Republic of Iraq
Ministry of Higher Education & Scientific research
Al-Mustaqbal University
Science College
Medical physics Department

Analytical Chemistry

For

First Year Student

Lecture 9

By

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2024-2025

Infrared spectrophotometric analysis

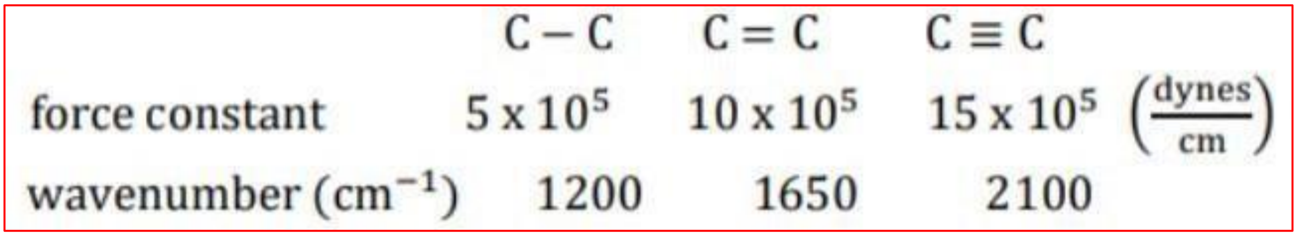
- Infrared spectroscopy is used in identification of functional groups in pure compounds.
- Infra-red (IR) does not have sufficient energy to induce electronic transition as seen in UV spectroscopy. When molecule absorbed electromagnetic radiation in IR region, undergoes vibrational or a rotational transitions which causes net change in the dipole moment in the molecule (IR active, for example HCl, CO etc), if dipole moment does not change in molecules then they are IR inactive (for example: O_2, H_2, N_2 etc.) means they does not absorb IR radiation. IR region ranges from 4000-400 cm^{-1}
- If the frequency of IR radiation matched with the vibrational frequency of molecule, then molecule absorb radiation.
- IR spectroscopy based on Hooke's law, suppose two atoms or masses are connected through spring (bond), then frequency of vibration can be represented by following equation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \quad \text{or} \quad \bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{\kappa}{\mu}}$$

- Where, κ is force constant of the bond, $\bar{\upsilon}$ is wave-number (cm^{-1}), ν is the frequency, c is speed of light and μ is reduce mass (m1 and m2 are the masses of atoms)

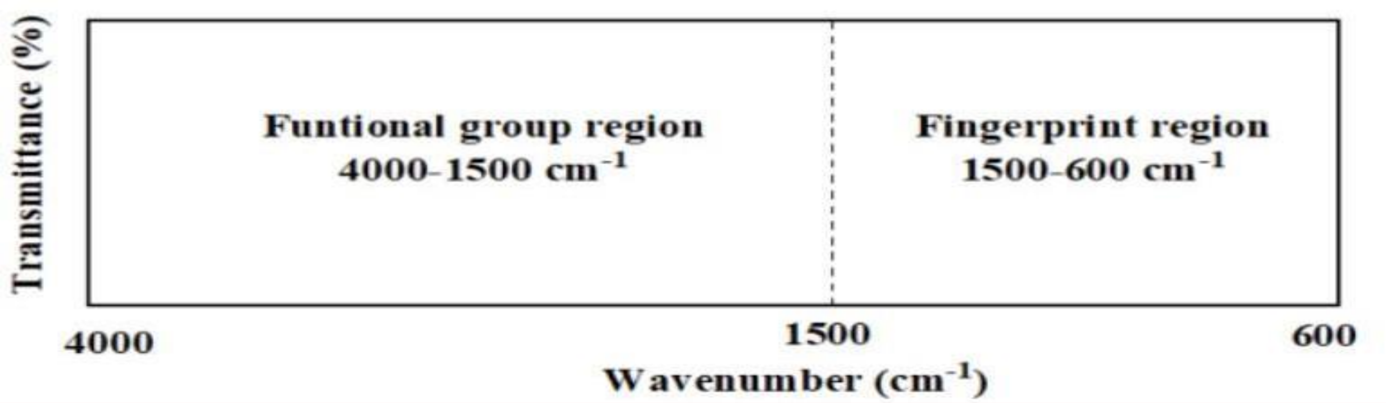
$$\mu = \frac{m_1 \times m_2}{(m_1 + m_2)}$$

- Stronger the bond, greater the value of force constant (κ), higher the frequency vibration or wave-number (cm^{-1}). For example,



