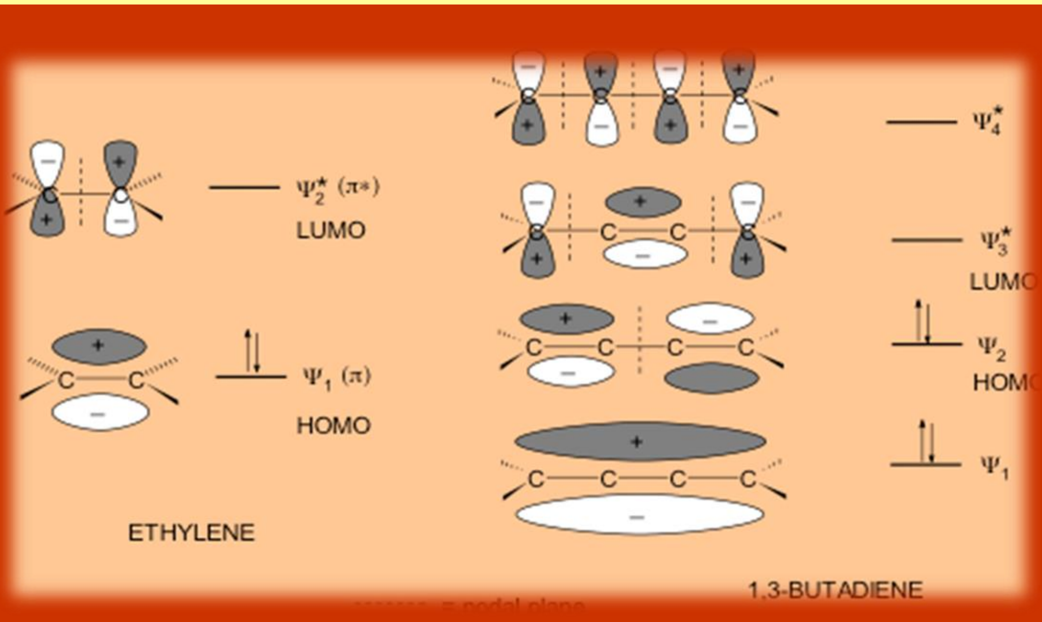
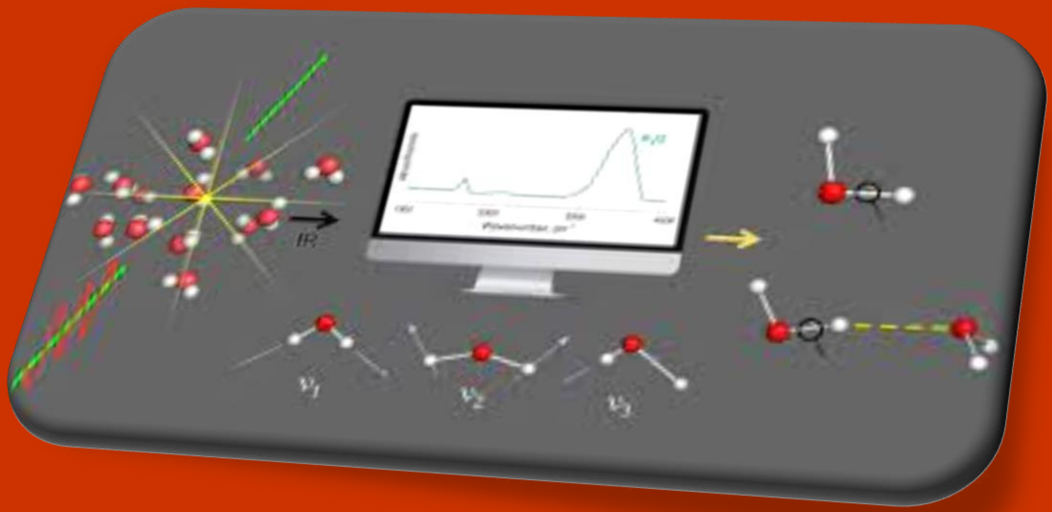
MSCCH-509

M.Sc. II Semester

SPECTROSCOPY-I





SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

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BLOCK-3 MOLECULAR SPECTROSCOPY-II

UNIT 1: FUNDAMENTALS OF SPECTROSCOPY

CONTENTS:

1.1 INTRODUCTION

The energy which is transmitted in the form of radiations from one body to another is known as radiant energy. This radiant energy possesses fields, electric as well as magnetic field. When light (radiation) falls on a molecule (matter), there is transition between the energy levels within the molecule that results from the interaction with the photon of radiation. Photons are the packets of energy in case of light/radiation. Let us consider a molecule having two energy levels, say E_1 and E_2. If a photon (radiation) of a particular frequency say ν falls on a molecule which is in the ground state having energy E_1, then by absorption of photon having energy ($E=h\nu$) there is transition from the energy level E_1 (ground state) to energy level E_2 (excited state) within the molecule. This will happen only when the energy difference ($\Delta E = E_2 - E_1$) between the molecular energy level is exactly equal to the energy of photon (hν) as shown in fig. 1.1.

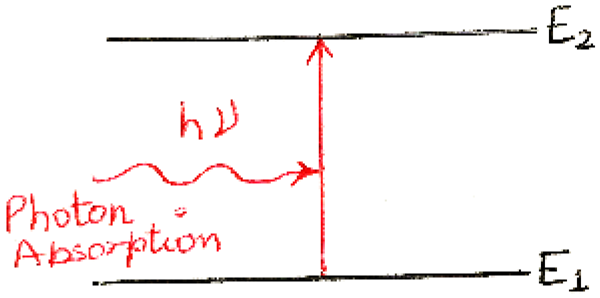

Fig. 1.1. Transition between energy levels on absorption of photon

This interaction between photons of radiations and moleculewhich results in the transition within the molecule give rise to one of the important branch of science which is known by the name spectroscopy. By this branch of science, we can gain knowledge about atomic and molecular structure along with measurement of energy difference between different energy level within the molecule. The present unit deals with the fundamentals of spectroscopy which includes recap of quantum mechanics, characteristics of electromagnetic radiations or spectrum. Here we will discuss the basic elements of spectroscopy which includes knowledge of types of spectroscopy, spectrum and its types. Along with this, we will discuss some basic principles (Heisenberg's uncertainty principle), Lambert- Beer's Law, coefficient (Einstein coefficients, integrated absorption coefficients). The idea of transition dipole moments with selection rules are also taken into consideration in order to make the unit more clear and easy to understand.

1.2 OBJECTIVES

After going through the unit thoroughly, you be able to

- Define the term Spectroscopy.
- Describe the types of Spectroscopy.
- Gain knowledge about the basic elements of Spectroscopy.
- Explain Heisenberg's uncertainty principle.
- Explain electromagnetic radiations along with electromagnetic spectrum.
- State Lambert-Beer's law.
- Gain knowledge about the selection rules that are involved in transitions.
- Explain the term line width and transition dipole moment

1.3 RECAPITULATION AND ROLE OF QUANTUM MECHANICS

Quantum mechanics is also knowns as wave mechanics. One of the important features of quantum mechanics is quantization of angular momentum and energy. The classical mechanics which deals with macroscopic particles like rigid bodies differ from quantum mechanics which deals with microscopic particles like electron, proton, atoms and molecules. According to quantum mechanics, "All microscopic particles possess both wave nature as well as particle nature (de Broglie concept)". The famous personalities like W. Heisenberg (Heisenberg uncertainty principle), E. Schrodinger (Schrodinger wave equation) played an important role in the field of quantum mechanics. In quantum mechanics there are limits on the value of a physical quantity that how accurately it can be predicted prior to its measurement. It allows the calculation of properties and behavior of physical systems. We discuss about wave function (ψ) which represents amplitude and square of ψrepresents the probability of finding an electron.According to S. Hawking "Quantum mechanics allows us principle to predict nearly everything around us within the limits set up by the uncertainty principle". Finally in order to understand the electronic structure of chemical compounds along with thermodynamics, mechanism and the kinetics of chemical reactions at the theoretical level, the concept of quantum mechanics is considered.

1.4 ELECTROMAGNETIC RADIATIONS: CHARACTERIZATION

The radiant energy present in space travels with the speed of light i.e. 3×10^8 ms^{-1} having oscillating electric and magnetic fields perpendicular to each other refers to electromagnetic radiations. Electromagnetic radiations are defined as simple harmonicwave that are propagated from the source and travels in straight line when not reflected or refracted. Electromagnetic radiation possesses dual nature (both particle nature as well as wave nature). Considering the wave nature of radiation, Maxwell in 1864 found that the oscillating charge produces oscillating electric field along with oscillating magnetic field which propagate as wave with two field perpendicular to one another. If E represents the electric field and M represents the magnetic field, the electromagnetic wave is represented as shown in fig. 1.2.

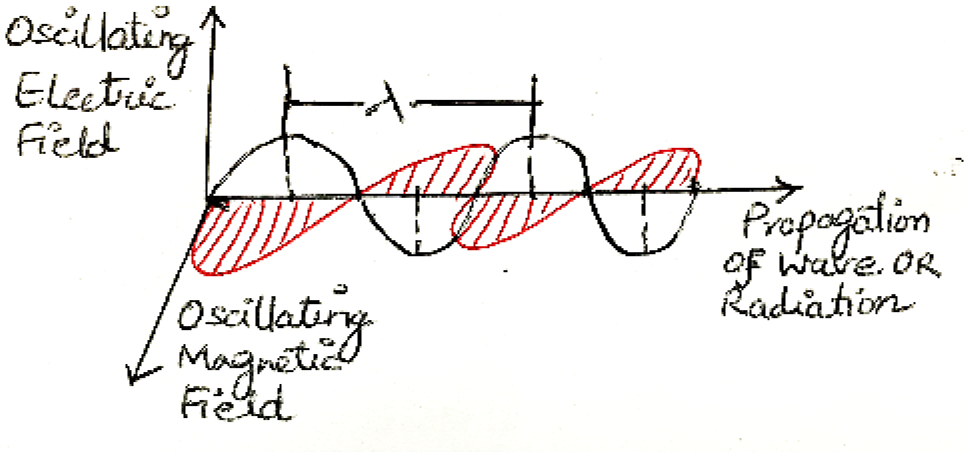

Fig.1.2. Electromagnetic wave

As no medium is involved considering wave nature of electromagnetic radiations thus these radiations can travel in vacuum. A particular wave is characterized by certain properties or parameters which are wavelength, frequency, wave number and velocity. Let's discuss one by one below:

- **Wavelength**: It is defined as the distance between two successive peaks or between two crests or two toughs. It is represented λ as shown in Figure 2. There are different unis by which we can express wavelength like Angstrom ($1A^0 = 10^{-10}m = 10^{-8}$ cm), nanometer ($1nm = 10^{-9}m = 10^{-7}cm$), micron ($1\mu = 10^{-6}$ m), meter (m), millimeter ($1mm = 10^{-3}m$).

- **Frequency**: The number of waves (wavelength) passing through a given point per second is known as frequency. It is represented by ν.

$$\text{Frequency } (\nu) = \text{Speed of light (c)/wavelength } (\lambda) = c/\lambda$$

The unit of frequency is cycles per second (1 cycle per second = 1 Hertz). Other units are megahertz (1 MHz = 10^6 Hz).By knowing the frequency of a particular radiation (visible light), we can determine its color. For example, 7.89×10^{14} Hz frequency corresponds to violet color.

- **Wave Number**: It is defined as a number of waves in a length of 1 cm. It is represented by $\bar{\nu}$ and is inverse of wavelength.The unit is cm^{-1}, which is known as Kaysers (K). $1\text{cm}^{-1} = 1\text{K}$

$$\bar{\nu} = 1/\lambda$$

- **Velocity**: Distance traveled by a wave in one second is called velocity of the wave. It is represented by v. As electromagnetic radiation possesses velocityequal to velocity of light, thus the velocity is represented by c($3 \times 10^8 \text{ms}^{-1}$). All electromagnetic radiations possess same velocity i.e. c but differ from each other in the value of wavelength.

Along with these parameters, phenomenon like reflection, refraction, interference show wave properties of a radiation. According to quantum theory of electromagnetic radiations, radiations consist of packets of energy known as photons. The energy of photon (quantum of energy) is directly proportional to the frequency of radiation.

$$E \propto \nu; \quad E = h\nu$$

Where h = Planck's constant = 6.626×10^{-34}Js

$$E = h\nu = hc/\lambda = hc\bar{\nu}$$

It is clear from above expression that radiations with high frequency have high energy and radiations with low frequency have low energy. Same is the case with wave number as like frequency; wave number is also directly proportional to the energy. On the other hand, radiations with high wavelength possess low energy and radiations with low wavelength possess high energy as both are inversely proportional. Electromagnetic radiations consist of both high frequency waves and low frequency waves which include cosmic rays, gamma rays, x-rays, ultra- violet rays, visible rays, infrared rays, microwaves and radiowaves.

1.4.1 Electromagnetic spectrum

When through a prism, a beam of light is passed, there is a dispersion of light into seven colors from red to violet and the set of colors is known as spectrum. Electromagnetic spectrum consists of different types of electromagnetic radiations that are arranged in order of their decreasing frequencies or increasing wavelengths. The frequencies of the radiations ranges from 10^7 to 10^{21} Hz and the wavelengths of these radiations ranges from $3x10^{-4}$ nm to $3x10^{10}$ nm in the spectrum which is given in table 1.1.

Table 1.1. Electromagnetic spectrum

Radiations	Cosmic Rays	Gamma Rays	X-Rays	Ultra-violet Rays	Visible	Infrared	Microwave	Radio wave
Frequency (Hz)	10^{21}	10^{19}	10^{17}	10^{15}	10^{13}	10^{11}	10^{9}	10^{7}
Wavelength (nm)	$3x10^{-4}$	$3x10^{-2}$	3	$3x10^{2}$	$3x10^{4}$	$3x10^{6}$	$3x10^{8}$	$3x10^{10}$

It is clear from Table 1 that cosmic rays possess highest frequency and lowest wavelength while the radio waves possess lowest frequency and highest wavelength. As frequency is directly proportional to energy thus in the spectrum, cosmic rays have highest energy while radio waves have lowest energy. Thus the order of electromagnetic radiations on the basis of decreasing frequencies or decreasing energies is: Cosmic rays> Gamma rays> X- rays> Ultra-violet rays> Visible rays> Infrared rays> Microwave > Radio waves. The order of electromagnetic radiations on the basis of increasing wavelength is: Cosmic rays < Gamma rays < X- rays< Ultra-violet rays< Visible rays< Infrared rays< Microwave < Radio waves.Corresponding to each electromagnetic radiations, there are different types of region in the spectrum. These are X- rays spectral region, ultra-violet region which is classified into near ultra-violet region and far ultra-violet region, visible region, infrared region which is classified into near infrared, mid infrared and far infrared region, microwave region and radio wave region.

1.4.2 Interaction of electromagnetic radiations with matter: Spectroscopy

When an electromagnetic radiation interacts with matter, both radiations and the matter undergo a change. These are as follows:

- By the process of reflection and refraction, the direction of incident beam of electromagnetic radiation can be changed.
- By the process of diffraction, double refraction and scattering, the beam of incident light can be transformed into other beam.
- Two types of scattering may occurs Rayleigh scattering (frequency of scattered radiationis same asthe frequency of incident radiation) or Raman scattering (frequency of scattered radiation and incident radiation is different either low or high).
- The intensity of the incident electromagnetic radiation when passed through the substance get lowered, this shows absorption of electromagnetic radiations.
- The absorption of electromagnetic radiations by atoms or molecules leads to excitation (rotational, vibrational and electronic) which is for short duration of about 10^{-8} second.

This interaction between electromagnetic radiation and matter give rise to the branch of branch of science known as spectroscopy. Thus spectroscopy is defined as the branch of science that deals with the interaction of electromagnetic radiation with matter.

By using the concept of spectroscopy, one can determine the atomic and molecular structures along with the analysis of different samples. Spectrophotometersare the instruments that are used to measure the relative energy that is emitted, transmitted or reflected. For recording the spectra automatically, special devices are connected to spectrophotometers, the block diagram of which is shown in fig.1.3. A continuous graph obtained by plotting absorbance or transmittance of electromagnetic radiations verses wavelength or wave number over a particular range refers to the spectrum of a molecule.

Fig. 1.3. Block Diagram of Spectrophotometer

There are two types of spectroscopy, atomic spectroscopy and molecular spectroscopy.

- **Atomic spectroscopy**: This spectroscopy deals with the interaction of electromagnetic radiations with atoms.

- **Molecular spectroscopy**: This spectroscopy deals with the interaction of electromagnetic radiations with molecules. This interaction results in transition between rotational, vibrational and electronic energy levels. Molecular spectra are more complicate than atomic spectra. When a molecule absorbs or emit a photon, following changes may occur:

  1) There may be change in rotational quantum number which gives rise to rotational spectra. This takes place in far infrared region and microwave regions of electromagnetic spectra.

  2) There may be change in vibrational quantum number along with the change in rotational quantum number which gives rise to other spectra known as vibrational-rotational spectra. This spectrum occurs in near infrared region of electromagnetic spectra.

  3) There may be change in electronic energy level which is accompanied by change in vibrational and rotational energy levels which give rise to electronic spectra. This spectra occurs in visible and ultra-violet regions of electromagnetic spectra.

  4) There may be change in the direction of nuclear spin quantum number in the presence of magnetic field, this give rise to type of molecular spectra known as nuclear magnetic resonance (NMR).

  5) There may be change in the direction of the resultant spin in the presence of a magnetic field, this give to electron spin resonance (ESR) type of molecular spectra. This type of spectra occur in microwave region of electromagnetic spectra.

  6) There may occur nuclear transition which gives rise to spectra known as Mossbauer spectra which occur in gamma rays region of electromagnetic spectra.

It is clear from above discussion that a molecule possesses translational energy (E_{trans}), rotational energy (E_{rot}), vibrational energy (E_{vib}), electronic energy (E_{el}), spin energy (E_{spin}) and nuclear energy ($E_{nuclear}$). Thus the total energy (E_{total}) is given by:

$$E_{total} = E_{trans} + E_{rot} + E_{vib} + E_{el} + E_{spin} + E_{nuclear}$$

All these energies are quantized except translational energy. Due to large difference in mass between electron and nucleus, it is permissible as approximation to consider the respective motion as mechanically separable. This approximation is known as Born-Oppenheimer approximation. According to Born-Oppenheimer approximation: $E_{total} = E_{rot} + E_{vib} + E_{el}$ .This expression do not contain translational energy because it is negligibly small.

1.5 LINE WIDTH

The width and intensity are the two factors which are considered in the analysis of spectrum of a molecule. For a particular transition, there is change in quantum number which are governed by certain rules known as selection rules. These rules have been obtained by using quantum theory of interaction of electromagnetic radiations with matter. The selection rule for a pure rotational transition is $\Delta J = \pm 1$, where J is the rotational quantum number. The selection rule for a pure vibrational transition is $\Delta v = \pm 1$, where v is the vibrational quantum number. On the basis of selection rules, transitions are classified as allowed or forbidden. Those transitions which obey selection rules are allowed transitions and are very intense while those transitions which do not obey selection rules are forbidden transitions and are very weak or less intense. In absorption or emission spectra, it has been observed that there are broad peaks in spite of sharp lines which may be due to mechanical slits in spectrophotometers which are not narrow resulting in blurred spectra. The resolving power of an instrument can be improved by doing improvement in the design of spectrophotometer but in any atomic and molecular transitions, there is a minimum width inherent beyond which no instrument can show sharp lines. This minimum width inherited is known as natural line width. For an atomic absorption line, the natural line width is of the order of 10^{-5} nm. In solution, the atomic absorption peaks are more intense or sharp than molecular absorption peaks. The effect namely collision broadening and Doppler broadening determines the natural line width. Collision broadening as the name predicts involves collision among the atoms causing small change in the energy levels of the ground state leading to broadening of the peaks or spectral lines in the spectrum. This effect is more pronounced in liquids than in gases. Doppler broadening on the other hand also causes broadening of peak that arises due to rapid motion of the absorber with respect to the source for those atoms that travels towards or away from the source. On the basis of direction of motion of a molecule relative to the instrument, the frequency becomes either lower or higher than the observed radiation frequency. This is known as Doppler broadening. This effect often determines the natural line width in gases. This is all about line width.

1.5.1 Heisenberg's Uncertainty Principle

Heisenberg's Uncertainty Principle is also known as indeterminacy principle or simply uncertainty principle. According to this principle "it is impossible to measure simultaneously the position and the velocity of a subatomic particle with absolute precession or accuracy". The more accurately we have known the value of one, the less accurately we know the value of other. It means that more accurately the position is measured, less accurately the velocity is measured. Mathematically,

$$\Delta x . \Delta p \geq h/4\pi$$

Where Δx is uncertainty in position, Δp is uncertainty in momentum, h is Planck's constant, π is 22/7. As Δp is equal to m x Δv, where Δv is uncertainty in velocity, then the above expression becomes:

$$\Delta x .m\Delta v \geq h/4\pi$$

This expression in the form of uncertainty in energy (ΔE) and uncertainty in life time of the energy level (Δt) is written as:

$$\Delta E. \Delta t \geq h/4\pi$$

Thus according to this principle, if a system exists in an energy state for a particular time Δt, then the energy of that particular state will be uncertain to an extent ΔE. Thus we can say that Heisenberg's uncertainty principle determines the lifetime broadening or the natural line width of a peak or spectral line. The ground state of a system is sharply defined as the system remains in the ground state for an infinite time. As for excited electronic state, the life time is about 10^{-8} sec.Therefore from Heisenberg's uncertainty principle:

$$\Delta E. \Delta t \geq h/4\pi \approx 10^{-34} Js$$

$$\text{As } \Delta t = 10^{-8} \text{ sec}; \Delta E = 10^{-34} / \Delta t = 10^{-34} / 10^{-8} \approx 10^{-26} \text{ J}$$

This shows that transition between the given excited state and the ground state possess an energy uncertainty ΔE having value 10^{-26} J. This ΔE is associated with natural line width (Δν) by relation: $\Delta E = h\,\Delta\nu$

From Heisenberg's uncertainty principle: $\Delta E.\ \Delta t \geq h/4\pi$

$$h\,\Delta\nu.\ \Delta t \geq h/4\pi$$

$$\Delta\nu \geq 1/4\pi\Delta t$$

This shows that for such transition from lowest energy state to excited state having life time of 10^{-8} sec, the uncertainty (Δν) is very small in comparison to the usual radiation frequency. It is concluded that line width of electronic transitions depends less on ΔE (uncertainty in energy) than on collision and Doppler broadening.

1.6 BASIC ELEMENTS OF SPECROSCOPY AND ITS ADVANTAGES

As discussed above under section 1.4.2, spectroscopy deals with the interaction and interpretation of electromagnetic radiations which are absorbed, scattered or emitted by atoms or molecules. Simply we can say that first of all there is interaction between electromagnetic radiations and matter then there is transition among different energy levels (vibrational, rotational, electronic etc) and finally absorption or emission bands are produced as a result of transition. The branch of science i.e. spectroscopy involves such techniques that are rapid and thus takes place quickly. The information given by spectrophotometer is recorded in the form of a permanent chart automatically. The spectroscopic techniques require very small amount of sample say milligram or micrograms to be tested or examined. These methods are more selective and sensitive in the analysis of highly complex mixtures and even detect trace amounts of impurities. The information provided by spectroscopy is reliable and more precise in determining the structural information of atoms or molecules.

1.7 EINSTEIN COEFFICIENTS

According to Albert Einstein, "In the formation of an atomic spectral line, three process takes place". These three processes are spontaneous emission, stimulated emission and absorption. Einstein coefficient is a measure of the probability of a particular process that occur, thus there are three Einstein coefficients. These coefficients explain the absorption or emission of photons via electronic transitions in atoms. Corresponding to each process, three coefficients are as follows:

- **Coefficient of spontaneous emission**: The coefficient corresponding to the process of spontaneous emission is known as coefficient of spontaneous emission. It is represented by A_{21}. It is defined as the probability per unit time for an atom that an atom in energy level 2 will spontaneously emit a photon and undergo a transition from energy level 2 (higher energy level) to energy level 1 (lower energy level). The unit of this coefficient is time^{-1} or second^{-1}. The process of spontaneous emission is shown in fig. 1.4.

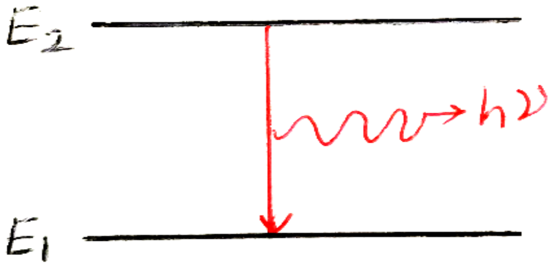

Fig. 1.4. Process of Spontaneous Emission

- **Coefficient of absorption:** The coefficient corresponding to the process of absorption is known as coefficient of absorption. It is represented by B_{12}. It is defined as the probability per unit time per unit mean intensity at frequency (ν_0) that an atom in energy level 1 (lower energy level) will absorb a photon of frequency $\nu_0$and get excited to energy level 2 (higher energy level). Its unit is sec^{-1}erg^{-1}cm^{2}sterad and the process of absorption is shown in fig. 1.5.

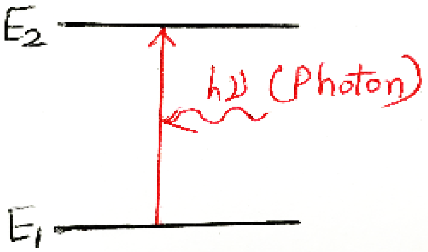

Fig. 1.5. Process of Absorption

- **Coefficient of stimulated emission:** The coefficient corresponding to the process of stimulated emission is known as coefficient of stimulated emission. It is represented by B_{21}. Here, the incoming photon cause a transition to energy level 1 from energy level 2 along with the emission of two photons. Its unit is $sec^{-1}erg^{-1}cm^2$sterad and the process is shown in fig.1.6.

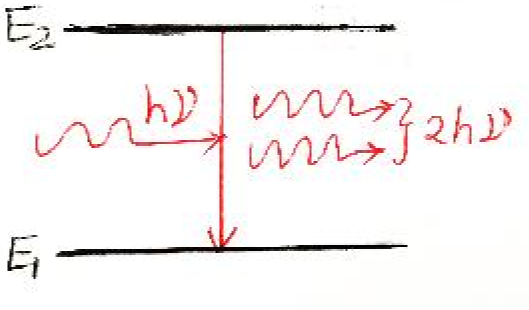

Fig. 1.6. Process of Stimulated Emission

Thus we can say that an Einstein coefficient explains the rate of transition that results from the interaction of electromagnetic radiation with different energy levels of the atoms.

1.8 LAMBET-BEER'S LAW: INTEGRATED ABSORPTION COEFFICIENTS

Photochemistry is defined as a branch of chemistry that deals with the process that involves absorption or emission of radiations. There are two fundamental laws of absorption namely Lambert's law and Beer's law.

- **Lambert's law:** This law was formulated by Johann Heinrich Lambert and according to this law "When a monochromatic light (light of single wavelength) is passed through a pure homogeneous medium, the decrease in the intensity of light with the thickness of the absorbing medium at any point is proportional to the intensity of the incident light". Mathematically the laws says:
  $-dI/dx \propto I$

Where I is intensity of incident radiation or light before entering the medium of small thickness dx,$-dI/dx$ is decrease in the intensity of light on passing through small thickness dx.

$-dI/dx = k\,I$ (k = constant of proportionality = absorption coefficient)

This coefficient depends upon the nature of the absorbing medium. Now in order to obtain integrated absorption coefficient, we have to integrate the above equation:

$$-dI/dx = k\,I$$

$$dI/I = -\,k\,dx$$

$$\text{when } x = 0,\ I = I_0$$

$$\int_{I_0}^{I} \frac{dI}{I} = \int_{x=0}^{x=x} -\,k dx$$

$$\ln I/I_0 = -\,kx$$

$$2.303 \log I/I_0 = -\,kx$$

$$\log I/I_0 = -\,kx / 2.303$$

$$\log I/I_0 = -\,k^1 x \quad (k^1 = k/ 2.303)$$

The above equation is integrated form of Lambert's law where $k^1$is integrated absorption coefficient or extinction coefficient of the substance or absorptivity of the substance.

- **Beer's law**: This law was formulated by August Beer and according to this law of absorption "When a monochromatic light is passed through a solution, there is decrease in the intensity of light with the thickness of the solution is directly proportional to the intensity of incident radiation or light along with the concentration of the solution". Mathematically the laws says:
  $-dI/dx \propto I\,c$

Where c is the concentration of solution, $-dI/dx$ is decrease in the intensity of light on passing through solution of thickness dx.

$-dI/dx = \varepsilon\, I\, c$ (ε = constant of proportionality = molar absorption coefficient)

The value of molar absorption coefficient depends on the nature of the absorbing medium along with the wavelength of light used. Now in order to obtain integrated absorption coefficient, we have to integrate the above equation:

$$-dI/dx = \varepsilon\ I\ c$$

$$dI/I = -\varepsilon\ c\ dx$$

$$\text{when } x = 0,\ I = I_0$$

$$\int_{I_0}^{I} \frac{dI}{I} = \int_{x=0}^{x=x} -\varepsilon\ c\ dx$$

$$\ln I/I_0 = -\ \varepsilon\ c\ x$$

$$2.303 \log I/I_0 = -\ \varepsilon\ c\ x$$

$$\log I/I_0 = -\ \varepsilon\ c\ x\ /\ 2.303$$

$$\log I/I_0 = -\varepsilon^1\ c\ x\ \ (\varepsilon^1 = \varepsilon\ /2.303)$$

The above equation is integrated form of Beer's law where $\varepsilon^1$is integrated absorption coefficient or molar extinction coefficient of the absorbing solution or molar absorptivity of the absorbing solution.

- **Lambert- Beer's law**: Lambert- Beer's law is also known as Beer- Lambert-Bouguer law or simply Beer's law. According to this law "For a given material, the thickness and concentration of the absorbing medium (solids) are directly proportional to the absorbance of the light". Mathematically:
  Absorbance $\propto$c x
  Absorbance (A) = ε^1 c x

  A = log I_0/I = ε^1 c x

Where c is concentration of the absorbing medium, x is the thickness, ε^1 is extinction coefficient of the absorbing medium and is defined as the log of the ratio of intensity of incident light to the transmitted light. According to Lambert- Beer's law, the absorbance is directly proportional to the concentration of the absorbing medium (solution). This shows that a plot between absorbance and concentration must be straight line but it was observed that there are positive and negative deviations in the plot that corresponds to concave upward and concave downward curve respectively (fig. 1.7).

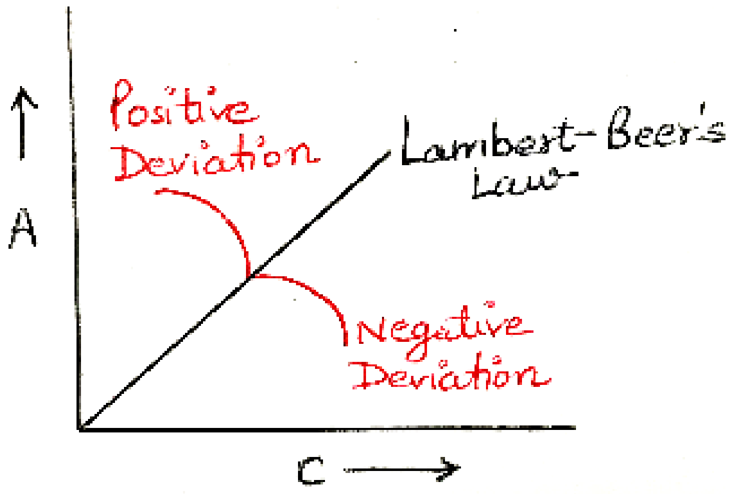

Fig. 1.7. Deviation from Lambert-Beer's Law

These deviations occur due to polymerization of species present in the solution, by not using monochromatic light, presence of impurities in the absorbing medium etc.

1.8.1 Applications

Beer's law finds several applications in the field of physical chemistry. By using Beer's law, the absorbance of the species present in the solution can be determined. Along with this by using this law, we can also determine the concentration of unknown sample by comparing it with a solution of known concentrated solution by using spectrophotometer.By recording the variation of absorbance with the change of wavelength of incident radiation, one can obtain the absorption spectrum of the compound.

1.8.2 Limitations

Along with several important applications, there are some limitations of the law. Firstly, this law is valid or applicable for solutions only. Secondly, this law works only when monochromatic light is used. Thirdly, when the intensity of incident radiation is very high then Beer-Lambert's law fails. Fourthly, when the concentration of the absorbing solution is high say greater than 0.01M, this law fails. This shows that Beer's law is a limiting law that is valid only when the concentration of the solution (absorbing medium) is low.

1.9 OSCILLATOR STRENGTHS

It is clear form above discussion that when electromagnetic radiations falls on an atom or molecule, they absorb or emit radiation that results in the transition from one energy level to another energy level. Oscillator strength shows the probability of absorption or emission of electromagnetic radiation in transition between the different energy levels of an atom or molecule. It has been found that large is the oscillator strength, bright is the transition. It is defined as the ratio of transition rate (Quantum mechanics) to the absorption or emission rate (classical mechanics) of a single electron oscillator having same frequency as that of the transition. Oscillator strength is represented by f and its magnitude for an electronic transition is directly proportional to the square of transition dipole moment $\{f \propto (e\ r)^2\}$. Here (e r) is transition dipole moment, where e is the electronic charge and r is the extent of charge displaced. In order to compare the strengths of transition between different types of quantum mechanical systems, the concept of oscillator strength is used. By using the concept of oscillator strength, one can calculate the dipole moment matrix elements, transition probabilities, validity of theoretical models and concentration of impurities.

1.10 TRANSITION DIPOLE MOMENT

Dipole moment arises due to the difference in the electronegativity between two chemically bonded atoms that leads to separation of charges that are equal in magnitude and opposite to each other. It is represented by μ and is a vector quantity i.e. it possess both magnitude and direction. For example, HCl is a dipole and possess dipole moment. Thus dipole moment is defined as the product of magnitude of charge (equal and opposite) and distance between the charges. Now let us talk about transition dipole, as the name indicates transition, when an electron undergoes transition from lower energy level to higher energy level, transition dipole results. As the distribution of charge in ground or lowest energy level is different from the distribution of charge in higher energy level, this difference in charge between two energy levels leads to the transition dipole like dipole moment. Transition dipole moment is also known as transition moment. Transition dipole moment is also given by the product of charge and the distance between the charges. Its unit is Coulomb- meter. The transition dipole moment is a vector quantity.

The direction and the square of magnitude of transition dipole moment measures the polarization of the transition which determine how the system interacts with an electromagnetic radiation of a particular given polarization and measures the strength of the interactions (transition intensity) due to the distribution of charge within the system respectively. When a beam of electromagnetic radiation is allowed to fall on an atom or molecule, there is transition between different energy levels under the influence of perturbing field of the incident radiation. If N_{12}represents the number of atoms passing from energy level 1 to energy level 2 by absorbing hν quantum of energy, then:

$$\text{Number of atoms passing from energy level 1 to energy level 2} = P_{12} N_1\rho (\nu_{12})$$

Where P_{12} is transition probability for absorption. The transition probability (probability of a system to change from one energy level to another energy level) depends on transition dipole moment. When the transition takes place from lower electronic state ψ_1 to higher electronic state ψ_2, the transition dipole moment is given by μ which is given by $[\mu] = \int \psi 2\mu \psi 1 \, d\tau$.Thus the rate of transition depends on transition dipole moment as well as on the electron density of the radiation. Transition dipole moment determines the intensity of an absorption band in electronic spectroscopy. More is the value of transition dipole moment, large will be the intensity of a band. One of the important applications of transition dipole moment is to determine whether the transition that takes place between energy levels are allowed or not. From the above discussion:

$$[\mu] = \int \psi 2\mu \psi 1 \, d\tau$$

If $[\mu] = 0$, transition is forbidden or not allowed

If $[\mu] \neq 0$, transition is allowed

1.11 SELECTION RULE BASED ON SYMMETRY IDEA

There are certain rules which decide whether the transition among different energy levels is allowed or not. These rules are known as selection rules. According to selection rule, transition between energy levels can occur only when one level has an odd quantum number and other level has an even quantum number. As we have to discuss the selection rule based on symmetry idea, therefore according to this rule,” Only those transitions between energy level take place that have different symmetry”. It means that one state or energy level possess symmetric wave function while the other state possess antisymmetric wave function. The transition between states both having symmetric wave function are forbidden. Likewise, the transition between states both having antisymmetric wave function are forbidden which is shown in fig. 1.8.

