

**B.Sc. (Honours) Part-I
Paper-IC**

**Topic: An Idea of Infrared
Spectroscopy**

UG

Subject-Chemistry

Dr. Laxman Singh

Asst. Professor

Department of Chemistry

R.R.S. College (PPU)

(Mokama, Patna)

An Idea of Infrared Spectroscopy

IR spectroscopy (which is short for infrared spectroscopy) deals with the infrared region of the electromagnetic spectrum, i.e. light having a longer wavelength and a lower frequency than visible light. Infrared Spectroscopy generally refers to the analysis of the interaction of a molecule with infrared light.

The IR spectroscopy concept can generally be analyzed in three ways: by measuring reflection, emission, and absorption. The major use of infrared

spectroscopy is to determine the functional groups of molecules, relevant to both organic and inorganic chemistry

OR

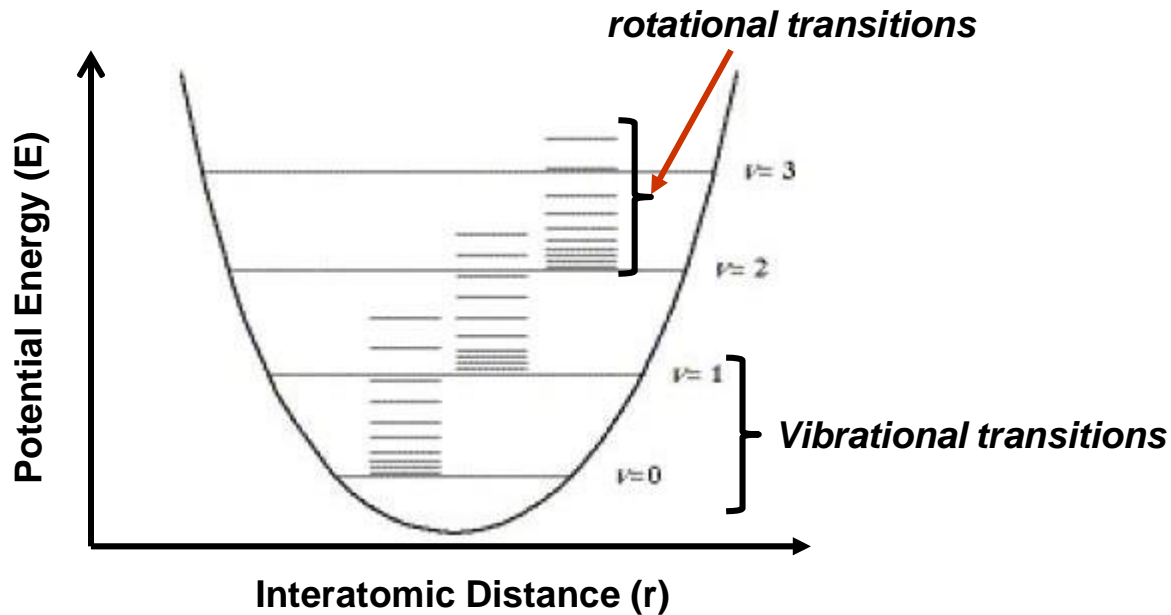
The infrared region of the spectrum encompasses radiation with wavenumbers ranging from about 12,800 to 10 cm^{-1} or wavelengths from 0.78 to 1000 μm . The infrared spectrum is divided into **near-**, **mid-**, and **far-**infrared radiation.

TABLE 16-1 IR Spectral Regions

Region	Wavelengths (λ), μm	Wavenumbers ($\bar{\nu}$), cm^{-1}	Frequencies (ν), Hz
Near	0.78 to 2.5	12800 to 4000	3.8×10^{14} to 1.2×10^{14}
Middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
Far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
Most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

Infrared Spectroscopy

Infrared (IR) spectroscopy: based on IR absorption by molecules as undergo vibrational and rotational transitions. Absorption of radiation in this region by a typical organic molecule results in the excitation of vibrational, rotational and bending modes, while the molecule itself remains in its electronic ground state.