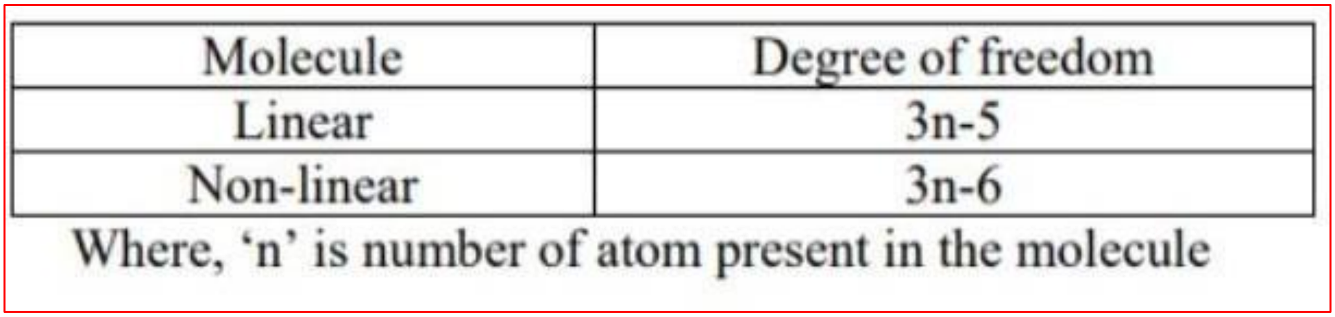
	$C-C$	$C=C$	$C\equiv C$	
force constant	5×10^5	10×10^5	15×10^5	$\left(\frac{dynes}{cm}\right)$
wavenumber (cm^{-1})	1200	1650	2100	

- IR spectrum is divided mainly into two region as follows;



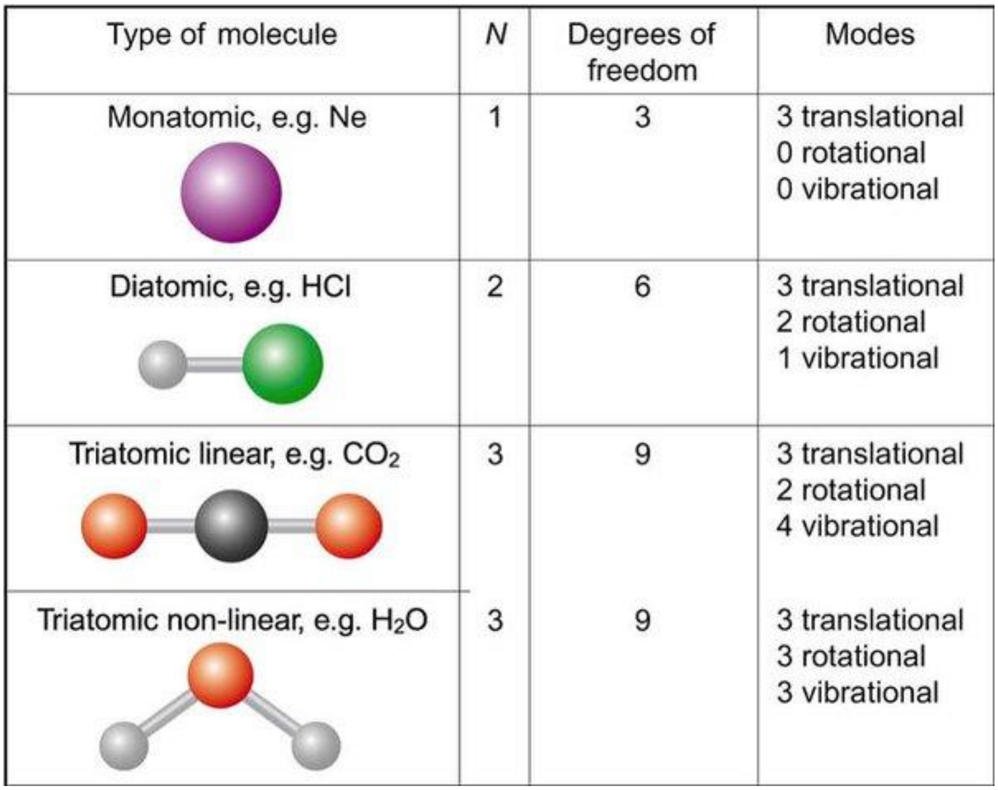
Fundamental Vibration

- These vibrations are arising when molecule promoted from ground state to lower excited state. The fundamental vibrations for linear and non-linear molecules are determined by following way:



Molecule	Degree of freedom
Linear	3n-5
Non-linear	3n-6

Where, ‘n’ is number of atom present in the molecule



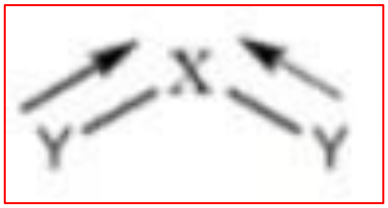
Type of molecule	*N*	Degrees of freedom	Modes
Monatomic, e.g. Ne	1	3	3 translational 0 rotational 0 vibrational
Diatomic, e.g. HCl	2	6	3 translational 2 rotational 1 vibrational
Triatomic linear, e.g. CO_2	3	9	3 translational 2 rotational 4 vibrational
Triatomic non-linear, e.g. H_2O	3	9	3 translational 3 rotational 3 vibrational

Fundamental Vibration

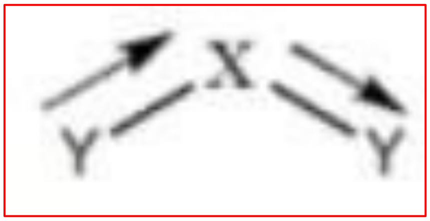
- **Stretching vibration**: Distance between two atom increase and decrease but bond angle remains constant.

Types of stretching vibrations

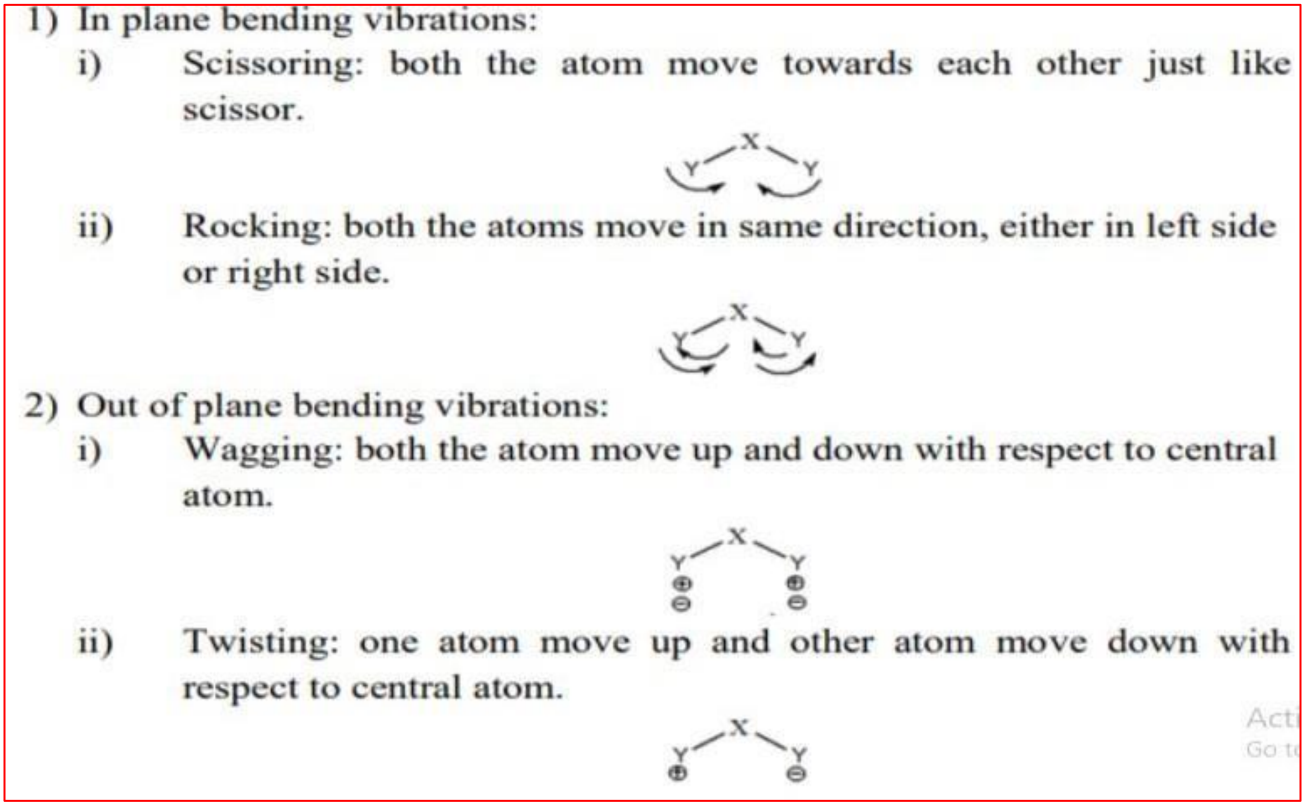
- **Symmetric stretching vibration**: In this case both the atoms stretched or compressed in same direction.