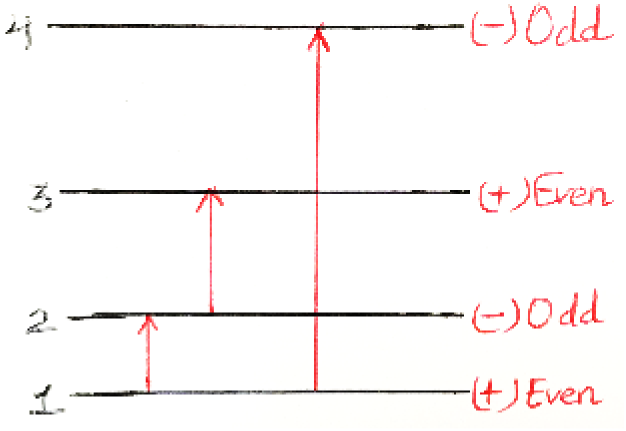

Fig.1.8. Symmetry Allowed Transitions

If (+) represents a state with symmetric wave function and (–) represents a state with antisymmetric wave function, then according to selection rule:

(+) ⟷ (–): Allowed transition

(+) ⟷ (+): Not allowed transition

(–) ⟷ (–): Not allowed transition

1.12 SELF-ASSESSMENT QUESTIONS (SAQ's)

Fill in the blanks:

1. Einstein coefficient of absorption and spontaneous emission is represented by ………. and ………. respectively.

2. Einstein coefficient explains the absorption and emission of ………. via ………. transitions in atoms.

3. According to Heisenberg's uncertainty principle, the ………. and ………. of a subatomic particle cannot be simultaneously measured with absolute accuracy.

4. According to Born-Oppenheimer approximation E_{total} =……….

5. Of all the energy possessed by a molecule, the ………. energy is negligibly small.

6. The spectroscopy helps in determining the information of atoms or molecules regarding the …

7. According to symmetry selection rule, only those transitions takes place for which one state has ………. wave function while the other state has ………. wave function.

8. If the integral value of transition dipole moment is equal to zero, then the transition is ……….

9. If the integral value of transition dipole moment is not equal to zero, then the transition is ……

10. The transition dipole moment is a ………. quantity.

11. The intensity of transition is measured by ………. of magnitude of transition dipole moment.

12. The large oscillator strength indicates ………. of the transition.

13. For both Lambert's law and Beer's law, ……. light is used.

14. According to Lambert- Beer's law, the absorbance is ……… proportional to the concentration of the absorbing medium.

15. Mathematically, Heisenberg's uncertainty principle is ……….

16. The natural line width refers to ………. of lines or peaks in the spectra.

17. The selection rule for pure rotational transition is ……….

18. The spectroscopy deals with the interactions of ………. with ……….

19. One of the important features of quantum mechanics is …of angular momentum and energy.

20. All electromagnetic radiations possess ………. velocity which is equal to velocity of ………

21. All electromagnetic radiations possess both ………. nature and ………. nature.

22. Each wave is associated with a particular ………., ………., and ……….

23. The arrangement of electromagnetic radiations in order of their ………. frequencies or ………. wavelength is known as ……….

24. In the electromagnetic spectrum, the cosmic rays possess ………. frequency and radio waves possess ………. frequency.

25. Only those transitions between energy level takes place that have different ……….

1.13 SUMMARY

In this unit we have discussed about the concept of spectroscopy with brief outline of the quantum mechanics. The characteristics of electromagnetic radiations were discussed with reference to wavelength, frequency, wave number and velocity. In addition to this, the fundamental laws of absorption were taken into account that includes Lambert's law and Beer's law. In order to compare the strengths of transitions between different types of quantum mechanical system, the concept of oscillator strength was discussed. In order to gain knowledge about the intensity of a band or peak in the spectra, the concept of transition dipole moment has been considered. The various selection rules that govern the transition between different states were discussed on the basis of transition dipole moment, quantum number and symmetry. Through spectroscopy, one can determine the information about atomic and molecular structure.

1.14 GLOSSARY

- **Spectroscopy:** Interaction between electromagnetic radiations and matter.
- **Monochromatic Light:** Light of single wavelength.
- **Spectrophotometer:** Instrument used to measure the relative energy that is emitted, transmitted or reflected.
- **Atomic Spectroscopy:** Interaction of electromagnetic radiations with atoms.
- **Molecular Spectroscopy:** Interaction of electromagnetic radiations with molecules.
- **NMR:** Nuclear magnetic resonance.
- **Electromagnetic Radiations:** Waves of high and low frequency having oscillating electric and magnetic field perpendicular to each other.
- **Electromagnetic Spectrum:** Arrangement of electromagnetic radiations in order of their decreasing frequencies.
- **Born-Oppenheimer Approximation:** $E_{total} = E_{rot} + E_{vib} + E_{el}$
- **Heisenberg's Uncertainty Principle:** Impossible to determine simultaneously the position and velocity of subatomic particles.
- **Einstein Coefficient:** Explain absorption and emission of photons via electronic transition in atoms.

- **Oscillator Strength:** Measures the probability of absorption or emission of electromagnetic radiations in transition.

1.15 POSSIBLE ANSWERS TO SAQ's

Fill in the blanks (Answer):

1. B_{12} and A_{21}; **2.** Photons, Electronic; **3.** Position, Velocity; **4.** $E_{rot} + E_{vib} + E_{el}$; **5.** Transitional; **6.** Structure; **7.** Symmetric' Antisymmetric; **8.** Forbidden; **9.** Allowed; **10.** Quantity; **11.** Square; **12.** Brightness; **13.** Monochromatic; **14.** Directly; **15.** $\Delta x . \Delta p \geq h/4\pi$; **16.** Broadening; **17.** $\Delta J = \pm 1$; **18.** Electromagnetic radiations, Matter; **19.** Quantization; **20.** Same, Light; **21.** Wave, Particle; **22.** Wavelength, Frequency, Wave number, Velocity; **23.** Decreasing; Increasing; Electromagnetic spectrum; **24.** Highest, Lowest; **25.** Symmetry

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1.17 TERMINAL QUESTIONS

1. Define electromagnetic spectrum and explain the characteristics of electromagnetic radiations.

2. Explain spectroscopy along with the fundamental laws of absorption.

3. Give selection rules based on symmetry ideas.

4. Explain Einstein coefficient.

UNIT 2: ATOMIC SPECTROSCOPY, XPS AND UPS

CONTENTS:

2.1 INTRODUCTION

Spectroscopy deals with the study of transition in a matter which results from the interaction of electromagnetic radiation (photons) with matter or chemical species like atom, molecule, ions etc. Due to this interaction, there is an absorption or emission of energy by the matter. In order to determine the atomic or molecular structures, various techniques in the field of spectroscopy are used to measure the energy difference between different energy levels. The atomic spectroscopy deals with the interaction of atom with the electromagnetic radiations that result in the transition of electron between energy levels in an atom. The electromagnetic radiations cause excitation of electrons which depends on the energy possessed by the photon or radiation. Electromagnetic radiations that possess low energy tend to excite the valence electron first. Photon with high energy results in the excitation of electrons to higher energy levels. We know that in the excited state electron is unstable therefore it tends to return in its ground state by emitting the energy. If the amount of energy absorbed can be measured in terms of the frequency and intensity of the electromagnetic radiation, the spectroscopy is known as atomic adsorption spectroscopy as there is absorption of radiations. If the amount of energy emitted by the excited electrons on returning to its ground state can be measured, the spectroscopy is known as atomic emission spectroscopy. Let us consider the structure of an atom which is given in fig. 2.1.

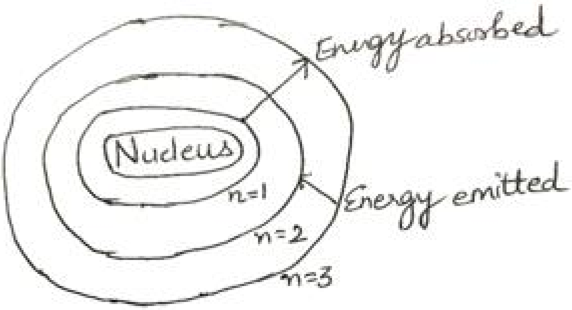

Fig. 2.1. Structure of an atom

It is to be noted that the energy gap for both the process i.e. absorption and emission is exactly the same. The sequence of energy levels with increasing energies is n =1< n =2 < n =3 <n =4 and so on. This atomic spectroscopy is useful in quantitative analysis of elements generally metals. The present unit deals with atomic spectroscopy which include the study of atomic states, term

symbols, microstates, spin factoring methods. Here we will focus on spin angular momentum, orbital angular momentum, total angular quantum number and their coupling. Further in this unit, we will discuss about different rules like Hund's rule, spin and orbital selection rule which decides the transition between different atomic energy levels. In order to have a clear understanding of the unit, we will study the spectra of a complex atom including Zeeman effect and Stark effect. In addition to this, a basic idea of atomic photoelectron spectroscopy will be provided that includes X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). As atomic spectroscopy is useful in qualitative analysis of elements, thus efforts are made to write the unit in a proper and interesting way.

2.2 OBJECTIVES

After going through the unit, you will be able to:

- Define atomic spectroscopy.
- Understand atomic absorption and atomic emission spectroscopy.
- Explain atomic states and terms symbols.
- Determine the microstate.
- Explain the coupling of spin angular momentum, coupling of orbital angular momentum, coupling of spin and orbital angular momentum.
- Explain the selection rules involved during the transition between different energy levels in atomic spectroscopy.
- State Zeeman and Stark effect.
- Explain photoelectron spectroscopy with reference to UPS and XPS.

2.3 ATOMIC STATES AND TERM SYMBOLS

The study of the electromagnetic radiation absorbed or emitted by the atoms is known as atomic spectroscopy. This spectroscopy finds its applications in pharmaceuticals, metallurgy and in the study of multidimensional elements. The atomic spectroscopy is classified into three types: emission, absorption and fluorescence spectroscopy. Let us discuss these types one by one:

- Atomic emission spectroscopy: In this type of spectroscopy, there is an explanation of electronic transition which involves the energy transfer from ground state to an excited state.
- Atomic absorption spectroscopy: In this type of spectroscopy, free electrons which are generated in an atomizer absorbs radiation at a particular frequency. The energy difference between the lower and higher energy levels should be identical.
- Atomic fluorescence spectroscopy: This type of atomic spectroscopy involves radiation of both excitation and de-excitation. Thus it is a combination of atomic absorption and atomic emission spectroscopy.

The electronic configuration of an atom does not provide the complete information about the filling of electrons in the orbitals. For example, there are two electrons in $2p^2$. This configuration do not show that whether the two electrons are present in the same orbital having same orientation of their orbital angular momenta or present in different orbitals having different orientations of their orbital angular momenta. As for p-orbital, the value of magnetic quantum number (m_l) has the value 0 to (n –1) i.e. +1, 0, –1. Similarly the electronic configuration of $2p^2$ does not decide the spin angular momenta or spin orientation of two electrons i.e. m_s= +1/2 or –1/2. The different ways in which the electrons can occupy the orbitals specified in the configuration are called the microstates of the configuration.

Let us consider a structure of atom which consist of a nucleus at the centre containing protons (positive charge particle) and neutrons (neutral particles) along with electrons (negatively charged) that revolve around the nucleus in the orbit. Thus the electrons moving in the orbit generates orbital angular momentum which is represented by l (small l) in addition to spin angular momentum (s). Let us discuss these angular momentum in detail.

2.3.1 Orbital angular momentum and its coupling

The orbital angular momentum which arises due to moving electron in an orbit is perpendicular to the plane of the orbit containing the electron and is a vector quantity. A vector quantity is a quantity which depends on the direction as well as on the magnitude. The orbital angular momentum is quantized and is given by an expression:

$$\text{Orbital angular momentum} = \sqrt{l\,(l+1)}\ h/2\pi$$

where h represents Planck's constant andl is an integer that represent the state of an electron in an atom. l is also known as azimuthal quantum number and its value may be zero or positive. For different orbitals, l- values are given below:

Orbitals	s	p	d	f
l- value	0	1	2	3

When orbital angular momentum have component along z-axis, then it is given by expression:

$$\text{Orbital angular momentum along z-axis} = l_z.\ h/2\pi$$

where $l_z$may be zero or integer that is along z-axis having value 2l + 1.The orbital angular momentum possessed by two or more electrons is added vectorially (couple together) to obtain total orbital angular momentum. This total orbital angular momentum is represented by capital L and is given by the expression:

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, \ldots\ldots\ldots\ldots.. |l_1 - l_2|$$

where $l_1$represents orbital angular momentum of one electron, l_2 represents orbital angular momentum of second electron and $|l_1 - l_2|$ represents absolute value. This coupling of orbital angular momentum of two electrons (1, 2) in an atom is known as l-l coupling. The L must be an integer and represents different atomic states as given below:

L-value	0	1	2	3	4	5
Atomic state	S	P	D	F	G	H

In order to understand the concept of l-l coupling, let us take an example of p^2 configuration. Here p represents the subshell where two electrons are present in an orbital. Simply we can say that there are two electrons in three p-orbitals in p-subshell. For p-orbital, l value is 1. Thus:

$$l_1 = 1; l_2 = 1$$

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, \ldots\ldots\ldots\ldots.. |l_1 - l_2|$$

$$L = |1 + 1|, |1 + 1 - 1|, \ldots\ldots\ldots\ldots.. |1 - 1|$$

$$L = 2, 1, 0$$

This shows that there are three values of L that represents three atomic state S, P, D corresponding to L value 0, 1 and 2 respectively. Similarly if there is d^2 configuration, the value of l is 2. Thus:

$$l_1 = 2;\ l_2 = 2$$

$$L = |l_1 + l_2|,\ |l_1 + l_2 - 1|,\ \ldots\ldots\ldots\ldots\ |l_1 - l_2|$$

$$L = |2 + 2|,\ |2 + 2 - 1|,\ \ldots\ldots\ldots\ldots\ |2 - 2|$$

$$L = 4, 3, 2, 1, 0$$

This shows that there are five values of L that represents five atomic state S, P, D, F, G corresponding to L value 0, 1, 2, 3 and 4 respectively.

2.3.2 Spin angular momentum and its coupling

The spin angular momentum like orbital angular momentum is a vector quantity which arises due to spinning or spin motion of an electron. The direction of spin angular momentum is along the spinning axis of the electron. The spin angular momentum is quantized and is given by the expression:

$$\text{Spin angular momentum} = \sqrt{s\,(s+1)}\ h/2\pi$$

When spinangular momentum have component along z-axis, then it is given by expression:

$$\text{Spin angular momentum along z-axis} = s_z.\ h/\ 2\pi$$

Where s_z is equal to + 1/2 or – ½. The spin angular momentum of different electrons is coupled together to obtain total spin angular momentum. This total spin angular momentum is represented by S and is given by the expression:

$$S = |s_1 + s_2|,\ |s_1 + s_2 - 1|,\ \ldots\ldots\ldots\ldots\ |s_1 - s_2|$$

Where the value of s is +1/2or –1/2. Here$s_1$represents spin angular momentum of one electron, s_2 represents spin angular momentum of second electron.This coupling of spin angular momentum of two electrons (1, 2) is known as s-s coupling. In order to understand the concept of s-s coupling, let us take an example of p^2 configuration where two electrons are present in two orbitals of p-subshell. Thus $s_1 = +1/2$ and $s_2 = +1/2$, therefore

$$S = |s_1 + s_2|, |s_1 + s_2 - 1|, \ldots\ldots\ldots\ldots. |s_1 - s_2|$$

$$S = |1/2 + 1/2|, |1/2 + 1/2 - 1|, \ldots\ldots\ldots\ldots. |1/2 - 1/2|$$

$$S = 1, 0$$

2.3.3 Total angular momentum

The total angular momentum of a single electron is the sum of orbital angular momentum and spin angular momentum.

$$\text{Total angular momentum} = \sqrt{j\ (j+1)}\ h/2\pi$$

Where j is a half integer having value 1/2, 3/2, 5/2 and so on. The coupling of total orbital angular momentum (L) and total spin angular momentum (S) give rise to a total quantum number which is represented by J. This coupling is known as spin-orbit coupling or Russell- Saunders coupling or LS coupling or RS coupling.

$$J = |L + S|, |L + S - 1|, \ldots\ldots\ldots\ldots. |L - S|$$

Where J is quantized and possesses positive value. Let us find the value of J for given value of L=2 and S = +1/2

$$J = |2 + 1/2|, |2 + 1/2 - 1|, \ldots\ldots\ldots\ldots. |2 - 1/2|$$

$$J = 5/2, 3/2$$

Thus J has two value 5/2 and 3/2. By using the concept of LS coupling, we can predict an atomic term symbol or term symbol of light atoms. Atomic term symbol is represented by $^{2S+1}L_J$. Here the value of L refers to atomic state and 2S+1 represent spin multiplicity which refers to number of orientations of the total spin and the number of lines possible in a state. If the value of spin multiplicity is one then the state is singlet state, if the value of spin multiplicity is two then the state is doublet state, if three then triplet state and so on. This spin multiplicity value i.e. 2S +1 represents different value of J. For example, if the value of spin multiplicity is one then the J will possess only one value, if the value of spin multiplicity is two then there will be two values of J. LS coupling determine atomic term symbols for those lighter atoms that have atomic number less than 30. For atoms having atomic number more than 30, another coupling i.e. j-j coupling is used.

2.3.4 Expression of term symbol

The expression of term symbol determined above by LS coupling is for a system that contains two electrons. For a particular atomic state, the term symbol is expressed by $^{2S+1}L_J$. Let us discuss some important rules that help in providing the expression of term symbol.

2.3.4.1 Hund's rule

There are three empirical rules for predicting the term symbol for a particular atom in the ground state (state in which all electrons in an atom are in the lowest energy) which refers to Hund's rule. According to Hund's first rule, "the term symbol with largest 2S+1 value or with largest multiplicity is the most stable state for an atom in a ground state". More is the stability, lower is the energy. Thus we can say that the ground term symbol of an atom possess lowest energy. For example, if an atom have term symbol having 2S+1 value 2 and 3, so according to Hund's first rule, the ground term symbol possess multiplicity of 3which is larger than 2. According to Hund's second rule, for a given value of total spin angular momentum (S), greater is the value of total orbital angular momentum (L), lower is the energy. Simply we can say that term symbol with largest L value is the most stable. For example, if for a particular atom the value of L are 0, 1 and 2 for which the atomic states are S, P and D. Thus according to Hund's second rule, the most stable state is with largest L value i.e. 2 which corresponds to atomic state D. According to Hund's third rule "the most stable state depends on the nature of subshell for which there is same value of L and S". The state with smallest value of J is the most stable provided that the subshell is less than half filled. When the subshell is more than half filled then the state with the largest value of J is the most stable. For example, if p-subshell contains less than three electrons (less than half filled), then the term symbol with lowest J value is more stable than the term symbol with higher J value. If p-subshell contains more than three electrons (more than half filled) then term symbol with largest J vale is the most stable. We can say that all three rules given by Hund explain the energy and stability concept of term symbol in order to predict ground term of an atom.

Thus in addition to Hund's rule, there are certain other points that we have to keep in mind while deciding the term symbol. These points are as follows:

- Those electrons which are in complete closed shell or closed subshell or orbitals do not contribute in the determination of term symbol. For these completely filled orbitals, the term symbol is always $^1S_0$.
- For more than half filled subshells, we use the term hole rather than the number of electrons actually present. In order to understand the concept of hole, let us consider the case of oxygen atom in the ground state. We know that there are eight electrons in oxygen atom, thus its electronic configuration is $1s^2$, $2s^2$, $2p^4$. This shows that it has p^4 configuration and it requires two more electron to fill its orbital of p-subshell completely. Thus we can say that in oxygen atom, there are two holes. The concept of holes should be considered only when the subshells are more than half filled. The term symbol of oxygen atom having p^4 configurationand carbon atom having has p^2 configuration are same. Thus it is concluded that for p-subshell, the pair of atoms having p^{6-n} and p^n configuration, the term symbols are same. Likewise for d-subshell, the pair of atoms having d^{10-n} and d^n configuration, the term symbols are same. For the above discussed example of carbon and oxygen, p^n is p^2 i.e. carbon atom and p^{6-n} is p^{6-2} i.e. p^4 where p^4 refers to oxygen atom. Thus p^2 and p^4 possess same term symbol. In the similar way, if n =2, then for d-subshell, d^n is d^2 and d^{10-n} is d^{10-2}i.e. $d^{8.}$ Thus according to above mentioned concept, d^2 and d^8 possess same term symbol.

Let us discuss an example of $p^{2,}$ p^3 and p^4 configuration. Here we will discuss Hund's rule and above points in determining the term symbols for these three different configuration p^2 (less than half filled), p^3 (exactly half filled)and p^4(more than half filled). Let us start with p^2 configurationthat is the configuration of carbon atom. There are six electrons in carbon atom having electronic configuration $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$. Here $1s^2$ and $2s^2$ orbitalsdo not contribute to term symbol as these orbitals are completely filled. Here $l_1 = 1$ and $l_2 = 0$.

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, \ \ldots\ldots\ldots\ldots\ldots \ |l_1 - l_2|$$

$$L = |1 + 0|, |1 + 0 - 1|, \ \ldots\ldots\ldots\ldots\ldots \ |1 - 0|$$

$$L = 1, 0$$

The above two value of L corresponds to two atomic states P and S for the value 1 and 0 respectively. Here $s_1 = +1/2$ and $s_2 = +1/2$, therefore

$$S = |s_1 + s_2|, |s_1 + s_2 - 1|, \ldots\ldots\ldots\ldots\ldots |s_1 - s_2|$$

$$S = |1/2 + 1/2|, |1/2 + 1/2 - 1|, \ldots\ldots\ldots\ldots\ldots |1/2 - 1/2|$$

$$S = 1, 0$$

For spin multiplicity, we have formula 2S + 1, thus

For S = 0, we have 2(0) + 1 = 1 (Singlet)

For S = 1, we have 2(1) + 1 = 3 (Triplet)

For a particular atomic state, the term symbol is expressed by $^{2S+1}L_J$. Thus form above L and 2S+1 value, we obtain term symbol ^1P, ^3P, ^1S and ^3S. Now let us find the value of J for determining the complete term symbol:

- For ^1P: L = 1, S = 0 (2S + 1= 1; thus S = 0)

$$J = |L + S|, |L + S - 1|, \ldots\ldots\ldots\ldots\ldots |L - S|$$

On putting the value of L and S:

$$J = |1 + 0|, |1 + 0 - 1|, \ldots\ldots\ldots\ldots\ldots |1 - 0|$$

J = 1, this corresponds to term symbol $^1P_1$

- For ^3P: L = 1, S = 1 (2S + 1= 3; thus S = 1)

$$J = |L + S|, |L + S - 1|, \ldots\ldots\ldots\ldots\ldots |L - S|$$

On putting the value of L and S:

$$J = |1 + 1|, |1 + 1 - 1|, \ldots\ldots\ldots\ldots\ldots |1 - 1|$$

J =2, 1, 0, this corresponds to term symbol $^3P_0$, $^3P_1$, $^3P_2$

- For ^1S: L = 0, S = 0 (2S + 1= 1; thus S = 0)

$$J = |L + S|, |L + S - 1|, \ldots\ldots\ldots\ldots\ldots |L - S|$$

On putting the value of L and S:

$$J = |0 + 0|, |0 + 0 - 1|, \ldots\ldots\ldots\ldots\ldots |0 - 0|$$

J = 0, this corresponds to term symbol $^1S_0$

- For ^3S: L = 0, S = 1 (2S + 1= 3; thus S = 1)

$$J = |L + S|, |L + S - 1|, \ldots\ldots\ldots\ldots. |L - S|$$

On putting the value of L and S:

$$J = |0 + 1|, |0 + 1 - 1|, \ldots\ldots\ldots\ldots. |0 - 1|$$

J = 1 this corresponds to term symbol $^3S_1$

Thus atomic term symbol for carbon or p^2configuration are $^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$, $^1S_0$ and $^3S_1$. Now let us find the ground term symbol for p^2configuration. According to Hund's first rule, the term with highest multiplicity is the ground term symbol. Therefore there are four term symbols ($^3P_0$, $^3P_1$, $^3P_2$ and $^3S_1$) having multiplicity equal to 3. From Hund's second rule, ground term symbol is with largest L value, thus the term symbols are $^3P_0$, $^3P_1$, $^3P_2$. Form Hund's third rule, the ground term symbol for carbon or p^2configuration is $^3P_0$ because in carbon, the p-subshell possesses two electrons which is the case of less than half filled where the smallest value of J represents ground term. Thus the ground term symbol for carbon or p^2configuration is $^3P_0$.

For p^3 configuration, L= 0; S = 3/2; J = 3/2; By using the above concept of determining the term symbol for p^2 configuration, the ground term symbol for p^3 configuration determined in the similar way is $^4S_{3/2}$.

For p^4 configuration, L= 1; S = 1; J = 0, 1, 2; By using the above concept of determining the term symbol for p^2 configuration, the term symbol for p^4 configuration determined in the similar way is $^3P_0$, $^3P_1$, $^3P_2$ and ground term symbol is $^3P_2$ as the subshell is more than half filled, therefore largest value of J corresponds to its ground term.

2.4 MICROSTATES

Microstates refer to different arrangement of each electron in a set of orbitals. The set of orbitals like in case of p-subshell, there are three set of orbitals (p_x ,p_y, p_z) having slightly different energy which can accommodate maximum six electrons. For d-subshell, there are five set of orbitals (d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$,d_{z^2}) having slightly different energy which can accommodate maximum ten electrons. Likewise, f-subshell possesses seven set of orbitals and so on. The slight difference in energy of orbitals is due to compact nature of atoms or molecules where the concept of inter electronic repulsion cannot be ignored. By knowing the number of orbitals and the number of electrons, we can calculate the number of microstates by the formula given below:

$$\frac{n_o!}{n_e!\,(n_o - n_e)!}$$

Where n_o is 2 multiplied by thenumber of orbitals, $n_e$represents the number of electrons while symbol ! represents factorial. Now using the above formula, let us find the number of microstates for p^1 configuration.Here p represents the subshell while 1 represents the number of electron. Thus:

$$n_e = 1,\ n_o = 2\times3 \text{ (number of orbitals in p-subshell)} = 6$$

$$\text{Number of microstates} = \frac{n_o!}{n_e!\,(n_o - n_e)!} = \frac{6!}{1!\,(6-1)!} = \frac{6!}{1!(5)!} = \frac{6\times5\times4\times3\times2\times1}{1\times5\times4\times3\times2\times1} = 6$$

Thus in p^1 configuration, there are six microstates or we can say that there are six different arrangement of one electron in the three orbitals of p-subshell.

Likewise for d^2 configuration:

$$n_e = 2,\ n_o = 2\times5 = 10$$

$$\text{Number of microstates} = \frac{n_o!}{n_e!\,(n_o - n_e)!} = \frac{10!}{2!\,(10-2)!} = \frac{10!}{2!(8)!} = \frac{10\times9\times8!}{2\times1\times8!} = 45$$

This shows that there are 45 different arrangements of two electrons in five orbitals of d-subshell. Similarly for p^2 configuration, the number of microstates calculated by the above formula is 15. For a given configuration, the value of magnetic quantum number (m_l) whose value vary from +l to –l including zero and spin quantum number (m_s) of the electrons specifies each permissible microstate. For p^2 configuration, the p-subshell for which the value of l is one possesses three value of m_li.e. +1, 0, –1 that refers to three set of orbitals while m_s value are +1/2 and –1/2. The given Table 2.1 shows different value of m_l and m_s that represents 15 possible microstates for p^2 configuration.

Table 2.1.**The value of m_l and m_s representing 15 possible microstates for p^2 configuration**

Microstate	Electron	Magnetic quantum number (m_l)	Spin quantum number (m_s)
1	1	+1	+1/2
	2	+1	–1/2
2	1	+1	+1/2
	2	0	+1/2
3	1	+1	+1/2
	2	0	−1/2
4	1	+1	−1/2
	2	0	+1/2
5	1	+1	−1/2
	2	0	−1/2
6	1	0	+1/2
	2	0	−1/2
7	1	+1	+1/2
	2	−1	+1/2
8	1	+1	+1/2
	2	−1	−1/2
9	1	+1	−1/2
	2	−1	+1/2
10	1	+1	−1/2
	2	−1	−1/2
11	1	0	+1/2
	2	−1	+1/2
12	1	0	+1/2
	2	−1	−1/2
13	1	0	−1/2
	2	−1	+1/2
14	1	0	−1/2
	2	−1	−1/2
15	1	−1	+1/2
	2	−1	−1/2

In this way by knowing the value of m_l and m_s, we can specify different number of microstates for a particular electronic configuration. The concept of microstate is useful in providing information regarding the spectra of an atom.

2.5 SELECTION RULES

There are certain rules which predict whether the transition between different energy levels or atomic states in spectra are allowed or not are known as selection rules. There are three selection rules:

- Rule 1: Those transitions in a spectrum are allowed for which there is any change in the value of n (principle quantum number or energy). In simple language we can say that Δn = any integer. Here Δ represents change. For example, let us consider an electron in the ground state (1s) that undergoes transition in p-state or p-orbital. According to this rule, 1s → np (n is equal to or greater than 2). Likewise the transition between 1s→2p is allowed as $\Delta n = 1$
- Rule 2: those transitions in spectra are allowed for which the orbital angular momentum (l) differs by only one unit. Simply $\Delta l = \pm 1$. Let us consider the transition of electron from 1s to 2p for which the value of l is 0 and 1 respectively. So according to this rule: $\Delta l = 1 - 0 = +1$. This shows that the transition of electron from 1s to 2p is allowed. When transition is from energy level having higher l value to energy level having lower l value, the value of $\Delta l = -1$.
- Rule 3: This rule is related to j which arises by the coupling of orbital and spin angular momenta of electrons. According to this rule,$\Delta j = 0, \pm 1$. For example, let us consider a transition from $^2S_{1/2}$ to $^2P_{1/2}$. Here $\Delta j = 0$ (1/2 – 1/2) which shows that the transition is allowed transition. Similarly for transition from $^2P_{3/2}$ to $^2D_{5/2}$ is allowed because

  $\Delta j = 5/2 - 3/2 = 2/2 = 1$, as selection rule is $\Delta j = 0, \pm 1$.

Thus by using these selection rules, we can explain the concept of allowed transitions.

2.6 SPECTRA OF ATOMS

There is an absorption or emission of light of a particular wavelength, as a result of transition of electron from one energy level to another energy level. The collection of these particular wavelengths of the atom gives rise to the atomic spectra of atoms. Thus we define atomic spectra as the spectrum of the electromagnetic radiation emitted or absorbed by an electron during transition between different energy levels within an atom. A diagram which shows the energies of the atomic states along with the transition between them refers to Grotrian diagram.

2.6.1 Hydrogen atom

The atomic spectra of hydrogen atom are the simplest one. As we know hydrogen atom contains only one electron which exist in 1s orbital. The electron in 1s orbital of hydrogen atom refers to its ground state. On the basis of selection rule discussed in the above topic, an electron in 1s orbital can undergo transition to any p-orbital and p electron can undergo transition to either d-state or s-state on the basis of selection rule provided that the value of n should be greater than or equal to 2 for np orbital. For hydrogen atom, one electron exist in 1s-orbital thereby the term symbol is $^2S_{1/2}$, where 2 represents spin multiplicity and ½ represents J value. The transition of electron takes place from 1s orbital to 2p orbital where 2p orbital possess term symbol $^2P_{1/2}$ and $^2P_{3/2}$. This shows that the spectra of hydrogen atom contains two lines (doublet) that arises from the following transition:$^2S_{1/2}$ to $^2P_{1/2}$ and from $^2S_{1/2}$ to $^2P_{3/2}$ obeying the selection rule $\Delta j = 0$ and $\Delta j = +1$ respectively.

Similarly the transition of electron can take place from 1s orbital to 3p, 4p, 5p on the basis of selection rule: $n \geq 2$. Likewise the transition of electron occurs from 2p orbital to 3s, 4s or to 3d, 4d in the following manner: For $\Delta j = 0$, the transition from $^2P_{3/2}$ to $^2D_{3/2}$ takes place while for $\Delta j = +1$, the transition from $^2P_{3/2}$ to $^2D_{5/2}$ and $^2P_{1/2}$ to $^2D_{3/2}$ takes place. The Grotrian diagram for hydrogen atom is shown in fig. 2.2.

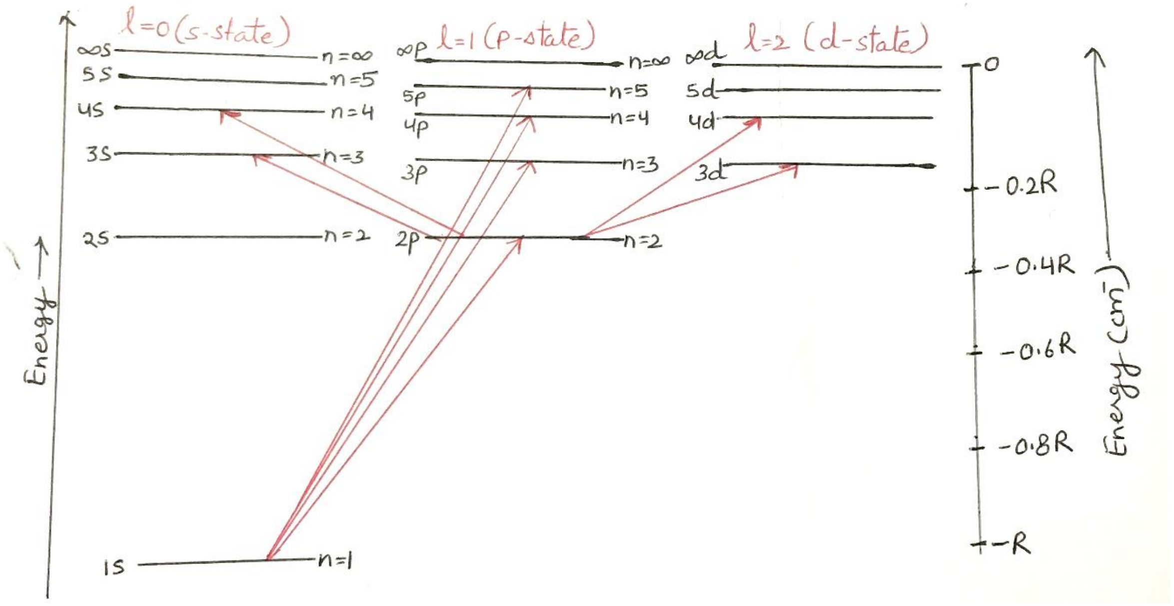

Fig. 2.2. Grotrian diagram for hydrogen atom

2.6.2 Lithium atom

We know that lithium atom contain three electrons having electronic configuration $1s^2$, $2s^1$. As 1s-orbital is completely filled, thus this orbital is not involved in transition normally. The spectra of lithium atom is nearby same as that of hydrogen atom, the difference lies only in the value of n. The value of n for lithium atom is 2 ($2s^1$) while for hydrogen atom, it is one ($1s^1$). In case of lithium atom, the transition of electron takes place from 2s-orbital to 2p-orbital, 3p-orbital, 4p-orbital and so on like hydrogen atom. Further the transition of electron takes place from 2p-orbital to 3s, 4s or 5s or 3d, 4d, 5d and so on. The transitions aresame like the transition in hydrogen atom. The spectra of lithium atom is shown in fig. 2.3.

