

INFRARED SPECTROSCOPY

- ❖ Infrared radiation stimulates molecular vibrations.
- ❖ Infrared spectra are traditionally displayed as %T (percent transmittance) versus wave number ($4000\text{-}400\text{ cm}^{-1}$).
- ❖ Provides information about the vibrations of functional groups in a molecule
- ❖ Useful in identifying presence or absence of functional groups.

INFRARED SPECTROSCOPY

What wavelength of electromagnetic radiation is involved in causing vibrations in molecules?

- Infrared (IR) electromagnetic radiation causes vibrations in molecules (wavelengths of 2500-15,000 nm or 2.5 – 15 μm)

How does the mass influence the vibration?

- The greater the mass - the lower the wave number

- ❖ Infrared region – wavelengths longer than visible
- ❖ Infrared wavelengths typically expressed in *micrometers* ($1\ \mu\text{m} = 1 \times 10^{-6}\ \text{m}$)
- ❖ Typical infrared spectrum covers between $2.5\ \mu\text{m}$ to $25\ \mu\text{m}$ ($2500\ \text{nm}$ to $25000\ \text{nm}$)
- ❖ region of infrared that is most useful lies between $2.5\text{-}16\ \mu\text{m}$ ($4000\text{-}625\ \text{cm}^{-1}$)
- ❖ depends on transitions between vibrational energy states
- ❖ Stretching
- ❖ bending

❖ Energy is inversely related to wavelength, so infrared light has less energy than visible light

❖ Typical units in infrared spectroscopy are *wavenumbers (ν) - the reciprocal of the wavelength (in centimeters)*

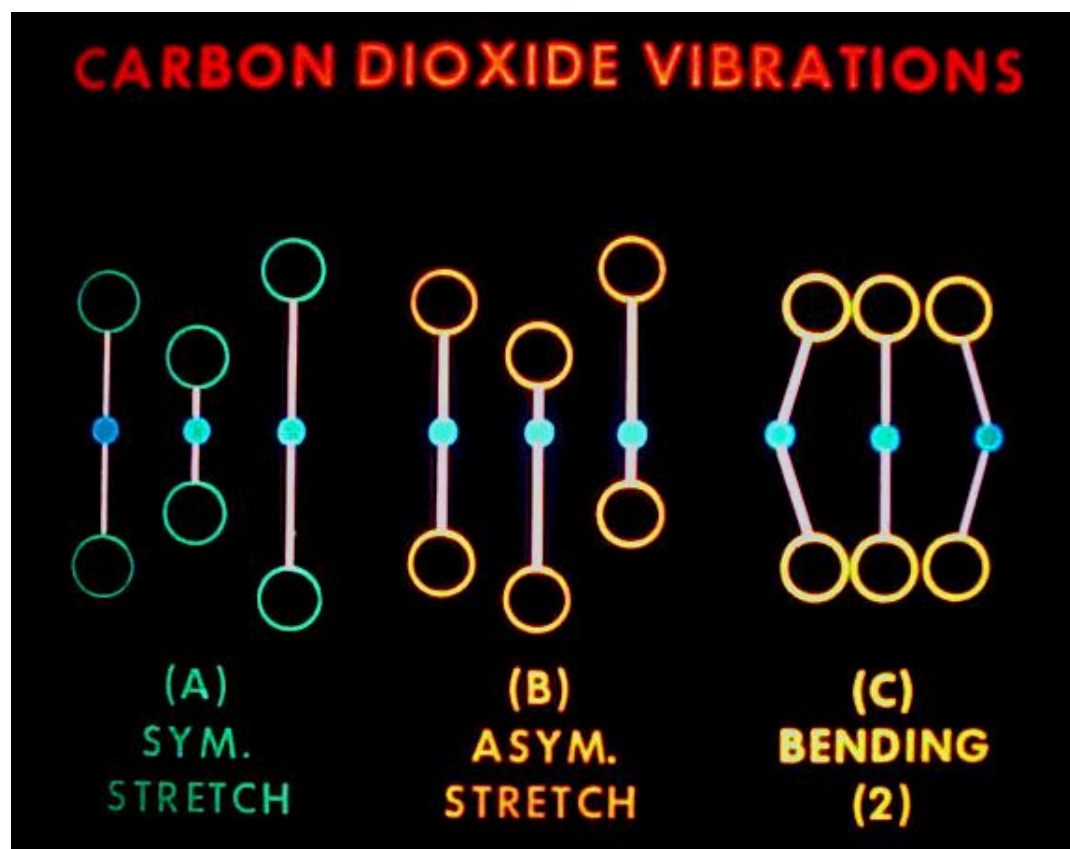
$$2.5 \mu\text{m} = 2.5 \times 10^{-4} \text{ cm} = 4000 \text{ cm}^{-1}$$

