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Subject: Engineering Chemistry

Unit: VI

Topic: Instrumental Techniques in  
Chemical Analysis

"WORKING TOWARDS BEING THE BEST"

## Unit 6 instrumental techniques in chemical Analysis

### Spectroscopy

#### Introduction

The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter. Visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength (Table 1).

**Table 1: The electromagnetic spectrum**

Radiation type	Wave length	Frequency	Applications
	$\lambda$ , (Å)	$\nu = c / \lambda$ , (Hz)	
radio	$10^{14}$	$3 \times 10^4$	
Nuclear magnetic resonance	$10^{12}$	$3 \times 10^6$	
Television	$10^{10}$	$3 \times 10^8$	Spin orientation
Radar	$10^8$	$3 \times 10^{10}$	
Microwave	$10^7$	$3 \times 10^{11}$	Rotational
Far infrared	$10^6$	$3 \times 10^{12}$	Vibrational
Near infrared	$10^4$	$3 \times 10^{14}$	
Visible	$8 \times 10^3$ - $4 \times 10^3$	$3.7 \times 10^{14}$ - $7.5 \times 10^{14}$	
Ultraviolet	$3 \times 10^3$	$1 \times 10^{15}$	Electronic
X-rays	1	$3 \times 10^{18}$	
Gamma rays	$10^{-2}$	$3 \times 10^{20}$	Nuclear transitions
Cosmic rays	$10^{-4}$	$3 \times 10^{22}$	

The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave traveling through space is represented by a sinusoidal trace (figure 1). In this diagram  $\lambda$  is the wavelength and distance A is known as the maximum amplitude of the wave. Although a wave is frequently characterized in terms of its wavelength  $\lambda$ , often the terms such as wavenumber ( $1/\lambda$ ), frequency ( $\nu$ ), cycles per second (cps) or hertz (Hz) are also used.

The unit commonly used to describe the wavelength is centimetres (cm), the different units are used to express the wavelengths in different parts of the electromagnetic spectrum. For example, in the ultraviolet and visible region, the units use are angstrom (Å) and nanometre (nm). In the infrared region, the commonly used unit is wavenumber ( $\bar{\nu}$ ), which gives the number of waves per centimetre.

$$\text{Wavelength } (\lambda) = 1 / \bar{\nu} = c / \nu$$

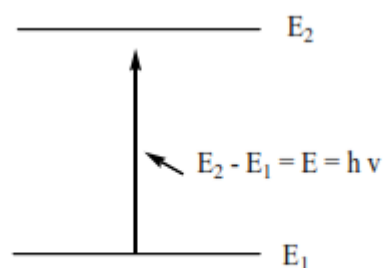
$$\text{Wave-number } (\bar{\nu}) = 1 / \lambda = \nu / c$$

$$\text{Frequency } (\nu) = c / \lambda = c \bar{\nu} \quad 1 \text{ cm} = 10^7 \text{ nm} = 10^8 \text{ \AA}$$

$$\text{Velocity } (c) = \nu \lambda = \nu / \bar{\nu} \quad 1 \text{ \AA} = 10^{-1} \text{ nm} = 10^{-8} \text{ cm}$$

### Absorption of Different Electromagnetic radiations by Organic Molecules

In absorption spectroscopy, though the mechanism of absorption of energy is different in the ultraviolet, infrared and nuclear magnetic resonance regions, the fundamental process is the absorption of a discrete amount of energy. The energy required for the transition from a state of lower energy ( $E_1$ ) to state of higher energy ( $E_2$ ) electromagnetic radiation that causes transition.



**Figure 2:** Energy transition for the absorption of any electromagnetic radiation

$$E = h\nu = hc / \lambda$$

Where  $E$  is energy of electromagnetic radiation being absorbed,  $h$  is the universal Planck's

$E_2 - E_1$  constant,  $6.624 \times 10^{-27}$  erg sec and  $\nu$  is the frequency of incident light in cycles per second (cps or hertz, Hz),  $c$  is velocity of light  $2.998 \times 10^{10}$  cm s<sup>-1</sup> and  $\lambda$  = wavelength (cm)

Therefore, higher is the frequency, higher would be the energy and longer is the wavelength, lower would be the energy. As we move from cosmic radiations to ultraviolet region to infrared region and then radio frequencies, we are gradually moving to regions of lower energies.

A molecule can only absorb a particular frequency, if there exists within the molecule energy transition of magnitude  $E = h\nu$

Although almost all parts of electromagnetic spectrum are used for understanding the matter, in organic chemistry we are mainly concerned with energy absorption from only ultraviolet and visible, infrared, microwave and radiofrequency regions.

**Ultraviolet – visible spectroscopy** ( $\lambda$  200 - 800 nm) studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from  $\pi$ - or non-bonding orbitals. It commonly provides the knowledge about  $\pi$ -electron systems, conjugated unsaturation's, aromatic compounds and conjugated non-bonding electron systems etc.

**Infrared spectroscopy** ( $\nu$  400-4000  $\text{cm}^{-1}$ ) studies the changes in the vibrational and rotation movements of the molecules. It is commonly used to show the presence or absence of functional groups which have specific vibration frequencies viz. C=O, NH, OH, CH, C-O etc.