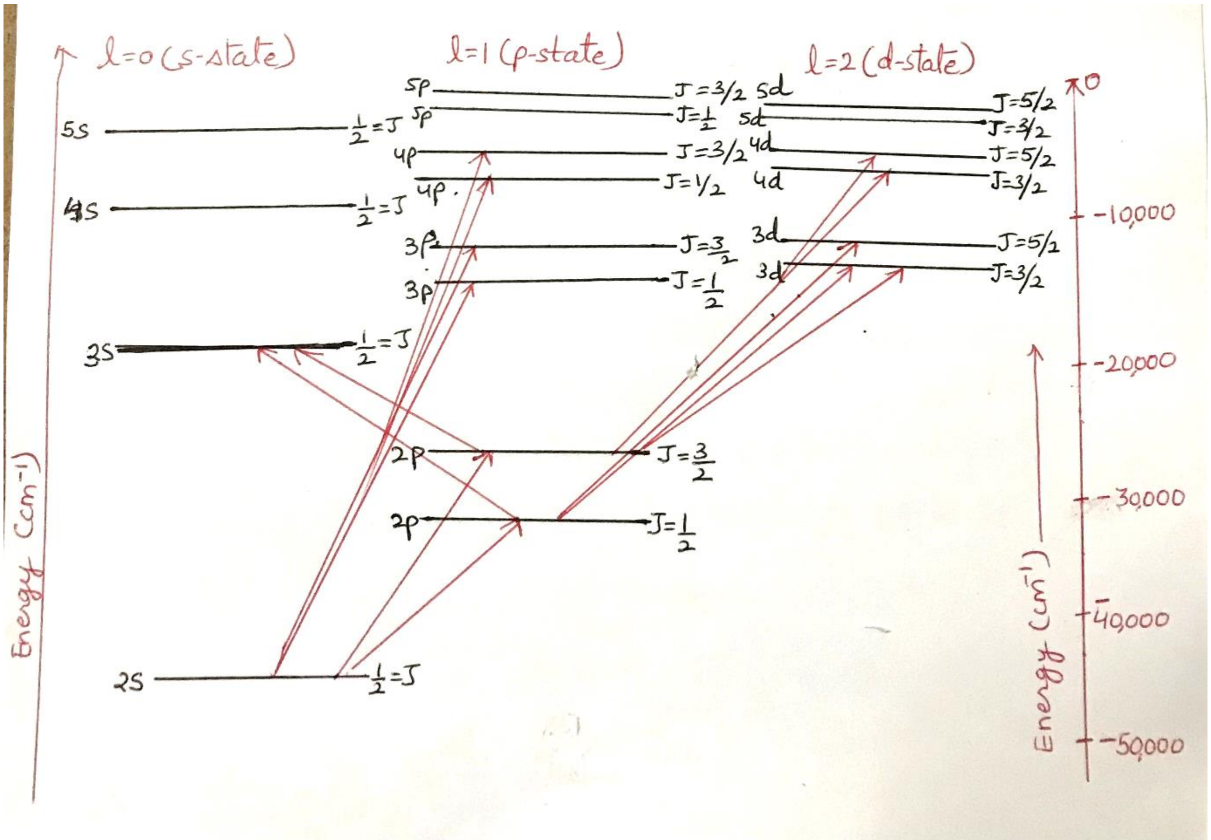

Fig. 2.3. Atomic spectra of lithium atom

2.6.3 Zeeman effect

The spinning and orbital motion of electron give rise to a magnetic moment (μ). In the presence of magnetic field (M), there is an interaction between μ and M which results in the splitting of lines in the spectra. This splitting of spectral lines in the presence of applied magnetic field is known as Zeeman effect. The interaction energy (E_{int}) is given by ($-\mu M$). This effect was observed by P. Zeeman. There are two types of Zeeman effect: normal Zeeman effect and anomalous Zeeman effect. In normal Zeeman effect, there is transition between the singlet terms and the spectral line split into three components. In anomalous Zeeman effect, transition takes place between the terms having spin multiplicity greater than one i.e. between doublet terms or triplet terms and the spectral line split into more than three components.

In the presence of magnetic field, a term with a particular J value splits inti 2J + 1 levels. Zeeman effect has a selection rule according to which $\Delta N_J = 0, \pm 1$. Here $\Delta N_J$is the component of J which is along the direction of the magnetic field. Let us understand Zeeman effect by considering $^1S_0$ to $^1P_1$ transition in the atomic spectra. For$^1S_{0,}$ the value of J = 0; L= 0 and S=0. According to Zeeman effect, there are 2J + 1 value. Thus for $^1S_{0,}$ 2J + 1 = 1. This shows that there is only one value of N_J i.e. 0. Likewise for $^1P_1$, 2J + 1 = 2 (1) + 1= 3, this shows that there are three value of N_J i.e. +1, 0 and –1. This results in the splitting of one spectral line of $^1P_1$into three lines which is shown in fig. 2.4.

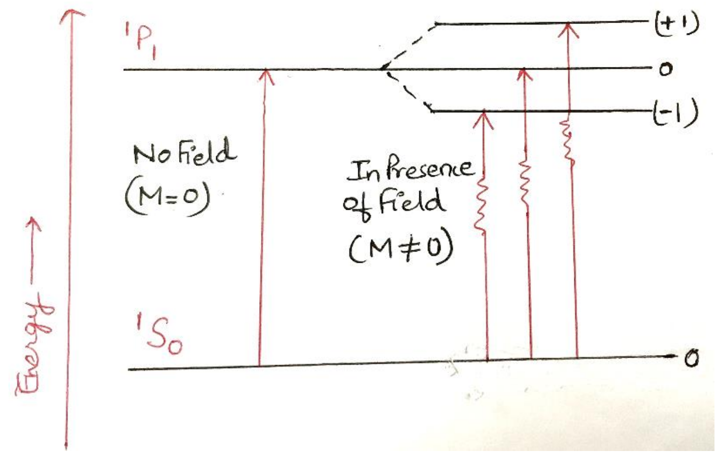

Fig. 2.4. Zeeman effect: Splitting of one spectral line of $^1P_1$into three lines

2.6.4 Stark effect

Zeeman effect as discussed above is the splitting of spectral lines in the presence of applied magnetic field. In the same way, the splitting of spectral lines in the presence of applied electric field (E) is known as Stark effect. In the presence of electric field, there is an interaction between applied electric field and induced electric dipole moment (μ) which arises due to polarization of electron. Here interaction energy (E_{int}) is given by ($-\mu E$). In Stark effect, the splitting of spectral line is proportional to the square of the applied electric field.

2.7 PHOTOELECTRON SPECTROSCOPY (XPS AND UPS)

Photons are the packets of electromagnetic radiations or light having energy (E) equal to hν, where h represents Plank's constant having value 6.62×10^{-34} Js and ν representsthe frequency of radiation in Hertz. When a photon strikes the surface of a material, there is transfer of energy from photon to the electrons of the materials. When the energy of the electron overcome the bond that holds or bind them in a material (binding energy), the electron form the surface get escape from the surface. The kinetic energy (E_k) of the emitted electron is detected by a spectroscopy which is known as photoelectron spectroscopy. In simple words, we can say that in photoelectron spectroscopy as the name indicates, a photon emits an electron fromthe surface of a material. The kinetic energy of the emitted electron (E_k) is given by the expression:

$$E_k = h\nu - E_b - \Phi$$

Where E_b is binding energy, ν is the frequency of radiation and Φ is the spectrometer work function. In photoelectron spectroscopy, we study XPS which is X-ray photoelectron spectroscopy and UPS which is ultraviolet photoelectron spectroscopy. In XPS, we use X-ray radiations having energy ranging from 200 to 2000 eV whereas in UPS, we use vacuum UV radiations having energy in the range of 10 to 45 eV for emitting the electron from the surface of a material. The commonly used source for X-ray are MgKα (1253.6 eV) radiation and Al Kα (1486.6 eV) radiation while for UPS, the source is Helium lamp (21.2eV). The complete setup of photoelectron spectroscopy is given in fig 2.5.

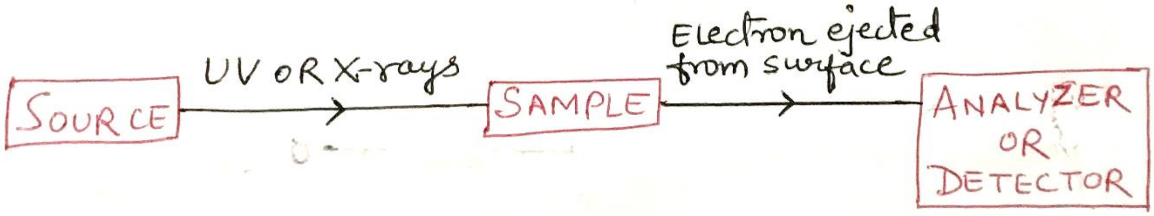

Fig 2.5. Setup of photoelectron spectroscopy

Here the analyzer, measures the kinetic energy of the ejected electrons while the detector counts the number of emitted electrons. By using photoelectron spectroscopy, we can determine the composition of the atom, stoichiometry and examine the contamination present on the surface of a material. In this way, we obtain spectra by plotting the number of electrons versus their binding energy.

2.8 SELF ASSESSMENT QUESTIONS (SAQ)

Fill in the blanks:

1. The value of magnetic quantum number for a given value of principle quantum number is ……….

2. The value of spin quantum number for an electron may be ………. and ……….

3. The value of azimuthal quantum number for p-orbital is ……….

4. The atomic state corresponding to zero value of total orbital angular momentum is ……….

5. There are ………. atomic states for an atom having p^2 configuration.

6. The total angular momentum is the sum of ………. and ……….

7. The multiplicity of a term symbol represents the number of ………. of total spin.

8. Atomic term symbol for a particular state is expressed as ……….

9. In an atomic term symbol, $2S + 1$ represents ………

10. According to Hund’s first rule, the most stable state for an atom is with ……… multiplicity.

11. Hund’s second rule says that for a given value of S, the ………. is the value of L, ………. is the energy.

12. When the subshell is less than half- filled, the state with ………. value of J is the most stable.

13. When the subshell is more than half- filled, the state with ………. value of J is the most stable.

14. The term symbol are same for ………. and ………. configuration.

15. The number of microstates refers to different arrangement of each electron in a set of ……….

16. For p^2-configuration, the number of microstates is ……….

17. The value of ………. and ………. specify each permissible microstates.

18. The selection rule for orbital angular momentum (l) involved in transition between different energy level is ………..

19. The transition from atomic state $^2S_{1/2}$ to $^2P_{3/2}$ are allowed by considering selection rule ………. and ……….

20. LS coupling scheme is used to determine term symbols for those atoms having atomic number ……….

21. ………. diagram shows the transition between the atomic states along with the energies.

22. In the spectra of hydrogen atom, the transition of electrons takes place from $^2S_{1/2}$ to ………. and ……….

23. The splitting of spectral lines in presence of an applied magnetic field is known as ………. effect.

24. The splitting of spectral lines in presence of an applied electric field is known as ………. effect.

25. In photoelectron spectroscopy, we discuss about ………. and ……….

2.9 SUMMARY

In this unit, we have discussed about atomic spectroscopy and photoelectron spectroscopy. In atomic spectroscopy which plays an important role in pharmaceutical, metallurgy and in determination of trace metals in different types of samples, we studied the concept of term symbols which includes orbital angular momentum, spin angular momentum, total angular momentum and its coupling. We learned how to determine term symbol by spin-orbit coupling. The concept of Hund's rule have been undertaken in order to predict the term symbol of a particular atom in the ground state. How different electrons can be arranged in a set of orbitals was discussed by taking the concept of microstate. In addition to this, different selection rules were discussed that predict the allowed transitions between different energy levels. The spectra of different atoms like hydrogen and lithium has been discussed particularly with reference to transition. Different effect like Zeeman, Stark was considered which are responsible for splitting of spectral lines in the presence of magnetic field and electric field respectively. Finally the unit concludes with the discussion of photoelectron spectroscopy that includes X-ray and ultraviolet radiations to eject an electron from the surface of a material.

2.10 GLOSSARY

- **Microstate**: Different arrangement of each electron in a set of orbitals.
- **Grotrian Diagram**: Diagram that shows the transitions between the atomic states along with the energies.
- **Spin Multiplicity**: Term 2S+1 in a term symbol.
- **Zeeman Effect**: Splitting of spectral lines in the presence of applied magnetic field.
- **Stark Effect**: Splitting of spectral lines in the presence of applied electric field.
- **Photoelectron Spectroscopy**: Photon in and electron out spectroscopy.
- **LS Coupling**: Determine atomic term symbols for those lighter atoms that have atomic number less than 30.

2.11 POSSIBLE ANSWERS TO SAQ's

Fill in the blanks:

1. 0 to (n –1); **2.** +1/2 and –1/2; **3.** One; **4.** S; **5.** Three; **6.** Total orbital angular momentum and total spin angular momentum; **7.** Orientations; **8.** $^{2S+1}L_J$; **9.** Spin multiplicity; **10.** Largest; **11.** Greater, Lower; **12.** Lowest; **13.** Highest; **14.** p^n and p^{6-n}; **15.** Orbitals; **16.** Fifteen; **17.** Magnetic quantum number and spin quantum number; **18.** $\Delta l = \pm 1$; **19.** $\Delta l = \pm 1$ and $\Delta j = 0, \pm 1$; **20.** Less than 30; **21.** Grotrian; **22.** $^2P_{1/2}$ and $^2P_{3/2}$; **23.** Zeeman; **24.** Stark; **25.** XPS and UPS

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2.13 TERMINAL QUESTIONS

1. Explain the concept of finding the expression of term symbol and determine the term symbol for p^2-configuration.

2. Define microstate. Calculate the number of microstate for p^1-configuration and p^2-configuration.

UNIT 3: ROTATIONAL SPECTROSCOPY

CONTENTS:

3.1 INTRODUCTION

Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. The spectra of polar molecules can be measured in absorption or emission by microwave spectroscopy or by far infrared spectroscopy. The rotational spectra of non-polar molecules cannot be observed by those methods, but can be observed and measured by Raman spectroscopy. Rotational spectroscopy is sometimes referred to as pure rotational spectroscopy to distinguish it from rotational-vibrational spectroscopy where changes in rotational energy occur together with changes in vibrational energy, and also from ro-vibronic spectroscopy (or just vibronic spectroscopy) where rotational, vibrational and electronic energy changes occur simultaneously.

For rotational spectroscopy, molecules are classified according to symmetry into spherical top, linear and symmetric top; analytical expressions can be derived for the rotational energy terms of these molecules. Analytical expressions can be derived for the fourth category, asymmetric top, for rotational levels up to $J = 3$, but higher energy levels need to be determined using numerical methods. The rotational energies are derived theoretically by considering the molecules to be rigid rotors and then applying extra terms to account for centrifugal distortion, fine structure, hyperfine structure and Coriolis coupling. Fitting the spectra to the theoretical expressions gives numerical values of the angular moments of inertia from which very precise values of molecular bond lengths and angles can be derived in favorable cases. In the presence of an electrostatic field there is Stark splitting which allows molecular electric dipole moments to be determined.

3.2 OBJECTIVES

After going through this unit you will be able to:

- To interpret rotational spectra, get information about molecular dimensions andatomic masses.
- Learn about rotational spectroscopy and the rigid rotator model to describe a rotating diatomic molecule.
- Selection rules and the appearance of their microwave spectra.

- To determine the bond lengths of diatomic molecules.
- The effect of isotopic substitution on rotational constants

3.3 THE ROTATION OF MOLECULES

Spectroscopy in the microwave region is concerned with the study of rotating molecules. The rotation of three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the centre of gravity-the principal axes of rotation. Thus a body has three principal moments of inertia, one about each axis, usually designated I_A, I_B and I_C.

Molecules may be classified into groups according to the relative values of their three principal moments of inertia. We shall describe this classification here.

1. Linear molecules. These, as the name implies, are molecules in which all the atoms are arranged in a straight line, such as HCl and OCS, illustrated below

H-Cl

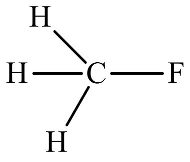
O-C-S

The three directions of rotation may be taken as (a) about the bond axis, (b) end over end rotation in the plane of the paper, and (c) end over end rotation at right angles to the plane.

For linear molecules we have:

$$I_B = I_{C,} \quad I_B = 0 \qquad \dots\dots 3.1$$

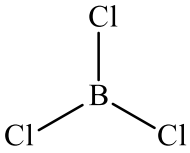
2. Symmetric tops. Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below:



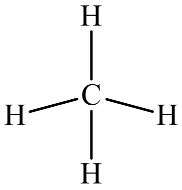
As in this case of linear molecules, the end over end rotation in, and out of, the plane of the paper are still identical and we have $I_B = I_C$. The moment of inertia about the C-F bond axis is now not negligible, however, because it involves the rotation of three comparatively massive hydrogen atoms off this axis. Such a molecule spinning about this axis can be imagined as a top, and hence the name of the class. We have then:

$$\text{Symmetric tops: } I_B = I_C \neq I_A \qquad I_A \neq 0 \qquad \ldots\ldots 3.2$$

There are two subdivisions of this class which may mention: if, as in methyl fluoride above, IB = IC > IA, the the molecule is said to be prolate symmetric top, where as if IB = IC < IA, the the molecule is said to be oblate symmetric top. Example BCl_3 . in this case $I_A = 2I_B = 2I_C$.



3. Spherical tops. When a molecule has all three moments of inertia identical, it is called a spherical top. Example CH_4. We have then:

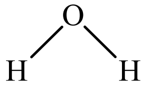


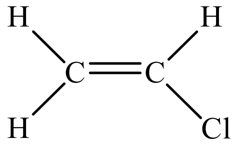
$$\text{Spherical tops: } I_A = I_B = I_C \qquad \ldots\ldots 3.3$$

4. Asymmetric tops. These molecules, to which the majority of substances belong, have all the moments of inertia different:

$$I_A \neq I_B \neq I_C \qquad \ldots\ldots 3.4$$

Simple examples are water and vinyl chloride.





3.4 ROTATIONAL SPECTRA

Rotational energy, along with all other forms of molecular energy is quantized: this means that a molecule cannot have any arbitrary amount of rotational energy but its energy is limited to certain definite values depending on the shape and size of the molecule concerned. The permitted energy values the so called rotational energy levels may in principle be calculated for any molecule by solving the schrodinger equation for the system represented by that molecule.

We shall consider each class of rotating molecule in turn, discussing the linear molecule in most detail, because much of its treatment can be directly extended to symmetrical and unsymmetrical molecules.

3.5 DIATOMIC MOLECULES

3.5.1 The rigid diatomic molecule

We start with this, the simplest of all linear molecules, shown in fig 3.1. masses m1 and m2 are joined by a rigid bar (the bond) whose length is

$$r_0 = r_1 + r_2 \qquad \ldots\ldots 3.5$$

The molecule rotates end-over-end about a point C, the centre of gavity: this is defined by the moment, or balancing, equation:

$$m_1 r_1 = m_2 r_2 \qquad \ldots\ldots 3.6$$

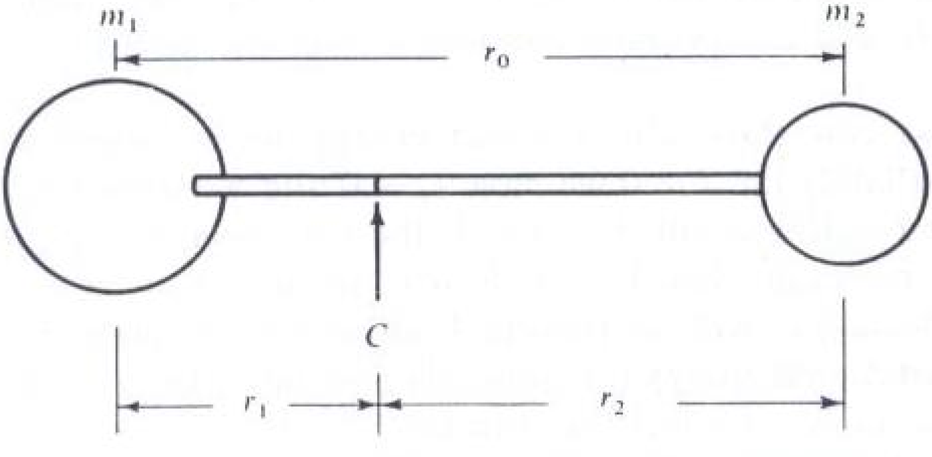


Fig. 3.1. A rigid diatomic molecule treated as two masses, m1 and m2, joined by a rigid bar of length $r_0 = r_1 + r_2$

The moment of inertia about C is defined by:

$$I = m_1 {r_1}^2 + m_2 {r_2}^2$$
$$= m_2 r_2 r_1 + m_1 r_1 r_2 \text{ (from Eq. 2.6)} \qquad \ldots\ldots 3.7$$

$$= r_1 r_2 (m_1 + m_2)$$

However, from Eqs (2.5) and (2.6):

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 + r_1)$$

Therefore,

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \text{ and } r_2 = \frac{m_1 r_0}{m_1 + m_2} \qquad \ldots\ldots 38$$

Replacing (2.8) in (2.7):

$$I = \frac{m_1 m_2}{m_1 + m_2} {r_0}^2 = \mu {r_0}^2 \qquad \ldots\ldots 3.9$$

where we have written $\mu = m_1 m_2 / m_1 + m_2$, and μ is called the reduced mass of the system. Equation (3.9) defines the moment of inertia conveniently in terms of the atomic masses and the bond length.

By the use of Schrodinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules} \quad \text{where } J = 0,1,2,\ldots \qquad \ldots\ldots 3.10$$

Here h is planck's constant and I is moment of inertia. The quantity J, which can take integral values from zero upwards, is called the rotational quantum number.

Equation (3.10) expressed the allowed energies in joules; we, however, are interested in differences between these energies, or, more particularly, in the corresponding frequency, $\nu = \Delta E/h$ Hz, or wavenumber, $\bar{\upsilon} = \Delta E/hc\ cm^{-1}$, of the radiation emitted or absorbed as a consequence of changes between energy levels. In the rotational region spectra are usually discussed in terms of wavenumber, so it is useful to consider energies expressed in these units. We write:

$$\epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I_c} J(J+1) \quad cm^{-1} \quad (J = 0,1,2 \ldots) \qquad \ldots\ldots 3.11$$

Equation (3.11) is usually abbreviated to:

$$\epsilon_J = B\,J(J+1) \quad cm^{-1} \quad (J = 0.1,2\ldots) \qquad \ldots\ldots 3.12$$

where B, the rotational constant, is given by

$$B = \frac{h}{8\pi^2 I_B C} J(J+1) \quad cm^{-1} \qquad \ldots\ldots 3.13$$

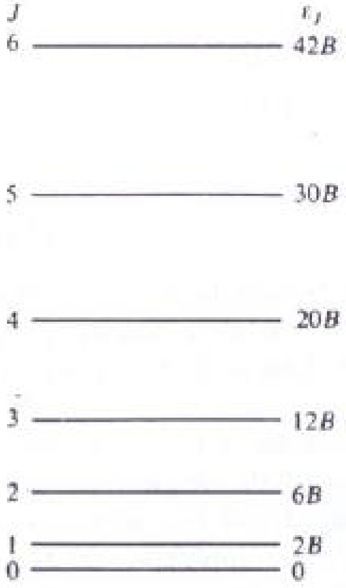


Fig. 3.2 The allowed rotational energies of a rigid diatomic molecule

From equation (3.12) we can show the allowed energy levels diagrammatically as in Fig.3.2. Plainly for J = 0 we have $\epsilon_j = 0$ and we would say that the molecule is not rotating at all. For J = 1, the rotational energy is $\epsilon_1 = 2B$ and a rotating molecule then has its lowest angular momentum. In practice, of course, there comes a point at which the centrifugal force of a rapidly rotating diatomic molecule is greater than the strength of the bond, and the molecule is disrupted, but this point is not reached at normal temperatures.

We now need to consider differences between the levels in order to discuss the spectrum. If we imagine the molecule to be in the J= 0 state (the ground rotational state, in which no rotation occurs), we can let incident radiation be absorbed to raise it to the J = 1 state. Plainly the energy absorbed will be:

$$\epsilon_{J=1} - \epsilon_{J=0} = 2B - 0 = 2B \ cm^{-1}$$

and therefore,

$$\bar{\upsilon}_{J=0\rightarrow J=0} = 2B\ \mathrm{cm}^{-1} \qquad \ldots\ldots 3.14$$

In other words, an absorption line will appear at $2B\ \mathrm{cm}^{-1}$. If now the molecule is raised from the J = 1 to the J = 2 level by the absorption of more energy, we see immediately:

$$\bar{\upsilon}_{J=1\rightarrow J=2} = \epsilon_{J=2} - \epsilon_{J=1} = 6B - 2B = 4B\ \mathrm{cm}^{-1} \qquad \ldots\ldots 3.15$$

In general, to raise the molecule from the state J to J+1, we would have:

$$\bar{\upsilon}_{J\rightarrow J+1} = B(J+1)(J+2) - BJ(J+1) = B[J^2 + 3J + 2 - (J^2 + J)]$$

$$\text{or} \qquad \bar{\upsilon}_{J\rightarrow J+1} = 2B(J+1)\ \mathrm{cm}^{-1} \qquad \ldots\ldots 3.16$$

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at 2B, 4B,6B,…. cm^{-1},while a similar lowering would result in an identical emission spectrum. This is shown in fig.3.3

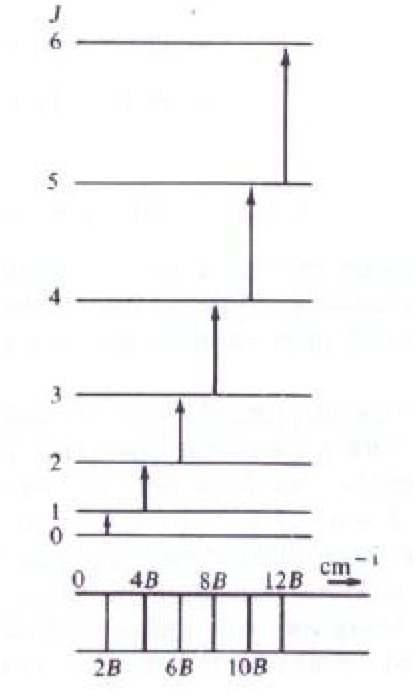


Fig. 3.3 Allowed transition between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

Selection rule for rigid diatomic rotator is given as:

$$\Delta J = \pm 1 \qquad \ldots\ldots 3.17$$

3.5.2 The Intensities of spectral lines

The relative intensities of spectral lines depends upon the relative populations of the energy levels. Even at room temperature many of the diatomic molecules are present in the excited state energy levels. Since the energy level population is given by the Boltzmann distribution, the intensity of rotational lines is evidently proportional to the Boltzmann distribution of molecules in the rotational energy levels, i.e.,

$$\text{Intesity} \propto \frac{N_J}{N_0} = e^{-E_J/kT} \qquad \ldots\ldots 3.18$$

Rotational energy levels are, however, degenerate, their degeneracy (g_J) for a diatomic molecule being given by

$$g_J = 2J + 1 \qquad \ldots\ldots 3.19$$

In other words, for a given value of J, the energy level is(2J + 1)-fold degenerate. For J = 0, $g_J = 1$; for $g_J = 1$, $g_J = 3$, for J=2, $g_J = 5$; and so on.

Hence, the intensity of rotational spectral lines is determined by the product of the degeneracy factor and the Boltzmann exponential factor.

Thus,

$$\text{Intesity} \propto \frac{N_J}{N_0} = (2J + 1)e^{-E_J/kT} \qquad \ldots\ldots 3.20$$

$$\text{Since} \qquad E_J = hcF(J) \qquad \ldots\ldots 3.21$$

$$\text{and} \qquad F(J) = BJ(J + 1) \qquad \ldots\ldots 3.22$$

$$\text{we have } N_J/N_0 = 2J(J + 1)e^{-BJ(J+1)hc/kT} \qquad \ldots\ldots 3.23$$

The quantity N_J/N_0 is plotted versus J for a rigid diatomic molecule at room temperature in fig.3.4.

We see that the relative intensity passes through a maximum. It can be shown that the value of J corresponding to the maximum in population is given by

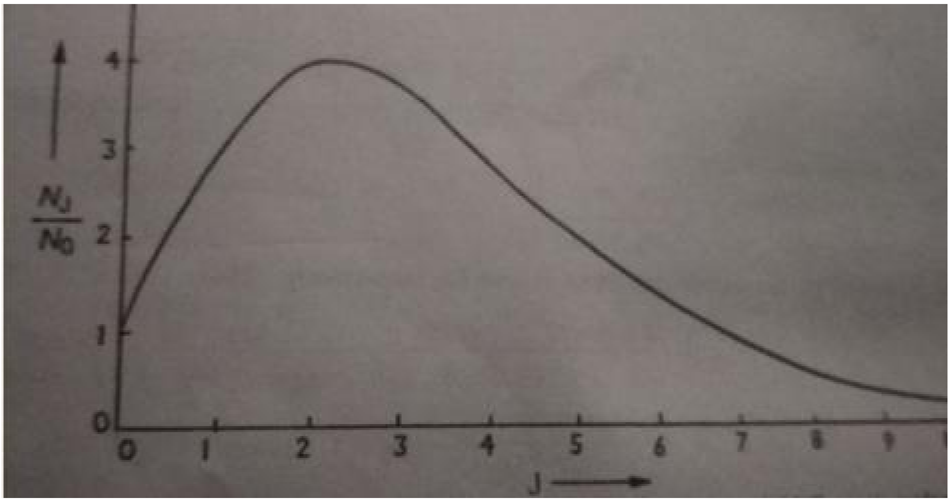


Fig.3.4 Plot of relative Boltzmann population versus J for a rigid diatomic molecule

$$J_{max} = \left(\frac{kT}{2hcB}\right)^{\frac{1}{2}} - \frac{1}{2} \qquad \ldots\ldots 3.24$$

The J_{max} should be rounded off to the nearest integral value.

3.5.3 The Effect of isotopic substitution

When a particular atom in a molecule is replaced by its isotope-an element identical in every way except for its atomic mass-the resulting substance is identical chemically with the original. In particular there is no appreciable change in internuclear distance on isotopic substitution. There is, however, a change in total mass and hence in the moment of inertia and B value for the molecule.

Considering CO as an example, we see that on going from $^{12}C\ ^{16}O$ to $^{13}C\ ^{16}O$ there is a mass increase and hence a decrease in the B value. If we designate the ^{13}C molecule with a prime we have $B > B^{I}$. This change will be reflected in the rotational energy levels of the molecule. Fig 3.5.

Observation of this decreased separation has led to the evaluation of precise atomic weights. Gilliam et al., as already stated, found the first rotational absorption of $^{12}C\ ^{16}O$ to be at

3.84235 cm^{-1}, while that of to $^{13}C\ ^{16}O$ was at 3.67337 cm^{-1}. The values of B determined from these figures are:

B = 1.92118 cm^{-1} and B^I = 1.82669 cm^{-1}

where the prime refers to the heavier molecule. We have immediately:

$$\frac{B}{B'} = \frac{h}{8\pi^2 I_C} . \frac{8\pi^2 I'_C}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12.00, we have:

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.999m'}{15.9994 + m'} \times \frac{12 + 15.9994}{12 \times 15.9994}$$

From which m', the atomic weight of carbon-13, is found to be 13.00007. This is within 0.02 percent of the best value obtained in other ways.

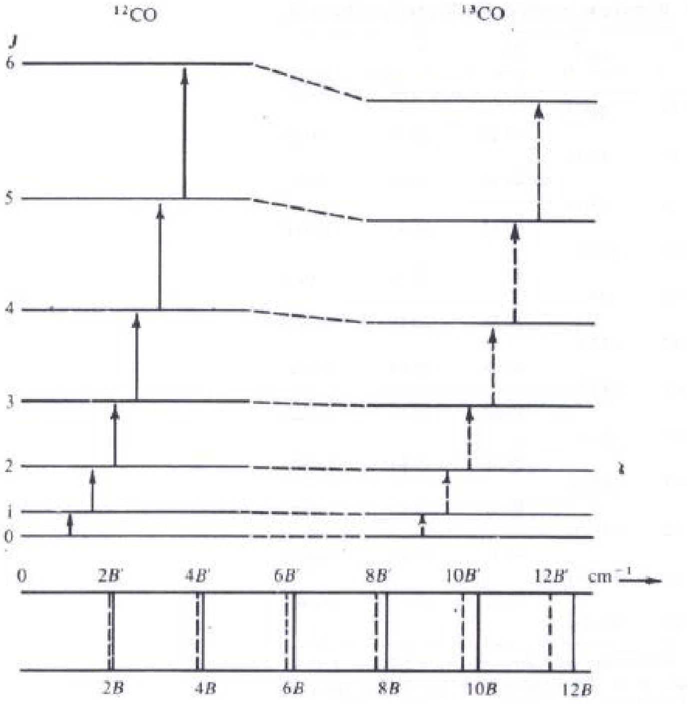


Fig. 3.5 The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as CO.

3.5.4 The Non-rigid rotator

So far we have considered the bond in a diatomic molecule to be a rigid bond. But this is only an approximation. However, all bonds are elastic to some extent. The elasticity results in some changes which are as follows:

(i) An elastic bond may have some vibrational energy.

(ii) Another consequence of elasticity is that the quantities r and B vary during a vibration.

3.5.5 The spectrum of a non-rigid rotator

The Schrodinger wave equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2\, J$$

or $$\varepsilon_J = {}^{E_J}\!/_{hc} = BJ\,(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \qquad \ldots\ldots 3.25$$

where the rotational constant, B, is as defined previously, and the centrifugal distortion constant, D, is given by:

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1} \qquad \ldots\ldots 3.26$$

which is positive quantity. Equation (2.24) applies for a simple harmonic field only; if the force field is anharmonic, the expression becomes:

$$\varepsilon_J = BJ\,(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \ \ldots.\text{cm}^{-1} \qquad \ldots\ldots 3.27$$

where H,K, etc., are small constants dependent upon the geometry of the molecule. They are, however, negligible compared with D and most modern spectroscopic data are adequately fitted by Eq. (3.25).

From the defining equations of B and D it may be shown directly that:

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\varpi^2} \qquad \ldots\ldots 3.28$$

where ϖ is the vibrational frequency of the bond.

Fig. 3.6 shows, much exaggerated, the lowering of rotational levels when passing from rigid to the non-rigid diatomic molecule. The spectra also compared, the dashed lines connecting corresponding energy levels and transitions of the rigid and the non-rigid molecules. It should be noted that the selection rule for the latter is still $\Delta J = \pm 1$.

We may easily write an analytical expression for the transitions:

$$\epsilon_{J+1} - \epsilon_J = \tilde{\upsilon}_J = B[(J+1)(J+2) - J(J+1)] - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \quad \ldots\ldots 3.29$$

$$= 2B(J+1) - 4D(J+1)^3 \quad cm^{-1}$$

where $\tilde{\upsilon}_J$ represents equally the upward treansition from J to J+1, or the downward from J+1 to J. Thus we see analytically, and from Fig. 3.6, that the spectrum of the elastic rotor to similar to that of rigid molecule except that each line is displayed slightly to low frequency, the displacement increasing with $(J+1)^3$.

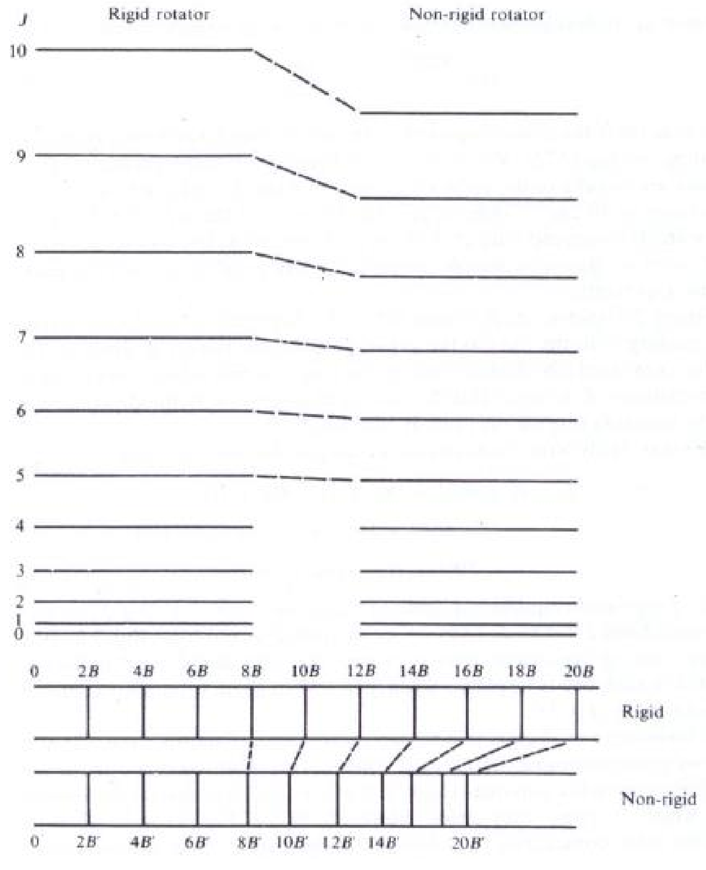


Fig. 3.6 the change in rotational energy levels and spectrum when passing from a rigid to a non-rigid diatomic molecule.

3.6 DETERMINATION OF BOND LENGTH FROM MICROWAVE DATA

For the sake of simplicity, consider the gaseous linear molecule OCS for which we want to determine the two bond distances 0-C and C-S. this can be done by isotopic substituation method. Consider first the molecule $^{16}O^{12}C^{32}S$. (Fig.3.7).

