UCB008 - APPLIED CHEMISTRY

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

SCBC-TIET

Infra-red Spectroscopy Series
Lecture - III

IR Spectroscopy - Principles

by

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Learning Outcomes

At the end of this session participants should be able to:

- Understand the principles of IR spectroscopy

Principles of IR spectroscopy

Criteria for a molecule to absorb IR radiation

- **Correct wavelength of radiation**
  - A molecule will absorb IR radiation when natural frequency of vibrations of some part of a molecule is same as that of the frequency of incident radiation.
- **Change in dipole moment**
  - A molecule is said to have an electric dipole when there is a slight positive and a slight negative charge on its component atoms.
  - **Vibrational motion of the molecule should be accompanied by change in (fluctuating) dipole moment i.e., dipole moment must change during the vibration**
  - With change in dipole moment, charge distribution of the molecule changes & it is the net change in charge distribution produced during stretching or bending which makes possible interaction between the molecule and IR radiations

Principles of IR spectroscopy

- **Type of vibration**
  - Stretching vibrations: **higher frequency**
  - Bending vibrations: **lower frequency**
- **Masses of the atoms in a bond [Atomic weight increases, Frequency decreases]**
- **Strength of the bond or bond order [Bond order increases, Frequency increases]**
- **Vibrational transition** that causes a significant change in the dipole moment of a chemical bond leads to strong absorption bands **– IR active transitions,** for example, Carbonyl gp
- Vibrations that result in no change in dipole moment does not give rise to any absorption band **– IR inactive,** for example, Homonuclear diatomic molecules

Vibrational modes

- For a molecule, number of possible vibrational modes depends on its vibrational degrees of freedom (DoF)
- Each atom has 3 DoF corresponding to the 3 cartesian coordinates (X, Y, Z)
- When atoms combine to form a molecule, no DoF is lost
- Total of DoF of a molecule = 3n (n → number of atoms)
- 3n Degree of Freedom = translational + rotational + vibrational
- A molecule, always, has 3 translational DoF
- A non-linear molecule has 3 rotational DoF but a linear molecule has only 2 rotational DoF, because rotation of linear molecule about its axis of linearity does not bring any change in the position of the atoms.

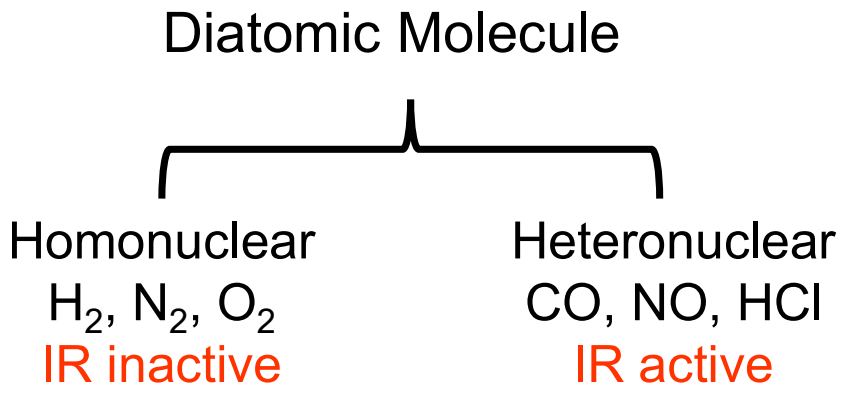
Vibrational modes

- **3n Degree of Freedom = translational + rotational + vibrational**
- Vibrational DoF for linear molecule = 3 + 2 + (3n-5)
- Vibrational DoF for non-linear molecule = 3 + 3 + (3n-6)

Molecule	Number of atoms	Total DoF	Translational DoF	Rotational DoF	Vibrational DoF
Carbon dioxide	3	3n = 3 x 3 = 9	3	2	9 – 5 = 4
H_2O	3	3n = 3 x 3 = 9	3	3	9 – 6 = 3
Benzene	12	3n = 3 x 12 = 36	3	3	36 – 6 = 30
Toulene	15	3n = 3 x 15 = 45	3	3	45 – 6 = 39
Acetylene	4	3n = 3 x 4 = 12	3	2	12 – 5 = 7