Potential energy resembles classic Harmonic Oscillator

2.) IR radiation is in the range of $12,800 - 10 \text{ cm}^{-1}$ or $\lambda = 0.78 - 1000 \text{ }\mu\text{m}$

- rotational transitions have small energy differences

• $\leq 100 \text{ cm}^{-1}, \lambda > 100 \text{ }\mu\text{m}$

- vibrational transitions occur at higher energies

- rotational and vibrational transitions often occur together

3.) Typical IR spectrum for Organic Molecule

Typical IR spectrum for Organic Molecule

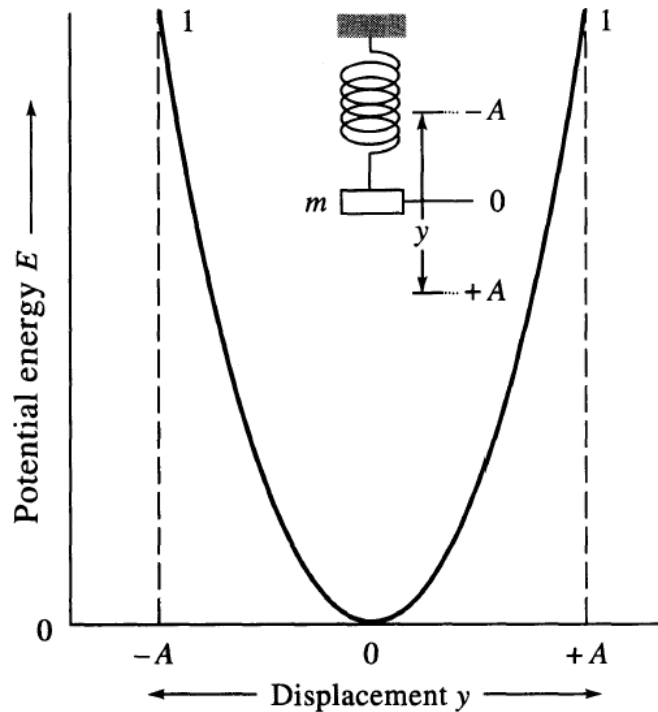
- many more bands than in UV-vis, fluorescence or phosphorescence
-
- bands are also much sharper
-
- pattern is distinct for given molecule
- - except for optical isomers
- good qualitative tool
- - can be used for compound identification
 - group analysis
- also quantitative tool
- - intensity of bands related to amount of compound present
 -
- spectra usually shown as percent transmittance (instead of absorbance) vs. wavenumber (instead of λ) for convenience

Theory of IR Absorption

1.) Molecular Vibrations

i.) Harmonic Oscillator Model:

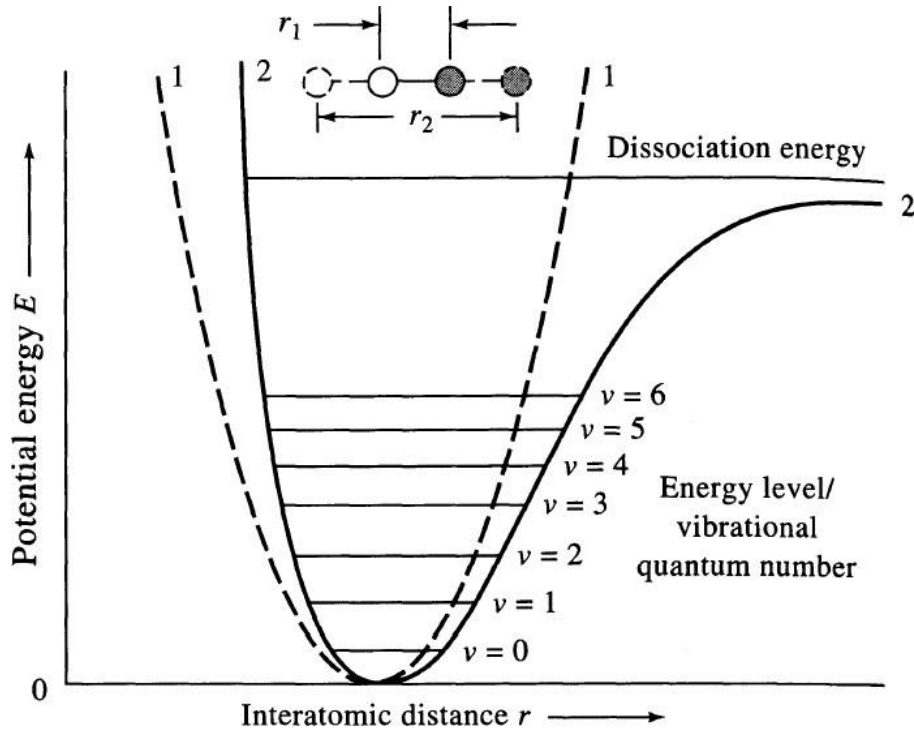
- approximate representation of atomic stretching
- two masses attached by a spring



$$E = \frac{1}{2} ky^2$$

where:

y is spring displacement
 k is spring constant



Vibrational frequency given by:

$$\nu = 1 / 2\pi \sqrt{k / m}$$

where:

