INFRARED SPECTROSCOPY

SEM-4, CC-8
PART-1, PPT-7

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INFRARED SPECTROSCOPY (PART-1, PPT-7)

Introduction

Infrared (IR) radiation refers to that part of the electromagnetic spectrum between the visible (400-800 nm) and microwave regions (1.0 -10 cm). IR spectrum contains a large number of absorption bands and it is impossible to assign all of them but those can be assigned correctly give a lot of information about the structure of the organic molecule.

Near IR (14000-4000 cm^{-1}): consists of overtones and combination bands resulting from vibrations in the mid IR region of the spectrum.

Mid IR (4000-400 cm^{-1}): provides structural information for most organic molecules.

Far IR (400-33 cm^{-1}): it has been used with inorganic molecules.

IR Regions

IR region: 2 μ - 25 μ = 2000 nm - 25000 nm

Organic compound generally absorb in the region: 2.5 μ - 15 μ.

In IR spectroscopy, units called wavenumbers are normally used to denote different types of light.

$$\overline{\nu} = \frac{1}{\lambda} \quad \text{where: } \overline{\nu} = \text{wavemumber}$$
$$\lambda = \text{wavelength}$$

$$\text{When } \lambda = 2.5 \text{ μ}, \overline{\nu} = \frac{1}{2.5 \text{ μ}} = \frac{1}{2.5 \times 10^{-4} \text{ cm}} = 4000 \text{ cm}^{-1}$$

$$\text{When } \lambda = 15 \text{ μ}, \overline{\nu} = \frac{1}{15 \text{ μ}} = \frac{1}{15 \times 10^{-4} \text{ cm}} = 667 \text{ cm}^{-1}$$

IR region (in terms of wavenumber) for organic compounds: 4000 cm^{-1} – 667 cm^{-1}

Theory of Molecular Vibration

IR radiation is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is quantized, but vibrational spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. Each transition appears as a single line but the lines obtained from vibrational and rotational transitions are very closely spaced. Consequently the spectrum consists of a family of lines which are usually so closely spaced that they merge (for low resolution) into a broad band.

When a molecule absorbs IR radiation, its chemical bonds vibrate. The bonds can stretch, contract, and bend. This is why IR spectroscopy is a type of vibrational spectroscopy.

A molecule is not a rigid assemblage of atoms. It can be said to resemble a system of balls of varying masses, corresponding to the atoms of a molecule, and springs of varying strengths, corresponding to the chemical bonds of a molecule ('Ball-and-Spring' Model).Therefore, several bonds in the molecule vibrate at a certain frequency.

There are two types of molecular vibrations:

(i) Stretching

(ii) Bending

More energy is required to stretch a bond than that required to bend it. Thus, stretching absorptions of a bond appear at high frequencies (higher energy) as compared to the bending absorptions of the same bond.

Fundamental Vibrations

Fundamental vibrations involve no change in the centre of gravity of the molecule.
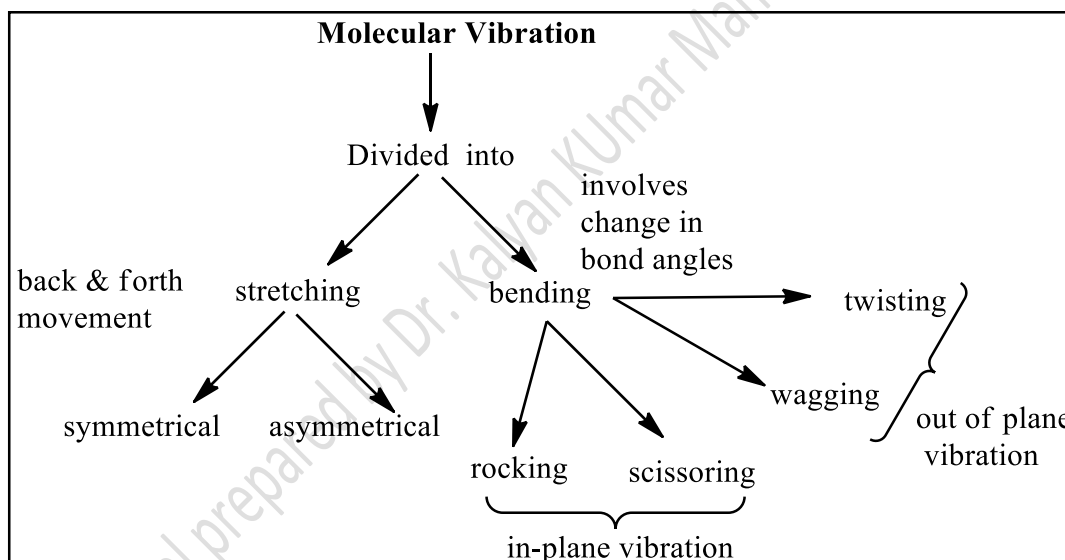
Stretching Vibration

