



SPECTROSCOPY

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Course Code-CHE- 504

Block – 3 : Infrared (IR) Spectroscopy

Lecture-2

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❖ **LEARNING OUTCOMES**

After studying this Chapter, you shall be able to:

- To understand the concept of Infra-red spectroscopy.
- To predict the number of fundamental modes of vibration of a molecule.

❖ INTRODUCTION:

The most frequent spectroscopic technique used by organic and inorganic chemists is infrared (IR) spectroscopy. It deals with the absorption of radiation in the infrared region of the electromagnetic spectrum. IR spectrum gives sufficient information about the structure (identification of functional groups) of a compound and can also be used as an analytical tool to assess the purity of a compound.

The absorption of infrared radiation by a molecule causes changes in their vibrational and rotational energy levels and hence IR-spectroscopy is also known as vibrational-rotational spectroscopy.

The infrared spectrum can be divided into three type of main regions:

- **Far infrared ($<400\text{ cm}^{-1}$)**
- **Mid-infrared ($4000\text{--}400\text{ cm}^{-1}$)**
- **Near-infrared ($13000\text{--}4000\text{ cm}^{-1}$)**

The mid IR region is of greatest practical use to the organic chemist, but the near- and far-infrared regions also provide important information about many compounds.

➤ **Mid IR region:**

The mid-infrared spectrum extends from 4000 to 400 cm^{-1} and results from vibrational and rotational transitions. This region is most useful for the organic chemist since most of the organic molecules absorb in this region.

The mid-infrared can be divided into two regions viz functional group region ($4000-1300\text{ cm}^{-1}$) and finger print region ($1300-600\text{ cm}^{-1}$).

(A). Functional group region ($4000-1300\text{ cm}^{-1}$):

Most of the functional groups present in organic molecules exhibits absorption bands in the region $4000-1300\text{ cm}^{-1}$, hence this is known as functional group region. In this region, each band can be assigned to a particular deformation of the molecule, the movement of a group of atoms, or the bending or stretching of a particular bond.

(B). Finger print region ($1300-600\text{ cm}^{-1}$):

The region from 1300 cm^{-1} to 600 cm^{-1} usually contains a very complicated series of absorptions. These are mainly due to molecular vibrations, usually bending motions that are characteristic of the entire

molecule or large fragments of the molecule. Except enantiomers, any two different compounds cannot have precisely the same absorption pattern in this region. Thus absorption patterns in this region are unique for any particular compound that is why this is known as finger print region.

➤ **Near-infrared region (12500–4000 cm^{-1}):**

The absorptions observed in the near-infrared region (12500–4000 cm^{-1}) are overtones or combinations of the fundamental stretching bands. Bands in the near infrared are usually weak in intensity. They are often overlapped and hence are less useful than the bands in mid-infrared region.

➤ **Far-infrared region (600-100 cm⁻¹):**

The far-infrared spectrum extends from 600 to 100 cm⁻¹. Organometallic and inorganic molecules contain heavy atoms and have weak bonds, therefore the fundamental vibrations of these molecules fall in this region. Lattice vibrations of crystalline materials occur in this region.