ν : frequency

k : force constant (measure of bond stiffness)

μ : reduced mass – $m_1 m_2 / m_1 + m_2$

If know ν and atoms in bond, can get k :

Single bonds:

$k \sim 3 \times 10^2$ to 8×10^2 N/m (Avg $\sim 5 \times 10^2$)

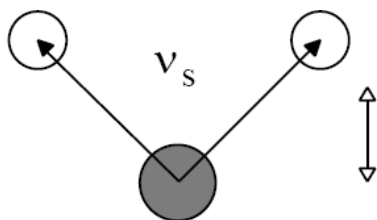
double and triple bonds $\sim 2x$ and $3x$ k for single bond.

$\nu \propto \sqrt{k}$ So, vibration ν occur in order:
single < double < triple

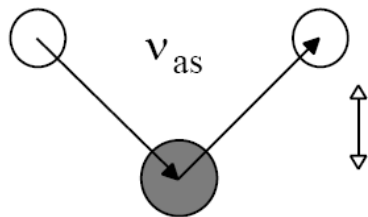
Types of Molecular Vibrations

Bond Stretching

symmetric

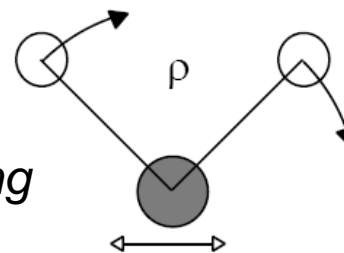


asymmetric

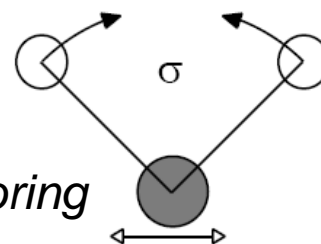


Bond Bending

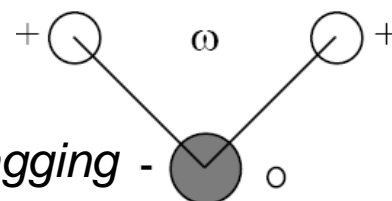
In-plane rocking



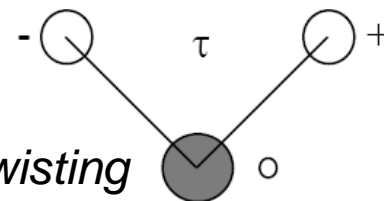
In-plane scissoring



Out-of-plane wagging



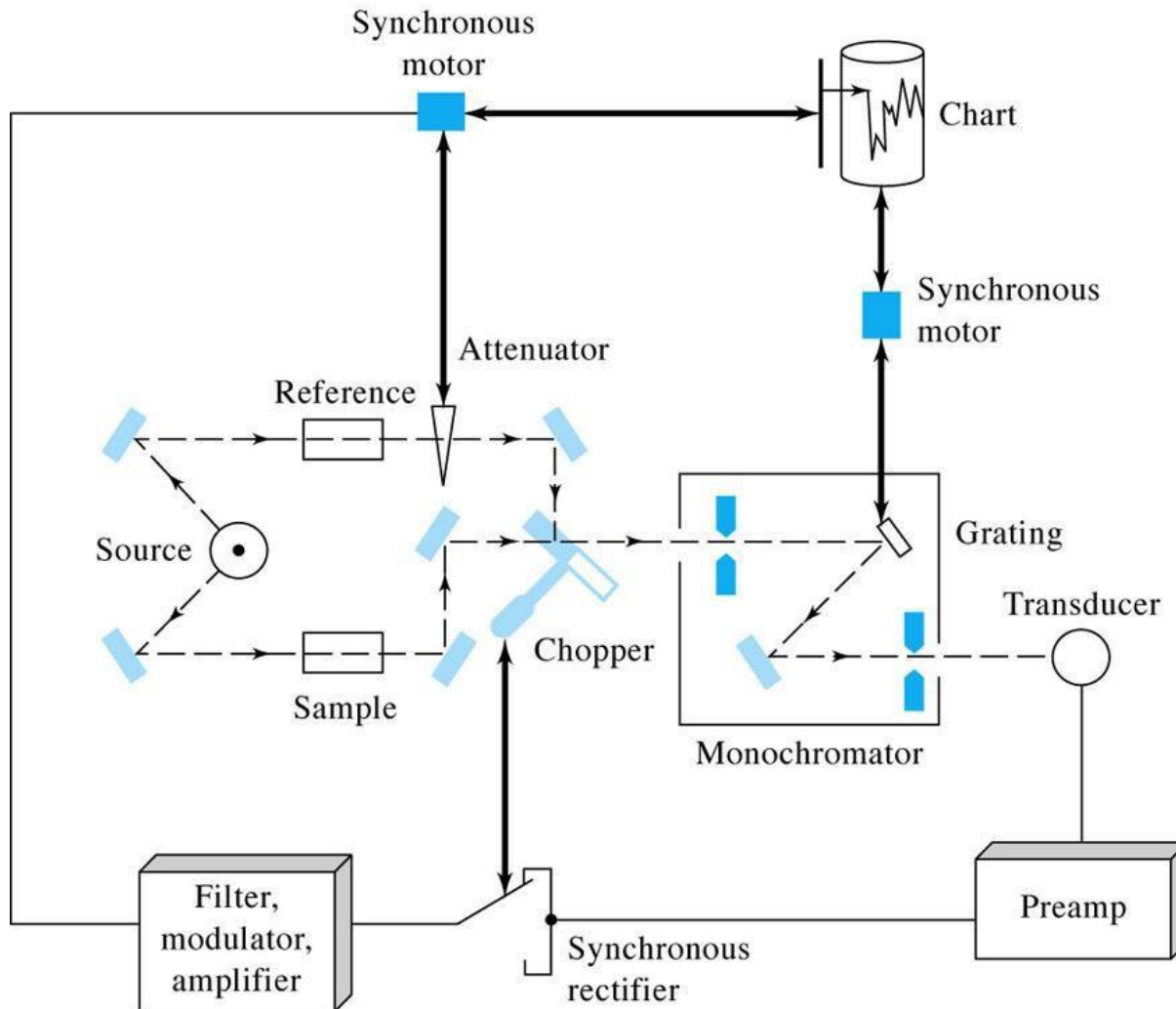
Out-of-plane twisting



Instrumentation of IR Spectroscopy

1.) Basic Design

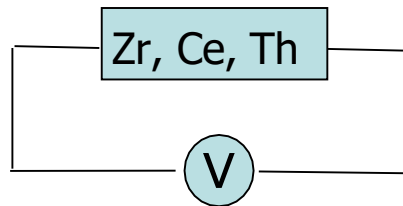
- normal IR instrument similar to UV-vis
- main differences are light source & detector



i.) Light Source:

- must produce IR radiation
- can't use glass since absorbs IR radiation
- several possible types

a) Nernst Glower



- rare earth metal oxides (Zr, Ce, Th) heated electrically
- apply current to cylinder, has resistance to current flow generates heat ($1200^{\circ} - 2200^{\circ} \text{C}$).
