Chapter 3

Infrared Spectroscopy IR

Infrared spectroscopy (IR

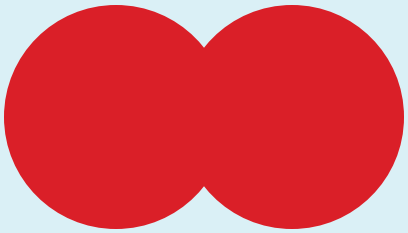
Infrared spectroscopy (IR)

measures the bond vibration frequencies in a molecule and is used to determine the functional group

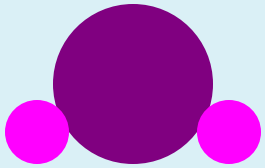
The IR Region

- Just below red in the visible region
- Wavelengths usually 2.5-25 μm
- More common units are wavenumbers, or cm^{-1}, the reciprocal of the wavelength in centimeters ($10^4/\mu m$ = 4000-400 cm^{-1})
- Wavenumbers are proportional to frequency and energy

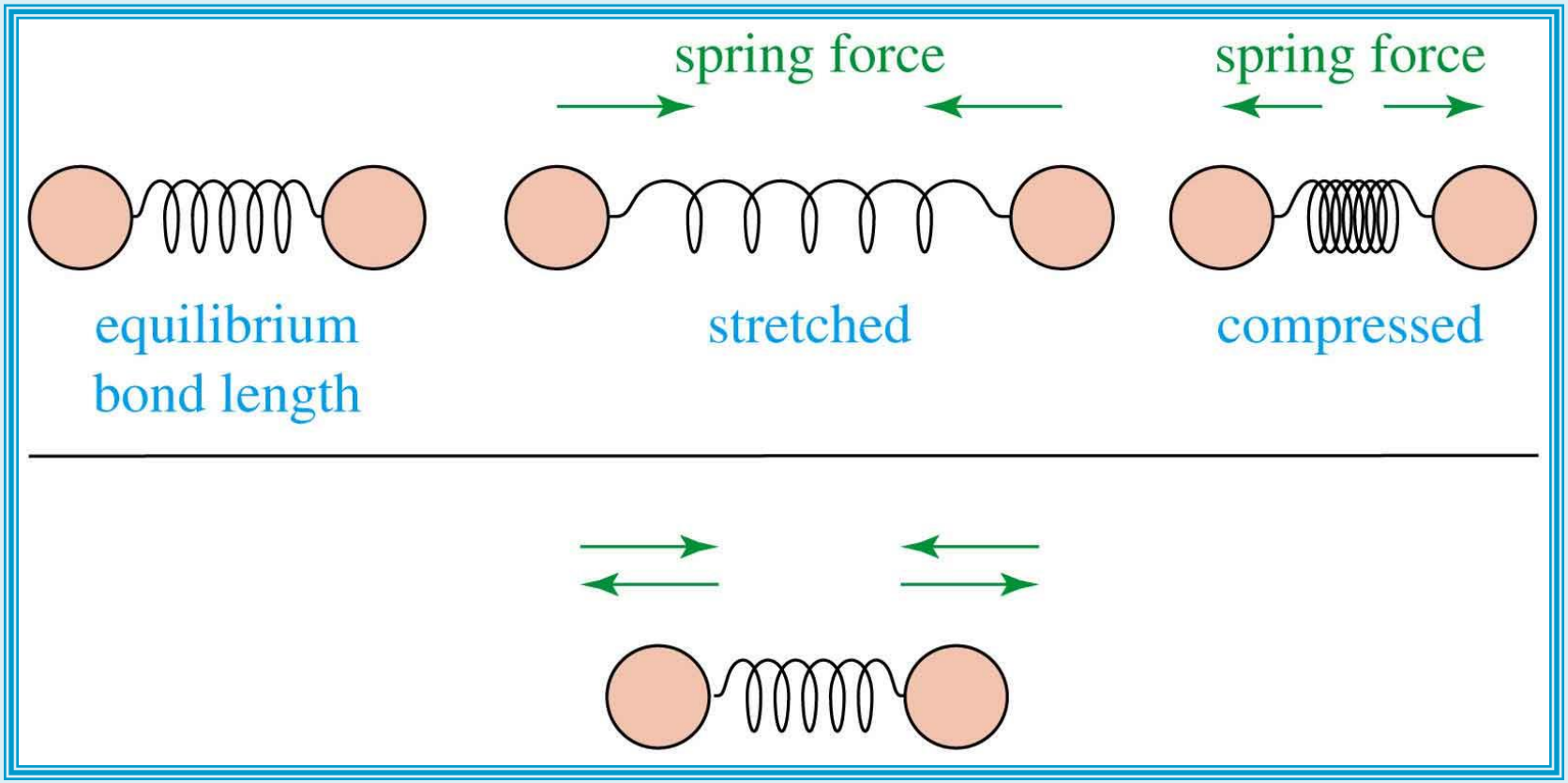
• The IR region is divided into three regions: the near, mid, and far IR. The mid IR region is of greatest practical use to the organic chemist.



Molecular Vibrations and IR Spectroscopy



Molecules are made up of atoms linked by chemical bonds. The movement of atoms and chemical bonds like spring and balls (vibration)



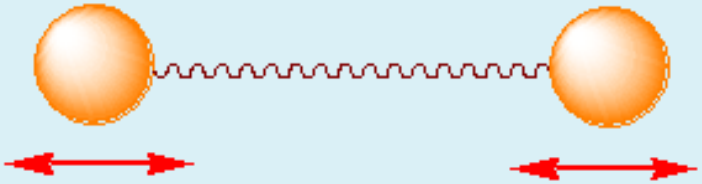
Vibrations

What is a vibration in a molecule?

Any change in shape of the molecule- stretching of bonds, bending of bonds, or internal rotation around single bonds

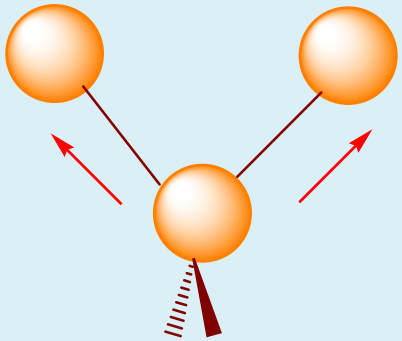
There are *two main vibrational modes* :

1. **Stretching:** change in bond length (higher frequency)

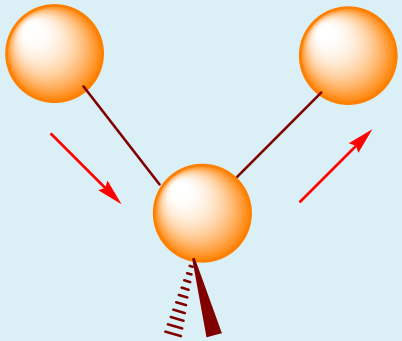


Stretching vibration

Stretching Types



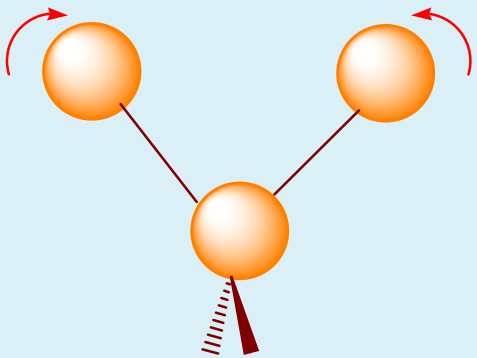
Symmetric



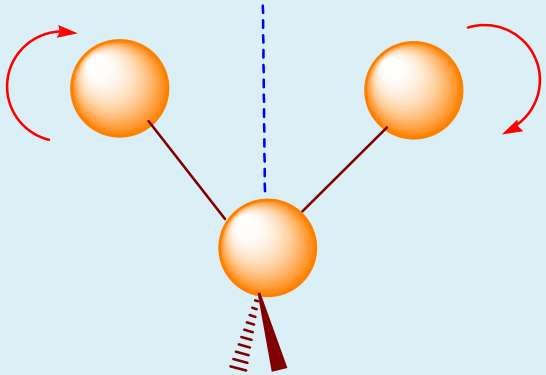
Asymmetric

2. Bending: change in bond angle (lower frequency)

Bending Types



In-plane (Scissoring)

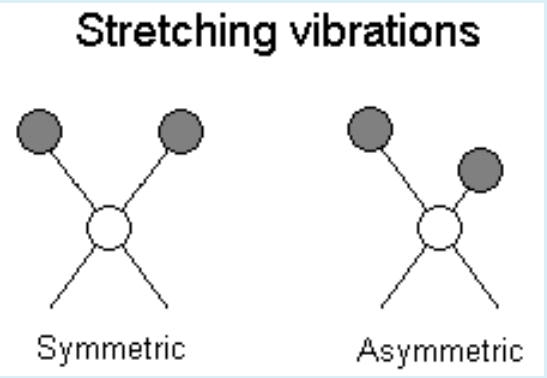


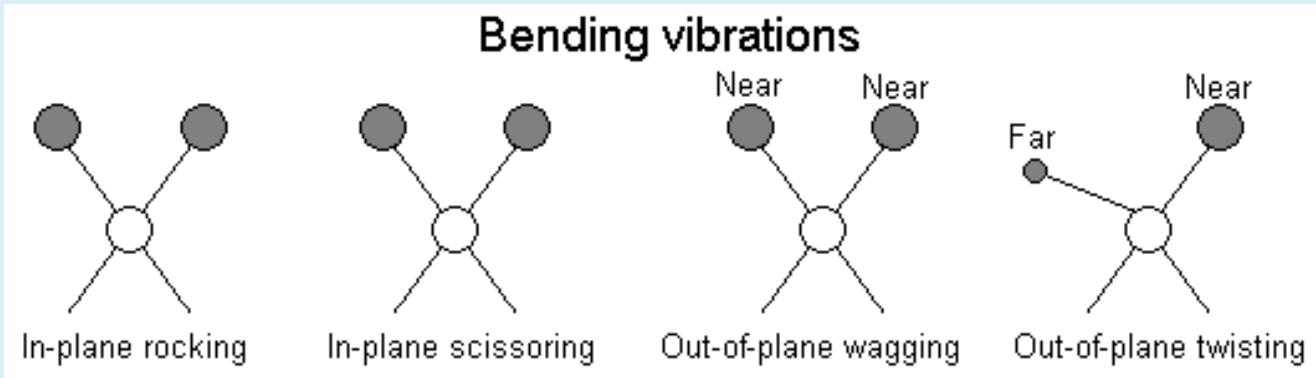
Out-plane (Twisting)

Modes of vibrations

Stretching: change in bond distance. Occurs at higher energy: 4000-1250 cm^{-1}.

Bending: change in bond angle. Occurs at lower energy: 1400-666 cm^{-1}.





H_2O

$-CH_2-$

- More complex types of stretching and bending are possible

Can a vibration change the dipole moment of a molecule?

- Asymmetrical stretching/bending and internal rotation change the dipole moment of a molecule. Asymmetrical stretching/bending are IR active.
- Symmetrical stretching/bending does not. Not IR active

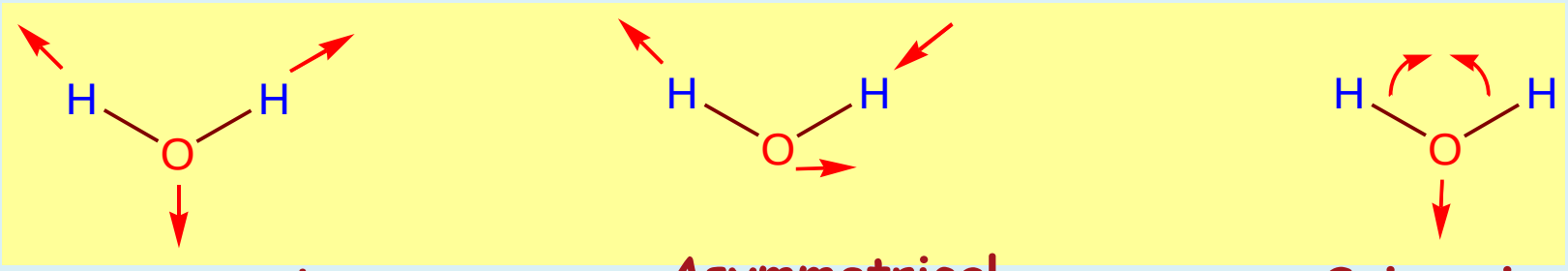
- *Infrared active* vibrations (those that absorb IR radiation) must result in a *change of dipole moment*

Fundamental Vibrations (Absorption Frequencies)

A molecule has as many as degrees of freedom as the total degree of freedom of its individual atoms.

- Each atom has 3 degree of freedom (x,y,z)
- A molecule of n atoms therefore has 3n degrees of freedom.
- Non linear molecules (e.g. H_2O)

Vibrational degrees of freedom or Fundamental Vibrations = 3n – 6

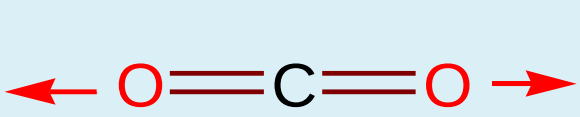


Symmetrical Stretching (υ_s OH) 3652 cm^{-1}

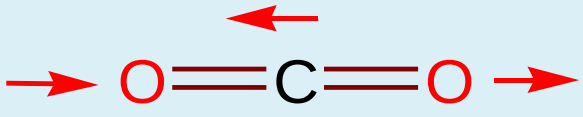
Asymmetrical Stretching (υ_{as} OH) 3756 cm^{-1}

Scissoring (δ_s HOH) 1596 cm^{-1}

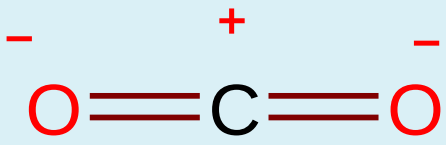
- **For linear molecule (e.g. CO_2) : Vibrational degrees of freedom or Fundamental Vibrations = 3n – 5**



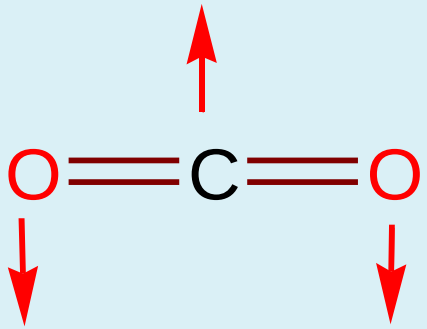
Symmetrical Stretching (υ_s CO_2) 1340 cm^{-1}



Asymmetrical Stretching (υ_{as} CO_2) 2350 cm^{-1}

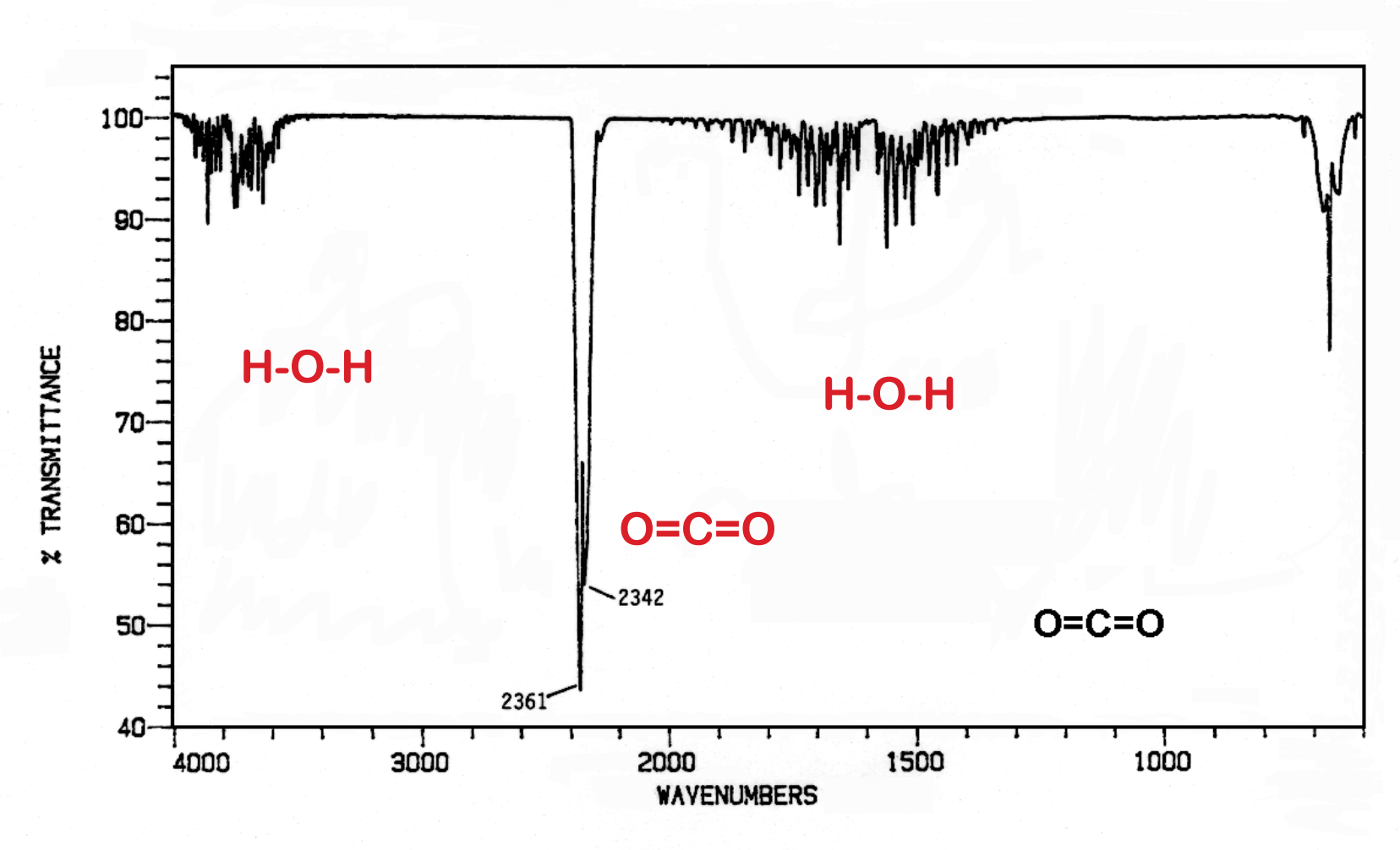


Scissoring (bending out of the plane of the paper) (δ_s CO_2) 666 cm^{-1}



Scissoring (bending in the plane of the paper) (δ_s CO_2) 666 cm^{-1}

Carbon Dioxide and Water



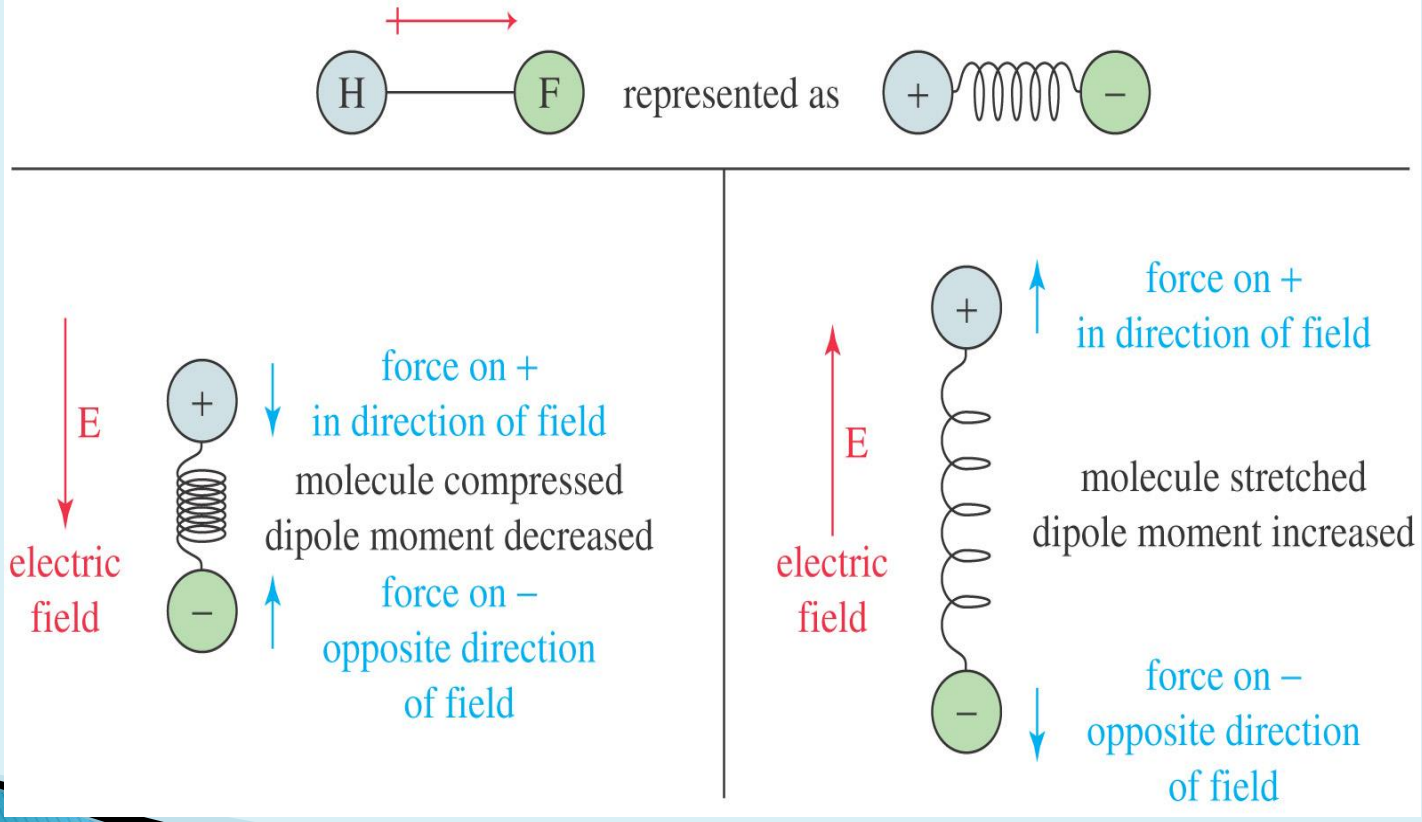
➢ The theoretical no. of fundamental vibrations will seldom be observed because overtones (multiples of a given frequencies) and combination tones (sum of two other vibrations) increase the no. of bands.

- Other phenomena reduce the no. of bands including:

- Fundamental frequencies that fall outside the 4000-400 cm^{-1} region.
- Fundamental bands that are too weak to be observed.
- Fundamental bands that are so close that they coalesce.
- The occurrence of a degenerate band from several absorptions of the same frequency in highly symmetrical molecules.
- The failure of certain fundamental vibrations to appear in the IR because of the lack of change in molecular dipole.

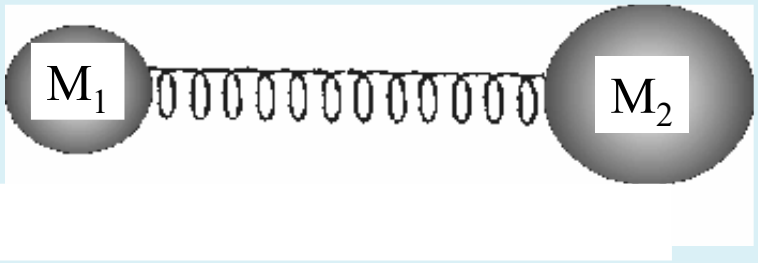
IR-Active and Inactive

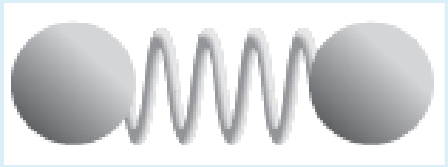
- A **polar** bond is usually **IR-active.**
- A **nonpolar** bond in a symmetrical molecule will absorb weakly or not at all **IR-inactive.**



Factors determining where a chemical bond absorb (Bond Properties)

Hooke's Law





$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}}$$

ύ = The vibration frequency (cm^{-1})

c = Velocity of light (cm/s)

f = force constant of bond (dyne/cm)

M1 and m2 are mass (gr) of atom M1 and M2

increasing μ

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

The CH strech occurs at about 3000cm-1. As the atom bonded to carbon increases in mass, the frequency of vibration decreases (wavenumbers get smaller)

2-How does the force constant of bond influence the vibration?

In general, triple bonds are stronger than double or single bonds between the same two atoms and have higher frequency of vibration (higher wave number)

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

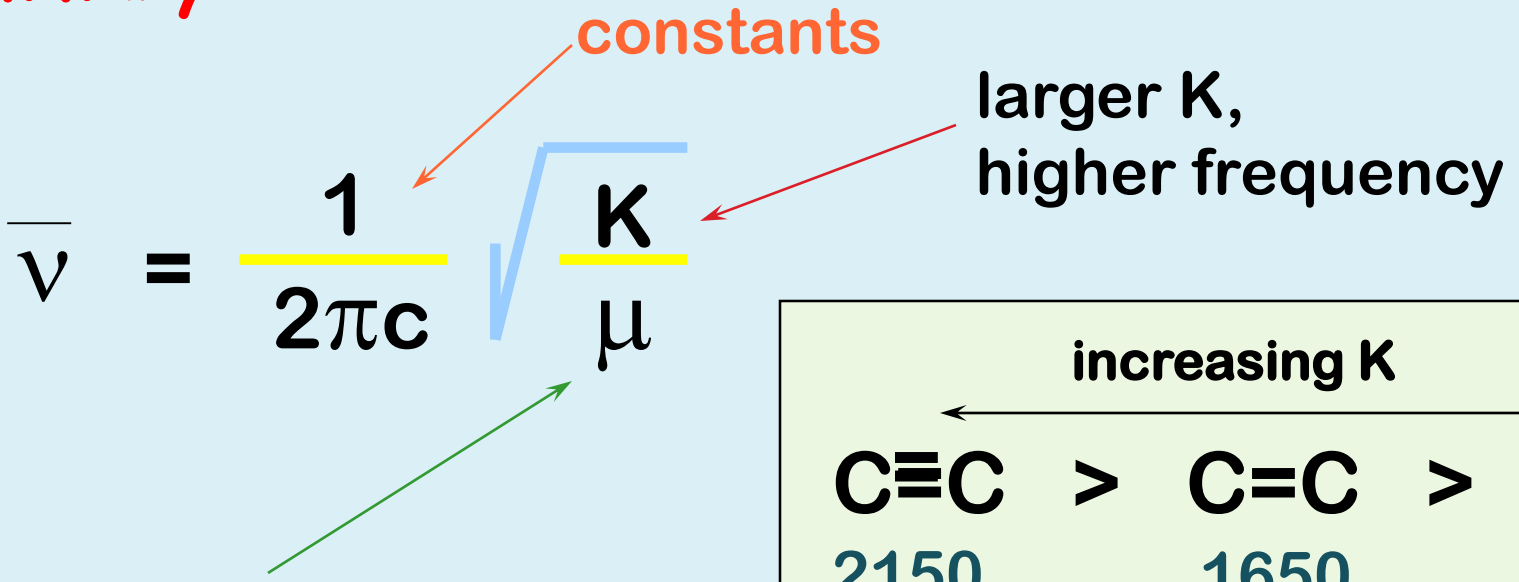
single bond	5×10^5 dyne/cm
double bond	10×10^5 dyne/cm
triple bond	15×10^5 dyne/cm

multiple bonds have higher K's

C≡C > C=C > C—C

2150cm-1 1650cm-1 1200 cm-1

Summary



increasing K

C≡C	>	C=C	>	C-C
2150		1650		1200

increasing μ

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

Stretching Frequencies

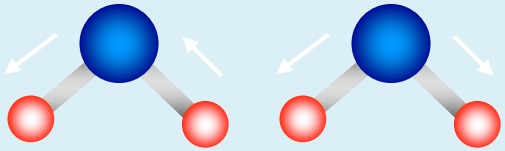
- Frequency decreases with increasing atomic mass.
- Frequency increases with increasing bond energy.

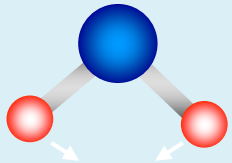
3-How does the type motions influence the vibration?

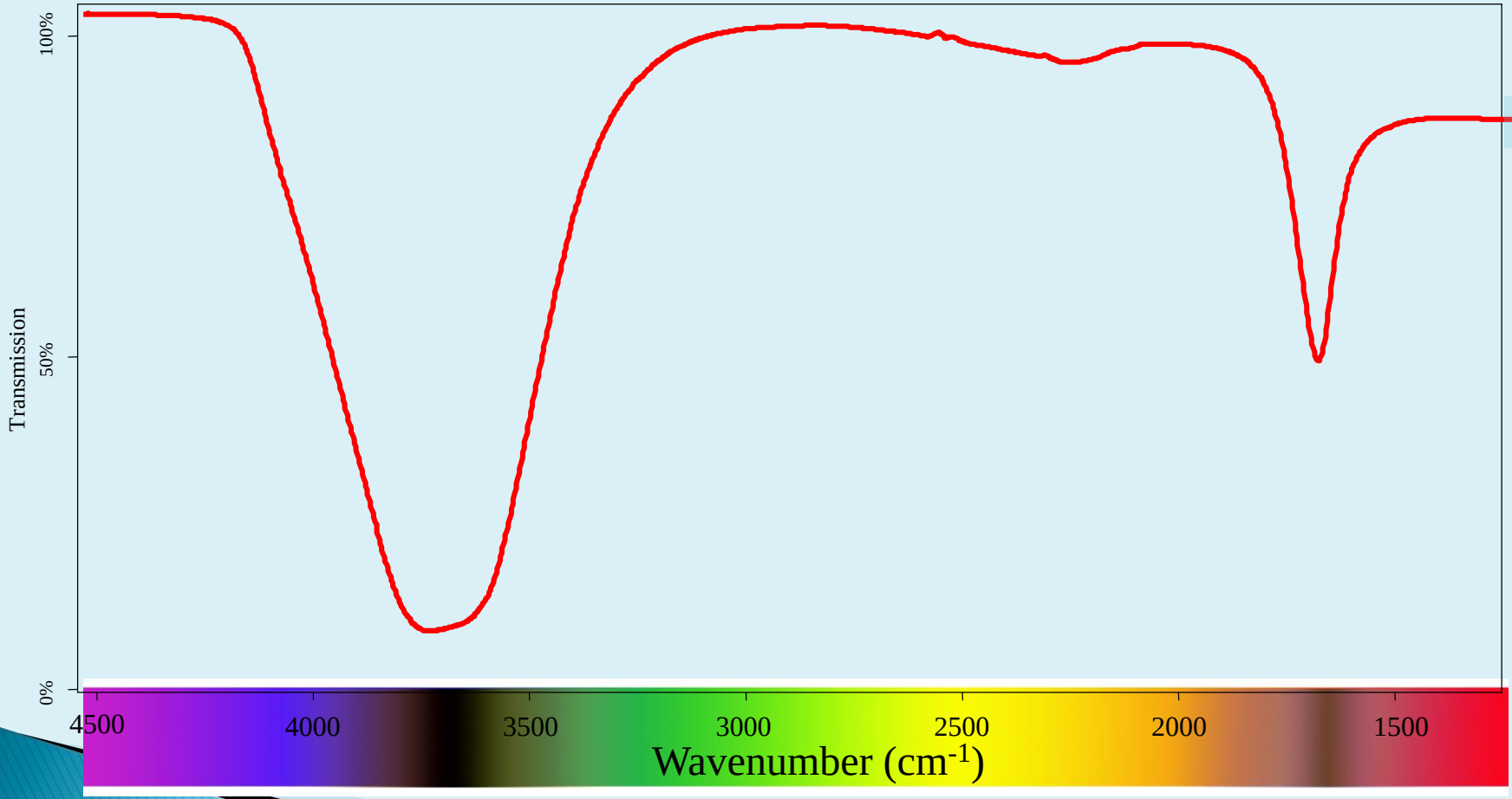
Bending motions occur at lower energy (lower frequency) than the typical streching because of the lower value for the bending force constant.