A stretching vibration is a rhythmical movement along the bond axis such that the inter-atomic distance is increasing or decreasing. In this type of vibrations, the distance between the atoms increases or decreases but the atoms remain in the same bond axis.

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

1. Symmetric stretching: In this type, the movement of the atoms with respect to a particular atom in a molecule is in the same direction. Therefore, in this mode of vibration both the bonds expand or contract at the same time.

2. Asymmetric stretching: In this vibrations, one atom approaches the central atom while the other departs from it. Therefore, in this mode of vibration, one bond expands while the other contracts.
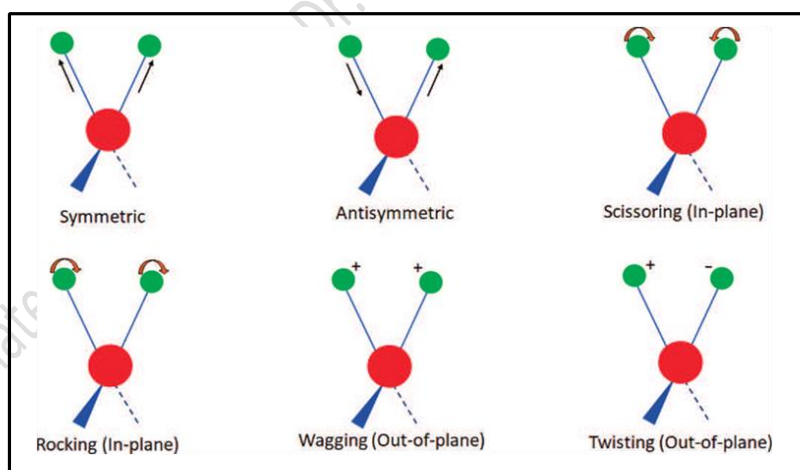
Bending Vibration

In this type of vibrations, the positions of the atoms change with respect to the original bond axis. It consists of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another.

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

1. Scissoring: In this type, two atoms approach each other.

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

3. Wagging: Two atoms move 'up and down' the plane with respect to the central atom.

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

Types of Vibrations

Modes of vibrations (normal modes)

A molecule has as many degrees of freedom as the total degrees of freedom of its individual atoms. Each atom has three degrees of freedom corresponding to the Cartesian coordinates (x, y, z) necessary to describe its position relative to other atoms in the molecule. A molecule of n atoms therefore has $3n$ degrees of freedom.

For nonlinear molecules, three degrees of freedom describe rotation and three describe translation; the remaining $3n - 6$ degrees of freedom are vibrational degrees of freedom or fundamental vibrations. Linear molecules have $3n - 5$ vibrational degrees of freedom, for only two degrees of freedom are required to describe rotation.

Number of Fundamental Vibration

A normal 3-atom molecule such as carbon dioxide (CO_2) has $(3 \times 3) - 5 = 4$ normal modes. The normal modes of CO_2 are a symmetric stretch, an asymmetric stretch, and two bending vibrations. Water is a nonlinear molecule, and has $(3 \times 3) - 6 = 3$ normal modes. The normal modes of H_2O consist of a symmetric stretch, an asymmetric stretch, and one bending vibration. When a molecule absorbs IR light and begins vibrating, it gives rise to an absorption band in the IR spectrum of the molecule at the wavenumber of light absorbed.

