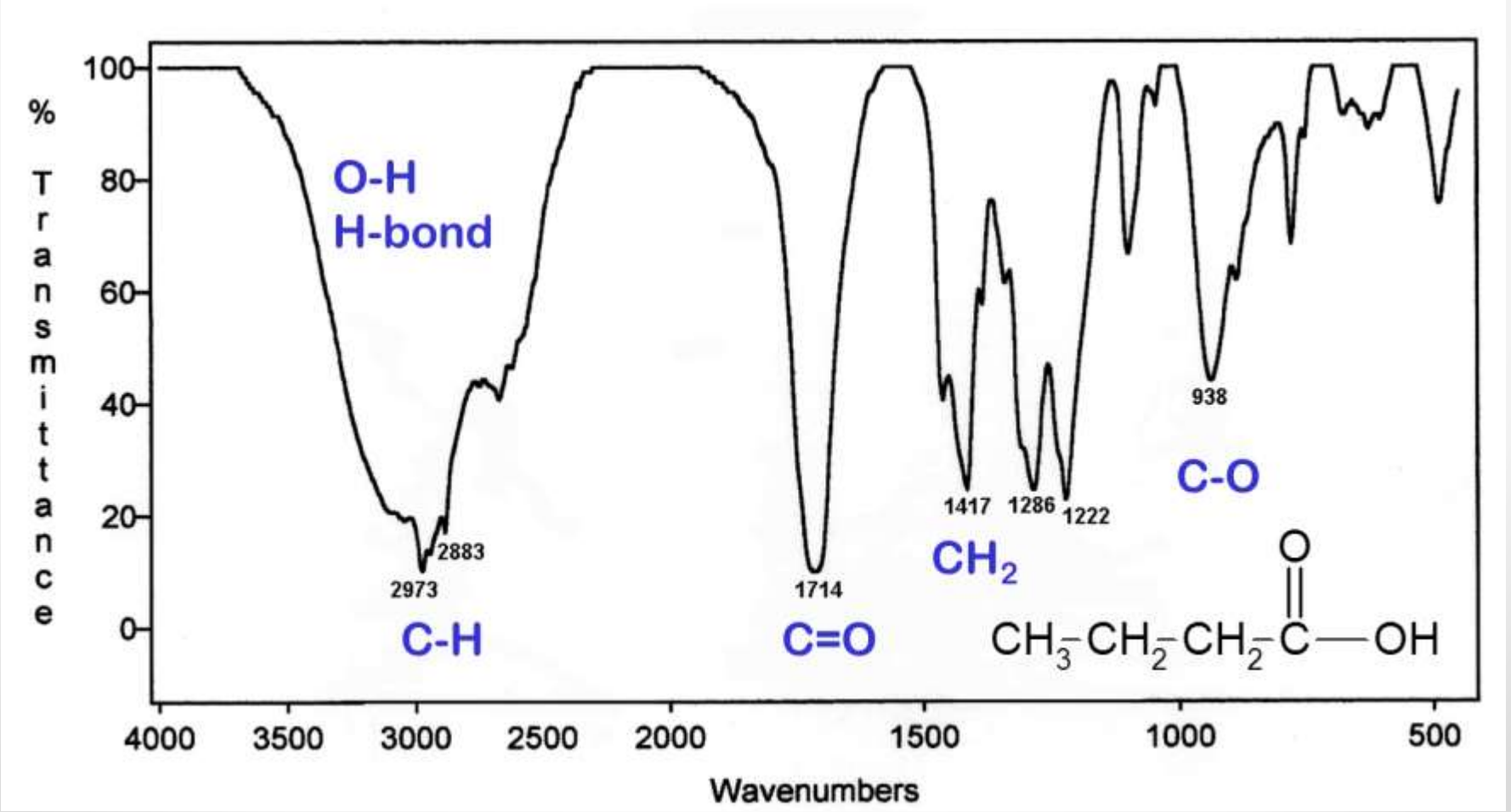
pure solution



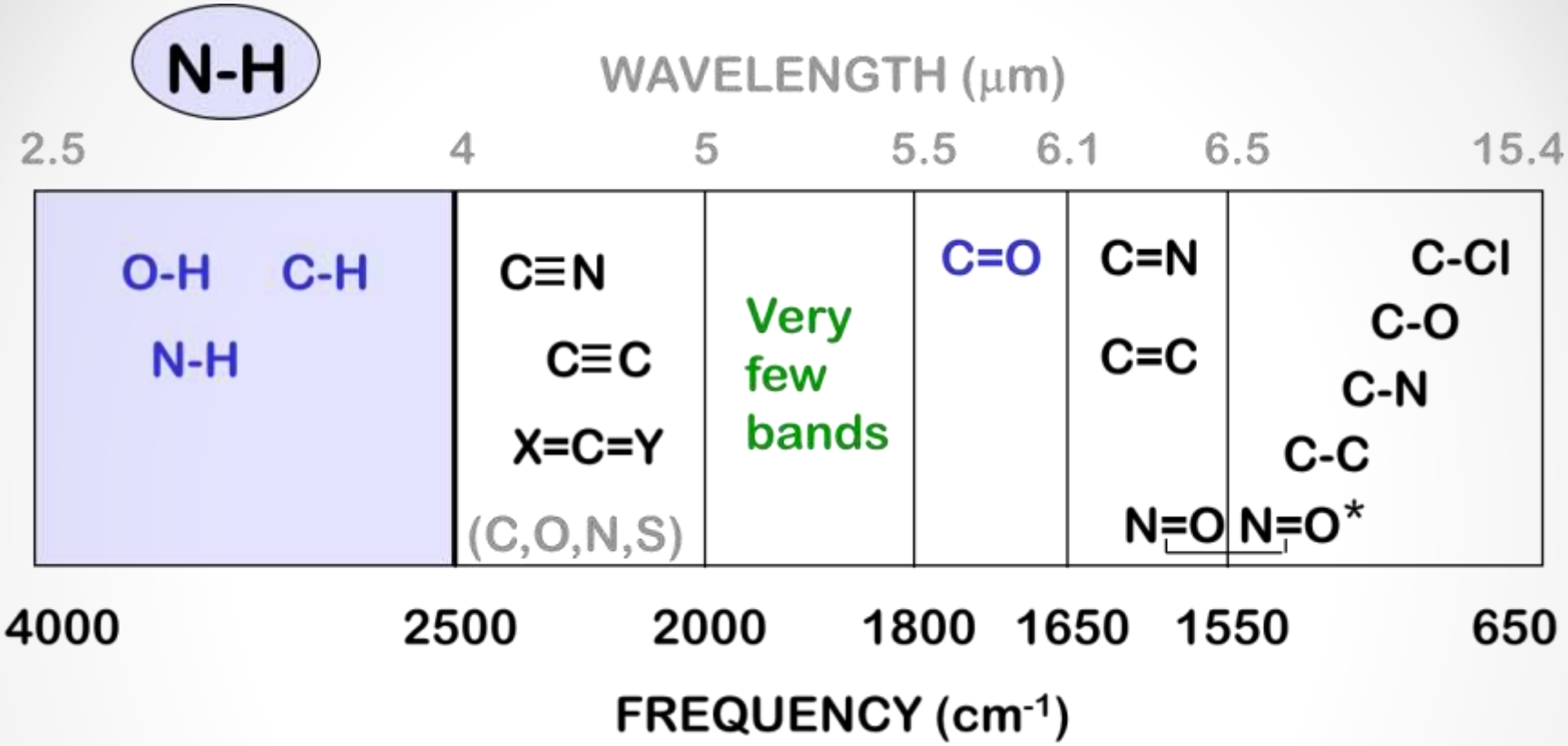
Carboxylic acid

Butanoic Acid

pure solution



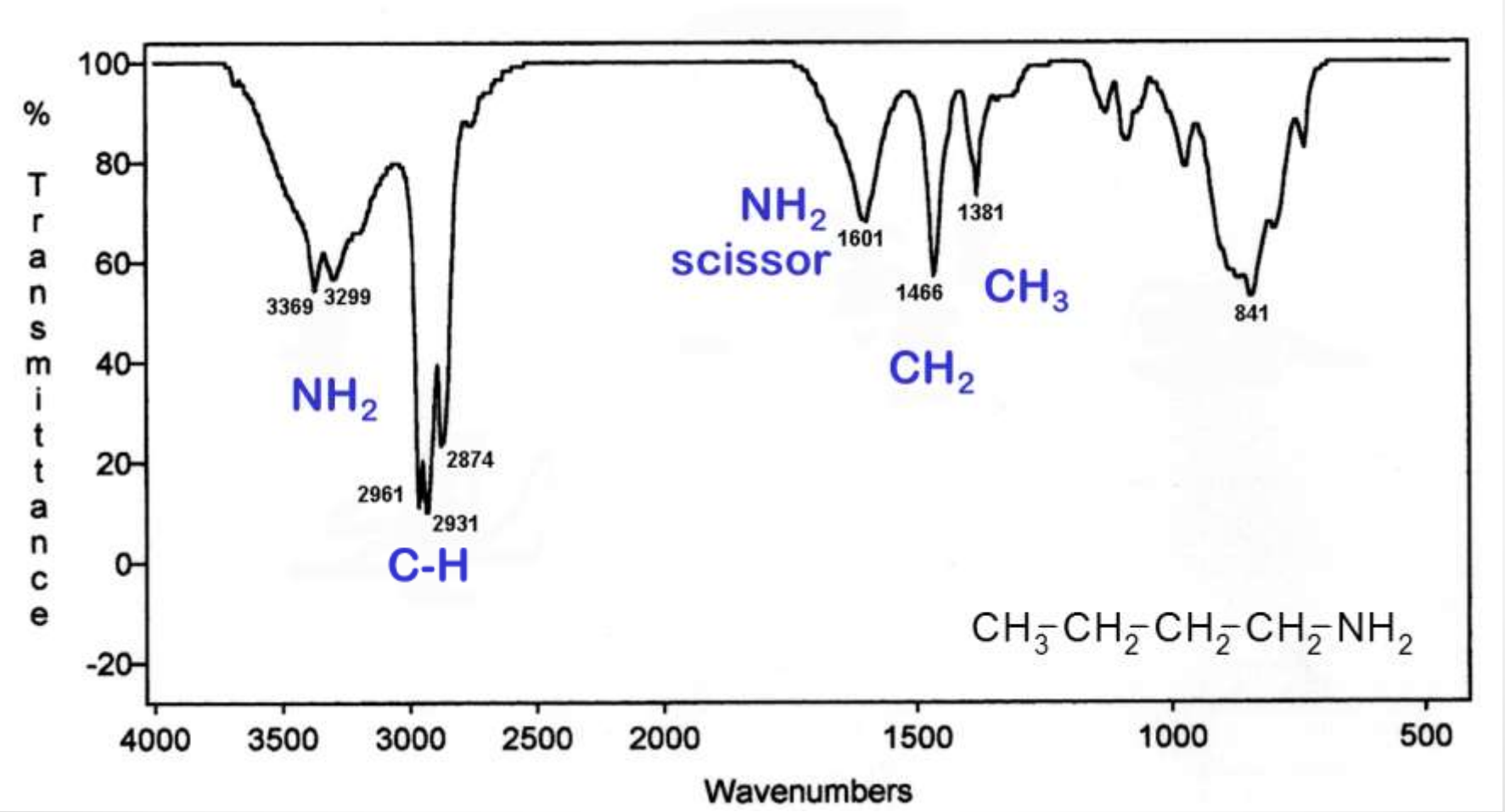
The N-H Stretching Region



- N-H 3300 - 3400 cm^{-1}
- Primary amines give two peaks
- Secondary amines give one peak
- Tertiary amines give no peak