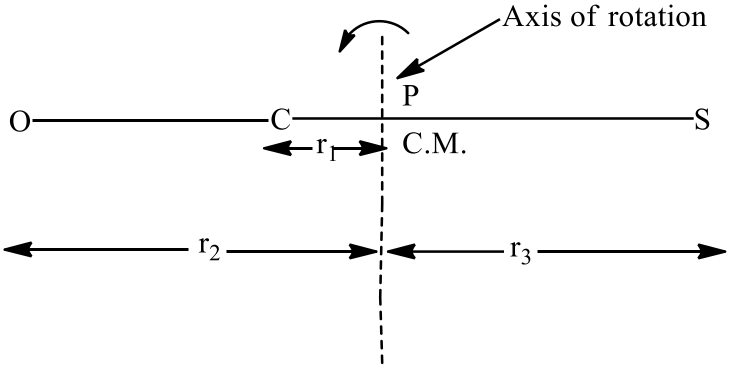


Fig.3.7 The rotation of $^{16}O^{12}C^{32}S$ molecule about an axis of rotation passing through its centre of mass (C.M)

Since the centre of mass is at P(from where the various distances are measured),

$$m_C r_1 + m_O r_2 = m_S r_3 \qquad \ldots\ldots 3.30$$

The moment of inertia is given by

$$I = m_C r^2{}_1 + m_C r^2{}_2 + m_S r^2{}_3 \qquad \ldots\ldots 3.31$$

$$\text{Also,} \quad r_2 = r_{CO} + r_1 \quad r_3 = r_{CS} - r_1 \qquad \ldots\ldots 3.32$$

where r_{CO} and r_{CS} are the two interatomic distances to be determined. Substituting Eqs.3.32 into Eq.3.30,

we have

$$m_C r_1 + m_O (r_{CO} + r_1) = m_S (r_{CS} - r_1) \qquad \ldots\ldots 3.33$$

On rearranging,

$$(m_C + m_O + m_S) r_1 = m_S r_{CS} - m_O r_{CO} \qquad \ldots\ldots 3.34$$

Since $m_C + m_O + m_S$ = M(the mass of OCS molecule), hence,

$$\mathrm{Mr_1 \;=\; m_S r_{CS} \;-\; m_O\, r_{CO}}$$

$$\therefore \mathrm{r_1} \;= \frac{\mathrm{m_S r_{CS} - \; m_O\, r_{CO}}}{\mathrm{M}} \qquad \ldots\ldots 3.35$$

By Substituting we have

$$\mathrm{I \;=\; m_C r^2{}_1 + m_O(r_{CO} + \;\; r_1\,)^2 \;+\;\; m_S(r_{CS} - \;\; r_1\,)^2} \qquad \ldots\ldots 3.36$$

we obtain

$$\mathrm{I} = \frac{\mathrm{m_S r^2{}_{CS} - m_O r^2{}_{CO} + 2m_O m_S r_{CO} r_{CS} - m_S r^2{}_{CS}}}{\mathrm{M}} \qquad \ldots\ldots 3.37$$

Eq.3.37 contains the unknowns $\mathrm{r_{CO}}$ and $\mathrm{r_{CS}}$.

Now we make an important assumption that isotopic substitution does not alter the interatomic distances. Applying this assumption to the $^{16}O^{12}C^{34}S$ molecule, we obtain a similar expression for the moment of inertia $I'$of this molecule:

$$\mathrm{I'} = \frac{\mathrm{m_S r^2{}_{CS} - m_O r^2{}_{CO} + 2m_O m_S r_{CO} r_{CS} - m_S r^2{}_{CS}}}{\mathrm{M}} \qquad \ldots..3.38$$

Thus, we can obtain both I and I' from the microwave spectra of $^{16}O^{12}C^{32}S$ and $^{16}O^{12}C^{34}S$ and from these moments of inertia, the unknown r_{CO} and r_{CS} can be determined.

3.7 ROTATIONAL SPECTRA OF POLYATOMIC MOLECULES

Let us first consider the different classes of molecules, their quantized energy levels, selection rules and rotational spectra.

3.7.1 Linear molecules

We have already seen that diatomic molecules show rotational spectra in which the lines are equally spaced and the rotational constant *B* can be extracted from the spacings. This allows us to calculate the moment of inertia and, consequently, the bond distance. Exactly the same energy level expression and selection rules hold for linear polyatomic molecules.

Thus, for diatomic (and other linear polyatomic molecules), $I_A = 0$ and $I_B = I_C$ and linear molecules have only two rotational degrees of freedom (all other molecules have three). In general, the rotational energy is contained in three dimensions, i.e.

$$E_{rot} = E_A + E_B + E_C = \frac{L^2{}_A}{2I_A} + \frac{L^2{}_B}{2I_B} + \frac{L^2{}_C}{2I_C} \qquad \dots\dots 3.39$$

We have seen that $I_A = 0$ for linear molecules, which implies that $L_A = I_A\omega$ is also zero. Equation 3.39 becomes

$$E_{rot} = \frac{L^2{}_B}{2I_B} + \frac{L^2{}_C}{2I_C} = \frac{L^2{}_B + L^2{}_C}{2I_B} \qquad \dots\dots 3.40$$

since $I_B = I_C$. Moreover, the total angular momentum squared is equal to the sum of the components, i.e.

$$L^2 = L^2{}_A + L^2{}_B + L^2{}_C = L^2{}_B + L^2{}_C, \qquad \text{since } L_A = 0$$

Therefore, equation (2) can be rewritten as

$$E_{rot} = \frac{L^2}{2I_B} = \frac{L^2}{2I} \qquad \dots\dots 3.41$$

if we let $I = I_B = I_C$. This is the expression we have been using for diatomic molecules.

We have seen that the energy levels are quantized and the allowed energy levels are

$$E_J = \frac{J(J+1)\hbar^2}{2I} = BJ(J+1) \qquad \dots\dots 3.42$$

We now move on to polyatomic linear molecules. Everything else is the same, except for the following:

(1) The masses are larger, and so are the moments of inertia. Hence, the rotational constants are smaller (~ 1 cm^{-1}) for polyatomic molecules as compared to diatomic molecules (~ 10 cm^{-1}).

(2) The selection rules remain the same. Only those molecules which possess a permanent dipole moment are microwave active. Thus, molecules like ethyne (H-C≡C=H) and carbon dioxide (O=C=O) are microwave inactive, while molecules lacking a centre of symmetry, such as H-C≡N and O=C=S, are microwave active. The selection rule $\Delta J = \pm 1$ is also the same and this

means that the rotational spectrum consists of equally spaced lines, but the spacing is smaller because of the smaller rotational constants.

(3) Molecules like OCS (fig.3.8) have two bond lengths to determine, but there is only one moment of inertia. The problem is solved by taking another isotopic form, which provides us with another equation to solve for the two unknowns.

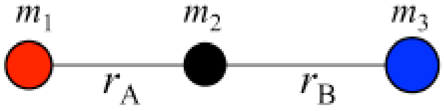


Fig. 3.8 A representation of a linear triatomic molecule with all three atoms different

If we assume that r_A and r_B are not altered by isotopic substitution, we can solve simultaneous equations for these bond lengths. One need not perform any more experiment, since ^{34}S is present to the extent of 4% in natural sulphur. For example, from data for $^{16}O-^{12}C-^{34}S$ and $^{16}O-^{12}C-^{32}S$ we get the following bond lengths: O-C: 0.1164 nm; C-S: 0.1559 nm.

3.7.2 Spherical top molecules

For these molecules, all three directions are equal. Thus

$$I_A = I_B = I_C$$

Hence

$$L_A = L_B = L_C$$

$$E_{rot} = \frac{L^2{}_A}{2I_A} + \frac{L^2{}_B}{2I_B} + \frac{L^2{}_C}{2I_C} = \frac{L^2{}_B + L^2{}_C + L^2{}_C}{2I_A} = \frac{L^2}{2I_A} \qquad \ldots\ldots 3.43$$

$$\because\ I_A = I_B = I_C \text{ and, } L^2 = L^2{}_A + L^2{}_B + L^2{}_C$$

The quantization condition applied to this equation yields the allowed energy levels

$$E_J = \frac{\hbar^2}{2I_A} J(J+1) = AJ(J+1) \qquad \ldots\ldots 3.44$$

$$\text{where,} \quad A = \frac{\hbar^2}{2I_A}$$

Since the three directions are equal, A = B = C, we could have equivalently written equation 2.44 in terms of B or C. However, by convention we follow the alphabetic order, and, here, since A is non-zero, it is conventional to write equation 2.44 in terms of A. However, since these molecules have zero dipole moment, they are microwave inactive.

3.7.3 Symmetric top Mmolecules

(i) Prolate symmetric tops

These molecules are characterized by

$$I_A < I_B = I_C$$

and

$$A > B = C$$

The expression for the rotational energy thus becomes

$$E_{rot} = \frac{L^2{}_A}{2I_A} + \frac{L^2{}_B}{2I_B} + \frac{L^2{}_C}{2I_C} = \frac{L^2{}_A}{2I_A} + \frac{L^2{}_B + L^2{}_C}{2I_B} = \frac{L^2{}_A}{2I_A} + \frac{L^2 - L^2{}_A}{2I_B} \quad \ldots\ldots 3.45$$

$$\because \; I_B = I_C \text{ and,} L^2 = L^2{}_A + L^2{}_B + L^2{}_C$$

We know that the total rotational angular momentum is quantized and its component in one of the directions is also quantized, thus

$$\hat{L}^2 \varphi_{rot} = J(J+1)\hbar^2 \varphi_{rot} \quad \ldots\ldots 3.46$$

$$L_z \varphi_{rot} = M_J \hbar \varphi_{rot}$$

In the absence of an external field, the 2J+1 values of M_J are all degenerate, but in the presence of an external field, the direction of the field becomes the unique direction and the degeneracy is lifted. In molecules that have axial symmetry, the unique direction is defined by this internal axis, in this case I_A. The rotational energy levels are quantized with respect to their components in this direction, too. We introduce another quantum number K, which has the same meaning as M_J, but the quantization is with respect to the internal axis. Like M_J, there are 2J+1 values of K. Thus, we may also add to equation 3.46.

$$L_A\varphi_{rot} = K\hbar\varphi_{rot} \qquad \ldots\ldots 3.47$$

with K = 0, ±1, ±2,…±J. Unlike an external axis, where the degeneracy is removed only on application of an external field, the internal axis is fixed on the molecule and the energy depends on K.

Substituting equations 3.46 and 3.47 in 3.45, we obtain

$$E_{rot} = = \frac{L^2{}_A}{2I_A} + \frac{L^2 - L^2{}_A}{2I_B} = \frac{K^2\hbar^2}{2I_A} + \frac{J(J+1)\hbar^2 - K^2\hbar^2}{2I_B}$$

$$= K^2\left(\frac{\hbar^2}{2I_A} - \frac{\hbar^2}{2I_B}\right) + \frac{(J+1)\hbar^2}{2I_B} \qquad \ldots\ldots 3.48$$

$$= K^2(A - B) + J(J+1)B$$

This expression is similar to that of a linear molecule, but with an additional term depending on K. All levels are displaced by an amount dependent on K^2. Thus, each level is split into J+1 levels. Since, for a prolate top molecule, A > B, this implies that each level is shifted up by an amount proportional to K^2 (Fig.3.9).

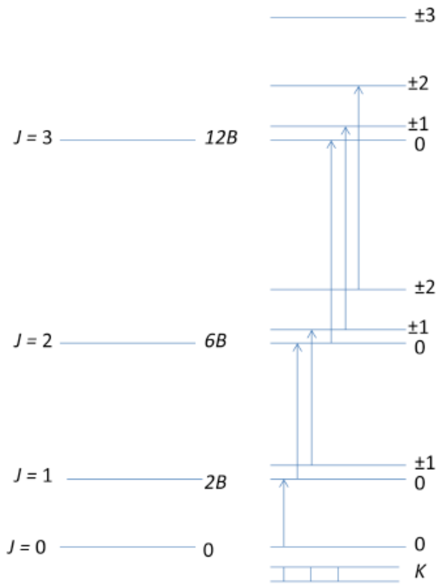


Fig. 3.9 Energy levels of a prolate top molecule

The selection rules are $\Delta J = \pm 1$

$\Delta K = 0$

The allowed transitions are shown in Fig.3.9. The ΔK= 0 selection rule ensures that the microwave spectrum consists of equally spaced lines just like that for linear molecules. The only difference is that each line here is actually a set of J+1 transitions of the same energy.

(ii) Oblate top molecules

For oblate top molecules,

$$I_A = I_B < I_C$$

and

$$A = B > C$$

Exactly the same type of reasoning, as above, results in the oblate analogue of equation 3.48

$$E_{rot} = K^2(C - B) + J(J + 1) \qquad \ldots\ldots 3.49$$

However, since C – B is negative, each level will be lowered by an amount proportional to K^2 , but because of the ΔK = 0 selection rule, the spacing will remain 2B, but each peak will consist of J+1 superimposed lines.

3.7.4 Asymmetric top molecules

Their rotational spectra are very complex, but most molecules can be classified as either near prolate or near oblate. Reduction in symmetry removes the ±K degeneracy, and each rotational J level is split into 2J+1 levels corresponding to different K.

We have seen that the rotational energy depends on the *J* quantum number, but each level has a degeneracy of 2J+1. When an external field is applied, this degeneracy is removed and the energy now also depends on the MJ quantum number. This effect is known as the Zeeman effect when the applied field is magnetic, and Stark effect if it is electric. Here we shall discuss the latter, which finds application in determination of accurate dipole moments of linear and symmetric top molecules.

3.8 APPLICATIONS OF ROTATIONAL SPECTRA

By determining the frequency separation ($\Delta\bar{\upsilon}$), it is possible to calculate the moment of inertia I of the molecule, using equation $B=h/8\pi^2Ic$. Then knowing the masses of the atoms present in the diatomic molecule, it is possible to calculate the distance between the atoms, r_0 (i.e., internuclear distance or bond length) using equation

$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^{\,2}$$

3.9 SUMMARY

- Pure rotational transitions are observed in the microwave region.
- There are two selection rules governing rotational transitions

  The gross selection rule is that the molecule must possess a permanent dipole moment.

  The second selection rule is that the rotational quantum number must change by one unit.
- The absorption spectrum gives rise to a spectrum containing lines with spacing equal to twice the rotational constant.
- The degeneracy of an energy level increases linearly with J, but the population decreases with increasing J. As a result, the population goes through a maximum at some J.
- The rotational level having the largest population shifts to higher J when the temperature is increased.
- It also depends on the value of the rotational constant. Smaller the rotational constant, larger is the Jmax.
- Microwave or rotational spectroscopy is applied to obtain accurate bond distances of heteronuclear diatomic molecules.
- Rotational lines of diatomic molecules are equally spaced and yield rotational constants, which are inversely proportional to the moment of inertia.

- The moment of inertia is proportional to the reduced mass of the molecule and the square of the bond distance.
- Isotopic substitution does not affect the bond length and, for molecules whose bond distances are known, the isotopic masses can be determined.
- The spacing between rotational lines decreases with increasing quantum number due to centrifugal distortion.
- Linear molecules exhibit rotational spectra in which the spacing between adjacent lines is 2B, from which the moment of inertia and bond length of a diatomic molecule can be extracted.
- However, for polyatomic molecules, there is more than one bond length to be determined, and only one rotational constant that can be obtained.
- Spherical top molecules do not possess a dipole moment and are hence microwave inactive.

3.10 TERMINAL QUESTIONS

1. Explain the relative intensities of the lines obtained in a pure rotational spectrum.

2. What is the effect of isotopic substitution on rotational spectra.

3.Discuss the rotational spectrum of Diatomic rigid rotator.

4. Explain the determination of bond length with the help of rotational spectroscopy.

5. Discuss the rotational spectrum of non- rigid rotator.

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UNIT 4: VIBRATIONAL SPECTROSCOPY-I: DIATOMIC MOLECULES

CONTENTS:

4.1 INTRODUCTION

Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemical substances. Samples may be solid, liquid, or gas. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) to produce an infrared spectrum. An IR spectrum can be visualized in a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wave numbers), with the symbol cm^{-1}. Units of IR wavelength are commonly given in micrometers (formerly called "microns"), symbol μm, which are related to wave numbers in a reciprocal way. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14000–4000 cm^{-1} (0.7–2.5 μm wavelength) can excite overtone or harmonic molecular vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

Infrared spectroscopy exploits the fact that molecules absorb frequencies that are characteristic of their structure. These absorptions occur at resonant frequencies, i.e. the frequency of the absorbed radiation matches the vibrational frequency. The energies are affected by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling. In particular, in the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are associated with the normal modes corresponding to the molecular electronic ground state potential energy surface. The resonant frequencies are also related to the strength of the bond and the mass of the atoms at either end of it. Thus, the frequencies of the vibrations are associated with a particular normal mode of motion and a particular bond type.

4.2 OBJECTIVES

After going through this unit you will be able to:

- Understand the essentials of Simple Harmonic Motion
- Understand the potential energy function of a real bond.
- Understand the concept of anharmonicity and the modified selection rules.
- Understand the meaning of fundamentals and overtones.
- Calculate dissociation energies of molecules.
- The breakdown of the Born-Oppenheimer approximation
- The influence of nuclear spin on rotational spectrum

4.3 THE VIBRATING DIATOMIC MOLECULE

4.3.1 The energy of diatomic molecule

When two atoms combine to form a stable covalent molecule, for example HCl, they may be said to do so because of some internal electronic reaarangement. There is repulsion between the positively charged nuclei of both the atoms, and between the negative electron clouds, on the other there is an attraction between the nucleus of an atom and the electrons of other, and vive versa. The two atoms settle at a mean internuclear distance such that these forces are just balanced and the total energy of the whole system is a minimum. Squeezing the atoms more closely together will cause the repulsive force to rise rapidly, while pulling them apart is resisted by the attractive force. Any attempt to distort the bond length requires an input of energy and we may plot energy against internuclear distance as in Fig.4.1, where we have ‘anchored’ the Cl atom on one axis and imagine pushing and pulling the H atom closer to or further from the Cl a bigger push or pull results in raising the energy more. At the energy minimum the internuclear distance is referred to as the equilibrium distance r_{req}, or more simply as the bond length.

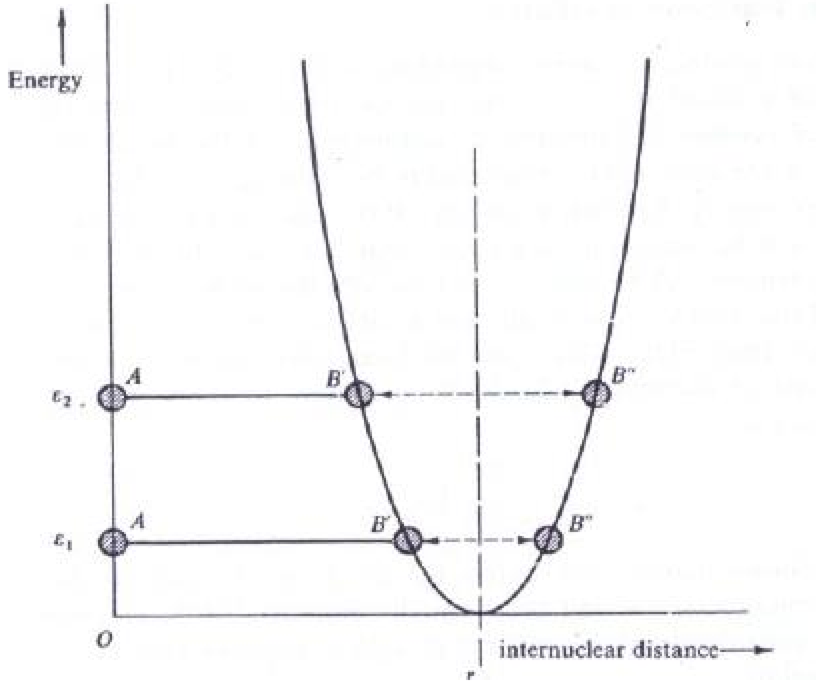


Fig. 4.1 Parabolic curve of energy plotted against the extension and compression of a spring obeying hook's law.

The compression and extension of a bond may be likened to the behavior of a spring, and we may extend the analogy by assuming that the bond, like a spring, obeys hook's law. We may write:

$$f = -k\left(r - r_{eq.}\right) \qquad \ldots\ldots 4.1$$

where f is the restoring force , k the force constant, and r the internuclear distance. In this case the energy curve is parabolic and has the form

$$E = \frac{1}{2}k(r - r_{eq.})^2 \qquad \ldots\ldots 4.2$$

This model of a vibrating diatomic molecule- the so called simple harmonic oscillator model- while only an approximation, forms an excellent starting point for the discussion of vibrational spectra.

4.3.2 The simple harmonic oscillator

In Fig.4.1 we have plotted the energy in the form of Eq.(4.2), i.e. as a parabola. The zero of curve and equation is at r = r_{eq}, and any energy in excess of this, for example at ε_2, arises because of extension or compression of the bond. The figure shows that if one atom (Cl) is considered to be stationary on the r = 0 axis, the other (H) will oscillate between H' and H''. in the case of HCl, it is a good approximation to say that, during vibrations, the heavy Cl atom stays virtually still and it is the much lighter H atom which moves. However, only the distance between the two atoms is important and for any diatomic molecule we can always imagine ourselves to be sitting on one atom and watching the other move- from our point of view the atom we are on is stationary and can be assumed fixed on the r = 0 axis. Thus diagrams like Fig.4.1 apply to any diatomic molecule.

If the energy of HCl molecule of Fig.4.1 is increased to ε_1 the oscillation will become more vigorous-that is to say the degree of compression and extension will be greater-but the vibrational frequepnt endency will not change. An elastic bond, like a spring, has a certain intrinsic vibrational frequency, dependent on the mass of the system and the force constant, but is independent of the amount of distortion. Classically it is simple to show that the oscillation frequency is:

$$\omega_{osc.} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ \text{Hz} \qquad \ldots\ldots 4.3$$

where μ is the reduced mass of the system. To convert this frequency to wave numbers, the unit most usually employed in vibrational spectroscopy, we must divide by the velocity of light, c, expressed in cm s^{-1}, obtaining:

$$\varpi_{osc.} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ \text{cm}^{-1} \qquad \ldots\ldots\ 4.4$$

Vibrational energies, like all other molecular energies, are quantized and the allowed vibrational energies for any particular system may be calculated from the Schrodinger equation. For the simple harmonic oscillator these out to be:

$$\mathrm{E}_v = \left(v + \frac{1}{2}\right) \mathrm{h}\omega_{\mathrm{osc.}} \text{ joules } \quad (v = 0,1,2, \ldots \qquad \ldots\ldots 4.5$$

where v is called the vibrational quantum number. Converting to the spectroscopic units, cm^{-1}, we have:

$$\varepsilon_v = \frac{\mathrm{E}_v}{\mathrm{hc}} = \left(v + \frac{1}{2}\right) \varpi_{\mathrm{osc.}} \ \mathrm{cm}^{-1} \qquad \ldots\ldots 4.6$$

as the only energies allowed to a simple harmonic vibrator. Some of these are shown in Fig.4.2.

In particular, we should notice that the lowest vibrational energy, obtained by putting $v = 0$ in Eq.4.5 or 4.6, is

$$\mathrm{E}_0 = \frac{1}{2} \mathrm{h}\omega_{\mathrm{osc.}} \text{ joules}$$

$$\text{or} \qquad \varepsilon_0 = \frac{1}{2} \varpi_{\mathrm{osc.}} \ \mathrm{cm}^{-1} \qquad \ldots\ldots 4.7$$

The implication is that the diatomic molecule can never have zero vibrational energy; the atoms can never be completely at rest relative to each other. The quantity $\frac{1}{2}\mathrm{h}\omega_{\mathrm{osc.}}\ \mathrm{cm}^{-1}$ is known as the zero-point energy; it depends on the classical vibrational frequency and hence on the strength of the chemical bond and the atomic masses.

Further use of Schrodinger equation leads to the simple selection rule for the harmonic oscillator undergoing vibrational changes:

$$\Delta v = \pm 1 \qquad \ldots\ldots 4.8$$

Applying the selection rule we have immediately:

$$\varepsilon_{v+1 \to v} = \left(v + 1 + \tfrac{1}{2}\right) \varpi_{\mathrm{osc.}} - \left(v + \tfrac{1}{2}\right) \varpi_{\mathrm{osc.}} = \varpi_{\mathrm{osc.}} \quad \mathrm{cm}^{-1} \qquad \ldots\ldots 4.9$$

Since the vibrational levels are equally spaced, transitions between any two neighbouring states will give rise to the same energy change. Further, since the difference between energy levels expressed in cm^{-1} gives directly the wavenumber of the spectral line absorbed or emitted

$$\bar{\upsilon}_{\mathrm{spectroscopic}} = \varepsilon = \varpi_{\mathrm{osc.}} \quad \mathrm{cm}^{-1} \qquad \ldots\ldots 4.10$$

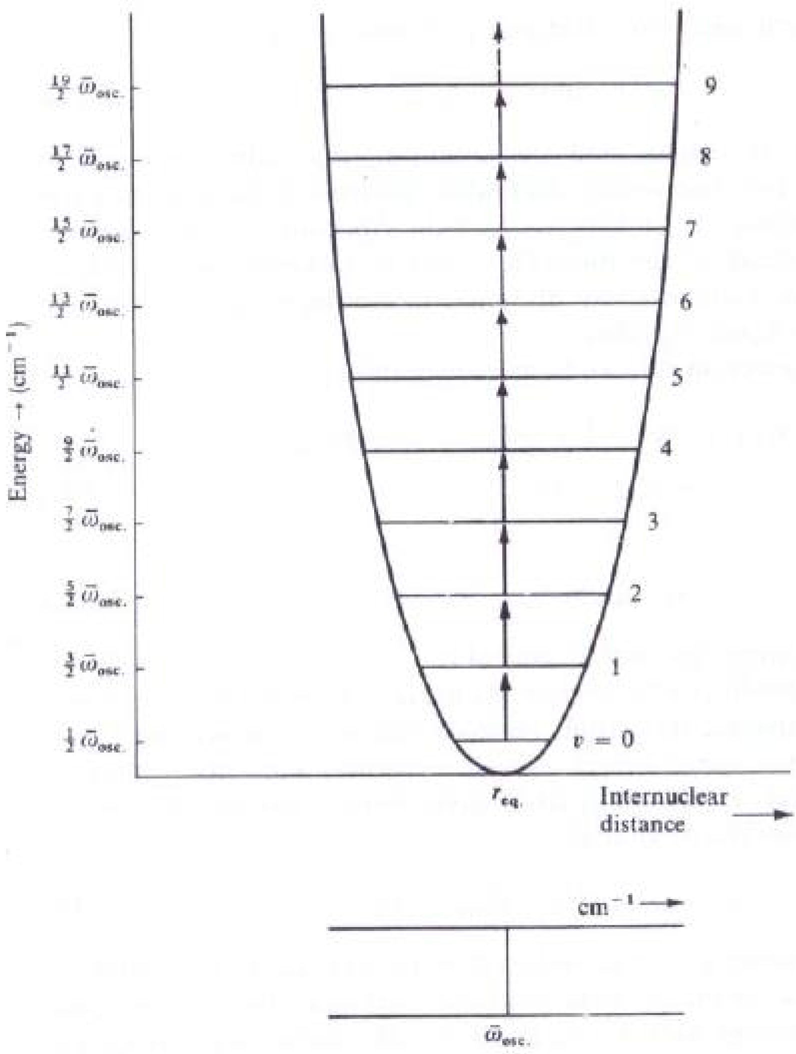


Fig. 4.2 The vibrational energy levels and allowed transitions between them for a diatomic molecule undergoing simple harmonic motion.

4.3.3 The anharmonic oscillator

Real molecule does not obey exactly the laws of simple harmonic motion; real bonds, although elastic, are not so homogenous as to obey Hook's law. If the bonds between atoms are stretched, for instance, there comes a point at which it will break-the molecule dissociates into atoms. Thus although for small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes-say greater than ten percent of the bond length-a much more complicated behavior must be assumed. Figure 4.3 shows, diagrammatically, the shape of energy curve for a typical diatomic molecule; together with (dashed) the ideal, simple harmonic parabola.

A purely empirical expression which fits this curve to a good approximation was derived by P.M.Morse, and is called the Morse function:

$$E = D_{eq.}[1 - \exp\{a(r_{eq.} - r)\}]^2 \qquad \ldots\ldots 4.11$$

where a is constant for a particular molecule and $D_{eq.}$ is the dissociation energy.

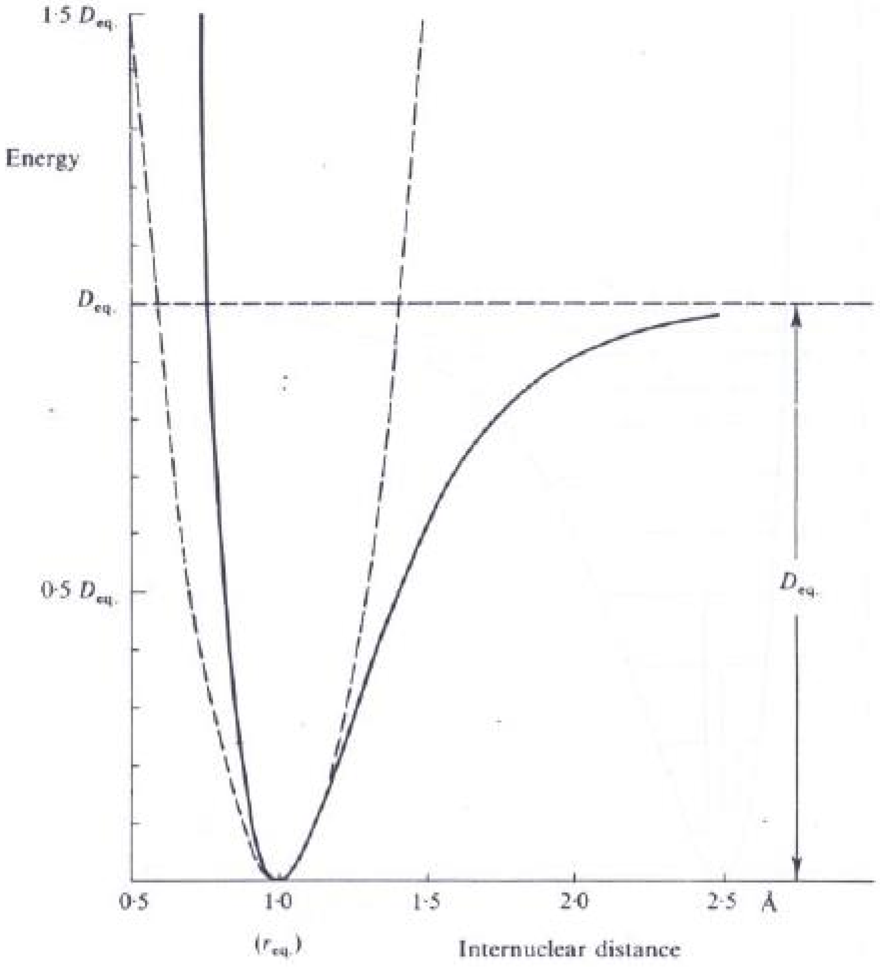


Fig. 4.3 the Morse curve: the energy of a diatomic molecule undergoing anharmonic extensions and compressions.

When Eq.4.11 is used instead of Eq.4.2 in the Schrodinger equation, the pattern of the allowed vibrational energy levels is found to be:

$$\varepsilon_v = \left(v + \frac{1}{2}\right)\varpi_e - \left(v + \frac{1}{2}\right)^2 \varpi_e \chi_e \ \ \mathrm{cm}^{-1} \quad (v = 0,1,2,\ldots) \qquad \ldots\ldots 4.12$$

where ϖ_e is an oscillation frequency (expressed in wavenumbers) which we shall define more closely below, and χ_e is the corresponding anharmonicity constant, for bond stretching vibrations, is always small and positive (≈+0.01), so that the vibrational levels crowd more closely together with increasing v. some of these levels are sketched in Fig.4.4.

It should be mentioned that Eq.4.12 like 4.11, is an approximation only; more precise expressions for the energy levels require cubic, quartic, etc., terms in (v+1/2) with anharmonicity constants y_e, z_e, etc., rapidly diminishing in magnitude. These terms are important only at large values of v, and we shall ignore them.

If we rewrite Eq.4.12, for the anharmonic oscillator as:

$$\varepsilon_v = \varpi_e \left\{1 - \chi_e\left(\mathrm{v} + \frac{1}{2}\right)\right\}\left(v + \frac{1}{2}\right) \qquad \ldots\ldots 4.13$$

and compare with energy levels of harmonic oscillator, we see that we can write:

$$\varpi_{\mathrm{osc.}} = \varpi_e \left\{1 - \chi_e\left(v + \frac{1}{2}\right)\right\} \qquad \ldots\ldots 4.14$$

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing v.

The selection selection rules for anharmonic oscillator are found to be:

$$\Delta v = \pm 1\,, \quad \pm 2, \pm 3, \ldots$$

There is a possibility of larger jumps in addition to what is observed in the harmonic oscillator. The larger jumps occur with decreasing probability with only the first three values of Δv (±1, ±2, ±3), showing observable intensity. These jumps are known as the fundamental, first and second overtone, respectively.

The next aspect to consider is the population. For rotational spectroscopy, several rotational energy levels are occupied, since the spacing between the energy levels is small. Applying the Boltzmann formula at room temperature (300 K) and considering IR radiation of frequency 3×1013 s^{-1}, one notes that

$$\frac{\mathrm{N_{v=1}}}{\mathrm{N_{v=0}}} = \exp\left\{-\frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 10^{3}}{1.38 \times 10^{-23} \times 300}\right\} = 0.008$$

1. $= 0 \rightarrow v = 1, \Delta v = +1$, with considerable intensity (the fundamental transition)

$$\Delta\varepsilon = \varepsilon_{v=1} - \varepsilon_{v=0} = \left(1+\frac{1}{2}\right)\varpi_e - \chi_e\left(1+\frac{1}{2}\right)^2\varpi_e - \left\{\frac{1}{2}\varpi_e - \left(\frac{1}{2}\right)^2\chi_e\varpi_e\right\}$$

$$= \varpi_e(1-2\chi_e)\mathrm{cm}^{-1} \qquad \ldots\ldots 4.15\mathrm{a}$$

2. $v = 0 \rightarrow v = 2, \Delta v = +2$, with small intensity (the first overtone transition)

$$\Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=0} = \left(2+\frac{1}{2}\right)\varpi_e - \chi_e\left(2+\frac{1}{2}\right)^2\varpi_e - \left\{\frac{1}{2}\varpi_e - \left(\frac{1}{2}\right)^2\chi_e\varpi_e\right\}$$

$$= 2\varpi_e(1-3\chi_e)\mathrm{cm}^{-1} \qquad \ldots\ldots\ 4.15\mathrm{b}$$

3. $v = 0 \rightarrow v = 3, \Delta v = +3$, with normally negligiblel intensity (the second overtone transition)

$$\Delta\varepsilon = \varepsilon_{v=3} - \varepsilon_{v=0} = \left(3+\frac{1}{2}\right)\varpi_e - \chi_e\left(3+\frac{1}{2}\right)^2\varpi_e - \left\{\frac{1}{2}\varpi_e - \left(\frac{1}{2}\right)^2\chi_e\varpi_e\right\}$$

$$= 3\varpi_e(1-4\chi_e)\mathrm{cm}^{-1} \qquad \ldots\ldots\ 4.15\mathrm{c}$$

4. $v = 1 \rightarrow v = 2, \Delta v = +1$, with normally very weakl intensity (the hot band transition)

$$\Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=1} = \left(2+\frac{1}{2}\right)\varpi_e - \chi_e\left(2+\frac{1}{2}\right)^2\varpi_e - \left\{\frac{3}{2}\varpi_e - \left(\frac{3}{2}\right)^2\chi_e\varpi_e\right\}$$

$$= \varpi_e(1-4\chi_e)\mathrm{cm}^{-1} \qquad \ldots\ldots 4.15\mathrm{d}$$

This transition is so called because increasing the temperature increases its intensity as more molecules go into the $v = 1$ level on raising the temperature. Also, molecules with lower vibrational frequencies are more likely to exhibit hot bands, since for them the population of the higher vibrational levels is higher.

4.4 OVERTONES AND COMBINATION BANDS

4.4.1 Overtones bands

Overtones occur when a vibrational mode is excited from v = 0 to v = 2, which is called the first overtone, or v = 0 to v = 3, the second overtone. The fundamental transitions, v = ±1, are the most commonly occurring, and the probability of overtones rapid decreases as the number of quanta (Δv = ± n) increases. Based on the harmonic oscillator approximation, the energy of the overtone transition would be n times larger than the energy of the fundamental transition frequency, but the anharmonic oscillator calculations show that the overtones are less than a multiple of the fundamental frequency. This is demonstrated with the vibrations of the diatomic HCl in the gas phase:

Table 4.1 HCl vibrational spectrum.

Transition	$\bar{\upsilon}_{\text{obs.}}(\text{cm}^{-1})$	$\bar{\upsilon}_{\text{harmonic}}\ (\text{cm}^{-1})$	$\bar{\upsilon}_{\text{anharmonic}}\ (\text{cm}^{-1})$
$0 \rightarrow 1$(fundamental)	2885.9	2885.9	2885.3
$0 \rightarrow 1$(first overtone)	5668.0	5771.8	5665.0
$0 \rightarrow 3$(second overtone)	8347.0	8657.7	8339.0
$0 \rightarrow 4$(third overtone)	10923.1	11543.6	10907.4
$0 \rightarrow 5$(fourth overtone)	13996.5	14429.5	13370.0

4.4.2 Combination bands

Combination bands involve changes in vibrational quantum numbers of more than one normal mode. These transitions are forbidden by harmonic oscillator selection rules, but are observed in vibrational spectra of real systems due to anharmonic couplings of normal modes. Combination bands typically have weak spectral intensities, but can become quite intense in cases where the anharmonicity of the vibrational potential is large. Broadly speaking, there are two types of combination bands.