- causes light production similar to blackbody radiation
- range of use $\sim 670 - 10,000 \text{cm}^{-1}$
- need good current control or overheats and damaged

b)

Globar

- similar to Nernst Glower but uses silicon carbide rod instead of rare earth oxides
- similar usable range

c) Incandescent Wire Source

- tightly wound nichrome or rodium wire that is electrically heated
- same principal as Nernst Glower
- lower intensity than Nernst Glower or Globar, but longer lifetime

d) CO₂ Laser

- CO₂ laser gas mixture consists of 70% He, 15% CO₂, and 15% N₂
- a voltage is placed across the gas, exciting N₂ to lowest vibrational levels.
- the excited N₂ populate the asymmetric vibrational states in the CO₂ through collisions.
- infrared output of the laser is the result of transitions between rotational states of the CO₂ molecule of the first asymmetric vibrational mode to rotational states of both the first symmetric stretch mode and the second bending mode
- gives off band of $\sim 100 \text{ cm}^{-1}$'s in range of 900-1100 cm^{-1}
- small range but can choose which band used & many compounds have IR absorbance in this region
- much more intense than Blackbody sources

e) Others

- mercury arc ($\lambda > 50 \mu\text{m}$) (far IR)
- tungsten lamp (4000 -12,800 cm^{-1}) (near IR)