- **Asymmetric stretching vibration**: In this vibration one atom undergoes stretching and other atom undergoes compression and vice versa.



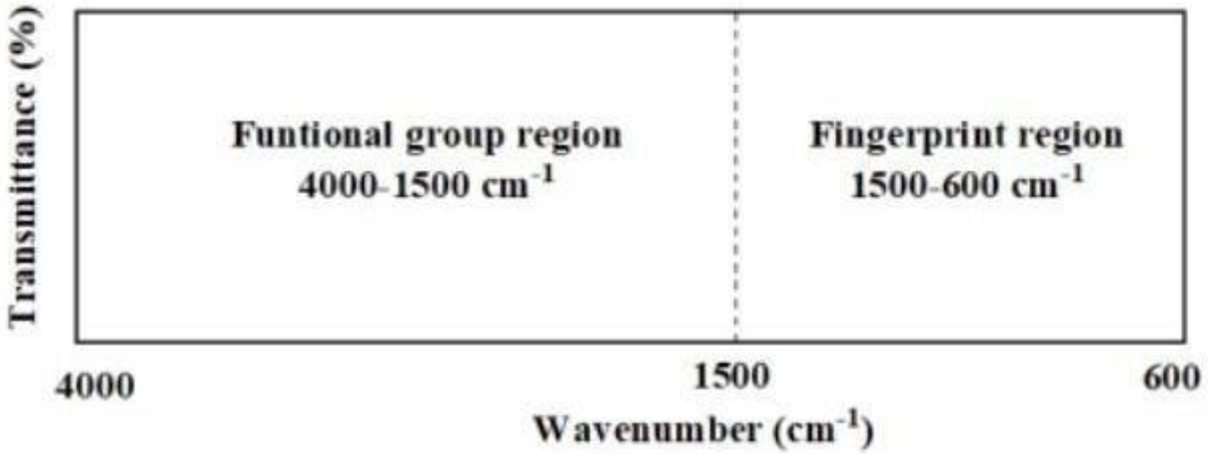
- **Bending vibrations:** Distance between two atom remains constant but bond angle changes. These vibrations can occur either in plane or out of plane