$$25 \mu\text{m} = 2.5 \times 10^{-3} \text{ cm} = 400 \text{ cm}^{-1}$$

Thus typical IR spectrum runs from 4000 to 400 cm^{-1}

INFRARED SPECTROSCOPY

- In the IR region of the electromagnetic spectrum, the absorption of radiation by a sample is due to changes in the vibrational energy states of a molecule.



INFRARED SPECTROSCOPY

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

What vibrations change the dipole moment of a molecule?

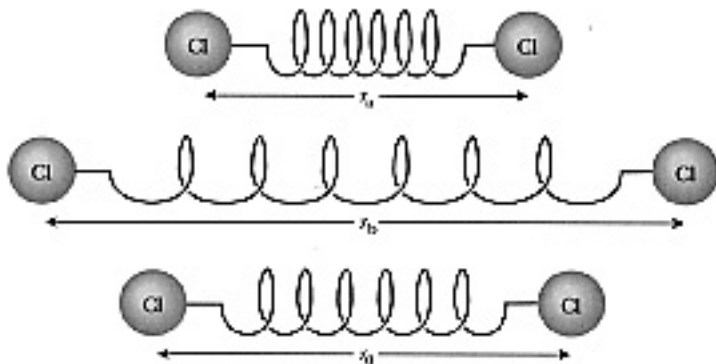
- Asymmetrical stretching/bending and internal rotation change the dipole moment of a molecule. Asymmetrical stretching/bending are IR active.
- Symmetrical stretching/bending does not. Not IR active

IR: Theory

A Model: Picture the atoms of a diatomic molecule as point masses connected by springs (bonds).

As a first approximation use Hooke's Law

$$F = -kx$$



F = force, restoring back to equilibrium position

k = characteristic ***stretching constant***

x = displacement from the equilibrium position

IR Stretching Frequencies of two bonded atoms:

The Frequency, ν , Depends On...

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_r}} \quad m_r = \frac{m_1 m_2}{m_1 + m_2}$$

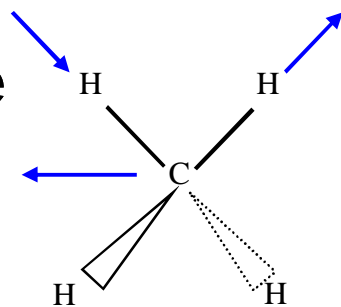
ν = frequency

k = spring strength (bond stiffness)

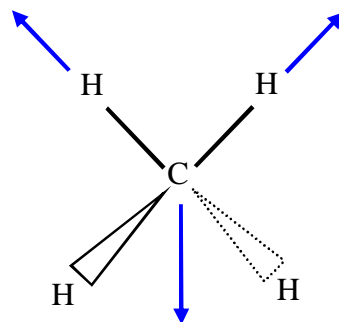
m_r = reduced mass (\sim mass of largest atom)

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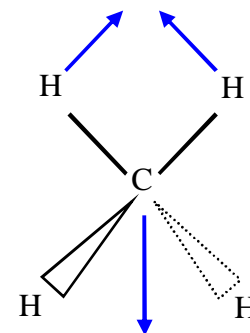
- Methane



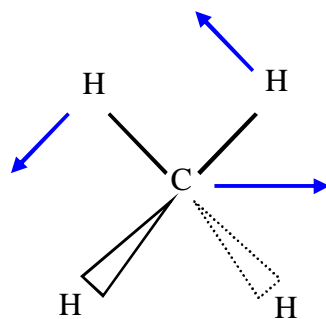
Asymmetrical stretching



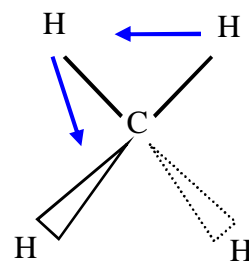
Symmetrical stretching



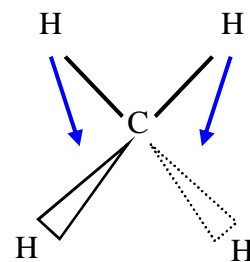
Bending or scissoring



Rocking or in plane bending



Twisting or out-of-plane bending



Wagging or out-of-plane bending

INFRARED SPECTROSCOPY

IR Stretching Frequencies: What Do they Depend On?