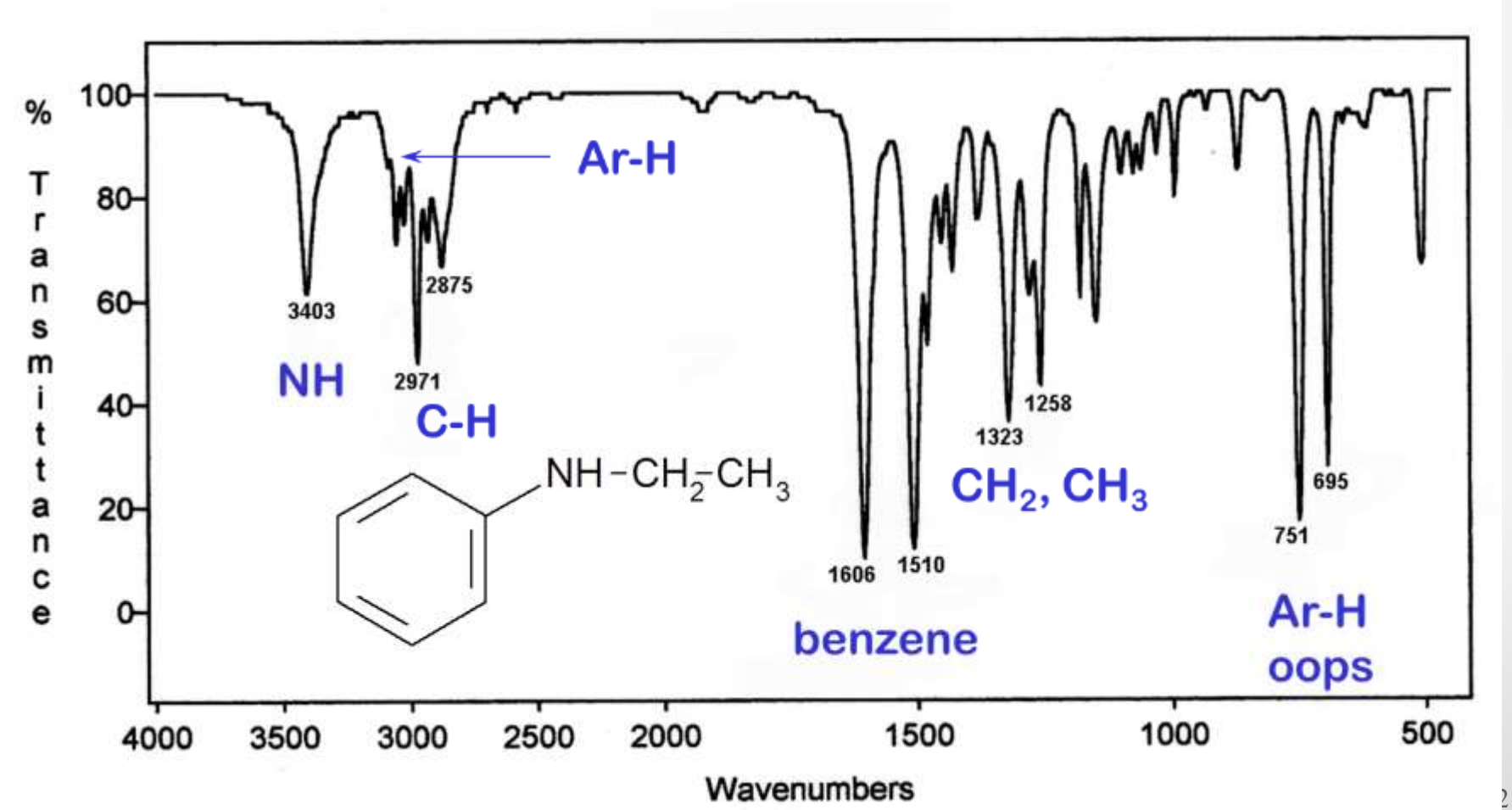
Primary amine

1-Butanamine



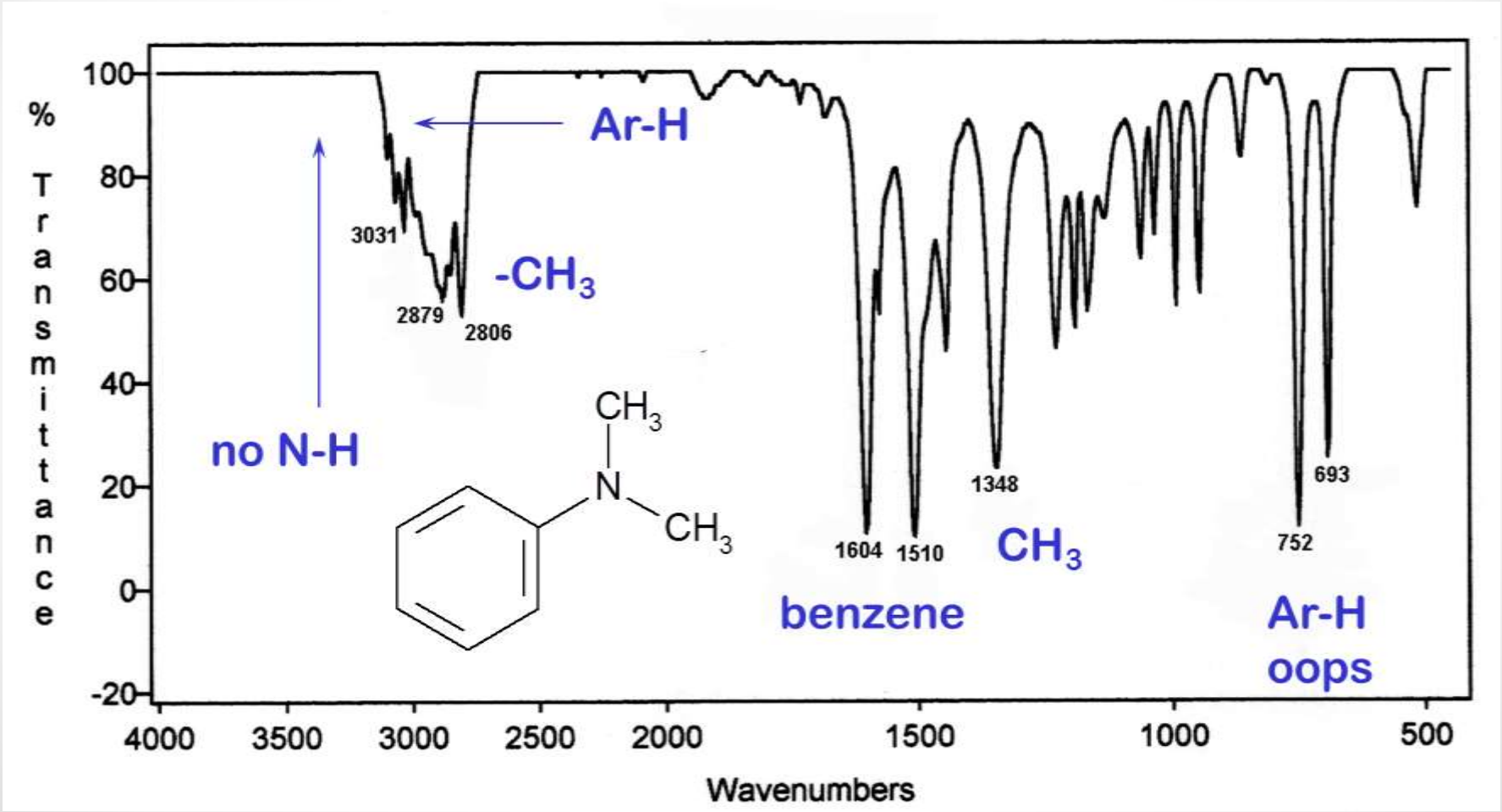
Secondary amine

N -Ethylbenzenamine

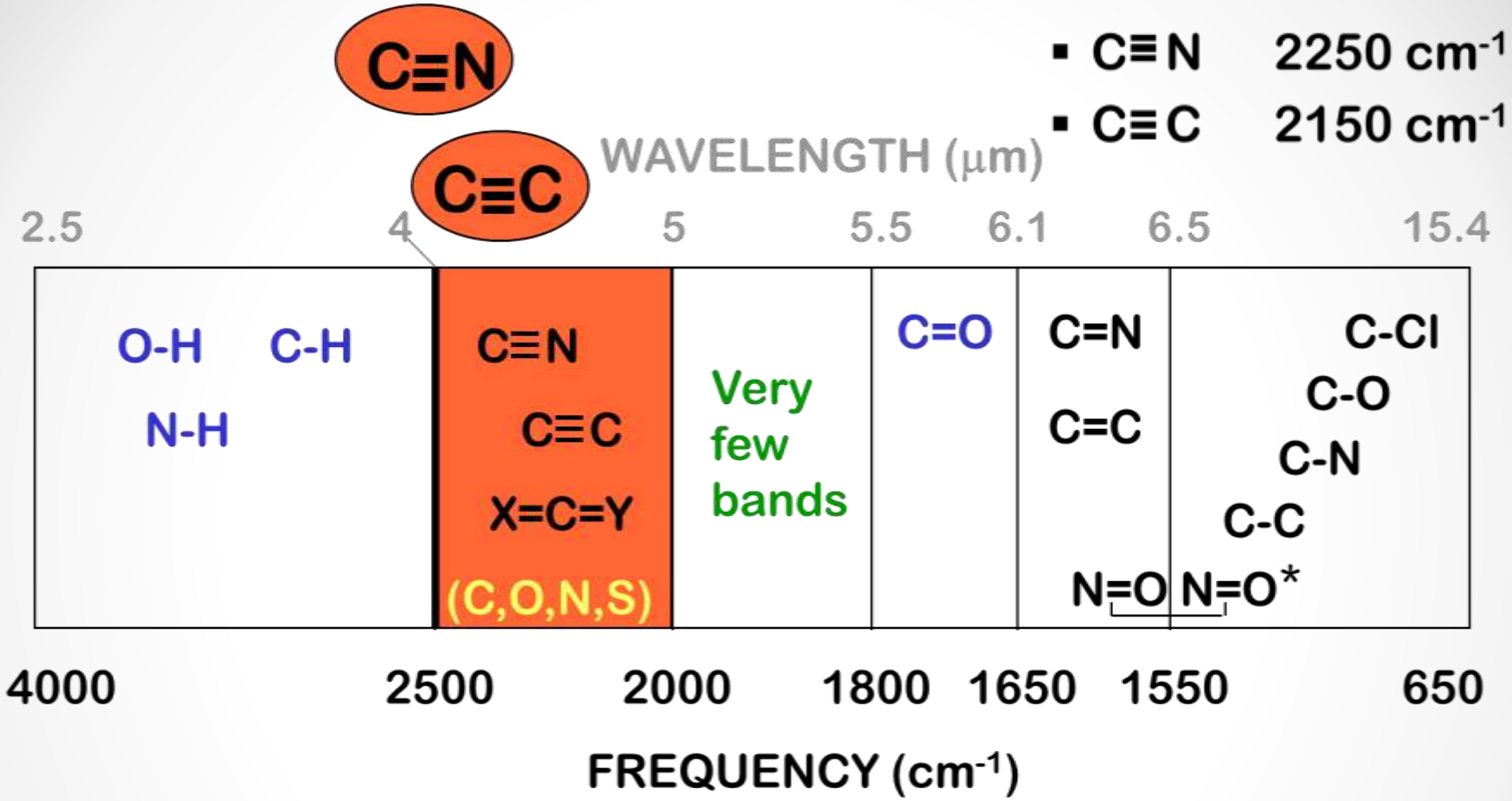


Tertiary amine

N,*N* -Dimethylaniline

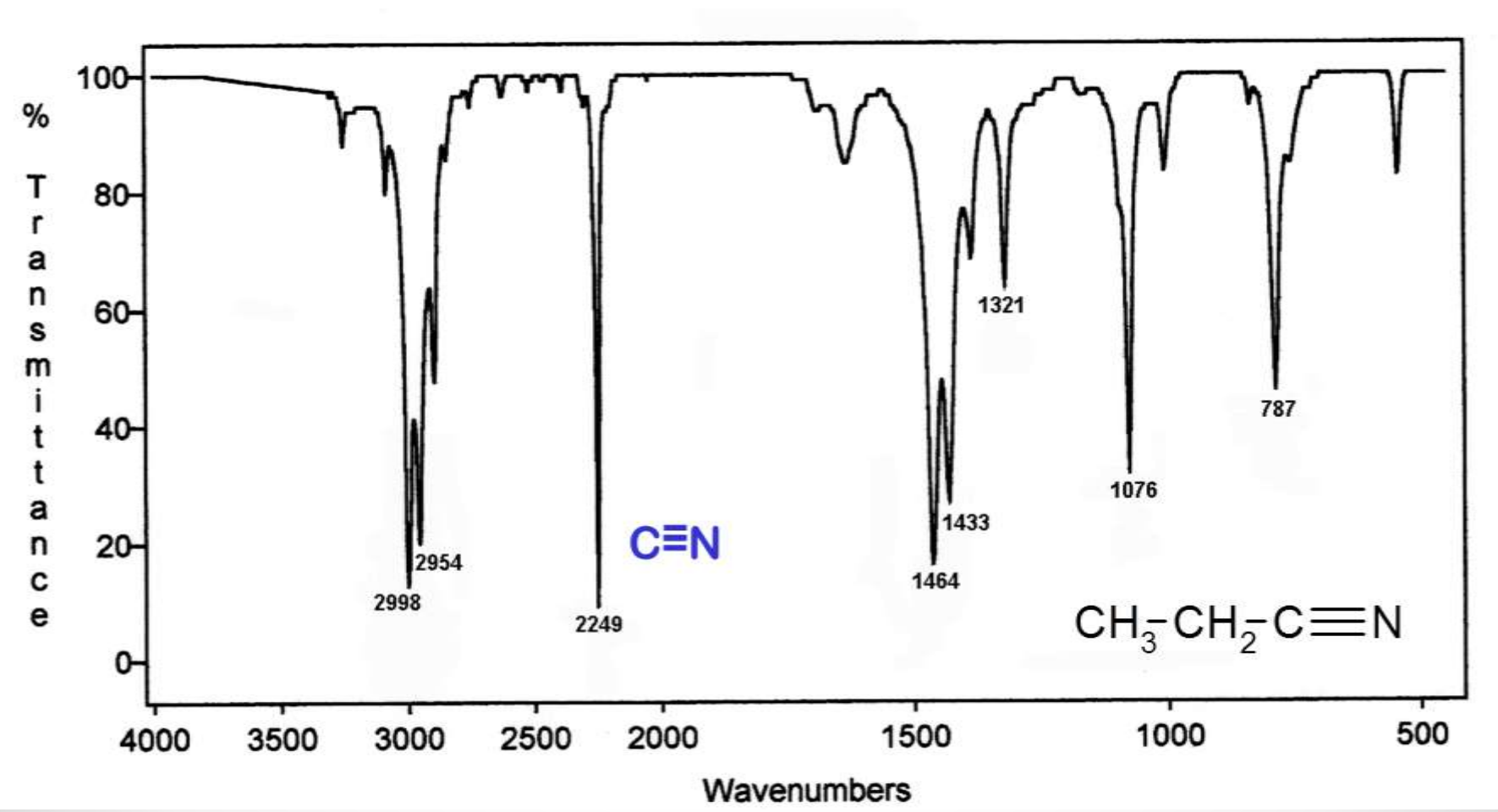


The Triple Bond Stretching Region

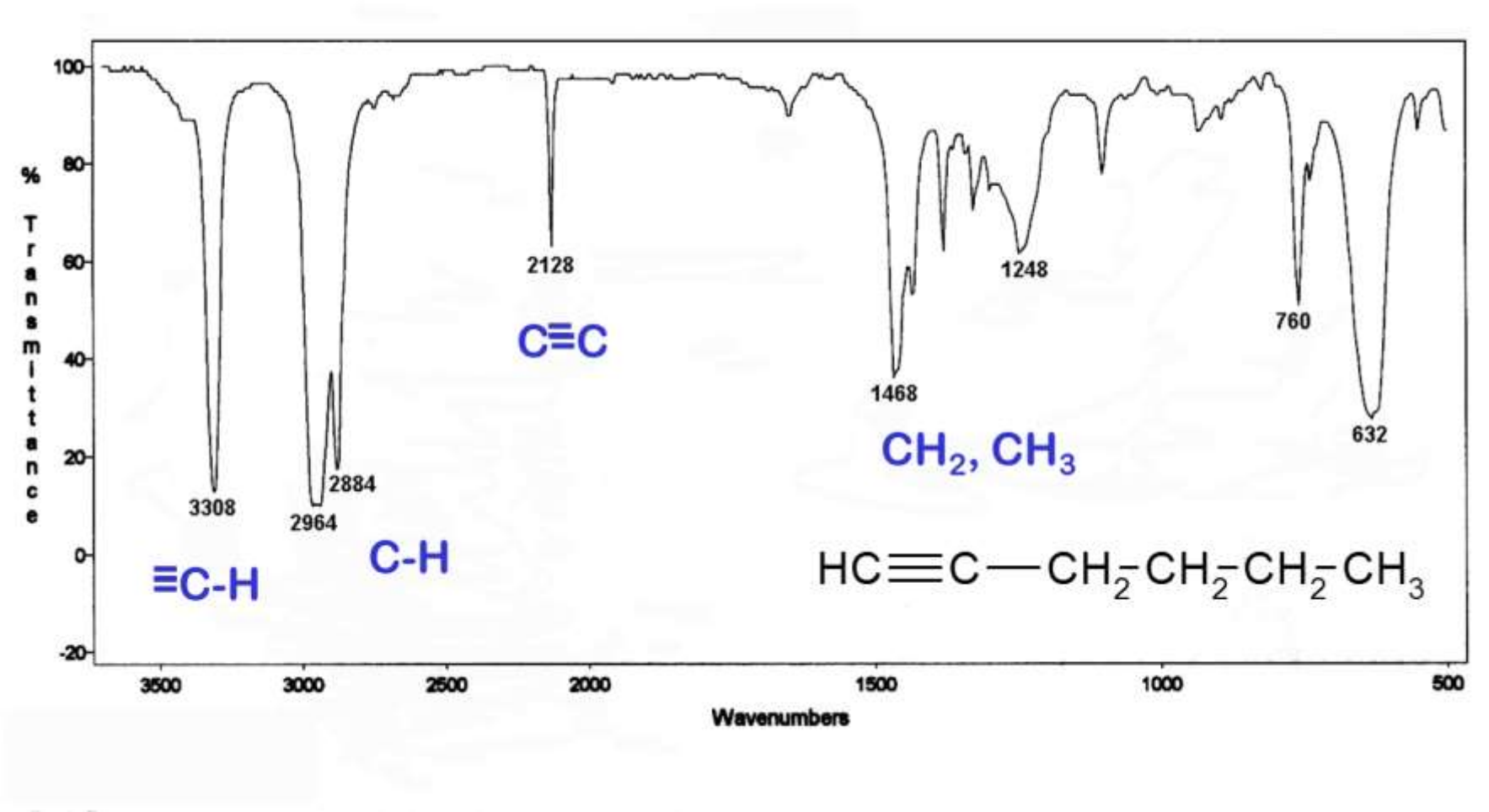


- The cyano group often gives a strong, sharp peak due to its large dipole moment.
- The carbon-carbon triple bond gives a sharp peak, but it is often weak due to a lack of a dipole.

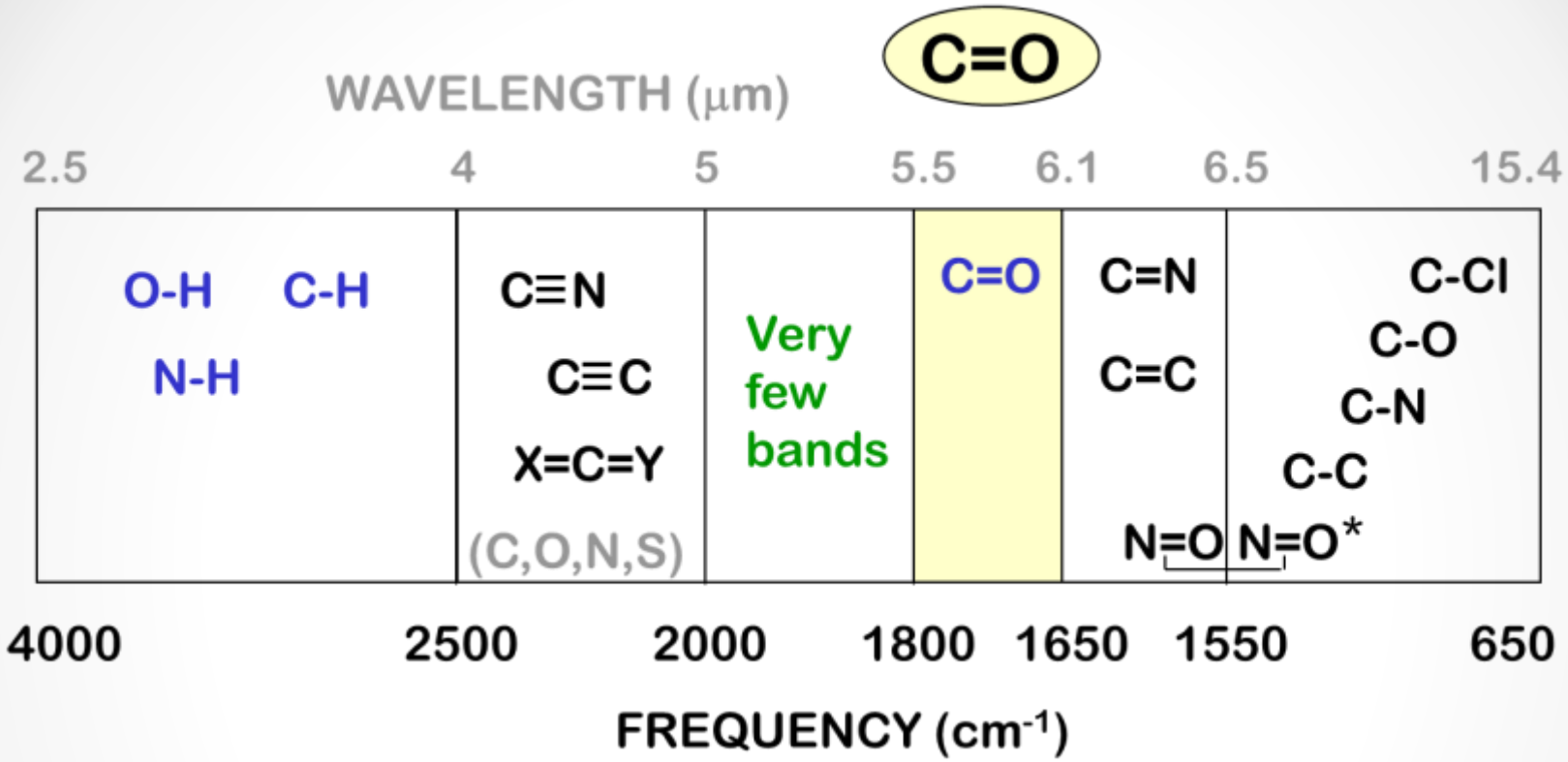
Propanenitrile

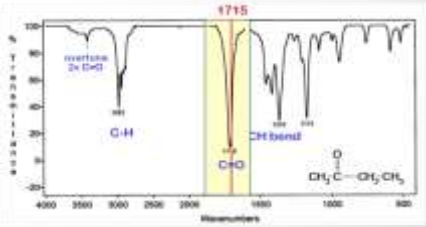


1-Hexyne


% Transmittance
100
80
60
40
20
0
-20
3500
3000
2500
2000
1500
1000
500
Wavenumbers
3308
2964
2884
2128
1468
1248
760
632
≡C-H
C-H
C≡C
CH2, CH3
HC≡C—CH2-CH2-CH2-CH3

The Carbonyl Stretching Region



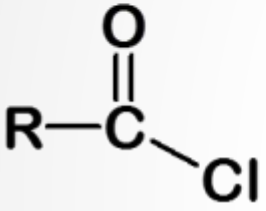


- This region stretches from about 1800 to 1650 cm^{-1}
- The base value is 1715 cm^{-1} (ketone).
- The bands are very strong !!! due to the large C=O dipole moment.
- C=O is often one of the strongest peaks in the spectrum.

37

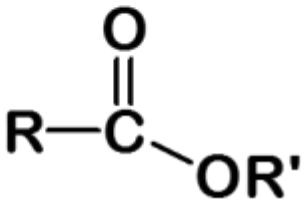
C=O is sensitive to its environment.

acid chloride



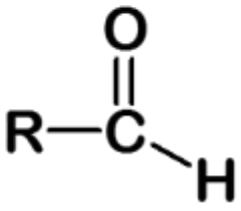
1800

ester



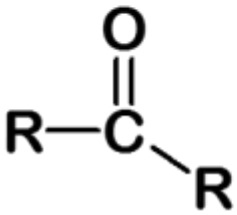
1735

aldehyde



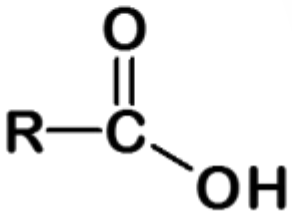
1725

ketone



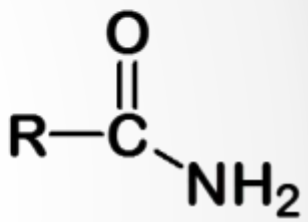
1715

carboxylic acid



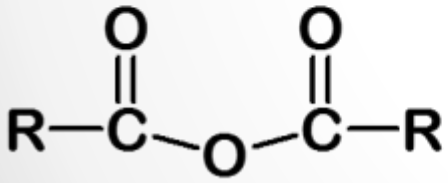
1710

amide



1690

anhydride

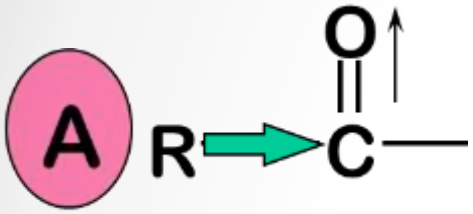


1810 and 1760

(two peaks)

Factors that influence the C=O absorption

Inductive and Resonance effects on the Carbonyl Frequency

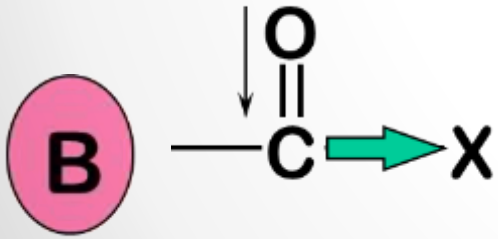


R = Me, Et, etc.

Electron-donating groups

weaken the carbonyl and

lower its absorption frequency

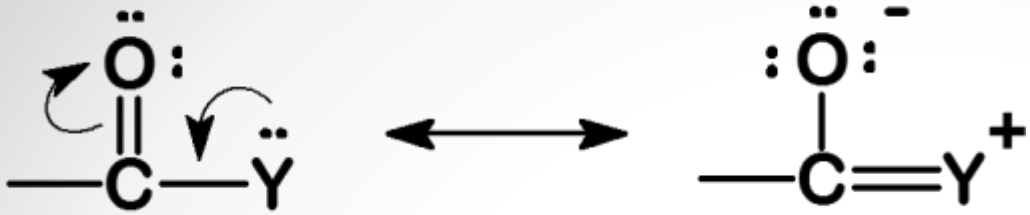


X = F, Cl, Br, O

Electron-withdrawing groups

strengthen the carbonyl and

raise its absorption frequency



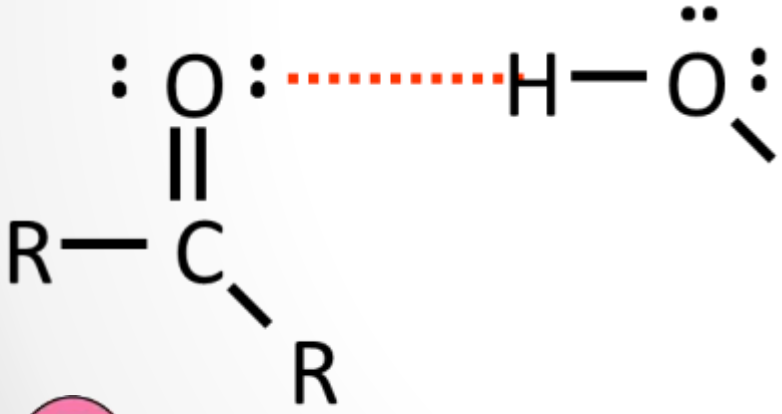
C

Y = N, O, or C=C

Resonance

weakens the carbonyl and

lowers its absorption frequency



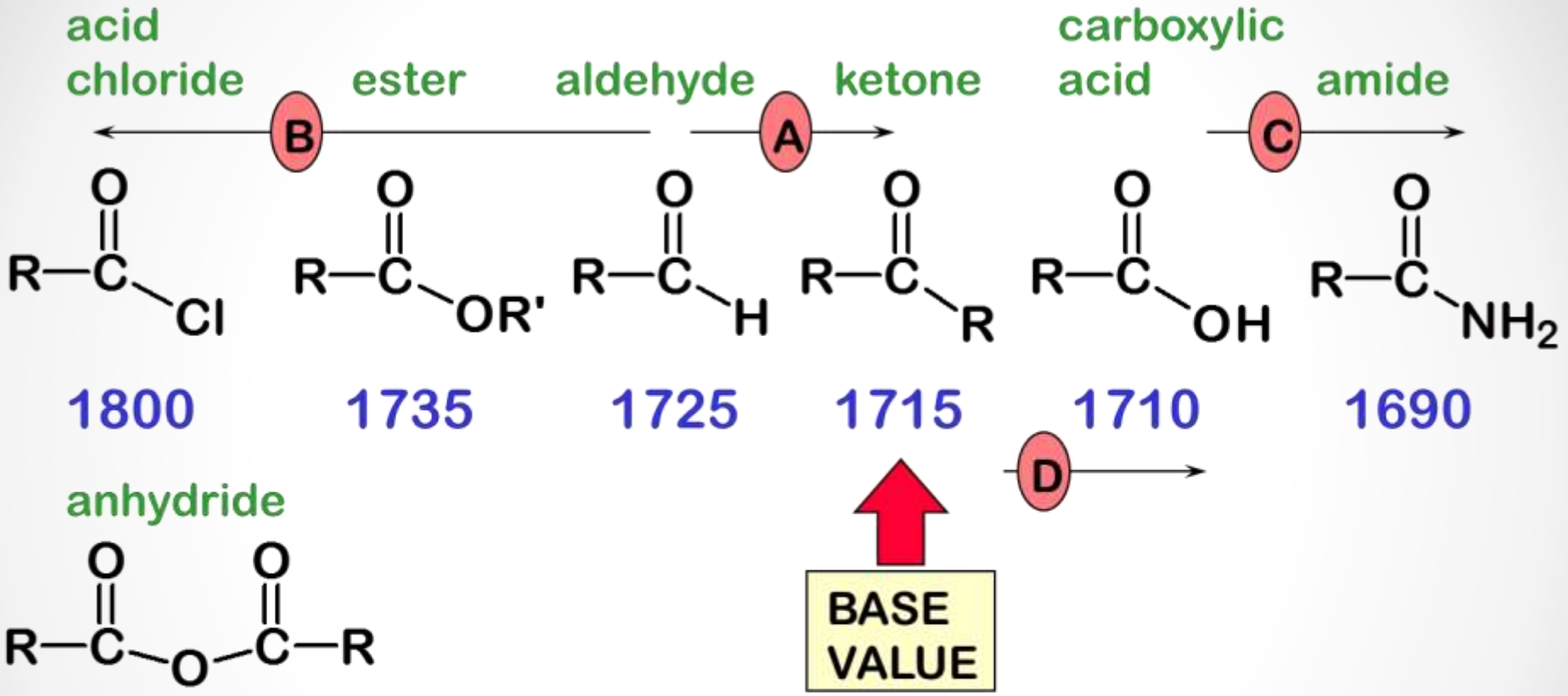
D

Hydrogen bonding

lengthens and weakens the C=O bond and

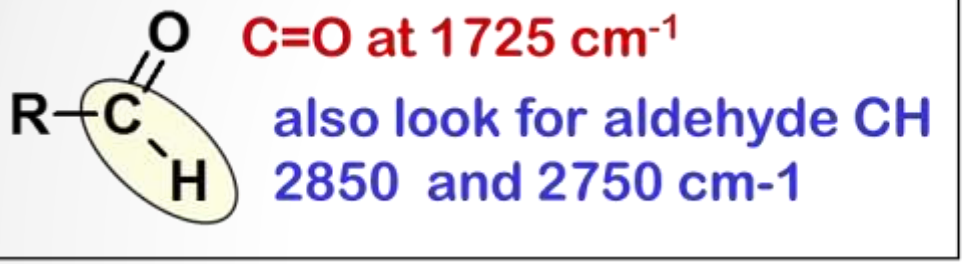
lowers its absorption frequency

How the Factors affect C=O



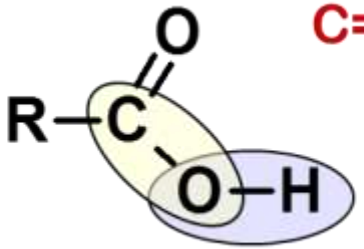
Confirmation of Functional group

- Every type of carbonyl compound has other places you can look to confirm your conclusion based on frequency alone.