**Nuclear magnetic resonance** (radiofrequency  $\nu$  60-600 MHz) provides the information about changes in magnetic properties of certain atomic nuclei.  $^1\text{H}$  and  $^{13}\text{C}$  are the most commonly studied nuclei for their different environments and provide different signals for magnetically non-equivalent nuclei of the same atom present in the same molecule.

## Ultraviolet and Visible Spectroscopy

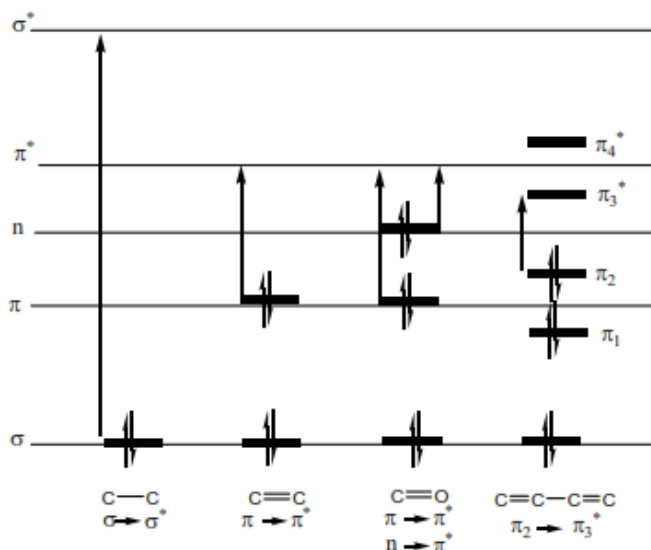
This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (VIS, 400-800 nm) regions. Since the absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule, it is also often called as electronic spectroscopy. The information provided by this spectroscopy when combined with the information provided by NMR and IR spectral data leads to valuable structural proposals.

### Nature of Electronic Transitions

The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding  $n$  or bonding  $\pi$  orbital) to an unoccupied molecular orbital (an antibonding  $\pi^*$  or  $\sigma^*$  orbital) of greater potential energy (figure 3). For most molecules, the lowest-energy occupied molecular orbitals are  $\sigma$  orbitals, which correspond to  $\sigma$  bonds. The  $\pi$  orbitals lie at relatively higher energy levels than  $\sigma$  orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies. The antibonding orbitals ( $\pi^*$  and  $\sigma^*$ ) are orbitals of highest energy. The relative potential energies of these orbitals and various possible transitions have been depicted in figure 3.

The saturated aliphatic hydrocarbons (alkanes) exhibit only  $\sigma \rightarrow \sigma^*$  transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies.

.Since all these transitions require fixed amount of energy (quantized), an ultraviolet or visible spectrum of a compound would consist of one or more well defined peaks, each corresponding to the transfer of an electron from one electronic level to another. If the differences between electronic energy levels of two electronic states are well defined i.e. if the nuclei of the two atoms of a diatomic molecule are held in fixed position, the peaks accordingly should be sharp. However, vibrations and rotations of nuclei occur constantly and as a result each electronic state in a molecule is associated with a large



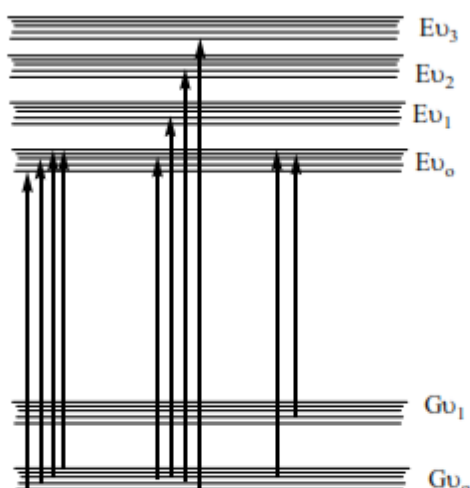
**Figure 3 :** Relative energies of orbitals most commonly involved in electronic spectroscopy of organic mole

The transition of an electron from one energy level to another is thus accompanied by simultaneous change in vibrational and rotational states and causes transitions between various vibrational and rotational levels of lower and higher energy electronic states. Therefore many radiations of closely placed frequencies are absorbed and a broad absorption band is obtained. When a molecule absorbs ultraviolet or visible light of a defined energy, an assumption is made that only one electron is excited from bonding orbital or non-bonding orbital to an anti-bonding orbital and all other electrons remain unaffected.

The excited state thus produced is formed in a very short time i.e. of the order of  $10^{-15}$  seconds. In accordance with Franck-Condon principle, during electronic excitation the atoms of the molecule do not move.

The most probable transition would appear to involve the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), but in many cases several transitions can be observed, giving several absorption bands in the spectrum. We can have a general view of the possible transitions prevailing in

compounds.



