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Principal Investigator		Co- Principal Investigator and Technical Coordinator
Prof A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		**Dr Vimal Rarh** Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi *Specialised in : e-Learning and Educational Technologies*
Paper Coordinator	**Content Writer**	**Reviewer**
Prof Diwan S Rawat Department of Chemistry University of Delhi	**Prof Diwan S Rawat** Department of Chemistry University of Delhi **Dr. Deepak Kumar** Assistant Professor Department of Chemistry University of Delhi	**Prof MSM Rawat** Department of Chemistry Hemwati Nandan Bahuguna Garhwal University
Anchor Institute : SGTB Khalsa College, University of Delhi		

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1. Learning Outcomes

After studying this module, 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.

2. 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. Unlike UV-spectroscopy which has very few peaks in their spectrum, IR spectroscopy provides spectrum with a large number of absorption bands and hence provide plenty of information about the structure of a compound. Different bands present in the spectra correspond to various functional groups and bonds present in the molecule.

The infrared spectrum can be divided into three type of main regions: the far infrared (<400 cm^{-1}), the mid-infrared (4000–400 cm^{-1}) and the near-infrared (13000–4000 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 cm^{-1}) and finger print region (1300-600 cm^{-1}).

Functional group region (4000-1300 cm^{-1}): Most of the functional groups present in organic molecules exhibits absorption bands in the region 4000-1300 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.

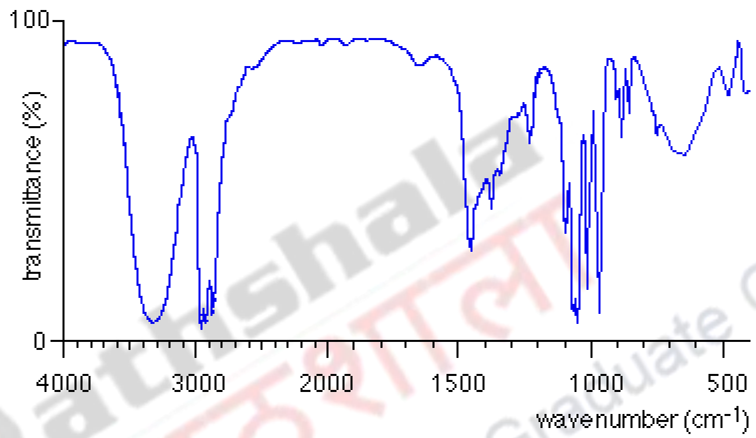
Finger print region (1300-600 cm^{-1}): The region from 1300 cm^{-1} to 600 cm^{-1} usually contains a very complicated series of absorptions. These are mainly due to molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule. Except 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.

It is very difficult to assign individual bands in this region. Two molecules having the same functional group but different bonding arrangements may show similar spectra in the functional group region but their spectra differ in the finger print region. Therefore both the regions are very useful for confirming the identity of a chemical substance. This is generally accomplished by comparing the spectrum of an authentic sample. When two compounds show a good match between the IR spectra in all frequency ranges, mainly in the fingerprint region, strongly indicates that they have the same molecular structures.

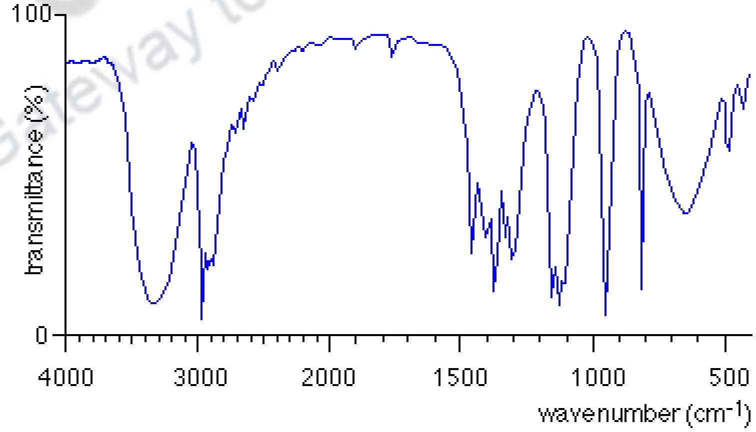
To understand the importance of finger print region to identify a compound, we can take the example of propan-1-ol and propan-2-ol.

Both the compounds are alcohols and contain exactly the same bonds. Now if you compare the infra-red spectra of these compounds, the functional group region is very similar for both the compounds but the fingerprint region is totally different. Therefore fingerprint region could be crucial to identify the compound.

infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$



infra-red spectrum of propan-2-ol, $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$



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.

NIR shows some similarities to UV-visible spectrophotometry and some to mid-IR spectrometry. Indeed the spectrometers used in this region are often combined UV-visible-NIR ones.

NIR is generally used for quantitative organic functional-group analysis. The NIR region has also been used for qualitative analyses and studies of hydrogen bonding, solute-solvent interactions, organometallic compounds and inorganic compounds

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.

3. Origin of Infra-red Spectroscopy

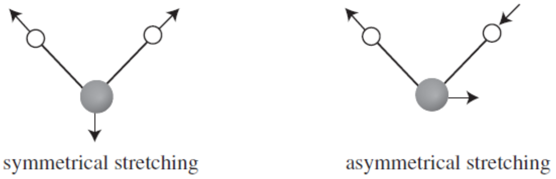
IR-spectroscopy gives the information about molecular vibrations or more precisely on transitions between vibrational and rotational energy levels. Since the absorption of infrared radiation leads to transition between vibrational and rotational energy levels, it is also vibrational-rotational spectroscopy.