❖ **ORIGIN OF INFRA-RED SPECTROSCOPY:**

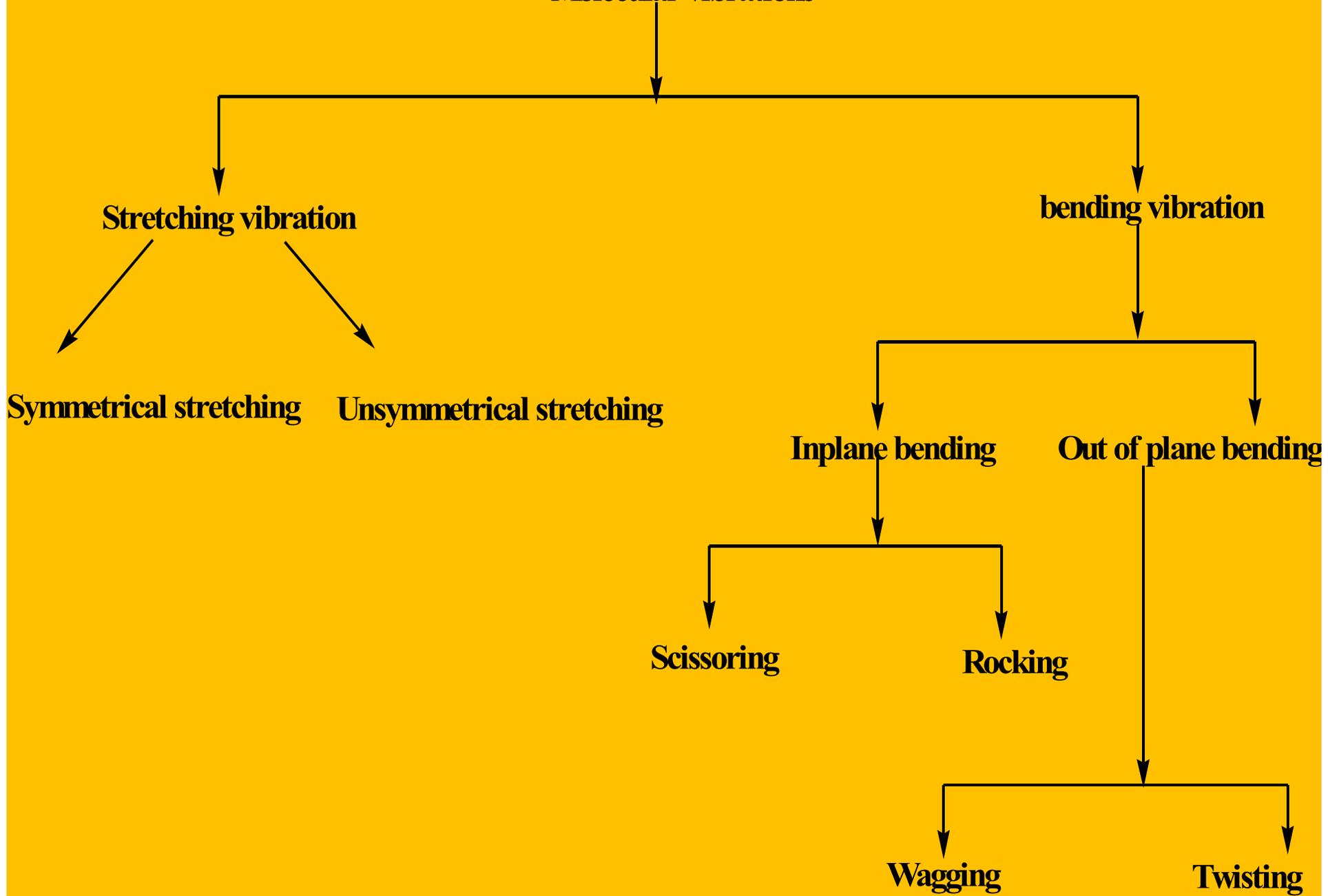
IR-spectroscopy gives the information about molecular vibrations or more precisely on transitions between vibrational and rotational energy levels. Since the absorption of infrared radiation leads to transition between vibrational and rotational energy levels, it is also vibrational-rotational spectroscopy.

When a molecule absorbs IR-radiation below 100 cm^{-1} , transitions between rotational energy levels take place. Since these energy levels are quantised, a rotational spectrum consists of discrete lines. If a molecule absorbs radiation in the range $100\text{--}10,000\text{ cm}^{-1}$, it causes transitions between vibrational energy levels. These energy levels are also quantised but vibrational spectra appear as bands rather than discrete lines. Each vibrational energy level is associated with a large number of closely spaced rotational energy levels or we can say that the energy difference between various rotational energy levels is very short than the energy difference between various vibrational energy levels.

❖ MOLECULAR VIBRATIONS:

If there occur the interaction between oscillating dipole moment of the compound and electronic vector of the Electromagnetic Radiation. In that case there will occur the absorption of IR radiation, which will give rise to the IR spectrum. When the IR radiation is passed through the sample, the electronic transition can also occur with the vibrational transition due to this reason IR spectra will also called as Vibrational-rotational spectra. When the molecule absorb the Irradiation then there are following types of transitions takes place.

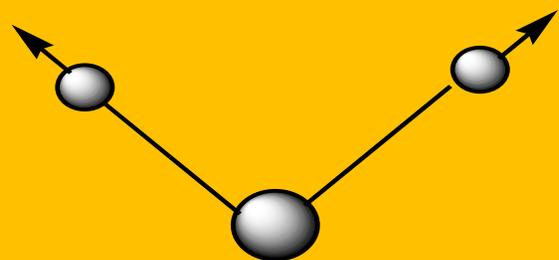
Molecular vibrations



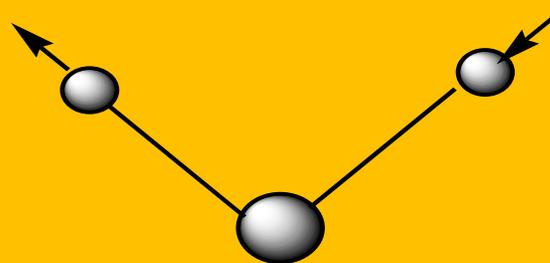
Flowchart of Molecular Vibrations

➤ **Stretching vibrations:**

It involves a rhythmic movement along a bond axis with a subsequent increase and decrease in bond length. Stretching vibrations are of two types *viz.*, *symmetrical stretching* and *asymmetrical stretching*.