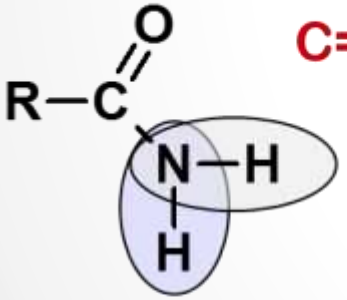
C=O at 1725 cm^{-1}

also look for aldehyde CH 2850 and 2750 cm-1



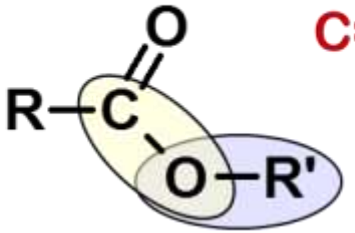
C=O at 1710 cm^{-1}

also look for OH (H-bonded) and C-O ~1200 cm-1



C=O at 1690 cm^{-1}

also look for two NH peaks at 3400 cm-1



C=O at 1735 cm^{-1}

also look for two C-O at 1200 and 1000 cm-1

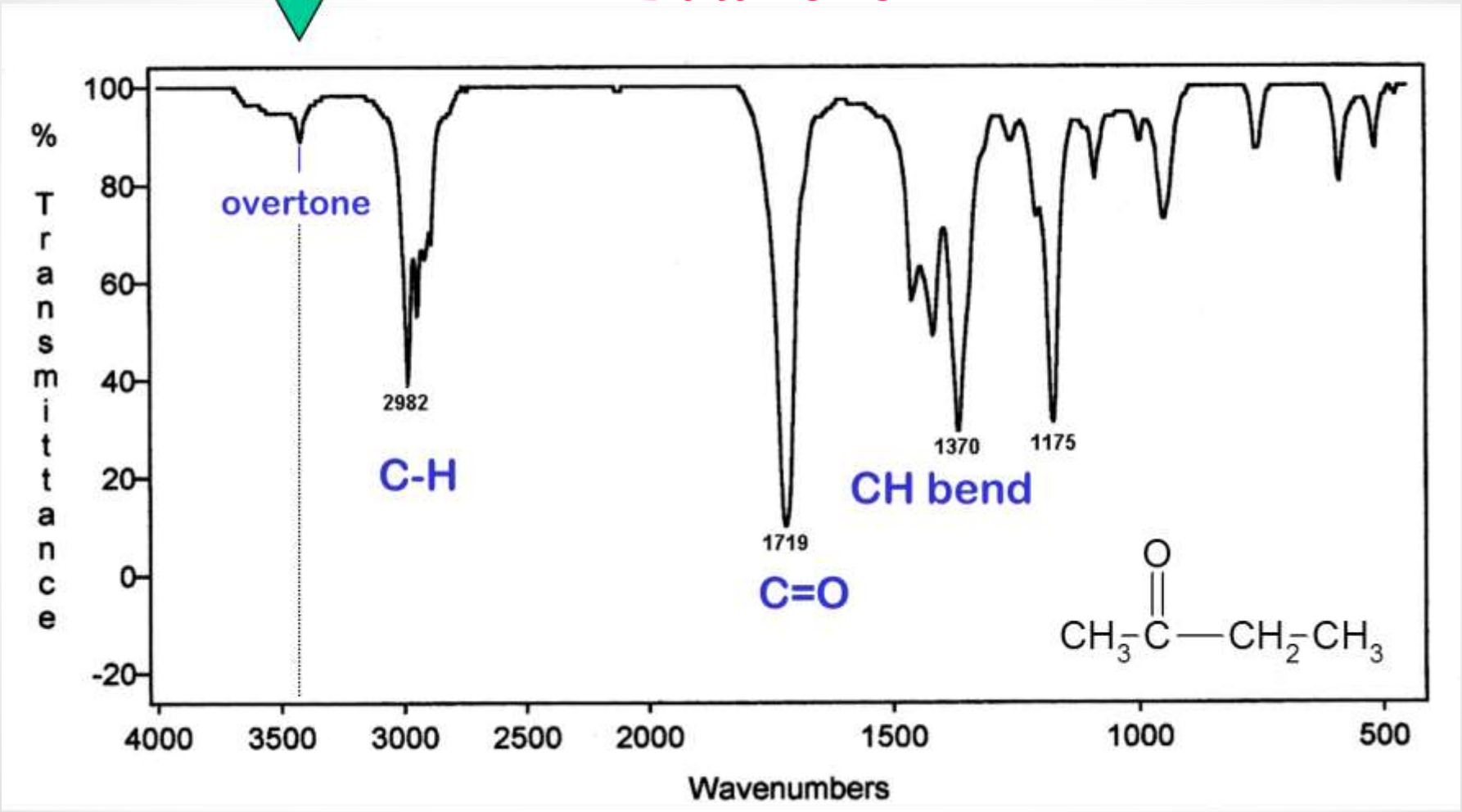
Ketones have C=O at 1715 cm^{-1} and no NH, OH, C-O or -CHO