(i) Difference transition

A difference transition, or difference band, occurs between excited states of two different vibrations. Using the 3 mode example from above, $010 \leftarrow 100$, is a difference transition. For difference bands involving transfer of a single quantum of excitation, as in the example, the frequency is approximately equal to the difference between the fundamental frequencies. The difference is not exact because there is anharmonicity in both vibrations. However the term "difference band" also applies to cases where more than one quantum is transferred, such as, $100 \leftarrow 020$.

Since the initial state of a difference band is always an excited state, difference bands are necessarily "hot bands"! Difference bands are seldom observed in conventional vibrational spectra, because they are forbidden transitions according to harmonic selection rules, and because populations of vibrationally excited states tend to be quite low.

(ii) Sum transition

A sum transition (sum band), occurs when two or more fundamental vibrations are excited simultaneously. For instance, $101 \leftarrow 000$ and , $012 \leftarrow 001$, are examples of sum transitions. The frequency of a sum band is slightly less than the sum of the frequencies of the fundamentals, again due to anharmonic shifts in both vibrations.

Sum transitions are harmonic-forbidden, and thus typically have low intensities relative to vibrational fundamentals. Also, sum bands can be, but are not always, hot bands, and thus may also show reduced intensities from thermal population effects, as described above. Sum bands are more commonly observed than difference bands in vibrational spectra.

4.5 DISSOCIATION ENERGIES FROM VIBRATIONAL DATA

The smallest energy required to break a bond is known as the dissociation energy. Whereas pure vibrational spectra yield inaccurate values of the dissociation energy due to the paucity of data, this is not the case for vibronic transitions, and both ground and excited state dissociation energies can be obtained. The latter are particularly useful since excited states are short-lived.

As shown in Fig.4.4, the ground and excited state potential energies are represented as Morse potential energy curves. We can see that the point of onset of dissociation equals the dissociation energy of the excited state plus the energy of the (0,0) transition, i.e. the energy of the pure electronic transition

$$\bar{\upsilon}_{\text{continuum}} = \bar{D}_0{}' + \tilde{\upsilon}_{0,0} \qquad \ldots\ldots 4.16$$

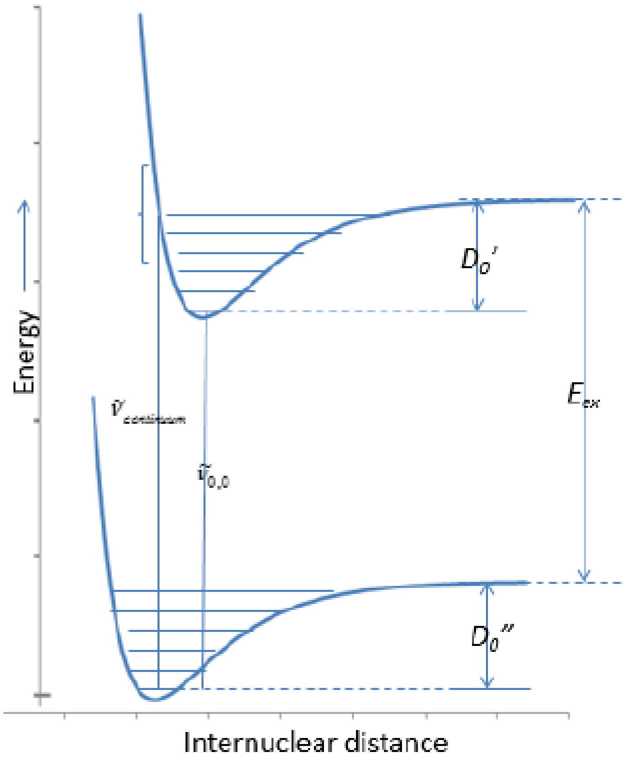


Fig.4.4 Dissociation energy

More often, the dissociation limit is not reached, but a number of vibronic transitions are observed. In such cases, too, the dissociation energies can still be extracted. The separation between adjacent lines of an anharmonic oscillator decreases with increasing vibrational quantum number, until it finally becomes zero when dissociation sets in. Use of the energy expression (eq. 4.17) for an anharmonic oscillator

$$G(v) = \omega_e{}'\left(v + \frac{1}{2}\right) - \chi_e \omega_e{}'\left(v' + \frac{1}{2}\right)^2 \qquad \ldots\ldots 4.17$$

gives $\Delta\bar{\upsilon} = \Delta G\left(v' + \frac{1}{2}\right) = G(v' + 1) - G(v') = \omega_e{}' - 2\chi_e{}'\omega_e{}'(v' + 1) \qquad \ldots\ldots 4.18$

This is the equation of a straight line. If we plot $\Delta\tilde{\upsilon}$ versus $(\upsilon + 1)$, a straight line with slope equal to $-2\chi_e{}'\omega_e{}'$and intercept $\omega_e{}'$ (Fig.4.5) should be obtained. Such a plot is known as a Birge-Sponer plot.

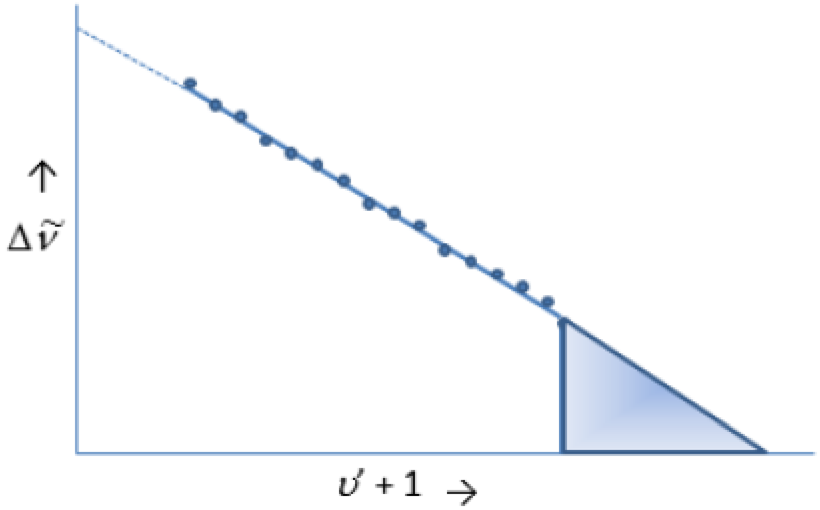


Fig. 4.5 Birge-Sponer plot

Extrapolation to the *x*-axis yields $v_{\max}{}' + 1$, where $v_{\max}{}' + 1$ is the maximum value of the vibrational quantum number for the upper electronic state, from which the continuum limit can be obtained using the values of $\omega_e{}'$ and $\chi_e{}'$obtained from the intercept and slope of the plot.

Alternately, rearrangement of equation (3.18) and setting $\Delta\tilde{\nu}$ equal to zero gives

$$v_{\max}{}' = \frac{1}{2\,\chi_e{}'} - 1 \qquad \ldots\ldots 4.19$$

This is equal to (–Intercept/Slope – 1). Application of eq.4.17 yields the continuum limit, from which the dissociation energy ($\overline{D}_0{}'$) of the upper electronic state can be obtained, or the expression for the spectroscopic dissociation energy of the anharmonic oscillator

$$\overline{D}_e{}' = \frac{\omega_e{}'}{4\,\chi_e{}'} = \frac{(\text{intercept})^2}{2 \times \text{slope}} \qquad \ldots\ldots 4.20$$

can be used. The thermochemical dissociation energy ($\overline{D}_0{}'$) can be obtained by subtracting the zero-point energy

$$\overline{D}_e{}' = \overline{D}_0{}' + \frac{1}{2}\omega_e{}' - \frac{1}{4}\chi_e{}'\,\omega_e{}' \qquad \ldots\ldots 4.21$$

4.6 THE DIATOMIC VIBRATING ROTATOR

Pure vibrational spectra can be observed only in liquids where interactions between molecules inhibit rotation. Since rotational energies are considerably smaller than vibrational energies, the freely moving molecules in the gaseous state are almost always rotating regardless of their vibrational state. Hence, molecules in gaseous state show rotational-vibrational spectra. The rotation and vibration are are, to a first approximation, independent of each other. This, which we shall call the Born-Oppenheimer approximation, is tantamount to assuming that the combined rotational-vibrational energy is simply the sum of separate energies:

$$\mathrm{E_{total}} = \mathrm{E_{rot.}} + \mathrm{E_{vib.}}\ \text{(joules)} \qquad \ldots\ldots 4.22$$

$$\varepsilon_{\mathrm{total}} = \varepsilon_{\mathrm{rot.}} + \varepsilon_{\mathrm{vib.}}\ (\mathrm{cm^{-1}}) \qquad \ldots\ldots\ 4.23$$

Taking the separate expressions for $\varepsilon_{\mathrm{rot.}}$ and $\varepsilon_{\mathrm{vib.}}$ we have:

$$\varepsilon_{\mathrm{J,v}} = \varepsilon_{\mathrm{J}} + \varepsilon_{\mathrm{v}}$$

$$= \mathrm{BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3} + \cdots \left(\mathrm{v} + \frac{1}{2}\right)\varpi_{\mathrm{e}} - \chi_{\mathrm{e}}\left(\mathrm{v} + \frac{1}{2}\right)^2 \varpi_{\mathrm{e}}\ \mathrm{cm^{-1}} \qquad \ldots\ldots 4.24$$

Initially, we shall ignore the small centrifugal distortion constants D, H,etc., and hence write:

$$\varepsilon_{\mathrm{total}} = \varepsilon_{\mathrm{J,v}} = \mathrm{BJ(J+1)} + \left(\mathrm{v} + \frac{1}{2}\right)\varpi_{\mathrm{e}} - \chi_{\mathrm{e}}\left(\mathrm{v} + \frac{1}{2}\right)^2 \varpi_{\mathrm{e}} \qquad \ldots\ldots 4.25$$

The rotational levels are sketched in Fig.4.6 for the two lowest vibrational level, $v = 0$ and $v = 1$. There is, however, no attempt at scale in this diagram since the separation between neighbouring J values is, in fact, only some 1/1000 of that between the v values. Note that since the rotational constant B in Eq.4.18 is taken to be the same for all J and v, the separation between two levels of given J is the same in the $v = 0$ and $v = 1$ states.

It may be shown that the selection rules for the combined motions are the same as those for each separately; therefore we have:

$$\Delta v = \pm 1,\ \pm 2, \text{etc.} \qquad \Delta \mathrm{J} = \pm 1 \qquad \ldots\ldots 4.26$$

In Fig. 4.7 we have drawn some of the relevant energy levels and transitions, designating rotational quantum numbers in the v = 0 states as $\mathrm{J''}$ and in the v = 1 state as $\mathrm{J'}$.

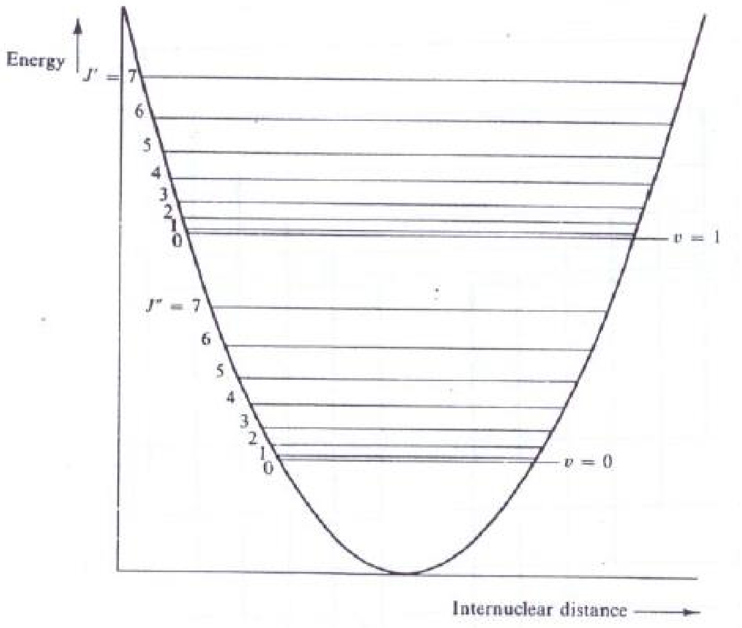


Fig. 4.6 The rotational energy levels for two different vibrational states of a diatomic molecule

Remember that the rotational levels J'' are filled to varying degrees in any molecular population, so the transition shown will occur with varying intensities. This is indicated schematically in the spectrum at the foot of Fig.4.7.

Considering only the $v = 0 \rightarrow v = 1$ transition we have in general:

$$\Delta\varepsilon_{J,v} = \varepsilon_{J'v=1} - \varepsilon_{J''v=0} = BJ'(J'+1) + 1\frac{1}{2}\varpi_e - 2\frac{1}{4}\chi_e\varpi_e - \left\{BJ''(J''+1) + \frac{1}{2}\varpi_e - \frac{1}{4}\chi_e\varpi_e\right\}$$
$$= \varpi_o + B\left(J' - J''\right)\left(J' + J'' + 1\right) \text{cm}^{-1}$$

Where, for brevity, we write ϖ_o for $\varpi_e(1 - 2\chi_e)$.

We should note that taking B to be identical in the upper and lower vibrational states is a direct consequence of the Born-Oppenheimer approximation-rotation is unaffected by vibrational changes.

Now we can have:

1. $\Delta J = +1$,that is $J' = J'' + 1$ or $J' - J'' = +1$; hence

$$\Delta\varepsilon_{J,v} = \varpi_o + 2B(J'' + 1)\text{cm}^{-1} \qquad J'' = 0,1,2,\ldots. \qquad \ldots\ldots\ 4.27a$$

2. . $\Delta J = -1$,that is $J'' = J' + 1$ or $J' - J'' = -1$; hence

$$\Delta\varepsilon_{J,v} = \varpi_o - 2B(J' + 1)\text{cm}^{-1} \qquad J' = 0,1,2,\ldots. \qquad \ldots\ldots\ 4.27b$$

These two expressions may conveniently be combined into:

$$\Delta\varepsilon_{J,v} = \bar{\nu}\,\text{spectroscopic} = \varpi_o + 2Bm \quad \text{cm}^{-1} \qquad m = \pm1, \pm2, \qquad \ldots\ldots 4.27c$$

where m, replacing $J'' + 1$and $J' + 1$ has positive values for $\Delta J = +1$ and is negative if $\Delta J = -1$. Note particularily that m cannot be zero since this would imply values of J' and J'' to be -1. The frequency ϖ_o is usually called the band origin or band centre.

Equation 4.27c, then represents the combined vibration-rotation spectrum.

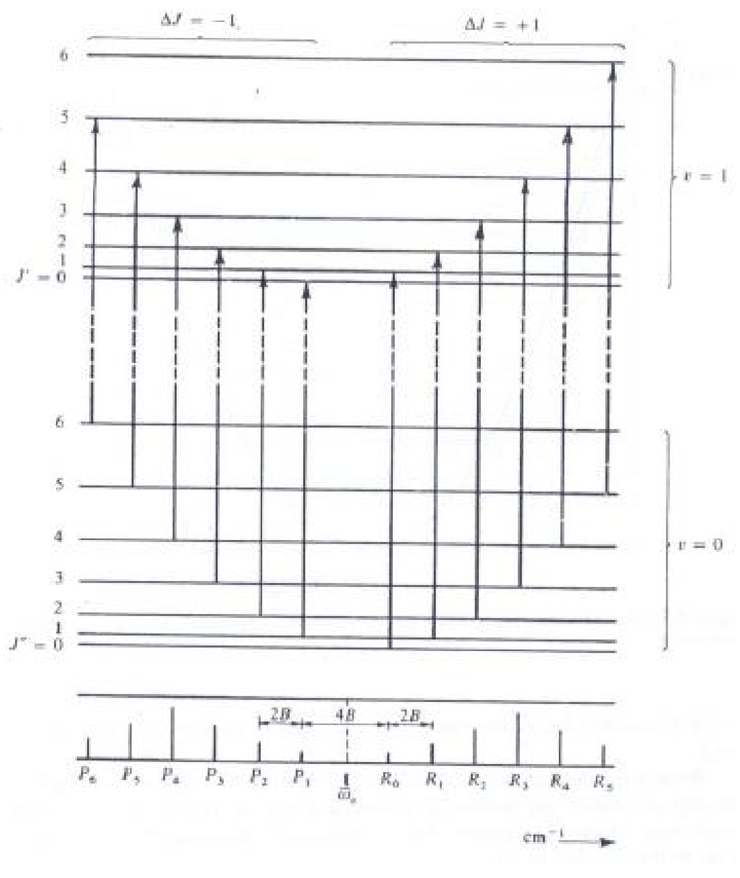


Fig. 4.7 Some transitions between the rotational-vibrational energy levels of a diatomic molecule together with the spectrum arising from them.

4.7 P, Q AND R BRANCHES OF ROTATIONAL-VIBRATIONAL SPECTRUM

In the case of rotational –vibrational spectrum:

(i) For $\Delta J = -1$, lines with frequency lower than the fundamental frequency are obtained. These lines are called P-branch of the spectrum (Fig.4.8)

(ii) For $\Delta J = +1$, lines with frequency greater than the fundamental frequency are obtained. These lines are called R-branch of the spectrum

(iii) For $\Delta J = 0$ i.e., when a vibrational transition occurs without being accompanied by rotational transition (e.g., in case of NO),

$$\Delta \bar{\nu} = \omega_0$$

i.e., a single line is expected at the centre. In actual practice, as the rotational constants of the two vibrational levels are slightly different, a cluster of closely spaced lines appears at the centre. This group of lines is called the Q-branch of the spectrum. When this type of transition is forbidden a gap appears at the centre.

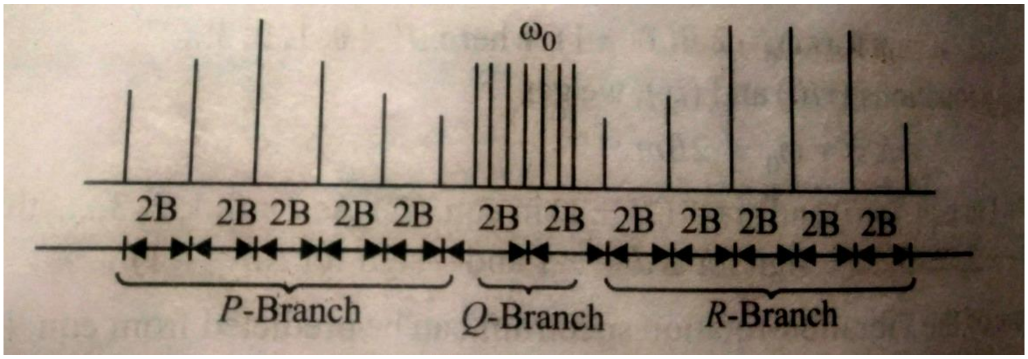


Fig. 4.8 P, Q and R branches of rotational-vibrational spectrum.

4.8 BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION

So far we have assumed that vibration and rotation can proceed quite independently of each other. A molecule vibrates some 10^3 times during the single course of rotation, however, so it is evident that the bond length also changes continually during the rotation. If the vibration is simple harmonic the mean bond length will be the same as the equilibrium bond length and it will not vary with vibrational energy; this is seen in Fig.4.1. however, the rotation constant B depends on $1/r^2$ and, the average value of this quantity is not the same as $1/r^2_{eq.}$, where $r_{eq.}$is the equilibrium length. Further, an increase in the vibrational energy is accompanied by an increase in the vibrational amplitude and hence the value of B will depend on the v quantum number.

In the case of anharmonic vibrations the situation is rather more complex. Now an increase in vibrational energy will lead to an increase in the average bond length-this is perhaps most evident from Fig.4.4. the rotational constant then varies even more with vibrational energy.

In general, it is plain that, since $r_{av.}$ increase with the vibrational energy, B is smaller in the upper vibrational state than in the lower. In fact an equation of the form:

$$B_v = B_e - \alpha\left(v + \frac{1}{2}\right) \qquad \ldots\ldots 4.28$$

Gives, to a high degree of approximation, the value of B_v, the rotational constant in vibrational level v in terms of the equilibrium value B_e and α, a small positive constant for each molecule.

Here we restrict our discussion to the fundamental vibrational change, i.e. the change $v = 0 \rightarrow v = 1$, and we may take the repective B values as B_0 and B_1 with $B_0 > B_1$. For this transition:

$$\Delta\varepsilon = \varepsilon_{J',v=1} - \varepsilon_{J'',v=0} = \varpi_o + B_1J'(J'+1) - B_0J''(J''+1) \quad cm^{-1}$$

where, as before $\varpi_o = \varpi_e(1 - 2\chi_e)$.

we then have two cases:

1. $\Delta J = +1\,,\ J' = J'' + 1$

$$\Delta\varepsilon = \bar{\nu}_R = \varpi_o + (B_1 + B_0)(J''+1) + (B_1 - B_0)(J''+1)^2 cm^{-1}\ (J'' = 0,1,2,\ldots.) \quad \ldots\ldots 4.29a$$

and

2. $\Delta J = -1\,,\ J'' = J' + 1$

$$\Delta\varepsilon = \bar{\nu}_P = \varpi_o - (B_1 + B_0)(J'+1) + (B_1 - B_0)(J'+1)^2 cm^{-1}\ (J' = 0,1,2,\ldots.) \quad \ldots\ldots 4.29b$$

where we have written $\bar{\upsilon}_P$ and $\bar{\upsilon}_R$ to represent the wavenumbers of the P and R branch lines, respectively. These two equations can be combined into the expression:

$$\bar{\upsilon}_{P,R} = \varpi_o + (B_1 + B_0)m + (B_1 - B_0)m^2 \ \text{cm}^{-1} \quad (m = \pm 1, \pm 2, \ldots\ldots) \qquad \ldots\ldots\ 4.29c$$

where positive m values refer to the R branch and negative to P.

In table 4.2 some of the data for CO are tabulated, together with the positions of lines calculated from the equation:

$$\bar{\nu}\,\text{spec} = 2143.28 + 3.813m - 0.0175m^2 \ \text{cm}^{-1}$$

from this we see that, for this molecule:

$B_1 = 1.898$ cm^{-1} $B_0 = 1.915$ cm^{-1}

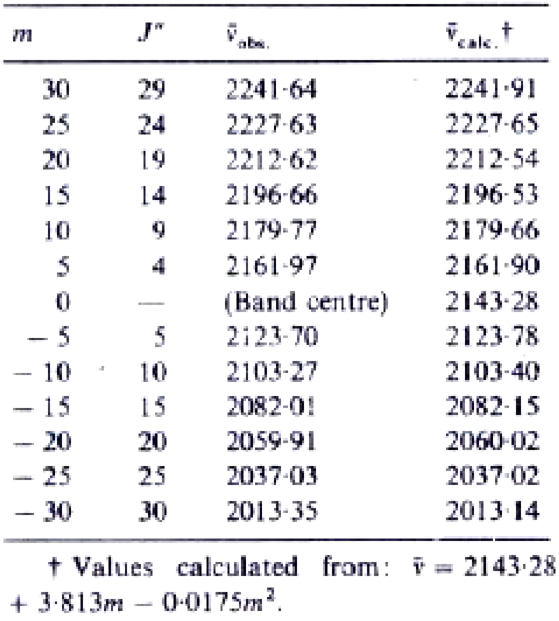
And hence, using Eq.3.22, we have:

$\alpha = 0.018$ $B_e = 1.924$ cm^{-1}

further, we can calculates ate the equilibrium bond length and the bond lengths in the $v = 0$ and $v = 1$ states to be:

$r_{eq} = 0.1130$ nm $r_0 = 0.1133$ nm $r_1 = 0.1136$ nm

Table 4.2 Obseved and calculated wavenumbers of some lines in the spectrum of CO



m	J''	$\bar{\nu}_{\text{obs.}}$	$\bar{\nu}_{\text{calc.}}$†
30	29	2241·64	2241·91
25	24	2227·63	2227·65
20	19	2212·62	2212·54
15	14	2196·66	2196·53
10	9	2179·77	2179·66
5	4	2161·97	2161·90
0	—	(Band centre)	2143·28
− 5	5	2123·70	2123·78
− 10	10	2103·27	2103·40
− 15	15	2082·01	2082·15
− 20	20	2059·91	2060·02
− 25	25	2037·03	2037·02
− 30	30	2013·35	2013·14

† Values calculated from: $\bar{\nu} = 2143{\cdot}28 + 3{\cdot}813m - 0{\cdot}0175m^2$.

4.9 NUCLEAR SPIN EFFECT

Centre of symmetry has an effect on the intensity of alternate lines in the P and R branches. The effect is due to the existence of nuclear spin and is an additional factor determining the populations of rotational levels. In the case of CO_2 every alternate rotational level is completely unoccupied and so alternate lines in the P and R branches have zero intensity. This leads to a line spacing of 4B instead of the usual 2B. that the spacing is indeed 4B can be shown in several ways, perhaps the most convincing of which is to examine the spectrum of the isotopic molecule $^{18}O\text{-}C\text{-}^{16}O$. Here there is no longer a centre of symmetry, nuclear spin does not now affect the spectrum and the line spacing is found to be just half that for normal CO_2.

In the case of acetylene, alternate levels have populations which differ by a factor of 3: 1so that the P and R branch lines show a strong, weak, strong, weak,… alternation in intensity, as shown in Fig.4.9.

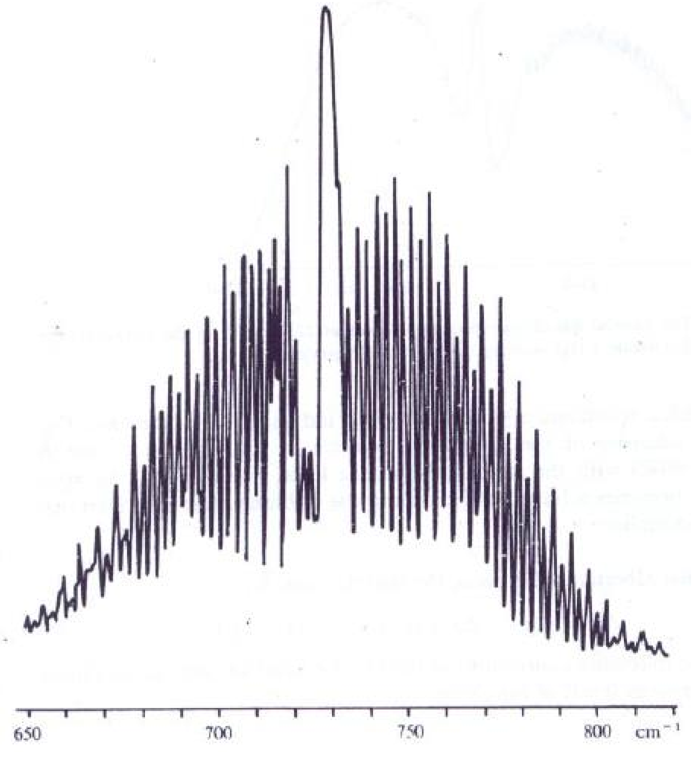


Fig.4.9 The spectrum of the bending mode of acetylene,CHCH, showing the strong, weak, strong,weak,…intensity alternation in the rotational fine structure due to the nuclear spin of the hydrogen atoms.

4.10 SUMMARY

- Vibrations on molecules are studied in the infrared region of the electromagnetic spectrum.
- The classical model of the Simple Harmonic Oscillator shows that the frequency of vibration depends on the force constant and reduced mass of the molecule.
- The spectrum of a real molecule does not resemble what is predicted by the harmonic oscillator model.
- The Morse potential is a satisfactory representation of the potential energy function of a real molecule.
- For this oscillator, larger quantum jumps are allowed and one sees the fundamental and, first and second overtones, as well as hot bands.
- Data from these spectra allow one to get an estimate of the dissociation energy.
- An approximation that can be used to understand vibration-rotation spectra is the Born-Oppenheimer approximation, which states that since the energy scales are different, the two motions can be treated independently.
- The two selection rules also remain the same. Application of the selection rules predicts two branches in the spectra, but the band centre itself is missing.
- However, analysis of the spectra yields information about the vibrational frequencies and rotational constants and all corresponding molecular parameters can be determined.
- However, analysis of real spectra shows a crowding of lines at the higher wavenumber R branches, and spacing out of the P branches with increasing *J*.
- This implies that the rotational constant is not independent of the vibrational quantum number and decreases with increasing v since the average bond length increases with increasing amplitude of vibration.

4.11 TERMINAL QUESTIONS

1. What type of potential energy curve is obtained for a simple harmonic oscillator and why.

2. What are P, Q and R branches of the vibration-rotation spectrum

3. Discuss the spectrum of simple harmonic oscillator.

4. Explain the overtone and fundamental bands.

5. Discuss effect of nuclear spin in vibrational spectroscopy

4.12 REFERENCES

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UNIT 5: VIBRATIONAL SPECTROSCOPY-II : POLYATOMIC MOLECULES

CONTENTS:

5.1 INTRODUCTION

IR spectroscopy also known as rotational-vibrational is a powerful analytical tool used by almost all the branches of Chemistry of for solving the problems related to structural elucidation and functionalities. Though organic compounds are studied by IR-spectroscopy, inorganic compounds containing polyatomic anions or cations also give very useful infra-red spectra. There are two requirements for the absorption of EMR by matters

(1) the Radiations must have precisely the correct energy to satisfy the energy requirements of the material

(2) There must be an interaction between the radiation and matter.

Radiation in the IR region has the proper magnitude of energy to cause vibrational transition, in molecules and the first requirement for absorption is satisfied if a given frequency of IR corresponds exactly to a fundamental vibrational frequency of a given molecule. To satisfy the second requirement for absorption, the molecule must undergo a change in **dipola moment** when the fundamental vibration occurs as the oscillating dipole resonates with EMR. If no change in dipole moment occurs when the molecule vibrates, there will be no interaction between the electro magnetic radiation and the non electromagnetic molecule and no absorption will take place regardless of the energy compatibility. Such a vibrations are said to be infrared inactive. The dipolemoment of two equal and opposite charges is defined as the product of the charge and the distance separating them

$\mu = e \times d$................. (1)

μ = dipole moment, e= charge and d= distance,

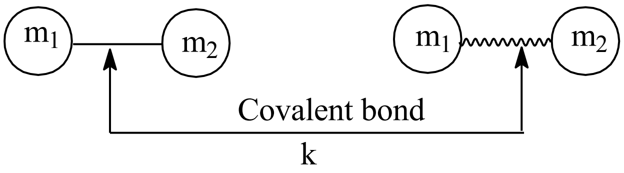
For a molecule, it is the effective centre of the positive and negative charges which is important, d being the distance between those centres. Fig.1 illustrates how the separation of charge in a polar molecule like water may be visualised. As will be shown momentarily, all the possible modes of vibration of a water molecule involve a change in dipole moment, and thus all its vibrational modes are infrared-active.With a linear molecule like CO_2 its dipole momement is zero. More important is that the change in dipolement is zero when the molecule is symmetrically stretched. Thus, the symmetrical stretch of CO_2 is infrared-inactive. On the other hand, an anti symmetrical (or asymmetrical) stretch involves a change in dipole moment, and thus this mode is IR-active.

5.2 OBJECTIVE

Objective of this unit are to introduce the principl of IR and FTIR spectroscopy. Intrpretation of molecular vibration, narration of functional group and fingerprint region, IR spectrum, Hook's law, factors effecting vibrational frequencies viz; conjugation, electronic effects like; inductive and mesmeric effects. Hydrogen bonding, Ring strain etc, interpretation of IR spectra of some classes of organic compounds.

5.3 HOOK'S LAW

Hooke's Law states that the force needed to compress or extend a spring is directly proportional to the distance you stretch it. In IR spectroscopy the the bond stretching is related to Hooks's law.Viz if a diatomic molecule absorb IR radation it starts vibrating. A vibrating diatomic (presuming the covalent bond behaving as a spring and the atoms having masses m_1 and m_2 respectively) molecule or less precisely a diatomic grouping (O-H, N-H, C-O etc) in a more complex molecule behaves as a simple harmonic oscillator, oscillating with the frequency ν as per the following Hook's equation.



$$\bar{\upsilon} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1.m_2}{m_1 + m_2}$$

$\bar{\upsilon}$= frequency μ= reduced mass

Where:-

ν^{-} = wave number in cm^{-1}=, corresponding to the vibrational frequency of the bond

c = Speed of light in cms^{-1}

k = force constant in dynes/cem.(a measure of bond strength, the stronger the bond, the larger the k)

μ = reduced mass gatom^{-1}

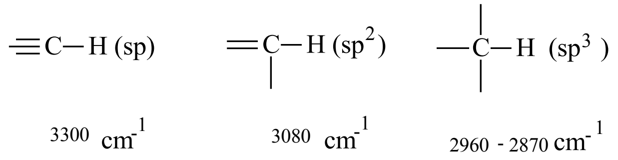
The Hook's equation in very important in IR-spectroscopy in order to predict the variation of vibrational frequencies of functional groups.

5.4 INFLUENCE OF FORCE CONSTANT ON VIBRATIONAL FREQUENCY OF A BOND

The force constant of a bond increases numerically with bond order and bond length and consquentlly decreases with the increase with the increase in bond length. It has been observed that the stretching vibrational frequency also increase as force constant increases.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]
[illegible]	[illegible]	2	[illegible]	[illegible]
[illegible]	[illegible]	3	[illegible]	[illegible]

Hybridization also affects the force constant k of the bond. The strength of bonds is in the order of sp > sp^2 > sp^3 and is illustrated by observed C-H stretching frequencies in the following partial structures of hydrocarbons (HC).

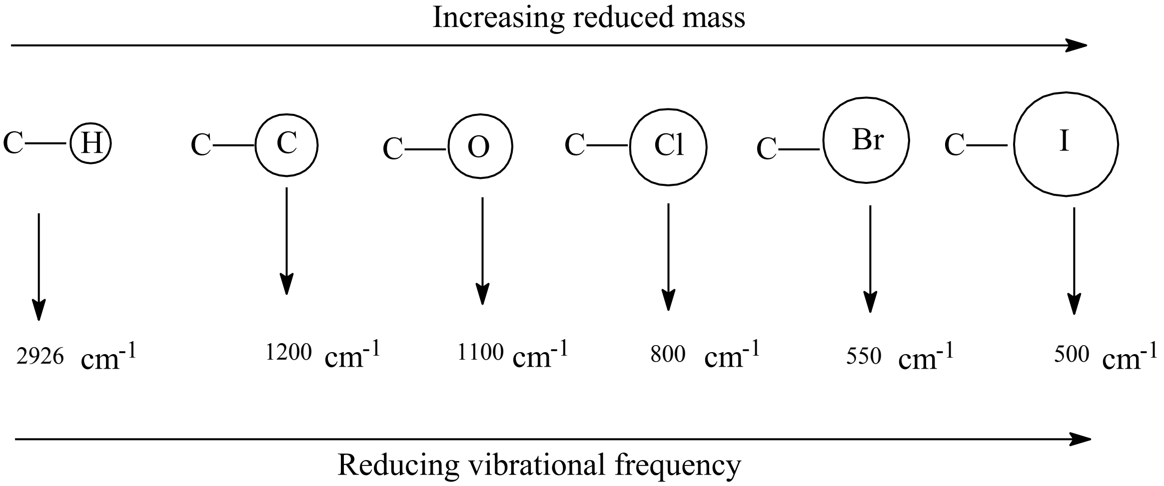


5.5 INFLUENCE OF REDUCED MASSE ON VIBRATIONAL FREQUENCY OF A BOND

Influence of As per the following equation bonds between atoms of higher masses will vibrate at lower frequencies than the bonds bearing the lighter atoms.

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

Viz; The O-H bond absorb near 3600cm^{-1} while O-D bond absorb near 2630cm^{-1} In this case the strength of bond is nearly same but the masses od O and D are different i.e. mass of D is higher than H. Similarly the C-H stretching occurs near 2960cm^{-1}. As the masses of the atoms attached covalently with carbon increases, the factor μ increases and consequently the frequency decreases as follow.



5.6 DEGREES OF FREEDOM OF POLYATOMIC MOLECULES

We already know that a diatomic molecule has only one fundamental vibration or one vibrational coordinate. This arises due to the stretching and compresssion of the bond connecting two atoms just like a spring (fig 5.1).

