UNIT-1 MPHYCC-10

Theory of IR

Molecular vibrational frequencies lie in the IR region of the electromagnetic spectrum, and they can be measured using the IR technique. In IR, polychromatic light (light having different frequencies) is passed through a sample and the intensity of the transmitted light is measured at each frequency. When molecules absorb IR radiation, transitions occur from a ground vibrational state to an excited vibrational state.

For a molecule to be IR active there must be a change in dipole moment as a result of the vibration that occurs when IR radiation is absorbed. Dipole moment is a vector quantity and depends on the orientation of the molecule and the photon electric vector. The dipole moment changes as the bond expands and contracts. When all molecules are aligned as in a crystal and the photon vector points along a molecular axis such as z. Absorption occurs for the vibrations that displace the dipole along z. Vibrations that are totally x or y polarized would be absent. Dipole moment in a heteronuclear diatomic molecule can be described as uneven distribution of electron density between the atoms. One atom is more electronegative than the other and has a net negative charge.

The dipole moment can be expressed mathematically as

$$\mu = er$$

The relationship between IR intensity and dipole moment is given as

$$I_{IR} \propto \left(\frac{d\mu}{dQ}\right)^2$$

relating this to intensity of the IR radiation, we have have the following equation below.

where μ is the dipole moment and Q is the vibrational coordinate. The *transition moment integral,* that gives information about the probability of a transition occurring, for IR can also be written as

$$\langle \psi i \, M | \psi f \rangle$$

i and f represent are initial and final states. Ψi is the wave function. Relating this to IR intensity we have

$$IIR \propto \langle \psi i \, M | \psi f \rangle$$

where M is the dipole moment and has the Cartesian coordinates, Mx, My, Mz. In order for a transition to occur by dipole selection rules, at least one of the integrals must be non zero.

Region of IR

The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 μm. Conventionally the IR region is subdivided into three regions, near IR, mid IR and far IR. Most of the IR used originates from the mid IR region. The table below indicates the IR spectral regions

Region	Wavelength	Wavenumbers (V), cm^{-1}	Frequencies (v), HZ
Near	0.78 -2.5	12800 - 4000	3.8 x 10^{14} - 1.2 x 10^{14}
Middle	2.5 - 50	4000 - 200	3.8 x 10^{14} - 1.2 x 10^{14}
Far	50 -100	200 -10	3.8 x 10^{14} - 1.2 x 10^{14}
Most Used	2.5 -15	4000 -670	3.8 x 10^{14} - 1.2 x 10^{14}

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm^{-1}). The cm^{-1} is the wave number scale and it can also be defined as 1/wavelength in cm. A linear wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process. The relationship is given below

$$\nu(cm{-1})=\frac{1}{\lambda} \times 10^4 \left(\frac{\mu m}{cm}\right) = \frac{v(Hz)}{c(cm/s)}$$

Near Infra Red Spectroscopy: Absorption bands in the near infrared (NIR) region (750 - 2500 nm) are weak because they arise from vibrational overtones and combination bands. Combination bands occur when two molecular vibrations are excited simultaneously. The intensity of overtone bands reduces by one order of overtone for each successive overtone. When a molecule is excited from the ground vibrational state to a higher vibrational state and the vibrational quantum number v is greater than or equal to 2 then an overtone absorption results. The first overtone results from v = 0 to v = 2. The second overtone occurs when v =0 transitions to v = 3. Transitions arising from the near IR absorption are weak, hence they are referred to as forbidden transitions but these transitions are relevant when non-destructive measurements are required such as a solid sample. Near IR spectra though have low absorption they have a high signal to noise ratio owing to intense radiation sources and NIR is able to penetrate undiluted samples and use

longer path lengths; it becomes very useful for rapid measurement of more representative samples.

Far InfraRed Spectroscopy: The far IR region is particularly useful for inorganic studies due to stretching and bending vibrations of bonds between the metal atoms and ligands. The frequencies, which these vibrations are observed, are usually lower than 650 cm^{-1}. Pure rotational absorption of gases is observed in the far IR region when there is a permanent dipole moment present. Examples include H_2O, O_3, HCl.

IR Analysis

Qualitative Analysis

IR spectroscopy is a great method for identification of compounds, especially for identification of functional groups. Therefore, we can use group frequencies for structural analysis. Group frequencies are vibrations that are associated with certain functional groups. It is possible to identify a functional group of a molecule by comparing its vibrational frequency on an IR spectrum to an IR stored data bank.

Here, we take the IR spectrum of Formaldehyde for an example. Formaldehyde has a C=O functional group and C-H bond. The value obtained from the following graph can be compared to those in reference data banks stored for Formaldehyde. A molecule with a C=O stretch has an IR band which is usually found near 1700 cm^{-1} and around 1400 cm^{-1} for CH_2 bend. It's important to note that this value is dependent on other functional groups present on the molecule. The higher 1700 cm^{-1} indicates a large dipole moment change. It is easier to bend a molecule than stretch it, hence stretching vibrations have higher frequencies and require higher energies than bending modes. The finger print region is a region from 1400-650 cm^{-1}. Each molecule has it's own characteristic print and is often cumbersome to attach any values to this region.

Wavelength (µm)

% Transmission

Wave Number (cm⁻¹)

C = 0