UCB008 - APPLIED CHEMISTRY

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

Infra-red Spectroscopy Series
Lecture - II

IR Spectroscopy – Molecular Vibrations

by

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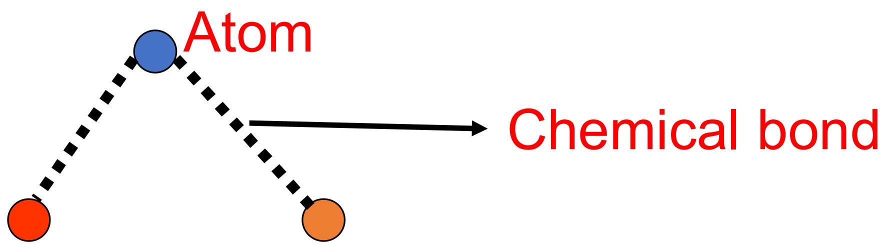
Learning Outcomes

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

- Distinguish various types of vibrational motions in a molecule
- Calculate vibrational frequency using Hooke's law

- Molecular Vibrations
  - The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and contracted.
  - Molecules - consisting of balls (atoms) of different sizes tied with springs (bonds) of varying strength.



Molecular Vibrations

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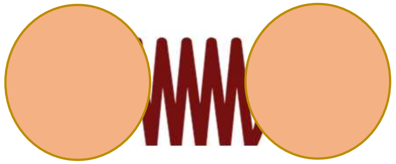
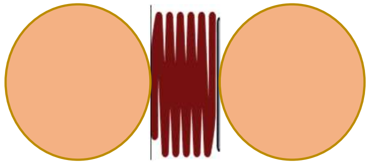
- Infrared radiation induces **vibrational transitions** in covalently bonded atoms or molecules.
- Diatomic molecules having covalent bond can be assumed as spring holding together two atoms.



Equilibrium bond length



Compressed covalent bond

Stretched covalent bond

Specific bonds respond to (absorb) **specific** frequencies of the photons of IR region

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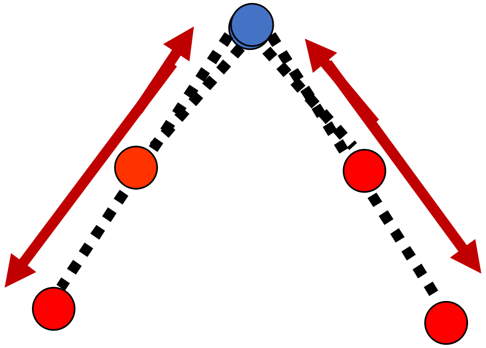
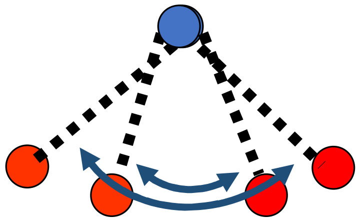
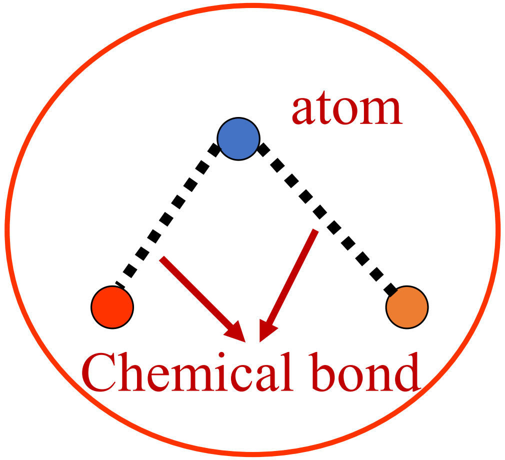
Molecular Vibrations

Stretching vibrations
(Distance between atoms changes)



Bending vibrations
(Bond angle changes)





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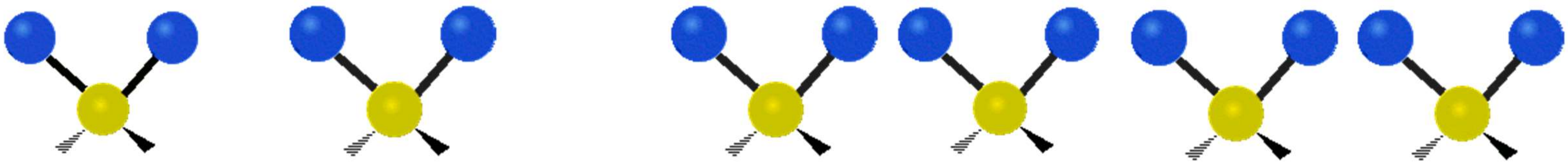
Molecular Vibrations

Stretching vibrations
(Distance between atoms changes)

- Symmetric stretching
- Asymmetric stretching

Bending vibrations
(Bond angle changes)

- Inplane
  - Scissoring
  - Rocking
- Out of plane
  - Wagging
  - Twisting



$\bar{\nu}_{Asym} > \bar{\nu}_{Sym} >> \bar{\nu}_{Bending}$

Animation courtesy: https://en.wikipedia.org/wiki/Molecular_vibration

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Molecular Vibrations

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- In addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms.
- Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations.
- Infrared spectrometers permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure.
- Frequency of absorption depends on

  1. Relative masses of the atoms
  2. Force constant – Bond strength
  3. Arrangement of atom within the molecule

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Hooke's Law and Molecular Vibrations

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Frequency of absorption - Calculation – Hooke's Law

$$\left[v = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \right] \text{Hz}$$

Where: ν = oscillating frequency (Hz)
k = force constant
μ = reduced mass of the atoms

$$\left[\bar{v} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \right] \text{cm}^{-1}$$

Where: $\bar{v}$ = Wave number (cm^{-1})
c = speed of light (3×10^{10} cm/s)

$$\mu = \frac{M_1 \times M_2}{M_1 + M_2}$$

Where: M_1 & M_2 = masses of atom in kg

IR spectra is recorded as transmittance vs wave number (cm^{-1})

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Hooke's Law and Molecular Vibrations

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$$\left[v = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \right] \text{Hz}$$

If Bond strength increases
or
Reduced mass (μ) decreases → vibrational frequency increases

If Bond Strength decreases
or
Reduced mass (μ) increases → vibrational frequency decreases

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In the next session……

- Principles underlying IR spectroscopy