Directly on the strength of the bonding between the two atoms ($\nu \sim k$)

Inversely on the reduced mass of the two atoms ($\nu \sim 1/m$)

Expect: ν will increase with increasing bond strength (bond order)
and decreasing mass

Examples of stretching frequencies and correlations with bond strengths (bond order)

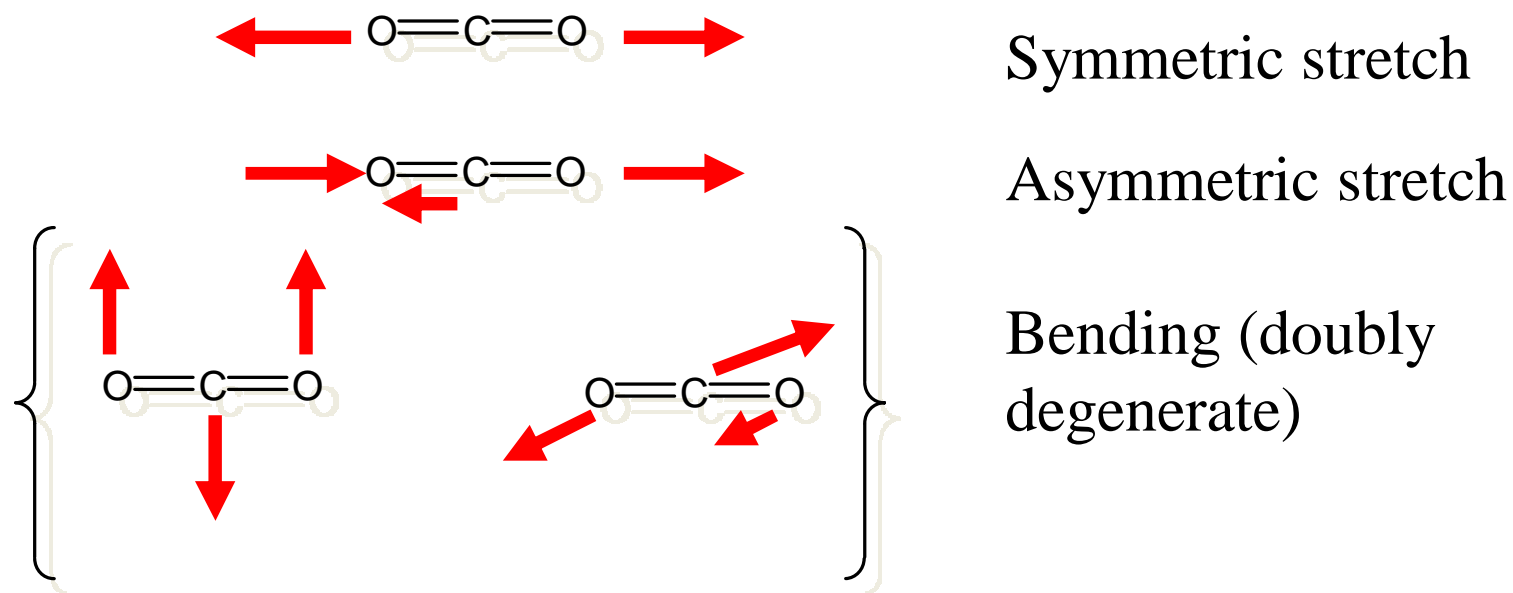
	Bond strength*	Bond order	ν
C-C	350	1	1000 cm ⁻¹
C=C	600	2	1600 cm ⁻¹
C≡C	840	3	2200 cm ⁻¹

*In kJ/mol

For same reduced mass!