C-H streching	C-H bending
~ 3000 cm-1	~ 1340 cm-1

Vibrational Spectroscopy







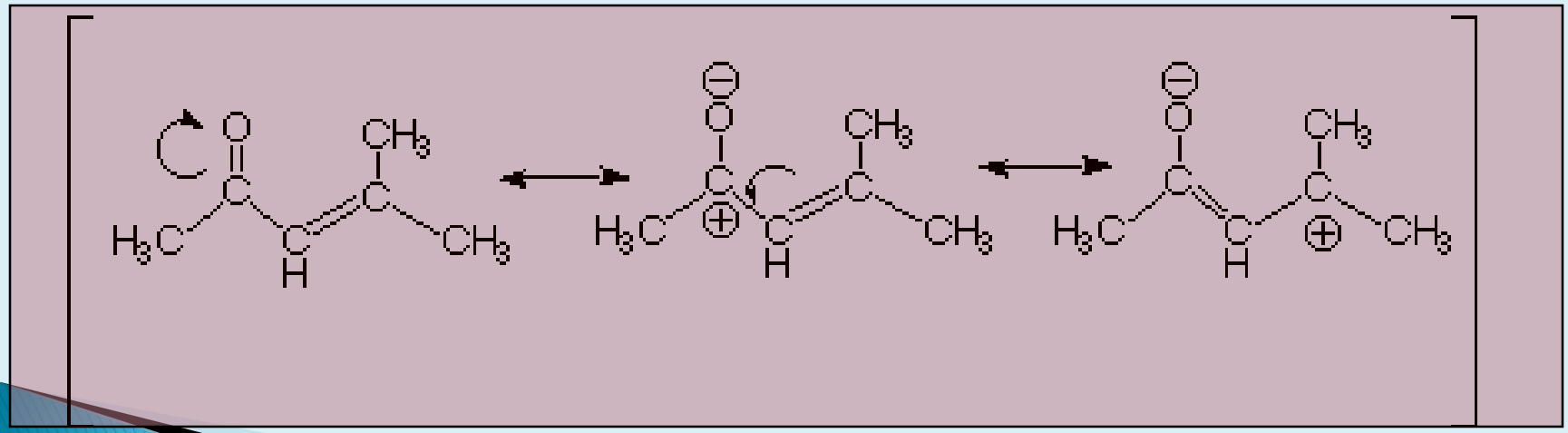
4-How does the hybridization influence the vibration?

Hybridization affects the force constant also. Bonds are stronger in the order sp> sp2 >sp3, and the observed frequencies of C-H vibration illustrate this nicely

≡C-H	>	=C-H	>	-C-H	
sp		sp2		sp3	
3300		3100		2900	cm-1

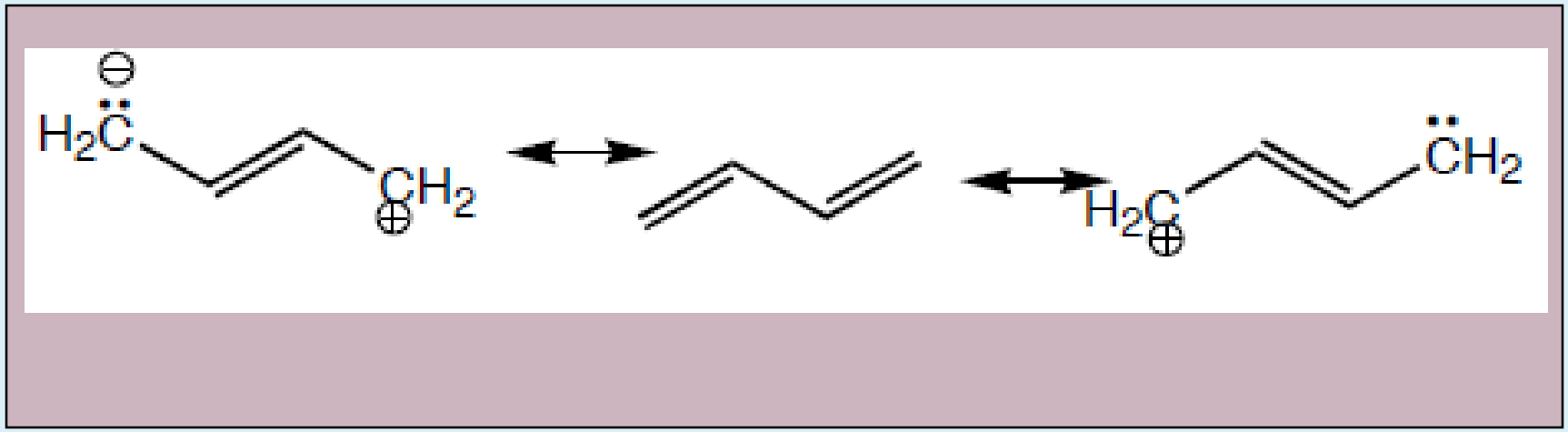
5-How does the resonance influence the vibration?

Resonance also affects the strength and length of a bond and hence its force constant. Thus, whereas a normal ketone has its C=O streching vibration at 1715 cm-1, a ketone that is conjucated with a C=C double bond absorb at a lower frequency, near 1675 to 1680 cm-1. That is because resonanace lengthens the C=O bond distance and gives it more single-bond character .

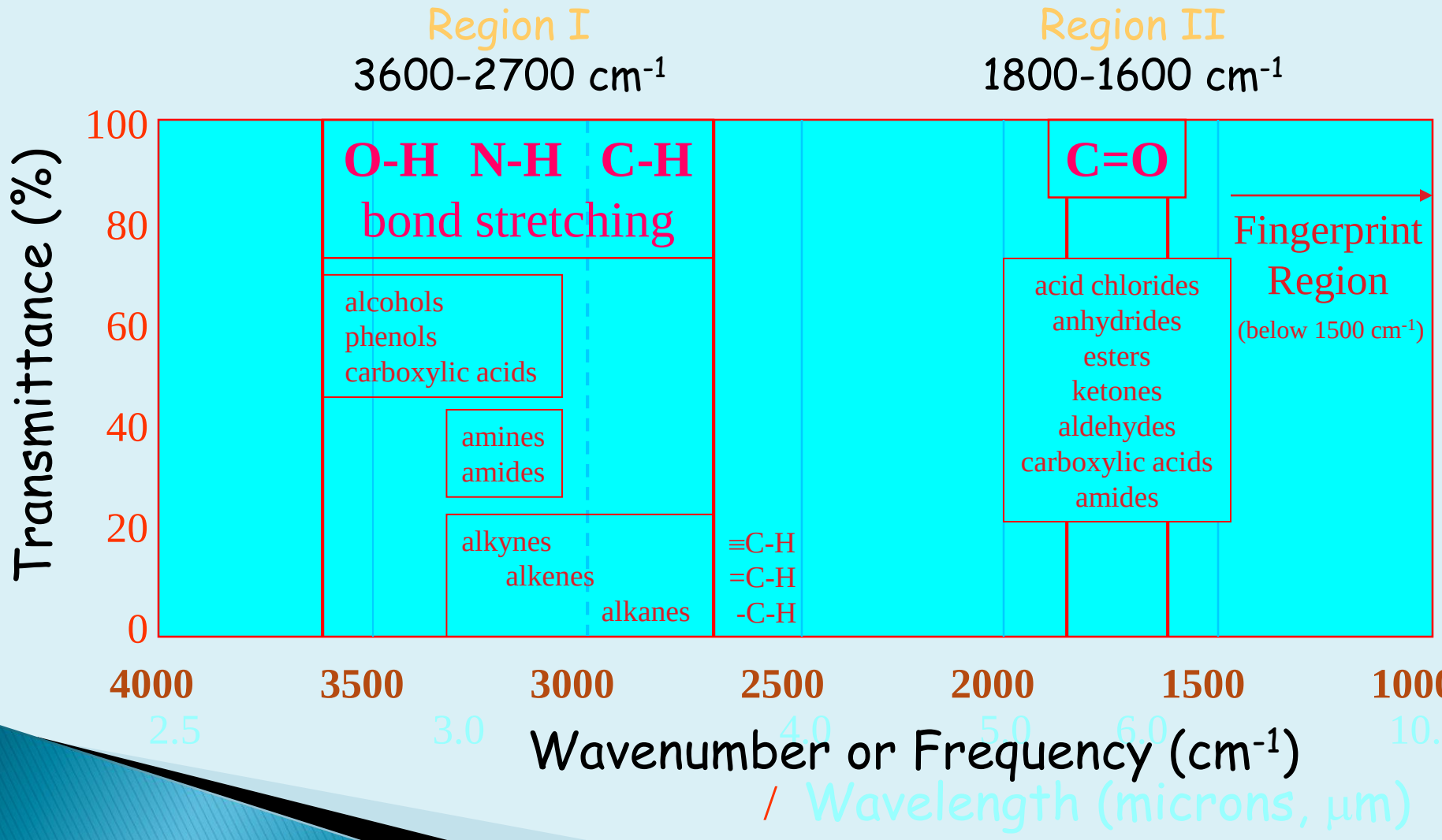


6- Conjugation effects

Conjugation of a C=C double bond with either carbonyl group or another double bond provides the mulptiple bond with more single-bond character (through resonnance, as shown in the following example), a lower force constant, and thus a lower frequency of vibration.

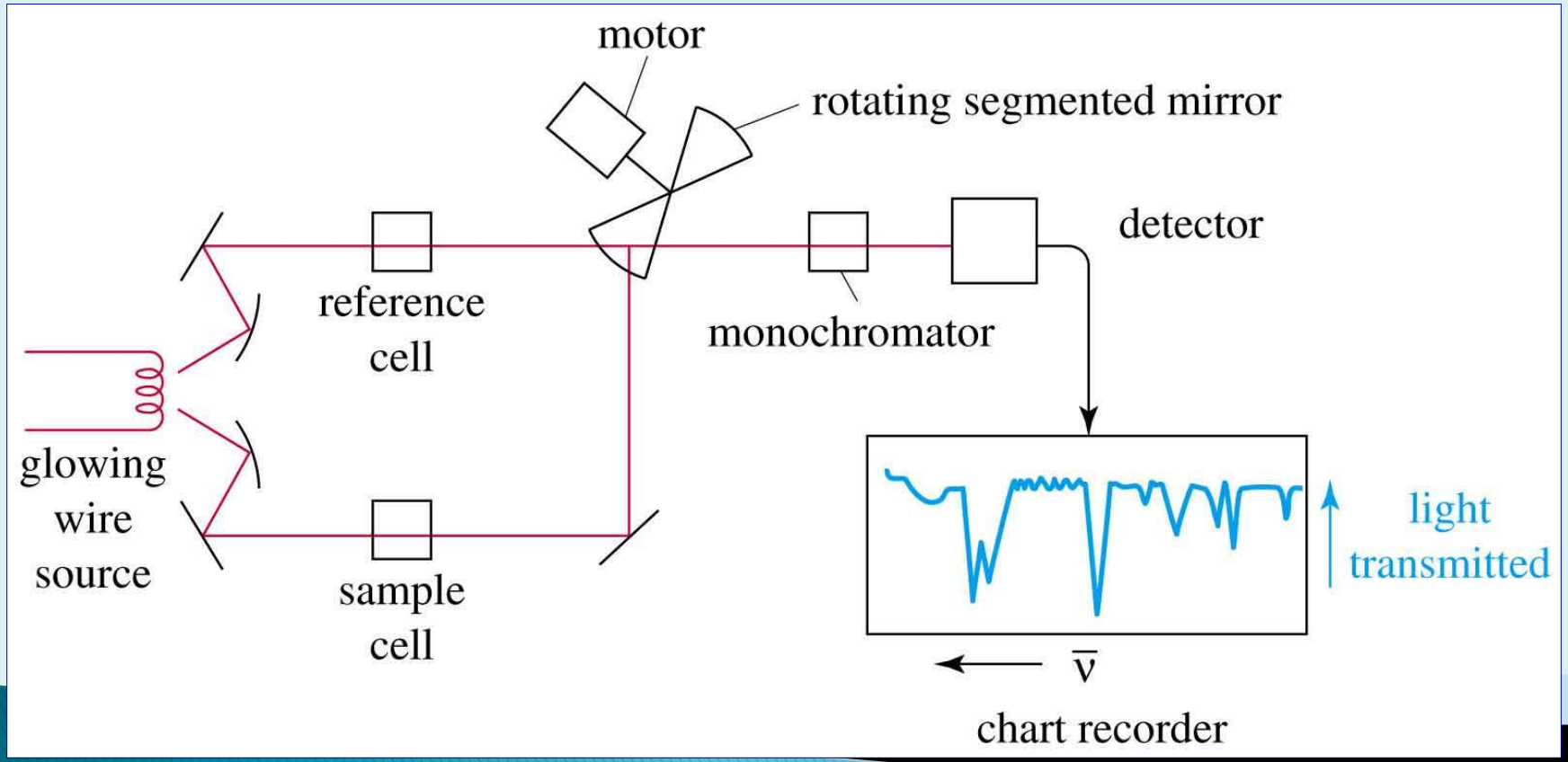


IR Correlation Diagram



Instrumentation

1. Radiation source
2. Monochromator
3. Solvents, sample cells, samples
4. Readout / Recorder



schematic diagram of a double beam double-grating infrared spectrophotometer

SOLVENTS, CELLS, SAMPLES

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

Cells

- NaCl or KCl cells may be used (moisture from air and sample should be avoided: even with care, [illegible] become fogged due to absorption of moisture)
- Very thin (path length = 0.1 to 1.0 mm)
- Sample concentration = about 0.1 – 10%

Preparation of Samples for IR spectroscopy

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 Neat (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.

Use of IR spectra

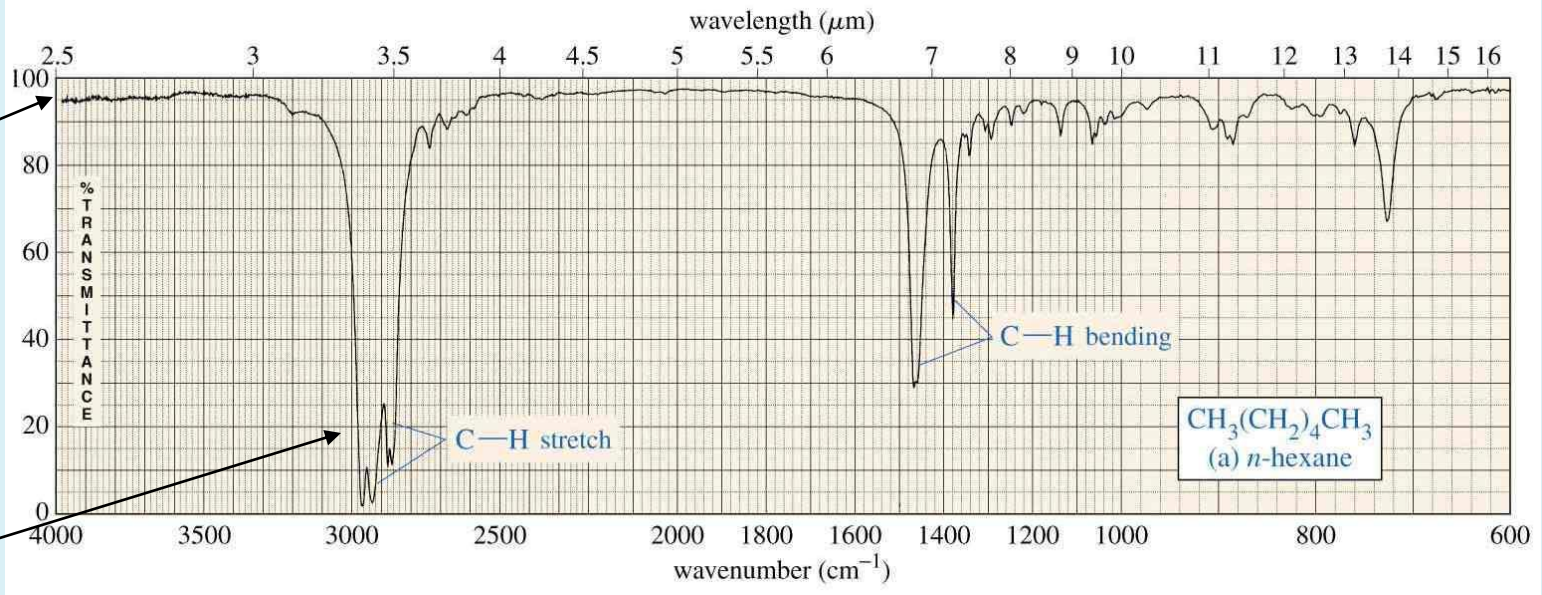
- Identification of functional groups on a molecule – this is a very important tool in organic chemistry
- Spectral matching can be done by computer software and library spectra
- Since absorbance follows Beer's Law, can do quantitative analysis

FEATURES OF AN IR SPECTRUM

- An IR spectrum is a plot of per cent transmittance (or absorbance) against wavenumber (frequency or wavelength). A typical infrared spectrum is shown below.

- A 100 per cent transmittance in the spectrum implies no absorption of IR radiation. When a compound absorbs IR radiation, the intensity of transmitted radiation decreases. This results in a decrease of per cent transmittance and hence a dip in the spectrum. The dip is often called an absorption peak or absorption band.
- Different types of groups of atoms (C-H, O-H, N-H, etc…) absorb infrared radiation at different characteristic wavenumbers.

IR Spectrum



- No two molecules will give exactly the same IR spectrum (except enantiomers)
- Simple stretching: 1600-3500 cm^{-1}
- Complex vibrations: 400-1400 cm^{-1}, called the "fingerprint region"

Describing IR Absorptions

IR absorptions are described by their frequency and appearance.

- *Frequency* (n) 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

How to approach the analysis of a spectrum

- When analyzing the spectrum of an unknown, concentrate your first effort on determining the presence (or absence) of a few major functional groups.
- The C=O, O-H, N-H, C-O, C=C, C≡C, C≡N and NO2 peaks which give structural information if they are present.
- Do not try to make a detailed analysis of the analysis of C-H absorption near 3000 cm-1, almost all compounds have these absorptions.
- D not worry about subtleties of the exact environment in which the functional group is found.
- Following is a major checklist of the important gross features

Is a carbonyl group is present?

The C=O group gives rise to a strong absorption in the region 1820-1660 cm-1. If C=O is present check the following types:

- **Acids:** Is O-H also present? Broad absorption near 2400-3400 cm-1 (usually overlaps C-H).
- **Amides:** Is N-H also present? Medium absorption near 3400 cm-1; sometimes a double peak with equivalent halves.
- **Esters:** Is C-O present? Strong-intensity absorption near 1000-1300 cm-1.
- **Aldehydes:** Is aldehydes C-H present? Two weak absorptions near 2750-2850 cm-1 on right side of the aliphatic C-H absorptions.
- **Anhydrides:** two C=O absortions near 1760-1810 cm-1.
- **Ketones:** The preceding five choices have been eliminated.

Is a carbonyl group is absent?

Check the following:

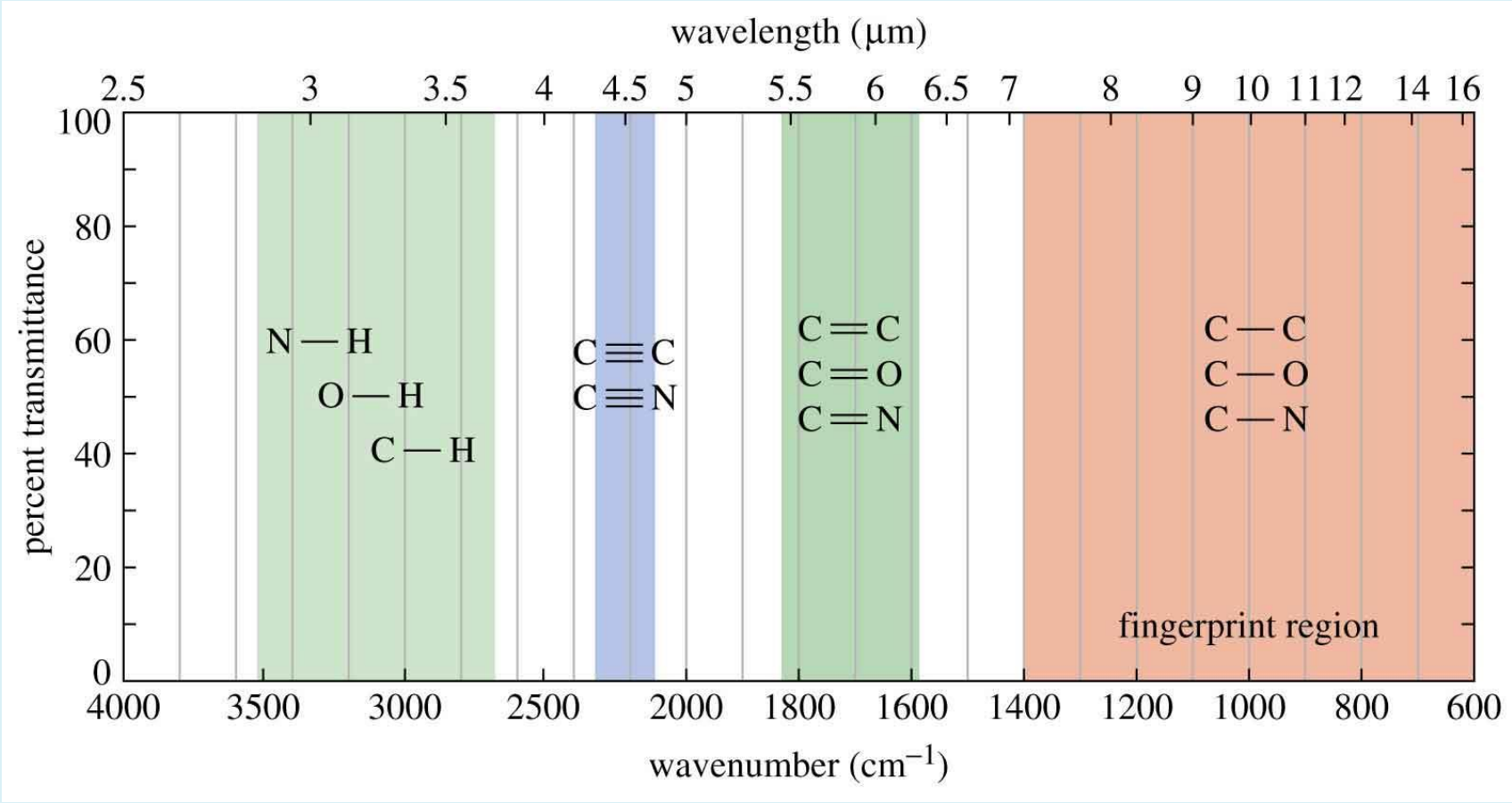
- **Alcohols; Phenols:** Check for O-H:
  * Broad absorption near 3300-3400 cm-1;
  * Confirm this by finding C-O near 1000-1300 cm-1.

- **Amines:** Check for N-H
  * Medium absorption(s) near 3400 cm-1.
- **Ethers:** Check for C-O near 1000-1300 cm-1 (and absence of O-H near 3400 cm-1).

- **Double bonds and/or aromatic rings:**
  - *C=C is a weak absorption near 1650 cm-1
  - * medium to strong absorptions in the region 1450-1600 cm-1; these often imply aromatic ring.
  - * Confirm the double bond or aromatic ring by consulting the C-H region on the left of 3000 cm-1.
- **Triple bonds:**
  - *C≡N: is a medium, sharp absorption near 2250 cm-1.
  - *C≡C: is a weak, sharp absorption near 2150 cm-1
  - * Check also for acetylenic C-H near 3300 cm-1
- **Hydrocarbons:**
  - *None of the preceding is found.
  - Major absorption are in C-H region near 3000 cm-1.
  - Very simple spectrum; the only other absorption appear near 1375-1460 cm1.

- 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. This part of the spectrum is unique to each compound and is often called the *fingerprint* region. It is rarely used for identification of particular functional groups.

Summary of IR Absorptions



BASE VALUES
(+/- 10 cm^{-1})

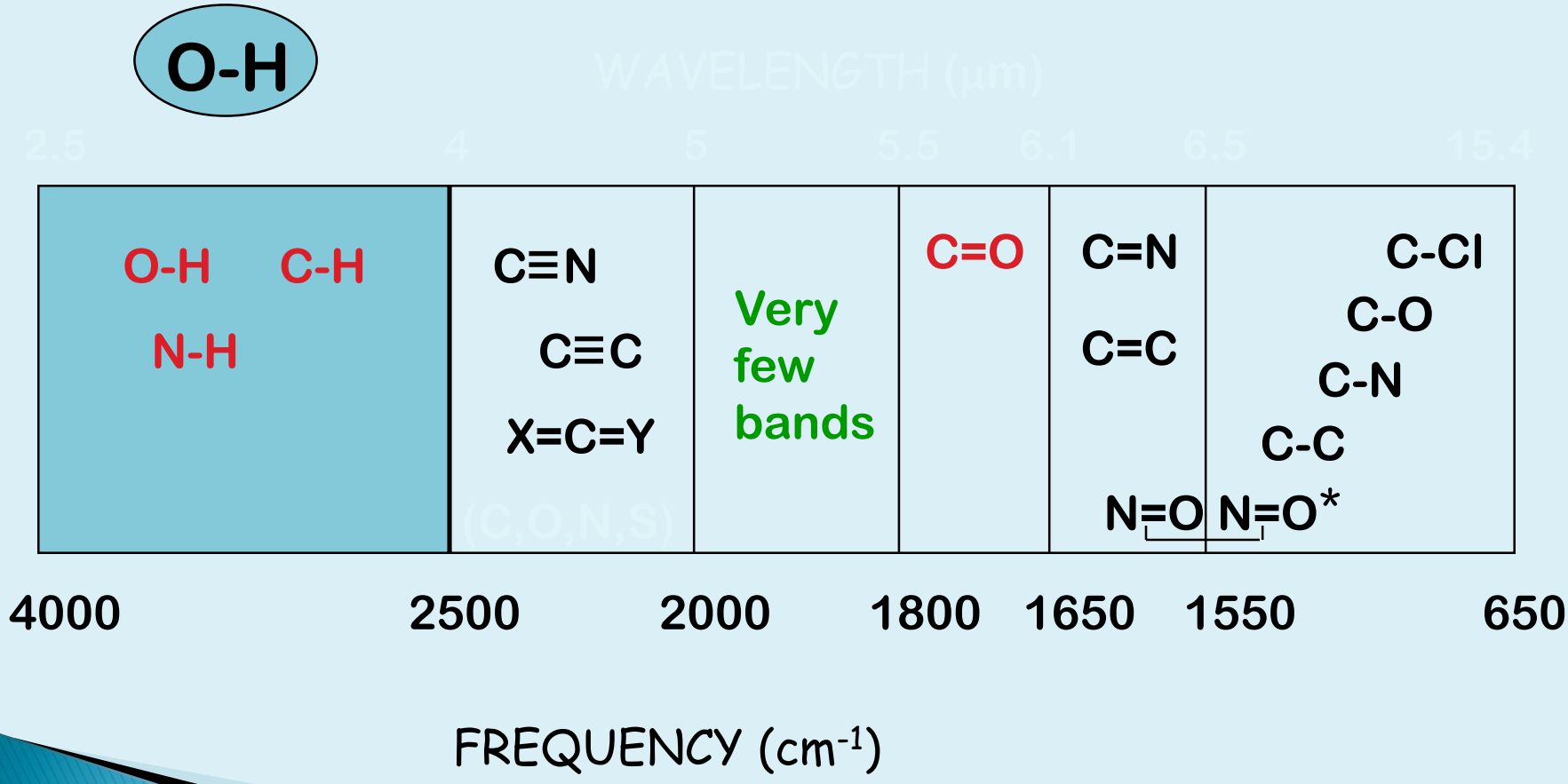
O-H	3600
N-H	3400
C-H	3000
C≡N	2250
C≡C	2150
C=O	1715
C=C	1650
C–O	~1100

These are the minimum number of values to memorize.

large range

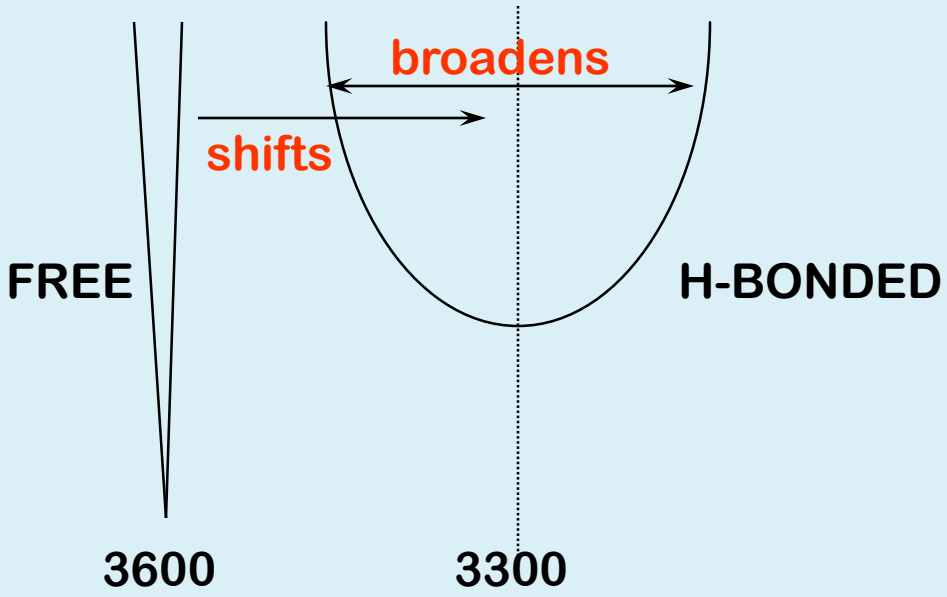
O-H STRETCH

Typical Infrared Absorption Regions

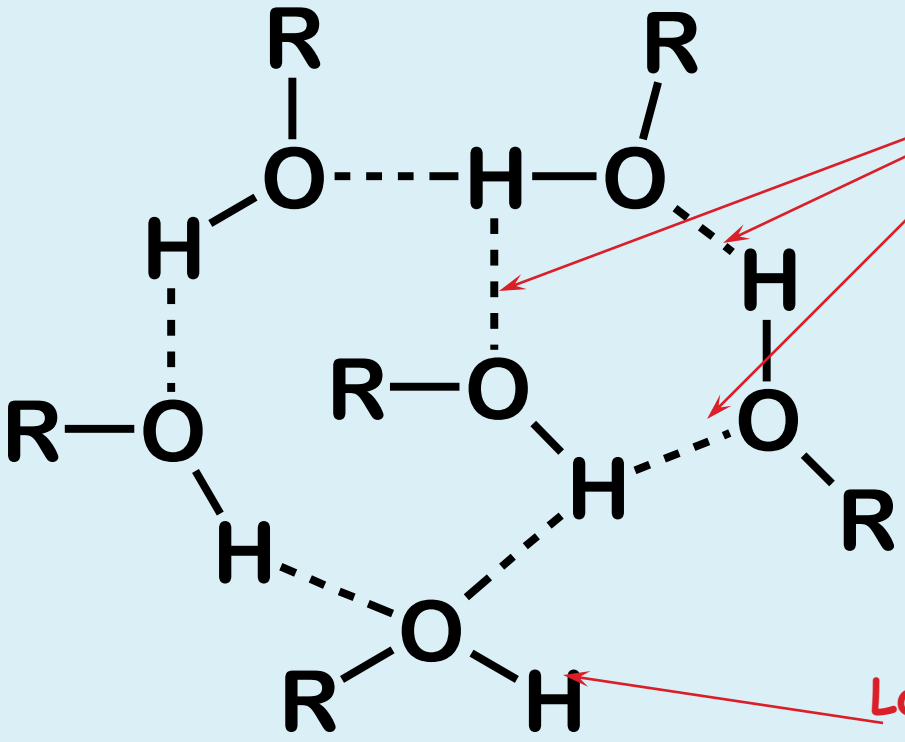


The O-H stretching region

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



HYDROGEN-BONDED HYDROXYL



Many kinds of OH bonds of different lengths and strengths This leads to a broad absorption.