Selection Rules (Active and Forbidden Vibrations)

The first necessary condition for a molecule to absorb IR light is that the molecule must have a vibration during which the change in dipole moment with respect to distance is non-zero, *i.e.,*

$$\partial\mu/\partial x \neq 0$$

   Where: $\partial\mu$ = change in dipole moment

    ∂x = change in bond distance

The second necessary condition for IR absorption to take place is that the energy of the light entering on a molecule must equal a vibrational energy level difference within the molecule, *i.e.,*

  $\Delta E_{vib} = h\nu = hc\bar{\nu}$

    Where: ΔE_{vib} = vibrational energy level difference in a molecule

  h = Planck's Constant (6.626×10^{-34} J.s)

     c = The speed of light (3×10^{10} cm/s)

  $\bar{\nu}$ = Wavenumber in cm^{-1}

IR Active Molecules

Molecular vibration which will lead to a change in the dipole moment of the molecule will give rise to absorption bands in the IR. Otherwise, they are said to be IR inactive and will show no absorption. If a molecule has a centre of symmetry, then the vibrations are centrosymmetric and are inactive in the IR. The vibrations which are not centrosymmetric are active in the IR.

The intensity of a fundamental absorpton depends upon the difference between the dipole moments of the molecule in the ground state and the vibrational excited state. Greater the difference, more is the intensity of absorption. The symmetrical stretching of the C=C bond in ethylene (a molecule with a centre of symmetry) will not produce a change in the dipole moment of the molecule. This mode of vibration is IR inactive. Therefore, *trans*-dichloroethylene shows no C=C stretching vibration whereas *cis*-isomer shows this band.

The symmetrical stretching mode of carbon dioxide produces no change in the dipole moment (μ) of the molecule and is, therefore, 'inactive' in the IR. The asymmetrical stretching mode produces a change in the dipole moment, is thus IR active. A large change in dipole moment will usually give rise to strong absorption. So, bands of hydrocarbons which are only composed of carbon and hydrogen atoms are weak.

Examples of IR Active/Inactive Molecules/Modes

trans-dichloroethylene

Acetylene

IR Inactive ($\mu = 0$)

Carbon dioxide
Symmetrical
stretching

cis-dichloroethylene

Carbon dioxide
Asymmetrical
stretching

IR Active ($\mu \neq 0$)
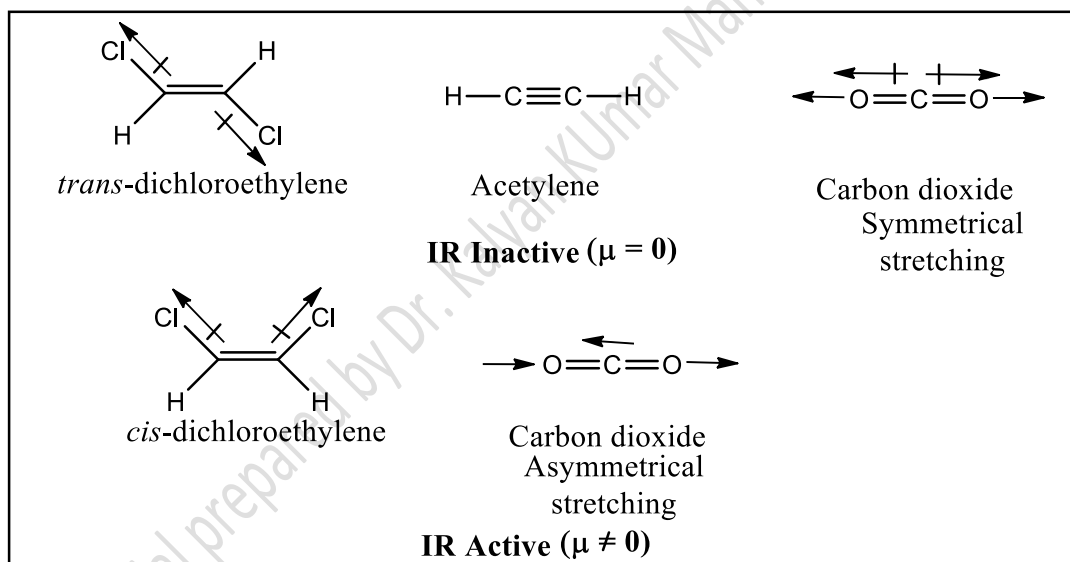
Vibrational Frequency

The value of a stretching vibrational frequency of a bond can be calculated fairly accurately by the application of Hooke's law. In the application of the law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring (ball-and-spring model). The value of vibrational frequency or wave number depends upon:

1. The stiffness of the bond expressed as the force constant (k or f)

2. The masses of the atoms at each end of the bond.

A molecule with a large force constant (a stiff or strong chemical bond) will absorb at a high wavenumber, and a molecule with heavy atoms (a large reduced mass) will absorb at low wavenumber.

