Subject: Chemistry
Semester VI
Paper No.: CHB-605
Topic: IR Spectroscopy (Module-1)
Lecture Notes: Dr. Diksha Katiyar

Introduction

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is the radiation between the visible and microwave regions. The IR spectroscopy theory utilizes the concept that molecules tend to absorb specific frequencies of light that are characteristics of the corresponding structure of the molecules. When energy in the form of IR radiation is applied then it causes the vibration between the atoms of the molecules and when applied infrared frequency equals natural frequency of vibration, then absorption of IR radiation takes place and a band or peak is observed in an infrared spectrum. IR spectroscopy is used by chemists to determine functional groups in molecules. It also helps chemist to obtain other useful structural information of the molecules. The infrared region is usually divided into three parts (**Table 1**); the near infrared, the mid infrared and the far infrared. Out of these, the region of greatest practical use to the organic chemist is the portion between 4000 cm^{-1} and 667 cm^{-1} (2.5-15 µm). In this region the number of molecular vibrations may be detected and measured in an infrared spectrum. The near and far infrared regions are not of much use for organic spectroscopy as only few useful absorption occur in these regions.

Table 1: Regions of the infrared

Region	Wavelength (µm)*	Frequency (cm^{-1})	Energy (kcal/mol)
Near IR	0.7 – 2.5	14290 – 4000	40.8 - 11.4
Mid IR	2.5 - 15	4000 - 667	11.4 - 1.9
Far IR	15 - 200	667 - 50	1.9 - 0.14

*(1 µm = 10^{-4} cm)

Theory

Infrared light is absorbed when the oscillating diploe moment (due to molecular vibration) interacts with the oscillating electric vector of the infrared beam. The absorbed radiation is converted by an organic molecule into energy of molecular vibrations. This absorption is quantized and vibrational spectra appear as bands because a single vibrational energy change is accompanied by a number of rotational energy changes. Vibrational bands for several functional groups appear at characteristic frequencies and the entire infrared spectrum can be used as a unique fingerprint of the compound under study. IR spectroscopy mainly concerned with those vibrational–rotational bands occurring between 4000 cm^{-1} and 667 cm^{-1}. The position of an absorption band in the spectrum may be expressed either in terms of wavelength (λ in microns) or very commonly in terms of wavenumber ($\bar{\upsilon}$ in cm^{-1}), which is the reciprocal of the wavelength. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds and the geometry of the atoms. The band intensities are expressed either as transmittance (T) or absorbance (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm, to the base 10, of the reciprocal of the transmittance:

$A = \log_{10} (1/T)$

Most often infrared spectra of organic compounds are plotted as percentage transmittance against wavenumber (Fig. 1). Each dip in a spectrum is called a band, represents absorption of infrared radiation at that frequency by the sample. A 100% transmittance means no absorption and if all the radiation is absorbed the transmittance is 0%. Wavenumbers are reciprocally related to wavelength as follows:

$\bar{\upsilon}$ in $\mathrm{cm}^{-1} = \frac{10000}{\text{wavelength in µm}}$ or $\bar{\upsilon}$ in $\mathrm{cm}^{-1} = \frac{1}{\text{wavelength in cm}}$

If wavelength (λ) is 2.5 µm = 2.5×10^{-4} cm, then

$\bar{\upsilon} = \frac{1}{2.5 \times 10^{-4}} = 4000\mathrm{cm}^{-1}$

similarly, the wavelength 15 µ correspends to wavenumber eaqual to 667 cm^{-1}.