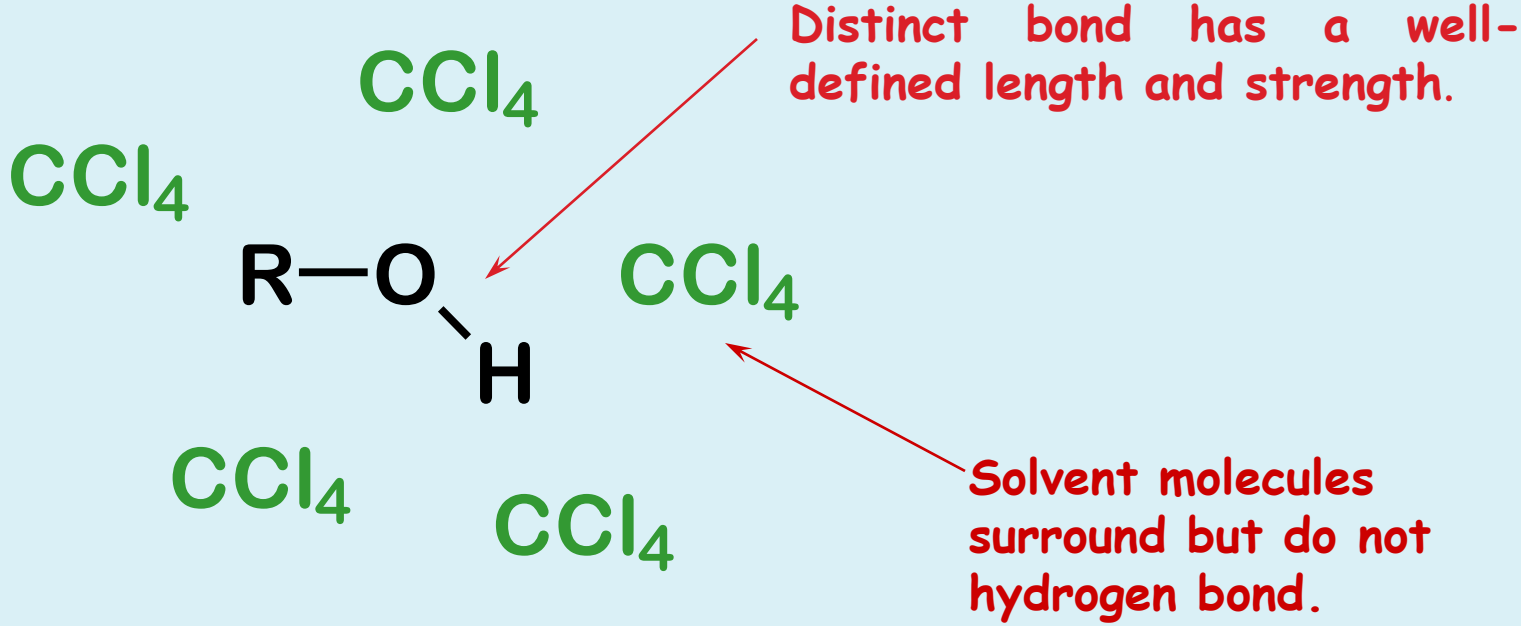
"Neat" solution.

Longer bonds are weaker and lead to lower frequency.

Hydrogen bonding occurs in concentrated solutions (for instance, undiluted alcohol).

"FREE" HYDROXYL

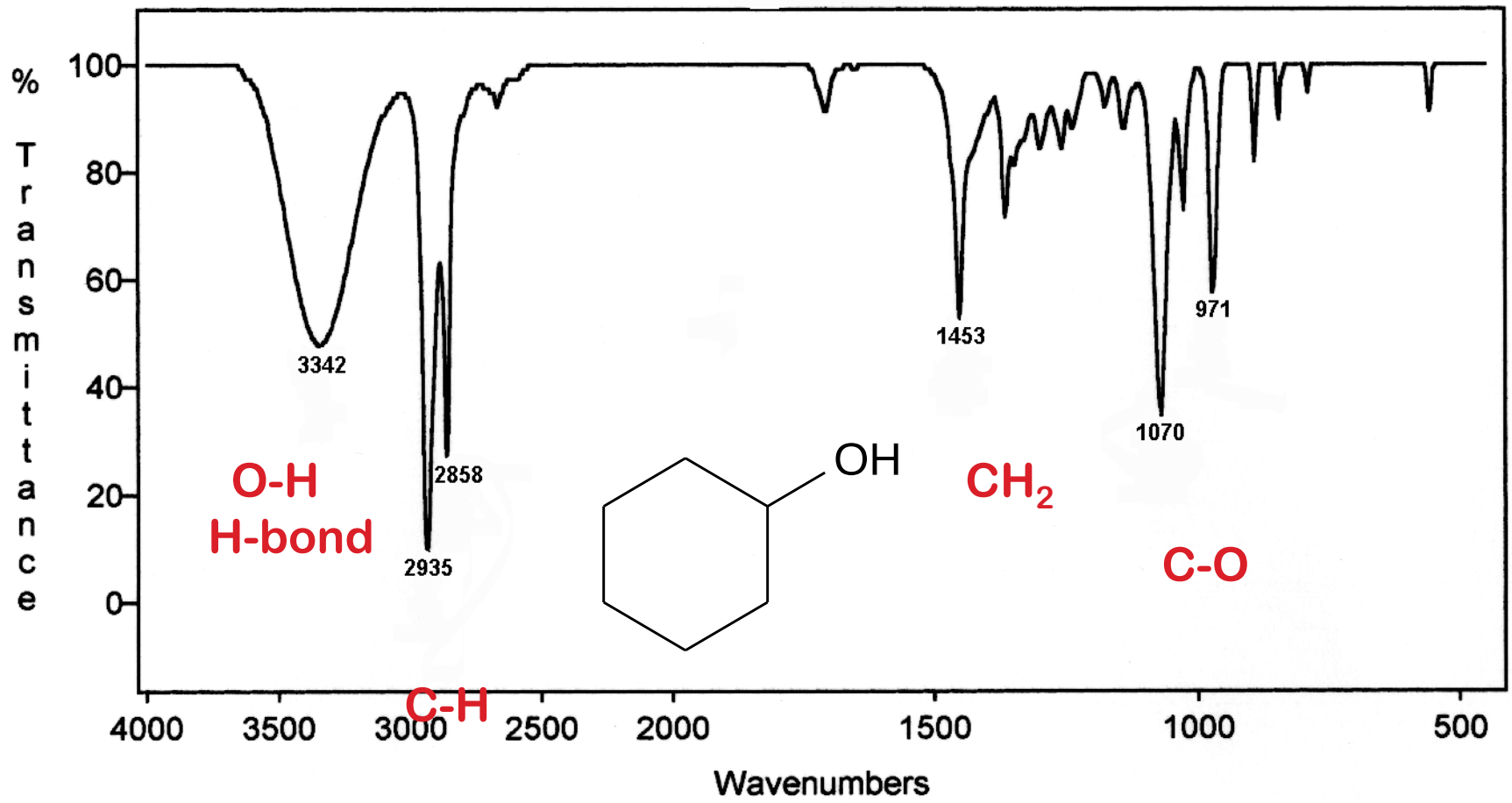
The "free" hydroxyl vibrates without interference from any other molecule.



Occurs in dilute solutions of alcohol in an "inert" solvent like CCl_4.

ALCOHOL

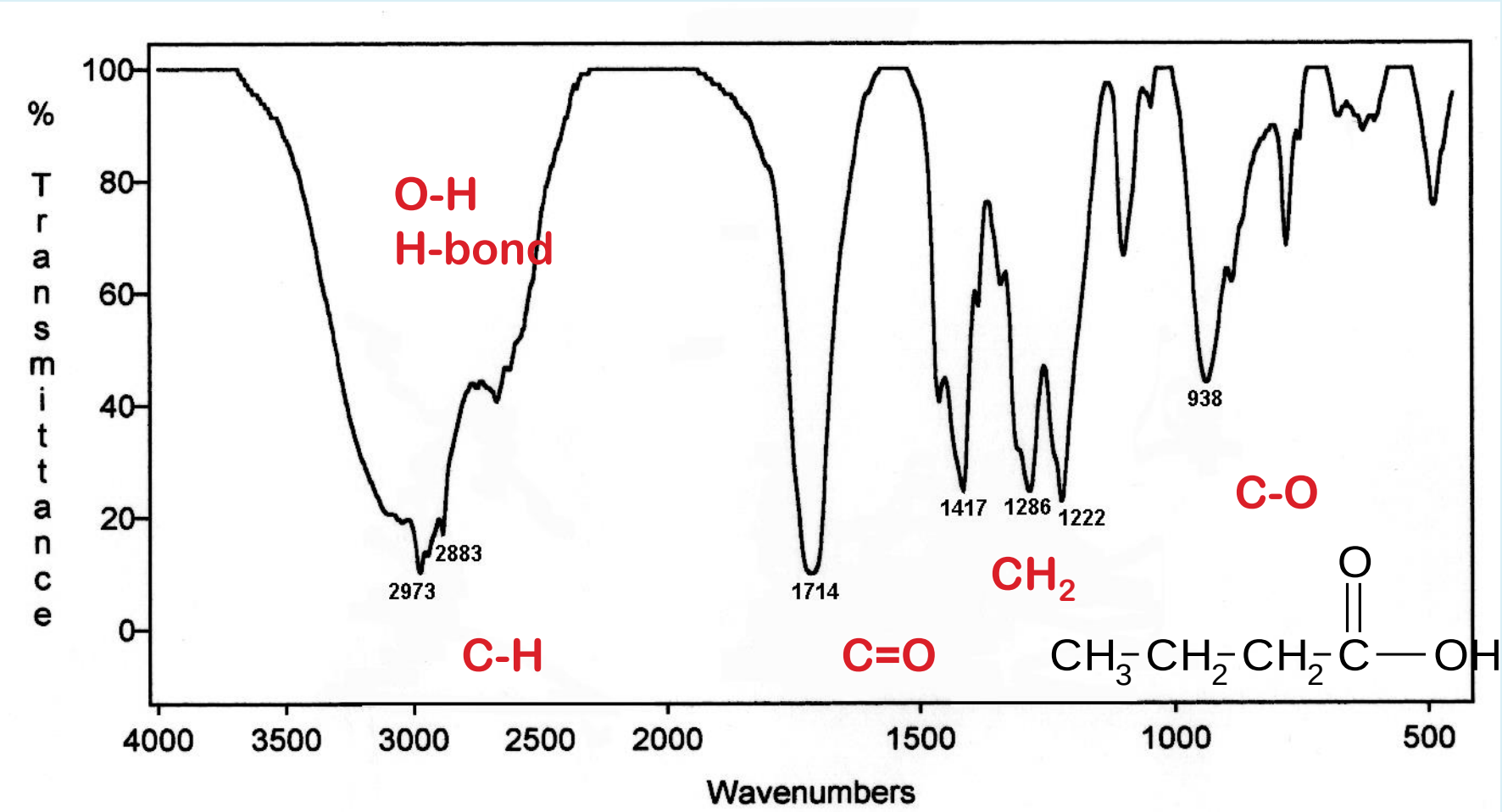
Cyclohexanol



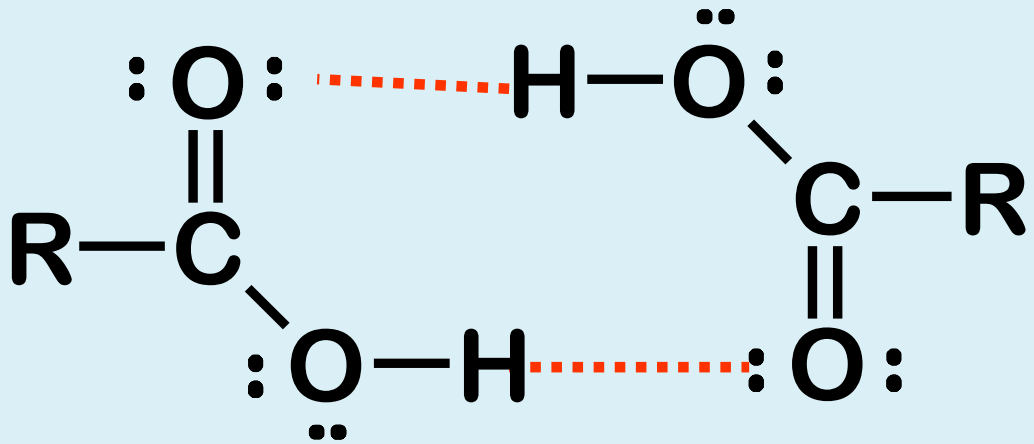
CARBOXYLIC ACID

Butanoic Acid

neat solution



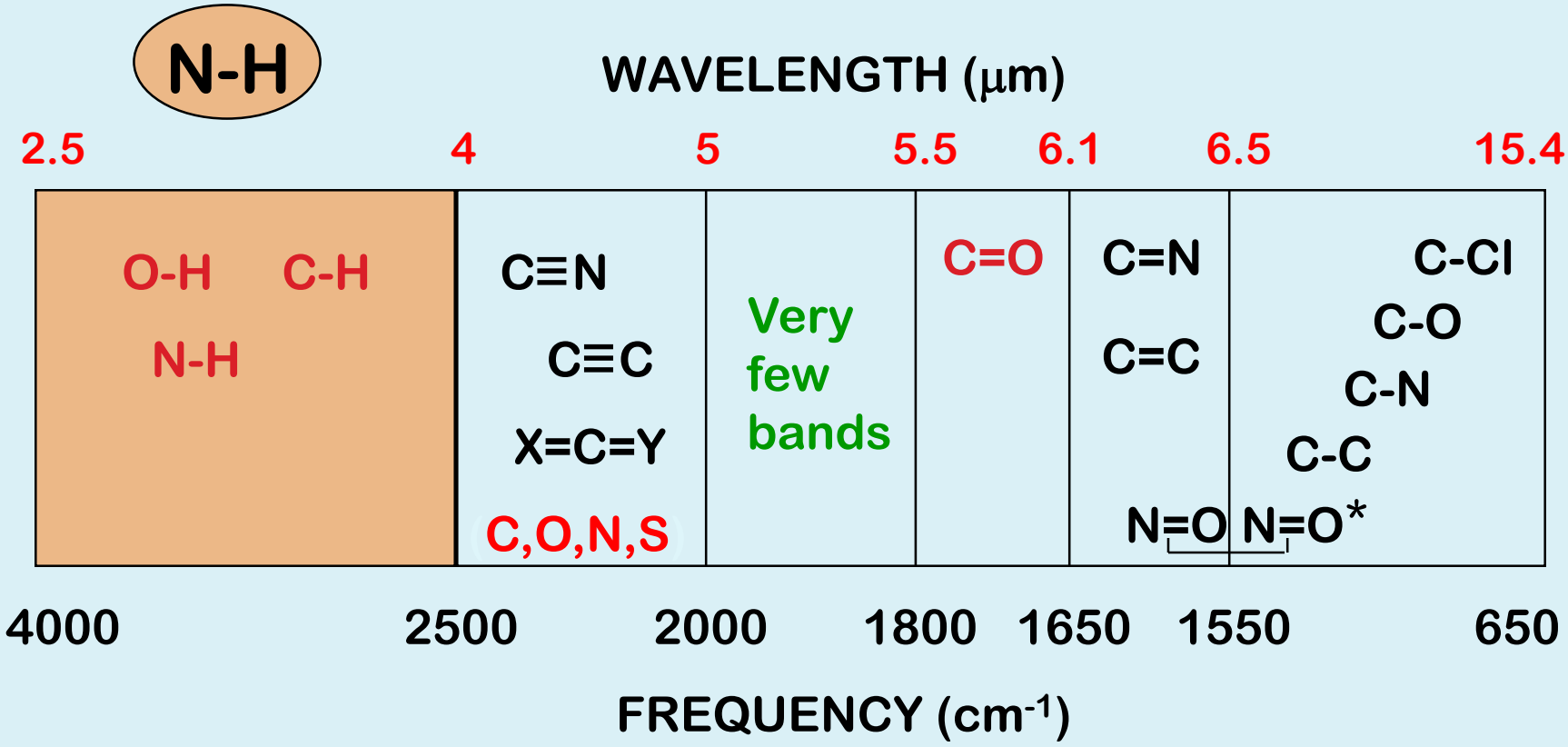
CARBOXYLIC ACID DIMER



Strong hydrogen bonding in the dimer weakens the OH bond and leads to a broad peak at lower frequency.