Symmetrical stretching

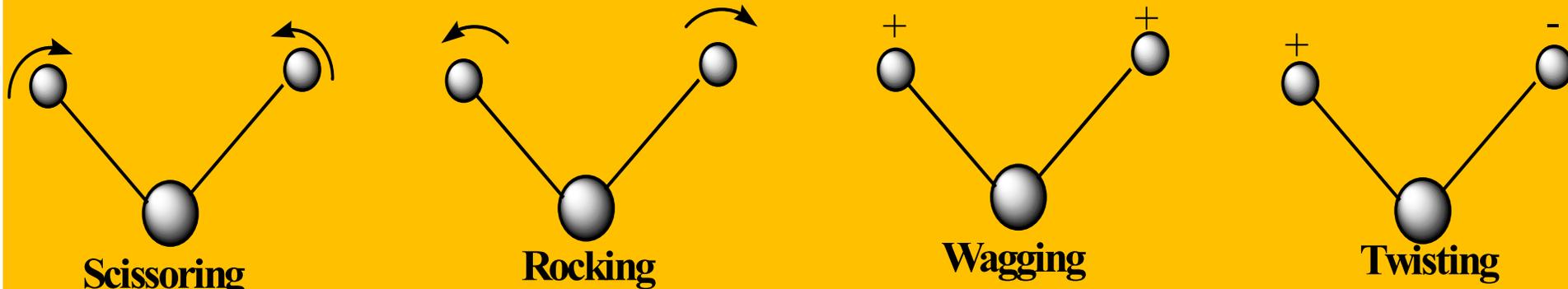


Unsymmetrical stretching

Stretching modes of H₂O

➤ **Bending vibrations:**

It involves a change in bond angle or movement of a group of atoms with respect to the rest of the molecule. Bending vibrations are of four types.



Bending vibrations of a CH₂ group

All the bonds in a molecule are not capable of absorbing infrared radiation but only those bonds which are accompanied by a change in the dipole moment will absorb in the infra-red region. Thus, vibrations which are associated with the change in the dipole moment of the molecule are called infra-red active transitions otherwise the vibration is said to be IR-inactive and do not show any absorption band in the IR-spectrum. Generally, larger the change in the dipole moment, the higher is the intensity of absorption.

Hence the vibrational absorption bands in simple hydrocarbons are weak while bands associated with bonds connecting atoms with considerable electronegativity difference give strong bands.

❖ *Selection Rule:*

IR-radiation is absorbed only when a change in dipole moment of the molecule takes place. Complete symmetry about a bond may eliminate certain absorption bands.

Therefore number of absorption bands observed is not exactly equal to the fundamental vibrations, some of the fundamental vibrations are IR-active while others are not. This is governed by selection rule described below.

1) In a molecule with a centre of symmetry, the vibrations symmetrical about the centre of symmetry are IR-inactive.

2) The vibrations which are not symmetrical about the centre of symmetry are IR-active.

Here are some examples which could explain the selection rule.

a) All the symmetrical diatomic molecules such as H_2 , N_2 and Cl_2 etc. are IR-inactive.

b) The symmetrical stretching of the $C=C$ bond in ethylene (centre of symmetry) is IR-inactive.

c) The symmetrical stretching in CO_2 is IR-inactive, whereas asymmetric stretching is IR-active.

d) Cis-dichloro-ethylene molecule shows $C=C$ stretching bands whereas

❖ FUNDAMENTAL AND OVERTONE BEND:

The energy of any molecule in a particular vibrational level can be given as :

When the molecule is absorbed energy in the IR radiation the excitef from one vibrational level to other vibrational level (Next vibrational level) then the energy difference can be given as:

$$E_v = \left(v + 1/2 \right) h\nu$$

Where E_v is the energy of corresponding vibrational level and v is equal to corresponding vibrational state i.e. $v = 1, 2, 3, 5, \dots$