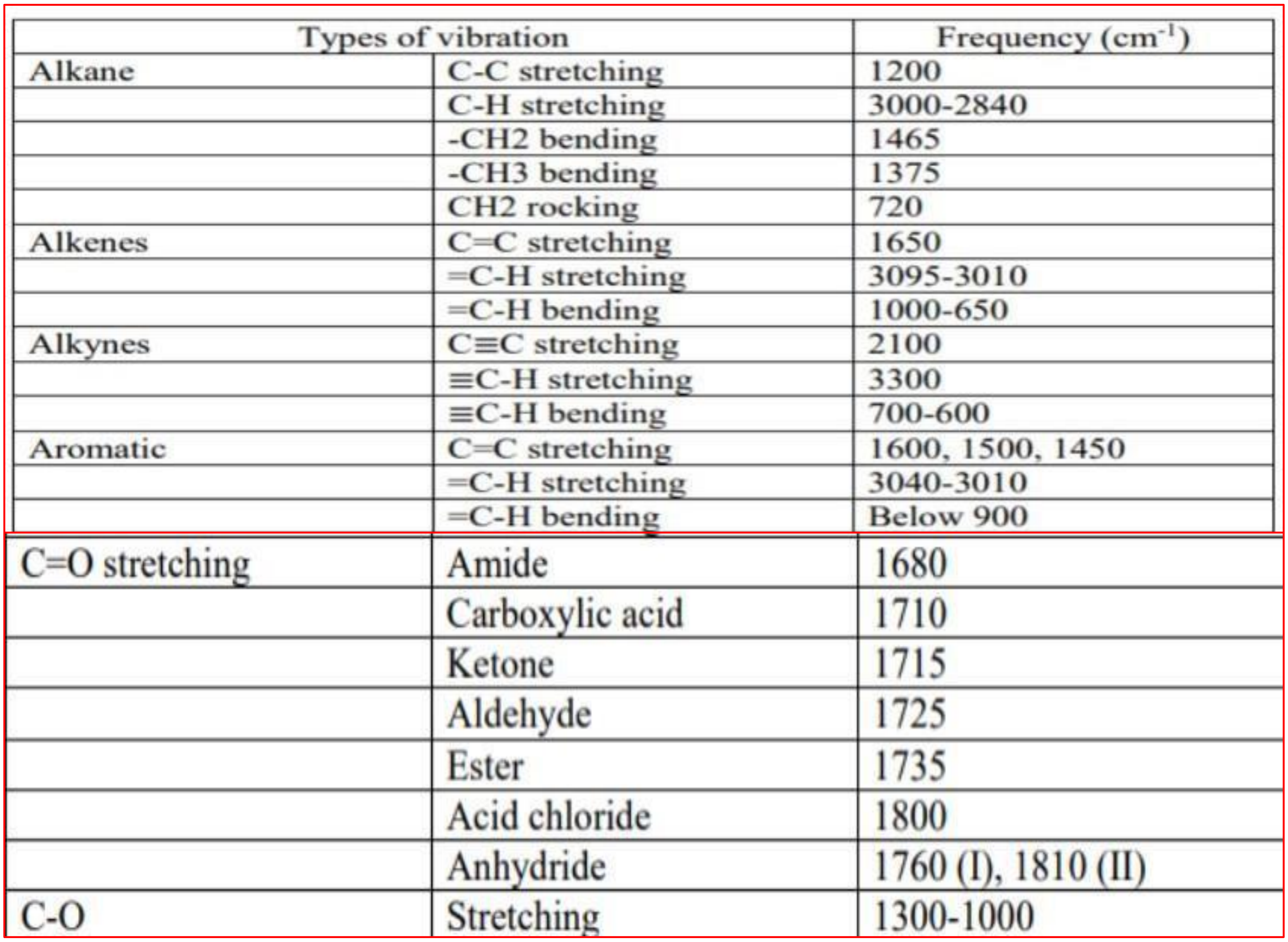
1) In plane bending vibrations:
   - i) Scissoring: both the atom move towards each other just like scissor.
   - ii) Rocking: both the atoms move in same direction, either in left side or right side.

2) Out of plane bending vibrations:
   - i) Wagging: both the atom move up and down with respect to central atom.
   - ii) Twisting: one atom move up and other atom move down with respect to central atom.

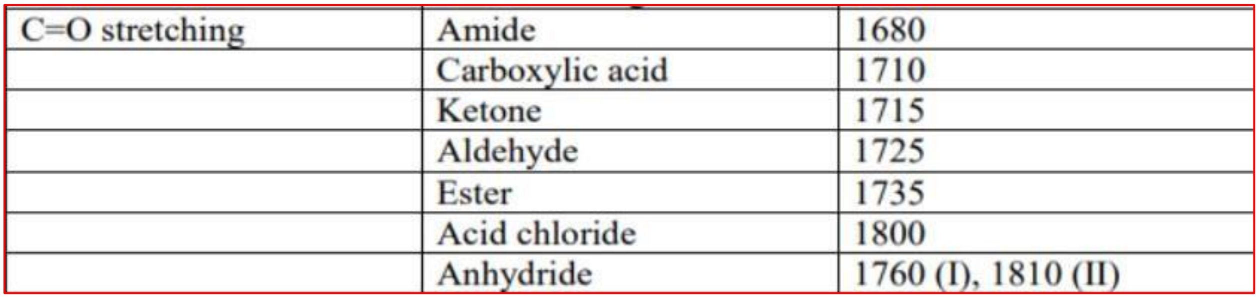
- The region from 1500-600 cm-1 in IR spectrum is known as **Fingerprint region**. In this region number of bending vibration is more than the number of stretching vibration.



- Number of molecules contains same functional group & show similar peak above 1500 cm^{-1} but they show different peak in finger print region. Therefore we can say that each and every molecule have unique peak or band which is observed in finger print region, it is just like the finger print of human.