N-H STRETCH

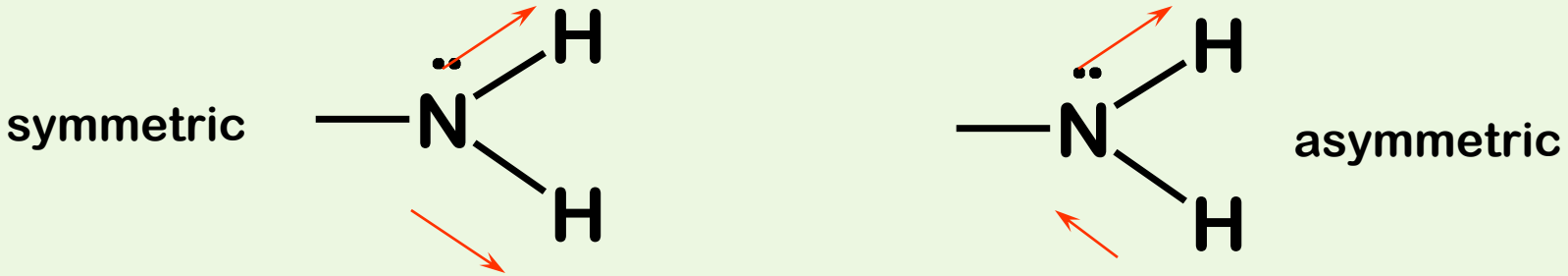
Typical Infrared Absorption Regions



The N-H stretching region

N-H 3300 - 3400 cm^{-1}

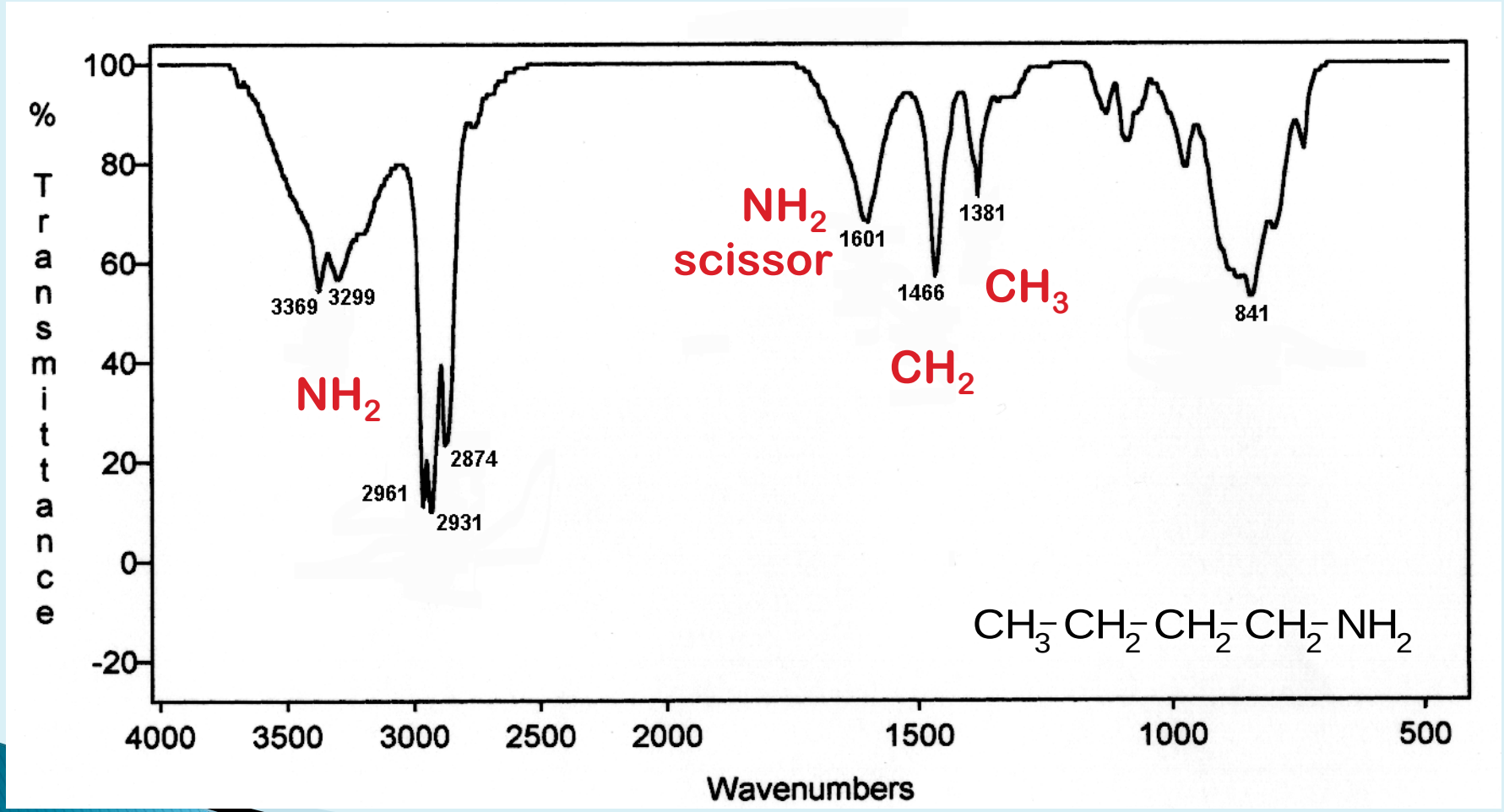
- Primary amines give **two peaks**



- Secondary amines give **one peak**
- Tertiary amines give **no peak**

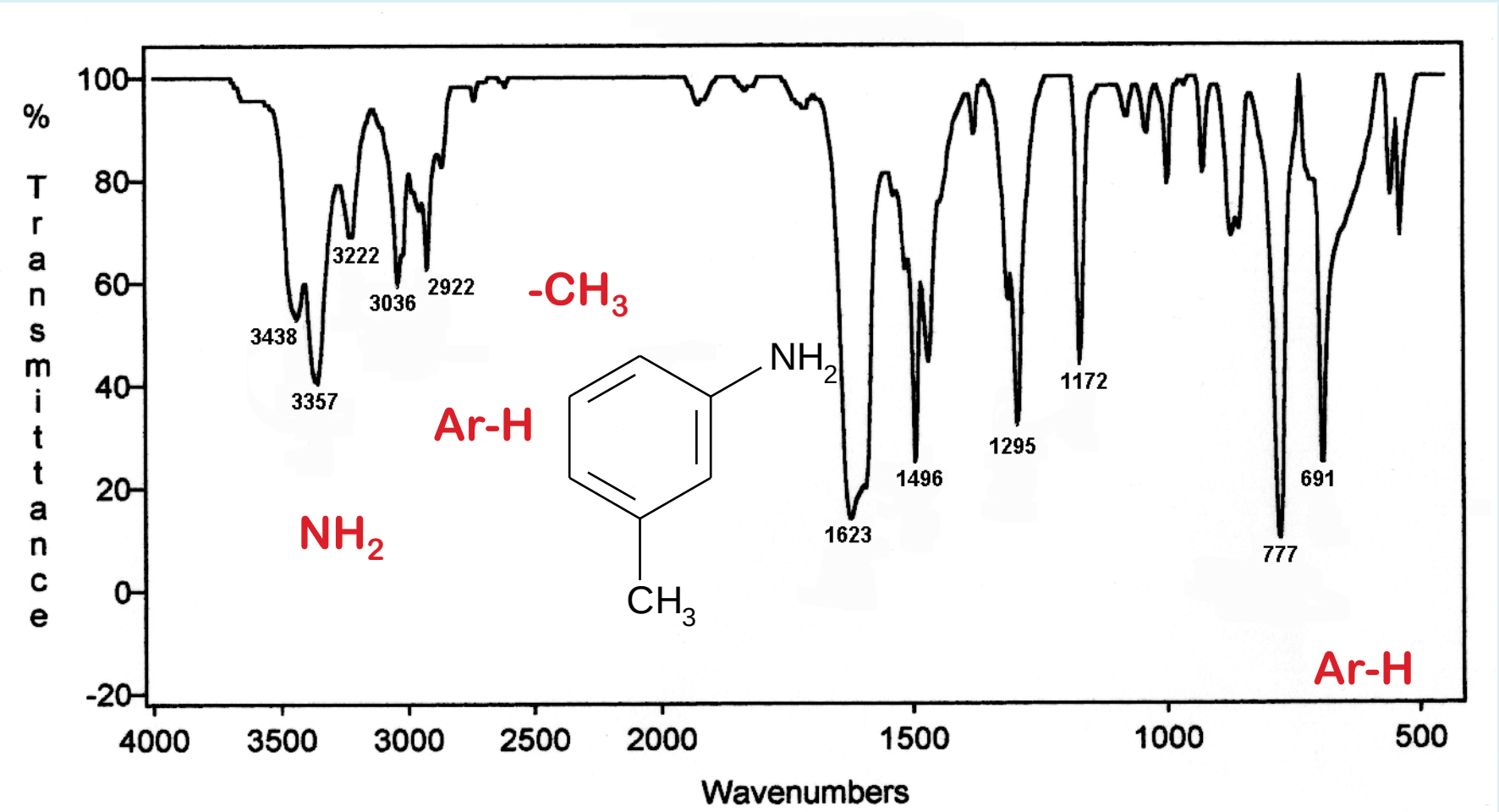
PRIMARY AMINE
aliphatic

1-Butanamine

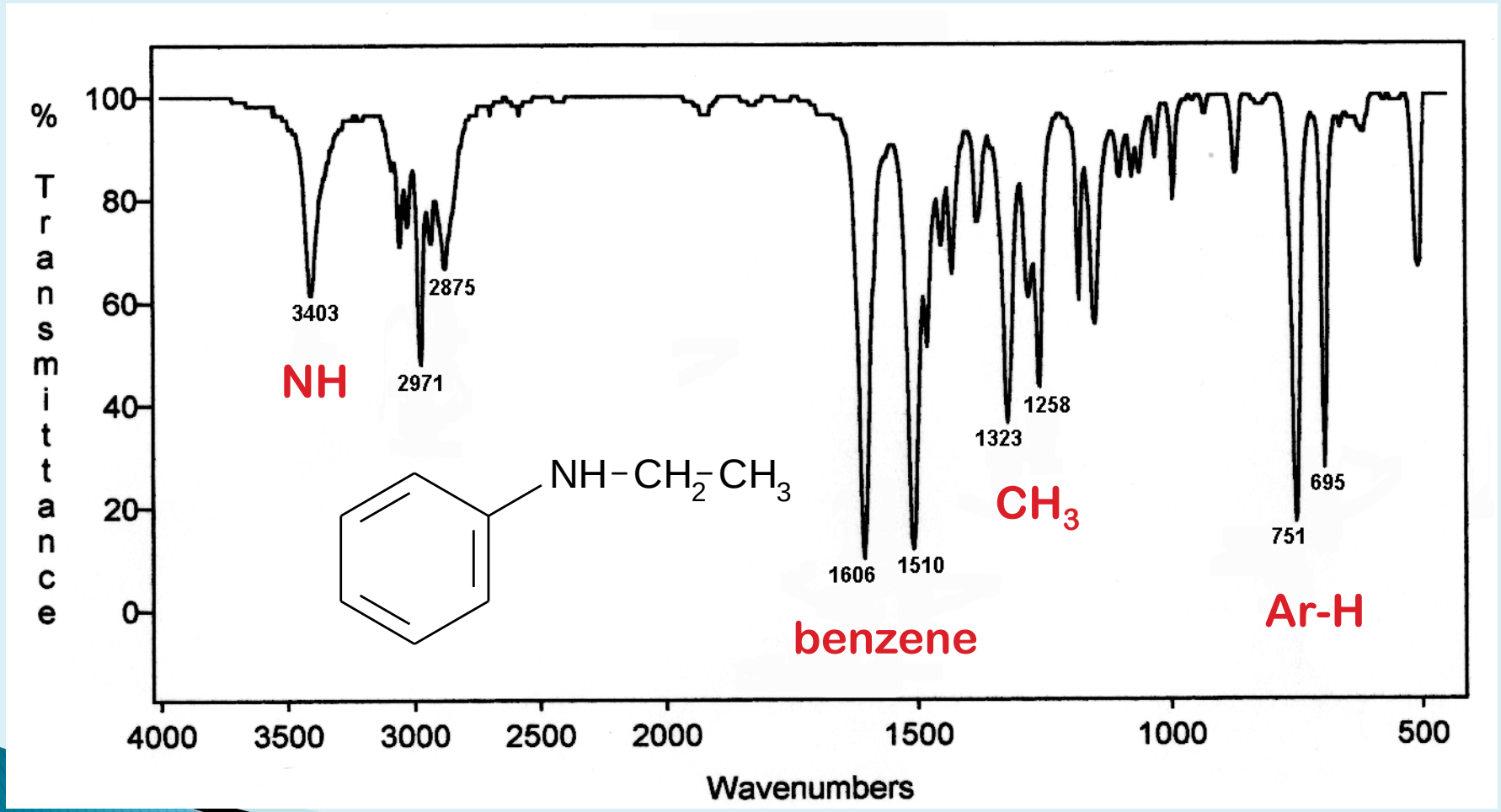


PRIMARY AMINE
aromatic

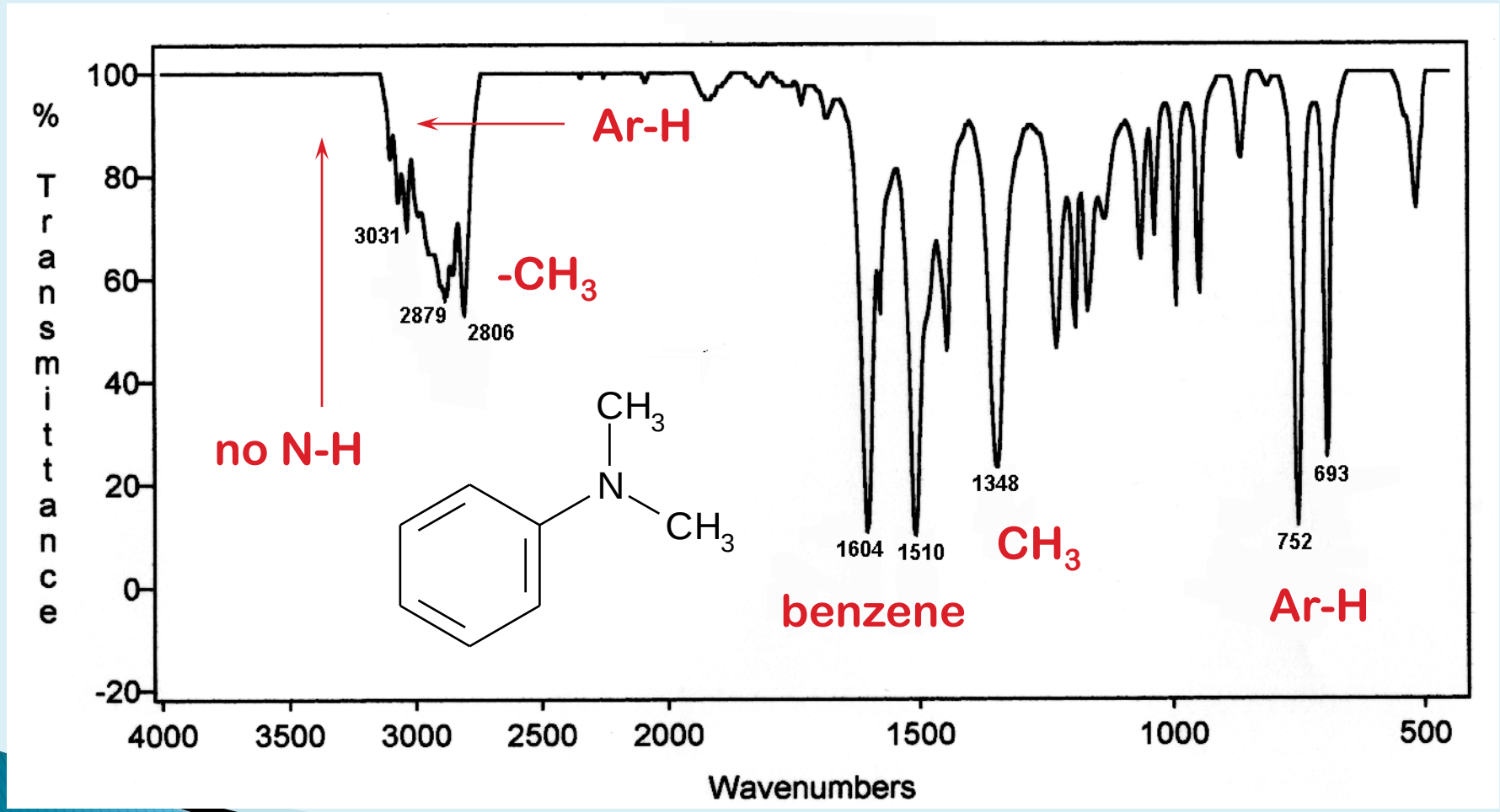
3-Methylbenzenamine



N -Ethylbenzenamine

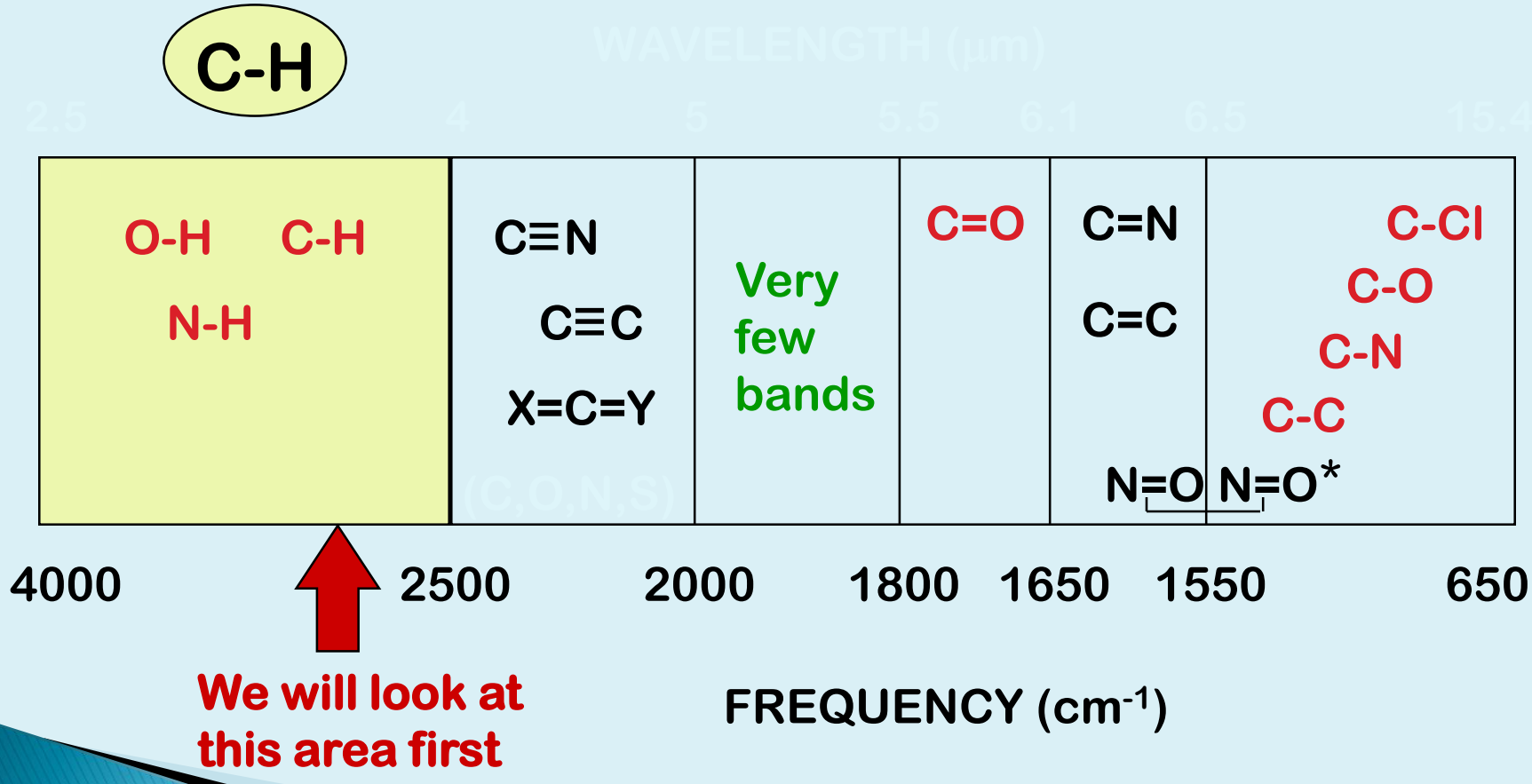


N,N-Dimethylaniline



C-H STRETCH

Typical Infrared Absorption Regions



The C-H stretching region

BASE VALUE = 3000 cm^{-1}

- **C-H sp stretch ~ 3300 cm^{-1}**
- **C-H sp^2 stretch > 3000 cm^{-1}**

UNSATURATED

3000 divides

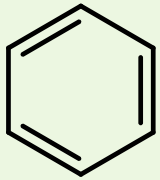
- **C-H sp^3 stretch < 3000 cm^{-1}**

SATURATED

- **C-H aldehyde, two peaks (both weak) ~ 2850 and 2750 cm^{-1}**

STRONGER BONDS HAVE LARGER FORCE CONSTANTS AND ABSORB AT HIGHER FREQUENCIES

increasing frequency (cm^{-1})

3300	3100	3000	2900
≡C-H		=C-H	-C-H
sp-1s		sp^2-1s	sp^3-1s

2850 2750
-CH=O (weak)
aldehyde

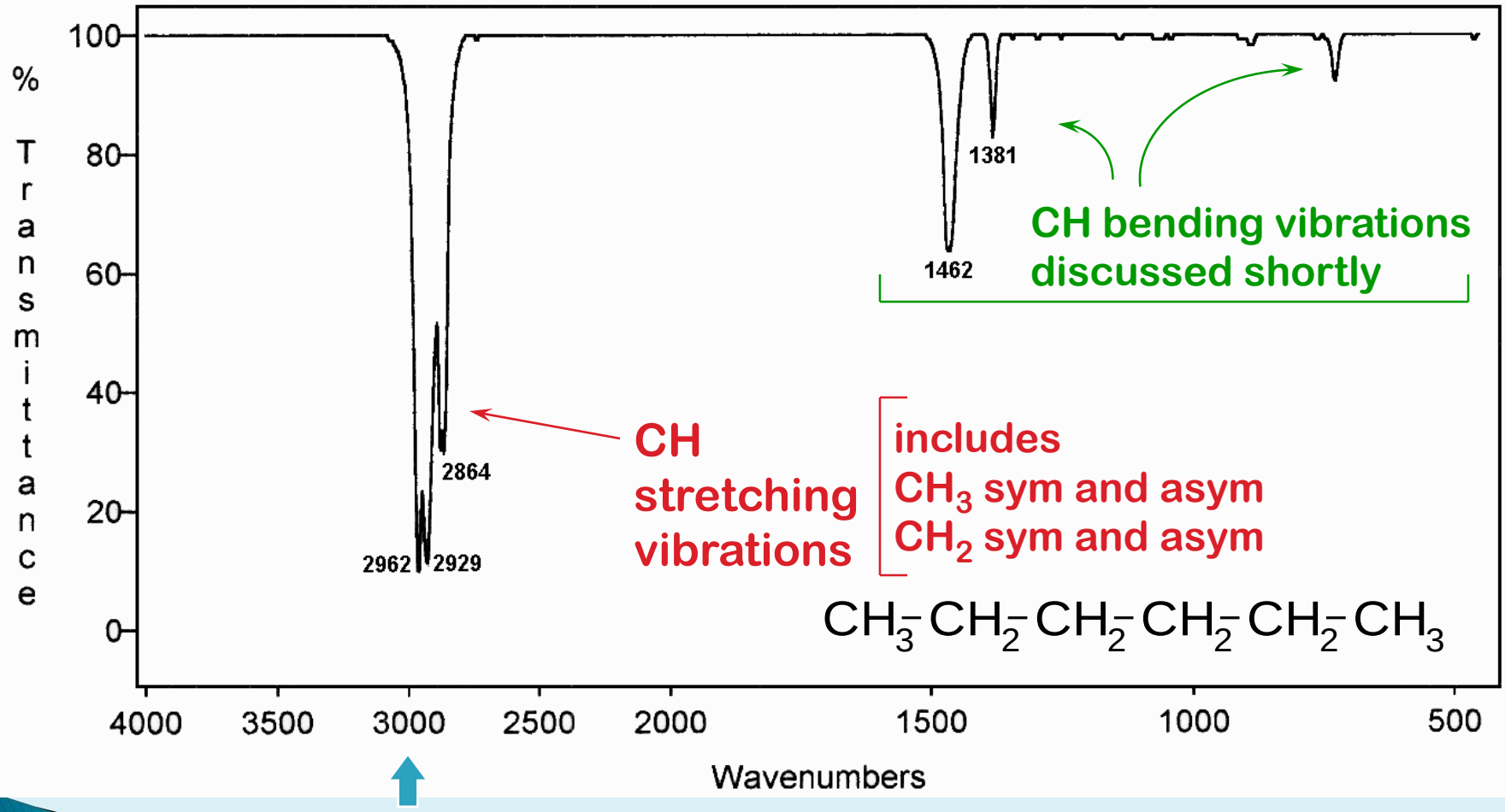
increasing s character in bond

increasing CH Bond Strength

increasing force constant K

CH BASE VALUE = 3000 cm^{-1}

Hexane


% Transmittance
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
2962
2929
2864
1462
1381
CH stretching vibrations
includes
CH3 sym and asym
CH2 sym and asym
CH bending vibrations discussed shortly
CH3 CH2 CH2 CH2 CH2 CH3

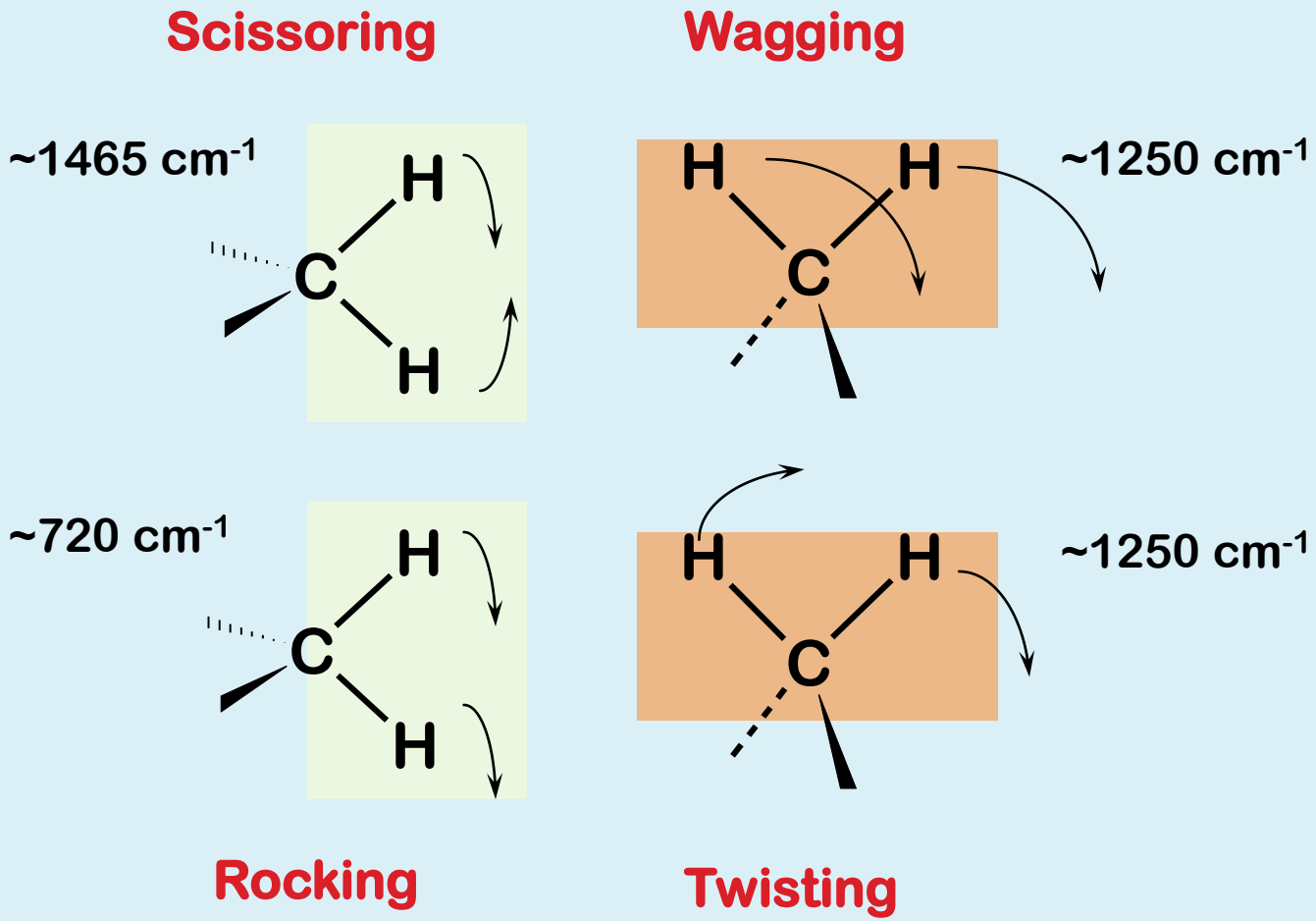
C-H BENDING

THE C-H BENDING REGION

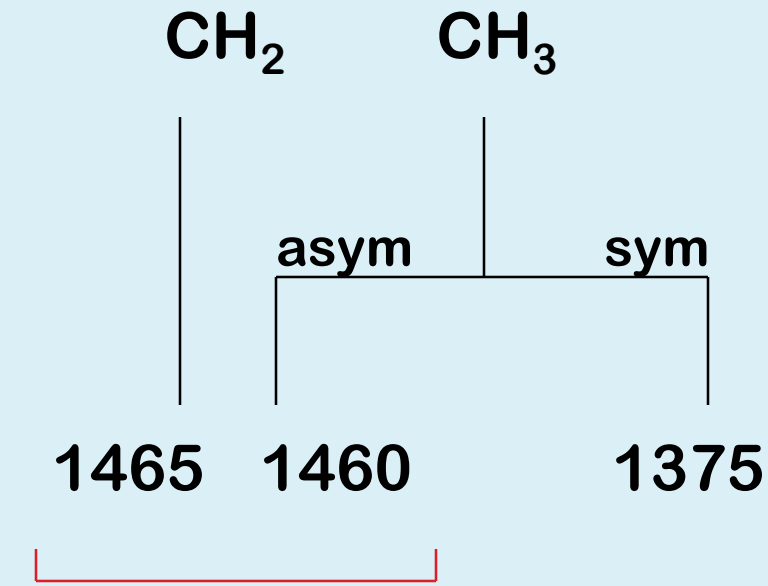
- CH_2 bending ~ 1465 cm^{-1}

- CH_3 bending (asym) appears near the CH_2 value ~ 1460 cm^{-1}
- CH_3 bending (sym) ~ 1375 cm^{-1}

METHYLENE GROUP BENDING VIBRATIONS

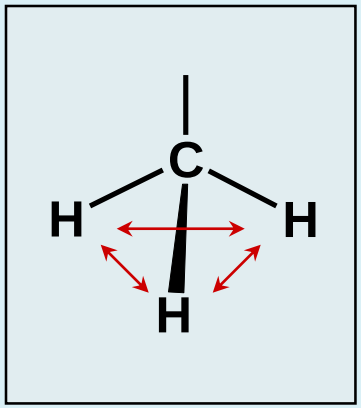


METHYLENE AND METHYL BENDING VIBRATIONS



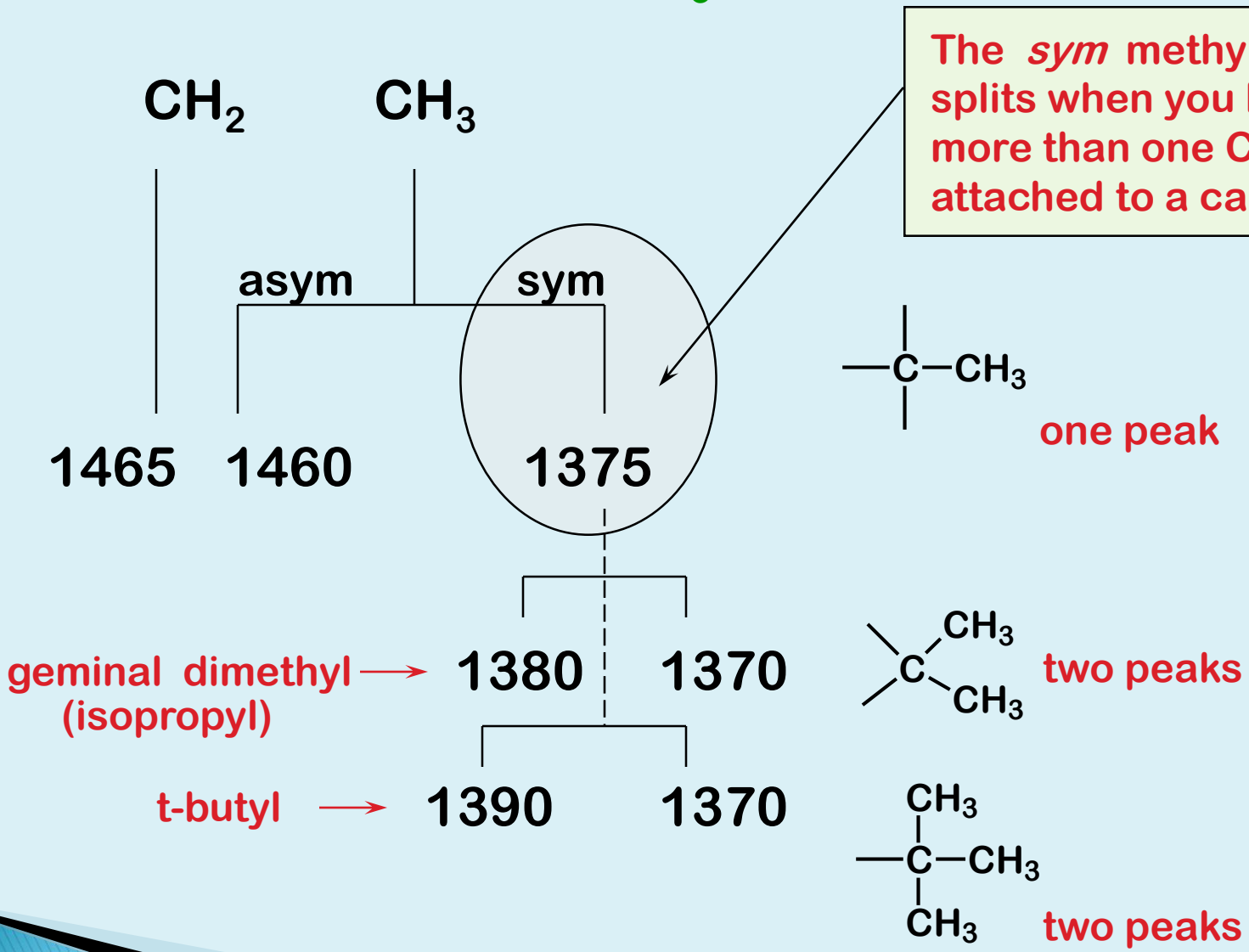
these two peaks frequently overlap and are not resolved

C-H Bending, look near 1465 and 1375 cm^{-1}



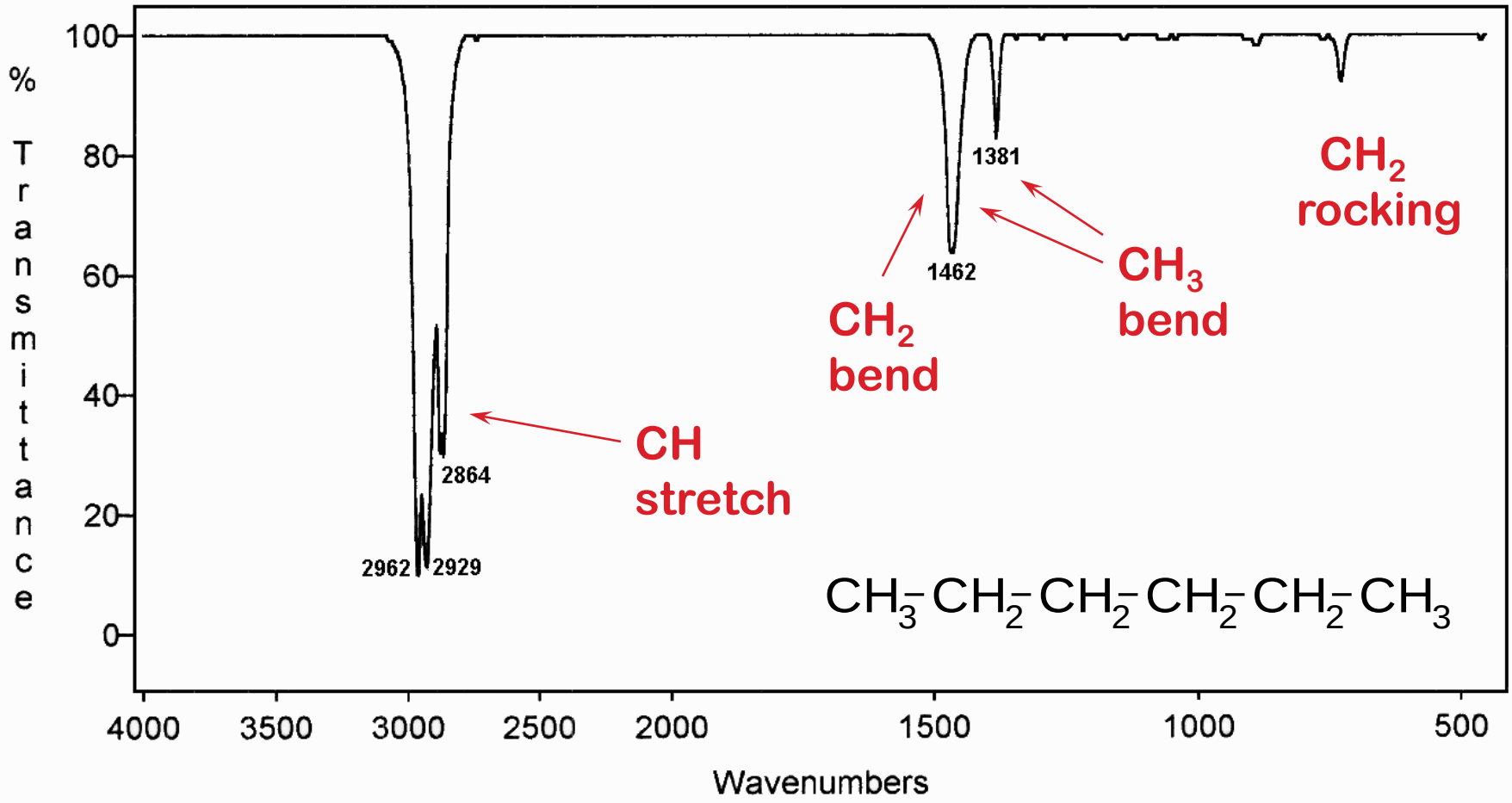
METHYLENE AND METHYL BENDING VIBRATIONS

ADDITIONAL DETAILS FOR SYM CH_3

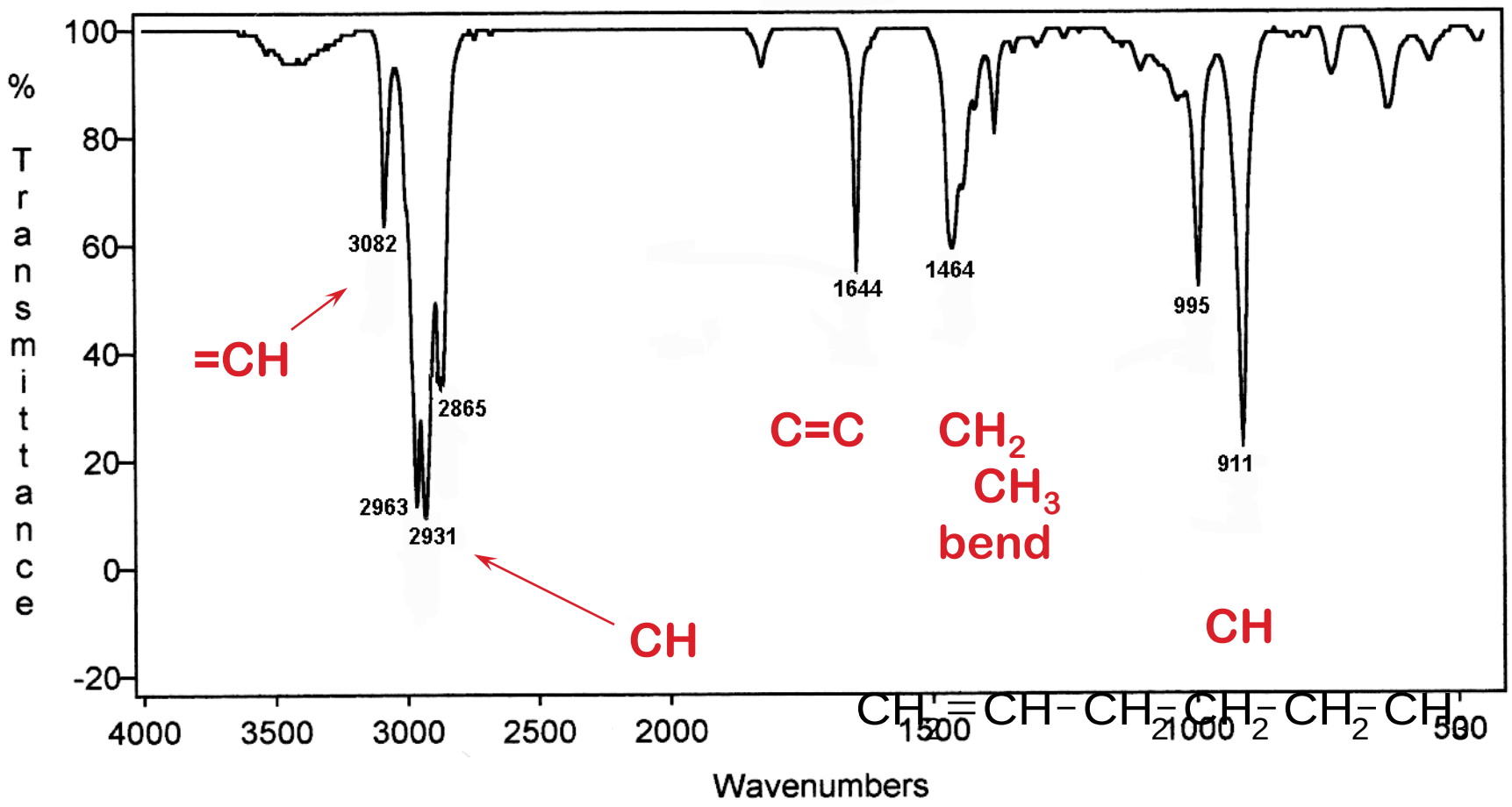


Hexane

ALKANE

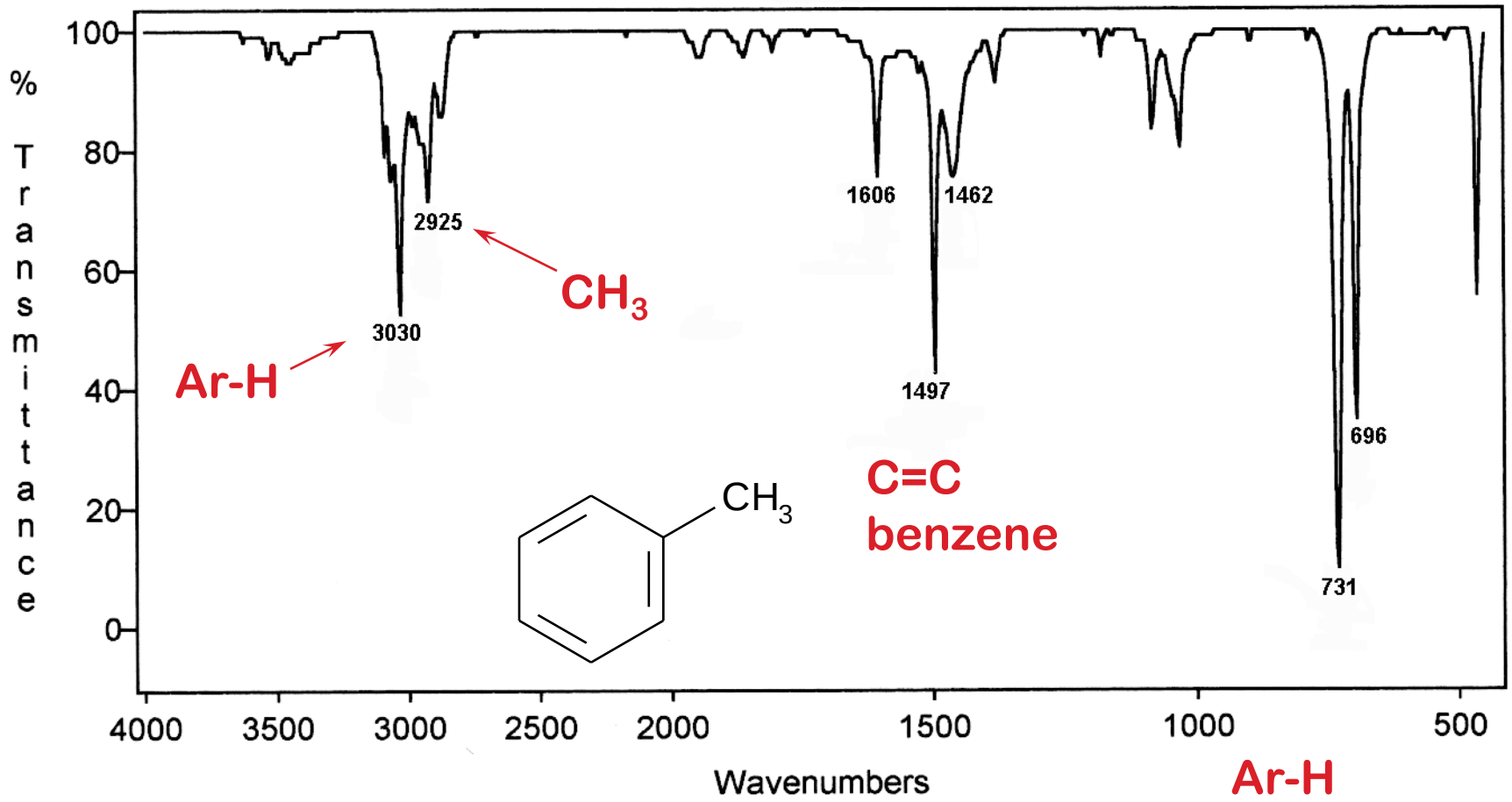


1-Hexene


% Transmittance
100
80
60
40
20
0
-20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
3082
2865
2963
2931
1644
1464
995
911
=CH
CH
C=C
CH2
CH3
bend
CH
CH2=CH-CH2-CH2-CH2-CH3