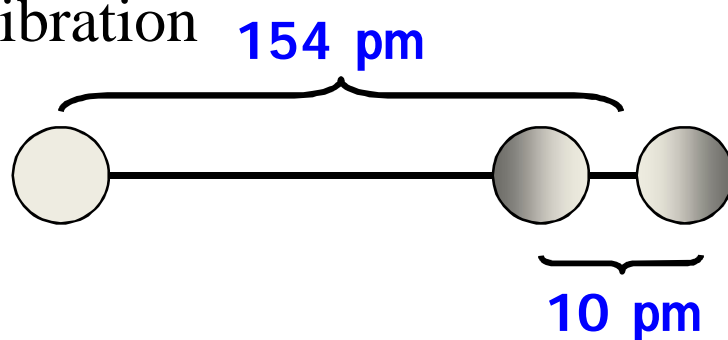
INFRARED SPECTROSCOPY

- Only vibrations that cause a change in 'polarity' give rise to bands in IR spectra – which of the vibrations for CO₂ are infrared active?



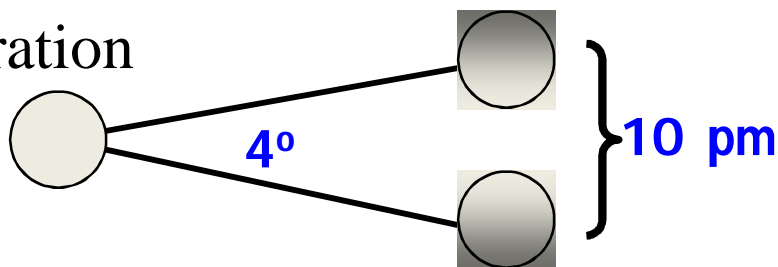
- How much movement occurs in the vibration of a C-C bond?

stretching vibration



For a C-C bond with a bond length of 154 pm, the variation is about 10 pm.

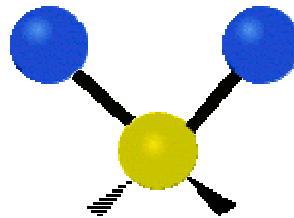
bending vibration



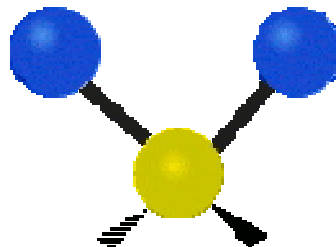
For C-C-C bond angle a change of 4° is typical. This moves a carbon atom about 10 pm.

Types of vibrations

❖ Symmetric stretching mode involves no dipole change and so is inactive in the IR region and no corresponding absorption of energy takes place. In this both bonds are shortened or elongated to the same extent simultaneously.

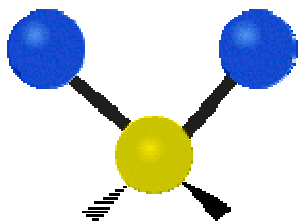


❖ Asymmetric stretching mode involves variation of bond length and hence involves dipole moment change, one of the bond is elongates and the other one is shortened.

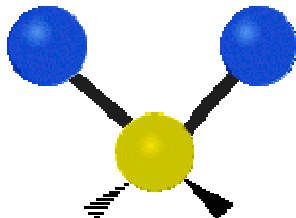


Types of vibrations

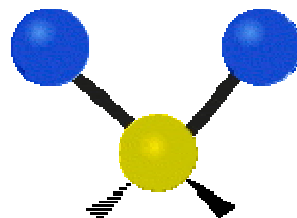
❖ Bending mode : It involves variation of bond angle and involves a dipole moment change (Rocking, scissoring, wagging, twisting) – change in angle between two bonds.



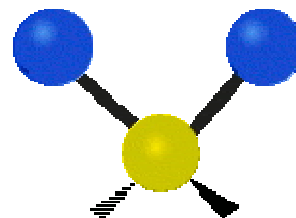
Rocking



scissoring



wagging



twisting

Vibrational coupling – interaction between vibrations (coupling) can occur.

Linear Molecules:

$(3N - 5)$ degrees of freedom

Non-Linear molecules:

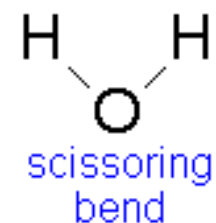
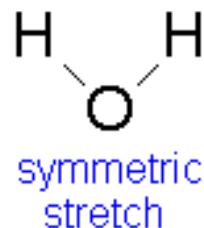
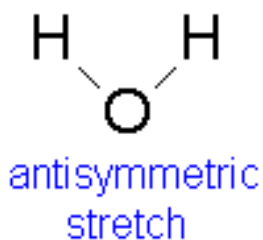
$(3N - 6)$ degrees of freedom