When a molecule absorb IR-radiation below 100 cm^{-1}, transitions between rotational energy levels takes place. Since these energy levels are quantised, a rotational spectrum consists of discrete lines. If a molecule absorbs radiation in the range 100-10,000 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. Therefore the vibrational spectra appears vibrational-rotational bands instead of discrete lines. Organic chemists are mainly concerned with these transitions especially with those occur in the range 4000-667 cm^{-1}.

4. Molecular Vibrations

The atoms in a molecule do not remain fixed at certain positions. The two nuclei can vibrate backwards and forwards or towards and away from each other around an average position. There are two types of fundamental molecular vibrations *viz.*, stretching (change in bond length) and bending (change in bond angle).

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.



Stretching modes of H_2O

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.

i.) Rocking

ii.) Scissoring
iii.) Wagging
iv.) Twisting

scissoring, or bending in-plane   twisting, or bending out-of-plane   rocking, or bending in-plane   wagging, or bending out-of-pla

Bending vibrations of a CH_2 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.

5. 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.

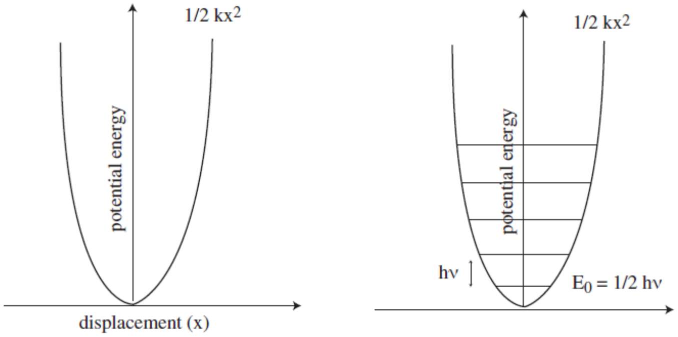
2) The vibrations which are not symmetrical about the centre of symmetry are IR-active.

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 trans molecule does not show this band.

6. Fundamental Vibrations

In the classical harmonic oscillator, $E = 1/2\boldsymbol{k}x^2 = h\nu$, 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.



Energy curve for a vibrating spring (left) and energy constrained to quantum mechanical model (right).

However, vibrational motion is *quantized*: it must follow the rules of quantum mechanics, and the only transitions which are allowed fit the following formula:

$$E = (n + 1/2)h\nu$$

where ν is the frequency of the vibration
n is the quantum number (0, 1, 2, 3, . . .)

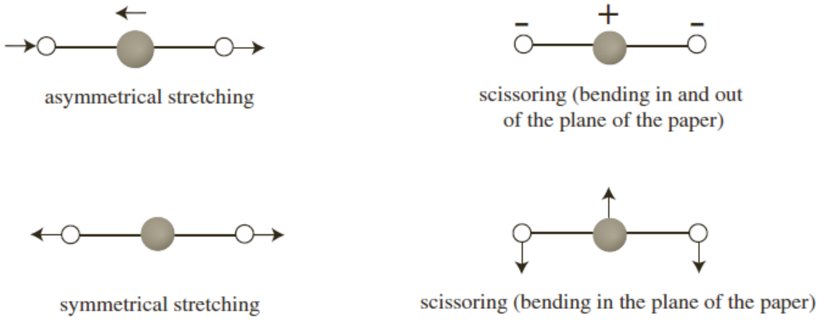
The lowest energy level is E_0 = 1/2 hν, the next highest is E_1 = 3/2 hν. According to the selection rule, only transitions to the next energy level are allowed; therefore molecules will absorb an amount of energy equal to 3/2 – 1/2 hν or hν. This rule is not inflexible, and occasionally transitions of 2 hν, 3 hν, 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 3*n* 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.

If the molecule is symmetrical such as hydrogen, nitrogen, and chlorine, the band is not observed in the IR spectrum. Asymmetrical diatomic molecules, e.g. CO and iodine chloride absorb in the IR spectrum.

It has been observed that in actual IR spectrum, the theoretical number of fundamental bands is seldom observed because there are certain factors which may increase or decrease the number of bands. Some fundamental vibrations lie outside the IR region (4000-400 cm^{-1}), whereas some are too weak to be observed. Few fundamental vibrations are too close that they merge into one another. The occurrence of degenerate bands (bands of same frequency) also cause decrease in the fundamental vibrational bands. This phenomena is called fermi resonance.

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}.



Streching and bending vibrational for CO_2

The appearance of certain types of non-fundamental (overtones, combinations of fundamental vibrations or difference of fundamental vibrations) bands increases the number of bands as compared to that expected from the theoretical number of fundamental bands. All these bands have very weak intensity than the fundamental vibration bands.

Overtones 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}.

A practical use for understanding overtones and combination bands is applied to organic solvents used in spectroscopy. Most organic liquids have strong overtone and combination bands in the mid-infrared region, therefore, acetone, DMSO, or acetonitrile should only be used in very narrow spectral regions. Solvents such at CCl_4, CS_2 and $CDCl_3$ can be used above 1200 cm^{-1}.

7. Summary

1. Absorption of electromagnetic radiation in infrared region can cause changes in the vibrational and rotational energy states.

2. A molecule consisting of n atoms has a total of 3n degrees of freedom.

3. The number of fundamental vibrational bands in a molecule is equal to the degree of freedom of a molecule however these numbers of bands is seldom obtained because of the occurrence of certain non-fundamental bands such as overtones, combinations of fundamental vibrations or difference of fundamental vibration bands.