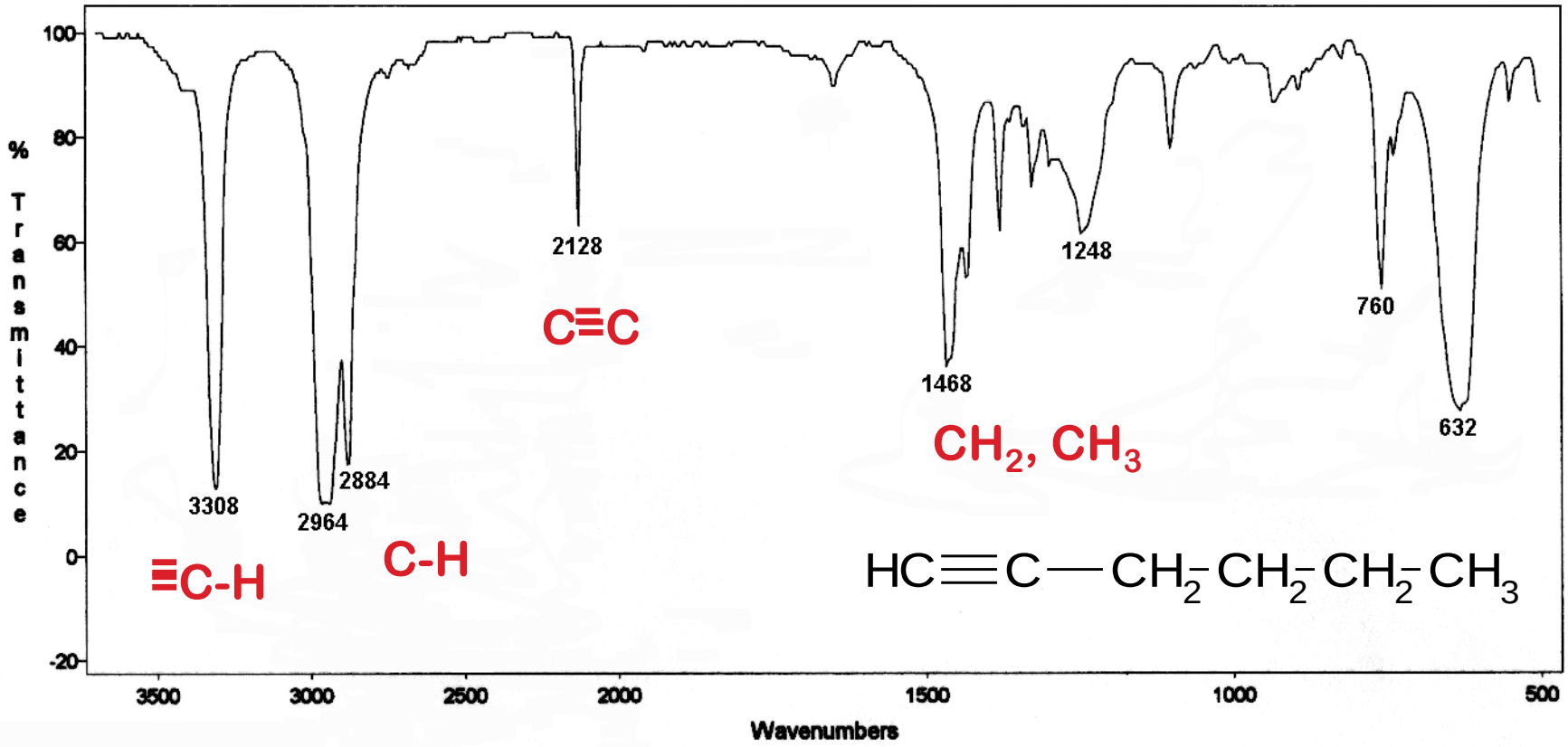
Toluene

AROMATIC

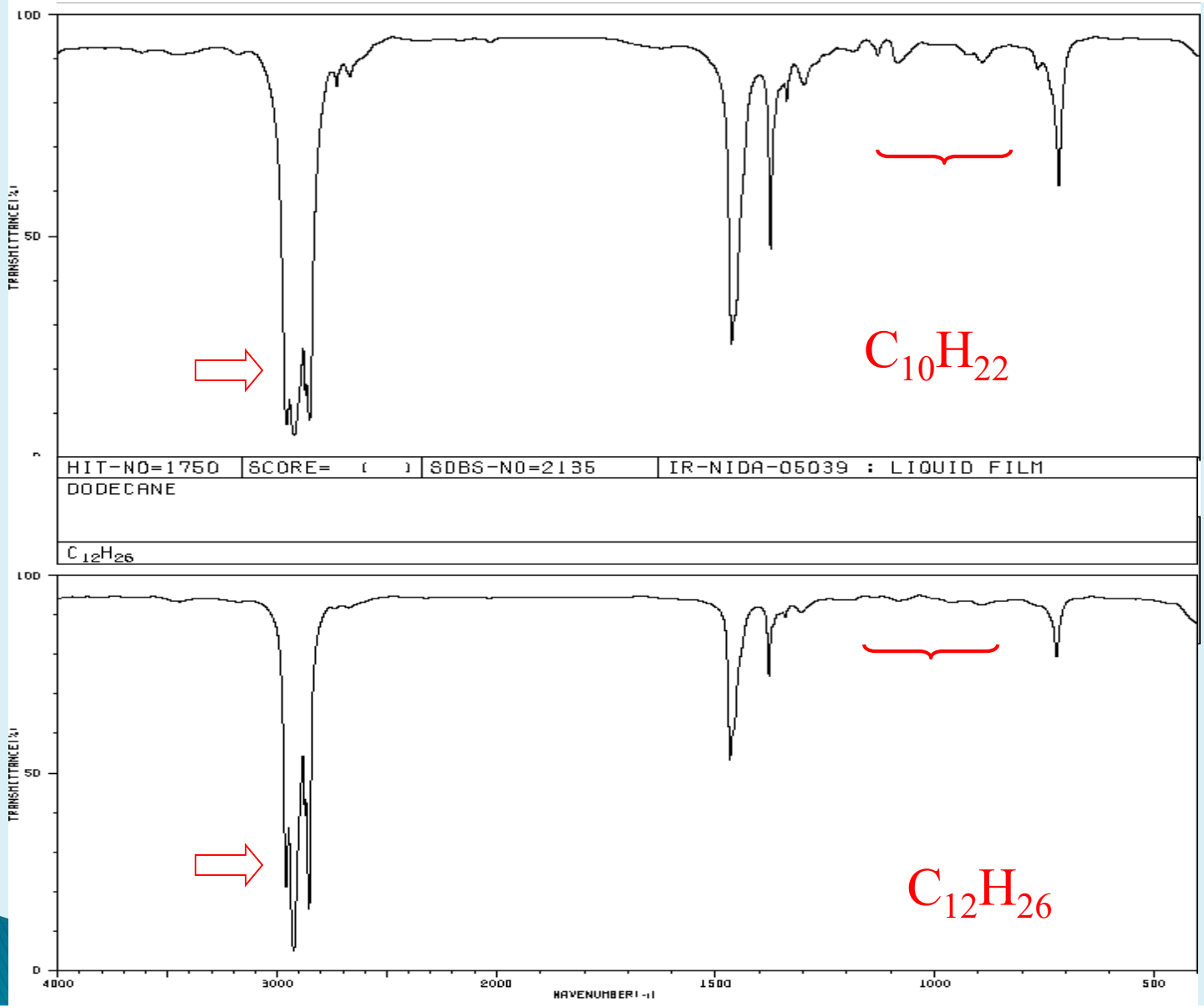


ALKYNE

1-Hexyne



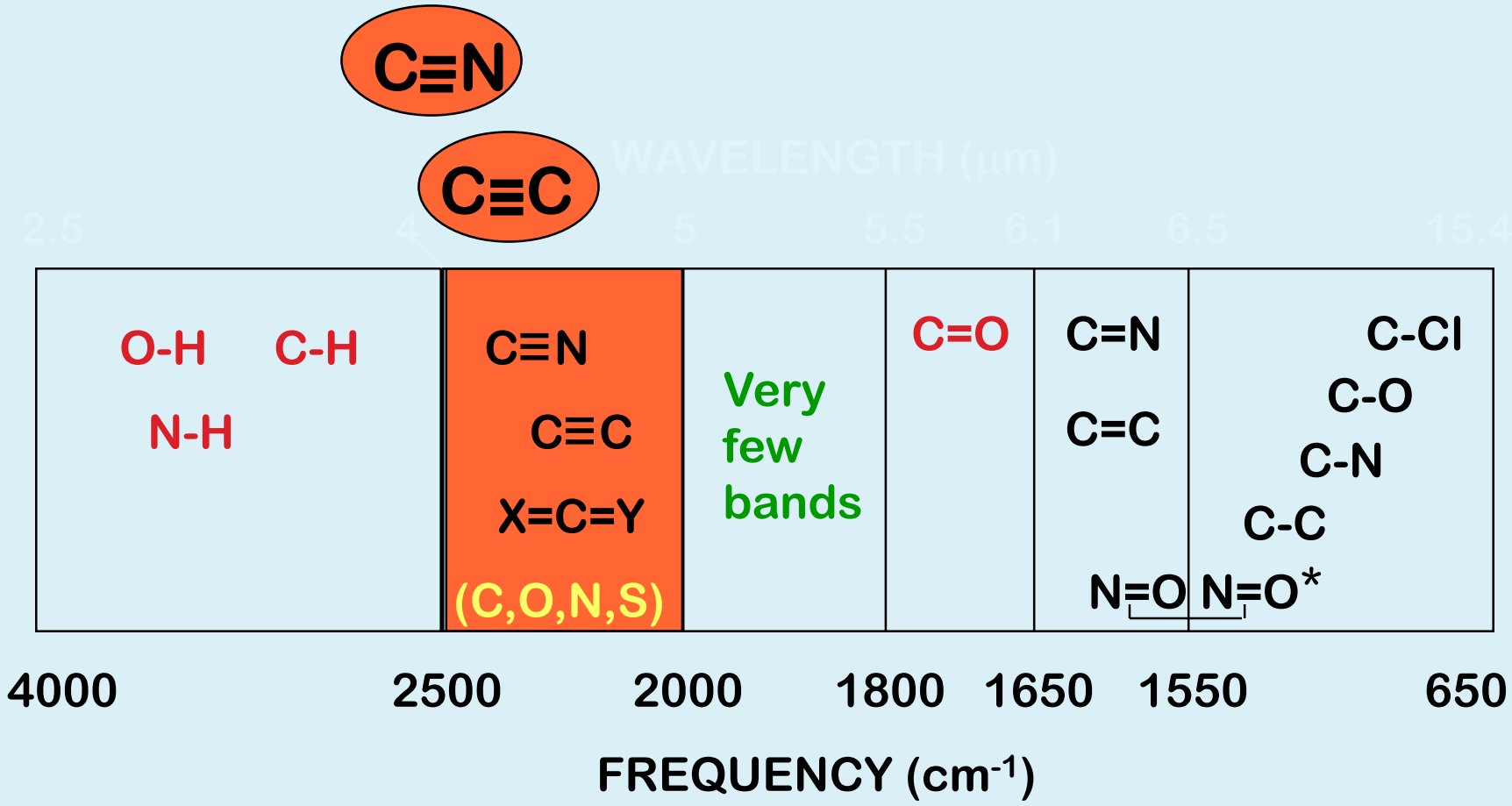
Fingerprinting



Similar But Not Identical

C≡N AND C≡C STRETCH

Typical Infrared Absorption Regions

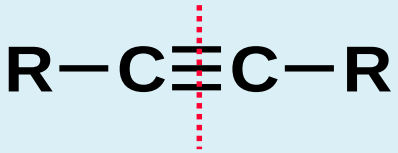


The triple bond stretching region

- C≡N 2250 cm^{-1}
- C≡C 2150 cm^{-1}

The cyano group often gives a strong, sharp peak due to its large dipole moment.

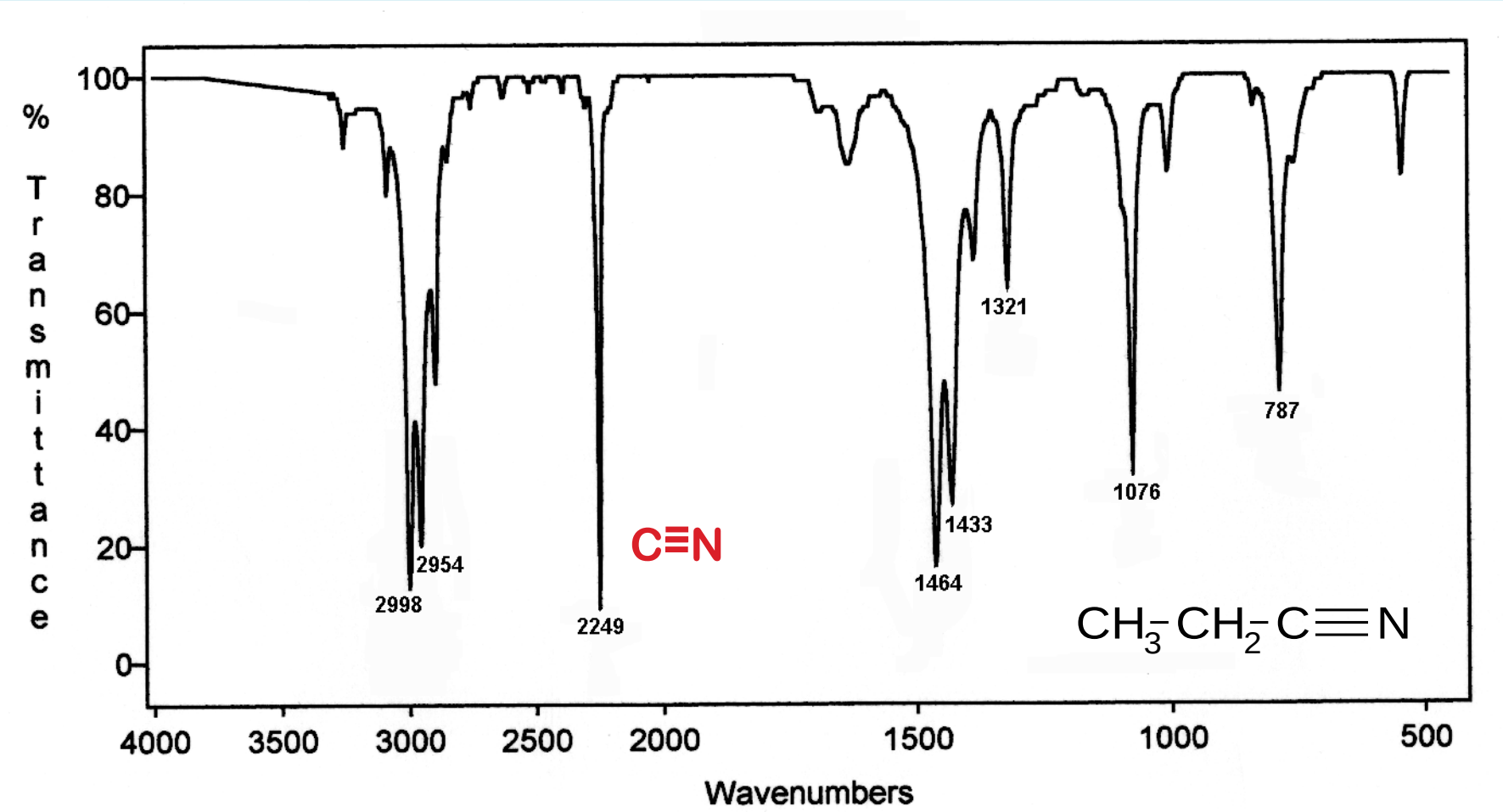
The carbon-carbon triple bond gives a sharp peak, but it is often weak due to a lack of a dipole. This is especially true if it is at the center of a symmetric molecule.



Propanenitrile

NITRILE

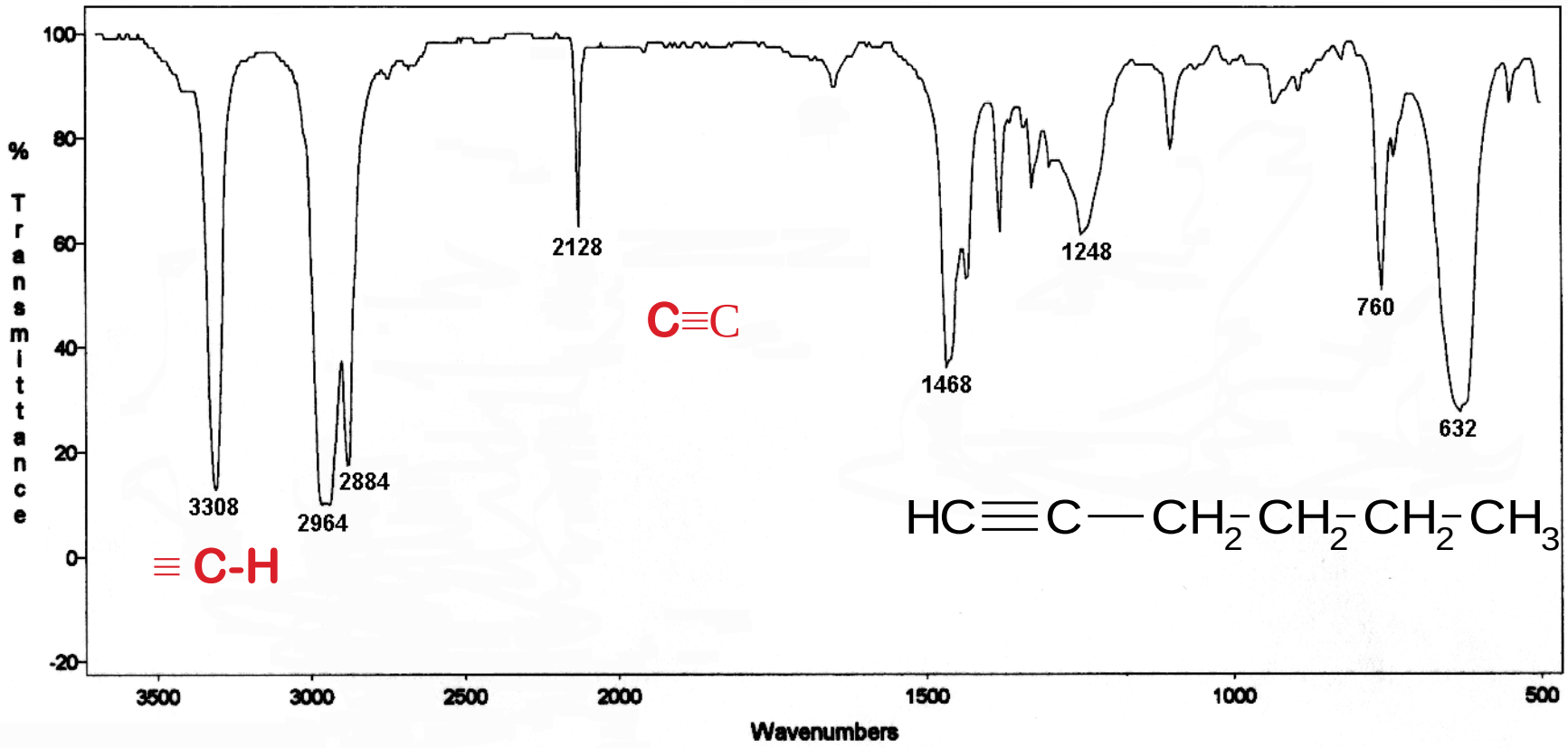
BASE = 2250



1-Hexyne

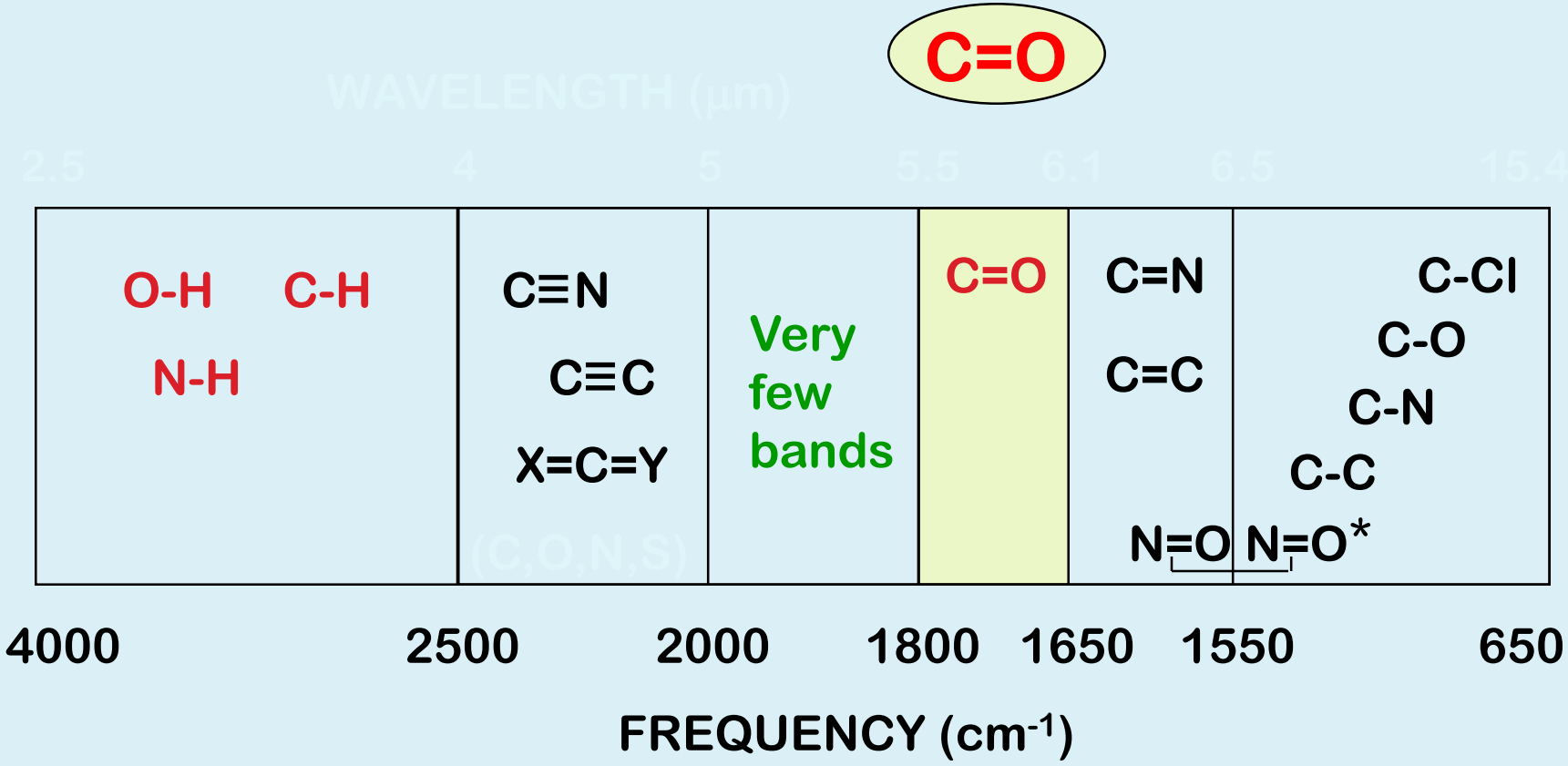
ALKYNE

BASE = 2150



C=O STRETCHING

Typical Infrared Absorption Regions



THE CARBONYL STRETCHING REGION

This region stretches from about 1800 to 1650 cm^{-1} RIGHT IN THE MIDDLE OF THE SPECTRUM

The base value is 1715 cm^{-1} (ketone)

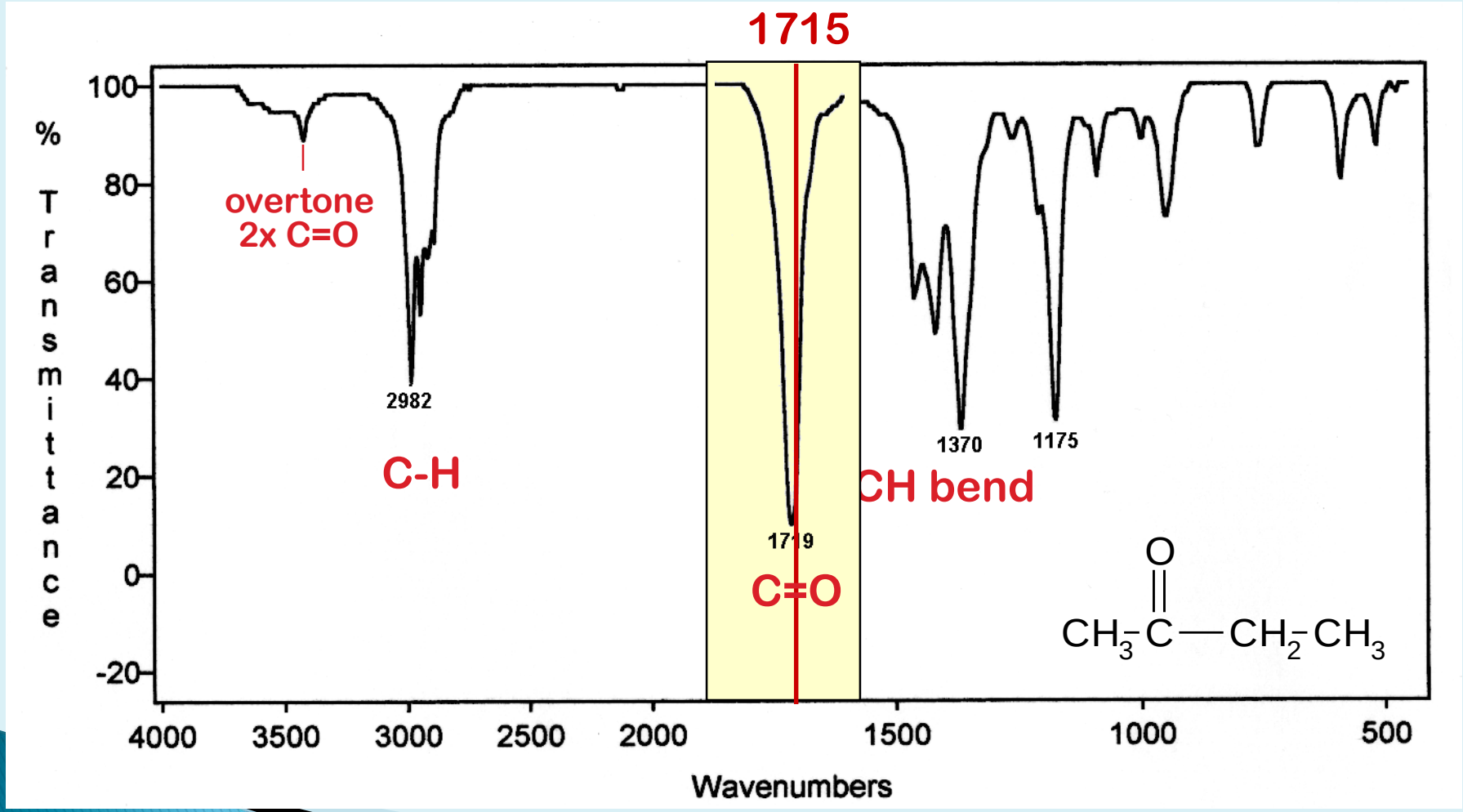
The bands are very strong !!! due to the large C=O dipole moment.

- C=O is often one of the strongest peaks in the spectrum

KETONE

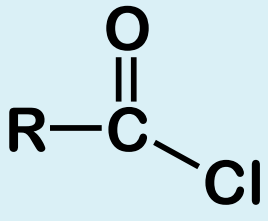
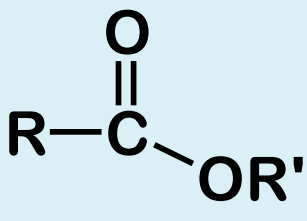
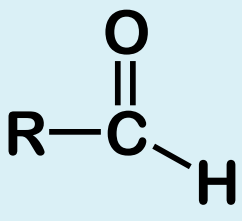
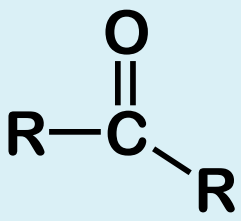
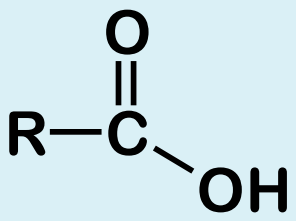
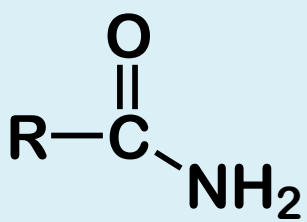
2-Butanone

BASE = 1715

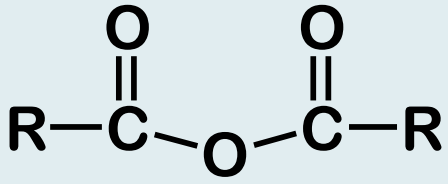


C=O IS SENSITIVE TO ITS ENVIRONMENT

EACH DIFFERENT KIND OF C=O COMES AT A DIFFERENT FREQUENCY

acid chloride	ester	aldehyde	ketone	carboxylic acid	amide
					
1800	1735	1725	1715	1710	1690

anhydride



1810 and 1760

(two peaks)

BASE VALUE

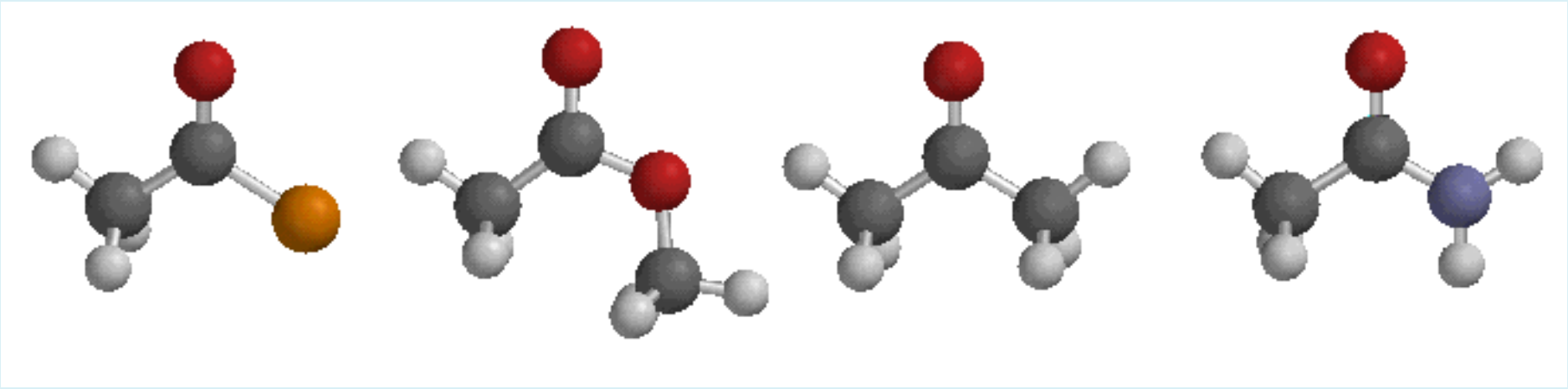
THESE VALUES ARE WORTH LEARNING

all are +/- 10 cm^{-1}

C=O BOND LENGTHS IN CARBONYL COMPOUNDS

shorter ← | → longer

1.225 A	1.231 A	1.235 A	1.248 A



acid chloride	ester	ketone	amide
1780 cm^{-1}	1735 cm^{-1}	1715 cm^{-1}	1680 cm^{-1}

SUMMARY

Ketones are at lower frequency than **Aldehydes** because of the second electron-donating alkyl group.