Anhydrides have two C=O peaks near 1800 cm^{-1} and two C-O

overtone of strong C=O peak
1719 x 2 = 3438

2-Butanone

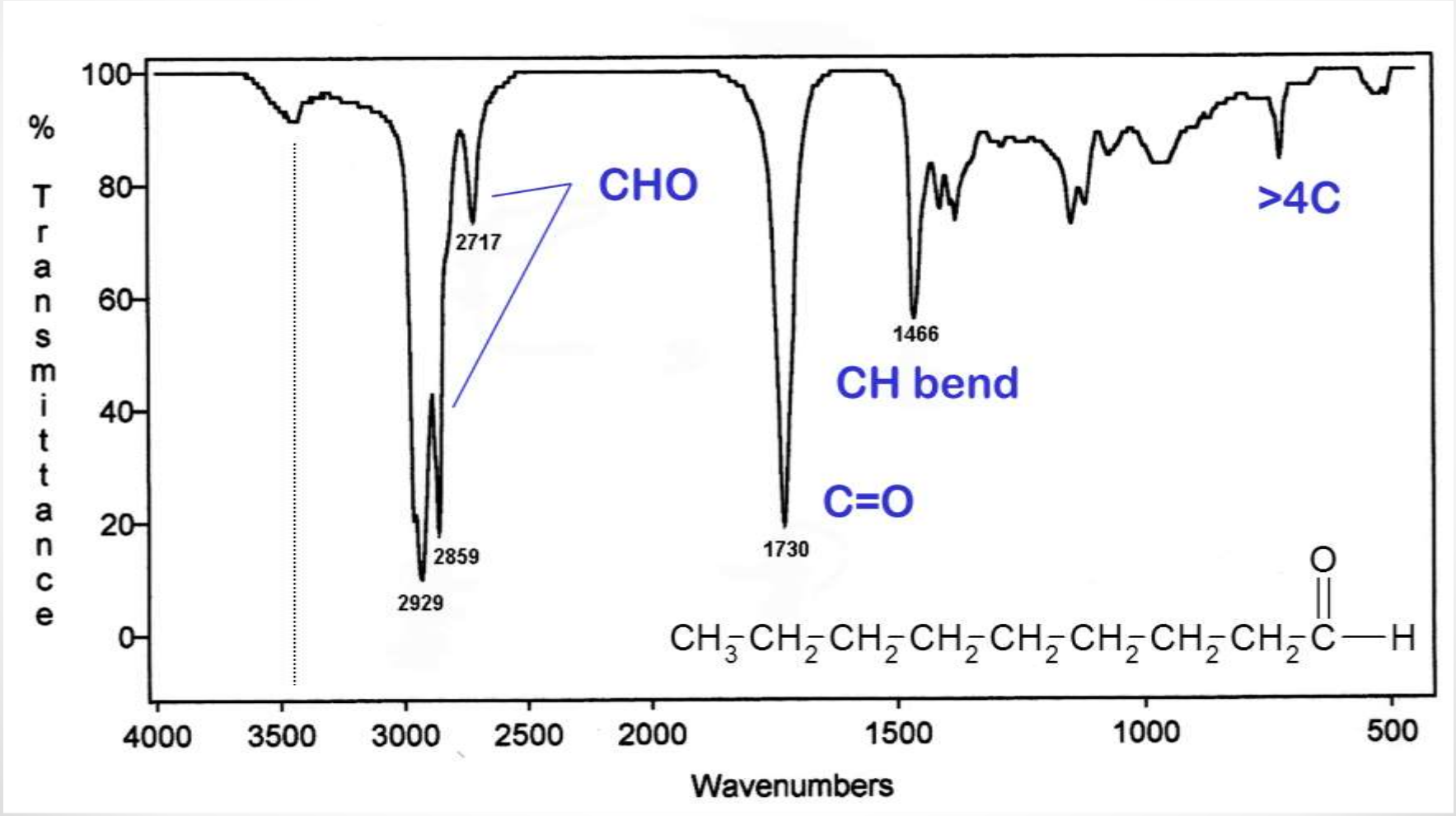
Ketone
Base = 1715



3438

Aldehyde
Base = 1725

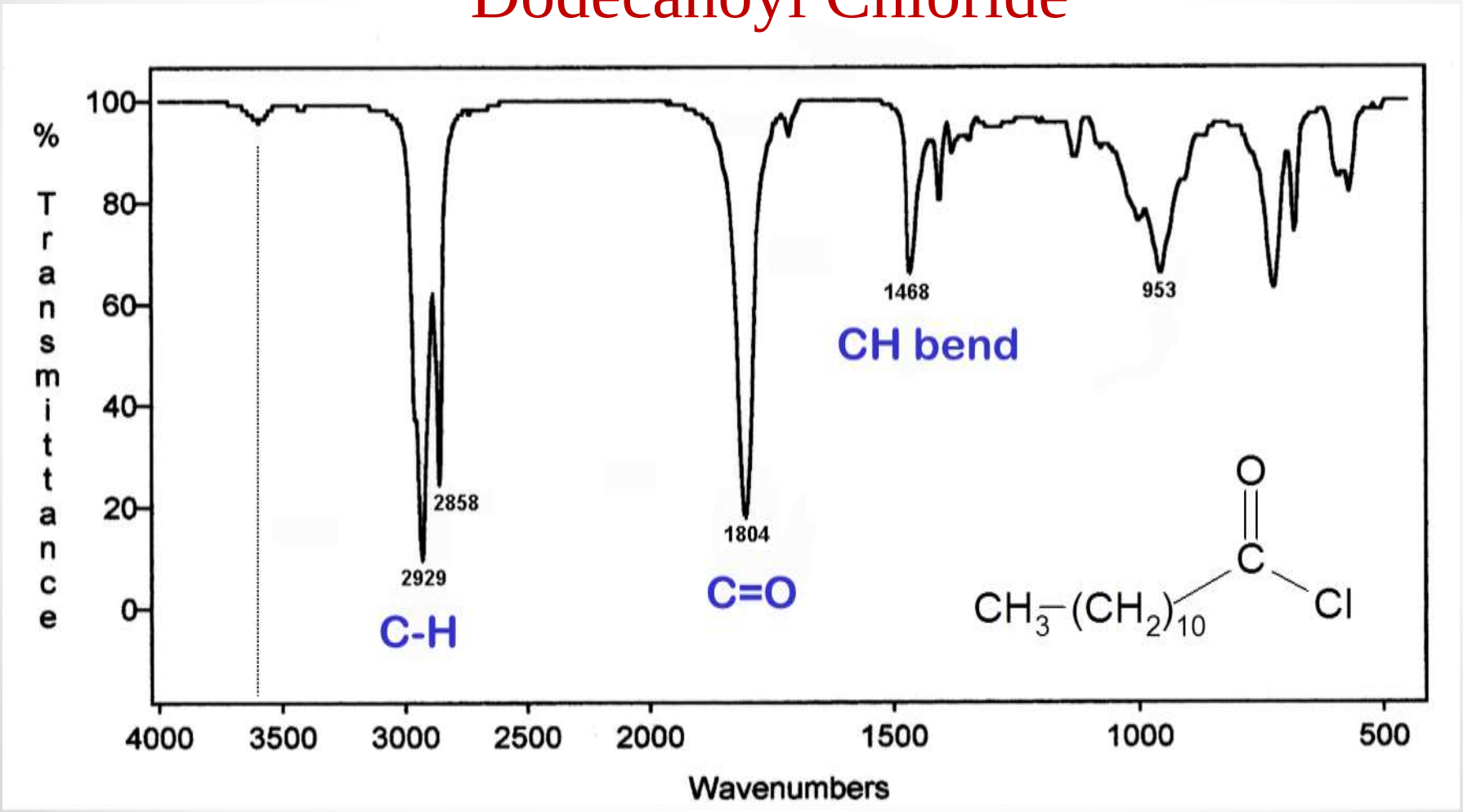
Nonanal



3460

Acid Chloride
Base = 1800

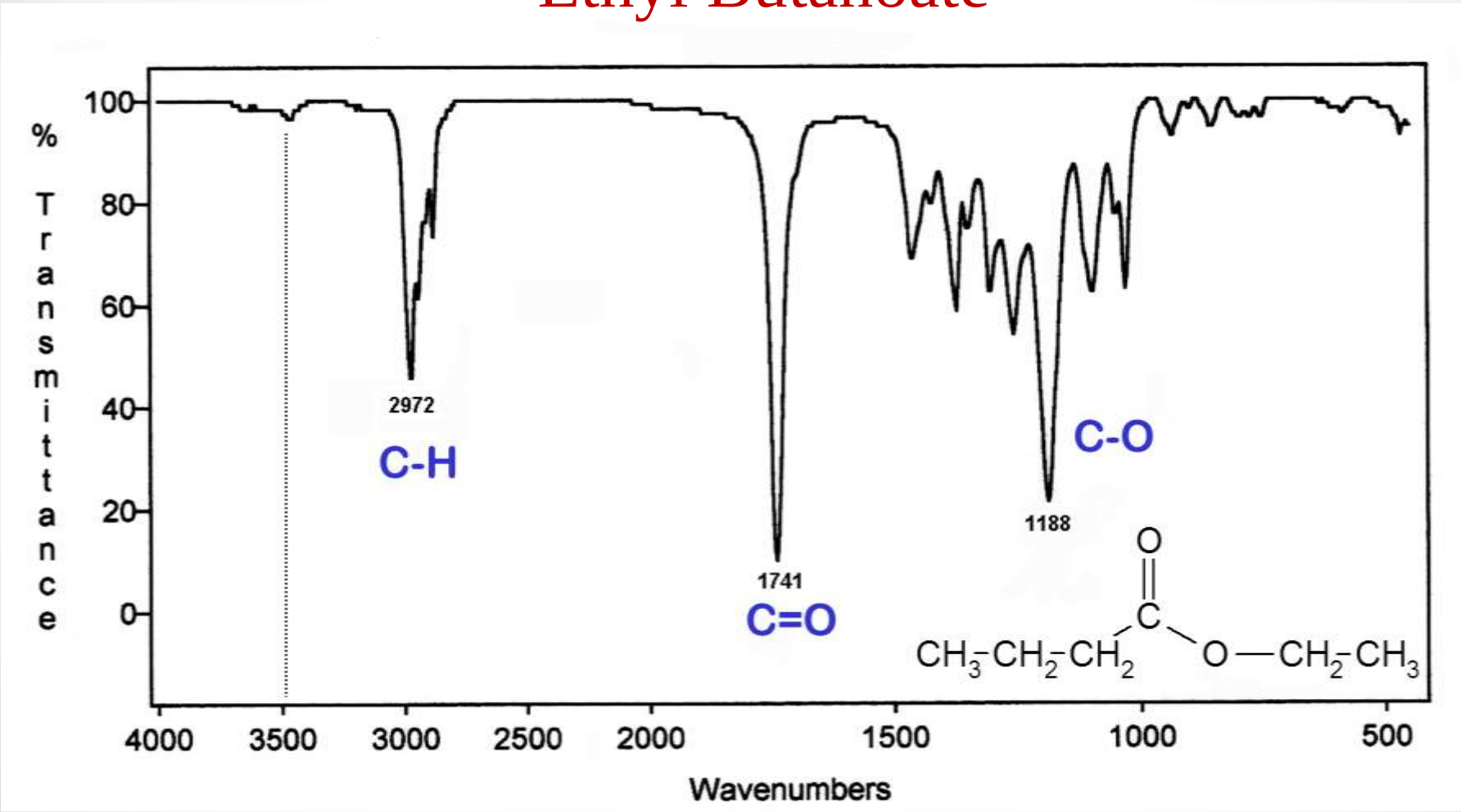
Dodecanoyl Chloride



Ester

Base = 1735

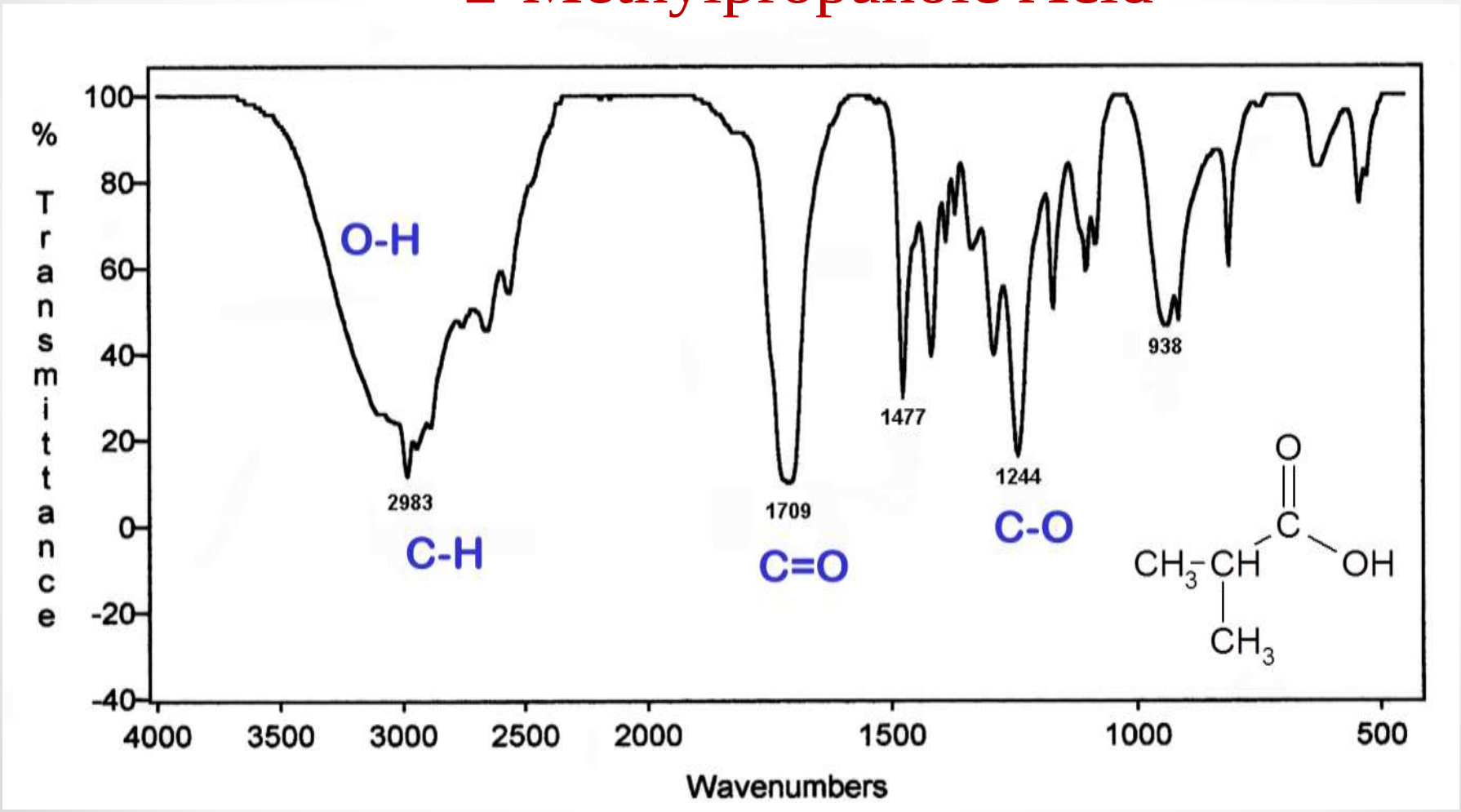
Ethyl Butanoate



3482

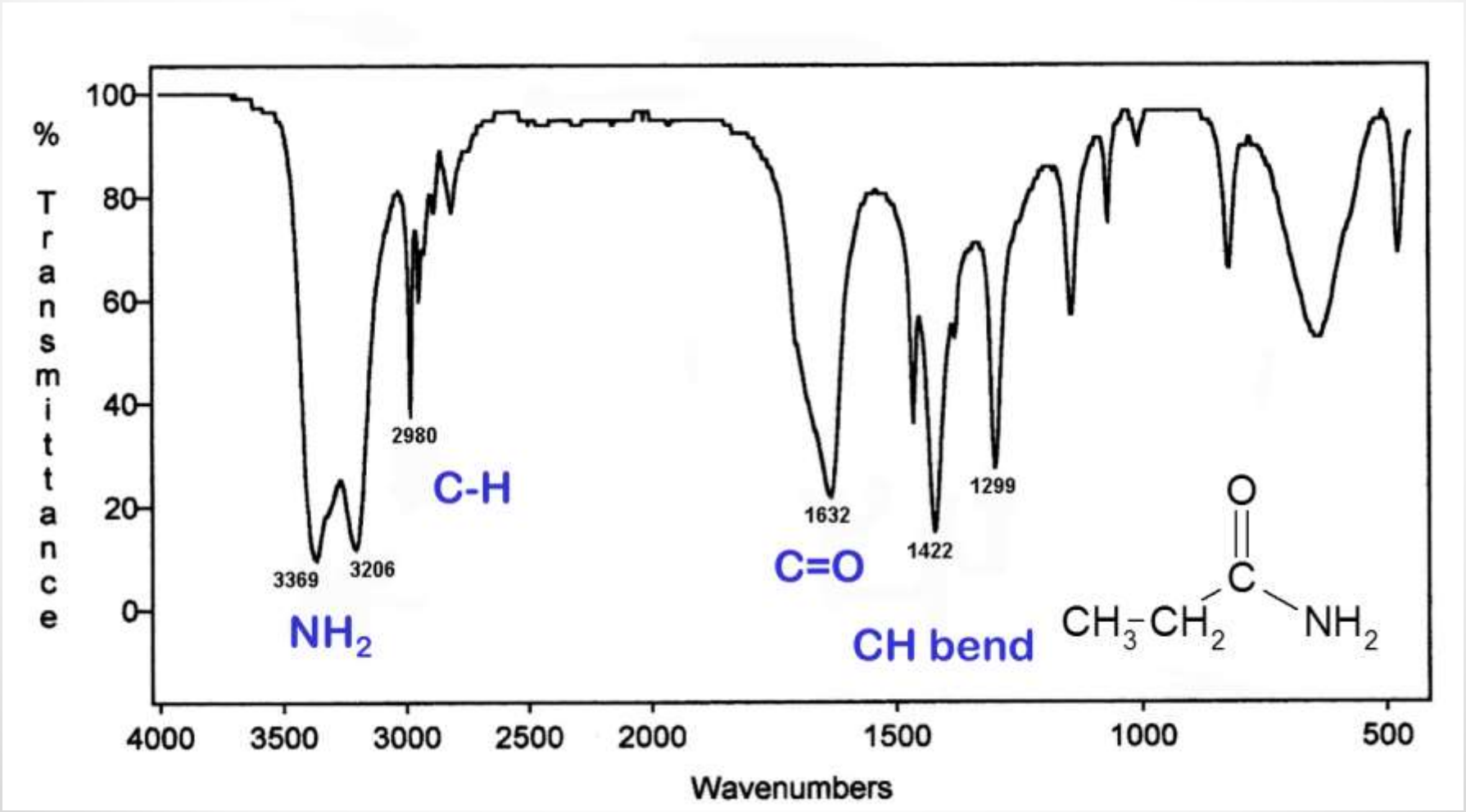
Carboxylic acid
Base = 1710

2-Methylpropanoic Acid



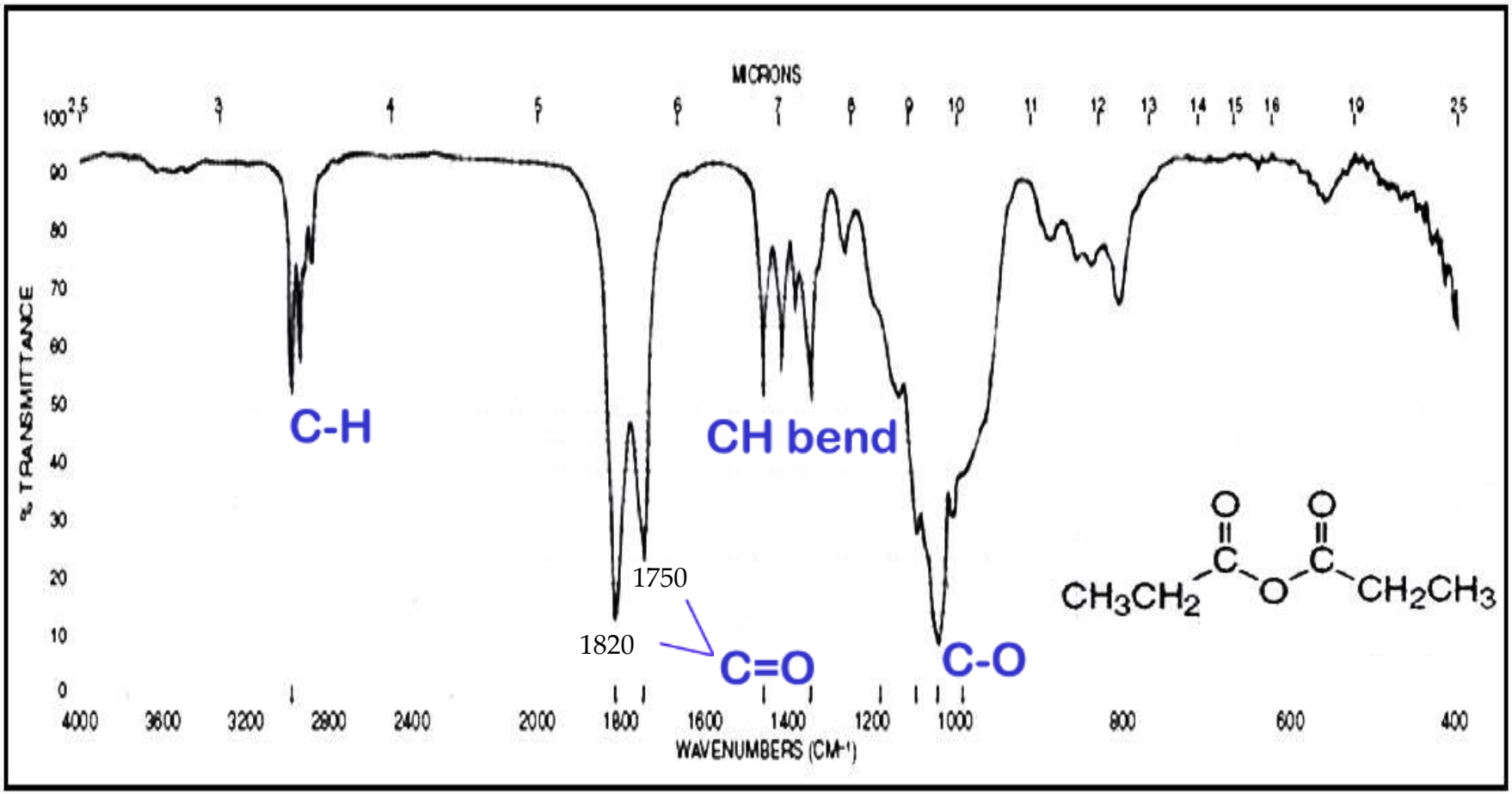
Amide
Base = 1690

Propanamide



Anhydride
Base = 1810 and 1760

Propionic anhydride



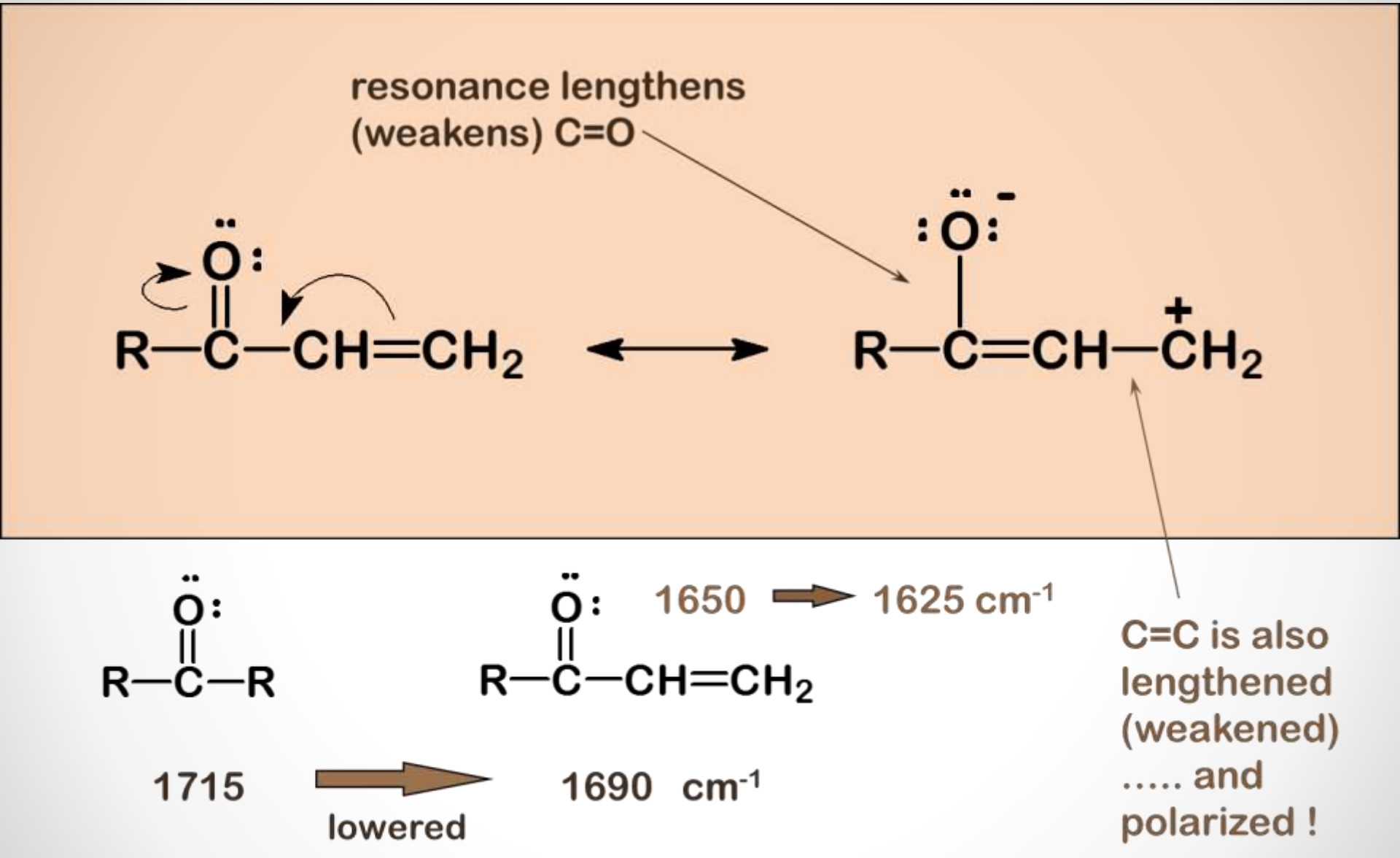
Conjugation of C=O with C=C

C=O 1715
C=C 1650

- Conjugation of a carbonyl with a C=C bond shifts values to lower frequencies.
- For aldehydes, ketones and esters, subtract about 25-30 cm^{-1} for conjugation with C=O.

- Conjugated ketone = 1690 to 1680 cm^{-1}
- Conjugated ester = 1710 to 1700 cm^{-1}

- C=C becomes quite strong!!



1715 → 1690 cm^{-1} lowered

1650 → 1625 cm^{-1}

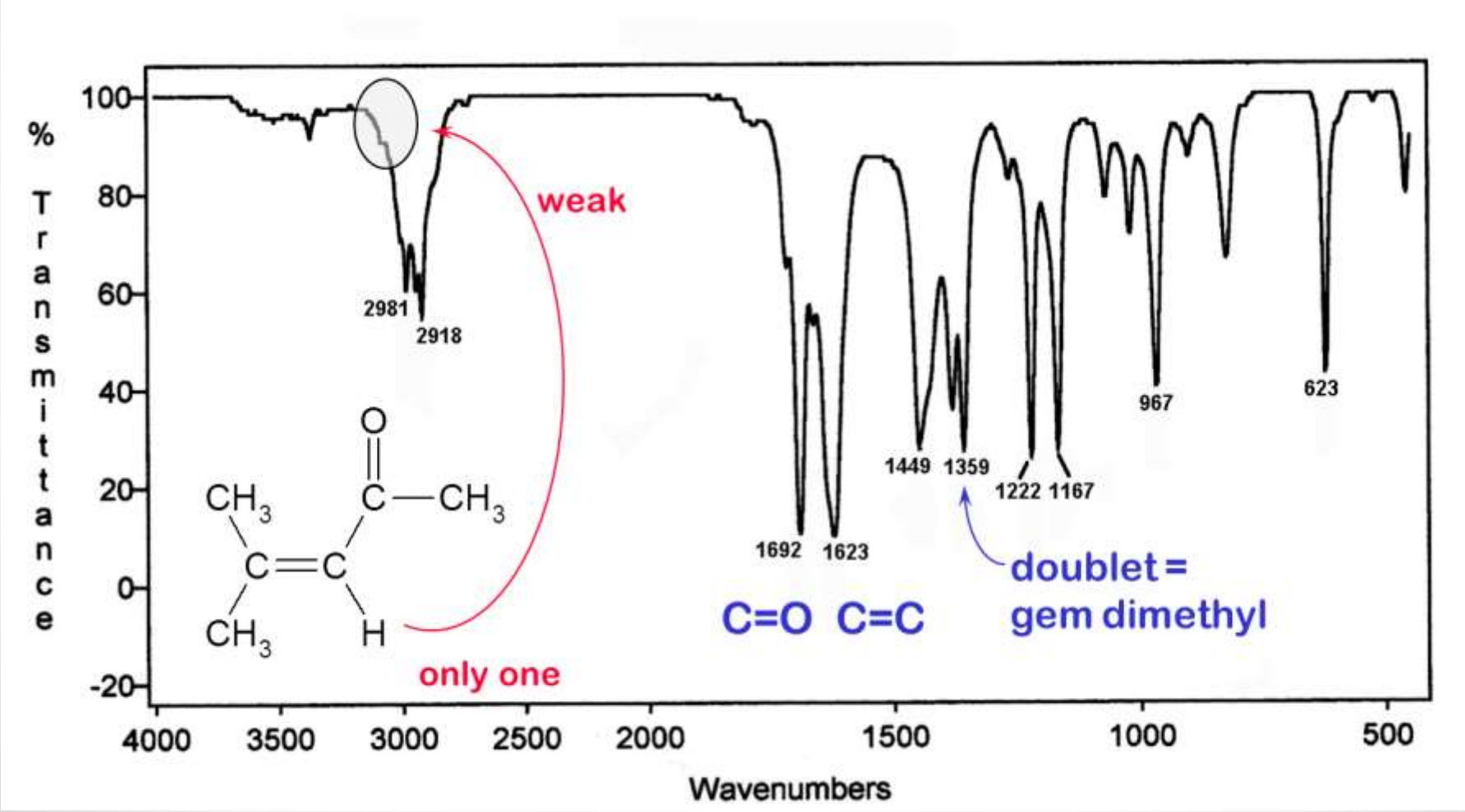
C=C is also lengthened (weakened) ….. and polarized !

C=O : 1715 - 30 = 1685

C=C : 1650 - 25 = 1625

Ketone conjugated

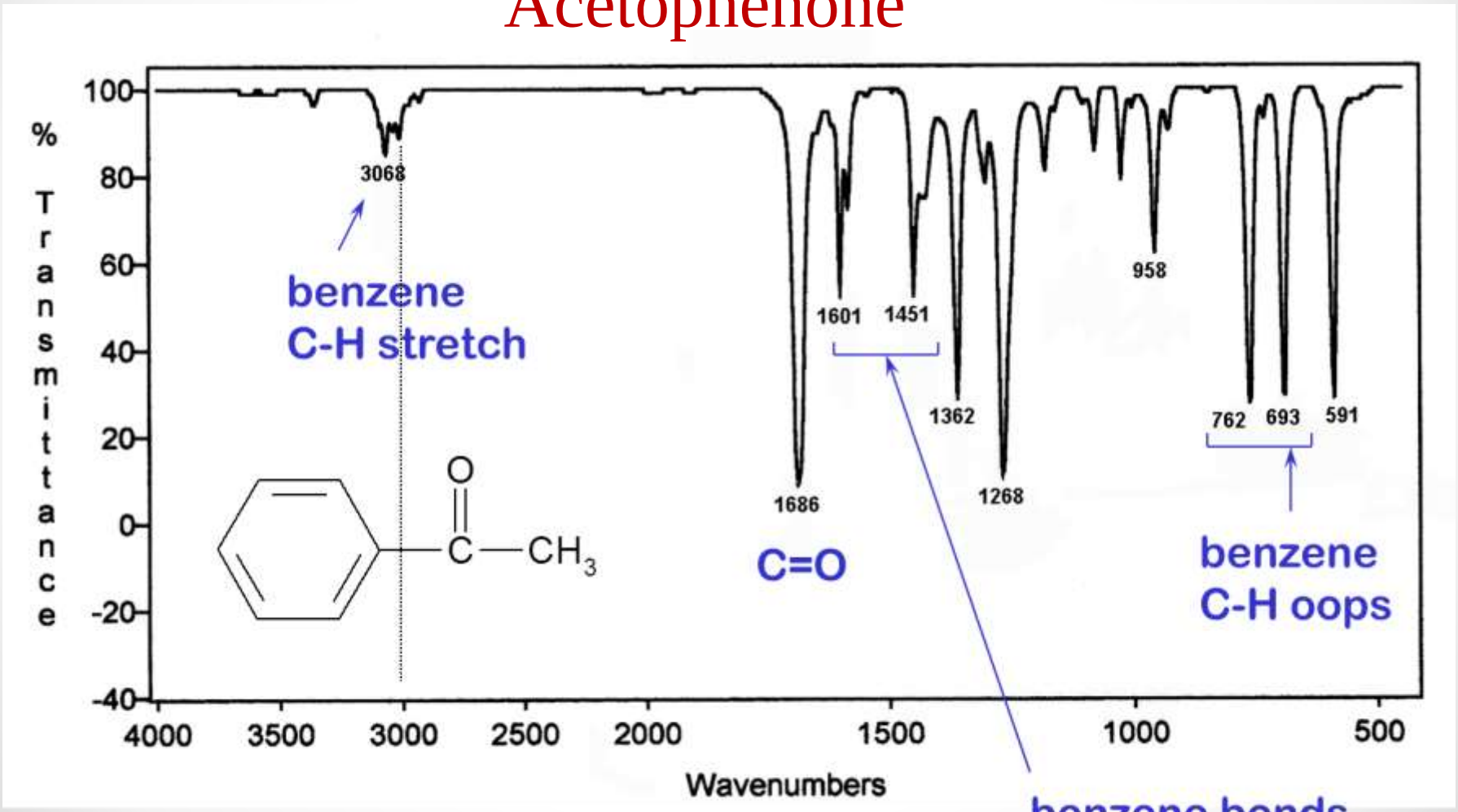
4-Methyl-3-penten-2-one



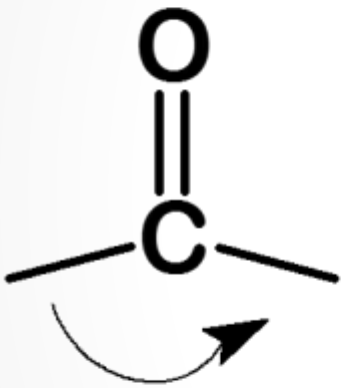
C=O : 1715 - 30 = 1685

Aromatic Ketone conjugated

Acetophenone

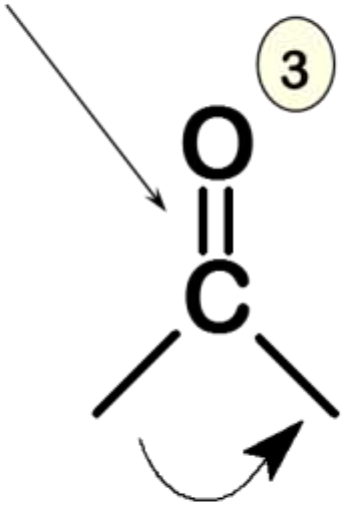


Angle Strain raises The Carbonyl Frequency



120° angle is normal

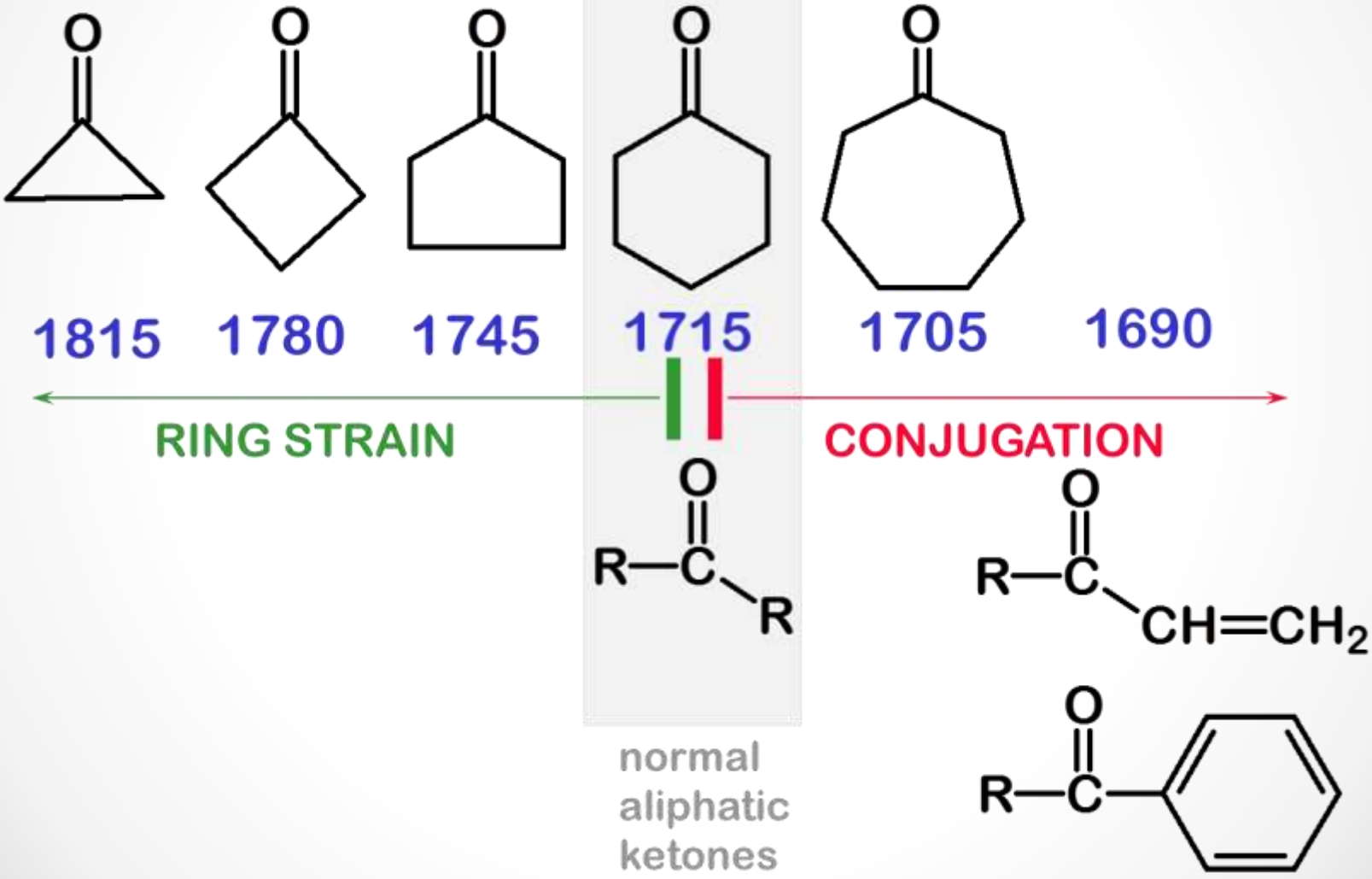
2 In response to more p character in the ring bonds, there is more s character in the bonds to C=O.



3 More s character leads to a shorter and stronger bond and a higher frequency.

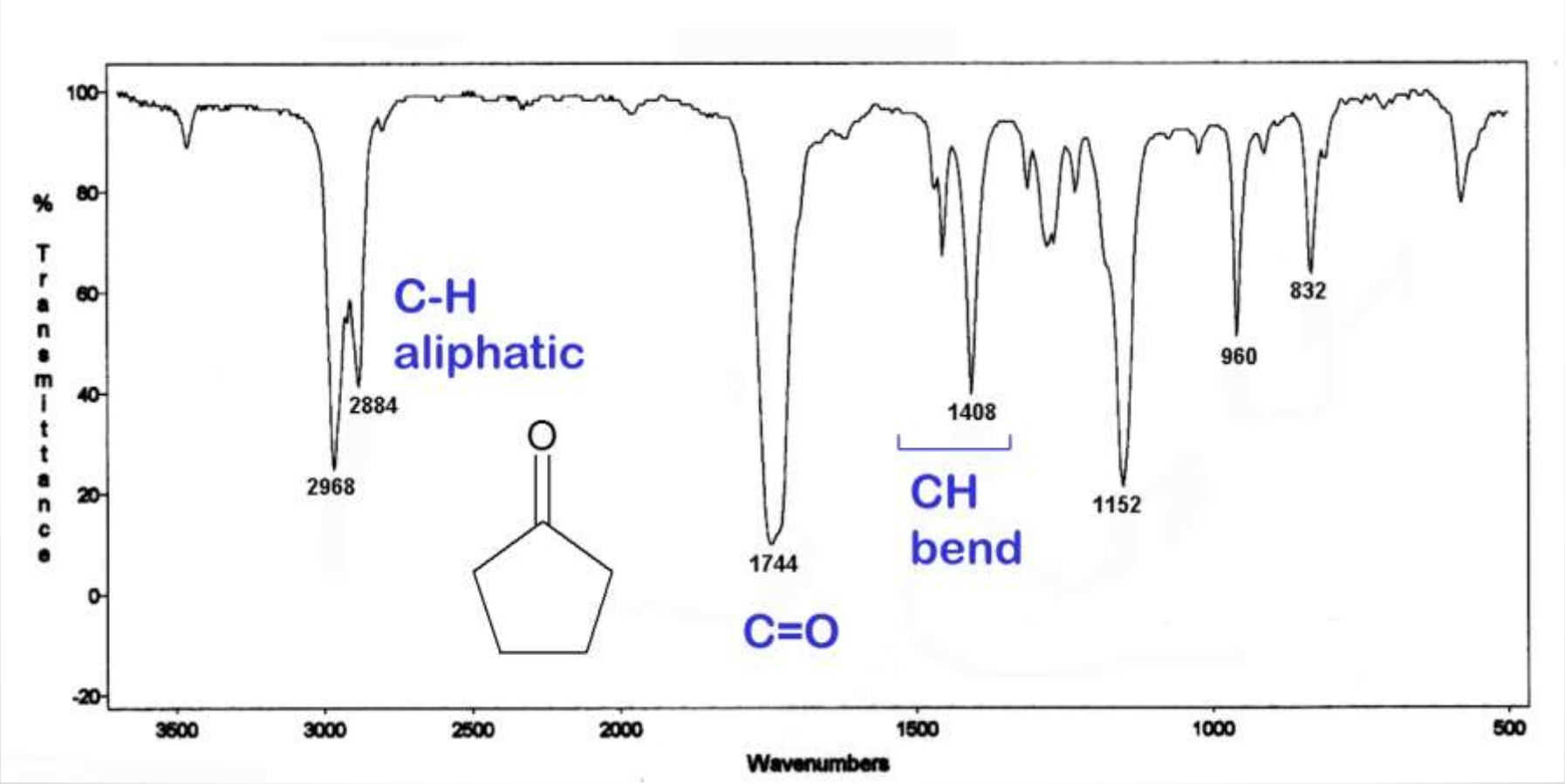
1 A smaller angle requires more p character in the hybrids forming the ring.