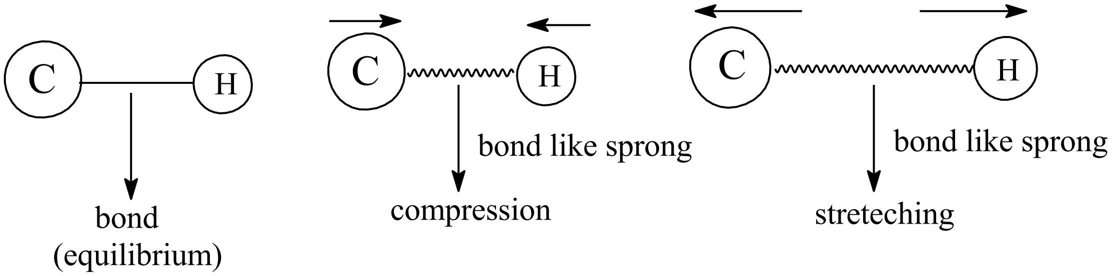


Fig.5.1. Stretching and compression of a simle diatomic molecule

Now let us cdculate the vibrational degrees of freedom of a polyatomic molecule. First let us presume that each atom is free to move in three perpendicular directions (along x, y, and z axes. Fig.5.2) and thus has three degrees of freedom. The degrees of freedom are the number of directions in which an atom can move freely independent of other atoms in the molecule. Hence, for molecule containisg N atoms, the total degrees of freedom are 3N. We know that a molecule has translational, rotational and vibrational motions. A molecule can have only three degrees of translational motion since centre of mass of the molecule can move only along three axial directions. That is, the whole molecule can move along the three axes. In addition, when the molecule is nonlinear, there are three degree5 of freedom due to otational motions about the three axes. Therefore, there remaid 3N - (3 +3) = (3N-6) coordinates which account for vibrational degrees of freedom for nonlinear polyatomic molecules.

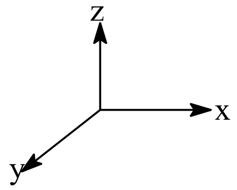


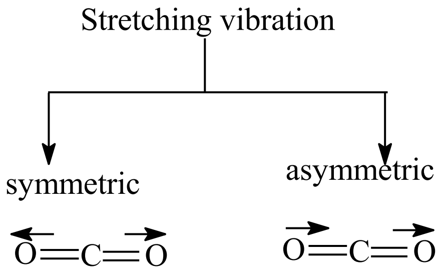
Fig 5.2. Three perpendicular coordinates for free independent movement of an atom

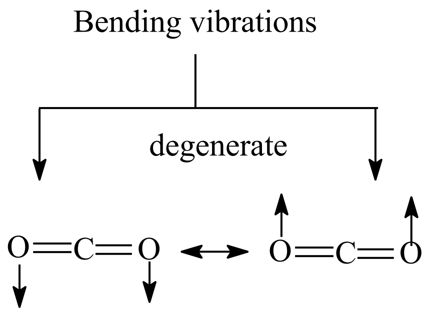
For a linear molecule, there are two rotational degrees'of freedoms as the rotations - about two axes perpendicular to internuclear bond axis only are allowed. The rotation about the internuclear axis is not possible since the moment of inertia along the internuclear axis is zero. Therefore a linear molecule possesses 3N - (3 + 2) = (3N-5) vibrational degrees of freedom. The details of the number of degrees of freedom for linear and nonlinear molecules are presented in Table 5.1.

Table 5.1: Degree of freedom in polyatomic molecules

Degree of freedom	Linear	Non-linear
Total	3N	3N
Translational	3	3
Rotational	2	3
Vibrational	3N – 5	3N-6

Persuing table 5.1 above, can you state the vibrational degrees of freedom of CO_2, H_2O and NH_3 molecules? It is worth recollecting that CO_2 is linear, H_2O is angular and NH_3 is pyramidal.CO_2 molecule has $(3 \times 3 - 5) = 4$ vibrational degrees of freedom; H_2O molecule has $(3 \times 3 - 6) = 3$ vibrational degrees of freedom and NH_3 molecule has $(3 \times 4 - 6) = 6$ vibrational degrees of freedom.





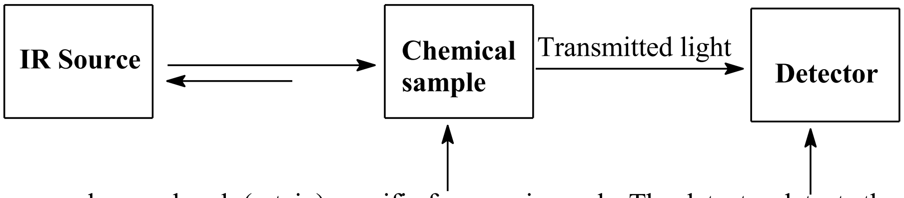
Selection rule: In rotational vibrational mode only those modes are IR- active which has change in dipole moment, i.e. molecules with non-centrosymmetry. The molecules with centre of symmetry will have zero change in oscillating dipole moment hence are IR-inactive like homodiatomic molecules like O_2,N_2, Cl_2.etc (table 5.2) All the functional groups in organic compounds are generally asymmetric in nature, hence can be detected simply by IR spectroscopy.

Table 5.2: Selection rule in IR-spectroscopy

Symmetry in the molecule	**IR**	**Raman**
Centrosymmetric	Inactive	Active
Non-centrosymmetric	Active	Inactive

5.7 TRANSMISSION VS. ABSORPTION

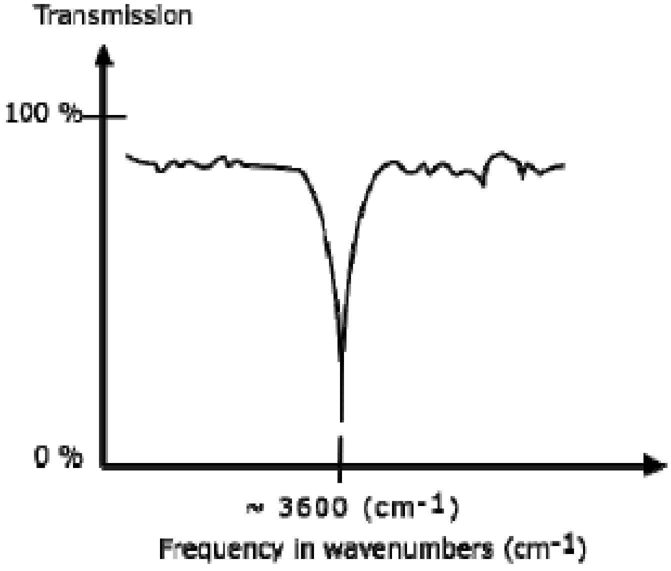
When a chemical sample is exposed to the action of **IR light from IR source**, it can **absorb** some requencies and **transmit** the rest. Some of the light can also be reflected back to the source.



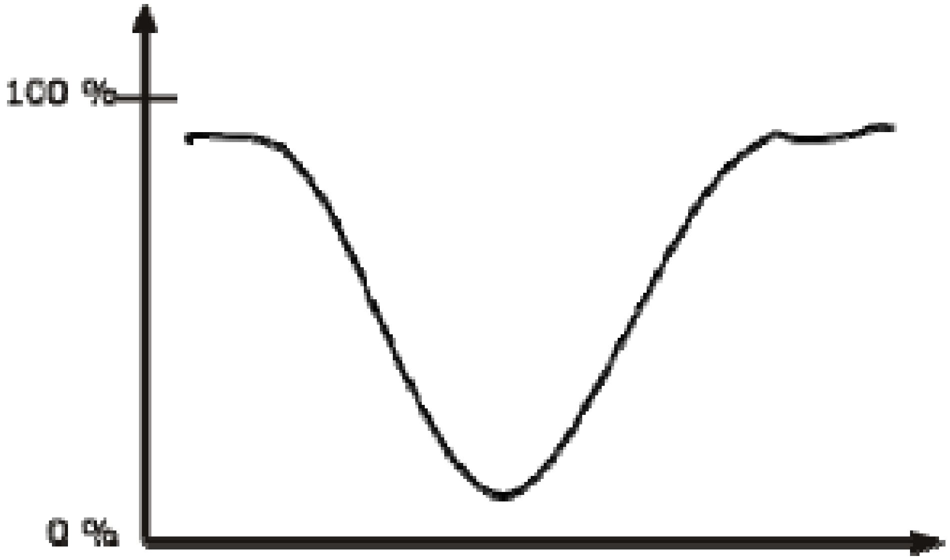
The sample can absorb (retain) specific frequencies and allow the rest to pass through it (transmitted light)

The detector detects the transmitted frequencies and by doing soalso reveals the values of the absorbed frequencies.

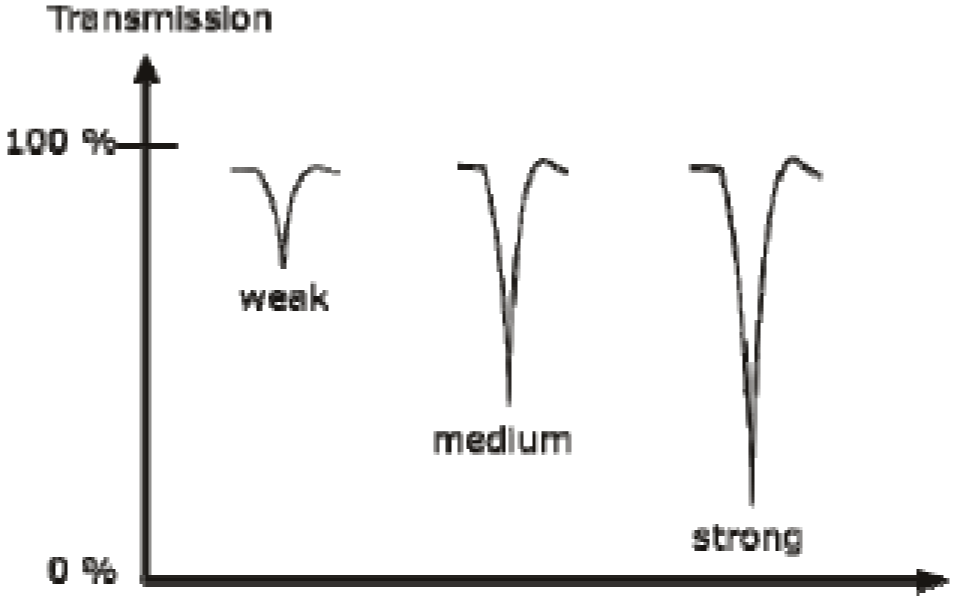
Finally we get the IR-spectrum as follow. The graph shows a spectrum in **transmission** mode.**This is the most commonly used representation** and the one found in most Chemistry and spectroscopy books.



The IR- band shapes are recorded commonly in the form of narrow and **broad** bands. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother. A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.



Based on their intensities the IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w),. A strong band covers most of the *y*-axis. A medium band falls to about half of the *y*-axis, and a weak band falls to about one third or less of the *y*-axis as follow.



5.8 IR-SPECTRUM

IR spectrum is a record of wave number (energy) along x-axis against transmittance (reciprocal of absorbance) along y-axis (fig.5.3). The spectrum has been divided into three regions. The overtone region, fundamental region and fingerprint region. Each regions with their energies in cm^{-1} has been presented in figure 5.4.

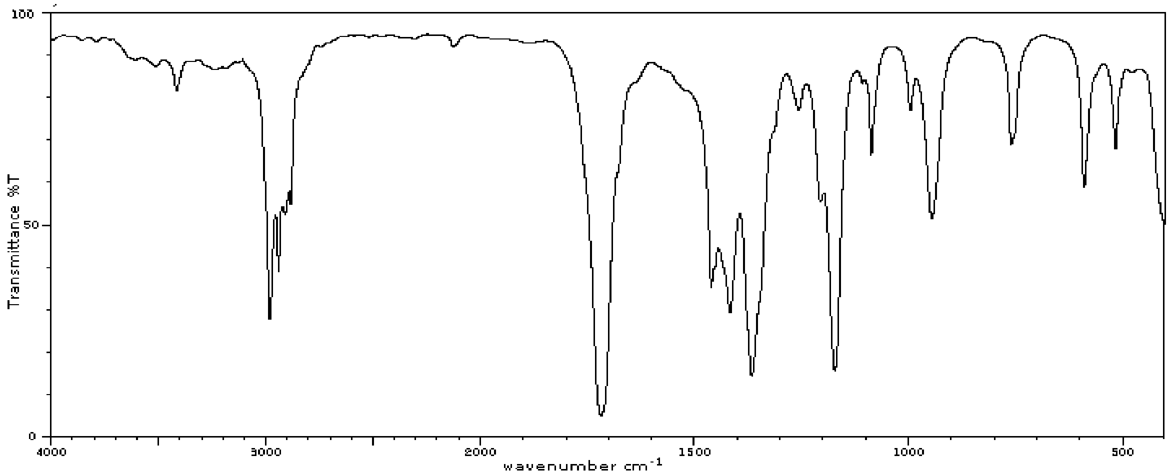


Fig.5.3. Infrared spectrum

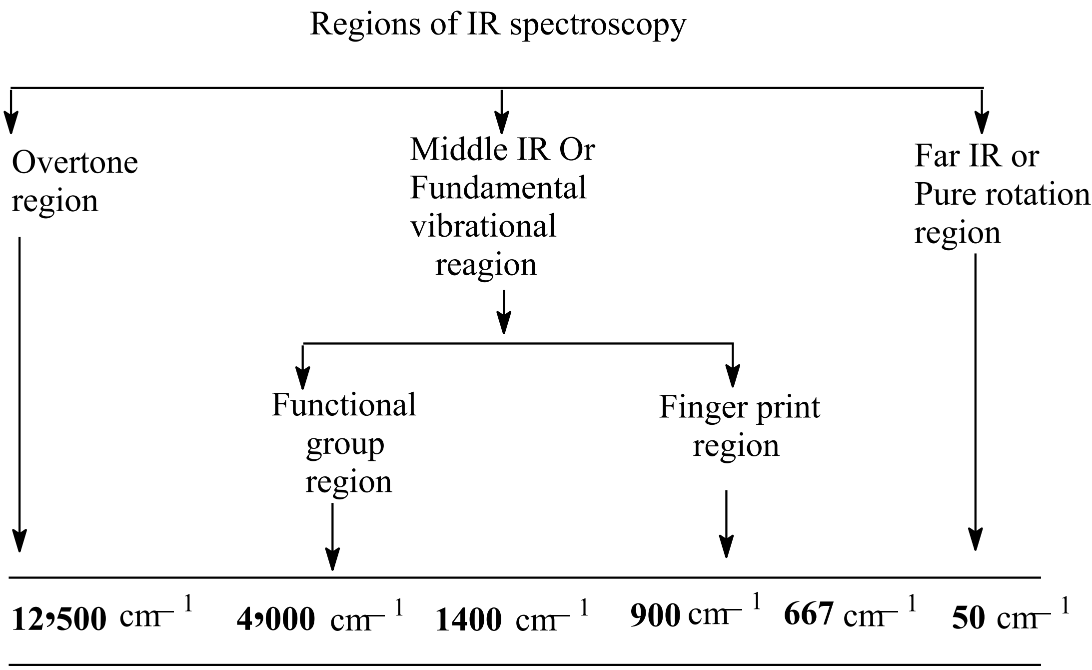


Fig 5.4. Various regions of IR-spectrum

5.9 GROUP FREQUENCIES AND ANALYSIS

A particular part of IR-spectrum generally middle IR can be divided into two parts as follow. The frequencies in each part are not expressed in Hz but in wave number, which is reciprocal of wavelength and is simply the number of waves/cm.

A. Functional group region: The region from 4000 cm^{-1} to approximately 1400 cm^{-1}(fig.5.5). Different functional group gives its peak in this region with different intensities. This region has diagnostic importance for functionalities in the molecules.

B. Fingerprint region: The region 1400 cm^{-1} to 650 cm^{-1} is referred as fingerprint region (fig 5).This region is very complex because apart from fundamental stretching and bending vibrations many bands resulting from the sum or difference of their vibrational frewuencies, This part of the spectrum is characteristic of a compound. Same molecule may have very similar spectra in the functional group region but certainly exhibit discerbible difference in the fingerprint region. Viz 1^0, 2^0 and 3^0 alcohols gives same O-H stretching in F.G region but may have different peaks in fingerprint region thus in spite of belonging to same homologus series the compounds can be distinguished in fingerprint region.

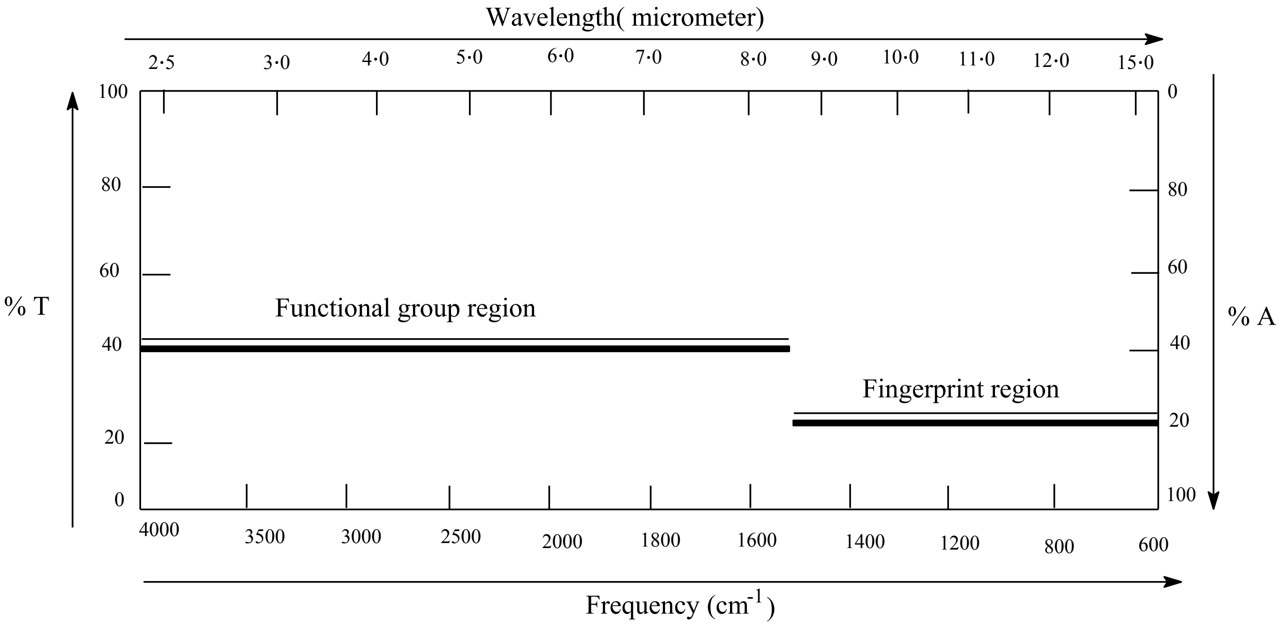
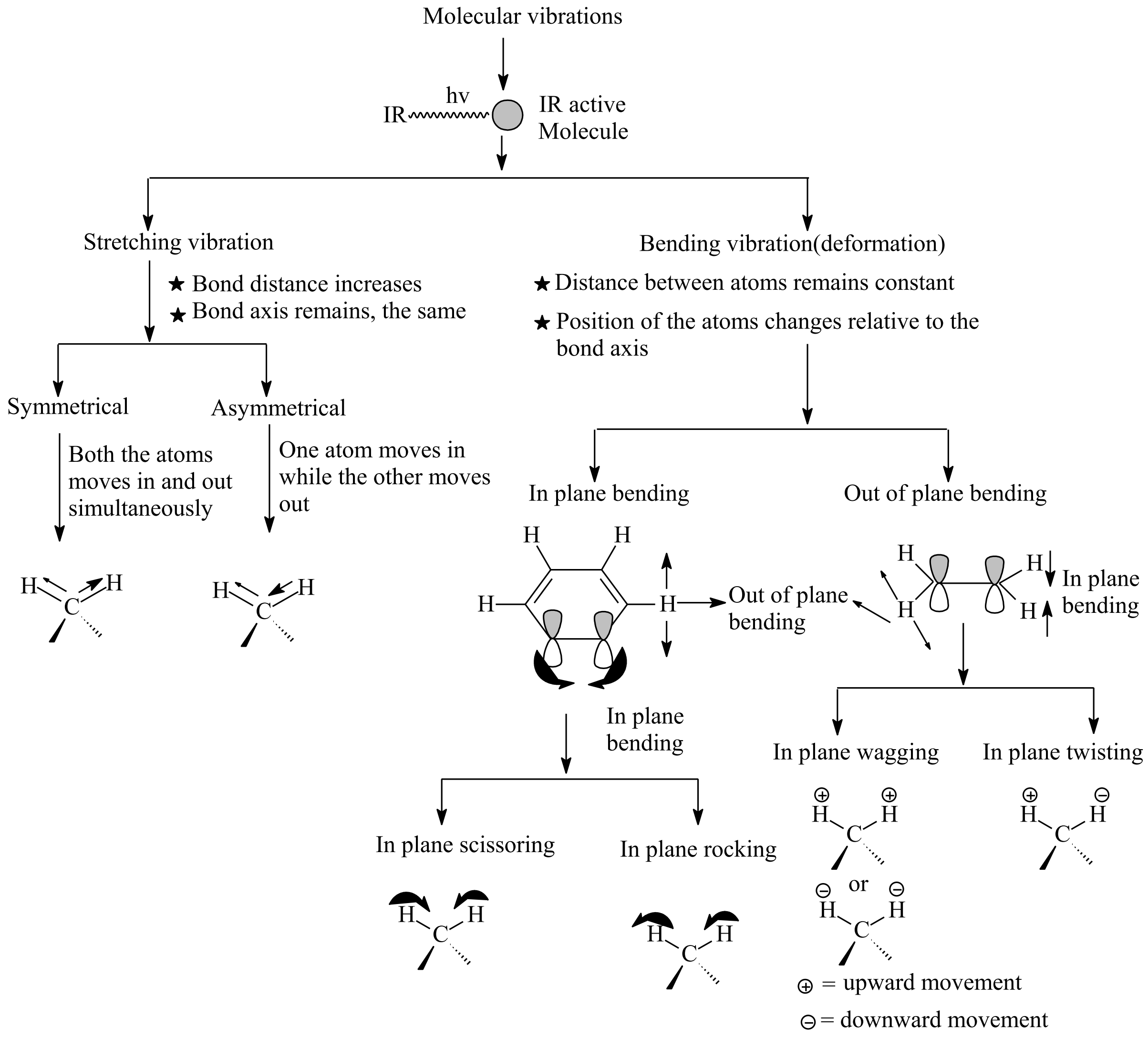


Fig 5.5 Group frequencies in IR-spectrum

5.10 MOLECULAR VIBRATIONS

The absorption of IR radiation corresponds to energy change in the range from 2-10kcl/mol. This energy encompasses the changes in vibrational and rotational levels of bonds in most covalent molecules. The IR radiation is absorbed when oscillating dipole moment due to molecular vibration encounter with the oscillating electer vector of IR-beam. These vibrations absorb IR at certain quantized frequencies and give characteristic bands.Amplitude of the vibration increased when IR light is absorbed. The following types of molecular vibrations generally take place upon absorbing IR radiation by an IR active molecule.



The IR bands are designated as

1. **Fundamental Bands:** The bands ariging due changes in vibrational levels at zeroth level ,v_0- v_1 at the room temperature are known as fundamental bands or simply IR peakes(fig 4). These bands arise due the intrection of oscillating dipole moment of the IR active molecule with IR-beam, generally because of harmonic oscillation. The number of fundamental bands basically depends upon degree of freedom of the molecule, which is 3N-5 for linear and 3N-6 for non linear molecules.
2. **Combination Bands:** The weak absorption occurring in IR spectrum because of the sum of two or more fundamental vibrational frequencies. These bands arise because of anharmonicities of the oscillation that lead to an intraction of the vibrational states in polyatomic molecules. The intensities of combination bands are weak compared to the fundamental and overtone bands.
3. **Overtone bands:** The term overtone is used in a general sense to apply to any multiple of a given fundamental vibration. The transition from $v_0 - v_2$ and $v_0 - v_3$ are the Ist and IInd overtones of the fundamental bands. These bands require twice and three times frequency (fig 5.6). Viz; the first overtone $2v_{c=o}$ for carbonyl fundamental $v_{c=o}$ at 1700cm^{-1} will be 3400cm-1.

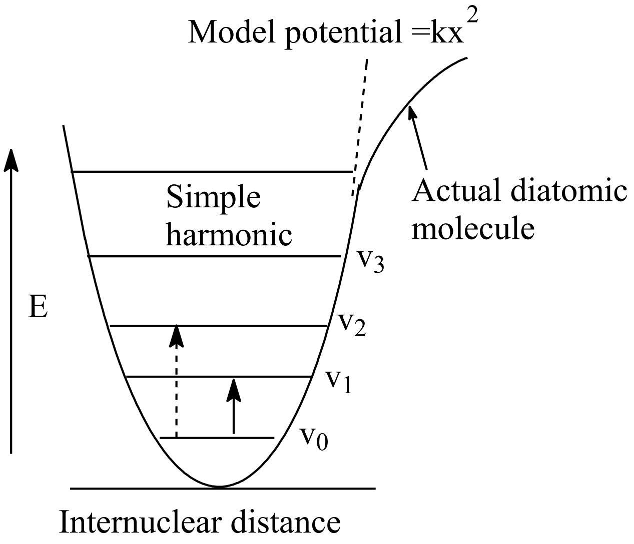


Fig.5.6. Potential energy curves for a model and an actual diatomic molecule, revealing fundamental ($v_0 - v_1$) transition and overtone ($v_0 - v_2$) transition

4. **Fermi Resonance:** It is basically interaction of fundamental –overtone bands. When an overtone or combination bands falls near a strong fundamental vibration, it cause a decrease in the intensity of the fundamental vibration and a large increase in the intensity of the overtone/combination vibration.Such interaction is known as Fermi resonance.Viz; appearance of two moderately intense bands in the region 2830-2695cm^{-1} in aldehydes is due to the interaction between the aldehydic C-H stretch and the first overtone of aldehydic C-H in plane bending which appears near 1390 cm^{-1}

5.10.1 Survey of different regions for detection of different functional groups

Each functional group in organic chemistry reveals its characteristic peaks in middle IR-regions. The intensity and position of IR peaks are related with the structure of the molecules and change in oscillating dipole moment while interacting with IR beam from source. The functional groups are non-centrocemetric in geometry and posses dipole moment. The change in dipole moment depends upon elemental composition of functional group which in turn unfluence the intensity of the IR peak i.e greater the change in dipole moment more intense will be the IR peak. Different functional groups have different values of force constant k and reduced mass μ hence accodring to Hook's law as stated above the position of IR peaks also vary. The different functional groups can be detected by matching their vibrational frequencies (table 5.3 A-I)

Table 5.3. Different regions for detection of different functional groups

A: 4000 - 3000 cm^1						
Vibratio--nal Frequen--cy cm^{-1}	**Intensity**		**F.G**	**Type of Str.**	**Compound**	**State**
3700-3584	medium	sharp	O-H	stretching	alcohol	free
3550-3200	strong	broad	O-H	stretching	alcohol	intermolecular bonded
3500-3400	medium	-	N-H	stretching	primary amine	-
3400-3300 3330-3250	medium	-	N-H	stretching	aliphatic primary amine	-
3350-3310	medium	-	N-H	stretching	secondary amine	-

3300-2500	strong	broad	O-H	stretching	carboxylic acid	usually centered on 3000 cm^{-1}
3200-2700	weak	broad	O-H	stretching	alcohol	intramolecular bonded
3000-2800	strong	broad	N-H	stretching	amine salt	-

B: 2400-2000 cm^{-1}

Vibrational Frequency cm^{-1}	Intensity		F.G.	Type of Molecular vibration	Compound	State
2349	strong	-	O=C=O	stretching	carbon dioxide	-
2275-2250	strong	broad	N=C=O	stretching	isocyanate	-
2260-2222	weak	-	CΞN	stretching	nitrile	-
2260-2190	weak	-	CΞC	stretching	alkyne	disubstituted
2175-2140	strong	-	S-CΞN	stretching	thiocyanate	-
2160-2120	strong	-	N=N=N	stretching	azide	-
2150	-		C=C=O	stretching	ketene	-
2145-2120	strong		N=C=N	stretching	carbodiimide	-
2140-2100	weak	-	CΞC	stretching	alkyne	monosubstituted
2140-1990	strong	-	N=C=S	stretching	Isothio-cyanate	-
2000-1900	medium	-	C=C=C	stretching	allene	-
2000	-	-	C=C=N	stretching	ketenimine	-

C: 2000-1650 cm^{-1}

Vibrational Frequency cm^{-1}	Intensity	Functional group	Type of Molecular vibration	Compound	State
2000-1650	weak	C-H	bending	aromatic compound	overtone

D: 1870-1540 cm^{-1}					
Vibrational Frequency cm^{-1}	**Intensity**	**F.G.**	**Type of Str.**	**Compound**	**State**
1818-1750	strong -	C=O	stretching	anhydride	-
1815-1785	strong	C=O	stretching	acid halide	-
1800-1770	strong	C=O	stretching	conjugated acid halide	-
1775- 1720	strong	C=O	stretching	conjugated anhydride	-
1770-1780	strong	C=O	stretching	vinyl / phenyl ester	-
1760	strong	C=O	stretching	carboxylic acid	monomer
1750-1735	strong	C=O	stretching	esters	6-membered lactone
1750-1735	strong	C=O	stretching	δ-lactone	γ: 1770
1745	strong	C=O	stretching	cyclopentanone	-
1740-1720	strong	C=O	stretching	aldehyde	-
1730-1715	strong	C=O	stretching	α,β-unsaturated ester	or formates
1725-1705	strong	C=O	stretching	aliphatic ketone	or cyclohexanone or cyclopentenone
1720-1706	strong	C=O	stretching	carboxylic acid	dimer
1710-1680	strong	C=O	stretching	conjugated acid	dimer
1710-1685	strong	C=O	stretching	conjugated aldehyde	-
1690	strong	C=O	stretching	primary amide	free (associated: 1650)
1690-1640	medium	C=N	stretching	imine / oxime	-
1685-1666	strong	C=O	stretching	conjugated ketone	-

1680	strong	C=O	stretching	secondary amide	free (associated: 1640)
1680	strong	C=O	stretching	tertiary amide	free (associated: 1630)
1650	strong	C=O	stretching	δ-lactam	γ: 1750-1700 β: 1760-1730

E: 1670-1600 cm^{-1}					
Vibrational Frequency cm^{-1}	**Intensity**	**F.G.**	**Type of Molecular vibration**	**Compound**	**State**
1678-1668	weak	C=C	stretching	alkene	disubstituted (trans)
1675-1665	weak	C=C	stretching	alkene	trisubstituted
1675-1665	weak	C=C	stretching	alkene	tetrasubstituted
1662-1626	medium	C=C	stretching	alkene	disubstituted (cis)
1658-1648	medium	C=C	stretching	alkene	vinylidene
1650-1600	medium	C=C	stretching	conjugated alkene	-
1650-1580	medium	N-H	bending	amine	-
1650-1566	medium	C=C	stretching	cyclic alkene	-
1648-1638	strong	C=C	stretching	alkene	Mono--substituted
1620-1610	strong	C=C	stretching	α,β-unsaturated ketone	-

F: 1600-1300 cm^{-1}					
Vibrational Frequency cm^{-1}	**Intensity**	**F.G.**	**Type of Molecular vibration**	**Compound**	**State**
1550-1500 1372-1290	strong	N-O	stretching	nitro compound	-
1465	medium	C-H	bending	alkane	methylene group

1450-1375	medium	C-H	bending	alkane	methyl group
1390-1380	medium	C-H	bending	aldehyde	-
1385-1380 1370-1365	medium	C-H	bending	alkane	gem dimethyl

G: 1400-1000 cm^{-1}					
Vibrational Frequency cm^{-1}	**Intensity**	**F.G.**	**Type of Molecular vibration**	**Compound**	**State**
1440-1395	medium	O-H	bending	carboxylic acid	-
1420-1330	medium	O-H	bending	alcohol	-
1415-1380 1200-1185	strong	S=O	stretching	sulfate	-
1410-1380 1204-1177	strong	S=O	stretching	sulfonyl chloride	-
1400-1000	strong	C-F	stretching	fluoro compound	-
1390-1310	medium	O-H	bending	phenol	-
1372-1335 1195-1168	strong	S=O	stretching	sulfonate	-
1370-1335 1170-1155	strong	S=O	stretching	sulfonamide	-
1350-1342 1165-1150	strong	S=O	stretching	sulfonic acid	anhydrous hydrate: 1230-1120
1350-1300 1160-1120	strong	S=O	stretching	sulfone	-
1342-1266	strong	C-N	stretching	aromatic amine	-
1310-1250	strong	C-O	stretching	aromatic ester	-
1275-1200 1075-1020	strong	C-O	stretching	alkyl aryl ether	-
1250-1020	medium	C-N	stretching	amine	-
1225-1200 1075-1020	strong	C-O	stretching	vinyl ether	-

1210-1163	strong	C-O	stretching	ester	-
1205-1124	strong	C-O	stretching	tertiary alcohol	-
1150-1085	strong	C-O	stretching	aliphatic ether	-
1124-1087	strong	C-O	stretching	secondary alcohol	-
1085-1050	strong	C-O	stretching	primary alcohol	-
1070-1030	strong	S=O	stretching	sulfoxide	-
1050-1040	strong broad	CO-O-CO	stretching	anhydride	-

H: 1000-650 cm^{-1}

Vibrational Frequency cm^{-1}	Intensity	F.G.	Str.	Compound	State
995-985; 915-905	strong	C=C	bending	alkene	monosubstituted
980-960	strong	C=C	bending	alkene	disubstituted (trans)
895-885	strong	C=C	bending	alkene	vinylidene
850-550	strong	C-Cl	stretching	halo compound	-
840-790	medium	C=C	bending	alkene	trisubstituted
730-665	strong	C=C	bending	alkene	disubstituted (cis)
690-515	strong	C-Br	stretching	halo compound	-
600-500	strong	C-I	stretching	halo compound	-

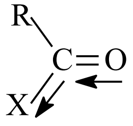
I: 900-700 cm

Vibrational Frequency cm-1	Intensity	F.G.	Str.	Compound
880 ± 20; 810 ± 20	strong	C-H	bending	1,2,4-trisubstituted
880 ± 20; 780 ± 20 (700 ± 20)	strong	C-H	bending	1,3-disubstituted
810 ± 20	strong	C-H	bending	1,4-disubstituted or 1,2,3,4-tetrasubstituted
780 ± 20; (700 ± 20)	strong	C-H	bending	1,2,3-trisubstituted
755 ± 20	strong	C-H	bending	1,2-disubstituted
750 ± 20; 700 ± 20	strong	C-H	bending	monosubstituted benzene derivative

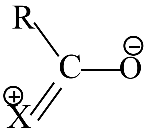
5.11 FACTORS INFLUENCING VIBRATIONAL FREQUENCIES

The vibrational frequencies of functional groups in IR-spectrum are affected by many factors as follow:

A. Inductive and mesomeric effect: Inductive and mesomeric effect associated with functional groups shift the vibrational frequencies in IR-spectrum. Viz; ketones, aldehydes, carboxylic acid, acyl halide, anhydride,ester, lactone,amide, lactam there is a significant shift of vibrational frequencies of carbonyl group if associated with inductive and mesomeric effect.The direction of shift depends upon the relative importance of the two effects i.e. predominance of inductive or mesomeric effect as follow.