Acid chlorides are at higher frequency than ketones because of the electron-withdrawing halide.

Esters are at higher frequencies than ketones due to the electron-withdrawing oxygen atom. This is more important than resonance with the electron pair on the oxygen.

Amides are at lower frequencies than ketones due to resonance involving the unshared pair on nitrogen. The electron-withdrawing effect of nitrogen is less important than the resonance.

Note that the electronegativity difference, O versus N, weights the two factors (resonance/ e-withdrawal) differently in esters than in amides.

Acids are at lower frequency than ketones due to H-bonding.

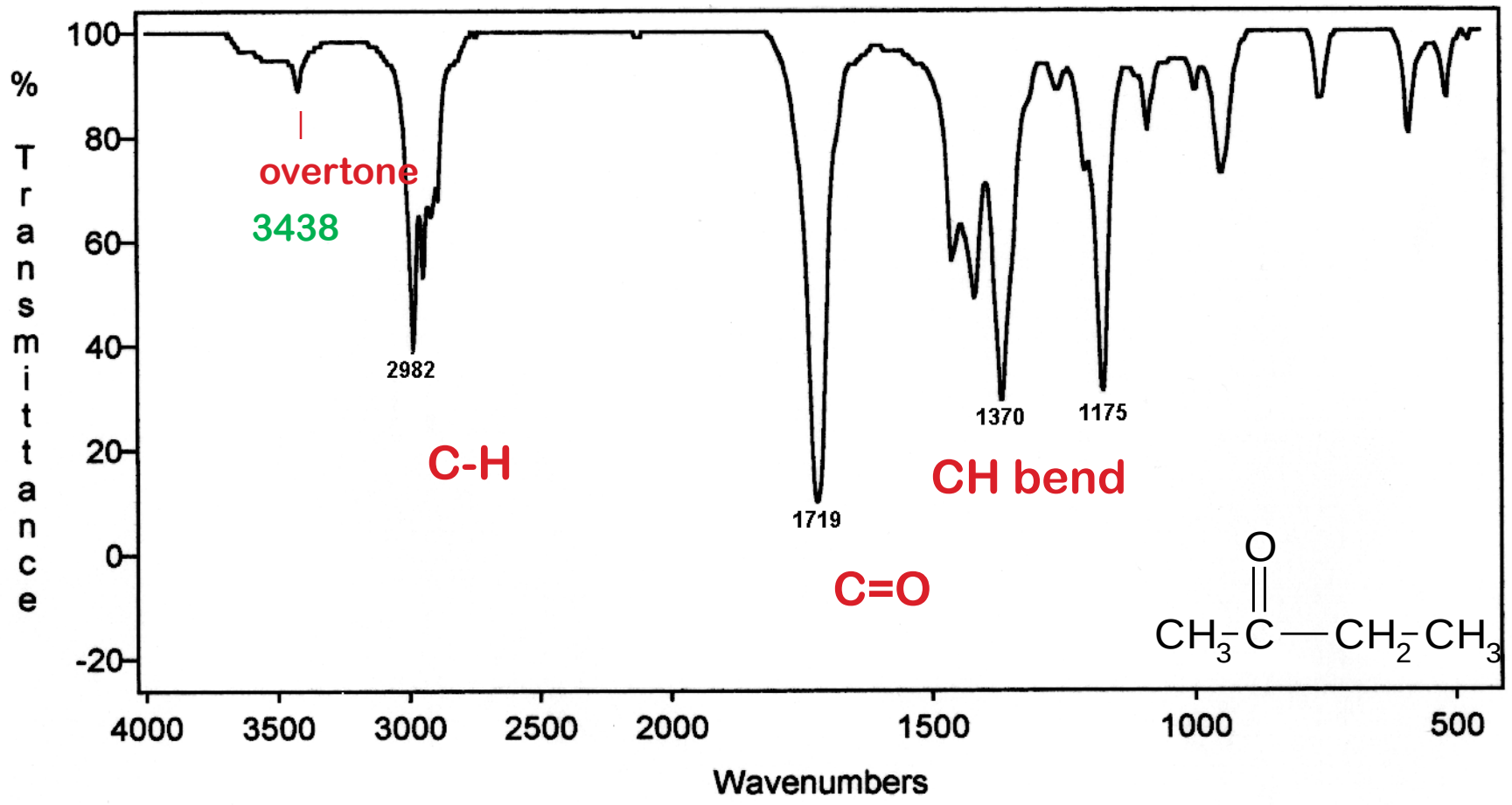
overtone of strong C=O peak

1719 x 2 = 3438

2-Butanone

KETONE

BASE = 1715



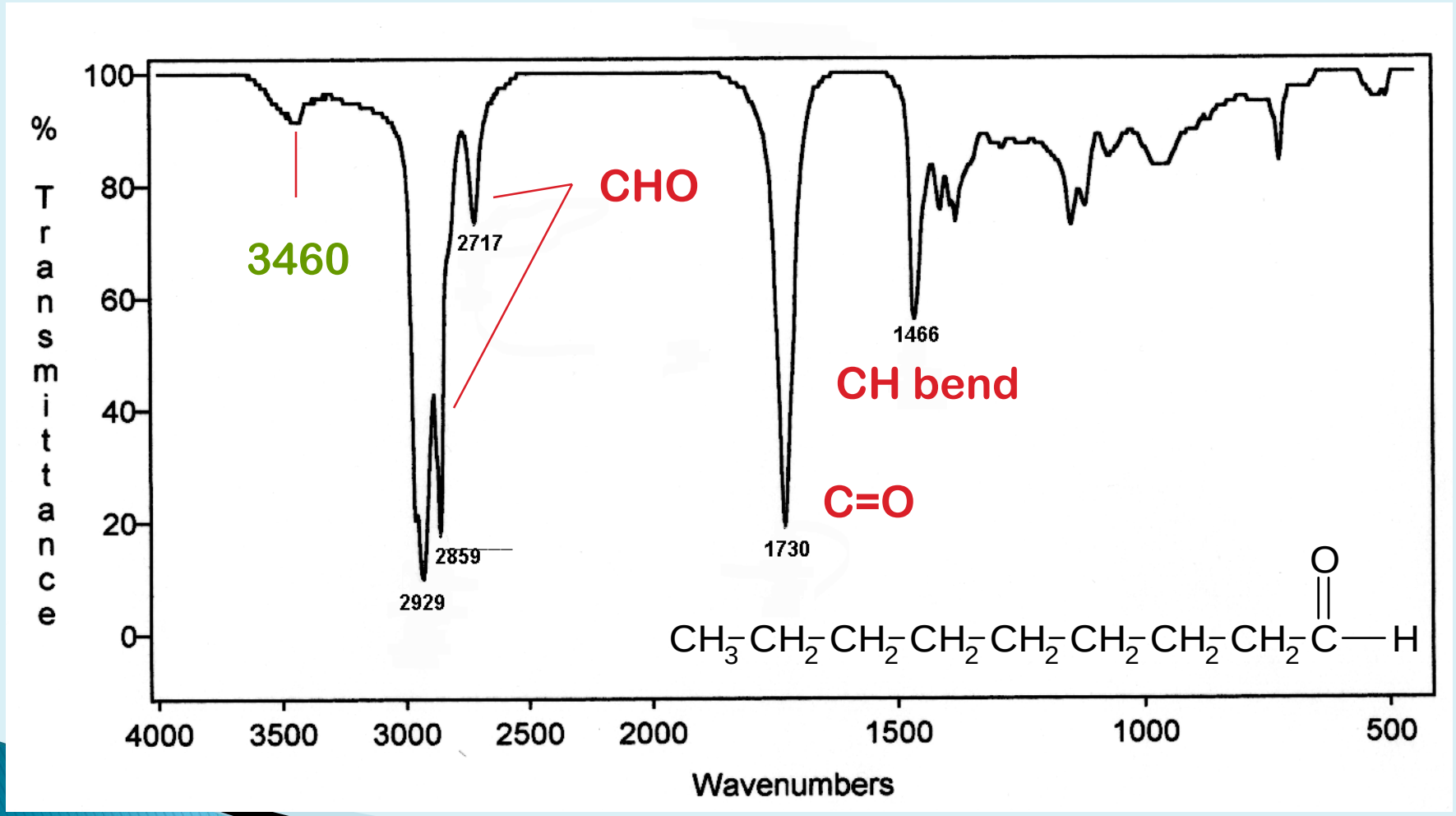
overtone of strong C=O peak

1725 x 2= 3460

ALDEHYDE

BASE = 1725

Nonanal



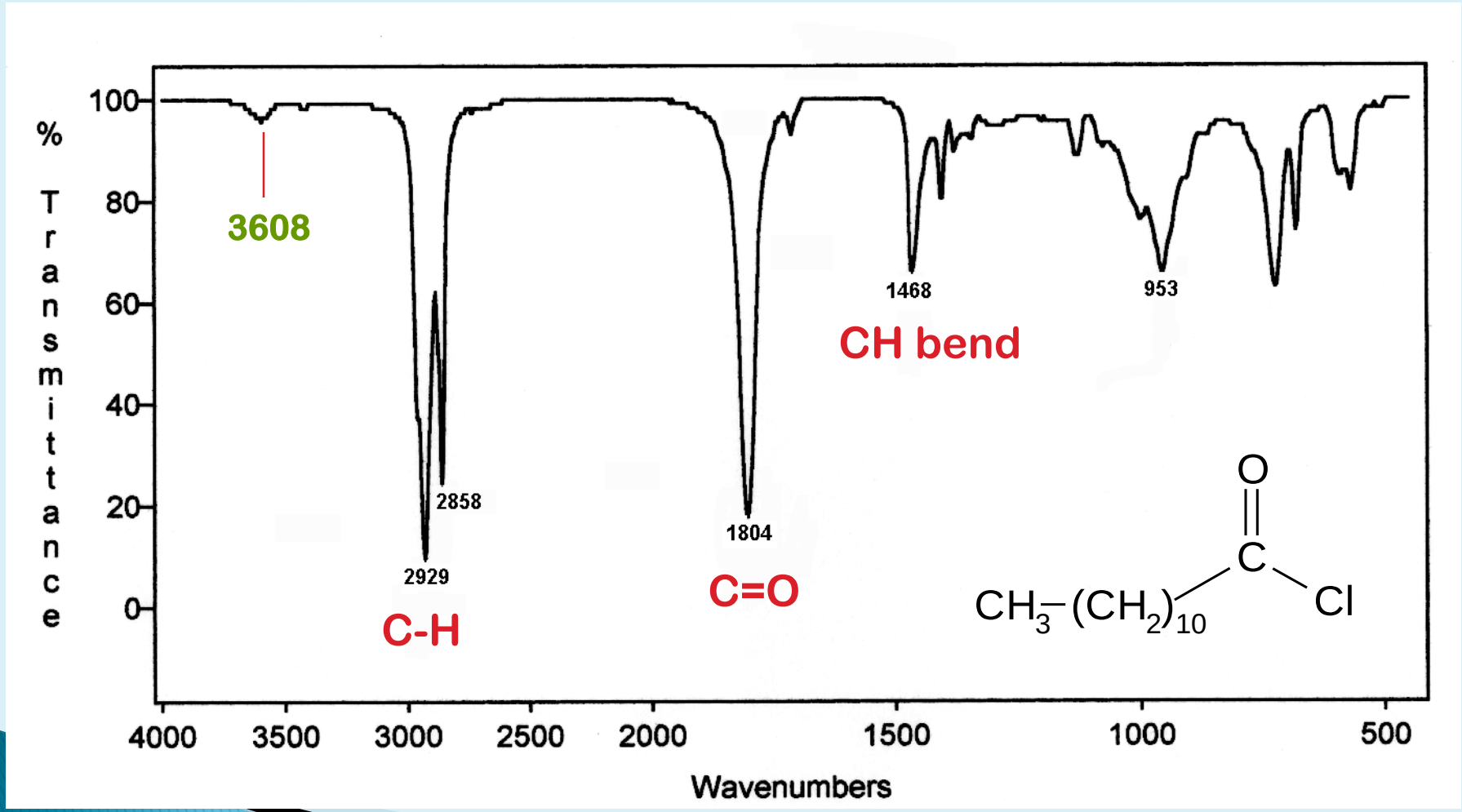
overtone of strong C=O peak

1800 x 2 = 3608

ACID CHLORIDE

Dodecanoyl Chloride

BASE = 1800



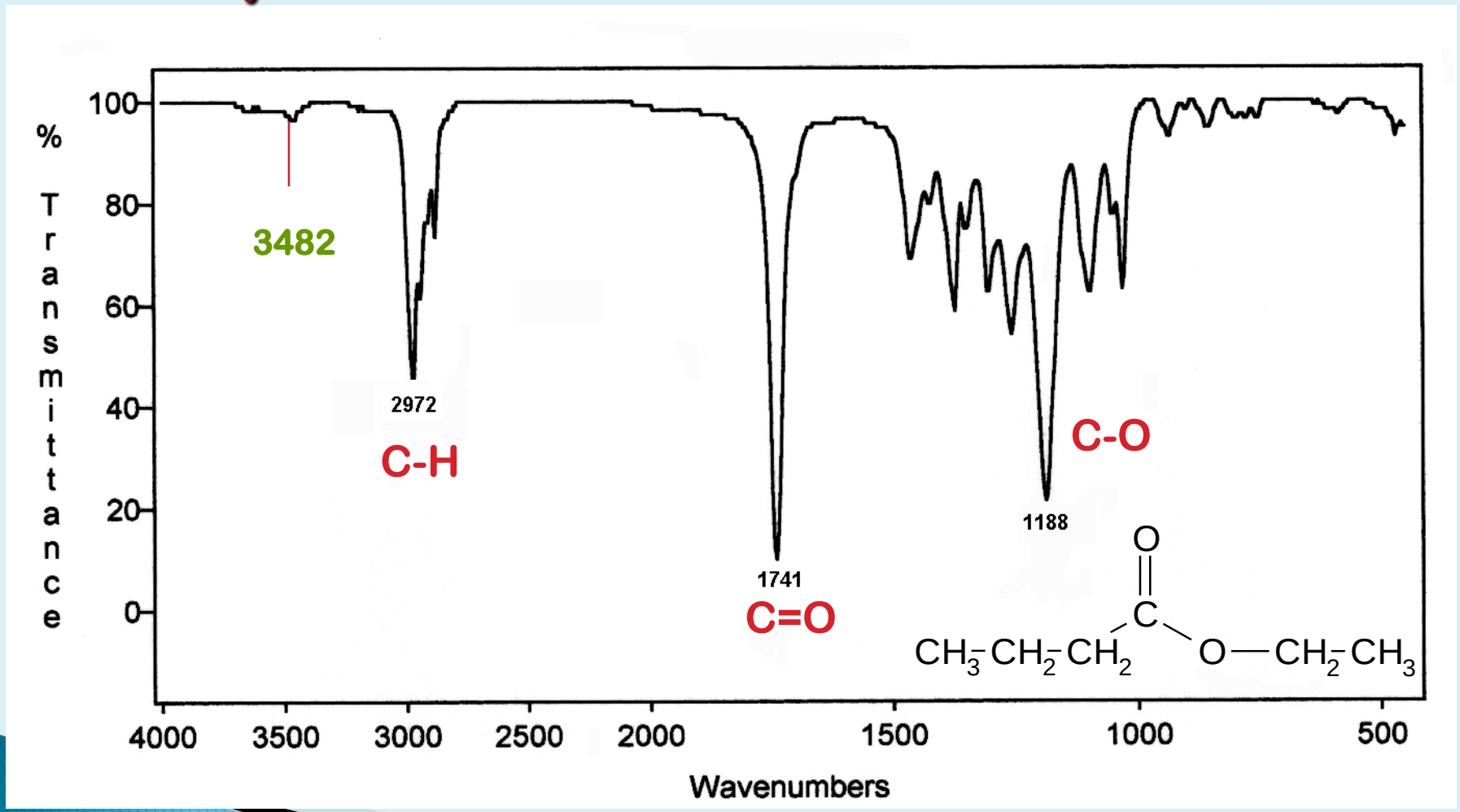
overtone of strong C=O peak

1735 x 2 = 3482

ESTER

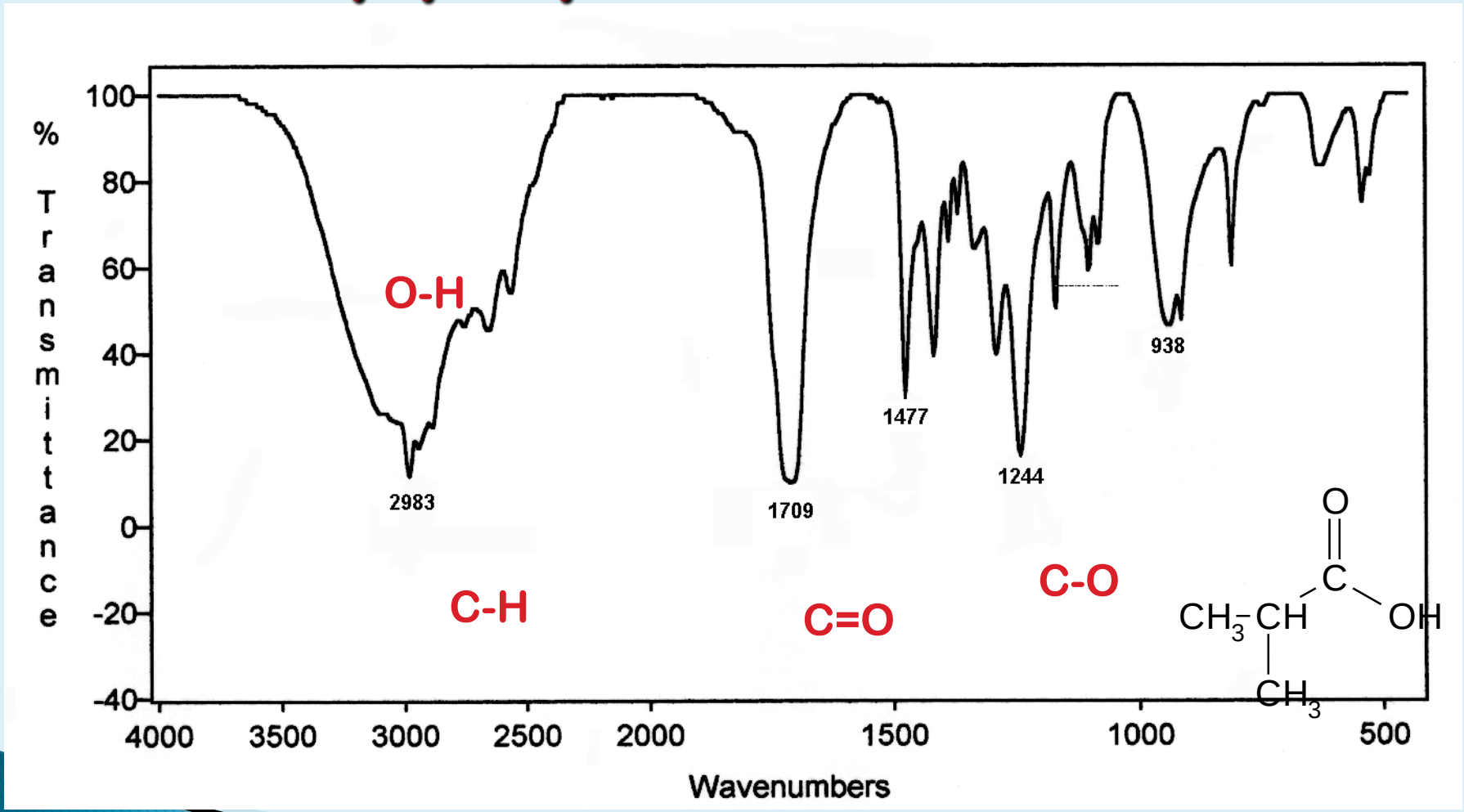
BASE = 1735

Ethyl Butanoate



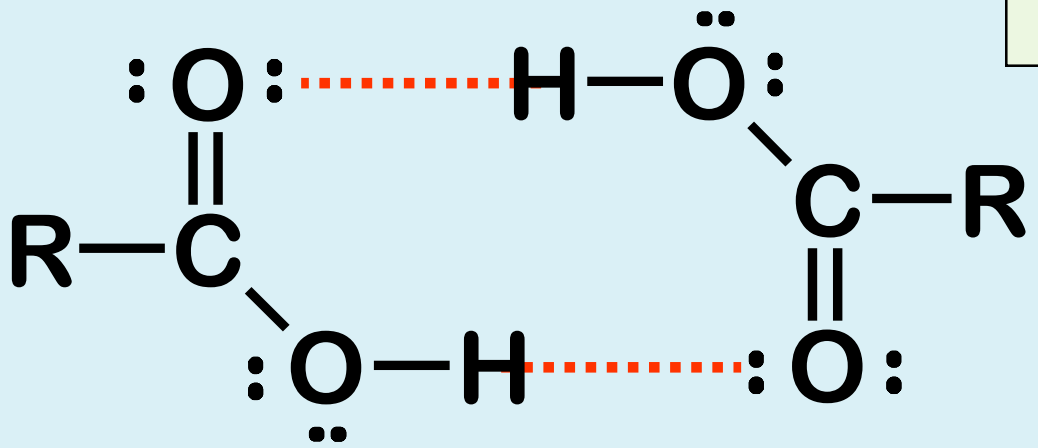
BASE = 1710

2-Methylpropanoic Acid



CARBOXYLIC ACID DIMER

RECALL



lowers frequency of C=O

and also of O-H

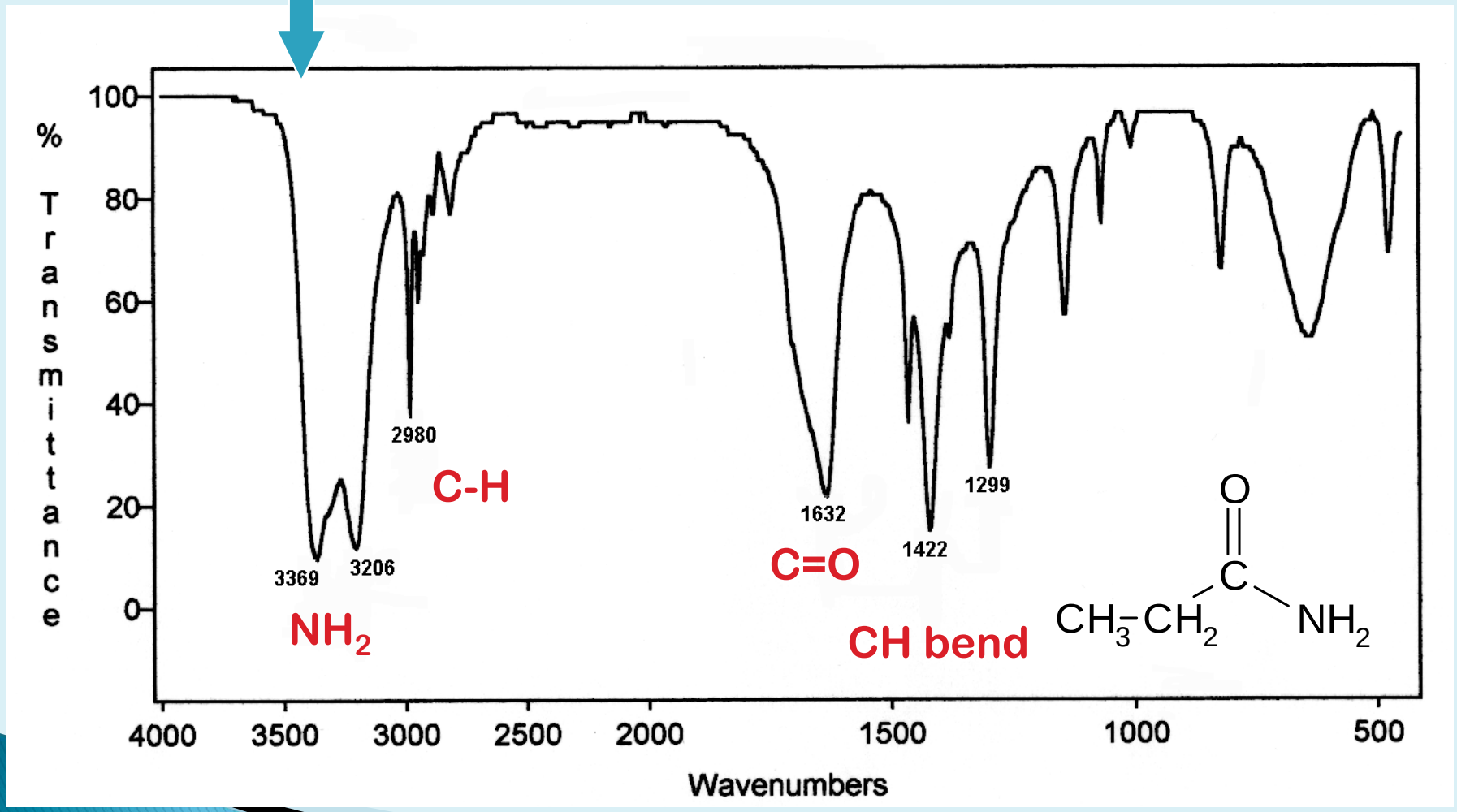
Strong hydrogen-bonding in the dimer weakens the O-H and C=O bonds and leads to broad peaks at lower frequencies.

Propanamide

AMIDE

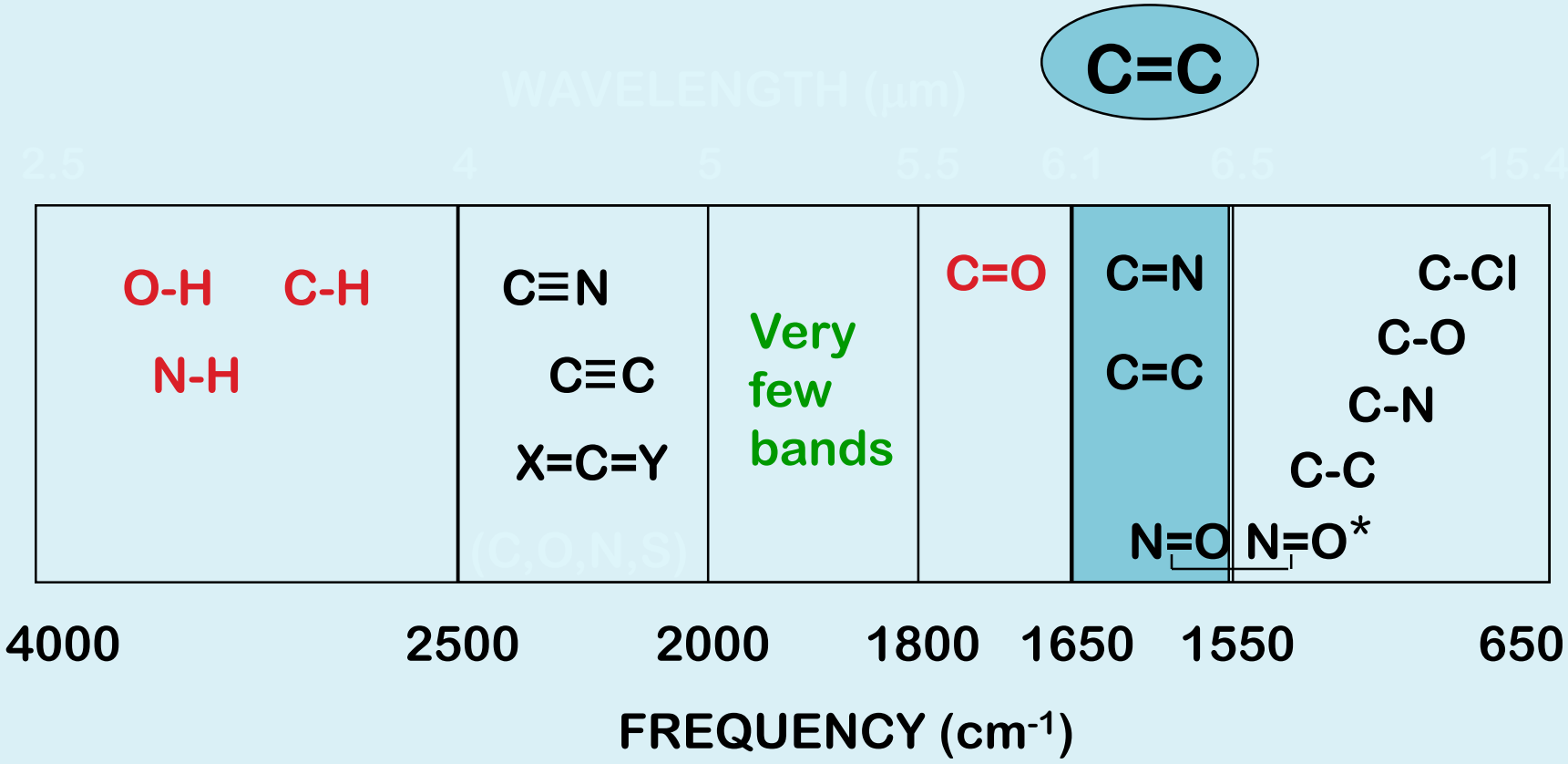
BASE = 1690

two peaks
sym / asym



C=C STRETCHING

Typical Infrared Absorption Regions

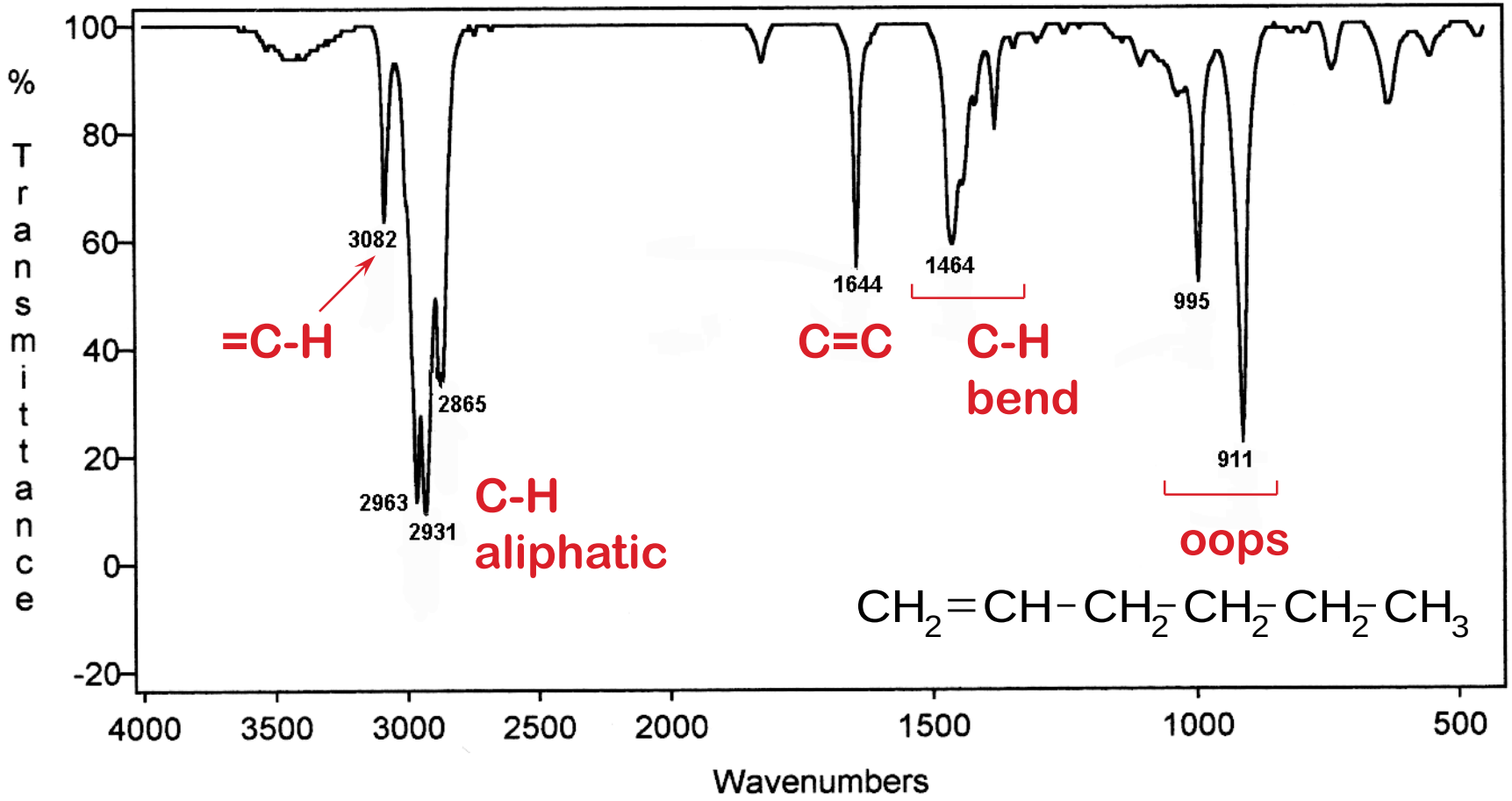


THE C=C STRETCHING REGION

- C=C double bond at 1650 cm^{-1} is often weak or not even seen.