**Figure 4 :** Energy level diagram showing excitation between different vibrational and rotational levels of two electronic states

## Types of transitions

1.  **$\sigma - \sigma^*$  transition;** Alkanes can only undergo  $\sigma - \sigma^*$  transitions. These are high-energy transitions and involve very short wavelength ultraviolet light ( $< 150$  nm). These transitions usually fall out-side the generally available measurable range of UV-visible spectrophotometers (200-1000 nm). The  $\sigma - \sigma^*$  transitions of methane and ethane are at 122 and 135 nm, respectively. In alkenes amongst the available  $\sigma - \sigma^*$  and  $\pi - \pi^*$  transitions, the  $\pi - \pi^*$  transitions are of lowest energy and absorb radiations between 170-190 nm.

2.  **$n - \pi^*$  transition;** In saturated aliphatic ketones the lowest energy transition involves the transfer of one electron of the nonbonding electrons of oxygen to the relatively low-lying  $\pi^*$  anti-bonding orbital. This  $n - \pi^*$  transition is of lowest energy ( $\sim 280$  nm) but is of low intensity as it is symmetry forbidden. Two other available transitions are  $n - \pi^*$  and  $\pi - \pi^*$ . The most intense band for these compounds is always due to  $\pi - \pi^*$  transition.

3. **In conjugated dienes the  $\pi - \pi^*$**  orbitals of the two alkene groups combine to form new orbitals – two bonding orbitals named as  $\pi_1$  and  $\pi_2$  and two antibonding orbitals named as  $\pi_3^*$  and  $\pi_4^*$ . It is apparent that a new  $\pi - \pi^*$  transition of low energy is available as a result of conjugation. Conjugated dienes as a result absorb at relatively longer wavelength than do isolated alkenes.

## Some important terms and definitions

(I) **CHROMOPHORE:** The energy of radiation being absorbed during excitation of electrons from ground state to excited state primarily depends on the nuclei that hold the electrons together in a bond. The group of atoms containing electrons responsible for the absorption is called chromophore. Most of the simple un-conjugated chromophores give rise to high energy transitions of little use. Some of these transitions have been listed in [table](#)

**Table 3: Absorption maxima of simple un-conjugated chromophores**

Chromophore	Transition	$\epsilon_{\max}$	$\lambda_{\max}$ (nm)
<i><math>\sigma</math> – bonded electrons</i>			
(C-C, C-H etc.)	$\sigma \rightarrow \sigma^*$		~ 150
<i>Lone pair electrons</i>			
-O-, -N-, -S-	$n \rightarrow \sigma^*$	100-1000	~ 190
C=O, C=N	$n \rightarrow \pi^*$	15	~300
	$\pi \rightarrow \pi^*$	500	~190
R-C $\equiv$ N	$n \rightarrow \pi^*$	5	~ 170
R-COOH, RCONH <sub>2</sub> , RCOOR	$n \rightarrow \pi^*$	50	~ 210

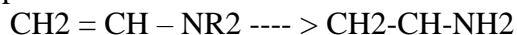
### Identification of chromophores:

There is no set rule for the identification of a chromophore. The change in position as well as the intensity of the absorption depends upon a large number of factors. Following points may be useful.

1. Spectrum having a band near 300 m $\mu$  may possess two or three conjugated units.
2. Absorption bands near 270-350 m $\mu$  with very low intensity  $\epsilon_{\max}$  10-100 are because of n- $\pi^*$  transitions of carbonyl group.
3. Simple conjugated chromophores like dienes or  $\alpha \beta$  –unsaturated ketones have  $\epsilon_{\max}$  values, i.e., from 10,000 to 20,000.
4. The absorption with  $\epsilon_{\max}$  value between 1,000-10,000 reveals the presence of an aromatic system. If aromatic nucleus is substituted with groups which can extend the chromophore, the absorption takes place at still higher value of extinction coefficients.

**AUXOCHROMES:** It is a group which itself does not act as a chromophore but when attached to a chromophore, it shifts the adsorption towards longer wavelength along with an increase in the intensity of absorption. Some commonly known auxochromic groups are: -OH, -NH<sub>2</sub>, -OR, -NHR, and -NR<sub>2</sub>. For example: When the auxochrome -NH<sub>2</sub> group is attached to benzene ring. Its absorption change from  $\lambda_{\max}$  225 ( $\epsilon_{\max}$  203) to  $\lambda_{\max}$  280 ( $\epsilon_{\max}$  1430)

All auxochromes have one or more non-bonding pairs of electrons. If an auxochrome is attached to a chromophore, it helps in extending the conjugation by sharing of non-bonding pair of electrons as shown below.



The extended conjugation has been responsible for bathochromic effect of auxochromes.