Principle of IR spectroscopy

- **Diatomic molecules**
- For a diatomic molecule, 3n = 3 x 2 = 6
- Vibrational DoF for diatomic molecule = 3n – 5 = 3 x 2 – 5 = **1**
- Thus, for a diatomic molecule – only stretching vibration is possible



Principle of IR spectroscopy

- **Triatomic molecules**
- For a molecule, number of possible vibrational modes depends on its vibrational degrees of freedom (DoF)
- Vibrational DoF increases with increase in number of atoms in a molecule
- Out of these all possible vibrational modes, only those which causes fluctuating dipole moment in molecule give rise to absorption in IR region
- If a molecule has center of symmetry, vibrations which are centro-symmetric are IR inactive
- Out of all possible vibrational modes, even if only one mode is active in IR region, molecule is said to be IR active
- Therefore, all triatomic and polyatomic molecules are IR active
- Except, homonuclear diatomics, all other molecules are IR active

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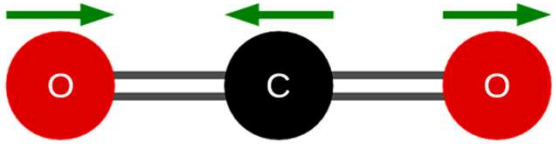
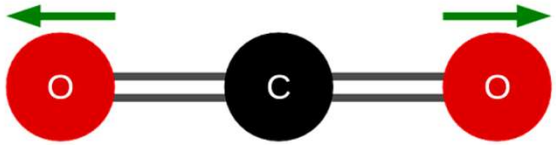
CO_2 – Vibrational Modes

- Asymmetric Stretch



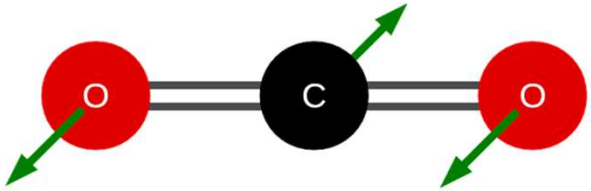
- Symmetric Stretch (not IR active)