Water

Nonlinear molecule

$3N-6$ degree of freedom

$$3(3)-6=3$$

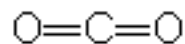


Carbon Dioxide

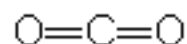
Linear molecule

$3N-6$ degree of freedom

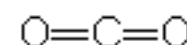
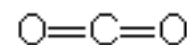
$$3(3)-5=4$$



inactive
no dipole change

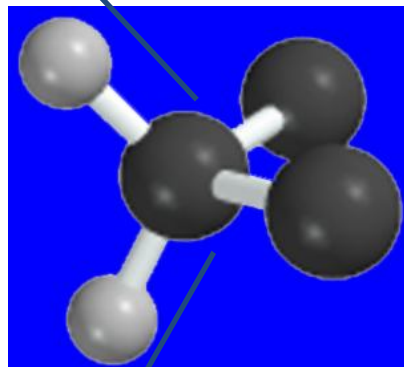


active

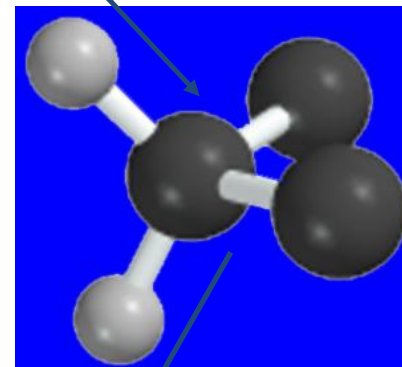


degenerate
same energy
one band

Stretching Vibrations of a CH₂ Group

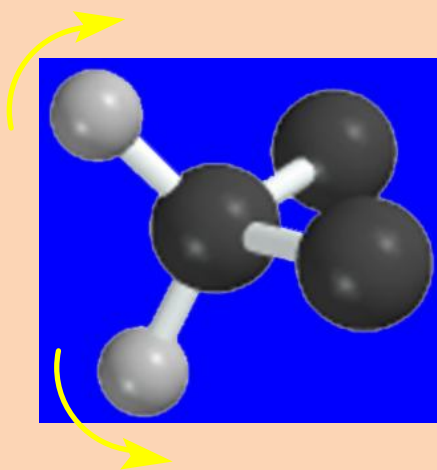


Symmetric

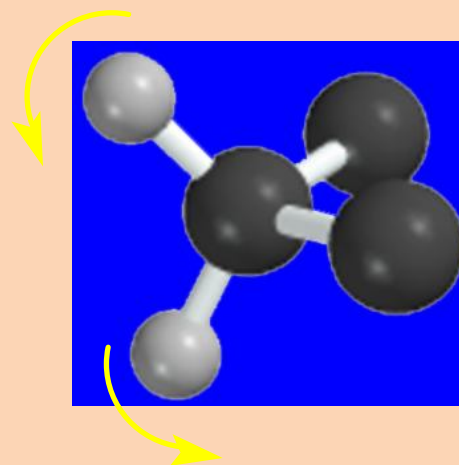


Antisymmetric

Bending Vibrations of a CH₂ Group

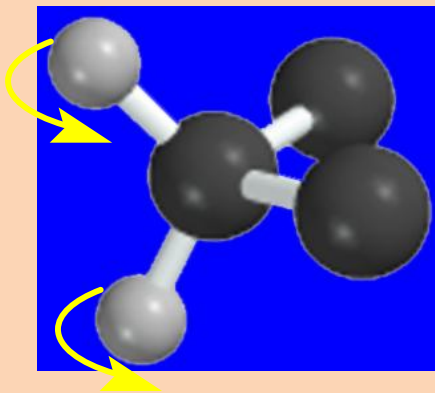


In plane

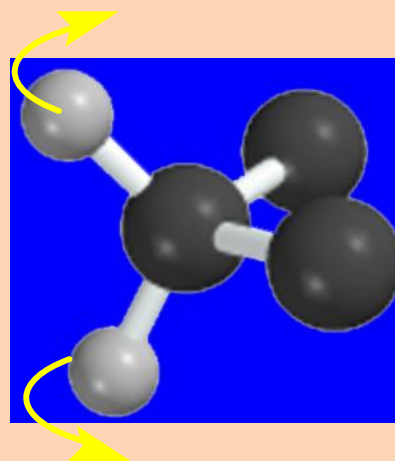


In plane

Bending Vibrations of a CH₂ Group



Out of plane



Out of plane

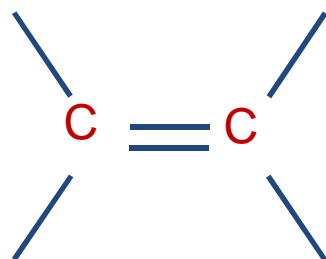
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp C—H	3310-3320
sp^2 C—H	3000-3100
sp^3 C—H	2850-2950
sp^2 C—O	1200
sp^3 C—O	1025-1200

Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
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Stretching vibrations (multiple bonds)



1620-1680



2100-2200



2240-2280

Infrared Absorption Frequencies

Structural unit

Frequency, cm^{-1}

Stretching vibrations (carbonyl groups)

Aldehydes and ketones

1710-1750

Carboxylic acids

1700-1725

Acid anhydrides

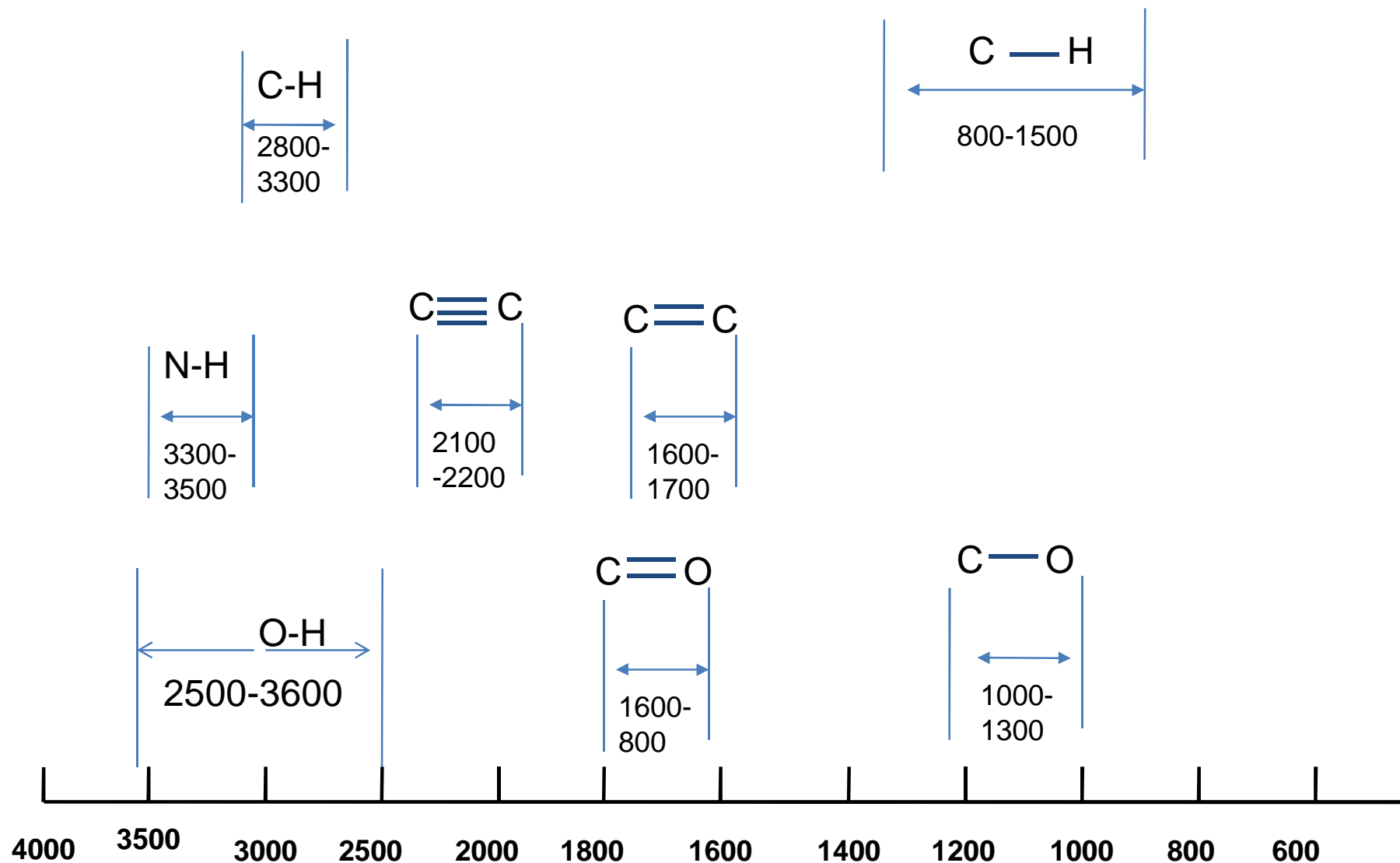