### Instrumentation:

**Source:** hydrogen discharge lamp is the source for UV rays and tungsten lamp for visible range.

**Monochromator:** it is for selection of a particular wave length for study transition.

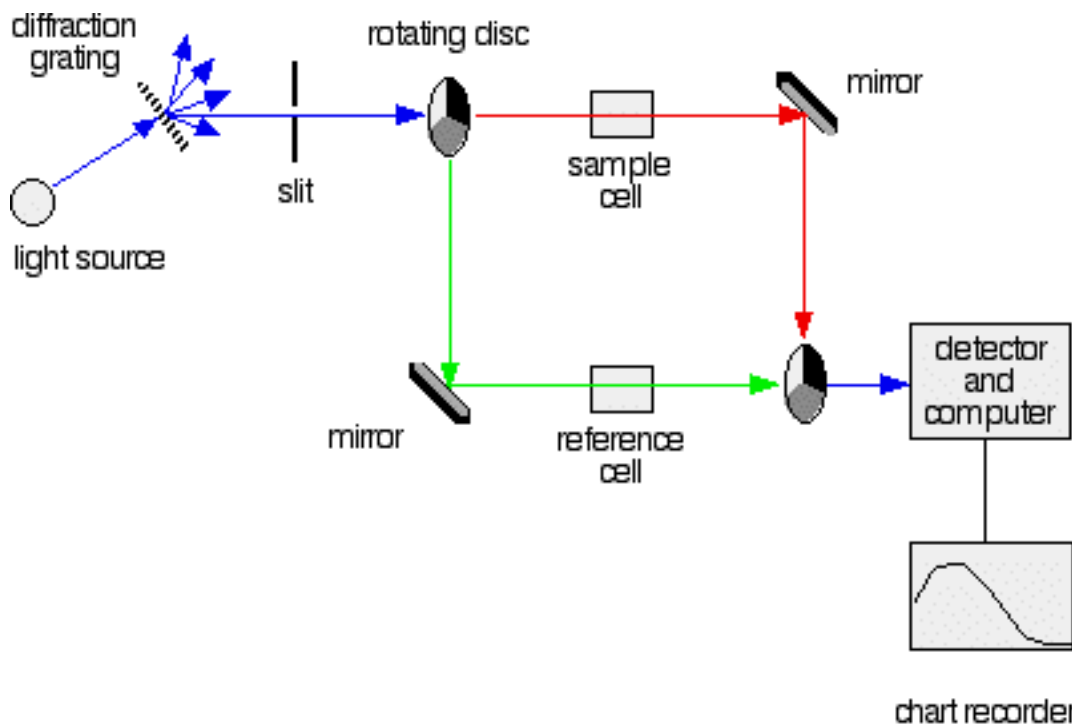
**Cuvette:** silica and quartz sample cells are used as they do not absorb in UV-Visible region.

**Amplifier :** for amplification of signals.

**Detector-** photomultiplier tube, photo cells, are used as detector.

Recording is done on computer in the form of a graph plotted between wavelength as abscissa and optical density on as ordinate.





The unknown compound is first dissolved in to suitable solvent like ethanol or ether. The sample call is exposed to UV radiation of appropriate wave length. The detector will measure optical density of solution . Then optical density is measured at different wavelengths. Graph is plotted between optical density and wavelength having peaks then it is compared with reference for its identification.

### Application of UV spetrscopy:

#### 1. Detection of Impurities

UV absorption spectroscopy is one of the best methods for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material. By also measuring the absorbance at specific wavelength, the impurities can be detected. Benzene appears as a common impurity in cyclohexane. Its presence can be easily detected by its absorption at 255 nm.

#### 2. Structure elucidation of organic compounds.

UV spectroscopy is useful in the structure elucidation of organic molecules, the presence or absence of unsaturation, the presence of hetero atoms. From the location of peaks and combination of peaks, it can be concluded that whether the compound is saturated or unsaturated, hetero atoms are present or not etc.

#### 3. Quantitative analysis

UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation. This determination is based on Beer's law which is as follows.

$$A = \log I_0 / I_t = \log 1 / T = - \log T = abc = \epsilon bc$$

Where  $\epsilon$  is extinction co-efficient, c is concentration, and b is the length of the cell that is used in UV spectrophotometer.



Other methods for quantitative analysis are as follows.

- a. calibration curve method
- b. simultaneous multicomponent method
- c. difference spectrophotometric method
- d. derivative spectrophotometric method

#### 4. Qualitative analysis

UV absorption spectroscopy can characterize those types of compounds which absorb UV radiation. Identification is done by comparing the absorption spectrum with the spectra of known compounds. UV absorption spectroscopy is generally used for characterizing aromatic compounds and aromatic olefins.

#### 5. Chemical kinetics

Kinetics of reaction can also be studied using UV spectroscopy.

## Infrared Absorption Spectroscopy

The two atoms joined together by a chemical bond (may be single, double or triple bond), macroscopically can be composed as two balls joined by a spring. The application of a force like

1. **Stretching** of one or both the balls (atoms) away from each other or closer to each other.
2. **Bending** of one of the atoms either vertically or horizontally and then release of the force results in the vibrations on the two balls (atoms). These vibrations depend on the strength of the spring and also the mode (stretching or bending) in which the force is being applied.

Similarly, at ordinary temperatures, organic molecules are in a constant state of vibrations, each bond having its characteristic stretching and bending frequencies. When infrared light radiations between 4000-400 cm<sup>-1</sup> (the region most concerned to an organic chemist) are passed through a sample of an organic compound, some of these radiations are absorbed by the sample and are converted into energy of molecular vibrations. The other radiations which do not interact with the sample are transmitted through the sample without being absorbed. The plot of % transmittance against frequency is called the infrared spectrum of the sample or compound.