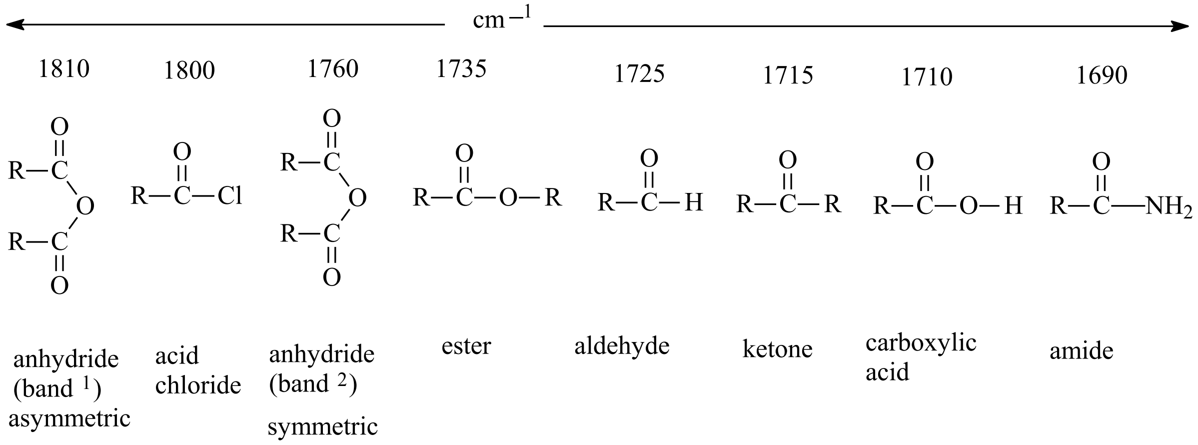


– I effect

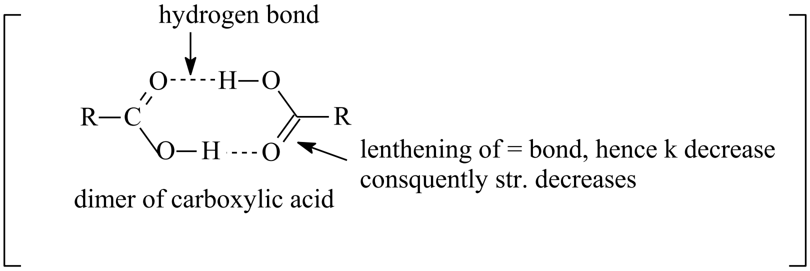


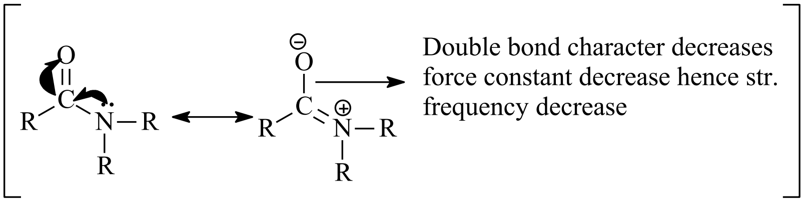
– M effect

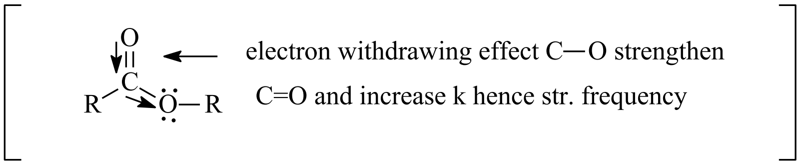
The electron pulling group like chloro, nitro, aldehydic etc suppress the polar polar contribution form of carbonyl group and enhance double bond charater which inturn increase force constant of the C=O bond as shown in –I effect above and consequently the vibrational frequency of absorption increases. Electron releasing group like amino, methyl etc attached covalently with carbonyl group tends to appurtenant the polar contributing form as shown in – M effect above and thus lowers the value of force constant of C=O group and consequently a decrease in carbonyl stretching frequency is observed. The shift in stretching frequency of carbonyl group in different class of organic compounds can be illustrated as follow.



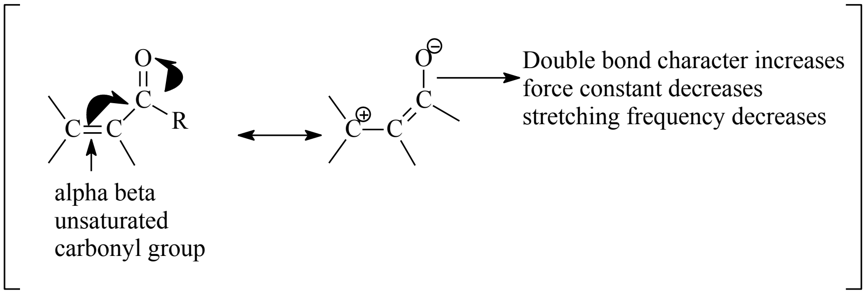
The least vibrational frequencies of carboxylic acid and amides is because of dimerization of carboxylic acid and +M effect of –NH$_2$ group which decrease k and consequently the stretching frequencies respectively while.In esters –I effect increase value of k as follow.

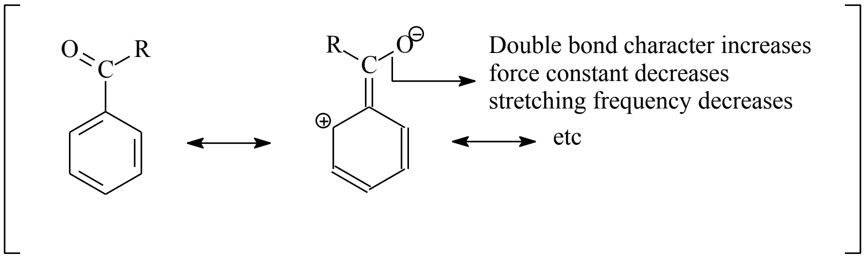






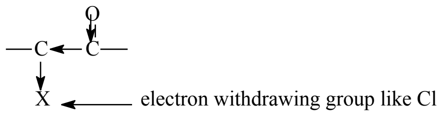
B. Conjugation: The conjugation lengthen double and shorten the double and accordingly change the value of force constant(k) which shift the vibrational frequencies in IR-spectrum, viz; the introduction of C=C adjacent to C=O results delocalization of π-electrons in the C=O and C=C bonds.

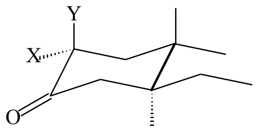




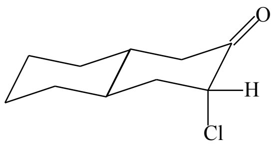
The conjugation increase single bond character of the C=O and C=C bonds in its canonical forms and hence lowers the values of force constant which result in lowering of C=O stretching frequency. Same pattern is observed in triple bond. Presence of double bond at α,β position of C=O result in 25 – 45 cm^{-1} lowering of frequency from the base value. Same lowering is observed if phenyl froup is attached. Addition of double bond at γ, δ and θ positioni in a conjugated system further lowers the stretching frequencies

C. Field effect (dipolar interaction through space): If the carbon atom next to carbonyl group is substituted by group like chlorine, the C=O band shift to a higher frequency, because of –I effect of chlorine.In cylic ketones two bands arise for C=O str. One arise from the conformationin which the chlorine is away from C=O group and other is due to the rotation next to C=O group. The lone pair of electron on halogen like Cl or Br repels the electron pair on oxygen of C=O group hence increase the force constant and thus absorbing towards higher frequency. In regid halocycloketones the C=O frequency is more if halogen viz; Cl is equatorially oriented because of electron pair repulsion, which increase k. In axial position there is no increase in k compared to equatorial hence C=O stretching is lower as follow

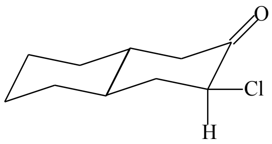




X	Y	Vc=o(cm^{-1})
H	H	1718
H	Br	1720
Br	H	1733
Br	Br	1735

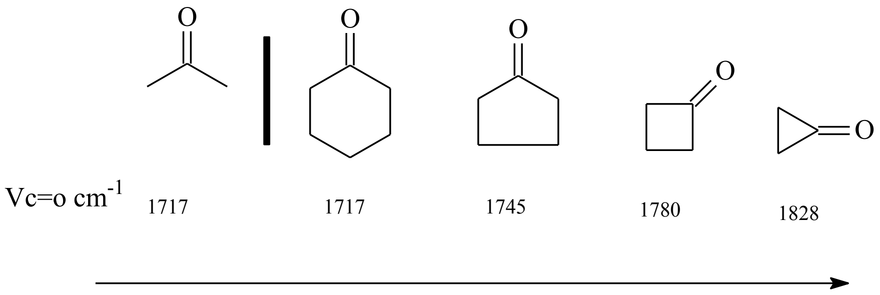


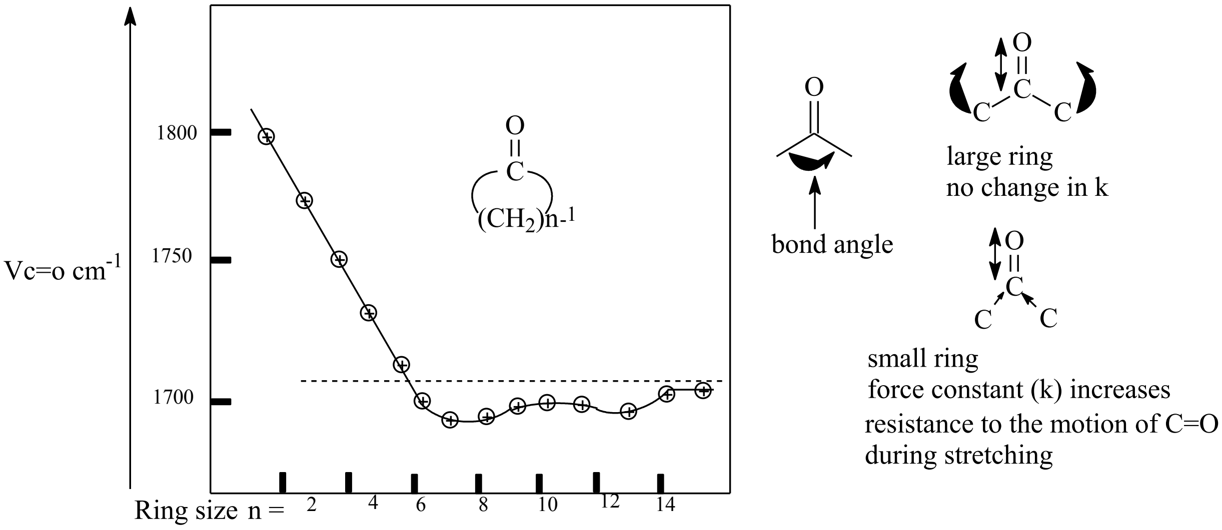
axial chlorine
1725 cm^{-1}
rigid system



equatorial chlorine
1750 cm^{-1}
rigid system

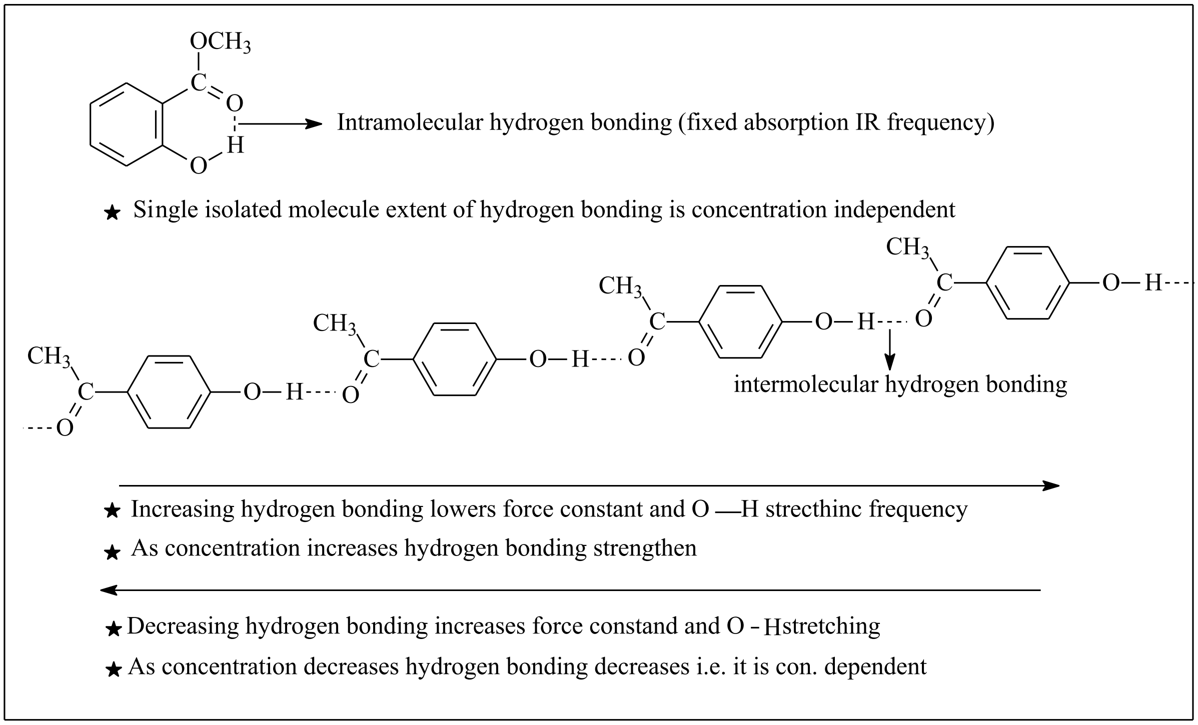
D. Ring size effect: The stretching and bending vibrations present in C=O bonds in strain free compounds i.e. planar with bond angle 120^0 are regarded as normal. However in the strained molecules or molecules substituted by bulky groups (steric hinderance) will shift the vibrational frequencies of the functional groups bound in the strained molecules as follow:





The vibrational frequency $^{V}{}_{C=O}$ =1717 cm^{-1}, represents unstrained system corresponding to n = 6 for the cyclic structure as represented above. In compounds with ring size smaller than n=6, the bond angle is less than 109.5^0 thus cause strain and shift the C=O stretching frequency. However the flexibility of larger rings permits the adaptation of strainless non-planar conformation, hence C=O stretching approximates to the value for cyclic long chain ketones (1717 cm^{-1})

E. Hydroen – bonding: Hydrogen bonding in carbonyl (C=O) group lengthens the C=O bond and lowers the stretching frequency, because as the hydrogen bonding lenthens the C=O the force constant decreases for example, a neat sample of $CH_3CH_2COCH_3$ absorb at 1715 cm^{-1} whereas a 10% solution of the compound in CH_3OH absorb at 1706 cm^{-1} Similarly O-H stretching frequency of phenol is lowered by 40-100 cm^{-1} in C_6H_6 solution compared to CCl_4 solution, because of hydrogen bonding between acidic hydrogen of phenol and the aromatic π-electron cloud(behaving as aLewis base). The shifting in stretching frequency also depends upon type of hydrogen bonding. The vibrational frequency in intramolecular hydrogen bonding is concentration independent while it is concentration dependent in intermolecular hydrogen bonding. Examination of varying concentrations of OH compounds in non-polar solvents immediately distinguishes inter and intramolecular hydrogen bonding. This concept can be understood as follow.



Intramolecular hydrogen bonding (fixed absorption IR frequency)

★ Single isolated molecule extent of hydrogen bonding is concentration independent

intermolecular hydrogen bonding

★ Increasing hydrogen bonding lowers force constant and O —H strecthinc frequency

★ As concentration increases hydrogen bonding strengthen

★ Decreasing hydrogen bonding increases force constand and O - Hstretching

★ As concentration decreases hydrogen bonding decreases i.e. it is con. dependent

5.12. FT-IR

The instrument in which IR spectra are obtained is lnown as IR spectrophotometer. There are two types of IR-spectrophotometr 1. Dispersive IR- spectrophometer and 2 Fourier transform

IR-spectrophotometer.Both the equipments provide similar information in the range of about 4000 cm^{-1} to 400 cm^{-1}. The FT-IR spectophometer provide IR-spectra more rapidly than dispersive spectrophotometer. To understand about FT-IR in my view we must have an idea about dispersive IR as represented in fig 5. As per the block diagram the a IR beam is emitted from the IR-sourse, which stricke to the reflecting mirror and is divided into two beams of same intensity. One beam pass through a reference cell while second pass through sample cell. The beams then pass into the monochromator (grating), which disperses each into a monochromatic frequencies of IR light.The gratting consist of rotating sector (beam chopper). The detector receives the ratio of intensities of reference and sample beams. In this way the detector determines which frequencies have been absorbed by the sample and which frequencies are unaffected by the light passing through the sample. The signals are amplified in amplifier and are recorded in frequency domain by the recorder (fig 5.7).

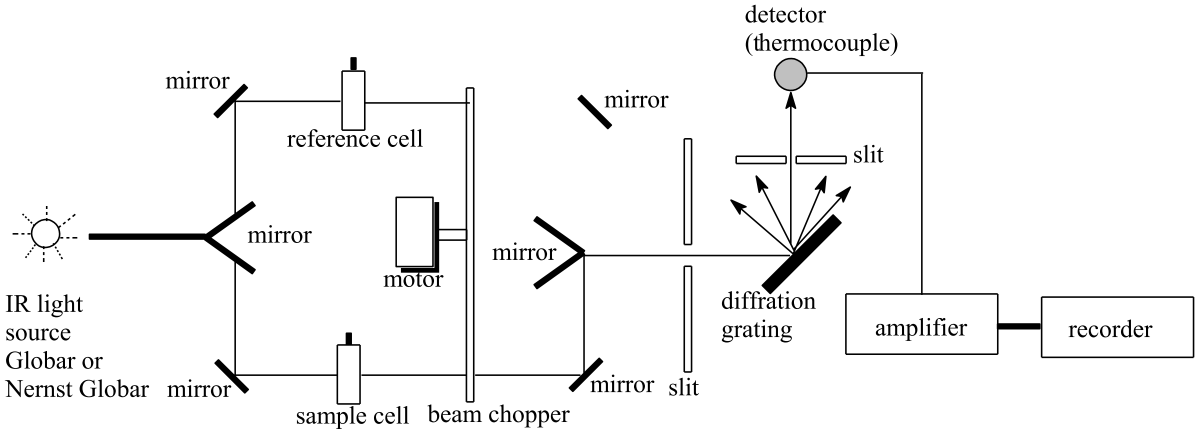


Fig.5.7. A schematic block diagram of a dispersive IR- spectrophotometer

Tne principle of IR-absorption inFourier transformation infrared (FT-IR) spectrophotometer is different from dispersive IR which is based on Michelson interferometer.It is also called *interferometric infrared spectroscopy*. In FT-IR spectrophotometer the monochromator or grating has been replaced by Michelsion interferometer. This technique was developed by Albert Michelson (German born American physicist) in 1887.The techniques has been extensively developed over past decade with very high resolution (<0.001cm^{-1}). In FT-IR we get time domain spectra which are recorded time v_s intensity these spectra are the converted to frequency domain by applying FT, the mathematical transformation and the spectra obtained frequency v_s intensity. In a Michelson interferometer adopted for FTIR, light from the polychromatic infrared source, approximately a black-body radiator, is collimated and directed to a beam splitter. Ideally 50% of the light is refracted towards the fixed mirror and 50% is transmitted towards the moving mirror. Light is reflected from the two mirrors back to the beam splitter and some fraction of the original light passes into the sample compartment. There, the light is focused on the sample. On leaving the sample compartment the light is refocused on to the detector. The difference in optical path length between the two arms to the interferometer is known as the *retardation* or *optical path difference* (OPD). An interferogram is obtained by varying the retardation and recording the signal from the detector for various values of the retardation. The form of the interferogram when no sample is present depends on factors such as the variation of source intensity and splitter efficiency with wavelength. This results in a maximum at zero retardation, when there is constructive interference at all wavelengths, followed by series of "squirm". The position of zero retardation is determined accurately by finding the point of maximum intensity in the interferogram. When a sample is present the background interferogram is modulated by the presence of absorption bands in the sample.The S/n ratio is enhanced. The schematic digram of FT-IR and Michelsion interferometer is given in fig 5.8, 5.9 [A] and [B].

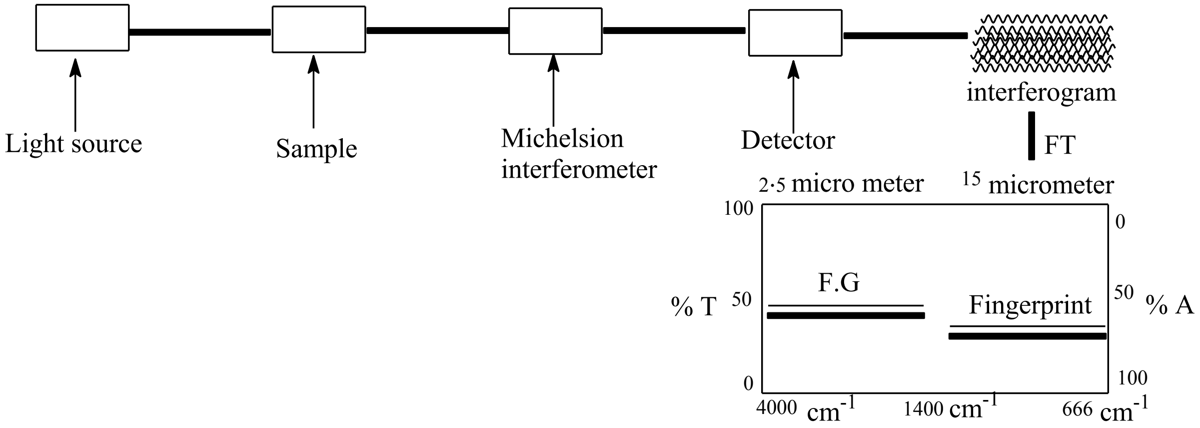


Fig 5.8. A schematic diagram of FT-IR spectrophotometer

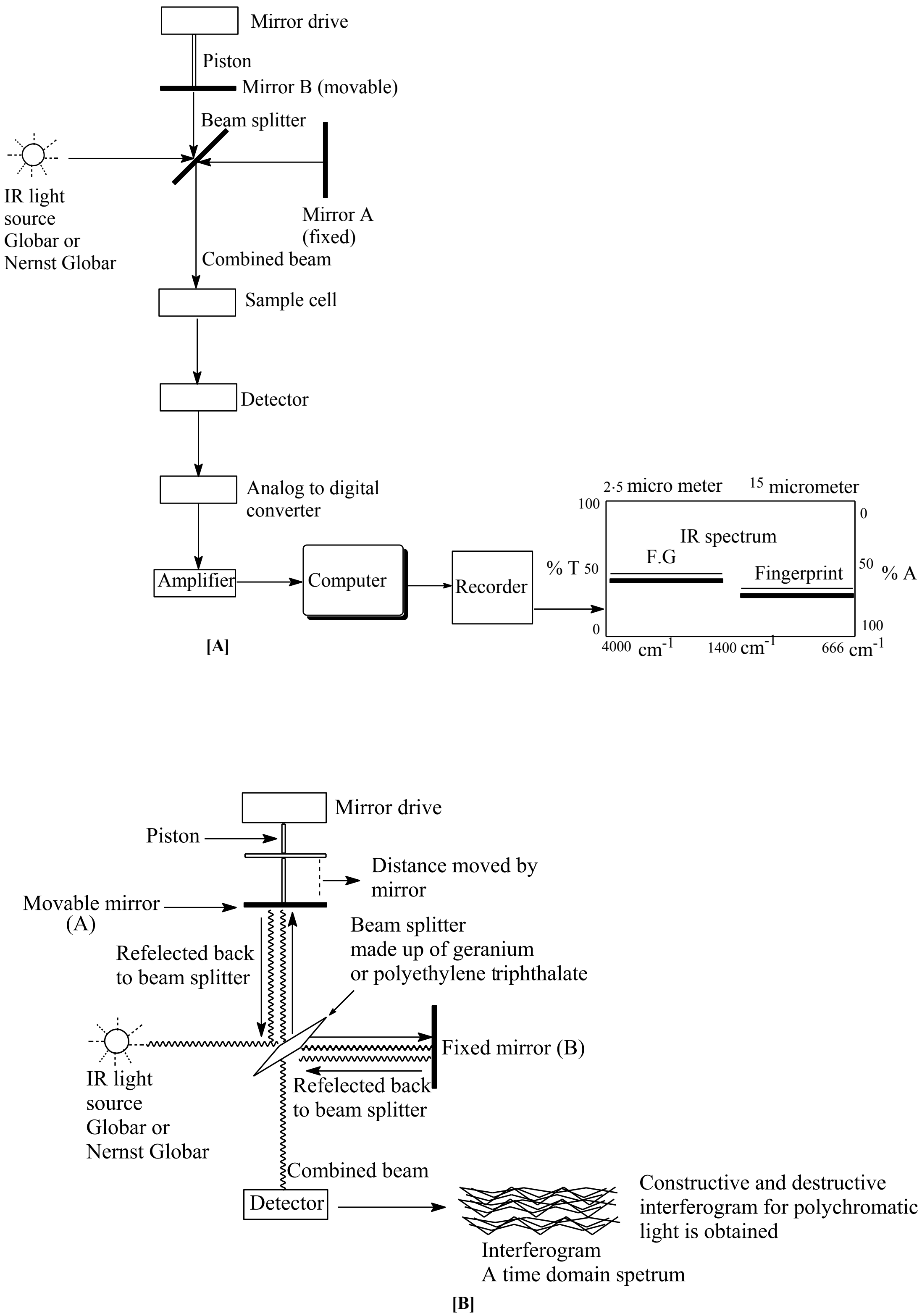
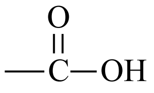
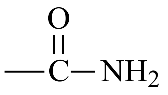
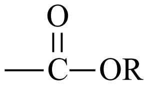
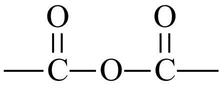
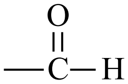
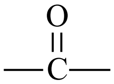
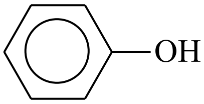


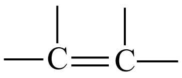
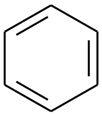
Fig. 5.9. FT-IR spectrophotometer [A] Michelson interferometer [B]

5.13 INTERPRETATION OF SPECTRA OF SOME CLASSES OF COMPOUNDS

While analyzing the IR- spectra of an unknown, compounds. Examine first the presence (or absence) of a few major functional groups. Like The C=O, O-H, N-H, C-O, C=C, C ≡ C, C ≡ N, and NO_2, which are the most conspicuous and give immediate structural information if they are present. Do not try to make a detailed analysis of the C – H absorption near 3000 cm^{-1}; almost all compounds have these absorptions. Do not worry about subtleties of the exact environment in which the fuctional group is found. Following are the key points to be considered during the interpretion of IR- spectra.

1.	Is a carbonyl group present? The C = O group gives rise to a strong absorption in the region 1820-1660 cm^{-1}. The peak is often the strongest in the spectrum and of medium width. You can't miss it.
2.	If C = O is present, check the following types (if it is absent, refer point no. 3).
ACIDS  $-\overset{\overset{O}{\|}}{C}-OH$	Is O – H also present? ➢ Broad absorption near 3400-2400 cm^{-1} (usually overlaps C – H)
AMIDES  $-\overset{\overset{O}{\|}}{C}-NH_2$	Is N – H also present? ➢ Medium absorption near 3400 cm^{-1}; sometimes a double peak with equivalent halves.
ESTERS  $-\overset{\overset{O}{\|}}{C}-OR$	Is C – O also present? ➢ Strong-intensity absorptions near 1300-1000 cm^{-1}.

ANHYDRIDES  $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	Two C = O absorptions near 1810 and 1760 cm^{-1}.
ALDEHYDES  $-\overset{O}{\overset{\|}{C}}-H$	Is aldehydes C – H present? ➢ Two weak absorptions near 2850 and 2750 cm^{-1} on right side of the aliphatic C – H absorptions.
KETONES  $-\overset{O}{\overset{\|}{C}}-$	The preceding five choices have been eliminated.
3.	If C = O is absent
ALCOHOLS, PHENOLS ROH 	Check for O – H. ➢ Broad absorption near 3400-3300 cm^{-1}. ➢ Confirm this by finding C – O near 1300-1000 cm^{-1}.
AMINES RNH_2/ $(R)_2NH$ $(R)_3N$	Check for N-H. ➢ Medium absorption(s) near 3400 cm^{-1}.
ETHERS	Check for C –O near 1300-1000 cm^{-1} (and absence of O – H

R—O—R		near 3400 cm^{-1}).
4.	Double bonds and/or aromatic rings	
 $-\overset{\vert}{C}=\overset{\vert}{C}-$ 		➢ C = C is a weak absorption in the region. ➢ Medium to strong absorptions in the region 1600-1450 cm^{-1}; thease often imply an aromatic ring. ➢ Confirm the double bond or aromatic ring by consulting the C – H region; aromatic and vinyl C – H occurs to the left of 3000 cm^{-1} (aliphatic C – H occurs to the right of this value).
5.	Triple bonds	
	$-C\equiv C-$	➢ C ≡ N is a medium, sharp absorption near 2250 cm^{-1}. ➢ C ≡ C is a weak, sharp absorption near 2150 cm^{-1}. ➢ Check also for acetylenic C – H near 3300 cm^{-1}.
6.	Nitro groups	
	NO_2	➢ Two strong absorptions at 1600-1530 cm^{-1} and 1390-1300 cm^{-1}
7.	Hydrocarbons	
	HC	➢ None of the preceding is found. ➢ Major absorptions are in C – H region near 3000^{-1}. ➢ Very simple spectrum; the only other absorptions appear near 1460 and 1375 cm^{-1}

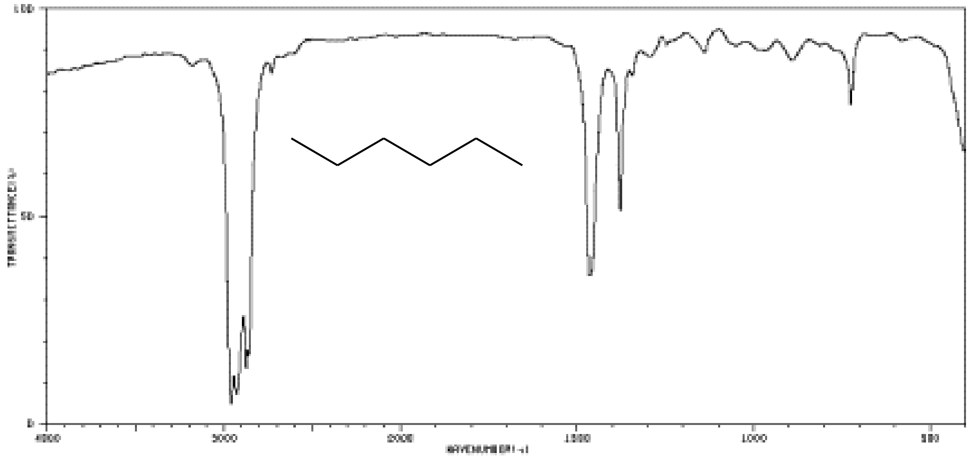
The beginners should resist the idea of trying to assign or interpret every peak in the spectrum. You simply will not be able to do it. Concentrate first on learning these major peaks and recognizing their presence or absence. For intrepriting IR spectra here some representative spectra of compounds are being described as follow.

Alkanes: Alkanes show very few absorption bands in the infrared spectrum. They yield four or more C – H stretching peaks near 3000 cm^{-1} plus CH_2 and CH_3 bending peaks in the range 1475-1365 cm^{-1}.

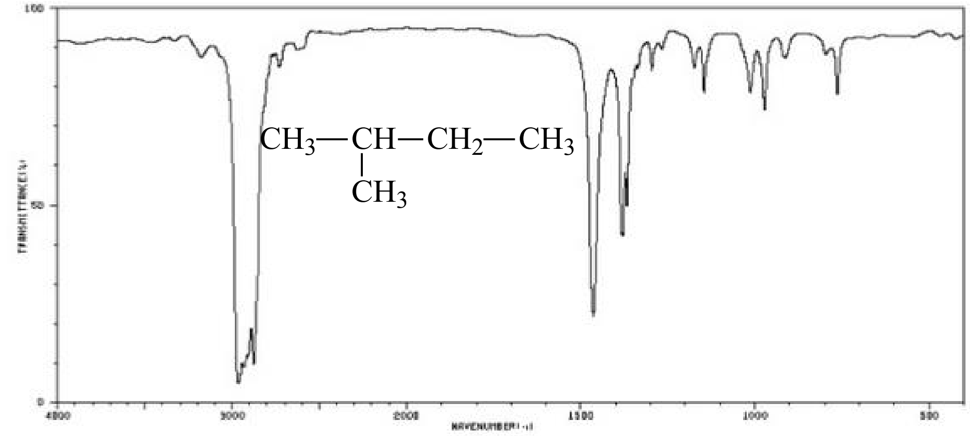
The spectrum is usually, with few peaks.

C – H	Stretch occurs around 3000 cm^{-1}.
	In alkanes (except strained ring compounds), sp^3 C – H absorption always occurs at frequencies less than 3000 cm^{-1} (3000-2840 cm^{-1})
	If a compound has vinylic, aromatic, acetylenic, or cyclopropyl hydrogens, the C – H absorption is greater than 3000 cm^{-1}. These compounds have sp^2 and sp hybridizations.
CH_2	Methylene groups have a characteristic bending absorption of approximately 1465 cm^{-1}
CH_3	Methyl groups have a characteristic bending absorption of approximately 1375 cm^{-1}
CH_2	The bending (rocking) motion associated with four or more CH_2 groups in an open chain occurs at about 720 cm^{-1} (called a long-chain band)
C – C	Stretch not interpretatively useful; many weak peaks.

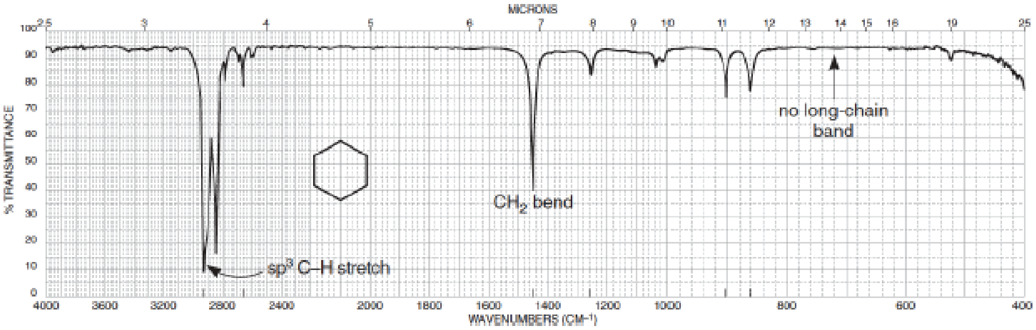
IR- of hexane



IR of isopentane



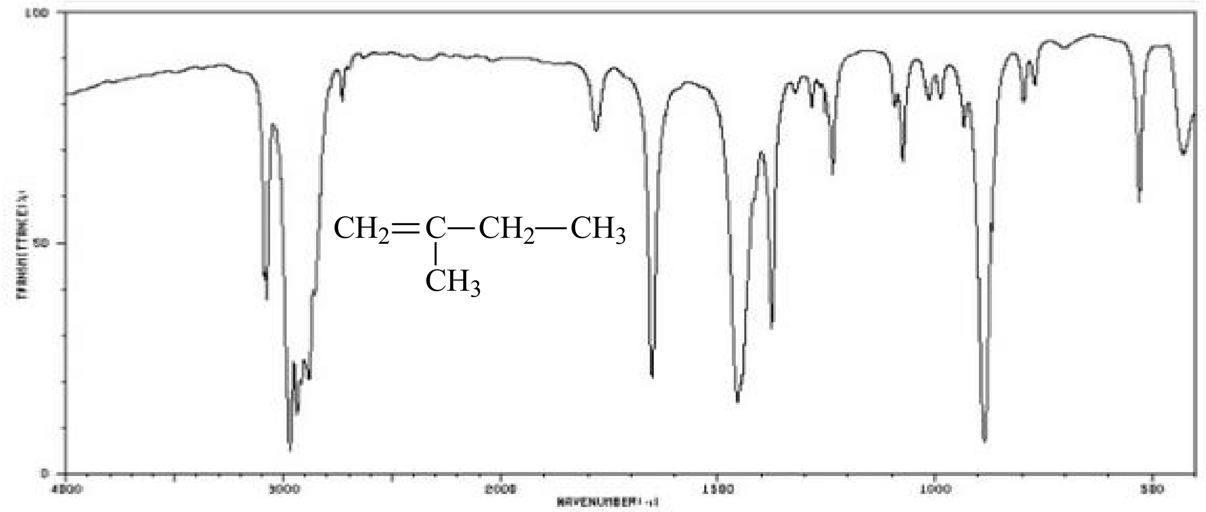
IR of cyclohexane



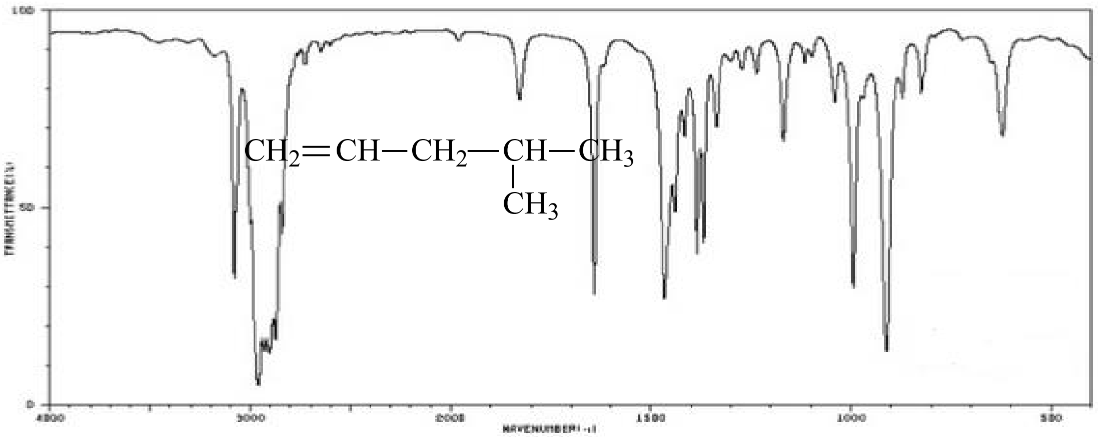
Alkenes: Alkenes exhibit many peaks, but the important diagonistic peaks are as follow.