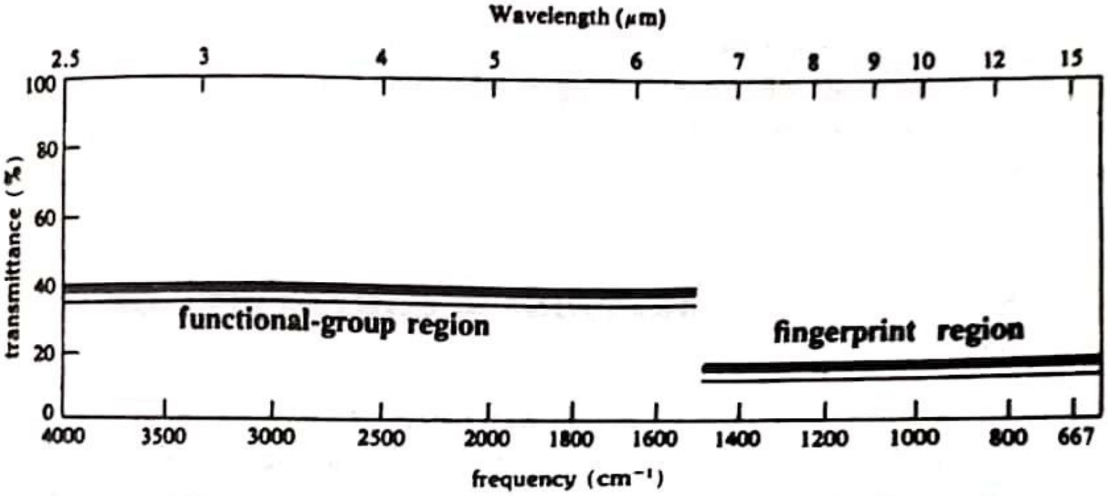


Fig. 1.

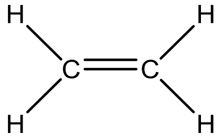
Regions of Infrared Spectrum

IR spectra can be divided into two regions

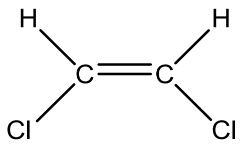
1. **Functional group region**: It comprises region between 4000-1450 cm^{-1} and gives information about the functional group present in the compound. This region is mainly associated with stretching vibrations of the functional groups. It contains relatively few bands.
2. **Finger print region:** The region from 1450-667 cm^{-1} is called finger print region, because this region of spectrum is almost unique to any particular compound. It contains absorption bands due to bending vibrations as well as absorption caused by C-C, C-O and C-N stretching vibrations. This region contains large number of absorption bands. This region is useful for the identification of compounds since no two compounds can give same infrared spectrum except enantiomers. Although the similar molecules may have similar absorption bands in functional group region, but there will always be clear difference in the absorption pattern in finger print region.

Molecular Vibrations

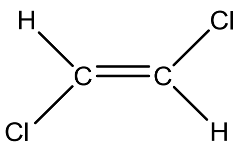
IR radiation causes atoms and group of atoms of organic compounds to vibrate faster about the covalent bonds which connect them. When the radiant energy matches the energy of specific molecular vibration, absorption occurs. It may be noted that the atoms in a molecule are not held rigidly. They can be considered as balls of varying masses connected to springs of varying strengths which in turn corresponds to covalent bonds. Thus, atoms in a molecule do not remain at fixed positions with respect to each other but actually vibrate back and forth about an average value of the interatomic distance. The vibrational energy of a chemical bond is quantized. At room temperature most of the molecules in a given sample are in the lowest vibrational state (ground state). However, on absorption of radiation of appropriate energy the transitions from the ground state (V = 0) to the first excited state (V = 1) takes place (Fig. 2). In this level the amplitude of the molecule vibration is greater. Generally, such absorption of an infrared light quantum can occur only if the dipole moment of molecule is different in the two vibrational levels. The variation of the dipole moment with the change in interatomic distance during the vibration corresponds to an oscillating electric field that can interact with the oscillating electric field associated with electromagnetic radiation. In general, molecular vibrations which lead to a change in the dipole moment of the molecule give rise to absorption bands in the infrared. Otherwise, they are said to be infrared inactive and show no absorption. For example, symmetrical stretching of C=C bond in ethylene (a molecule with a center of symmetry) does not produce a change in dipole moment of the molecule. This mode of vibration is therefore IR inactive.



Trans dichloroethylene shows no C=C stretching whereas cis isomer shows this band. While both compounds show bands for C-H and C-Cl stretchings.



Cis



Trans

Molecules with a permanent dipole moment such as water, CO, HCl and NO are infrared active. Whereas H_2, N_2, Cl_2 and other symmetrical diatomics do not give IR spectra. A large change in dipole moment gives rise to strong absorption. Bands of hydrocarbons are weak, whereas bands associated with bonds connecting atoms differing considerably in electronegativity e.g. C=O are usually quite strong.