1800-1850 and 1740-1790

Esters

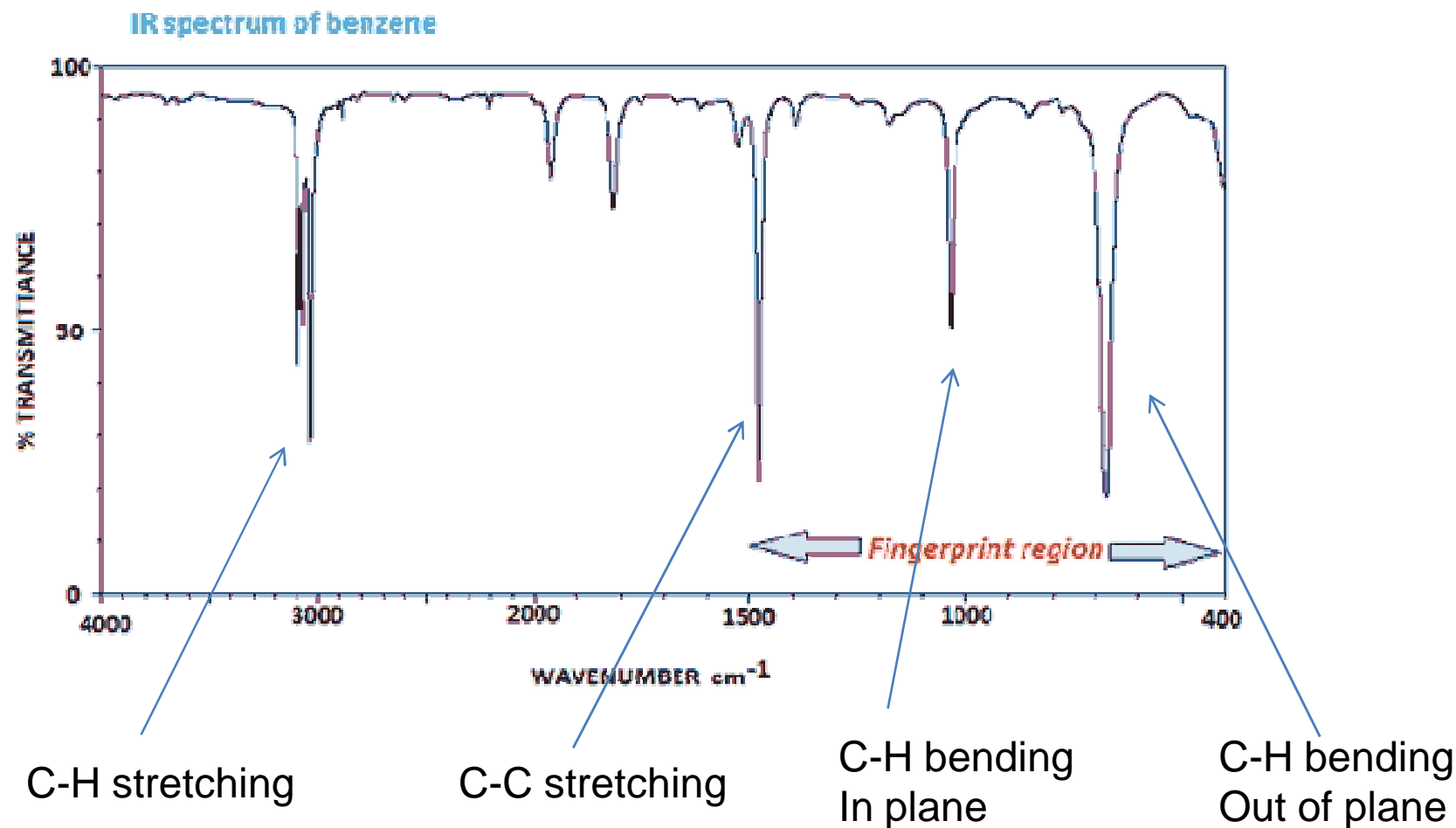
1730-1750

Amides

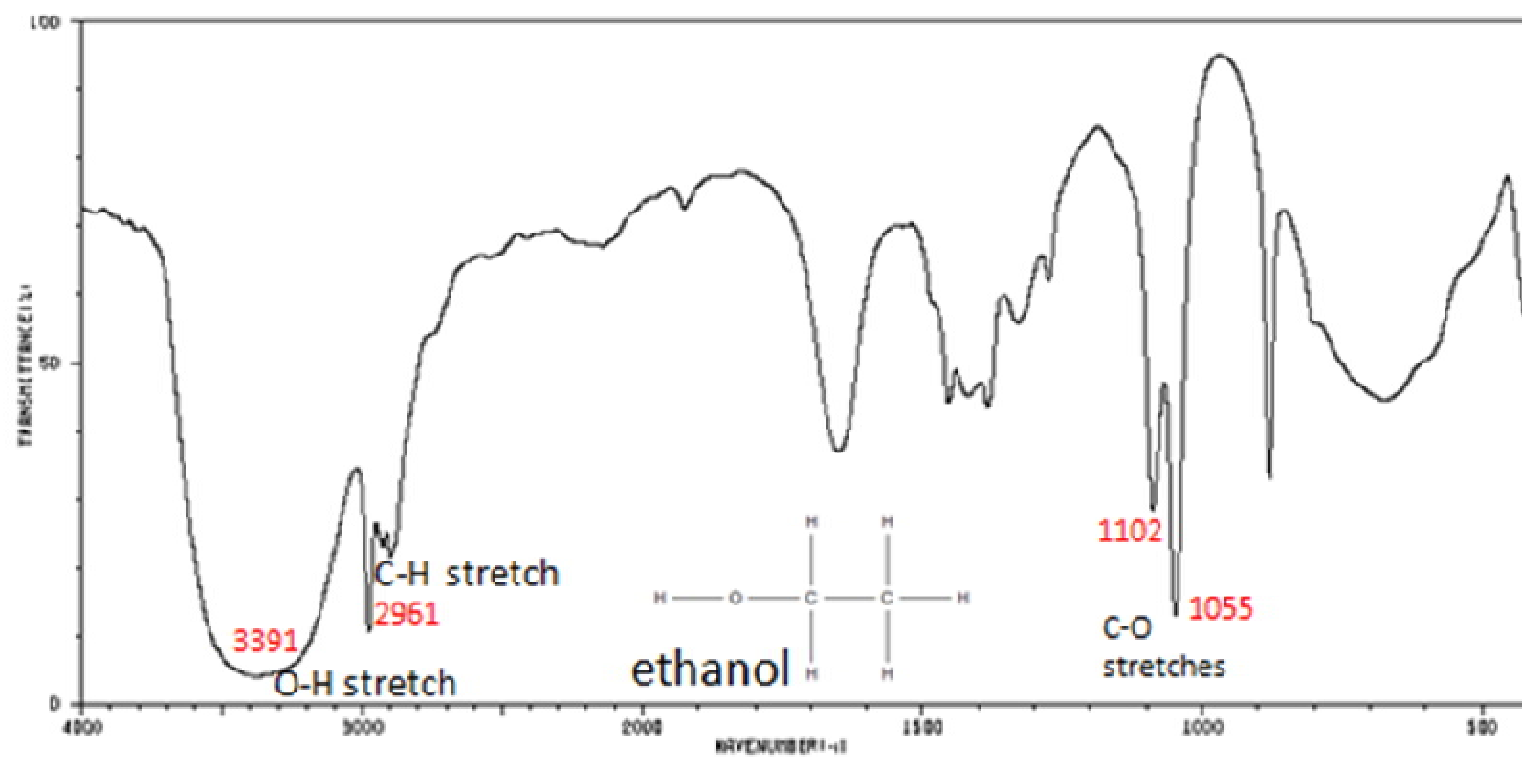
1680-1700



IR spectrum of Benzene



IR spectrum of Ethanol



Applications of IR spectroscopy

- ❖ To identify given compound: The spectra of a unknown compound can be compared with that of known compounds.
- ❖ Detection of impurities in the sample: The spectrum of impure samples will exhibit extra absorption bands.
- ❖ To confirm hydrogen bonding in molecule under study: Intermolecular or intramolecular hydrogen bonding can be confirmed.
- ❖ IR spectra provides information on molecular symmetry, dipole moments, bond length etc.
- ❖ Isomerism in compounds can be studied.
- ❖ It can be used for quantitative analysis of mixture of compounds.