Types of vibration		Frequency (cm^{-1})
Alkane	C-C stretching	1200
	C-H stretching	3000-2840
	-CH2 bending	1465
	-CH3 bending	1375
	CH2 rocking	720
Alkenes	C=C stretching	1650
	=C-H stretching	3095-3010
	=C-H bending	1000-650
Alkynes	C≡C stretching	2100
	≡C-H stretching	3300
	≡C-H bending	700-600
Aromatic	C=C stretching	1600, 1500, 1450
	=C-H stretching	3040-3010
	=C-H bending	Below 900
C=O stretching	Amide	1680
	Carboxylic acid	1710
	Ketone	1715
	Aldehyde	1725
	Ester	1735
	Acid chloride	1800
	Anhydride	1760 (I), 1810 (II)
C-O	Stretching	1300-1000



C=O stretching	Amide	1680
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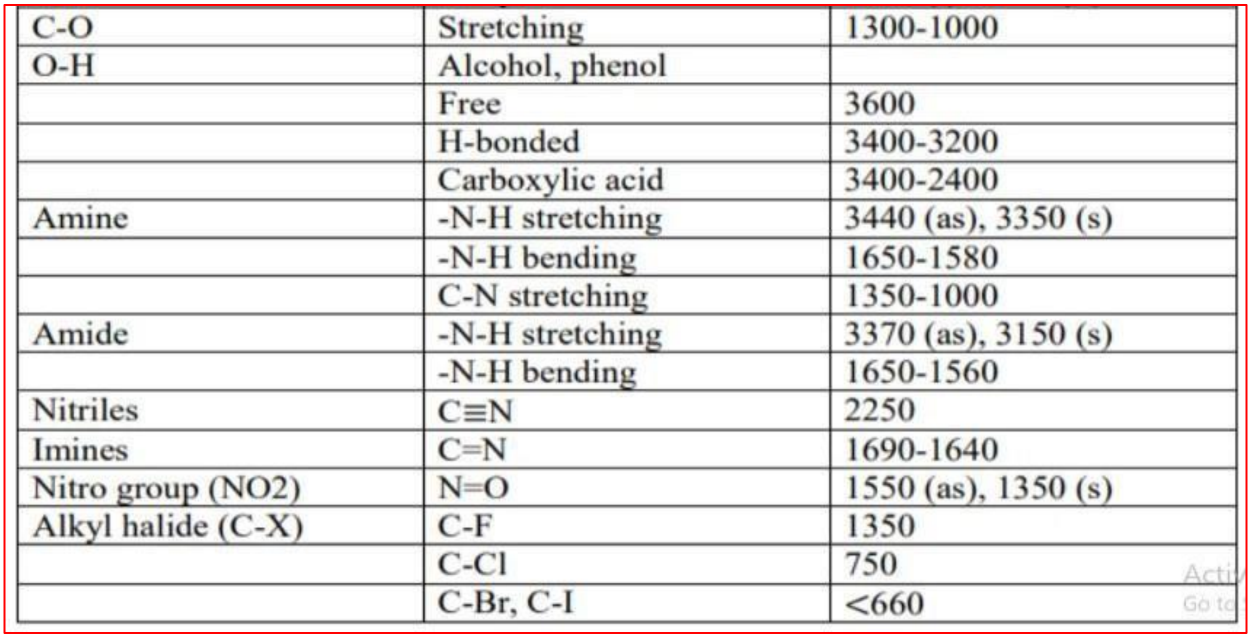
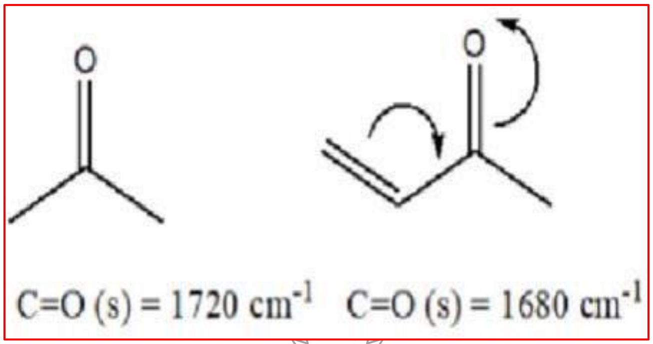


C-O	Stretching	1300-1000
O-H	Alcohol, phenol	
	Free	3600
	H-bonded	3400-3200
	Carboxylic acid	3400-2400
Amine	-N-H stretching	3440 (as), 3350 (s)
	-N-H bending	1650-1580
	C-N stretching	1350-1000
Amide	-N-H stretching	3370 (as), 3150 (s)
	-N-H bending	1650-1560
Nitriles	C≡N	2250
Imines	C=N	1690-1640
Nitro group (NO2)	N=O	1550 (as), 1350 (s)
Alkyl halide (C-X)	C-F	1350
	C-Cl	750
	C-Br, C-I	<660