HOOKE'S LAW

The following equation, derived from Hooke's law, states the relationship between frequency of vibration, atomic masses, and the force constant of the bond. The vibrational frequency of a bond will increase as 1) the strength of the bond increases and/or 2) the reduced mass (μ) decreases.

$$\bar{v} = \frac{1}{2\pi c} \left[\frac{k}{m_x m_y / (m_x + m_y)} \right]^{1/2}$$

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

where, $\bar{v}$ = wave number (in cm^{-1})

c = velocity og light (in cm/s)

k = force constant of the bond (in dyne/cm)

m_x and m_y = masses (in g) of the atoms x and y, respectively in a particular bond

μ = reduced mass = $m_x m_y / (m_x + m_y)$

k (or f) for single bond = 5 x 10^5 dyne/cm

k (or f) for double bond = 10 x 10^5 dyne/cm

k (or f) for triple bond   = 15 x 10^5 dyne/cm

Calculation of the wave number of stretching vibration

Atomic mass of carbon = 12 amu

Reduced mass (μ) = $\dfrac{m_x m_y}{m_x + m_y}$ = $\dfrac{12 \times 12}{12 + 12}$

= 6 amu = $\dfrac{6}{6.023 \times 10^{23} \text{ g}}$ = 9.962 x 10^{-24} g

Wave number, $\bar{v}$ = $\dfrac{1}{2\pi c} \left[\dfrac{k}{\mu} \right]^{1/2}$ c = 3 x 10^{10} cm/s

= 1189 cm^{-1} k = 5 x 10^5 dyne/cm

$\bar{v}_{C = C}$ = 1189 x 2$^{1/2}$ = 1682 cm^{-1}

$\bar{v}_{C \equiv C}$ = 1189 x 3$^{1/2}$ = 2059 cm^{-1}

$\bar{v}_{C - H}$ = 3031 cm^{-1}

Home Work: Calculate for

(i) $\bar{v}_{C - O}$ (ii) $\bar{v}_{C = O}$ (iii) $\bar{v}_{O - H}$ (iv) $\bar{v}_{N - H}$

FACTS

If one of the bonded atoms (m_1 or m_2) is a hydrogen (atomic mass =1), the mass ratio in the equation is roughly unity, but for two heavier atoms it is much smaller. Consequently, C-H, N-H and O-H bonds (with lower reduced mass) have much higher stretching frequencies than do corresponding bonds to heavier atoms (C-C, C-N, C-O, etc.).

Application of the formula to C-H stretching places the frequency of the C-H bond vibration at 3031 cm^{-1}. Actually, C-H stretching vibrations, associated with methyl and methylene groups, are generally observed in the region between 2960 cm^{-1} and 2850 cm^{-1}. The calculation is not highly accurate because effects arising from the environment of the C-H within a molecule have been ignored.

Calculation of wave number for C=O gives a lower value than that of C=C. Here, strength of the said bonds are different, whereas, calculation using Hooke's Law uses same k value for both C=O and C=C.

Force Constant (k)

The force constant (k) is proportional to the strength of the covalent bond linking m_1 and m_2. In the analogy of a spring, it corresponds to the spring's stiffness. For example, a C=N double bond is about twice as strong as a C-N single bond, and the C≡N triple bond is similarly stronger than the double bond. The IR stretching frequencies of these groups vary in the same order, ranging from 1100 cm^{-1} for C-N, to 1660 cm^{-1} for C=N, to 2220 cm^{-1} for C≡N.

Force constant is defined as the restoring force when a bond is displaced by one unit. Force constant reflects the strength of the bond. More is the force constant, stronger is the bond. Hence, we can say that a triple bond has higher value of force constant than a double bond, which in turn has a higher value of force constant than a single bond.