Conjugation and Ring Size Effects

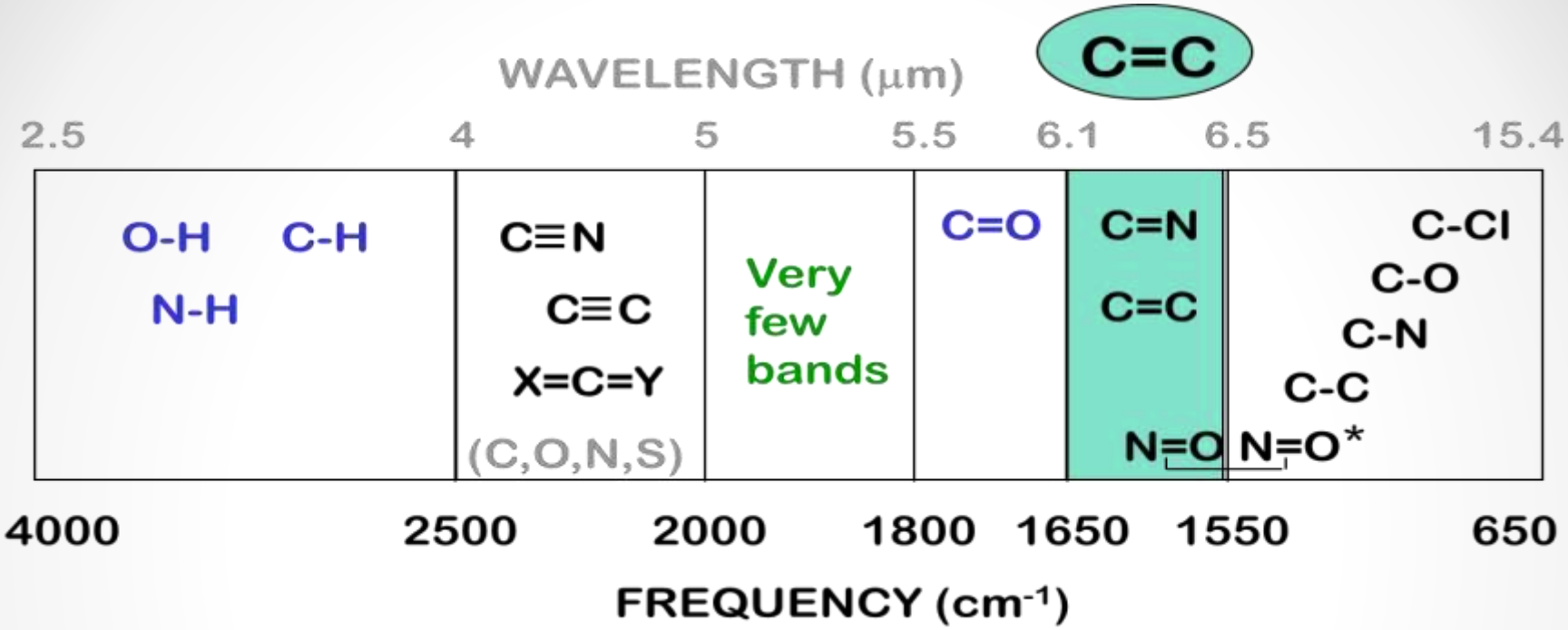


Cyclic Ketone
5-ring

Cyclopentanone



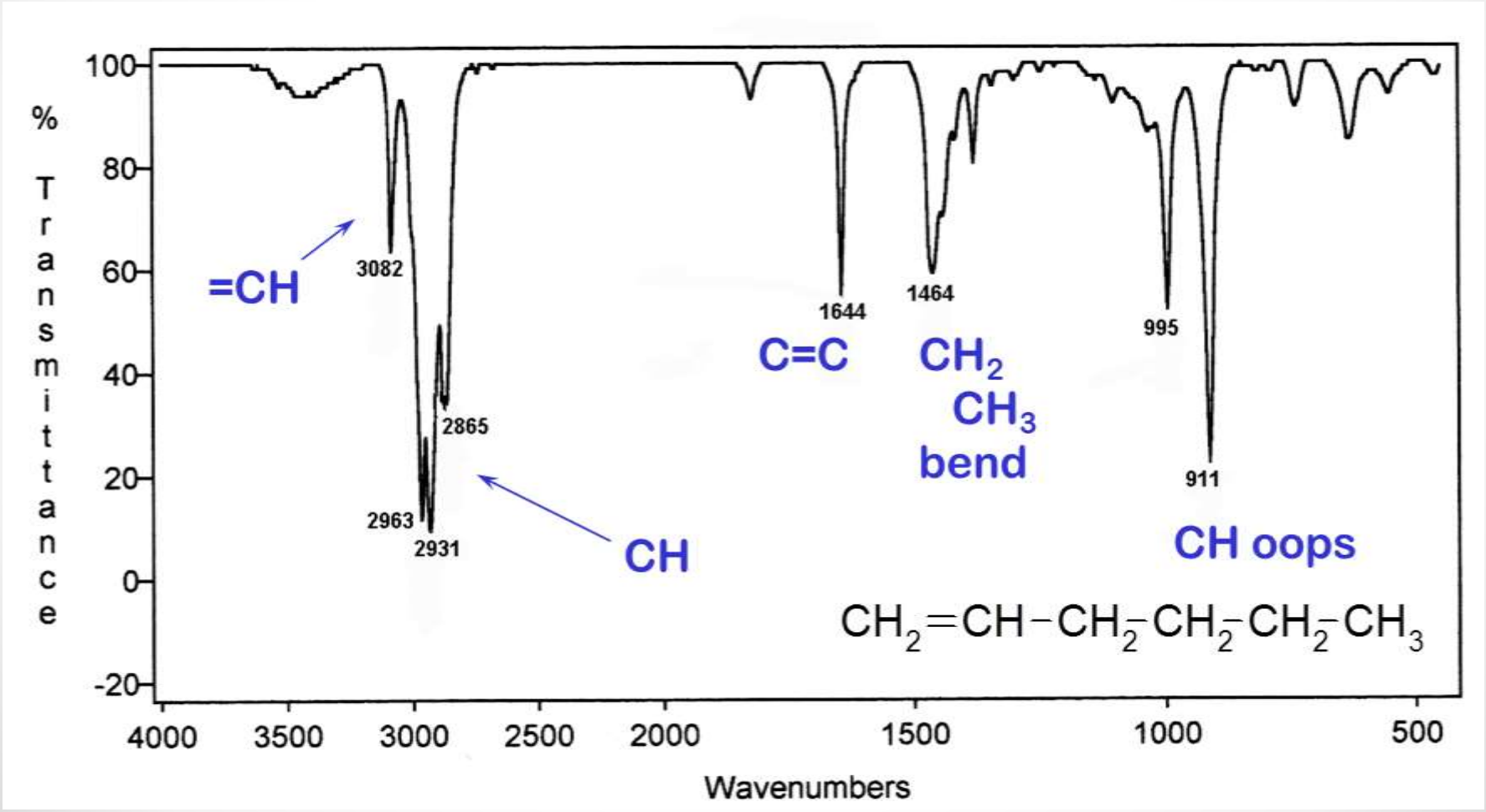
The C=C stretching region



- C=C double bond at 1650 cm^{-1} is often weak or not even seen.
- C=C benzene ring shows peak(s) near 1600 and 1475 cm^{-1} , one or two at each value - Conjugation lowers the value.
- When C=C is conjugated with C=O it is stronger and comes at a lower frequency.

Alkene

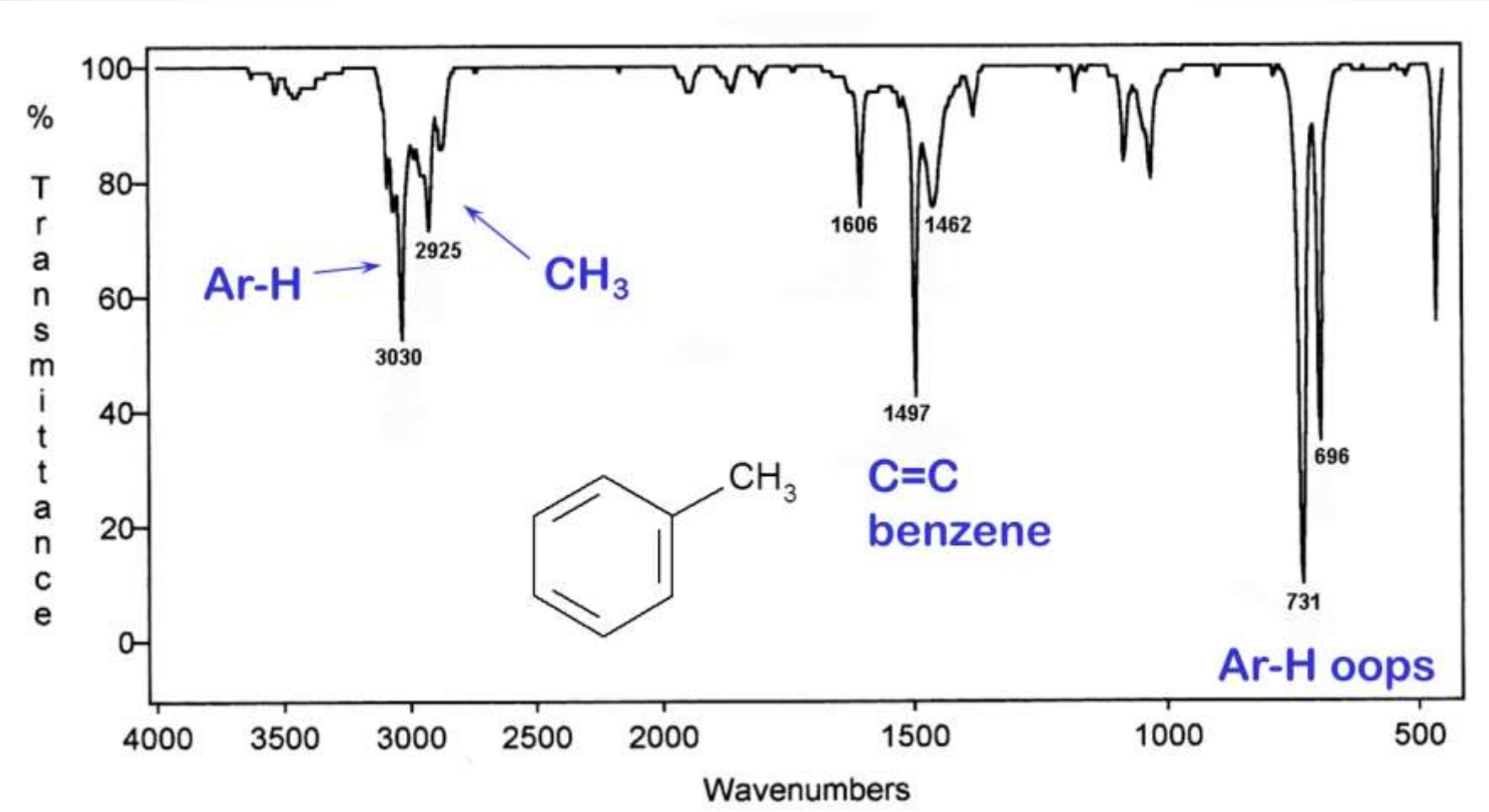
1-Hexene



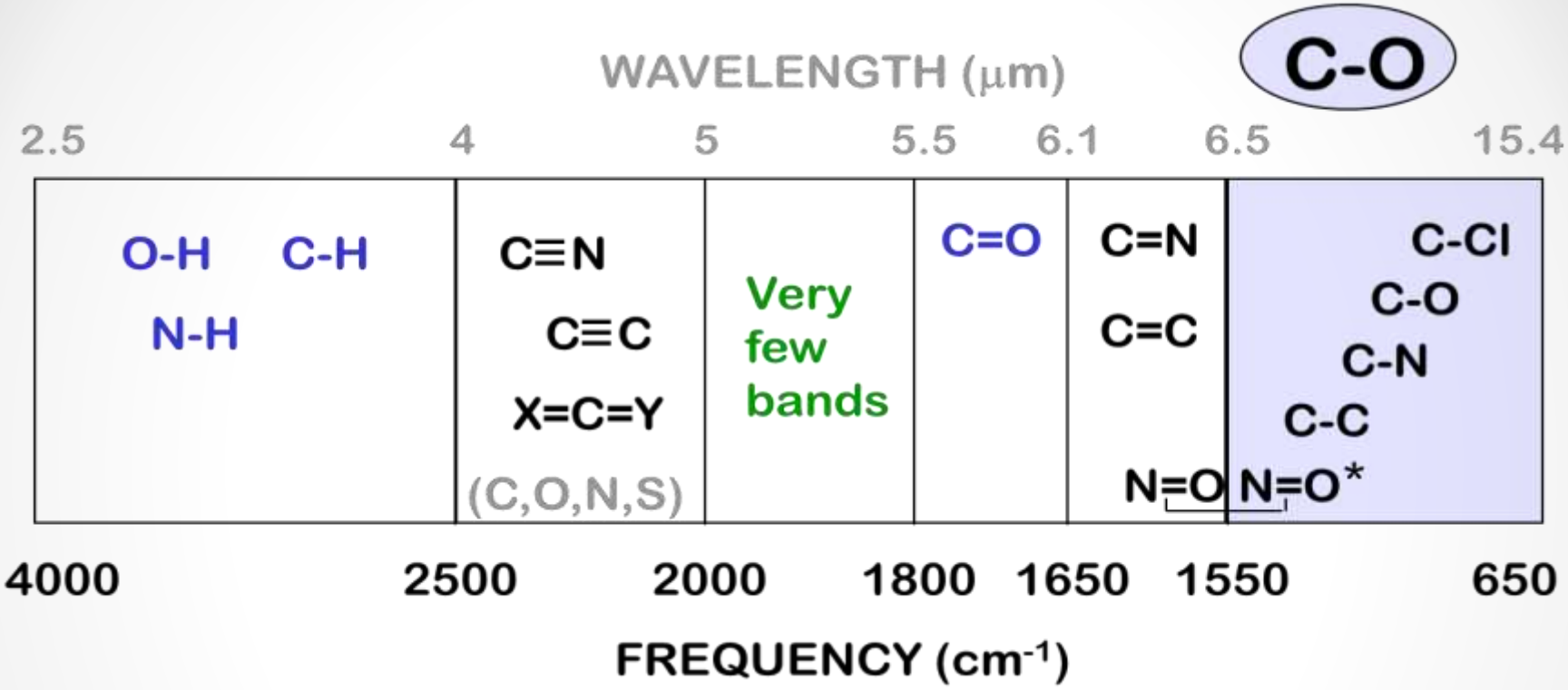
58

Aromatic

Toluene



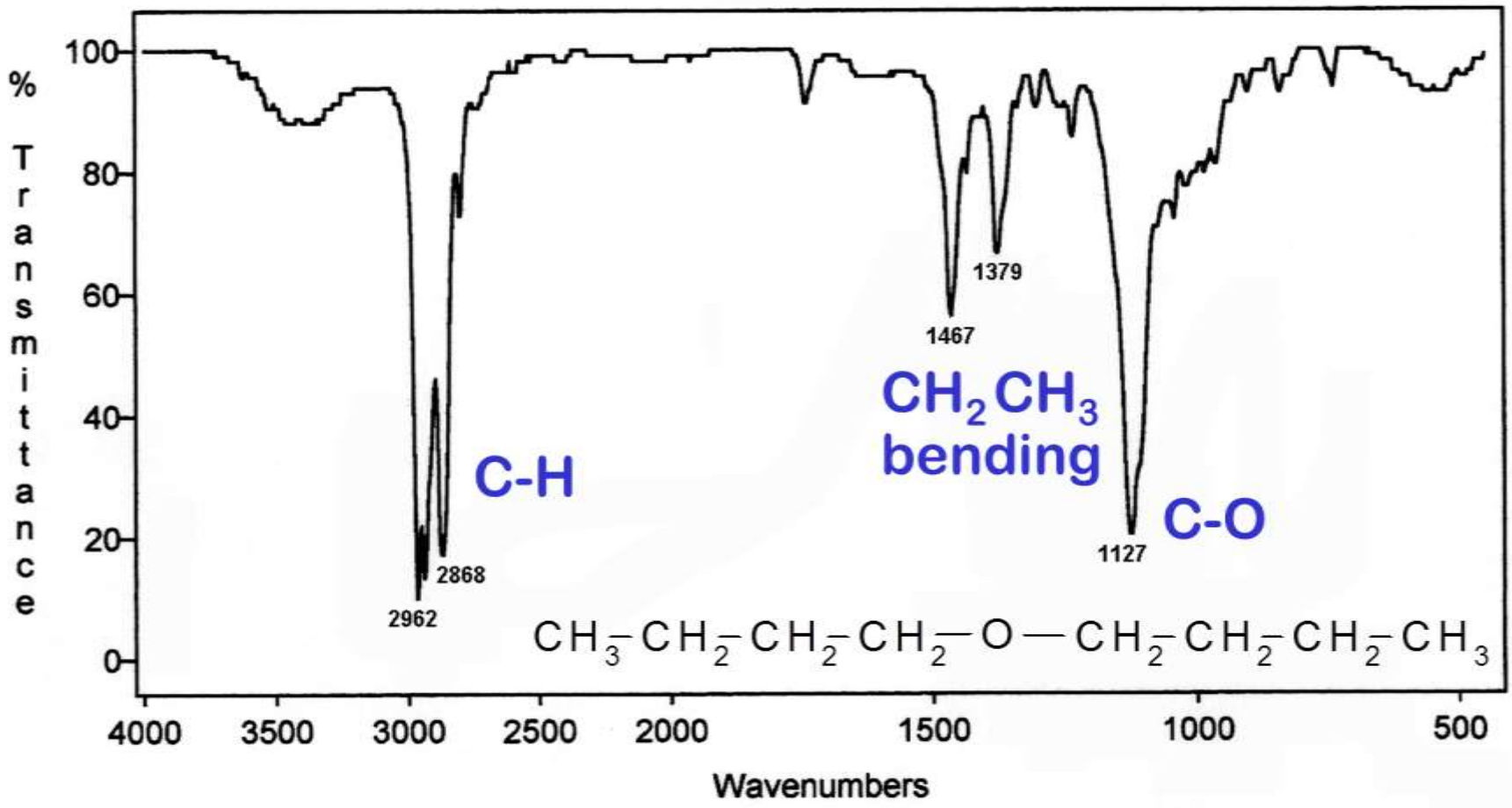
The C-O stretching region



- The C-O band appears in the range of 1300 to 1000 cm^{-1}.
- Look for one or more strong bands appearing in this range!
- Ethers, alcohols, esters and carboxylic acids have C-O bands.