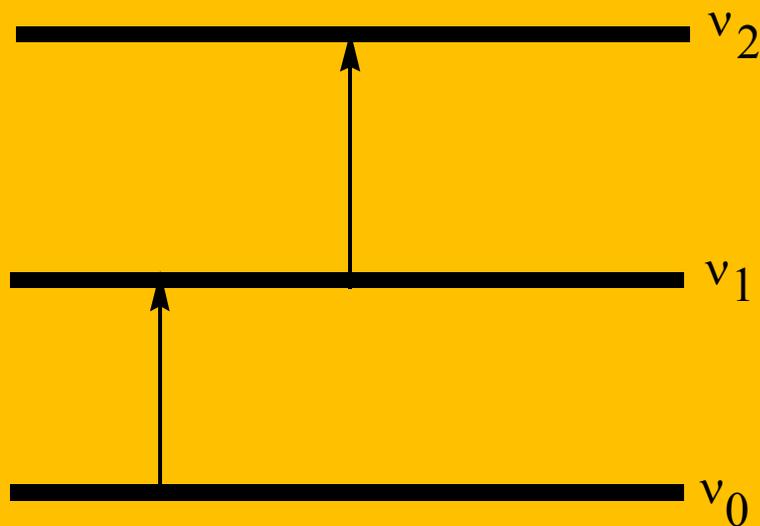
Thus according to above energy gap between two vibrational state there are two types of band are appear, which are given below.

➤ Fundamental Vibrations:

In the classical harmonic oscillator,

$$E = 1/2kx^2 = h\nu$$

Where x is the displacement of the spring. Thus, the energy or frequency is dependent on how far one stretches or compresses the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.



The lowest energy level is $E_0 = 1/2 h\nu$, the next highest is $E_1 = 3/2 h\nu$. According to the selection rule, only transitions to the next energy level are allowed; therefore molecules will absorb an amount of energy equal to $3/2 - 1/2 h\nu$ or $h\nu$. This rule is not inflexible, and occasionally transitions of $2 h\nu$, $3 h\nu$, or higher are observed.

These correspond to bands called overtones in an IR spectrum. They are of lower intensity than the fundamental vibration bands. The IR spectrum of a compound may show more than one vibrational absorption bands. The number of these bands corresponds to the number of fundamental vibrations in the molecule which can be calculated from the degree of freedom (DOF) of the molecule. A molecule comprising of n atoms has a total of $3n$ DOF. In a nonlinear molecule, three of these degrees of

freedom are rotational and three are translational and the remaining $(3n-6)$ correspond to vibrational degree of freedom or fundamental vibrations. Whereas in a linear molecule, only two degrees of freedom are rotational (because rotation about its axis of linearity does not change the positions of the atoms) and three are translational. The remaining $(3n-5)$ degrees of freedom are vibrational degree of freedom or fundamental vibrations.

➤ **Fermi Resonance:** The Fermi resonance effect usually leads to two bands appearing close together when only one is expected. When an overtone or a combination band has the same frequency as, or a similar frequency to, a fundamental, two bands appear, split either side of the expected value and are of about equal intensity.

The effect is greatest when the frequencies match, but it is also present when there is a mismatch of a few tens of wavenumbers. The two bands are referred to as a Fermi doublet.

For example:

Carbon dioxide, CO_2 is linear and has four fundamental vibrations but actually it shows only two bands (666 cm^{-1} and 2350 cm^{-1}). The symmetrical stretching vibration of CO_2 is inactive in the IR because this vibration produces no change in the dipole moment of the molecule. The two scissoring or bending vibrations are equivalent and therefore have the same frequency (degenerate) at 666 cm^{-1} . The asymmetrical stretch of CO_2 gives a strong band in the IR at 2350 cm^{-1} .

Overtone bands:

In addition to the fundamental vibrations, other frequencies can be generated by modulations of the fundamental bands. An overtone band occurs when the molecule makes a transition from the ground state ($v=0$) to the second excited state ($v=2$), where v is the vibrational quantum number. The intensity of the overtone band is very low as compared to the fundamental band and they are usually found in the near infrared region. Based on the harmonic oscillator approximation it has been found that the energy of the overtone transition is about n times of the fundamental vibration associated with that particular transition. Suppose a compound shows strong absorptions at x and y cm^{-1} then it may also give rise to weaker absorptions at $2x$, $2y$, $3x$ and $3y$ cm^{-1} , respectively.

The intensity of overtones bands decreases as the order of the overtone increases, i.e. the intensity of 3x or 3y overtones will be less than the 2x and 2y. Therefore second and third overtones are rarely observed.

➤ **Combination Bands:**

Combination bands are observed when two or more than two fundamental vibrations are excited simultaneously. If there are two fundamental vibrations at x and y cm^{-1} then it may also give rise to absorption bands at $(x+y)$, $(x+2y)$, $(2x+y)$ cm^{-1} .

➤ **Difference bands:**

It is also possible to have a difference band where the frequencies of two fundamental bands are subtracted, i.e. $(x-y)$, $(x-2y)$, $(2x-y)$ cm^{-1} .

THANK YOU