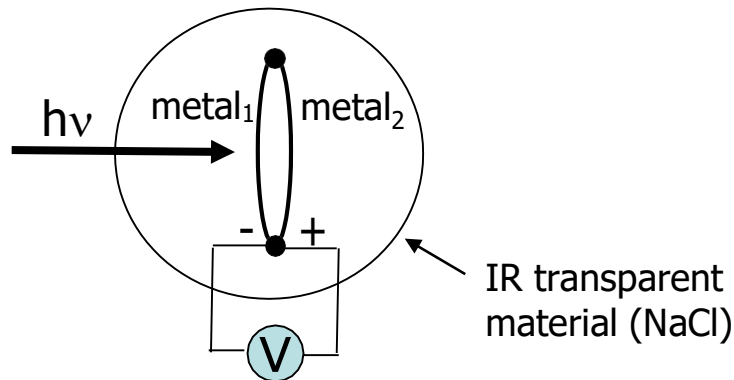
ii.) Detectors:

- two main types in common IR instruments

a) Thermal Detectors

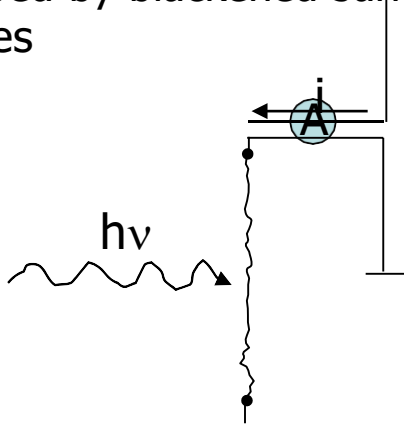
1.) *Thermocouple*

- two pieces of dissimilar metals fused together at the ends
- when heated, metals heat at different rates
- potential difference is created between two metals that varies with their difference in temperature
- usually made with blackened surface (to improve heat absorption)
- placed in evacuated tube with window transparent to IR (not glass or quartz)
- IR "hits" and heats one of the two wires.
- can use several thermocouples to increase sensitivity.



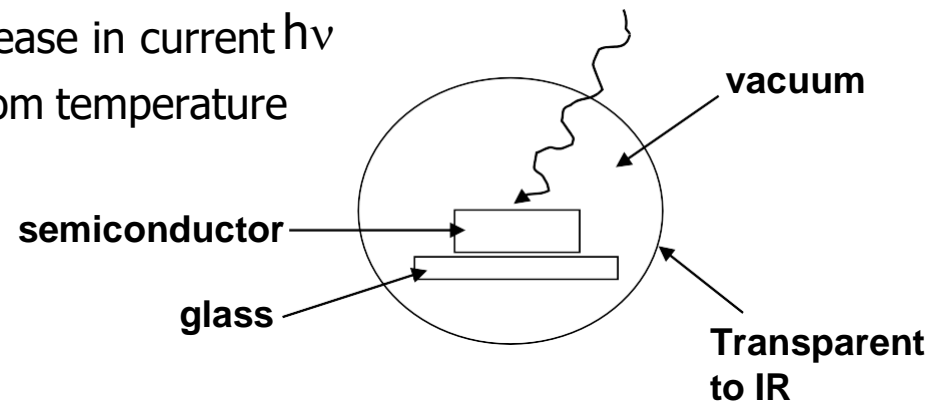
2.) Bolometer

- strips of metal (Pt, Ni) or semiconductor that has a large change in resistance to current with temperature.
- as light is absorbed by blackened surface, resistance increases and current decreases
- very sensitive



b) Photoconducting Detectors

- thin film of semiconductor (ex. PbS) on a nonconducting glass surface and sealed in a vacuum.
- absorption of light by semiconductor moves from non-conducting to conducting state
decrease in resistance \rightarrow increase in current $h\nu$
- range: $10,000 - 333 \text{ cm}^{-1}$ at room temperature



c) Pyroelectric Detectors

- pyroelectric (ceramic, lithium tantalate) material get polarized (separation of (+) and (-) charges) in presence of electric field.
- temperature dependent polarization
- measure degree of polarization related to temperature of crystal
- fast response, good for FTIR