This study of vibrations of bonds between different atoms and varied multiplicities which depending on the electronegativity, masses of the atom and their geometry vibrate at different but specified frequencies; is called infrared spectroscopy. The presence of such characteristic vibrational bands in an infrared spectrum indicates the presence of these bonds in the sample under investigation.

### Hooke's law and Absorption of radiations

The band positions in the IR spectrum are presented in wave numbers ( $\nu$ ) whose unit is the reciprocal centimetre (cm<sup>-1</sup>). Wave no. is proportional to the energy of vibration.

$$\Delta E = h\nu = hc / \lambda = hc\nu$$

Therefore, **in principle, absorption of radiation in the infrared region is quantized and should appear as sharp line.** However, each vibrational transition within the molecule is associated with number of rotational energy changes and thus appears as combination of Vibrational-rotational bands. The analogy of a chemical bond with two atoms linked through a spring can be used to rationalize several features of the infrared spectroscopy.

The approximation to vibration frequency of a bond can be made by the application of Hooke's law. In Hooke's law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring and frequency of vibration is stated as

Therefore, **the vibrational frequency of a bond would increase with the increase in bond strength.** Consequently, we can expect that C=C and C=O stretching will have higher frequencies than C-C and C-O stretching, respectively.

Therefore, **the vibrational frequency of a bond would increase with the decrease in reduced mass** of the system. It implies that C-H and O-H stretching absorptions should appear at higher frequencies than C-C and C-O stretching frequencies.

Similarly, O-H stretching should appear at higher frequency than O-D stretching. Further, in parallel with the general knowledge that the stretching of the spring requires more energy than to bend it, the stretching absorption of a band always appear at higher energy than the bending absorption of the same band..

$$\bar{\nu} \propto \sqrt{\frac{\text{bond strength}}{\text{mass}}}$$

$$\text{then } \bar{\nu} = \frac{1}{2\pi c} \sqrt{\left( \frac{K}{(m_1 m_2) / (m_1 + m_2)} \right)} \quad \text{eq. 1}$$

Where  $\bar{\nu}$  = the vibrational frequency ( $\text{cm}^{-1}$ )  
 $c$  = velocity of light ( $\text{cm/s}$ )  
 $K$  = force constant of the bond ( $\text{dyne/cm}$ )  
 $m_1$  and  $m_2$  = masses of the two atoms

The quantity  $(m_1 m_2) / (m_1 + m_2)$  is often expressed as  $\mu$ , the reduced mass of the system.

$$\therefore \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad \text{eq. 2}$$

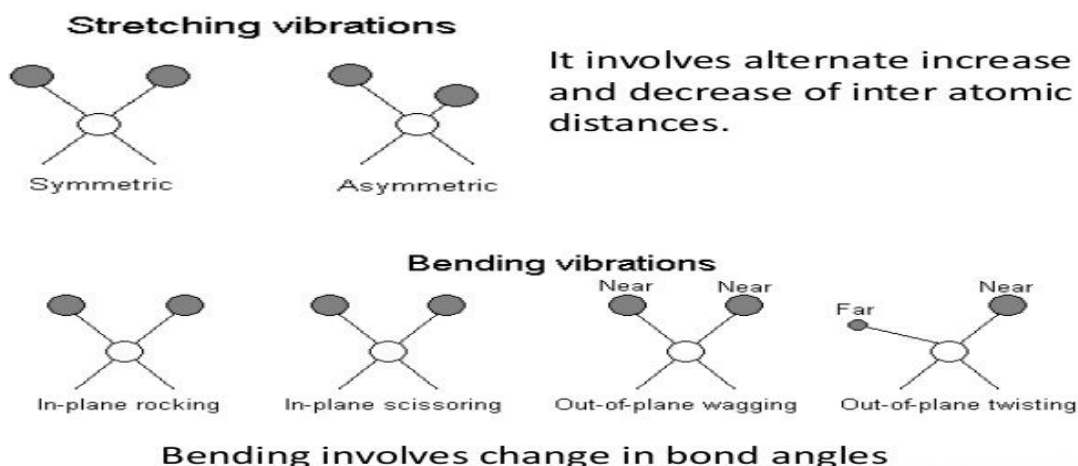
Since, according to equation 2

$$\bar{\nu} \propto \sqrt{K}$$

Types of vibrations:

1. stretching – change in bond length occurs.
  - a. Symmetric b. Asymmetric

2. bending- change in bond angle occurs.
  - a. Rocking b. scissoring c. twisting d. wagging



### Sample Preparation

For recording an IR spectrum, the sample may be gas, a liquid, a solid or a solution of any of these. The samples should be perfectly free of moisture, since cell materials (NaCl, KBr, CsBr etc.) are usually spoiled by the moisture.