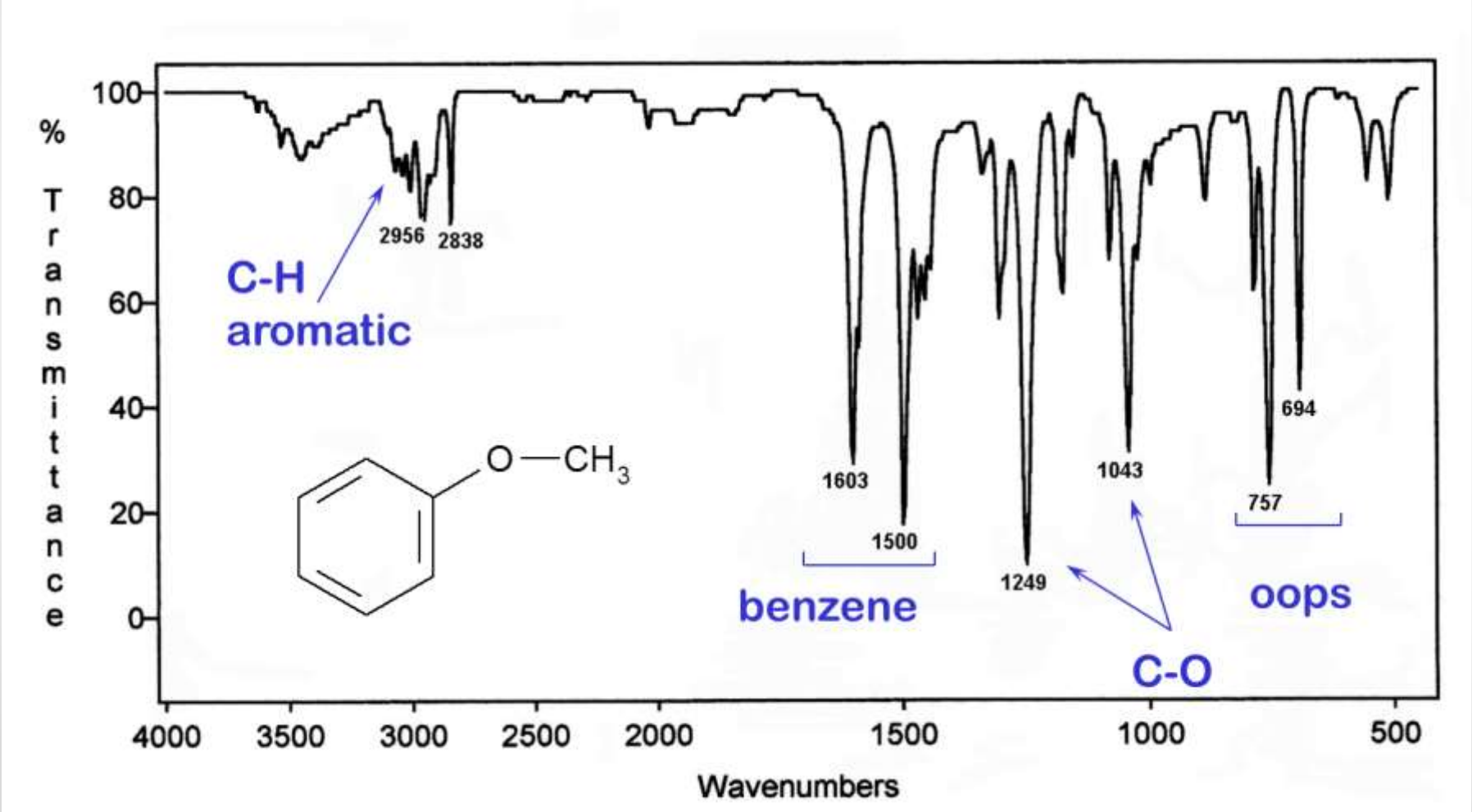
Ether
Base = 1100

Dibutyl Ether



Aromatic Ether
Base = 1100

Anisole

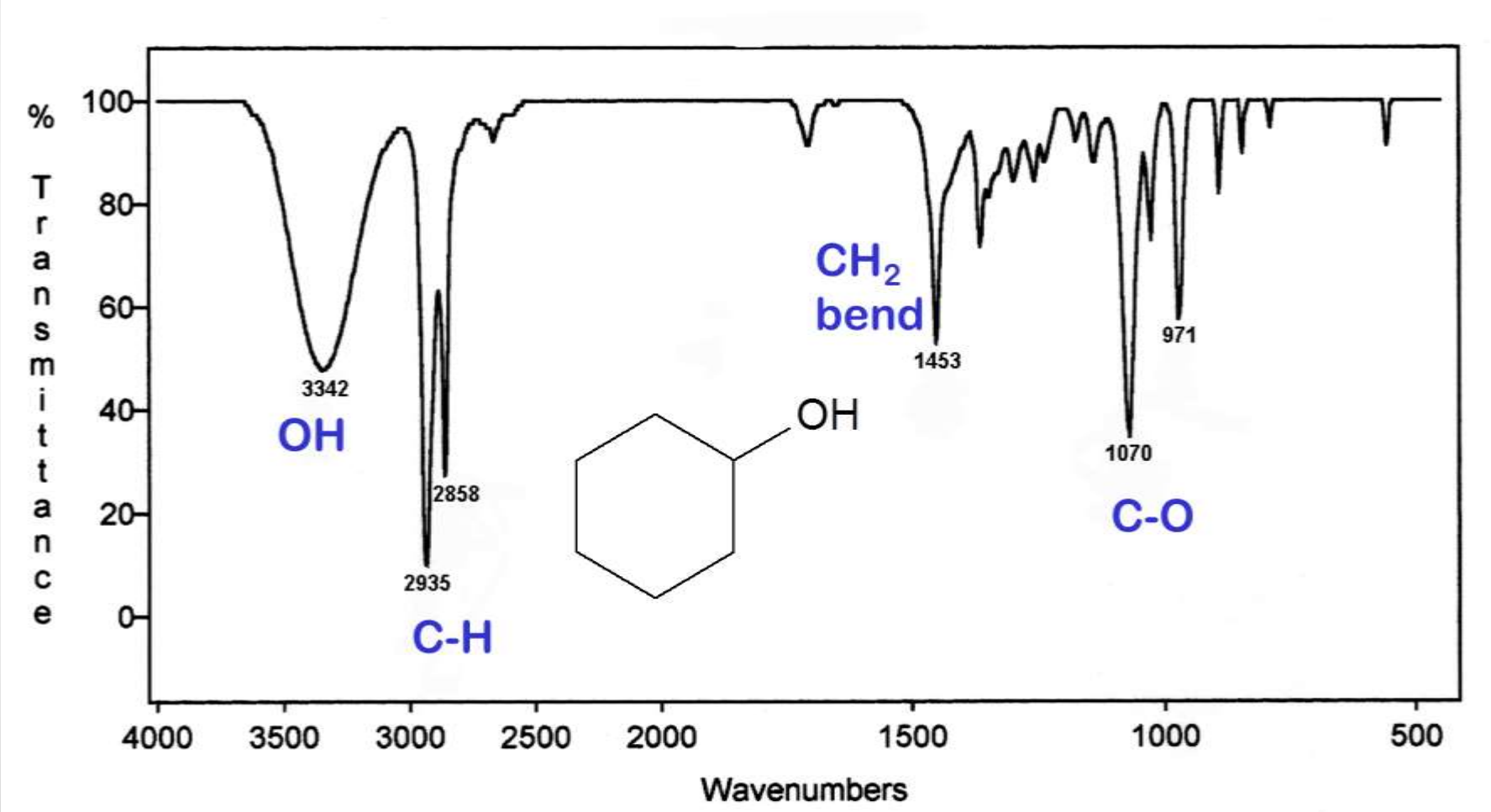


Alcohol

Base = 3600

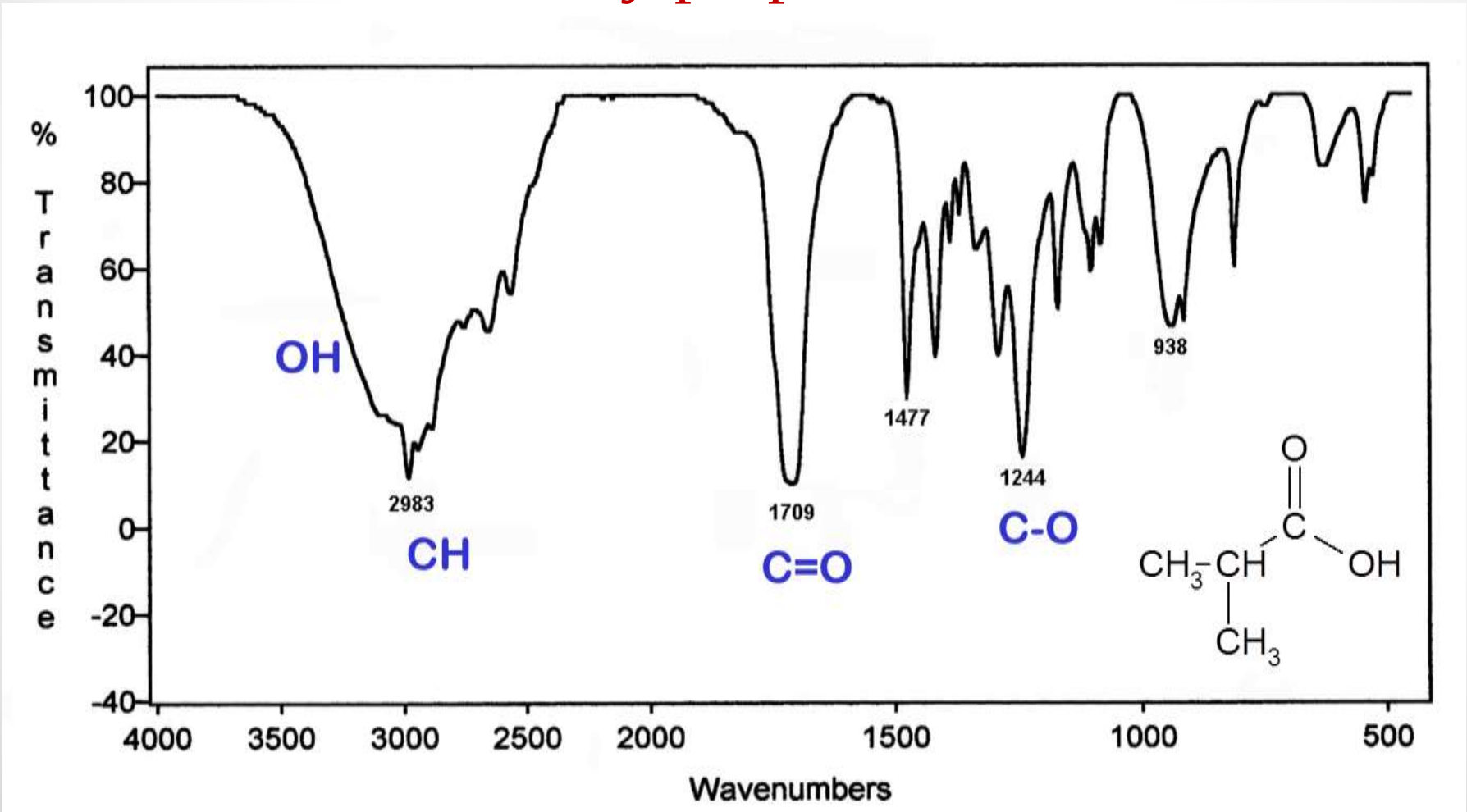
Base = 1100

Cyclohexanol

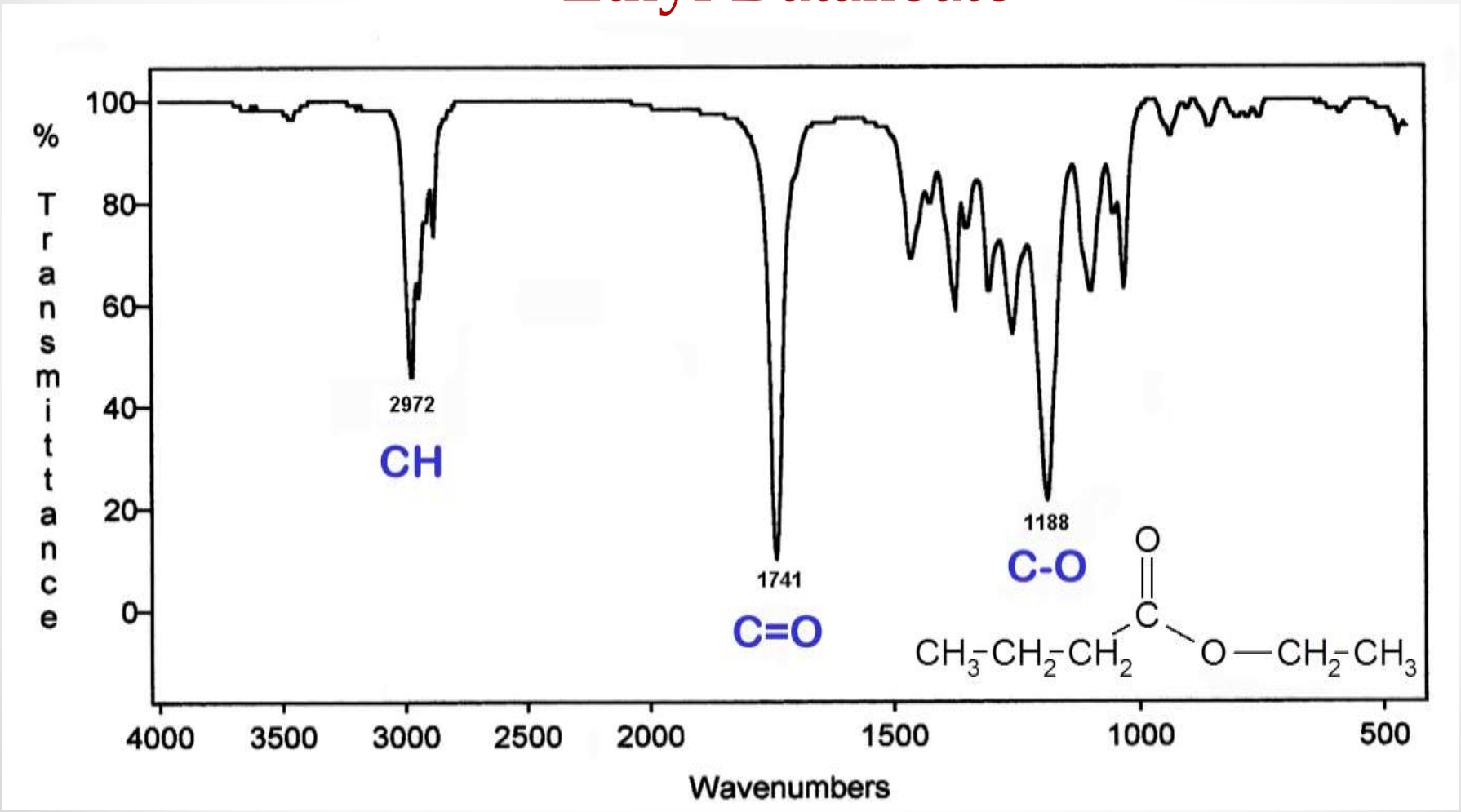


Carboxylic acid

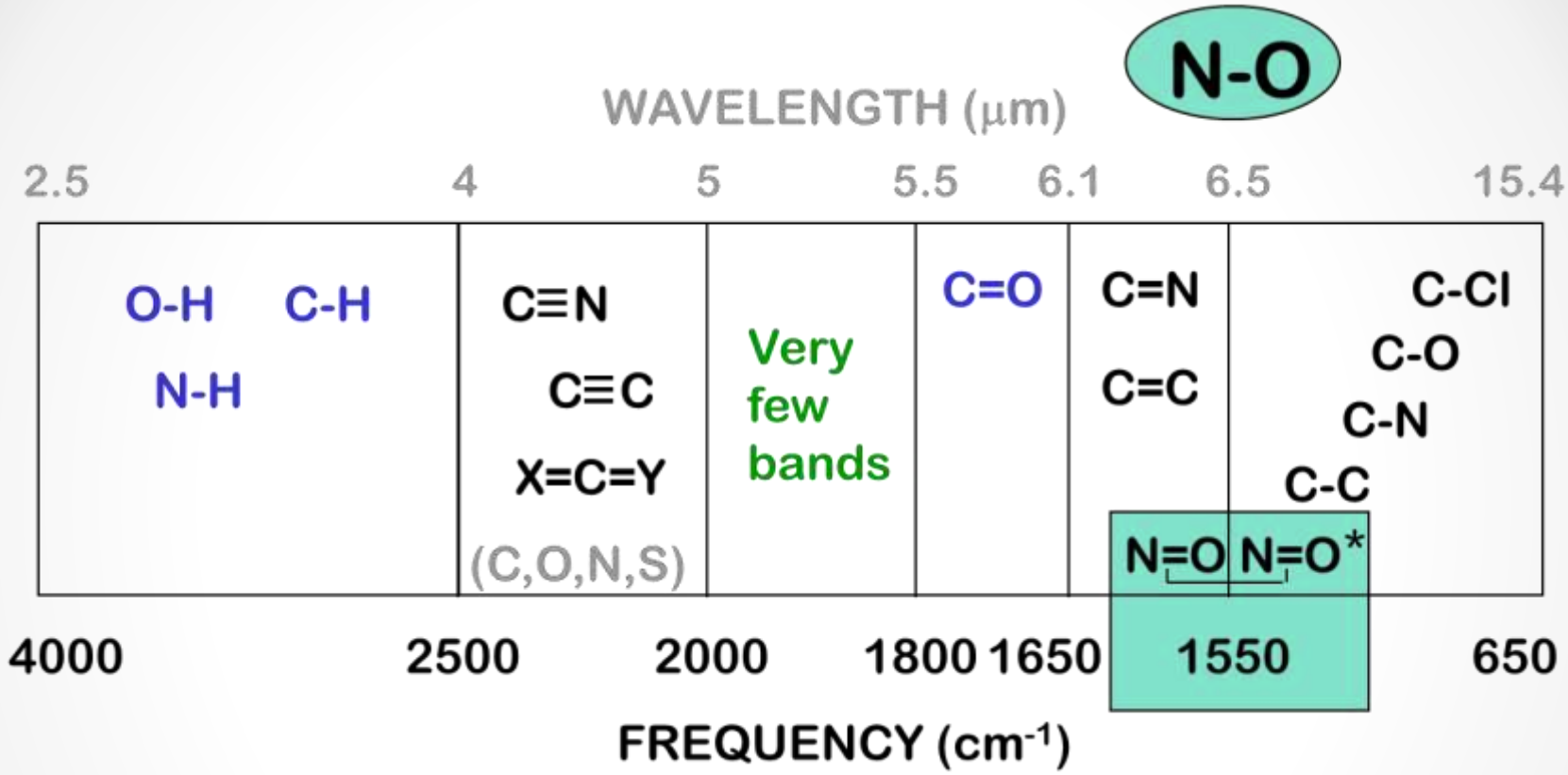
2-Methylpropanoic Acid



Ethyl Butanoate

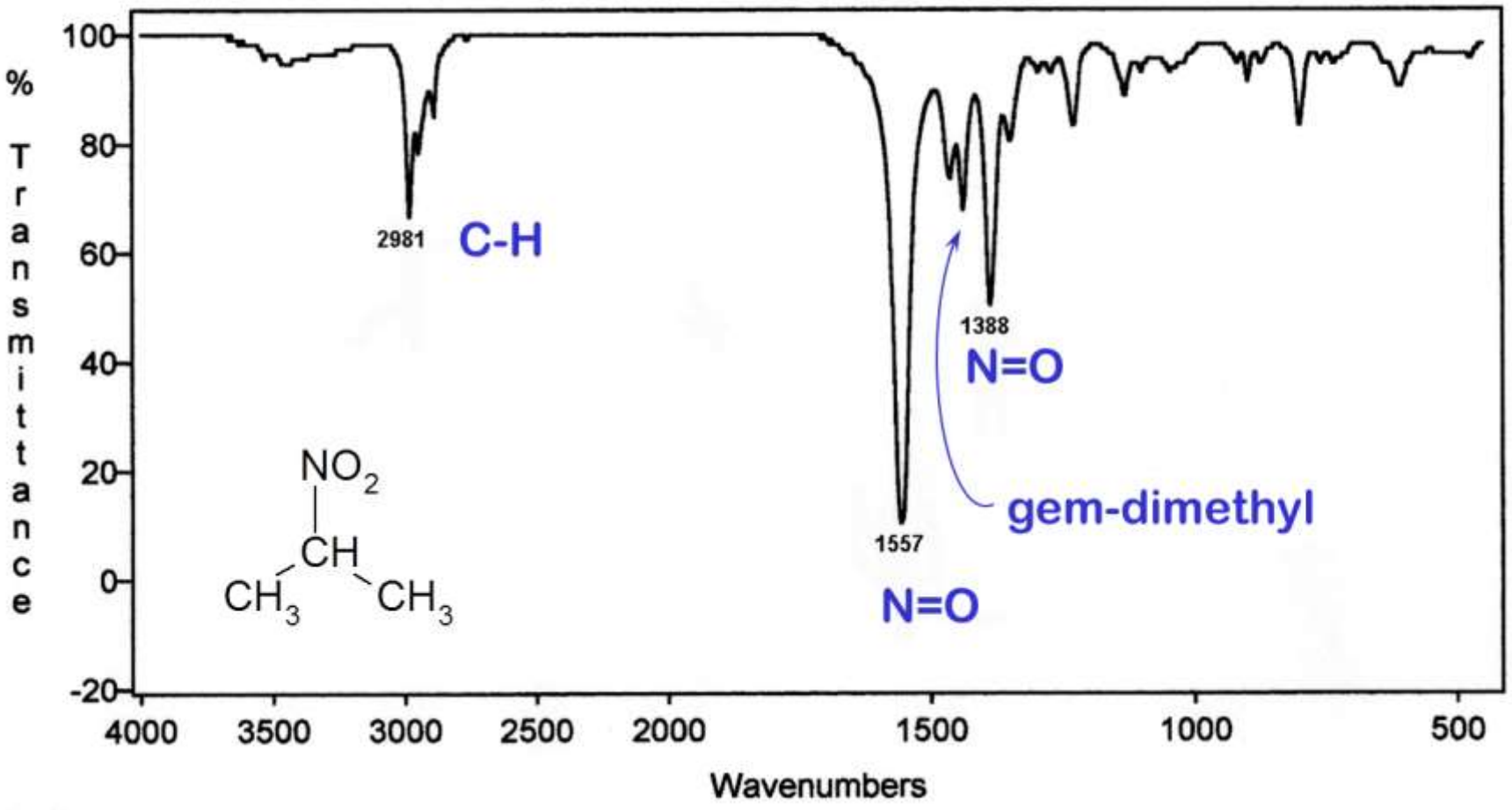


The N=O stretching region

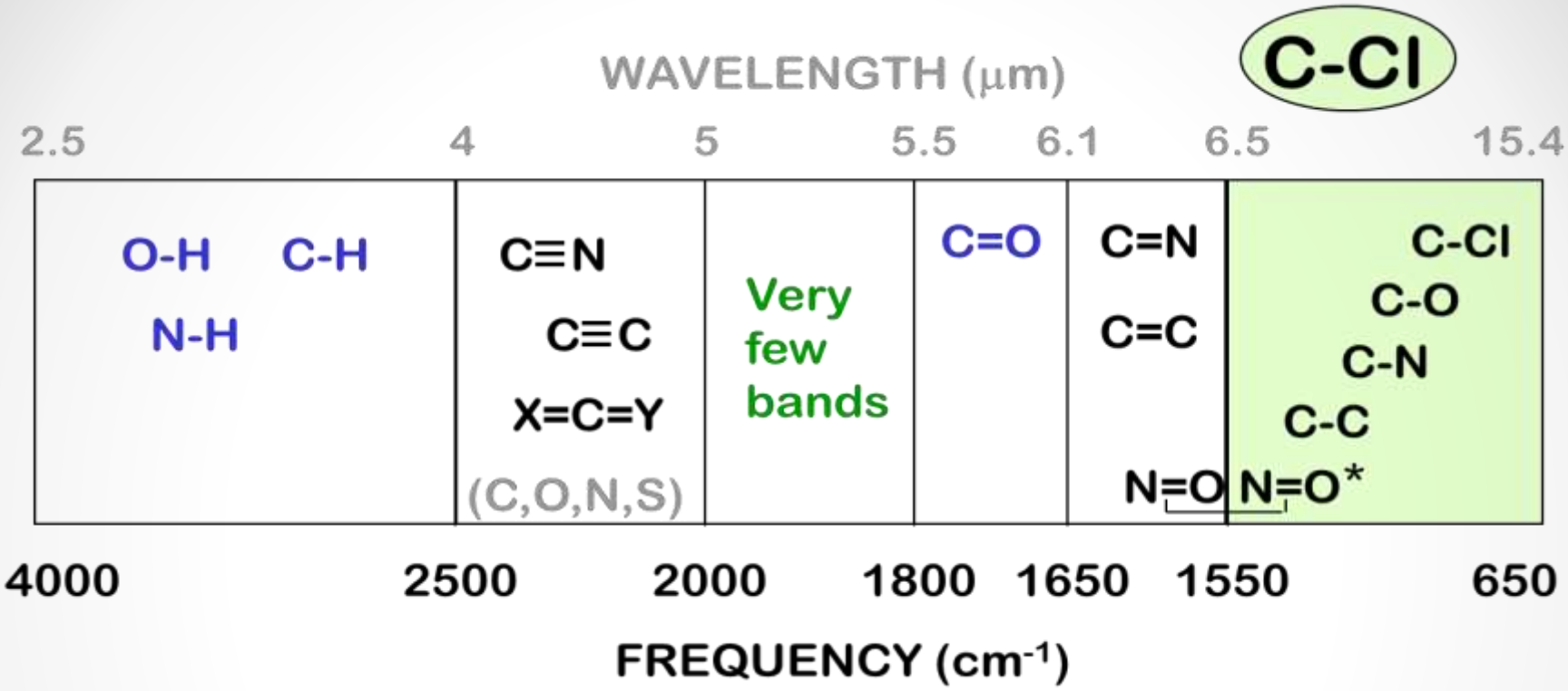


- N=O stretching : 1550 and 1350 cm^{-1} asymmetric and symmetric stretching.
- Often the 1550 cm^{-1} peak is stronger than the other one.