Factor affecting vibrational frequency

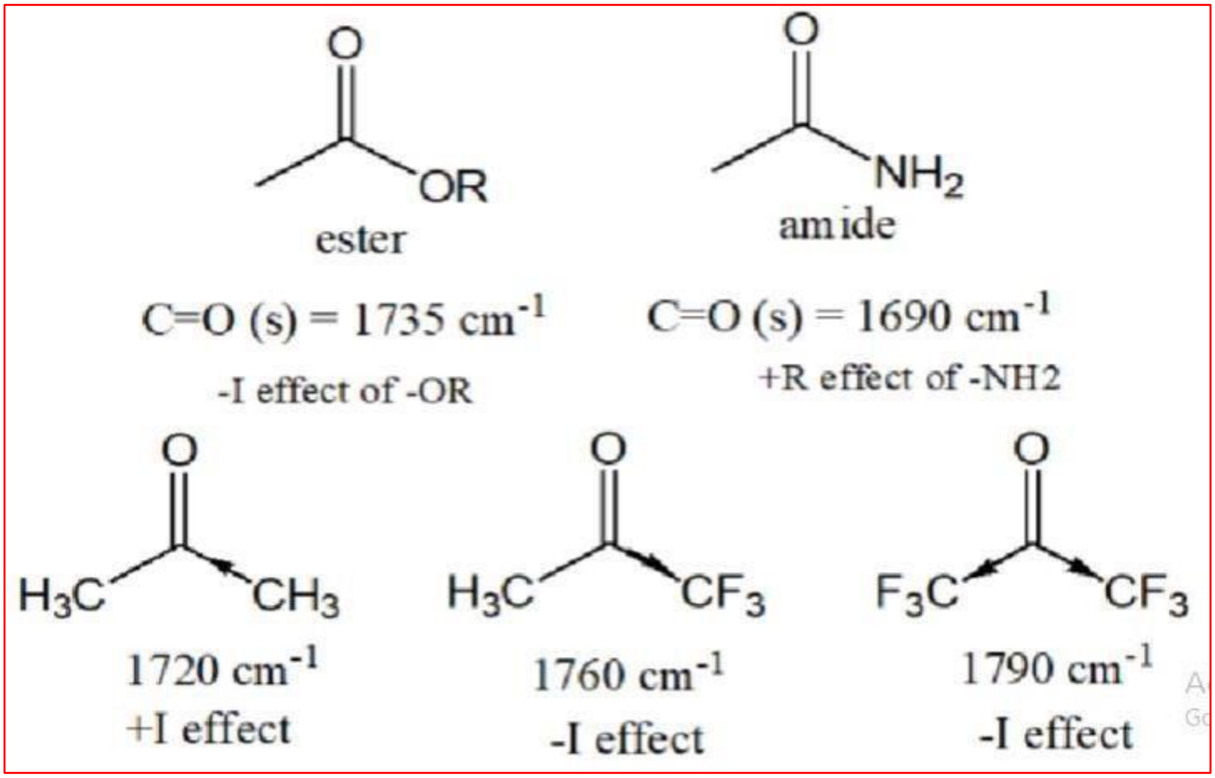
1- Conjugation:

As the conjugation increase, stretching frequency decreases , because force content decrease due to conjugation.



2-Inductive effect and resonance effect:

Oxygen is more electronegative than nitrogen, therefore nitrogen easily donate electron or lone pair of nitrogen undergoes delocalization with C=O bond. Due to delocalization double bond of C=O changes into partial double bond therefore force constant decreases which decrease the C=O stretching frequency.



3-Hydrogen bonding:

Intermolecular hydrogen bonding weakens the O- H bond, thereby shifting the band to lower frequency. For example, in neat solution O-H stretching vibration of phenol observed in the range from 3400- 3300 cm-1. When solution is dilute then O-H frequency shifted towards higher frequency at 3600 cm-1