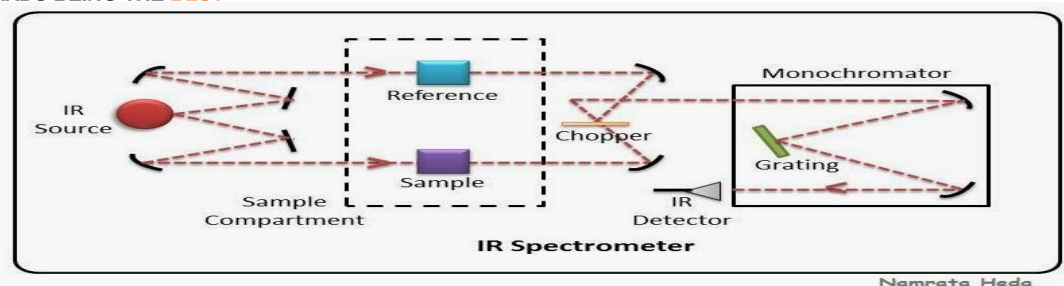
Liquids are studied neat or in solution. In case of neat liquid, a thin film of < 0.01 mm thickness is obtained by pressing the liquid between two sodium chloride plates and plates are subjected to IR beam. Spectra of solutions are obtained by taking 1-10 % solution of the sample in an appropriate solvent in cells of 0.1-1 mm thickness. A compensating cell, containing pure solvent is placed in the reference beam of the instrument.

The choice of solvent depends on the solubility of the sample and its own minimal absorption in IR region. Carbon tetrachloride, chloroform and carbon disulfide are preferred solvents.

The spectrum of a solid can be obtained either as a mull or as an alkali halide pellet. Mulls are obtained by thoroughly grinding 2-5 mg of a solid sample with a drop of mulling agent usually Nujol (mixture of paraffinic hydrocarbons) or fluorolube (a completely fluorinated polymer). The suspended particles must be less than 2  $\mu\text{M}$  to avoid excessive scattering of radiations. The mull is placed between two sodium chloride plates and plates are subjected to IR beam.

For preparing, an alkali halide pellet, 1-2 mg of dry sample is ground with ~ 100 mg of KBr powder. The mixture is then pressed into a transparent pellet with a special die under a pressure of 10,000-15,000 psi. KBr pellet is then mounted on holder and is placed in sample beam of IR spectrophotometer.

### Instrumentation:



**Source:** globar filamentis made of silicon carbide, nerst filament made of zirconium and thorium oxide.

**Cuvette:** cesium bromide, potassium bromide cuvette does not absorb in IR region..

**Detector-**The device that measures radiant energy by means of its heating effect is known as detector. The bolometer changes its resistance on heating, while in thermocouple emf produced between two junctions is proportional to the degree of heating.

**Monochromator-** grating or prism is used to obtain light of different wavelength for study different samples.

**Recorder-**spectrum of given compound between transmittance and frequency and is obtained on computer.

### Applications IR:

1. Identification of functional groups in organic molecules.
2. Identification of type of bonding between molecules.
3. Detection of impurity in a sample.
4. Identification of unknown compound.
5. Identification of type of substitution present in aromatic compounds.

### Rotational Spectroscopy

Introduction Free atoms do not rotate or vibrate. For an oscillatory or a rotational motion of a pendulum, one end has to be tied or fixed to some point. In molecules such a fixed point is the centre of mass. The atoms in a molecule are held together by chemical bonds. The rotational and vibrational energies are usually much smaller than the energies required to break chemical bonds. The rotational energies correspond to the microwave region of electromagnetic radiation ( $3 \times 10^{10}$  to  $3 \times 10^{12}$  Hz; energy range around 10 to 100 J/mol) and the vibrational energies are in the infrared region ( $3 \times 10^{12}$  to  $3 \times 10^{14}$  Hz; energy range around 10 kJ/mol) of the electromagnetic radiation. For rigid rotors (no vibration during rotation) and harmonic oscillators (wherein there are equal displacements of atoms on either side of the center of mass) there are simple formulae characterizing the molecular energy levels. In real life, molecules rotate and vibrate simultaneously and high speed rotations affect vibrations and vice versa. However, in our introductory view of spectroscopy we will simplify the picture as much as possible. We will first take up rotational spectroscopy of diatomic molecules.

### Rotational Spectra of diatomic

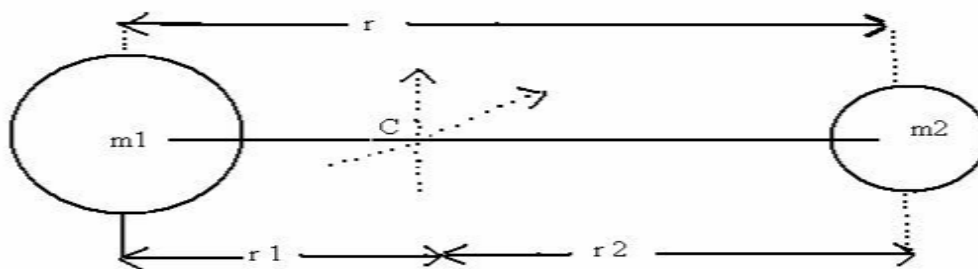


Fig. A rigid diatomic with masses  $m_1$  and  $m_2$  joined by a thin rod of length  $r = r_1 + r_2$ . The centre of mass is at C.