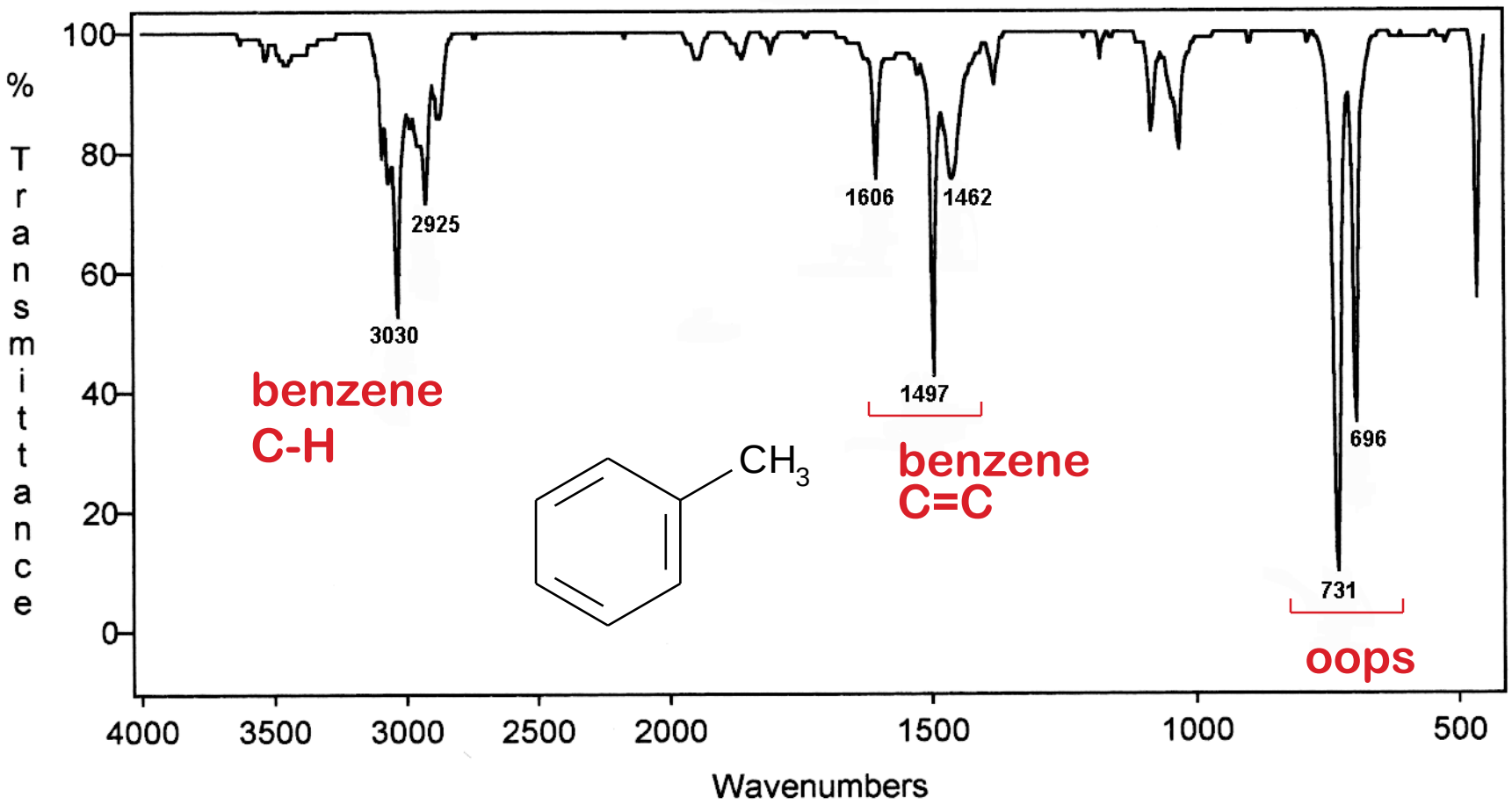
- C=C benzene ring shows peak(s) near 1600 and 1400 cm^{-1} , one or two at each value - CONJUGATION LOWERS THE VALUE.
- When C=C is conjugated with C=O it is stronger and comes at a lower frequency.

1-Hexene

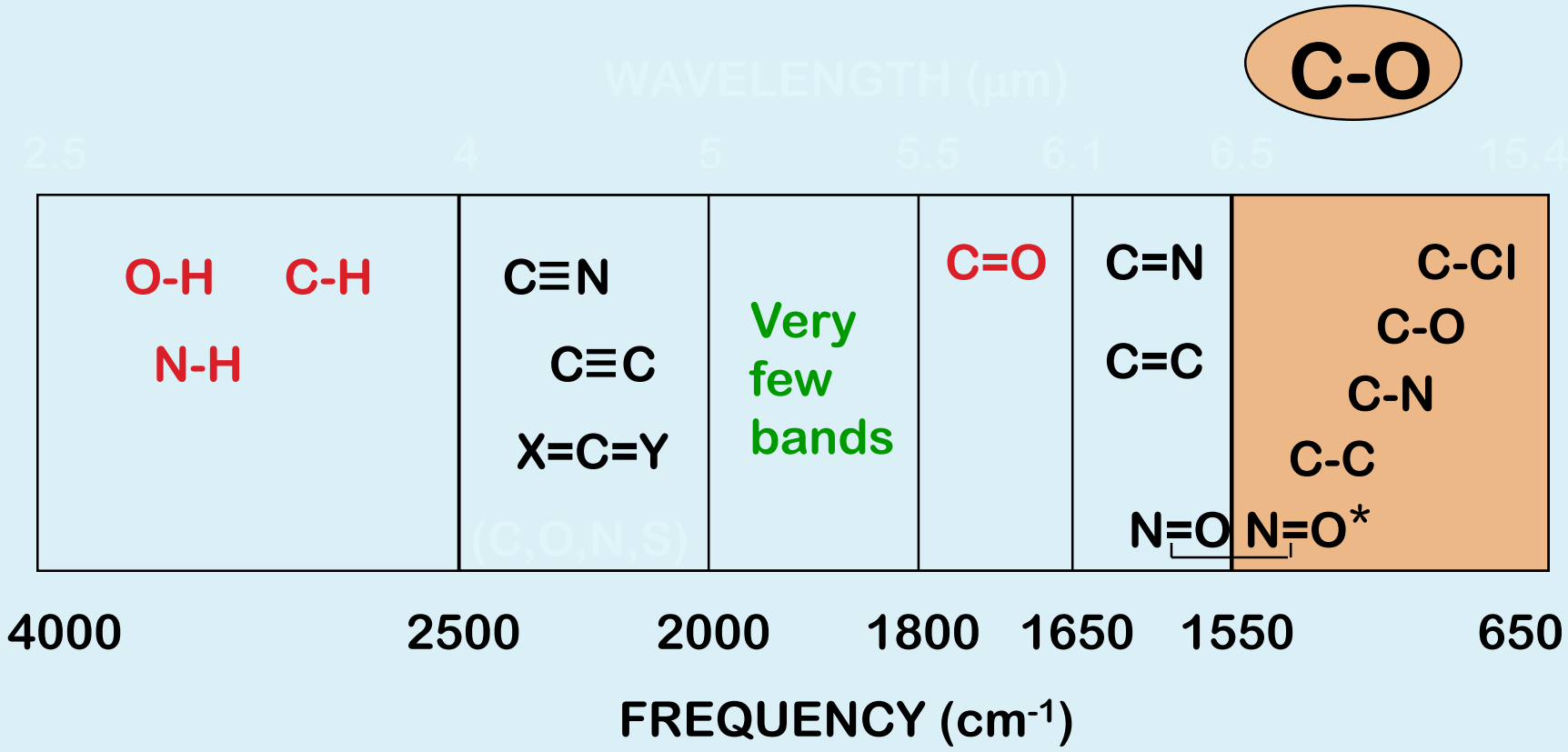

% Transmittance
100
80
60
40
20
0
-20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
3082
2963
2931
2865
1644
1464
995
911
=C-H
C-H aliphatic
C=C
C-H bend
oops
CH2=CH-CH2-CH2-CH2-CH3