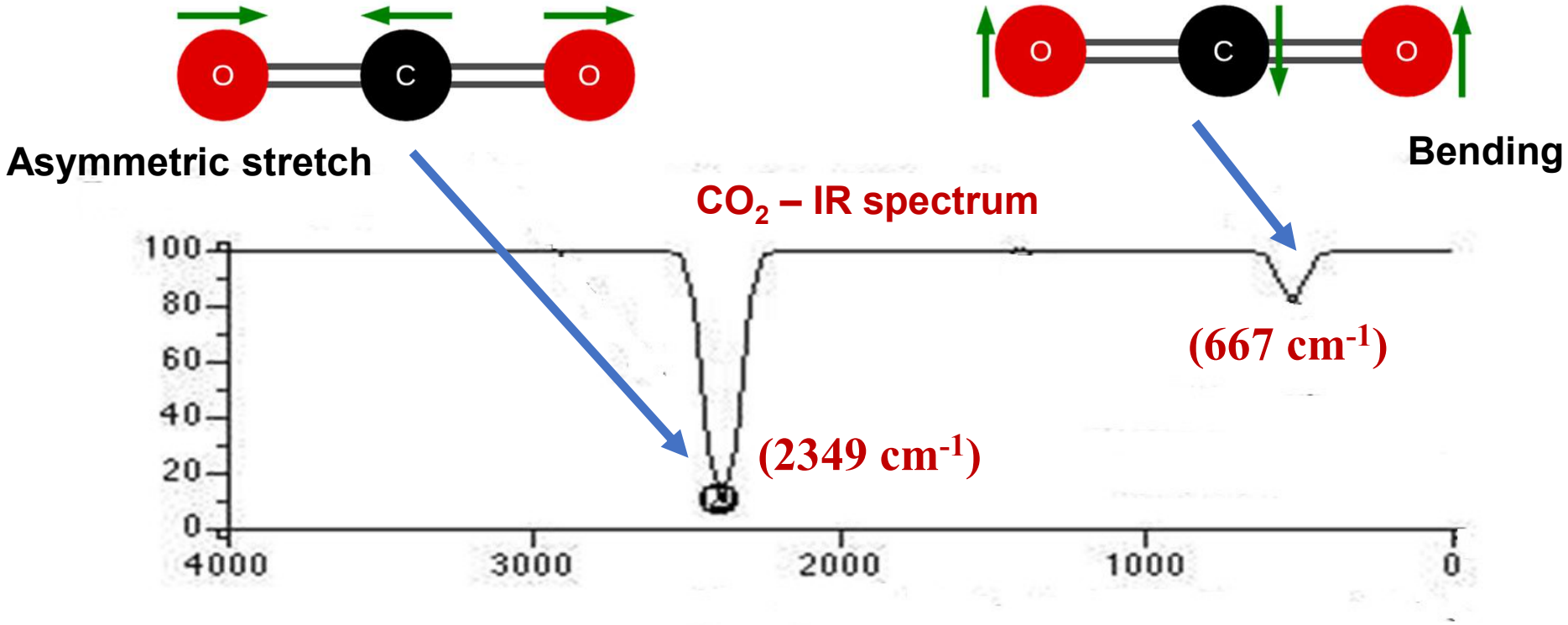
- Vertical Bend

- Horizontal Bend

  (A degenerate mode with same motion as above but rotated by 90°)

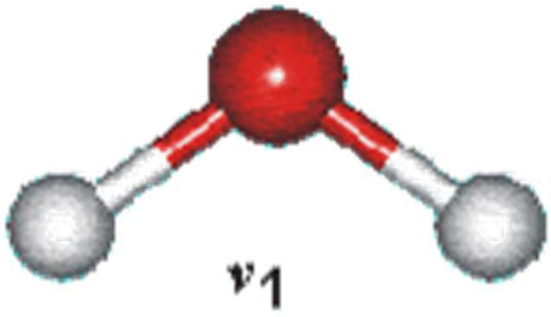


CO_2 – IR Spectrum



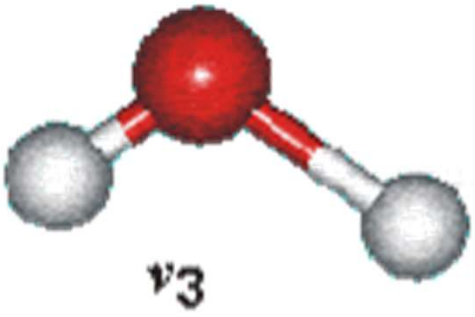
- Number of possible vibrational modes = 3n – 5 = 3 x 3 – 5 = 4
- Number of IR active vibrational modes = 3 (symmetric stretching – IR inactive)
- Number of bands in IR spectrum = 2 (both bending modes are degenerate)

H_2O – Vibrational Modes



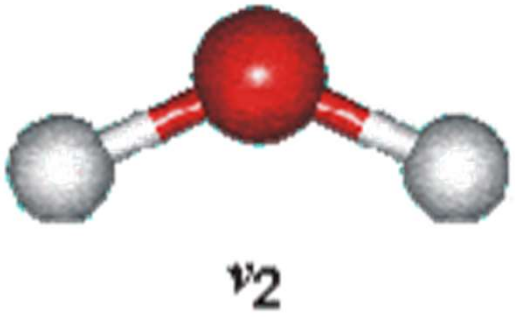
ν_1

symmetric stretch



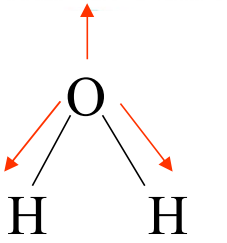
ν_3

asymmetric stretch

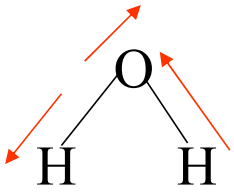


ν_2

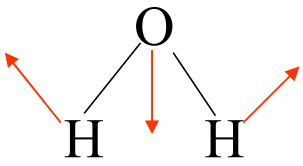
bend



Symmetric



Asymmetric



Bending

- All three modes of vibration in H_2O are not centrosymmetric and hence IR active
- Therefore, water cannot be used as solvent, in case of IR spectroscopy

Source: http://www1.lsbu.ac.uk/water/water_vibrational_spectrum.html

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In the next session…..

- Instrumentation associated with IR spectroscopy