The two independent rotations of this molecule are with respect to the two axes which pass through C and are perpendicular to the "bond length"  $r$ . The rotation with respect to the bond axis is possible only for "classical" objects with large masses. For quantum objects, a "rotation" with respect to the molecular axis does not correspond to any change in the molecule as the new configuration is indistinguishable from the old one.

The center of mass is defined by equating the moments on both segments of the molecular axis.

$$m_1 r_1 = m_2 r_2$$

The moment of inertia is defined by

$$\begin{aligned}
 I &= m_1 r_1^2 + m_2 r_2^2 \\
 &= m_2 r_2 r_1 + m_1 r_1 r_2 \\
 &= r_1 r_2 (m_1 + m_2)
 \end{aligned}$$

Since  $m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$ ,  $(m_1 + m_2) r_1 = m_2 r$  Therefore,

$$r_1 = \frac{m_2 r}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r}{m_1 + m_2}$$

Substituting the above equation in (13.3), we get

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)} = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Where  $\mu$ , the reduced mass is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The rotation of a diatomic is equivalent to a "rotation" of a mass  $\mu$  at a distance of  $r$  from the origin C. The kinetic energy of this rotational motion is  $K.E. = L^2/2I$  where  $L$  is the angular momentum,  $I\omega$  where  $\omega$  is the angular (rotational) velocity in radians/sec. The

operator for  $L^2$  is the same as the operator  $L^2$  for the angular momentum of hydrogen atom and the solutions of the operator equations  $L^2 Y_{lm} = l(l+1) Y_{lm}$ , where  $Y_{lm}$  are the spherical harmonics. The quantized rotational energy levels for this diatomic are

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

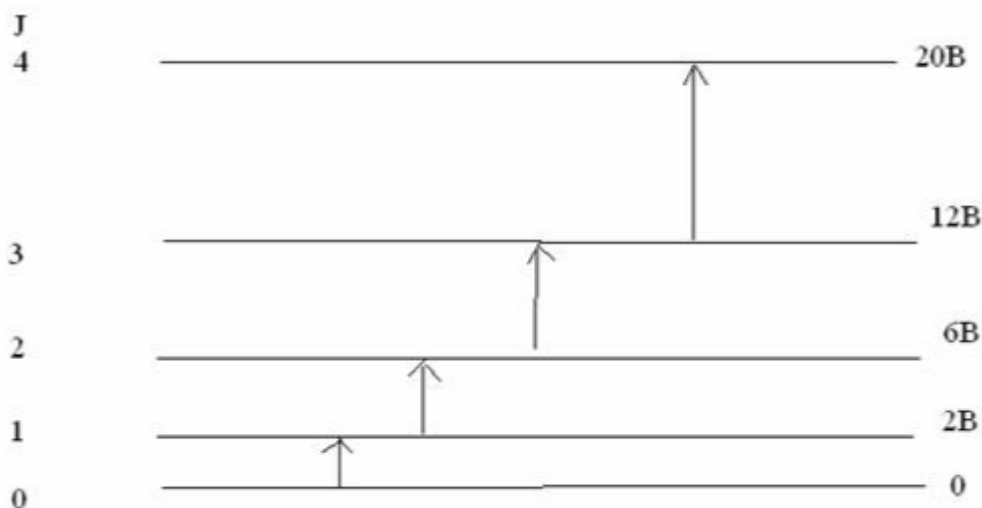
The energy differences between two rotational levels is usually expressed in  $\text{cm}^{-1}$ . The wave number corresponding to a given  $\Delta E$  is given by

$$\nu = \Delta E / hc, \text{ cm}^{-1}$$

The energy levels in  $\text{cm}^{-1}$  are therefore,

$$E_J = B J(J+1) \text{ where } B = \frac{h}{8\pi^2 I c}$$

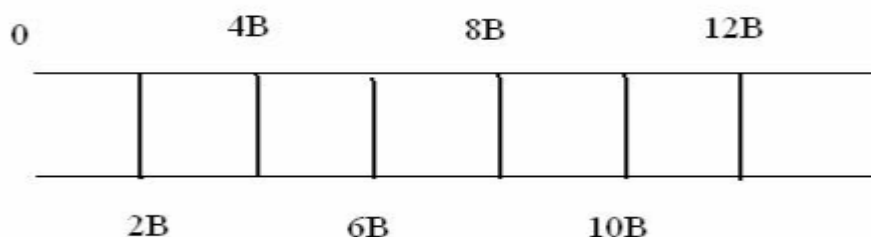
The rotational energy levels of a diatomic molecule are shown in Fig.