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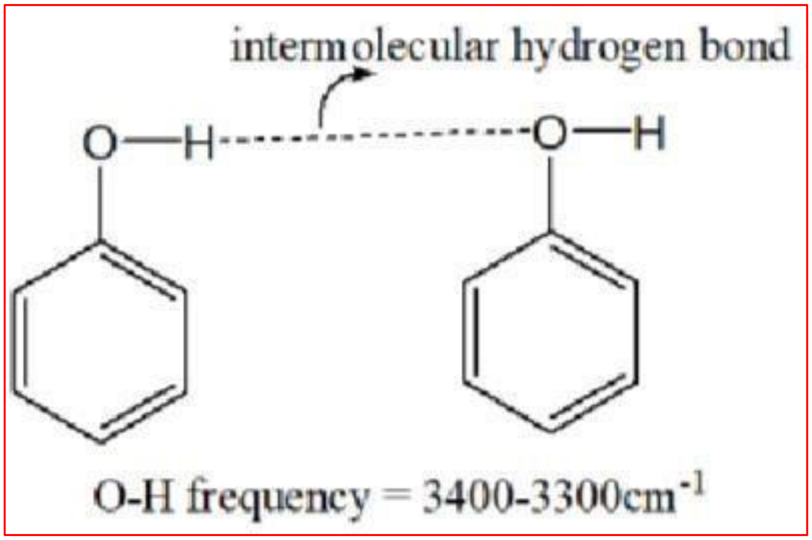
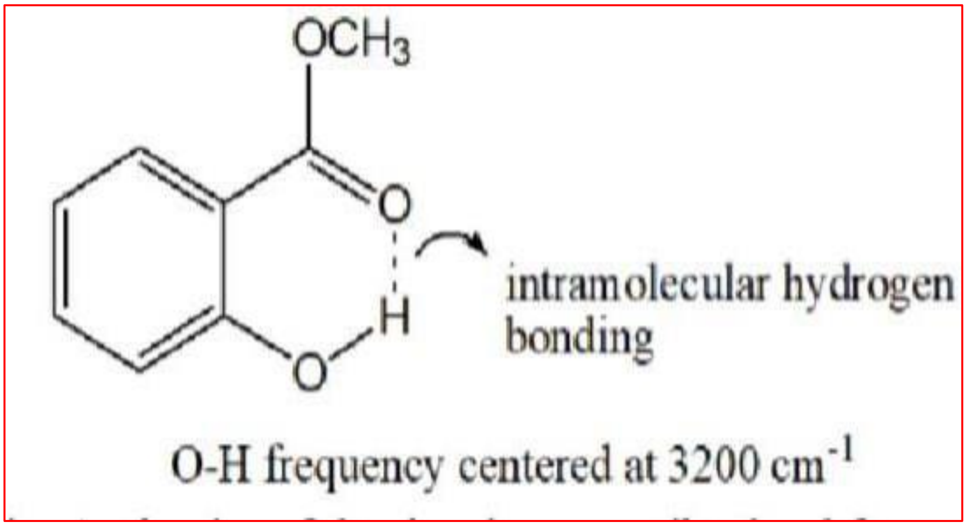


O-H frequency = 3400-3300cm^{-1}

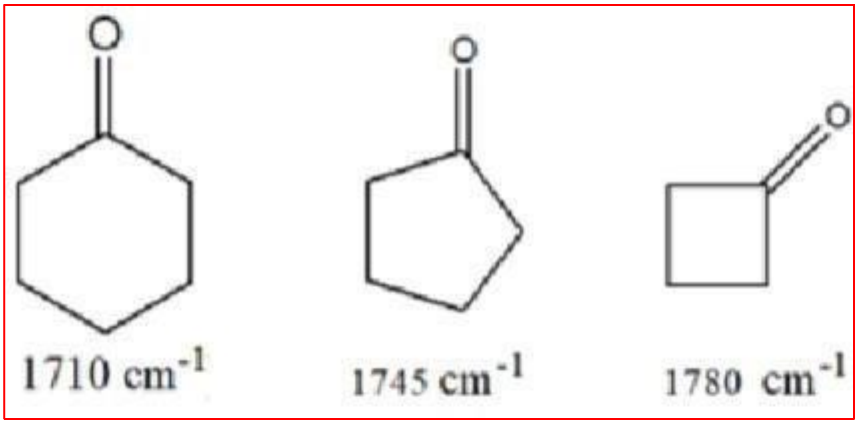
- Whereas in case of methyl salisilate, intramolecular hydrogen bonding lower down the stretching frequency of O-H at 3200 cm^{-1} . Intramolecular hydrogen bonding does not change its frequency even in very dilute solution because upon dilution structure of compound does not change.



O-H frequency centered at 3200 cm^{-1}

4-Ring strain:

As the size of the ring decrease, vibrational frequency of C=O increase. For example.



Application of IR Spectroscopy

- Identification of different functional group
- Distinction between intermolecular and intra- molecular hydrogen bonding.
- Identification of purity of the compound, if compound is impure then additional peaks are observed in the IR spectrum
- Study of chemical reaction:
- Identification of geometrical isomers (cis- trans).