Toluene

AROMATIC



Typical Infrared Absorption Regions



C-O STRETCHING

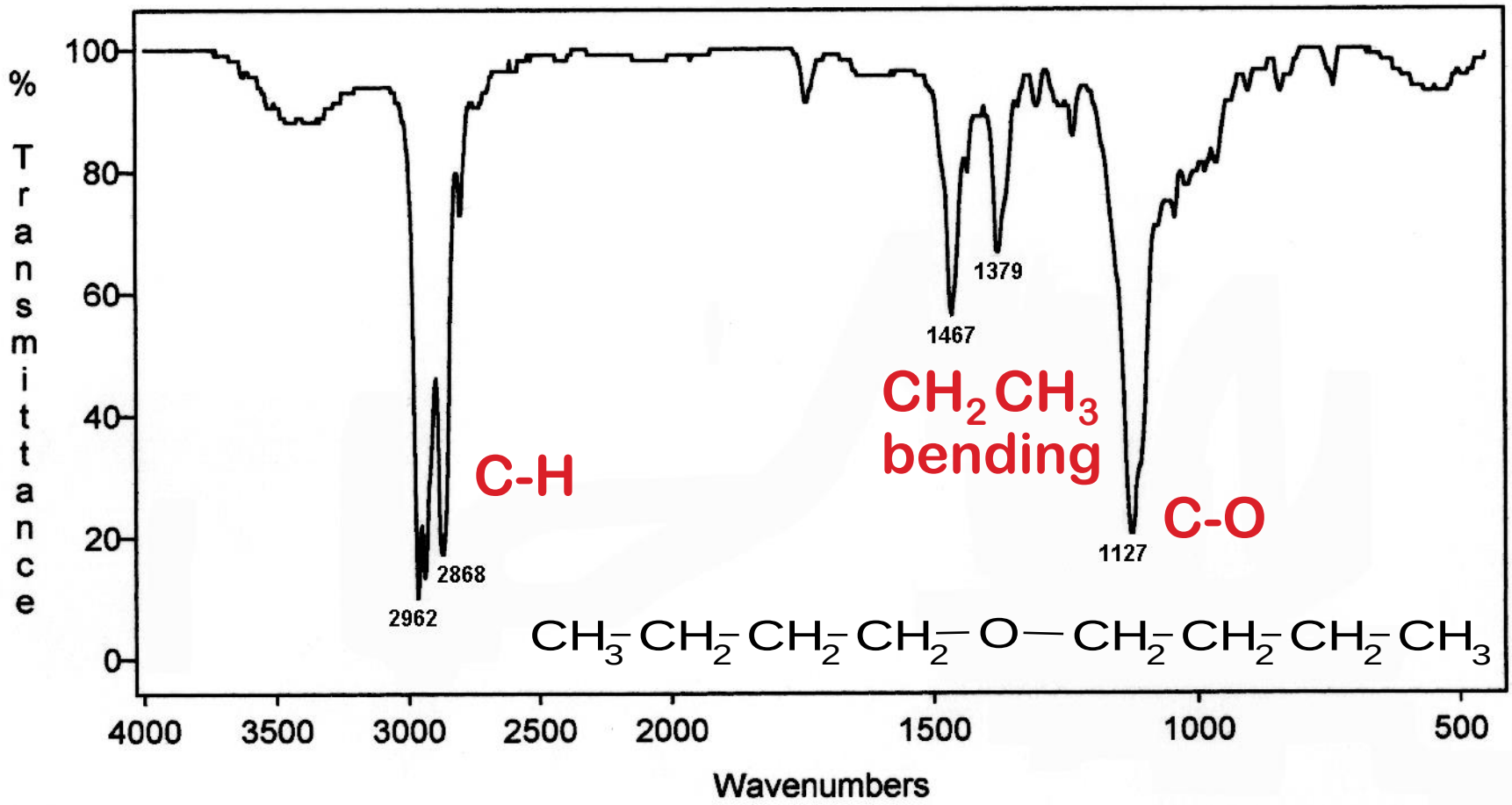
The C-O stretching region

- 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

Dibutyl Ether

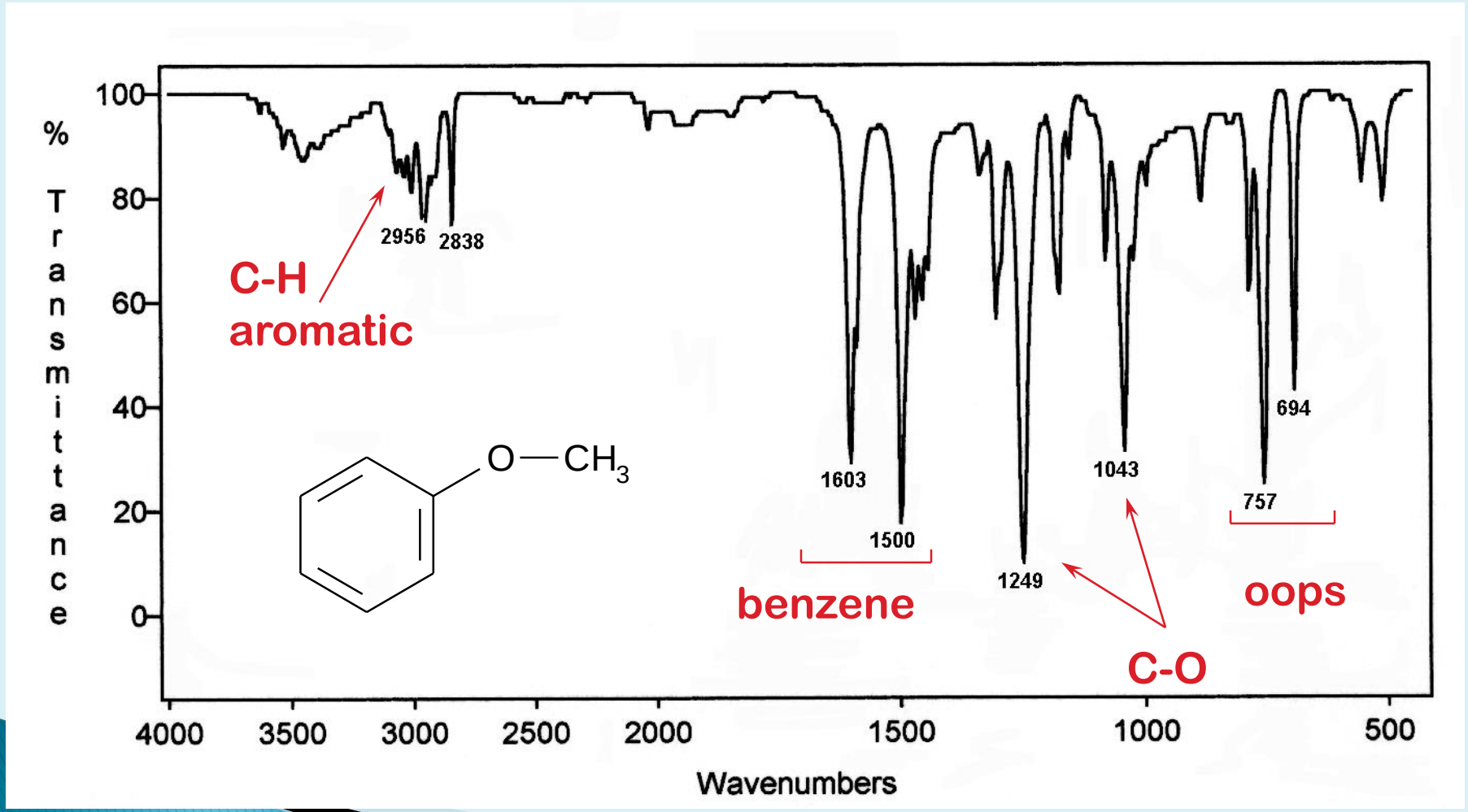
BASE = 1100



Anisole

AROMATIC ETHER

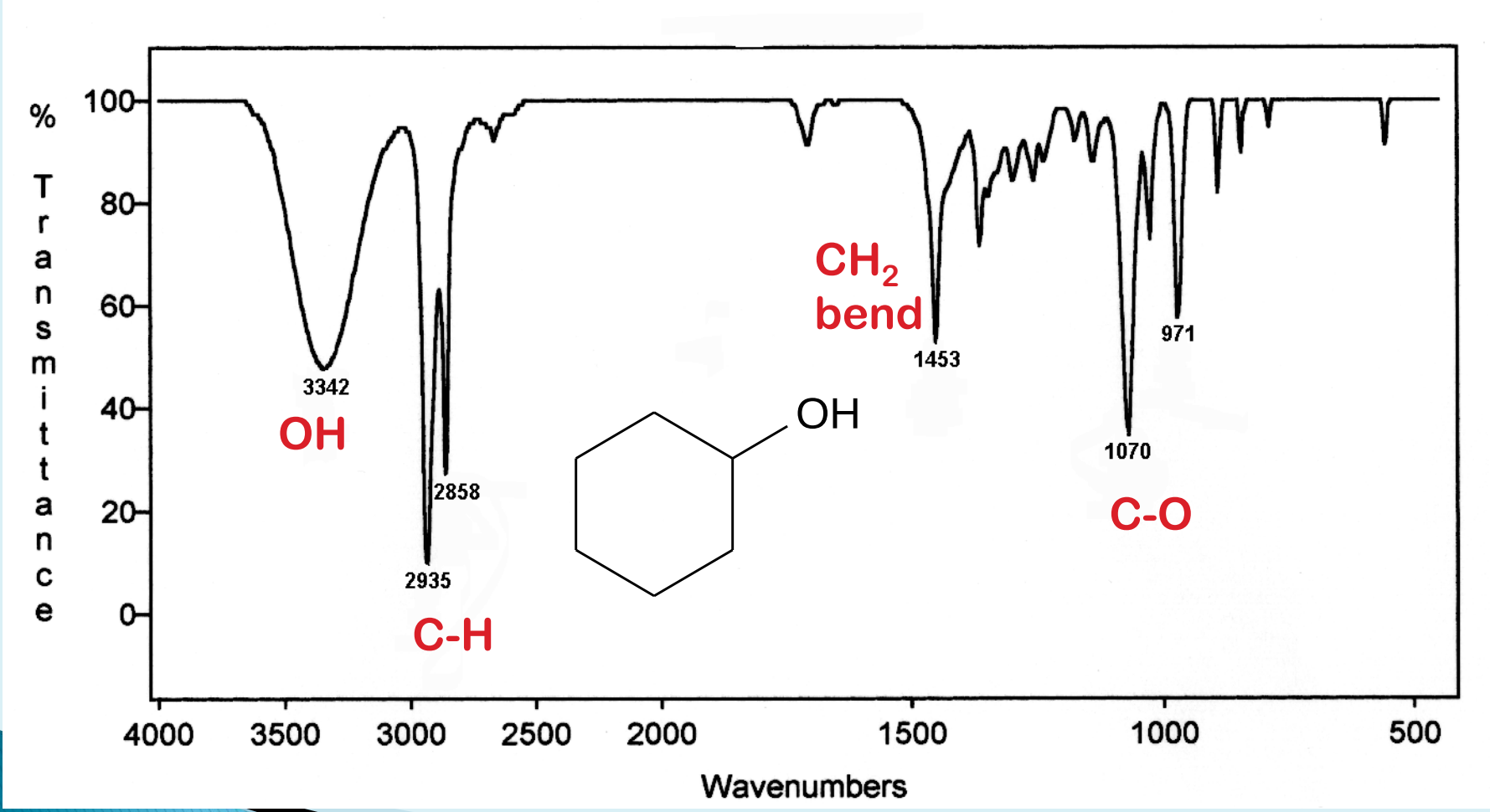
BASE = 1100



Cyclohexanol

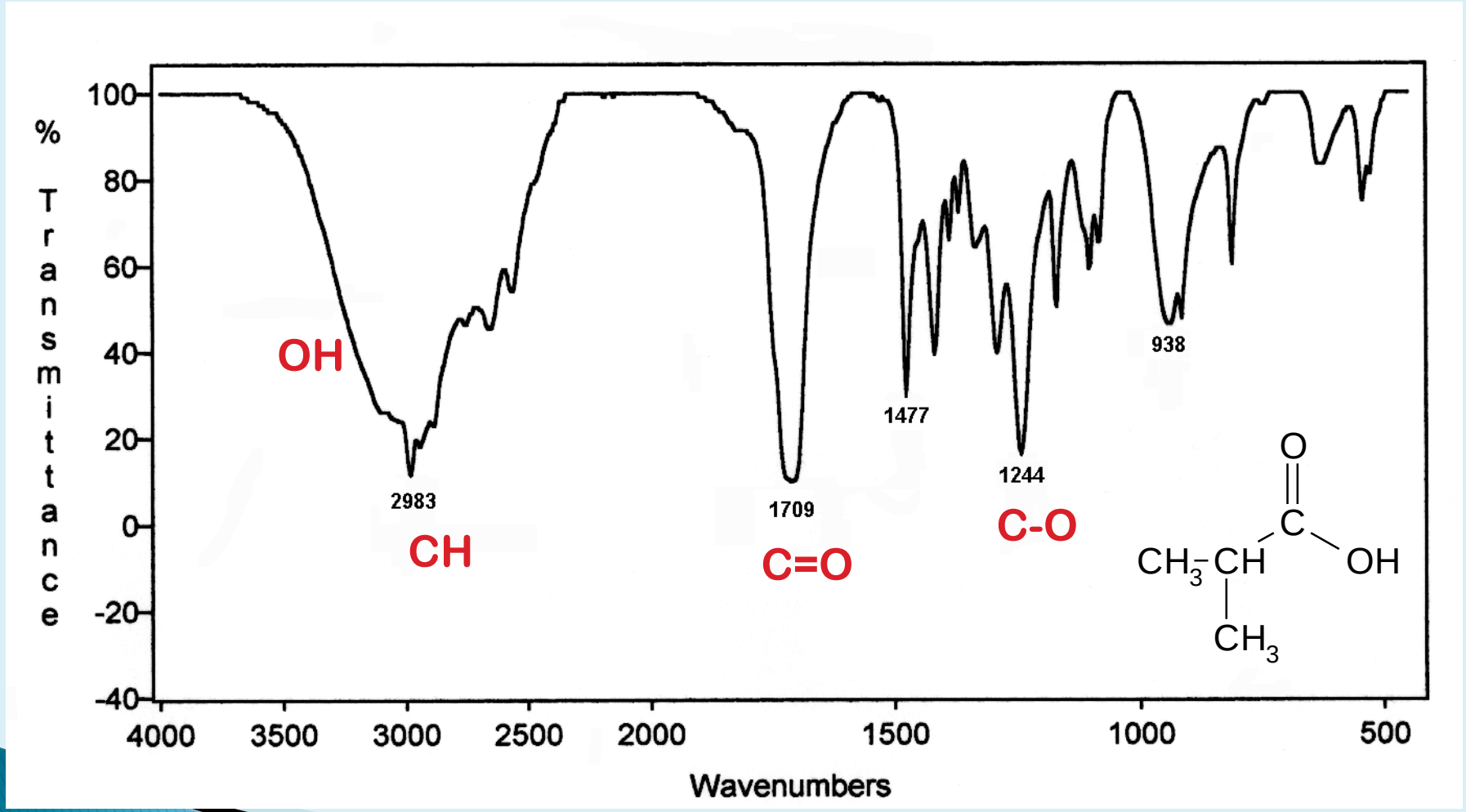
ALCOHOL

BASE = 3600
BASE = 1100



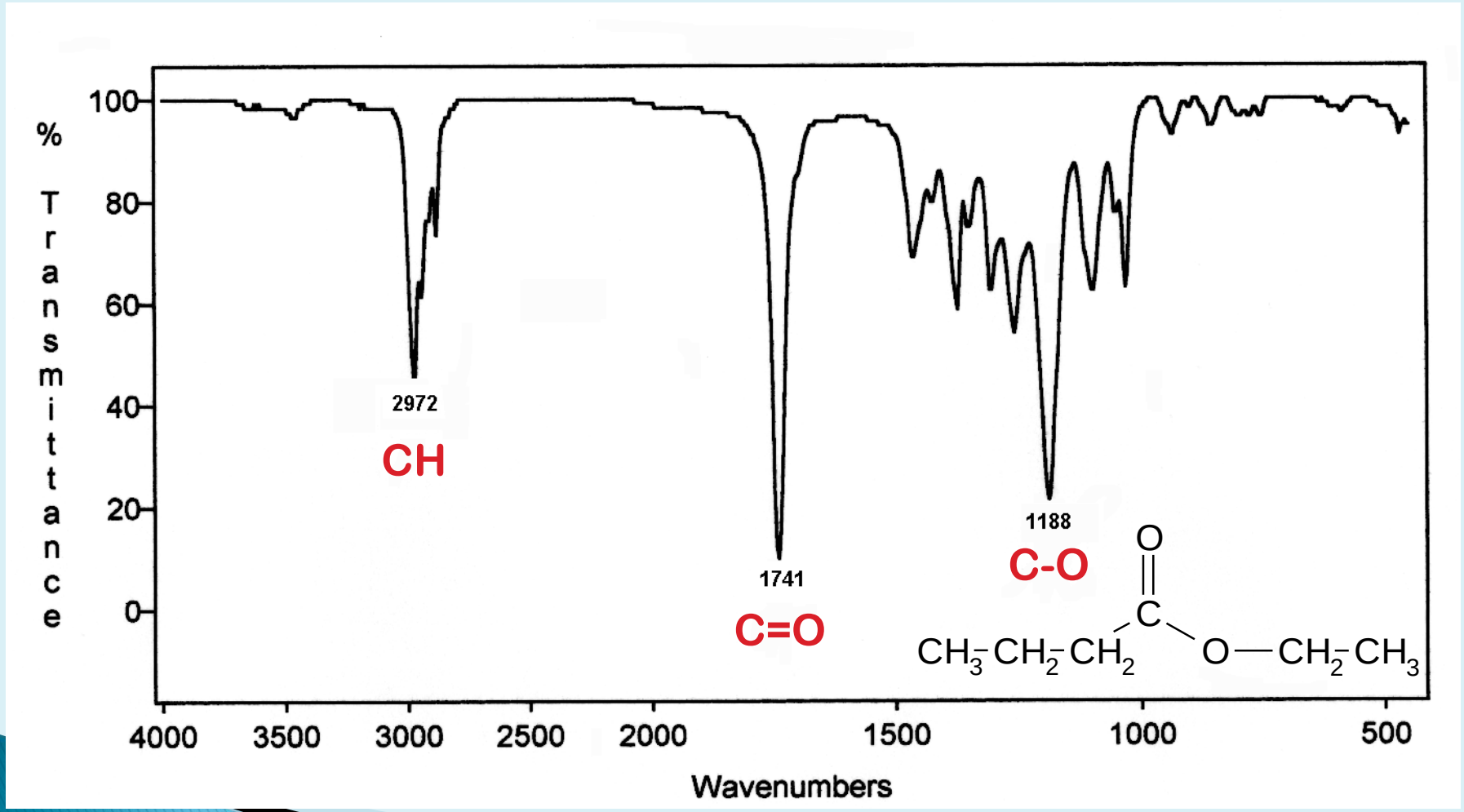
CARBOXYLIC ACID

2-Methylpropanoic Acid



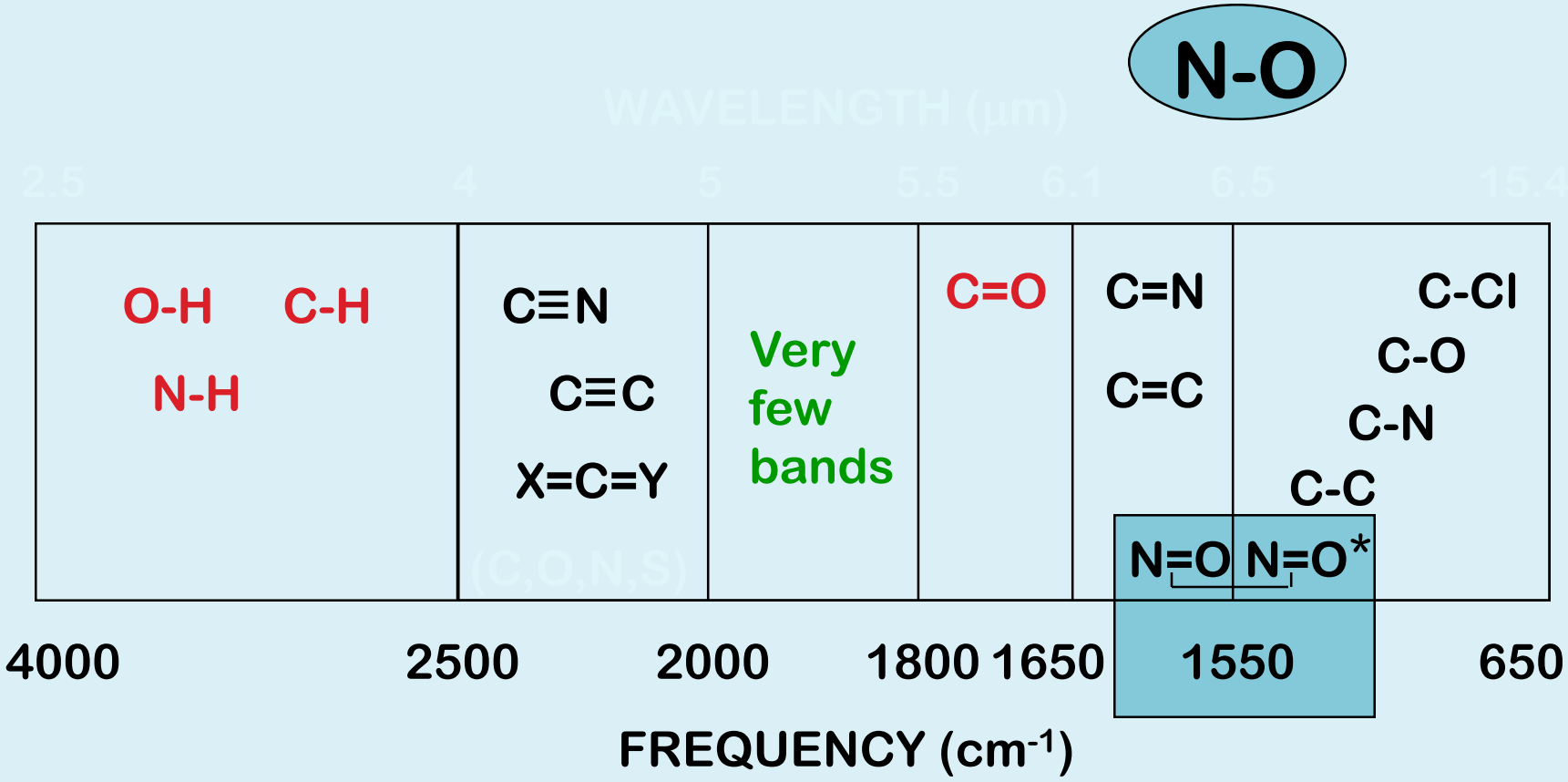
Ethyl Butanoate

ESTER



N=O STRETCHING

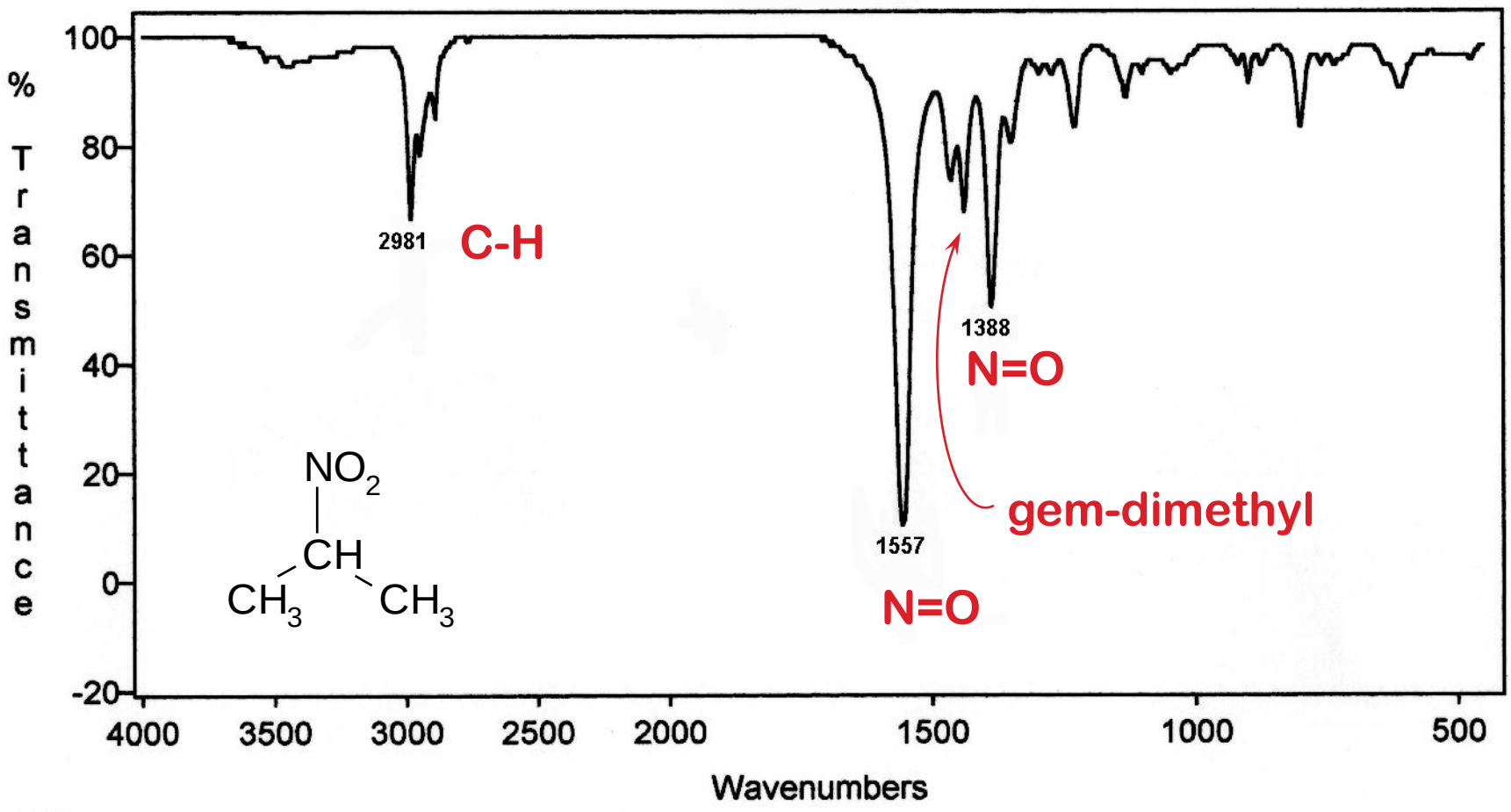
Typical Infrared Absorption Regions



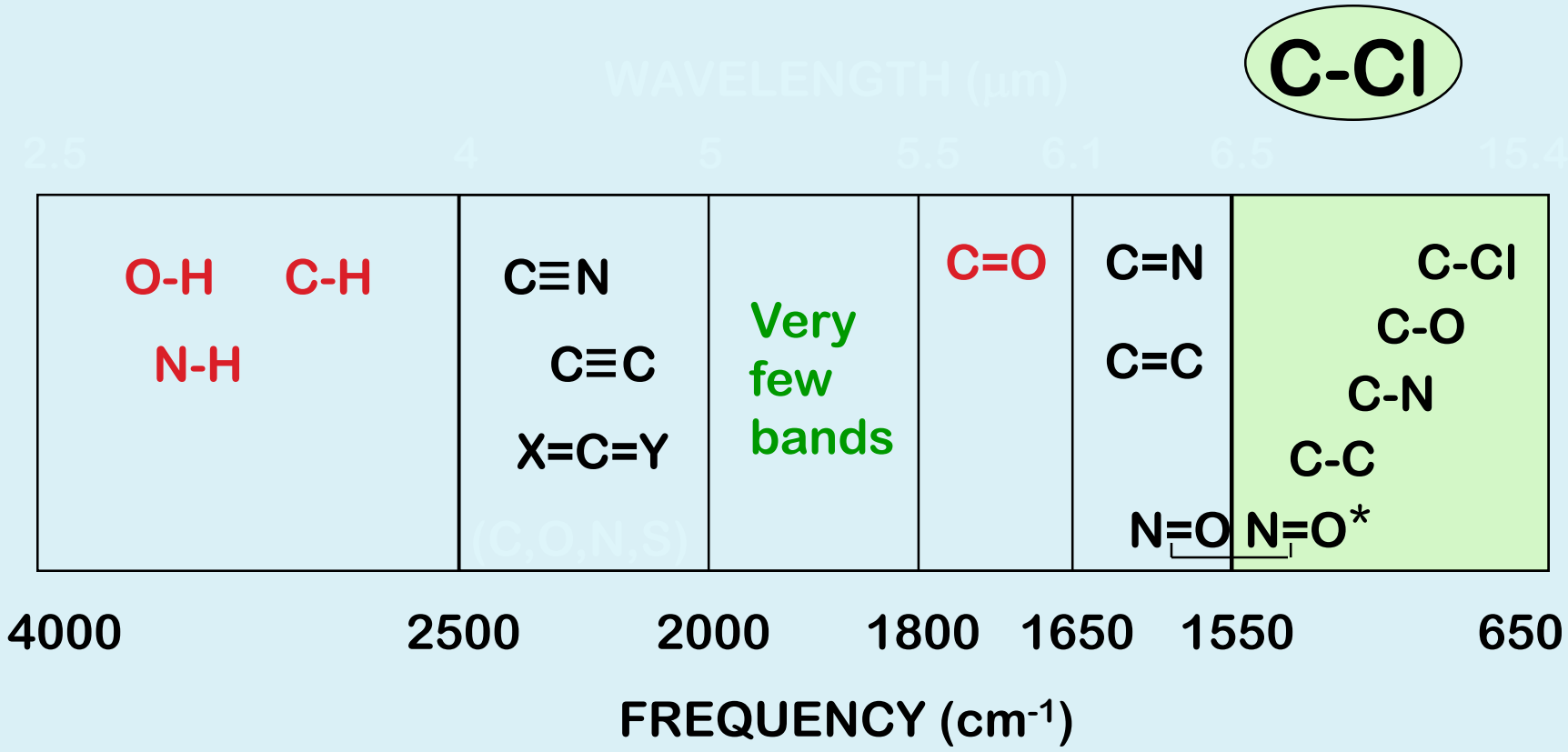
The N=O stretching region

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

2-Nitropropane



Typical Infrared Absorption Regions

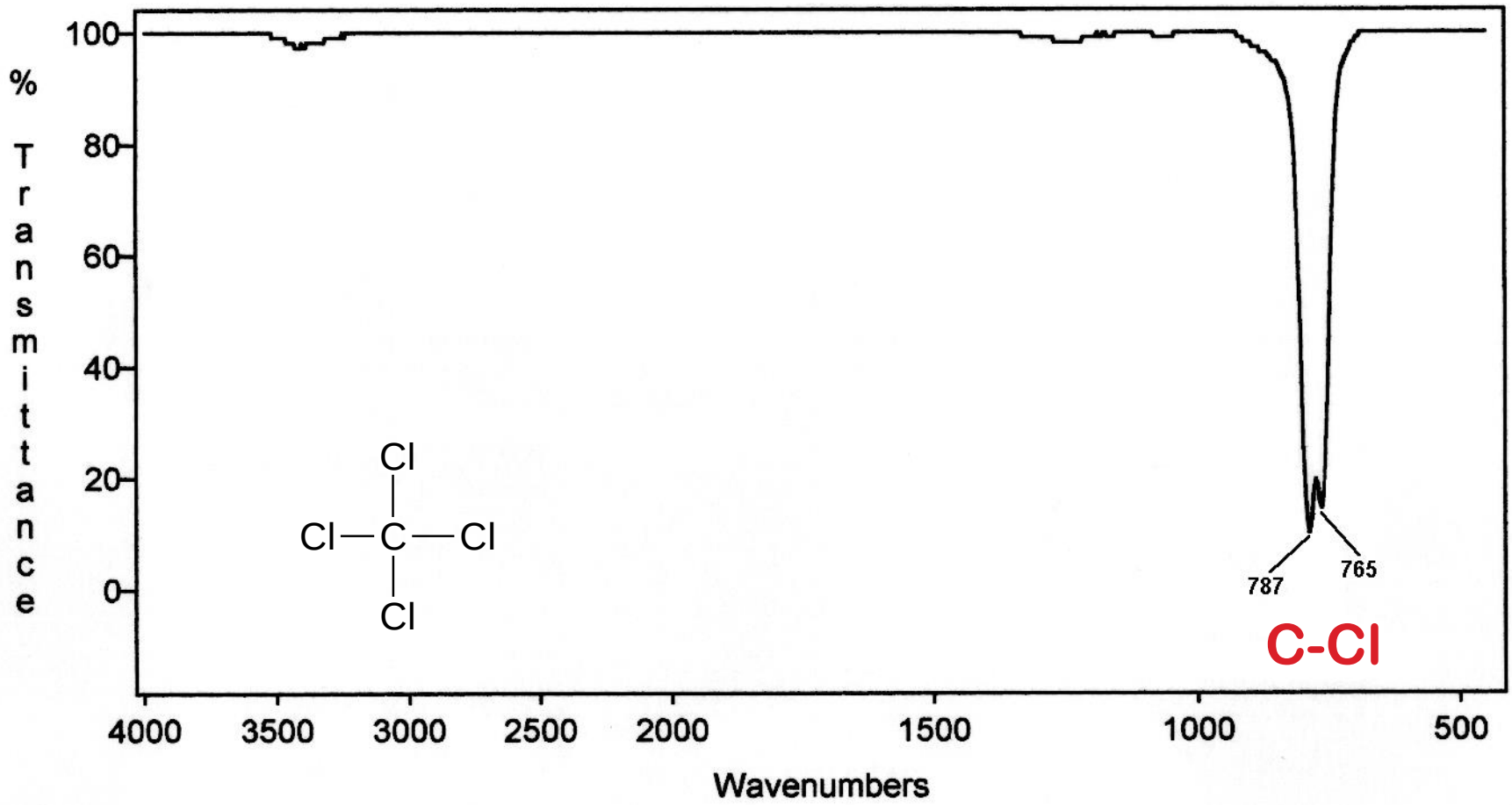


The C-X stretching region

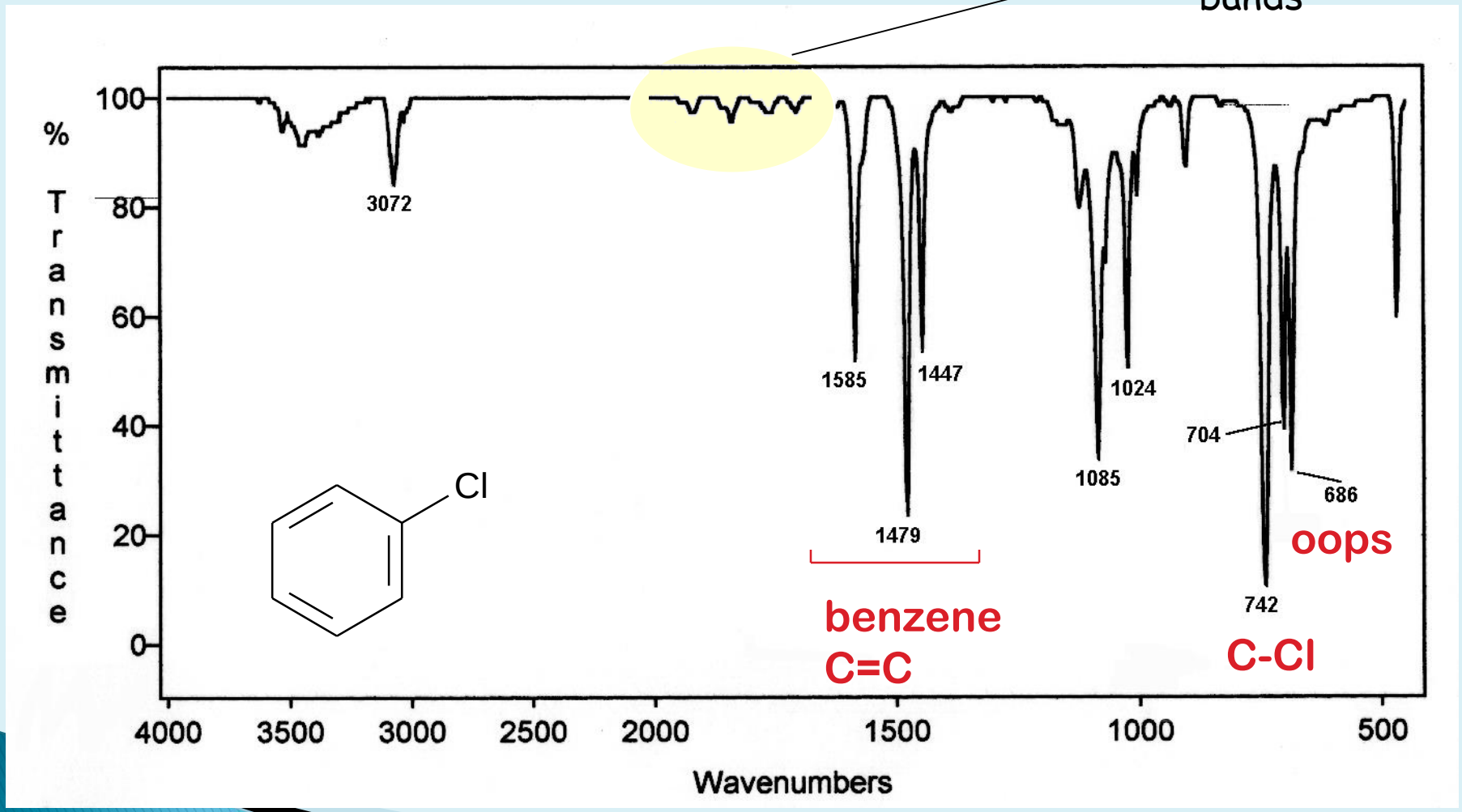
- C-Cl 785 to 540 cm^{-1}, often hard to find amongst the fingerprint bands!!
- C-Br and C-I appear outside the useful range of infrared spectroscopy.
- C-F bonds can be found easily, but are not that common.

Carbon Tetrachloride

Often used as a solvent for IR spectra.
When it is used, spectra show **C-Cl** absorptions.

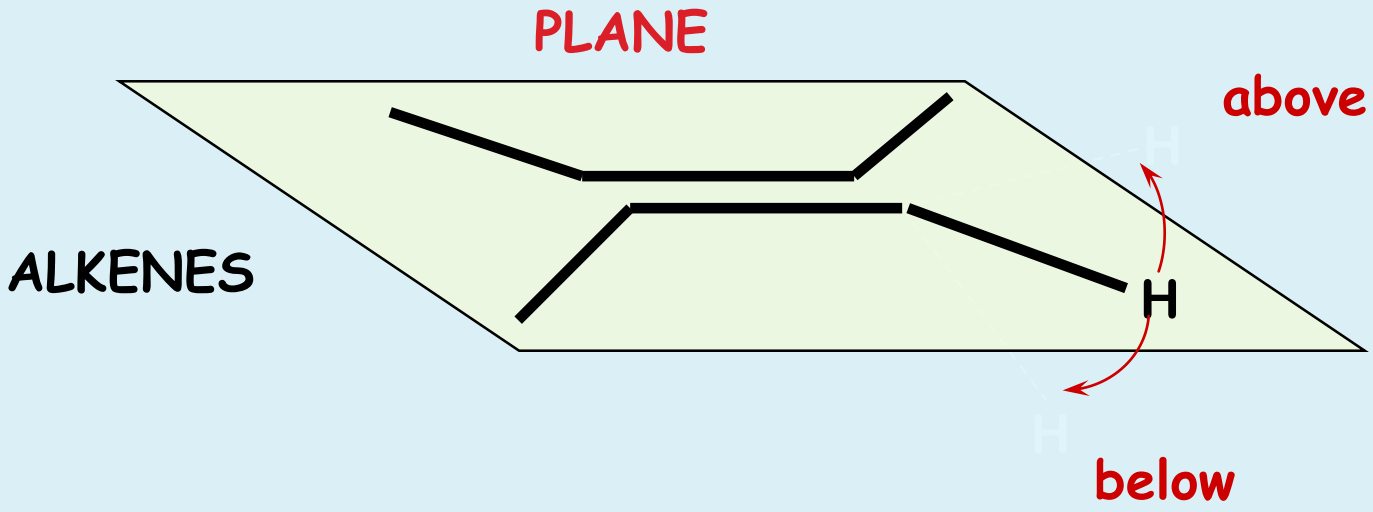


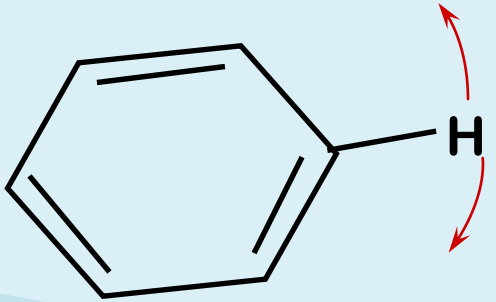
Chlorobenzene



=C-H OUT OF PLANE BENDING

OUT-OF-PLANE BENDING
(OOPS)





also with benzenes

ALKENES

Monosubstituted

Disubstituted

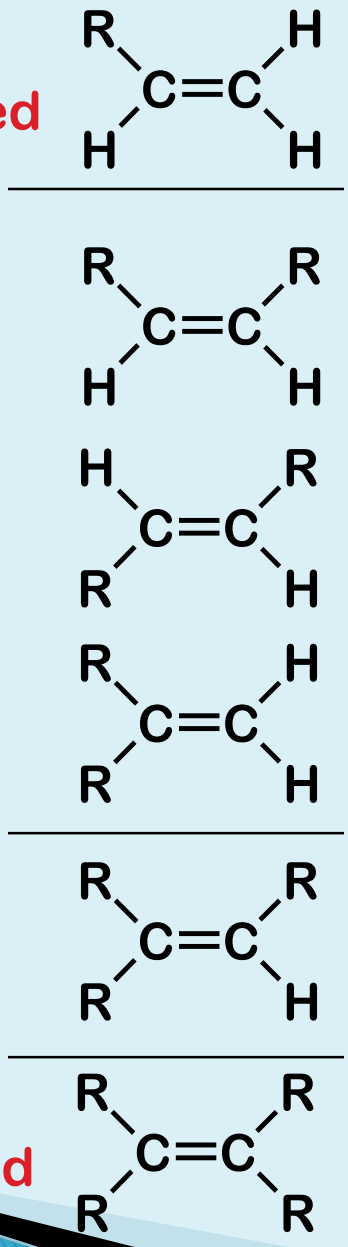
cis-1,2-

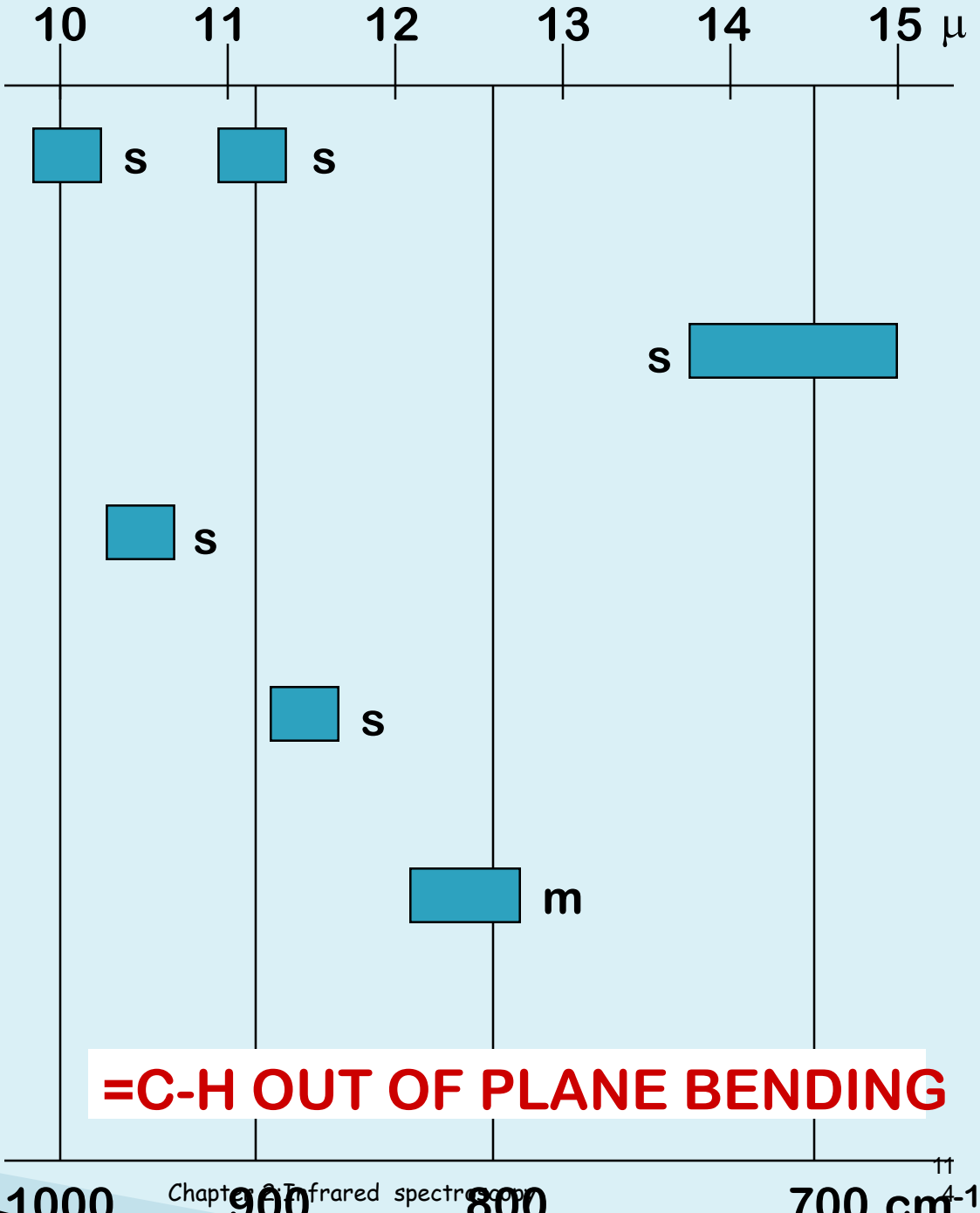
trans-1,2-

1,1-

Trisubstituted

Tetrasubstituted





=C-H OUT OF PLANE BENDING

BENZENES

Monosubstituted

Disubstituted

ortho
meta

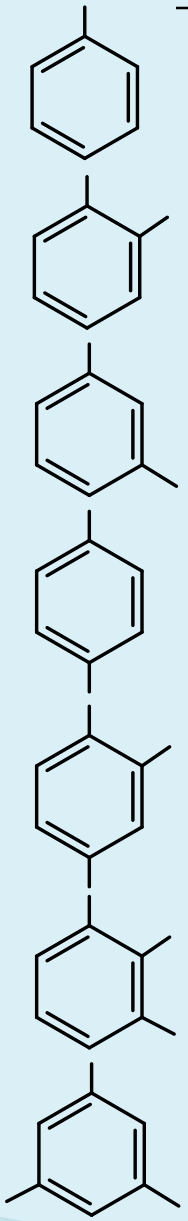
para

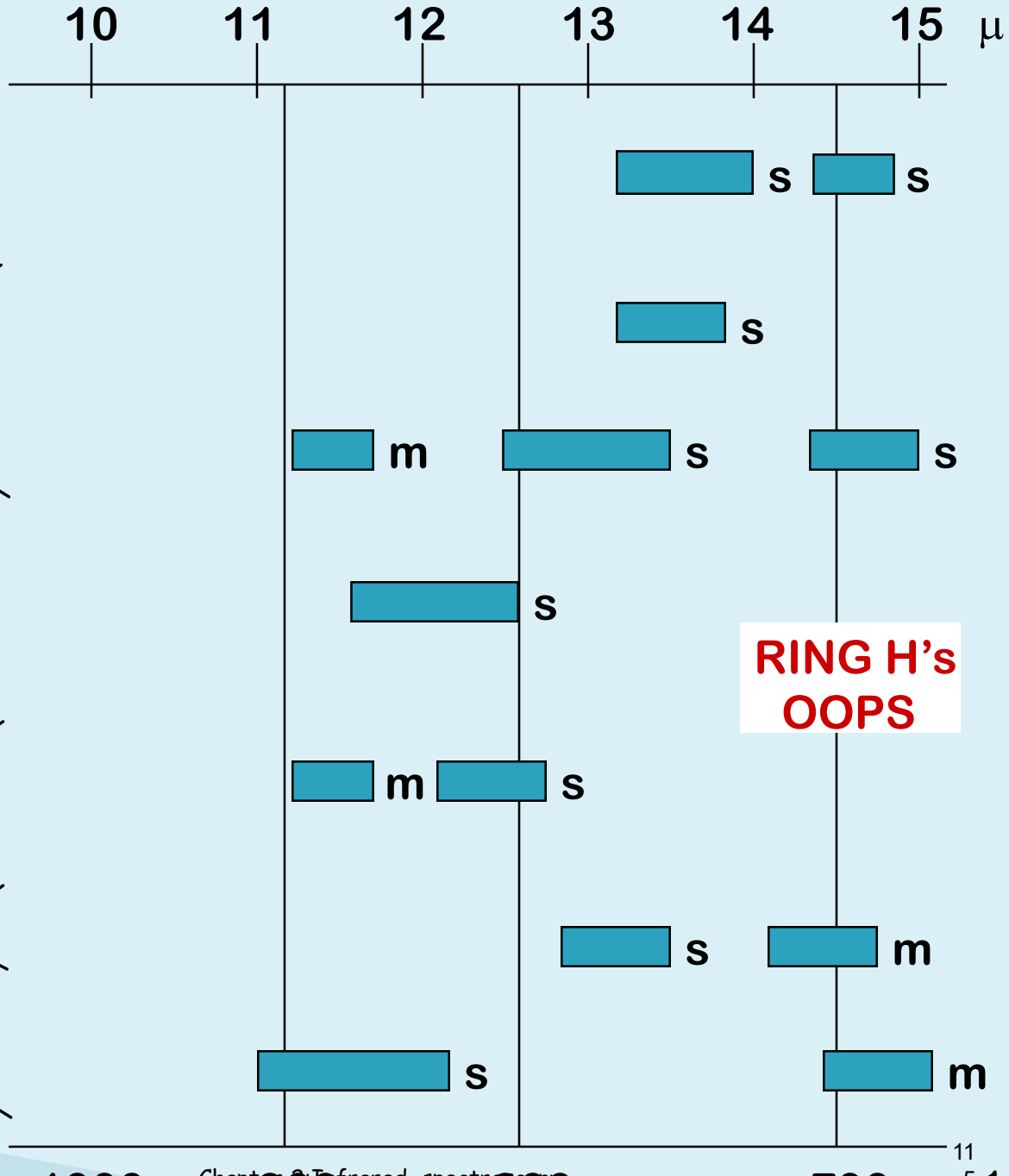
Trisubstituted

1,2,4

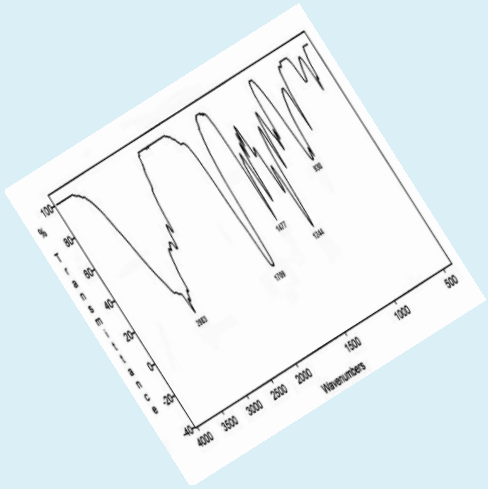
1,2,3

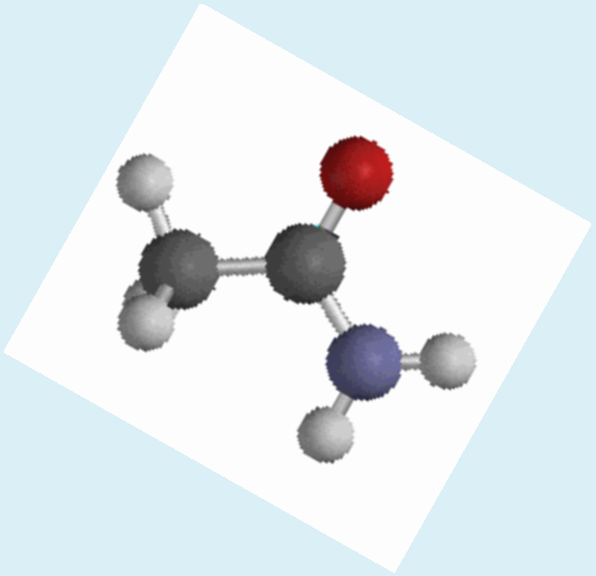
1,3,5





combination bands





END OF CHAPTER 2