**Rotational energy levels of a rigid diatomic molecule and the allowed transitions.**

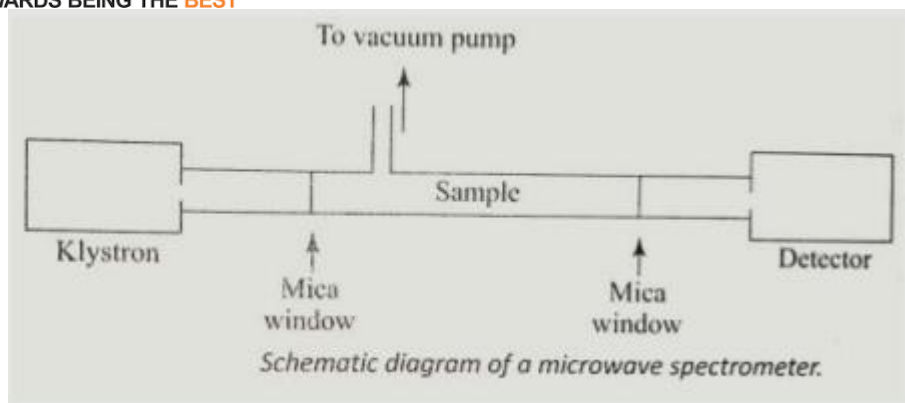
The selection rule for a rotational transition is,  
 $\Delta J = \pm 1$

In addition to this requirement, the molecule has to possess a dipole moment. As a dipolar molecule rotates, the rotating dipole constitutes the transition dipole operator  $\mu$ . Molecules such as HCl and CO will show rotational spectra while  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{CO}_2$  will not. The rotational spectrum will appear as follows



**Instrumentation:**





**Source:** klystron is a monochromatic source emits microwaves over a narrow frequency range (30cm-8mm).

**Beam guides:** achieved by using rectangular waveguides present inside which radiation is confined.

**Wave meters:** measures wavelength or frequency.

**Vacuum:** prevent atmospheric water to enter.

**Sample:** liquid as well as solid can be studied..

**Detector:** detector can be a radio receiver or crystal detector.

**Output:** spectra in the form of signals in which absorption is plotted against frequency.

### Beer-Lambert Law Statement

The Beer-Lambert law states that: for a given material sample path length and concentration of the sample are directly proportional to the absorbance of the light.

The Beer-Lambert law is expressed as:

$$A = \epsilon Lc$$

where,

A is the amount of light absorbed for a particular wavelength by the sample

$\epsilon$  is the molar extinction coefficient

L is the distance covered by the light through the solution

c is the concentration of the absorbing species

Following is an equation to solve for molar extinction coefficient:

$$\epsilon = ALc$$

But Beer-Lambert law is a combination of two different laws: Beer's law and Lambert law.

#### Beer's Law

Beer's law was stated by August Beer which states that concentration and absorbance are directly proportional to each other.

#### Lambert Law

Lambert law was stated by Johann Heinrich Lambert which states that absorbance and path length are directly proportional.

#### Beer-Lambert Law Formula

$$I = I_0 e^{-\mu(x)}$$

Where,

I is the intensity



$I_0$  is the initial intensity  
 $x$  is the depth in meters  
 $\mu$  is the coefficient of absorption

Absorption of energy causes the absorption of light as well usually by electrons. Different forms of light such as visible light and ultraviolet light get absorbed in this process. Therefore, change in the intensity of light due to absorption, interference, and scattering leads to:

$$\Delta I = I_0 - I_T$$

The following equations are necessary for us to obtain our ultimate derivative equation. Transmittance is measured as the ratio of light passing through a substance. It can be calculated as  $I_T/I_0$ . To calculate the of transmittance percentage we can do so by:

$$\%T = \frac{100I_T}{I_0}$$

Percent Transmittance is absorbance that is defined as the amount of light absorbed. This is usually calculated as the negative of transmittance and is given by:

$$A = \log_{10} \frac{I_0}{I_T} = \log_{10} \left( \frac{1}{T} \right) = -\log T = 2 - \log(\%T)$$

Absorbance (A) The rate of decrease in the intensity of light with the thickness of the material the light is directly proportional to the intensity of the incident light. Mathematically, it can be expressed as:

$$-\frac{dI}{db} \propto I \text{ or } -\frac{dI}{db} = k' I$$

As  $k'$  = Proportionality constant

Taking in the reciprocal of the equation we get,

$$-\frac{db}{dI} = \frac{1}{k'I}$$

Integrating the above equation we also

$$-b = \frac{1}{k'} \ln I_T + C$$

In the above equation,  $b$  and  $C$  is the constant of integration and  $I_T$  is the intensity being transmitted at the thickness

In order to solve the above equation with the constant of integration, we then get,

$$C = -\frac{1}{k'} \ln I_0$$

While solving for  $C$  in the equation will give us,

$$-b = \frac{1}{k'} \ln I_T - \frac{1}{k'} \ln I_0$$

$$\ln \frac{I_0}{I_T} = k'b$$

Converting to log<sub>10</sub> we get,

$$\log \frac{I_0}{I_T} = \frac{k'b}{2.303}$$

Rearranging the equation we get,

$$A = \frac{k'b}{2.303}$$

Thus, Lambert's law was formed and it states that the monochromatic radiation changes exponentially and decreases when it passes through a medium of uniform thickness.

### Limitations of the Beer-Lambert law

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at **high concentrations (>0.01M)** due to electrostatic interactions between molecules in close proximity
- **scattering of light due to particulates** in the sample
- **fluorescence or phosphorescence** of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light

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