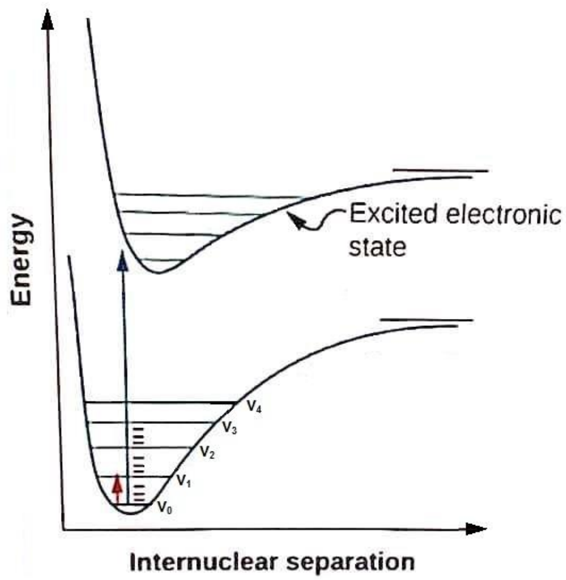


Fig. 2

Two kinds of fundamental vibrations are:-

(i) **Stretching**: In this type of vibrations, the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.

(ii) **Bending:** In this type of vibrations, the positions of the atoms change with respect to the original bond axis.

Stretching vibrations require higher energy and occur at higher frequency. Bending vibrations require lower energy and occurs at lower frequency. For instance, all C=O stretching bands of simple saturated aldehydes occur near 1730 cm^{-1} and bending vibrations occur at about 1200 cm^{-1}.

Types of stretching vibrations: There are two types of stretching vibrations:

(i) Symmetric stretching: In this type movement of the atoms with respect to a particular atom in a molecule is in the same direction.

(ii) Asymmetric stretching: In these vibrations, one atom approaches the central atom while the other departs from it.

Asymmetrical Stretching (v_{as} CH_2) Symmetrical Stretching (v_s CH_2)

STRETCHING VIBRATIONS

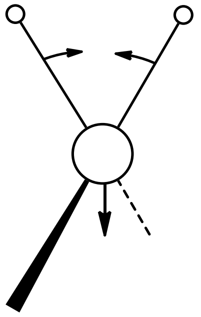
Types of bending vibrations (deformations): Bending vibrations are of four types:

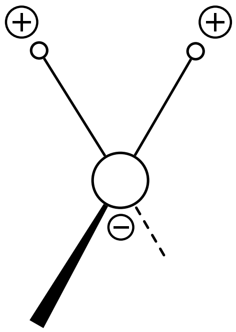
(i) Scissoring: Two atoms approach each other.

(ii) Rocking: In this type, the movement of the atoms takes place in the same direction.

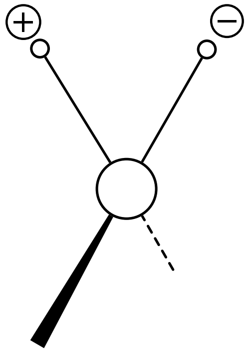
(iii) Wagging: Two atoms move up and below the plane with respect to the central atom.

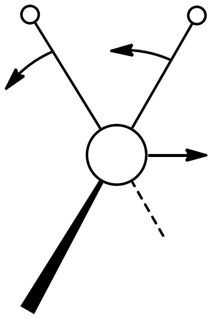
(iv) Twisting: In this type, one of the atoms moves up the plane while the other moves down the plane with respect to the central atom.





In-plane bending or scissoring (δ_s CH_2) Out-of-plane bending or wagging (ω CH_2)





Out-of-plane bending or twisting (τ CH_2) In-plane bending or rocking (ρ CH_2)

BENDING VIBRATIONS

Reference books

1. Spectrometric Identification of Organic Compounds by Robert M. Silverstein and Francis X. Webster, Wiley, Sixth edition (2006).
2. Applications of Absorption Spectroscopy of Organic Compounds by John R. Dyer (1987) Prentice Hall.
3. Elementary Organic Spectroscopy by Y. R. Sharma: Principles and Chemical Applications, S. Chand and Company Ltd.