2-Nitropropane

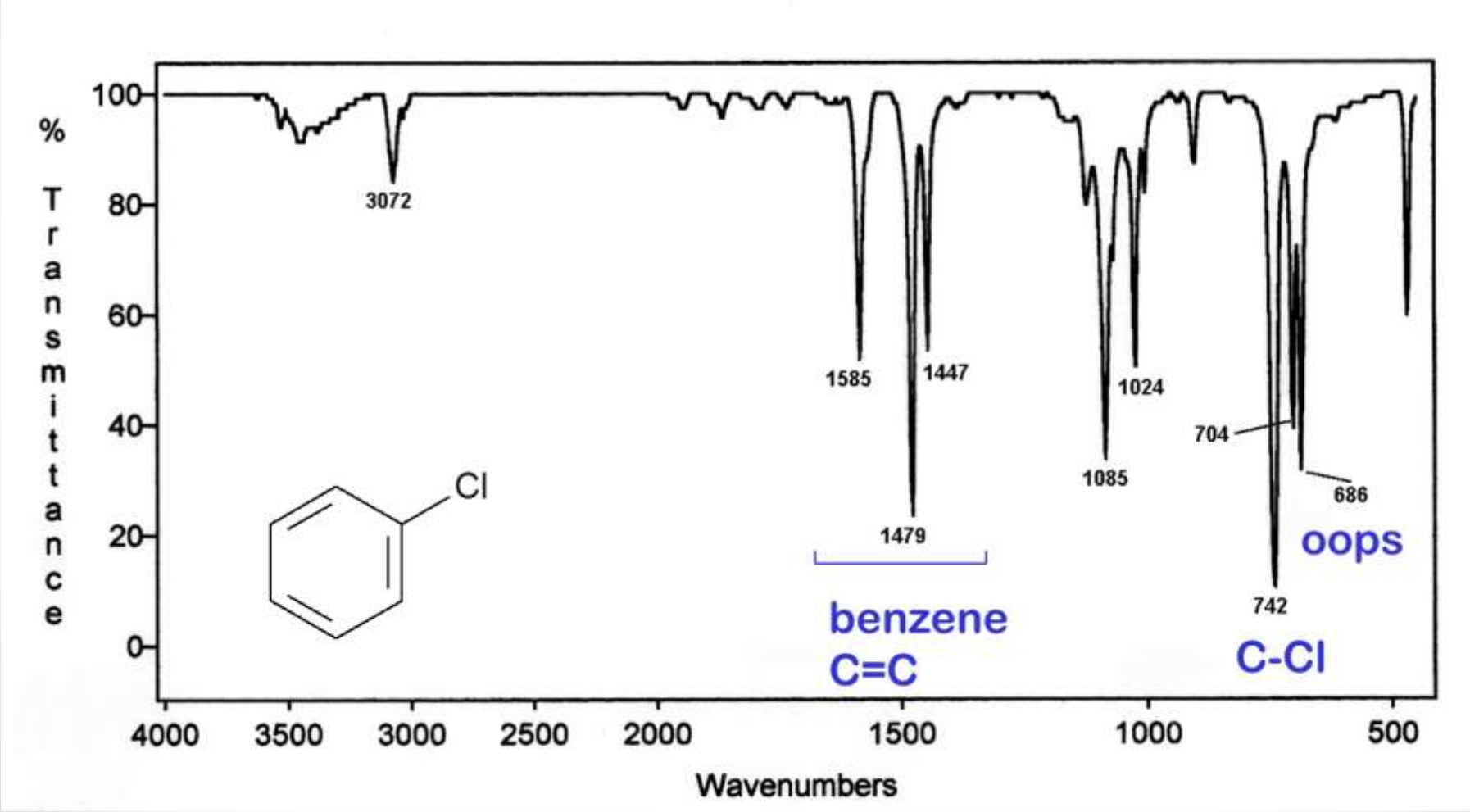


The C-X stretching region



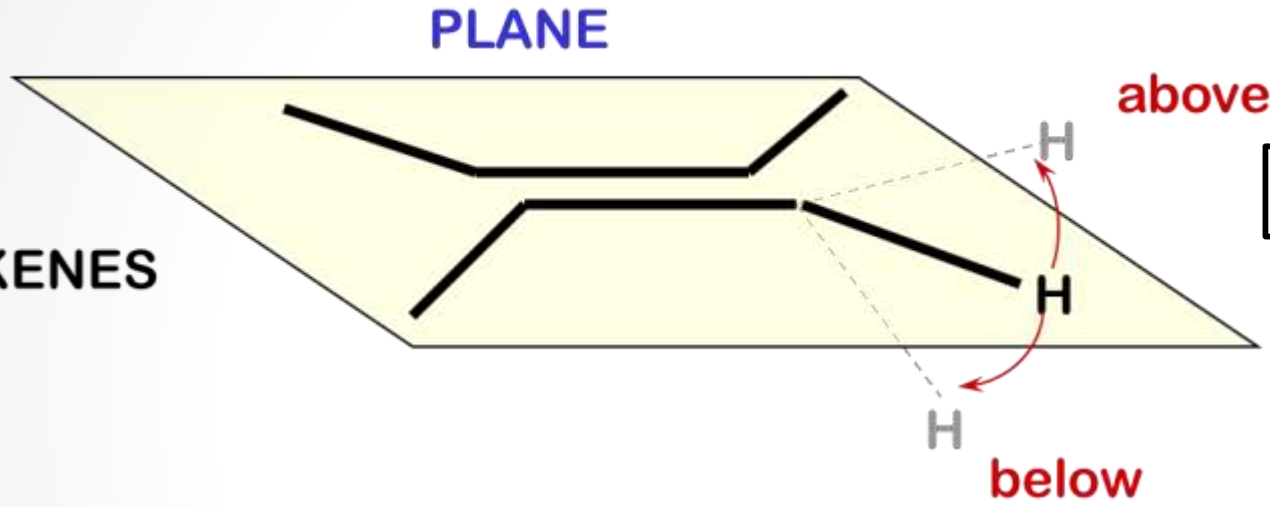
- C-Cl 785 to 540 cm^{-1},
  often hard to find amongst the fingerprint bands!!
- C-Br and C-I
  appear outside the useful range of infrared spectroscopy.
- C-F bonds can be found easily, but are not that common.

Chlorobenzene



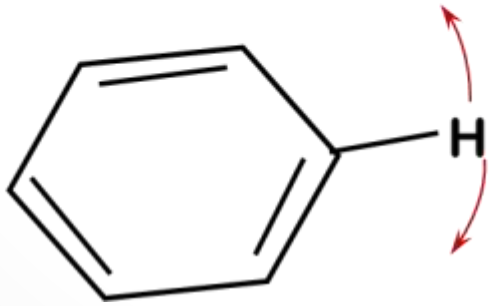
C-H Out-of-Plane Bending

(OOPS)



ALKENES

1000 to 650 cm^{-1}



also with

BENZENES

900 to 690 cm^{-1}

Alkenes

Monosubstituted

Disubstituted

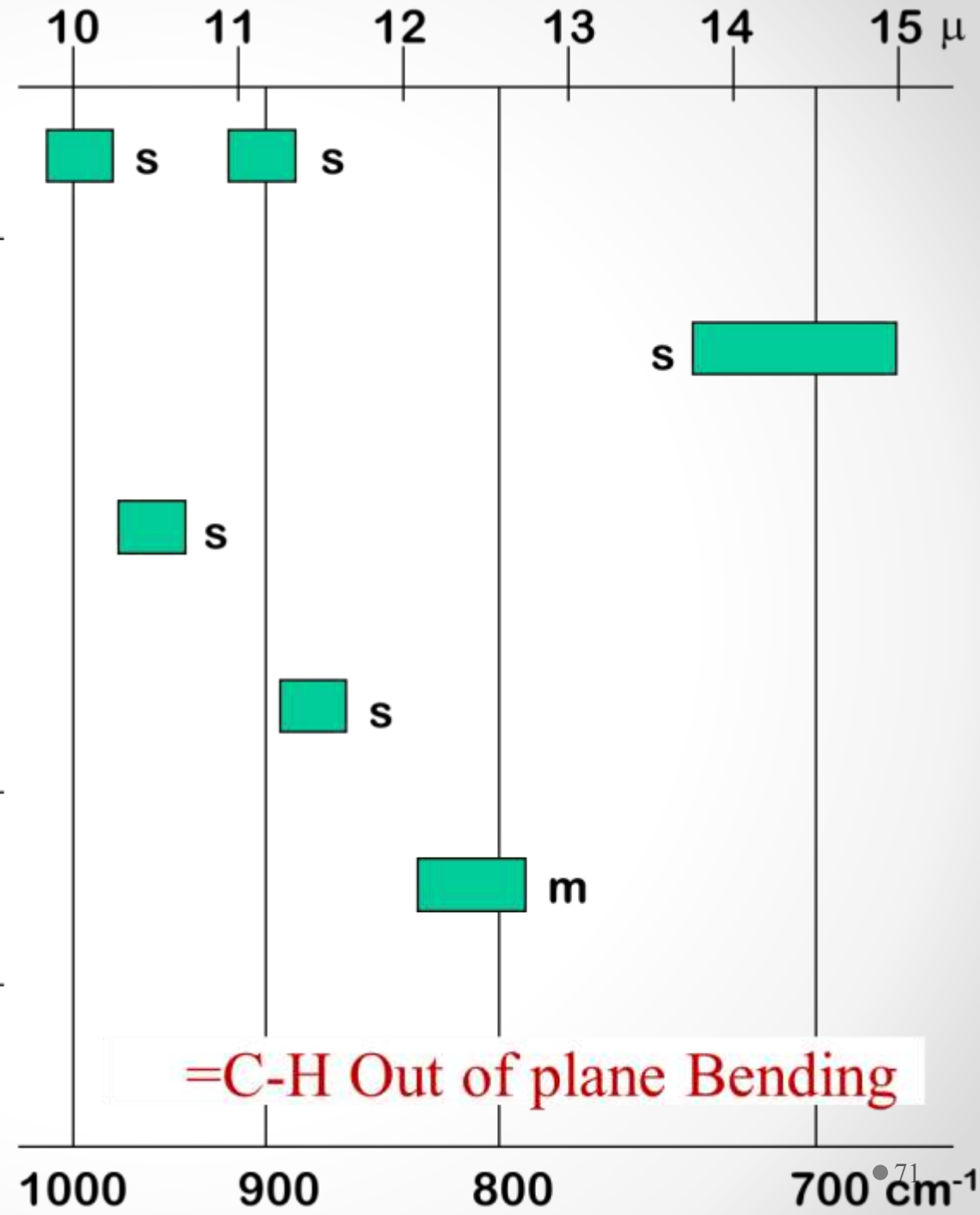
cis-1,2-

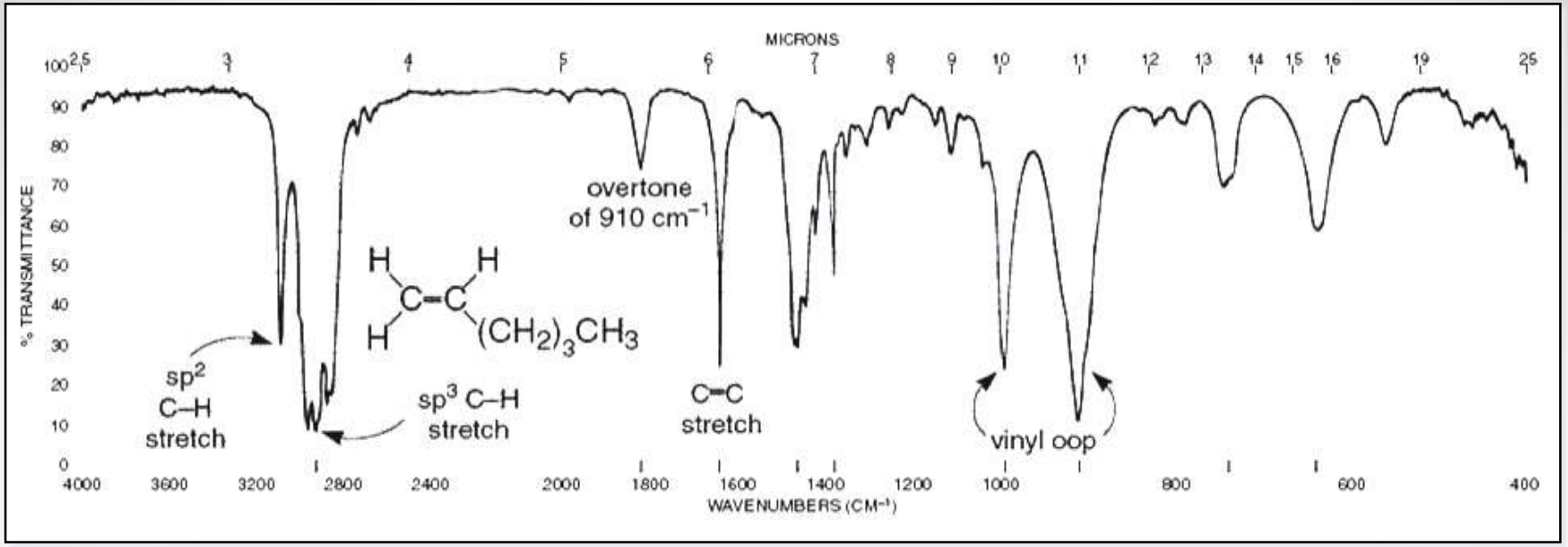
trans-1,2-

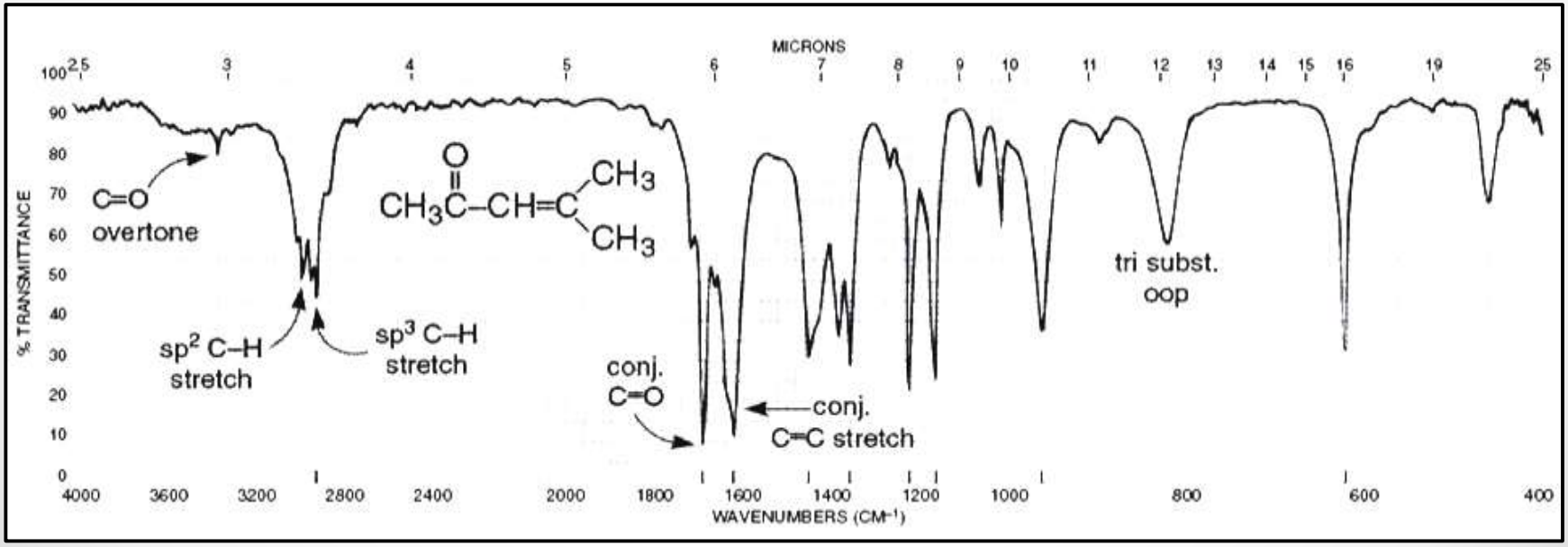
1,1-

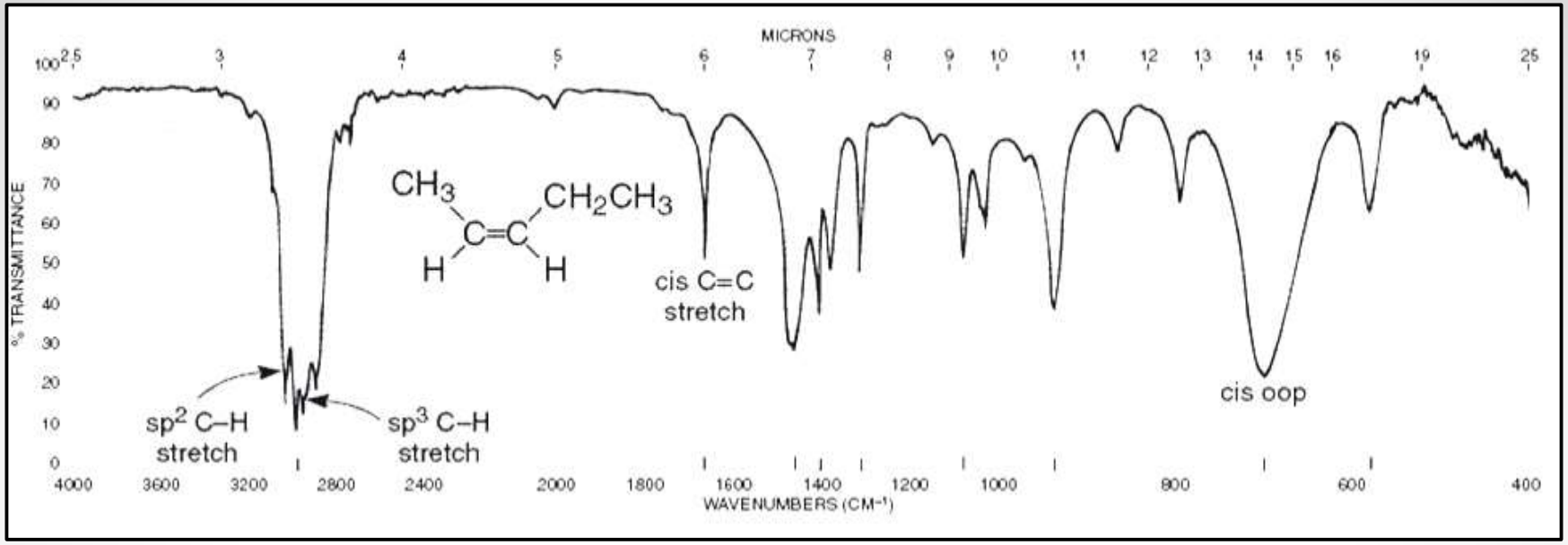
Trisubstituted

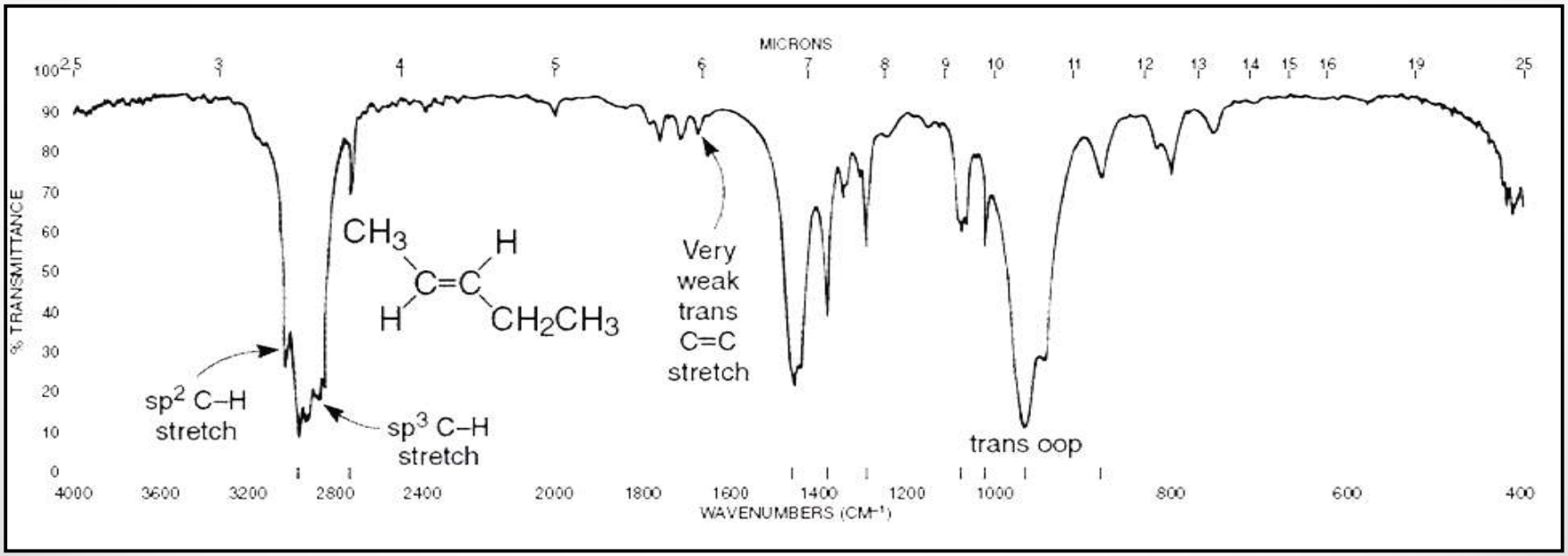
Tetrasubstituted



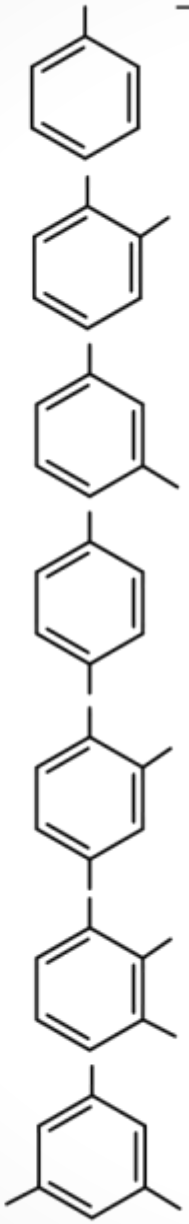

MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
overtone of 910 cm⁻¹
sp² C–H stretch
sp³ C–H stretch
C=C stretch
vinyl oop


MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
C=O overtone
sp² C–H stretch
sp³ C–H stretch
conj. C=O
conj. C=C stretch
tri subst. oop


MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
CH3
CH2CH3
C=C
H
H
cis C=C stretch
cis oop
sp2 C–H stretch
sp3 C–H stretch


MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
CH3
H
C=C
H
CH2CH3
Very weak trans C=C stretch
trans oop
sp2 C–H stretch
sp3 C–H stretch

Benzenes



Monosubstituted

Disubstituted

ortho

meta

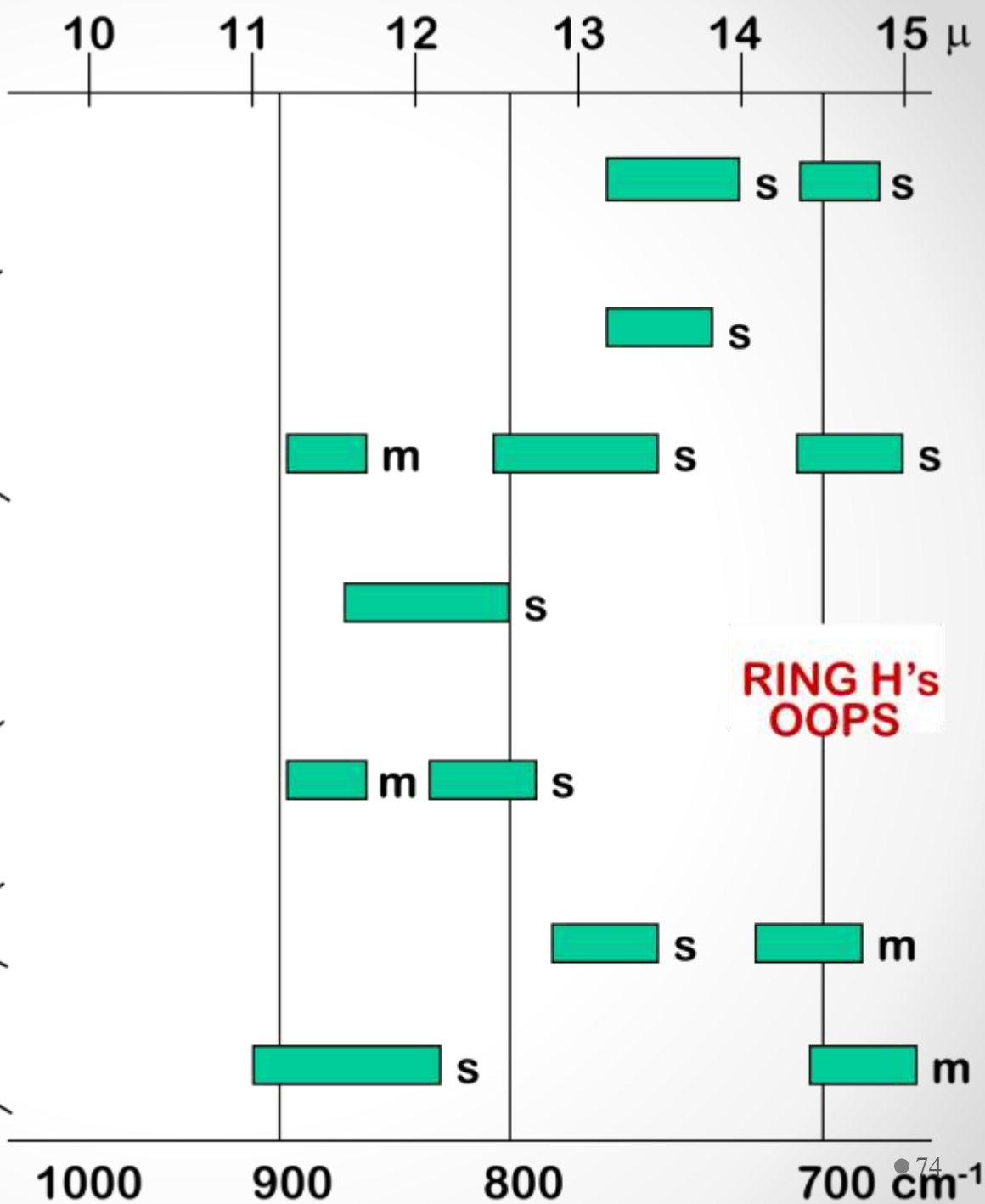
para

Trisubstituted

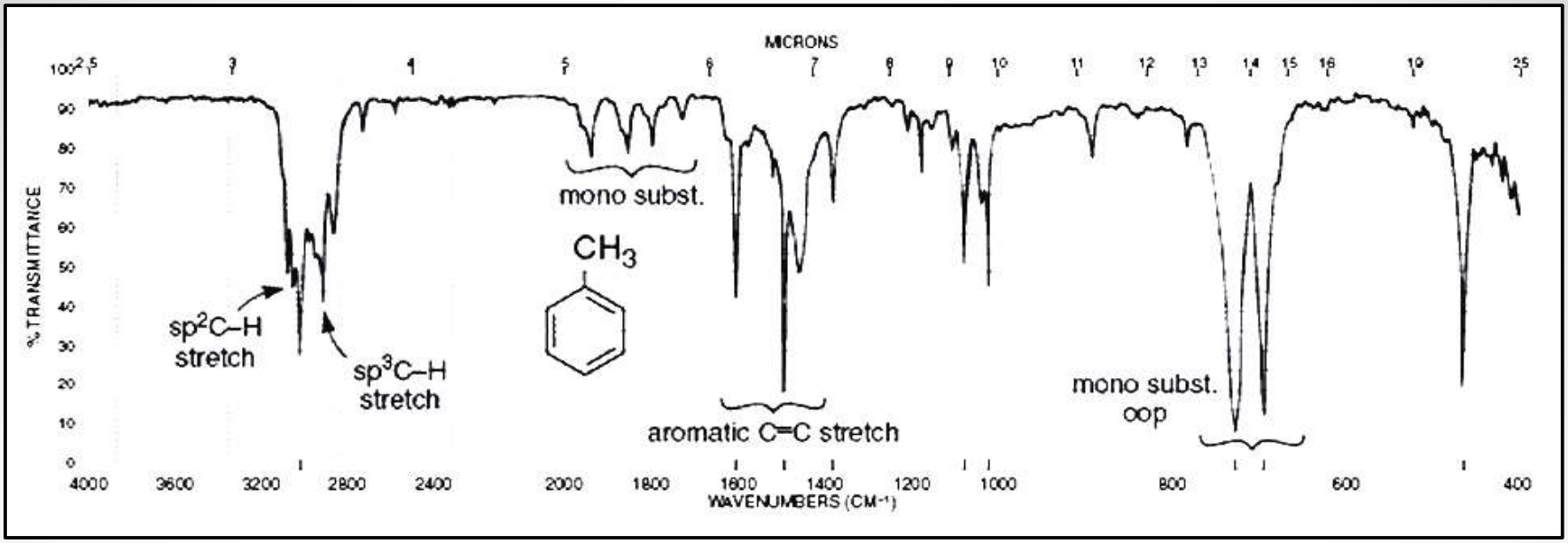
1,2,4

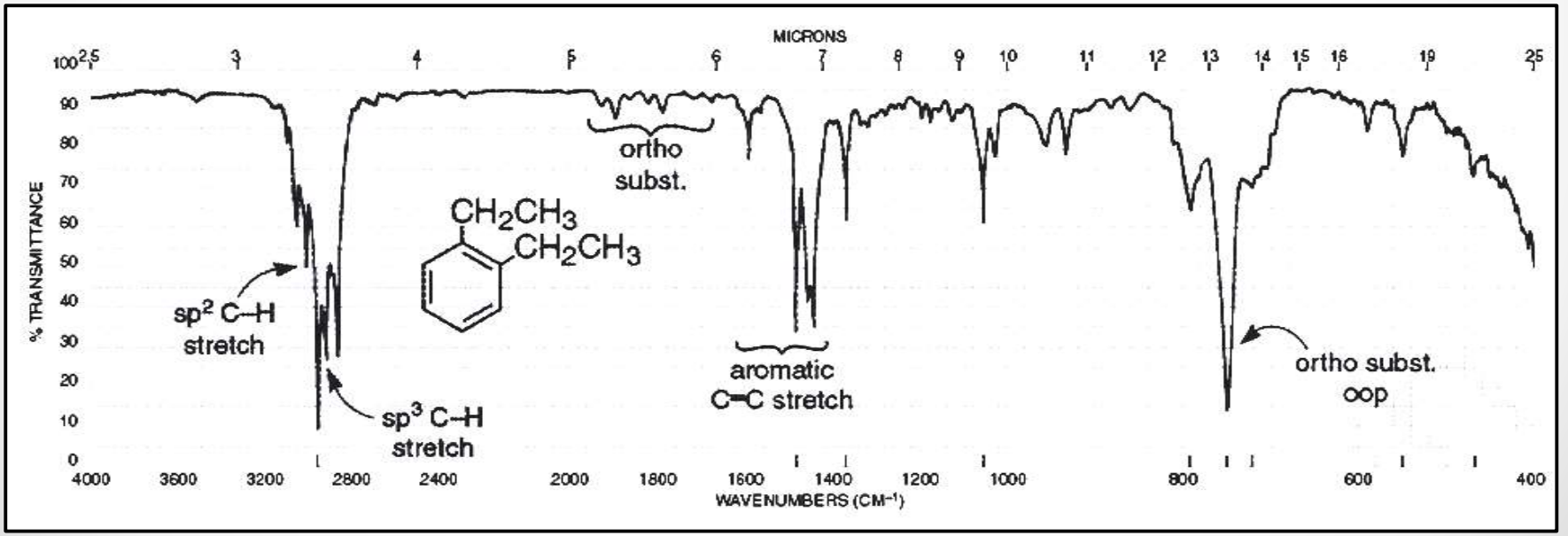
1,2,3

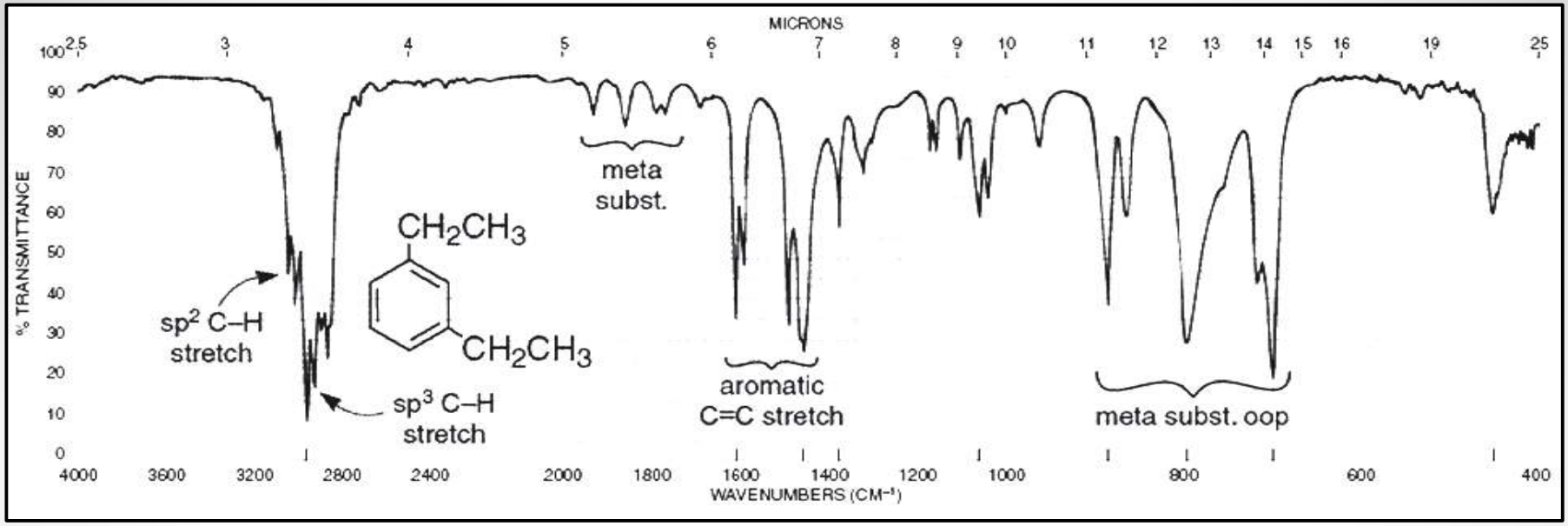
1,3,5

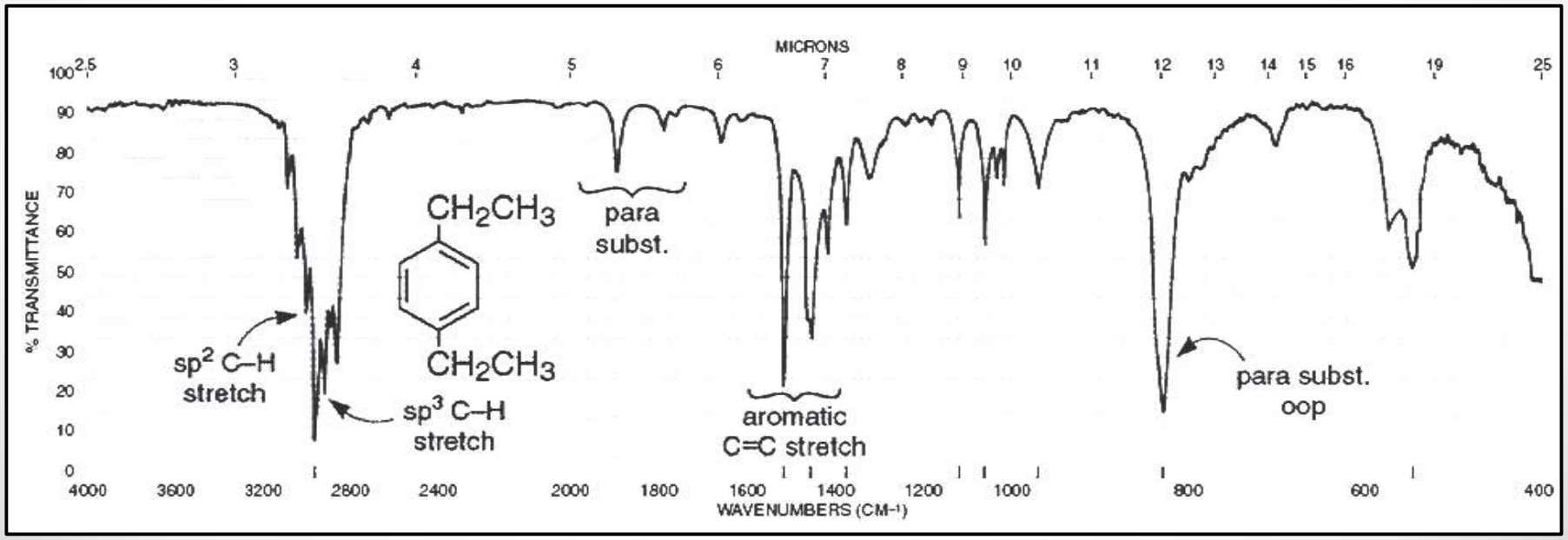


combination bands

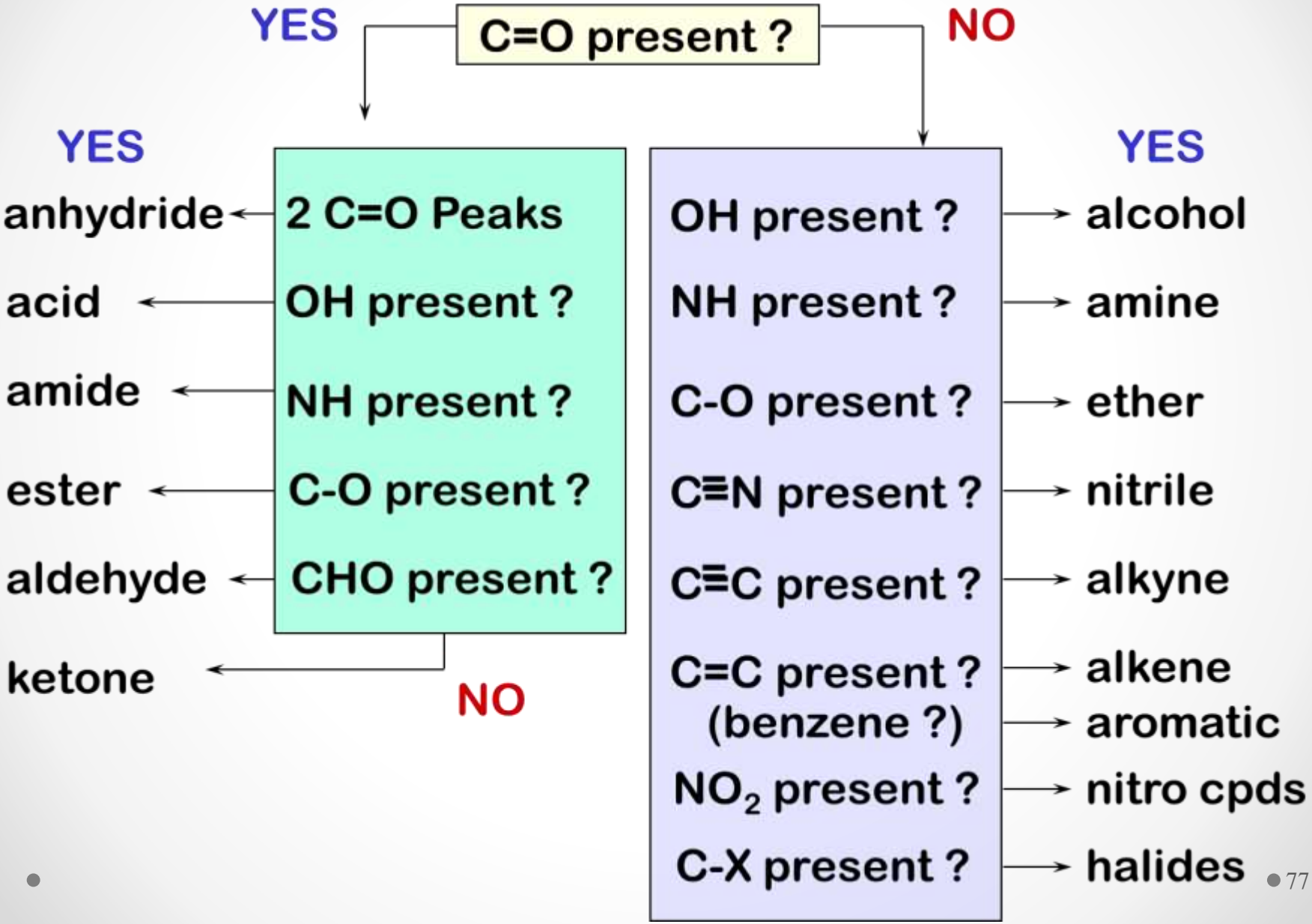

MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
mono subst.
CH3
sp2C–H stretch
sp3C–H stretch
aromatic C=C stretch
mono subst. oop


MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
ortho subst.
CH2CH3
CH2CH3
sp2 C–H stretch
sp3 C–H stretch
aromatic C=C stretch
ortho subst. oop

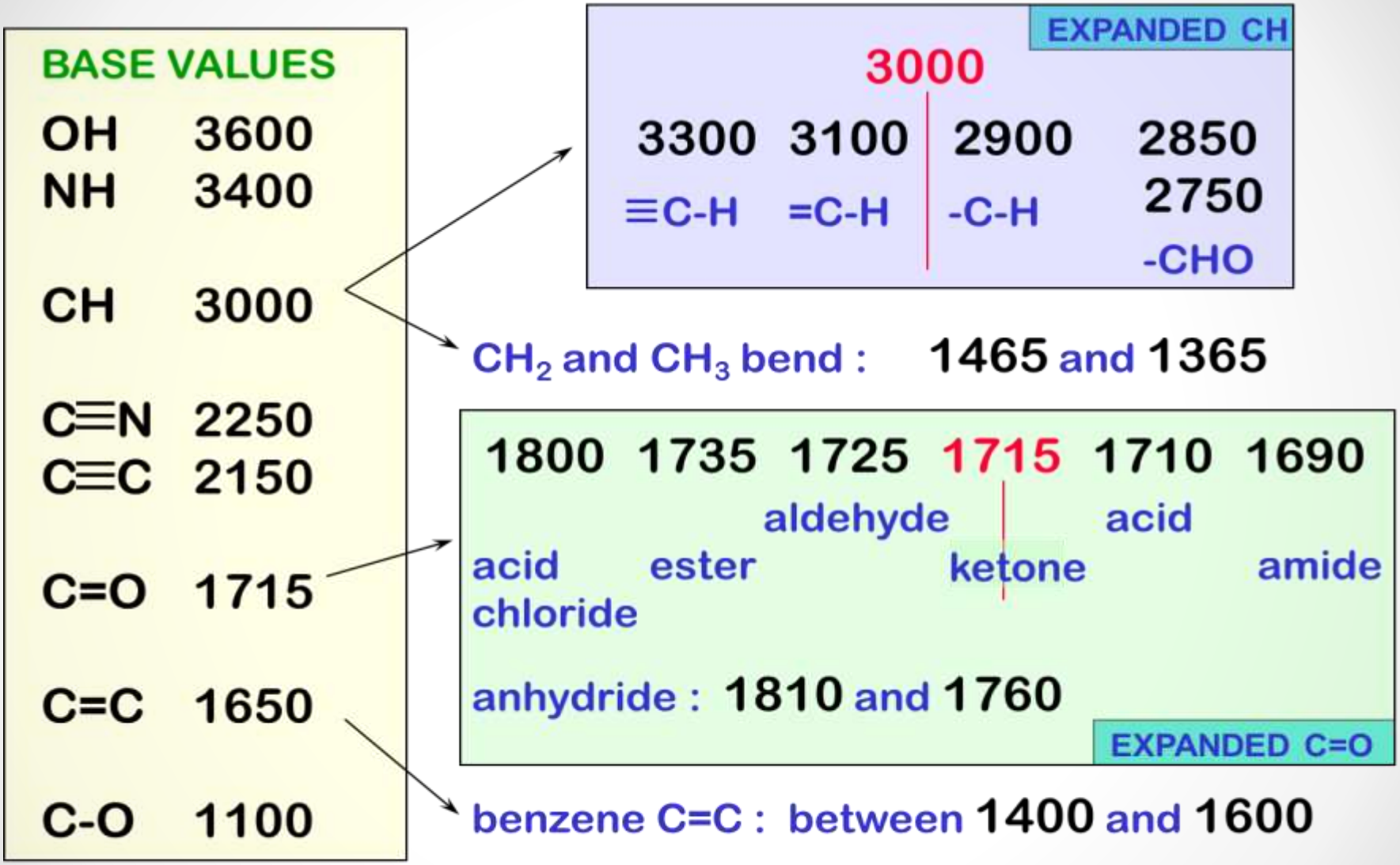

MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
meta subst.
sp² C–H stretch
sp³ C–H stretch
aromatic C=C stretch
meta subst. oop
CH₂CH₃
CH₂CH₃


MICRONS
% TRANSMITTANCE
WAVENUMBERS (CM⁻¹)
para subst.
sp² C–H stretch
sp³ C–H stretch
aromatic C=C stretch
para subst. oop
CH₂CH₃
CH₂CH₃

Final Summary



The minimum you need to know



Know also the effects of H-bonding, conjugation and ring size.