= C- H	Stretch for sp^2 C – H occurs at values greater than 3000 cm^{-1}. (3095-3010 cm^{-1})
= C – H	Out-of-plane (oop) bending occurs in the range 1000-650 cm^{-1}.
These bands can be used to determine the degree of substitution on the double bond (see discussion).	
C = C	Stretch occurs at 1660-1600 cm^{-1}; often conjugation moves C = C stretch to lower frequencies and increases the intensity.
	Symmetrically substituted bonds (e.g. 2,3-dimethyl-2-butene) do not absorb in the infrared (no dipole change).
	Symmetrically disubstituted (trans) double bonds are often vanishing weak in absorption; cis are stronger.

IR of 2-methyl-1-butene



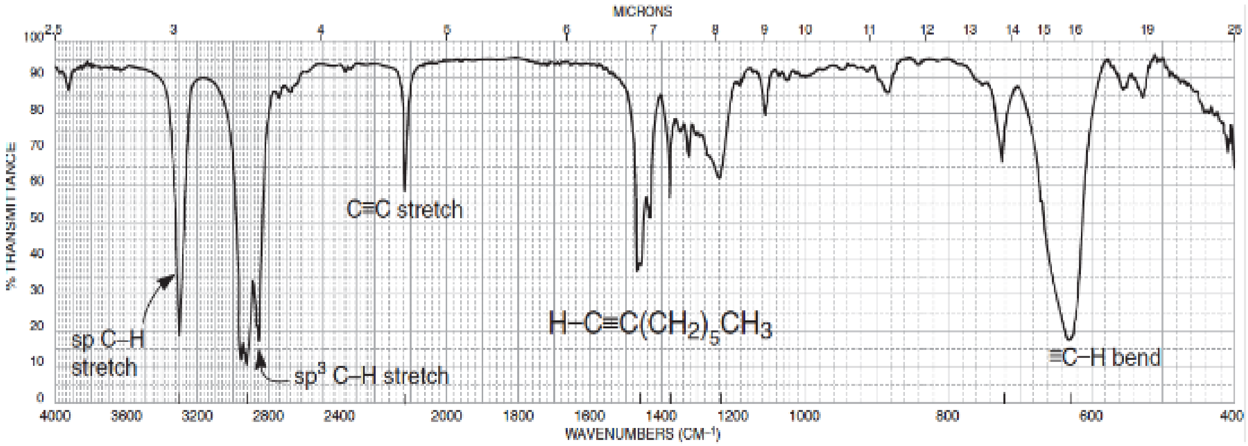
IR of 4-methyl 1- pantene



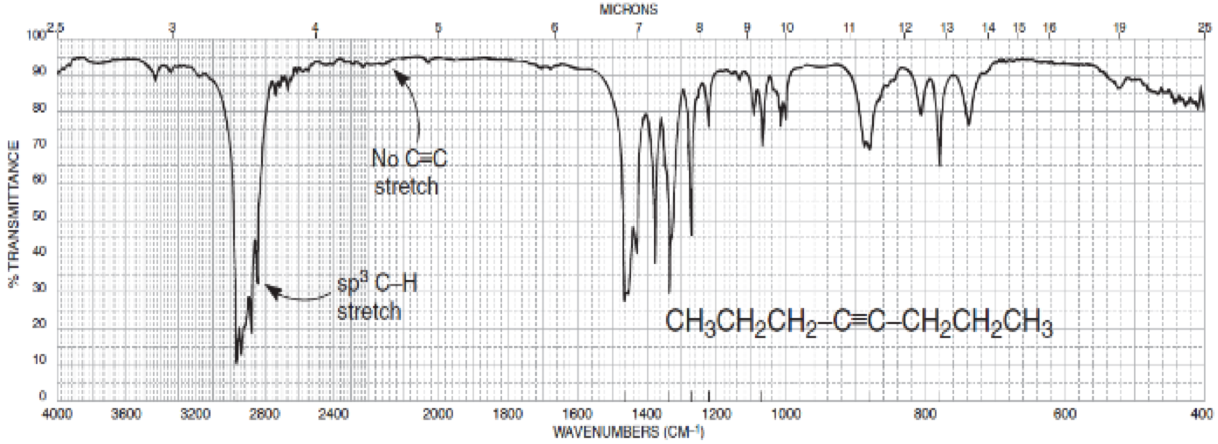
Alkynes: The terminal alkynes show peak at 3300 cm^{-1} and is not given by non terminal alkynes. Besides following peaks alkynes give C-H stretching for sp^3 carbon atoms.

$\equiv C-H$	C-H stretching at about 3300cm^{-1}
$C\equiv C$	It occur at about 2150 cm^{-1}, however conjugation move it towards lower frequency. Symmetrically substituted triple bond ether do not gives absorption or gives weak absorption.

IR spectrum of octyne-1:

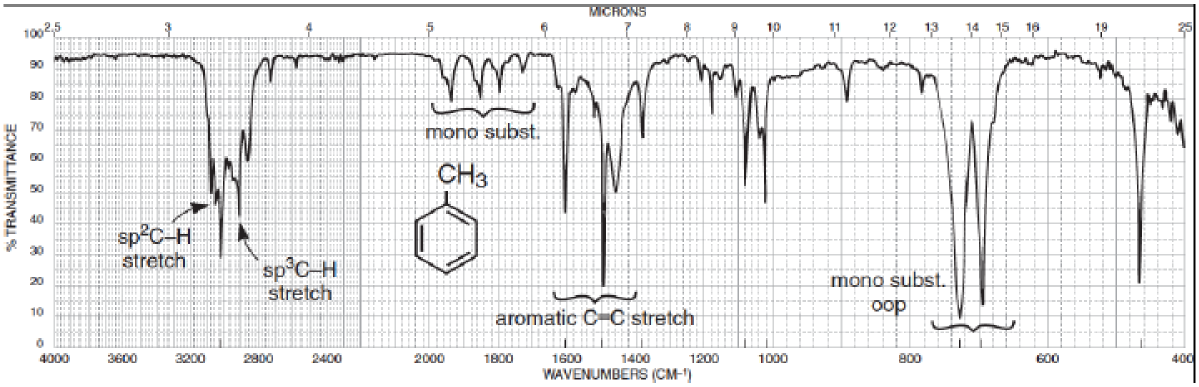


IR spectrum of 4-octyne:



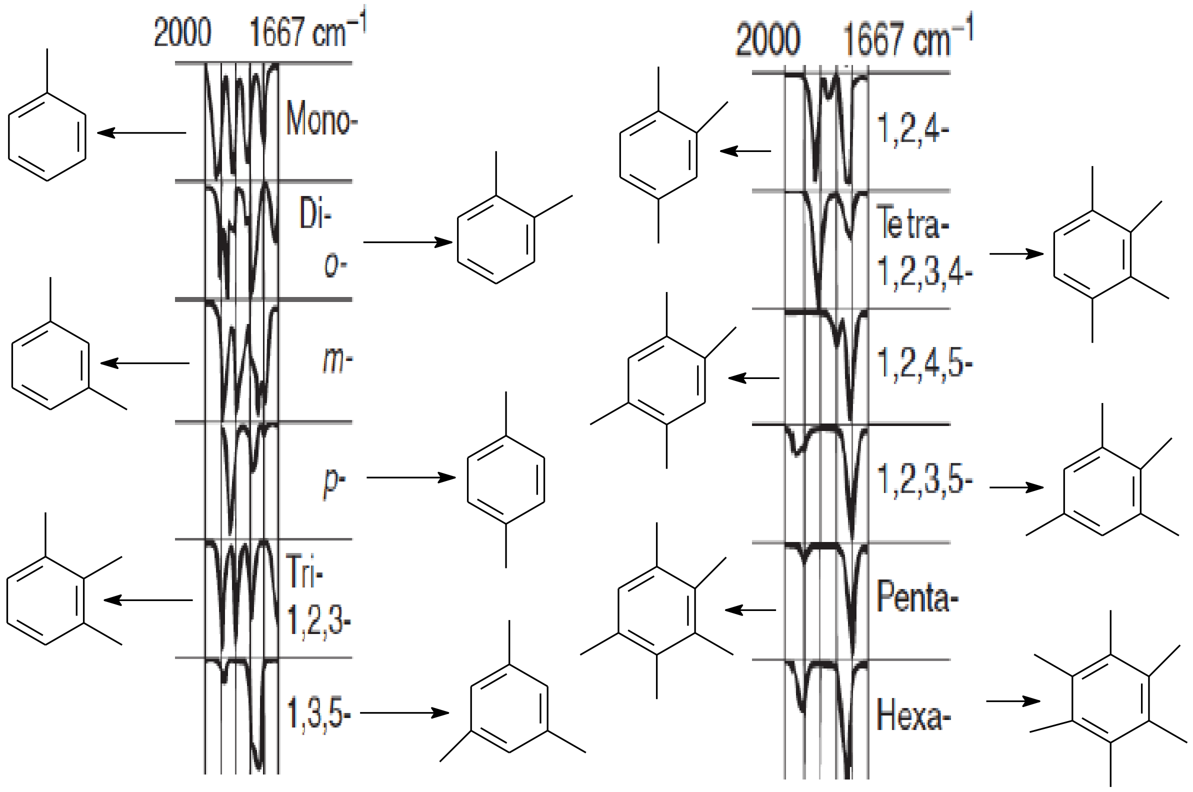
Aromatic compounds: The aromatic compounds show many absorption peaks in IR. All the peaks donot has diagnostic value. The peak for sp^2 carbon appears at higher at about 3000-31080cm^{-1}. The major diagnostic peaks in aromatic compounds are as follow with subsequent spectra of representative compounds.

=C-H	For sp^2 C-H. It occur at about 3000-3080 cm-1
=C-H	900- 690 cm^{-1} very important region tells about the pattern of substitution in aromatic compound. These bands appear because of oop (Out-of-plane) bending
C=C	Appears in pair at 1600 cm^{-1} and 1475 cm^{-1}
	A weak absorption pattern known as overtone region for aromatic compounds appears between 2000- 1667 cm^{-1} This is again highly informative region.

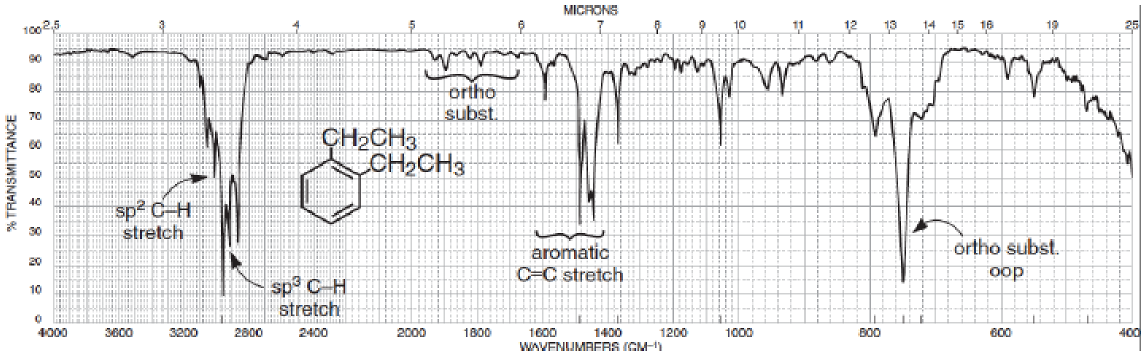


IR spectrum of toluene

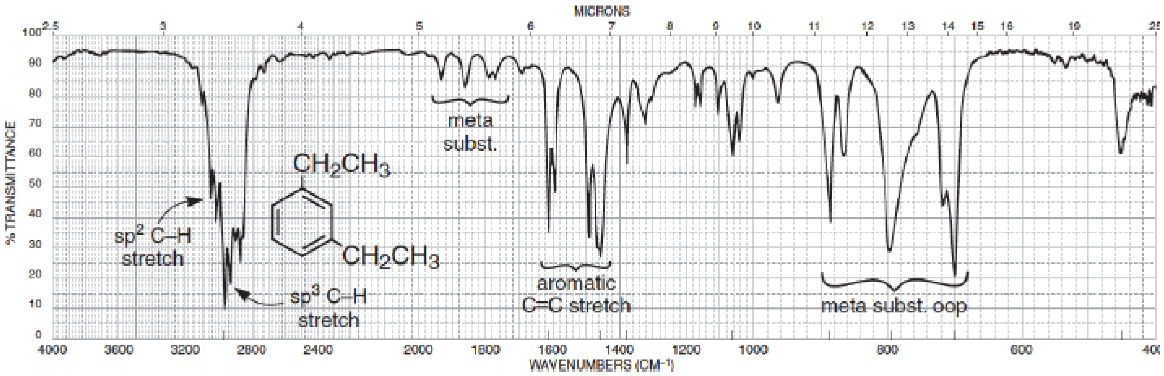
Substituted pattern: The following substitution pattern is observed in aromatic system



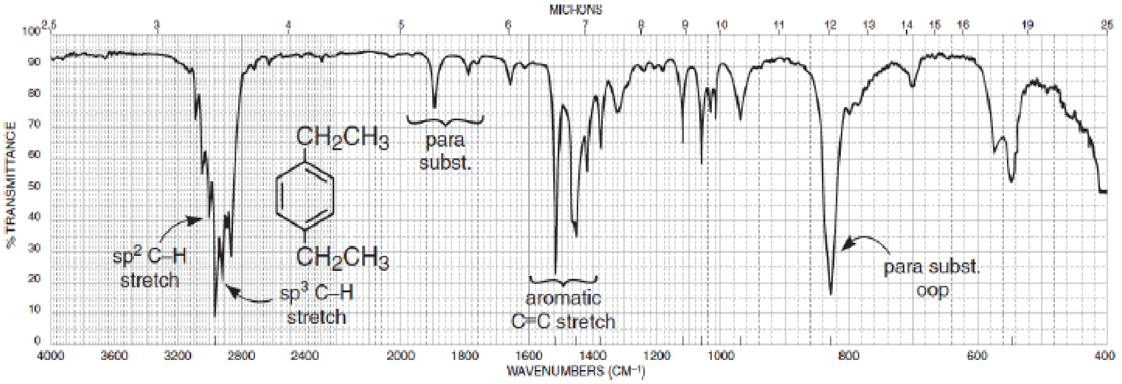
IR of ortho-diethyl benzene:



IR of meta-diethyl benzene:

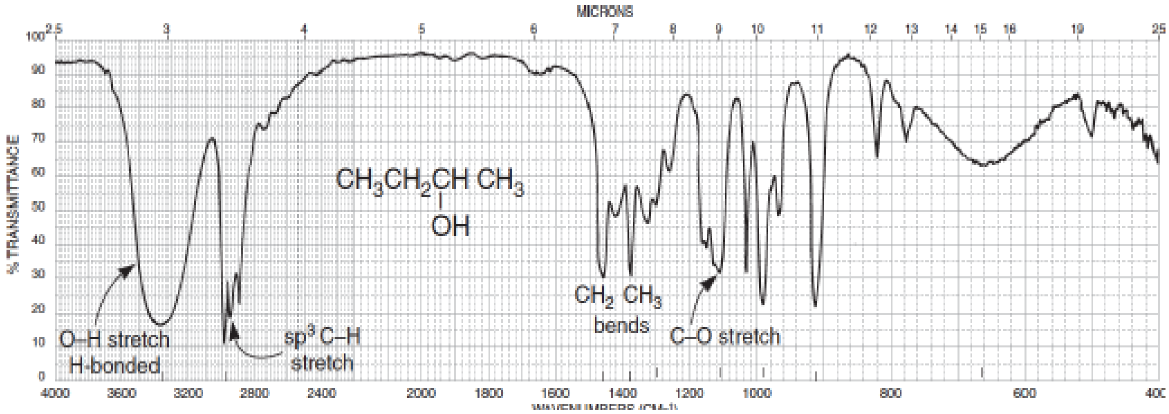


IR of para-diethyl benzene:

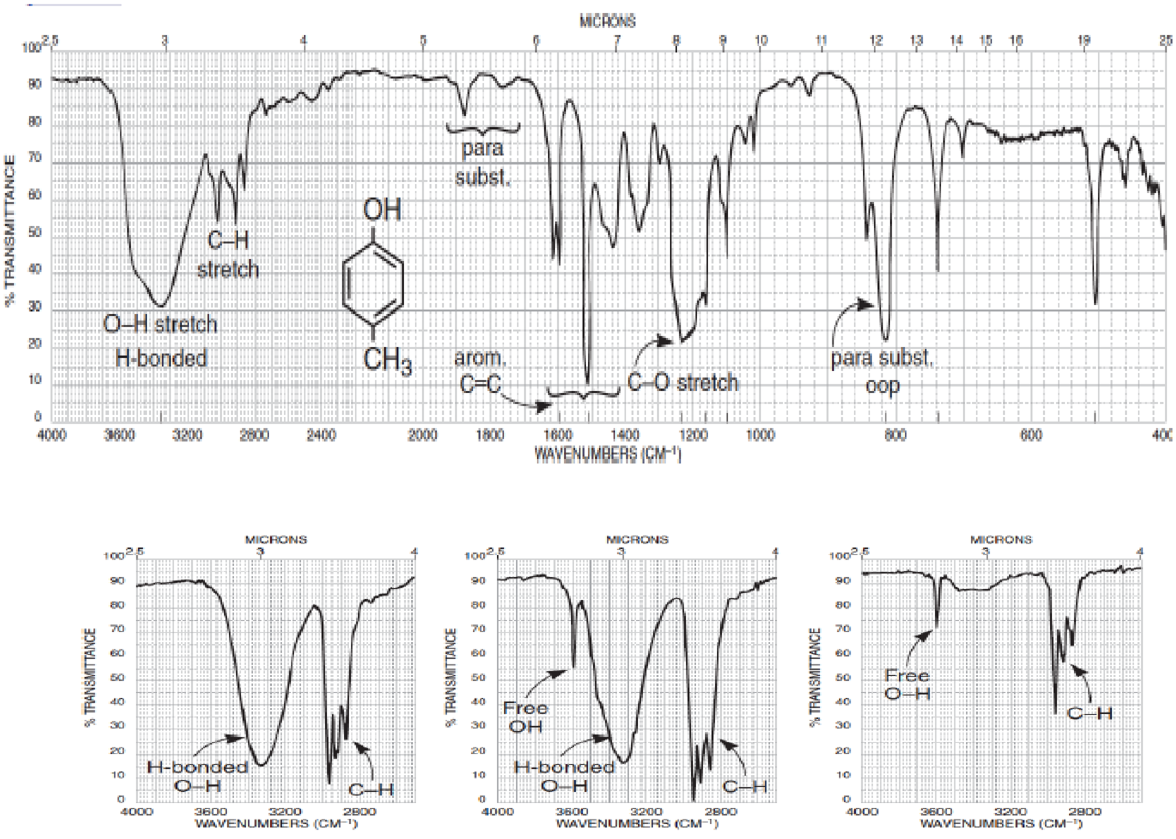


Alcohols and phenols: the –OH group of alcohol (R-OH) and phenol (Ph-OH) show –O-H stretching band at about 3400-3300 cm^{-1} in solution form. However in gaseous phase the free O-H stretching at 3600 cm^{-1} is observed. The shifting of O-H stretching towards lower frequency is because of hydrogen bonding, which weakes the force constant (k). The other diagonistic peak for C-O stretching is also observed between 1200-1000 cm^{-1}. In consolidated tabular representation of major diagonistic peaks alcohols and phenols are being described as under:

O-H	Free O-H stretch at 3650-3600 cm^{-1}. The hydrogen-bonded O-H bank is a broad peak at 3400-3300 cm^{-1}. This band is usually the only one present in an alcohol that has not been dissolved in a solven (near liquid). When the alcohol is dissolved in a solven, the free O-H and hydrogen-bonded O-H bands are present together, with the relatively weak free O-H
C-O-H	Bending appears as a broad and weak peak at 1440-1220 cm^{-1} often obscured by the CH_3 bendings.
C-O	Stretching vibration usually occurs in the range 1200-1000 cm^{-1}. This band can be used to assign a primary, secondary, or tertiary structure to an alcohol (see discussion) refer following examples.



Effect of hydrogen bonding: Hydrogen bonding always weakens the force constant and cause shifting of IR peak towards lower wavelength and shape of peak is broad. However the free O-H stretching is sharp in shape and appears towards higher wavelength (fig.5.10).

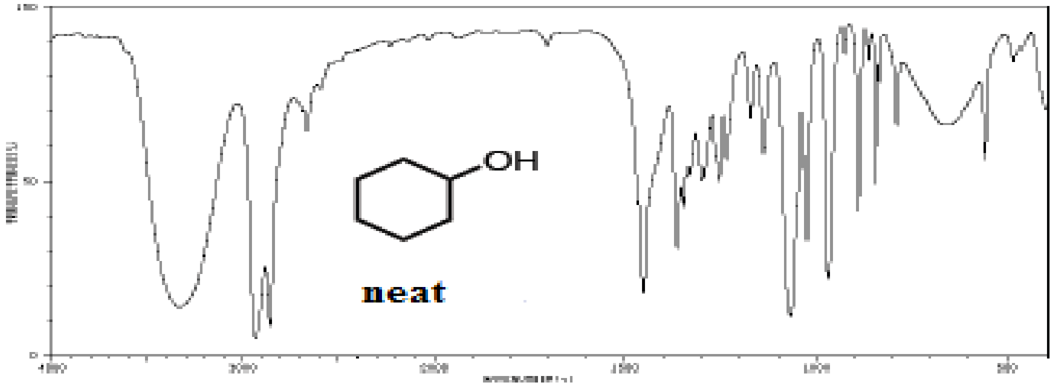


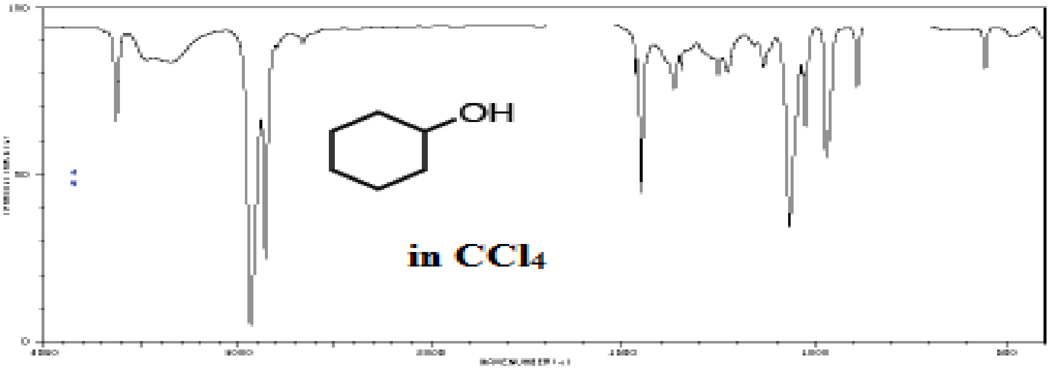
hydrogen bonded OH

free and hydrogen bonded OH (dilute solution)

free and hydrogen bonded OH (very dilute solution)

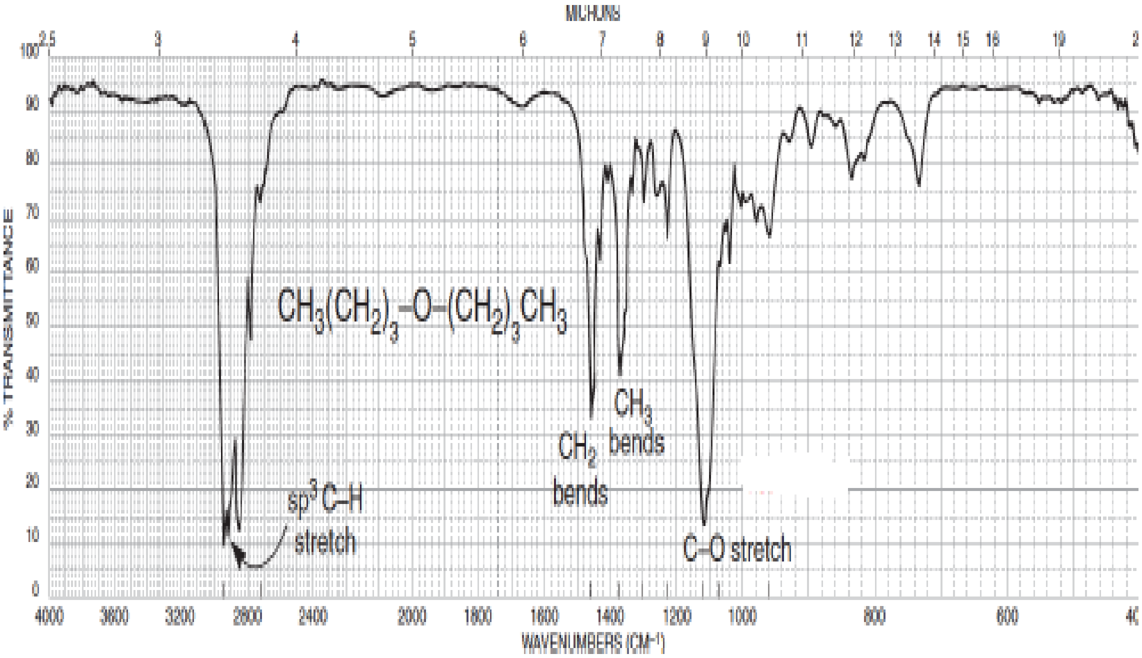
Fig 5.10. Shape and position of O-H stretching (free and hydrogen bonded)



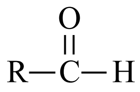
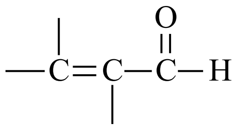
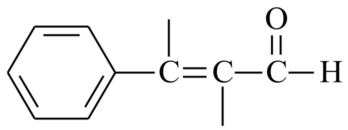


Ethers: The IR spectra of ethers generally look like to those of alkane; however can be distinguished by C-O stretching which appears between 1300-1000 cm^{-1} as shown in following spectra.

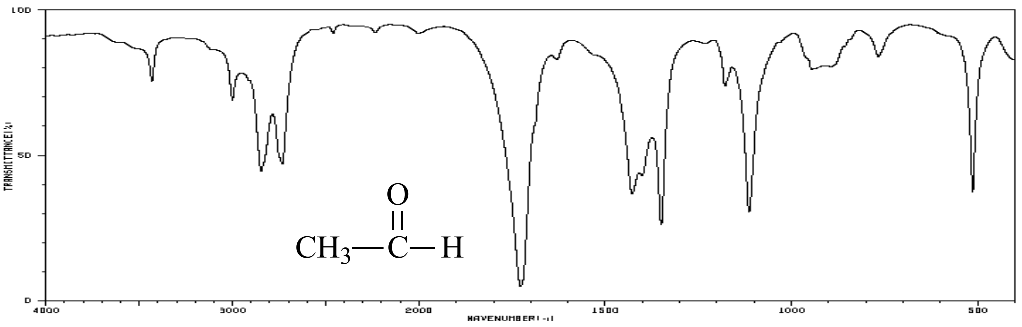
C-O	The most prominent band is that due to C-O stretch. 1300-1000 cm^{-1}. Absemce of C=O and O-H is required to ensure that C-O stretch is not due to an ester or an alcohol. Phenyl alkyl ethers give two strong bands at about 1250 and 1040 cm^{-1}, while aliphatic ethers give one strong band at about 1120 cm^{-1}.

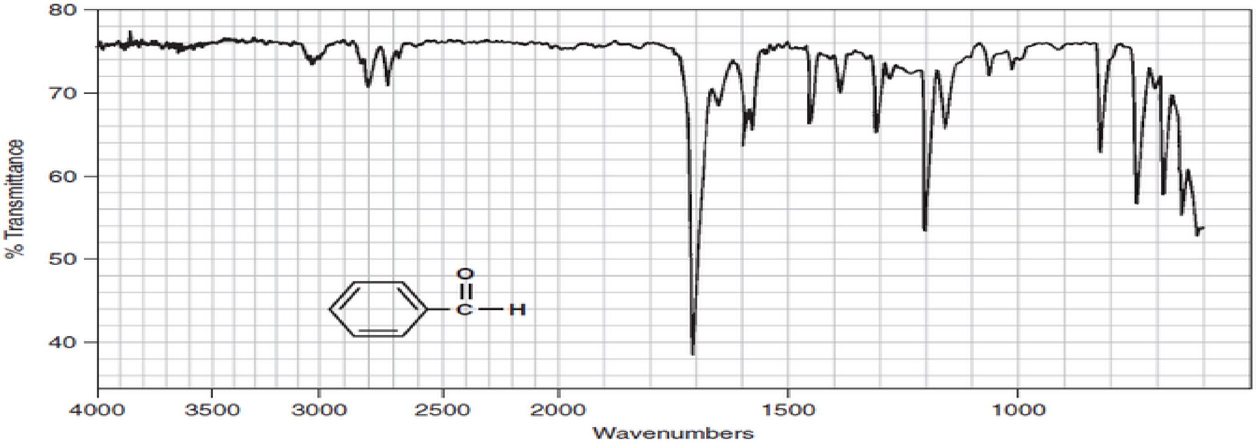


Aldehydes: Aldehydes give strong C=O peak in the range of 1740-1725 cm^{-1} This band is shifted towards lower frequency in presence of conjugation because of lengthening of C=O bond as a function of force constant. A doublet for C-H stretching known as overtone around 2850-2750 cm^{-1} is observed which differ aldehydes rom other carbony compounds.

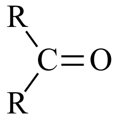
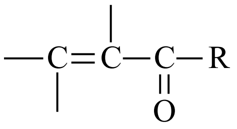
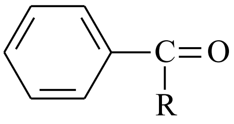
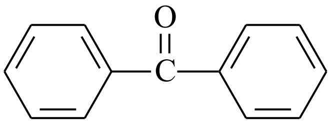
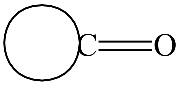
 $\mathrm{R-\overset{\overset{O}{\|}}{C}-H}$	C=O stretch gives peak in the range of 1740-1725 cm^{-1} for normal aliphatic aldehydes.
 $\mathrm{-\overset{|}{C}=\underset{|}{C}-\overset{\overset{O}{\|}}{C}-H}$	Conjugation of C=O with α, β C=C; 1700-1680 cm^{-1} for C=O and 1640 cm^{-1} for C=C
	Conjugation of C=O with phenyl; 1700-1660 cm^{-1} for C=O and 1600-1450 cm^{-1} for ring.
	Longer conjugated system; 1680 cm^{-1} for C=O
C-H	Stretch, aldehyde hydrogen (-CHO), consists of a pair of weak bands, one at 2860-2800 cm^{-1} and the other at 2760-2700 cm^{-1} . It is easier to see the band at the lower frequency because it is not obscured by the usual C-H bands from the alkyl chain. The higher-frequency aldehyde C-H stretch is often buried in the aliphatic C-H bands.

Some of the IR spectra of aldehydes are being presented here as follow:

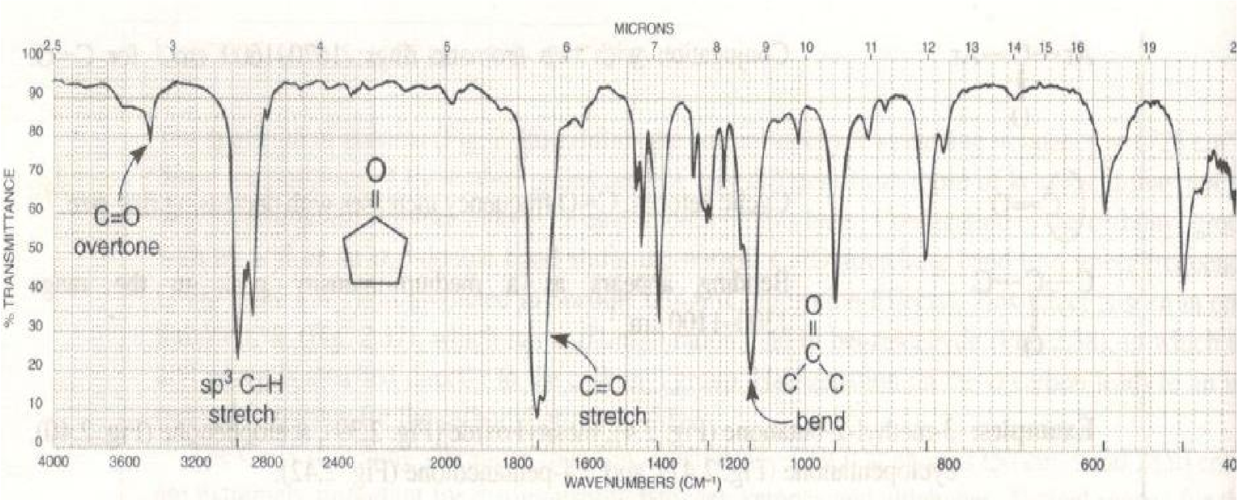


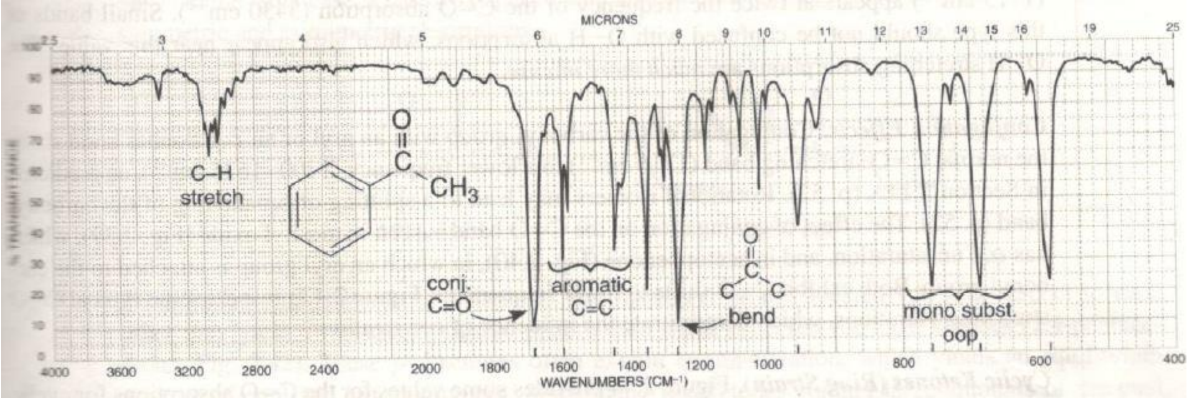


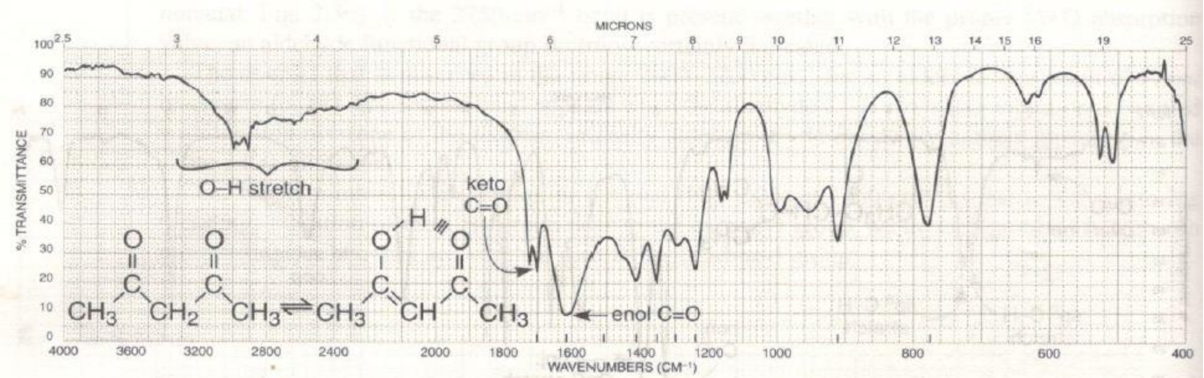
Ketones: Ketone is a very important function group in organic compound it gives the stretching peak in the range of 1720-1708 cm^{-1} subject to the structural feature of the compound.The position of peak shift towards lower frequencies with conjugation or phenyl group. However the electron withdrawing groups like halogen at α- position shift the C=O peak towards higher frequency. Similarly ring strain moves it towards higher frequency.

	C=O stretch, 1720-1708 cm^{-1}
	C= O stretching ;1700 – 1675 cm^{-1} for α, β C=C 1644 – 1617 cm^{-1}
	C=O with phenyl 1700-1680 cm^{-1} and 1600-1450 cm^{-1} for ring.
	1670 – 1600 cm^{-1} with conjugation having two phenyl rings.
	C=O increases as ring strain increases i.e. ring size decreases

IR of some representative compounds are given as follow:

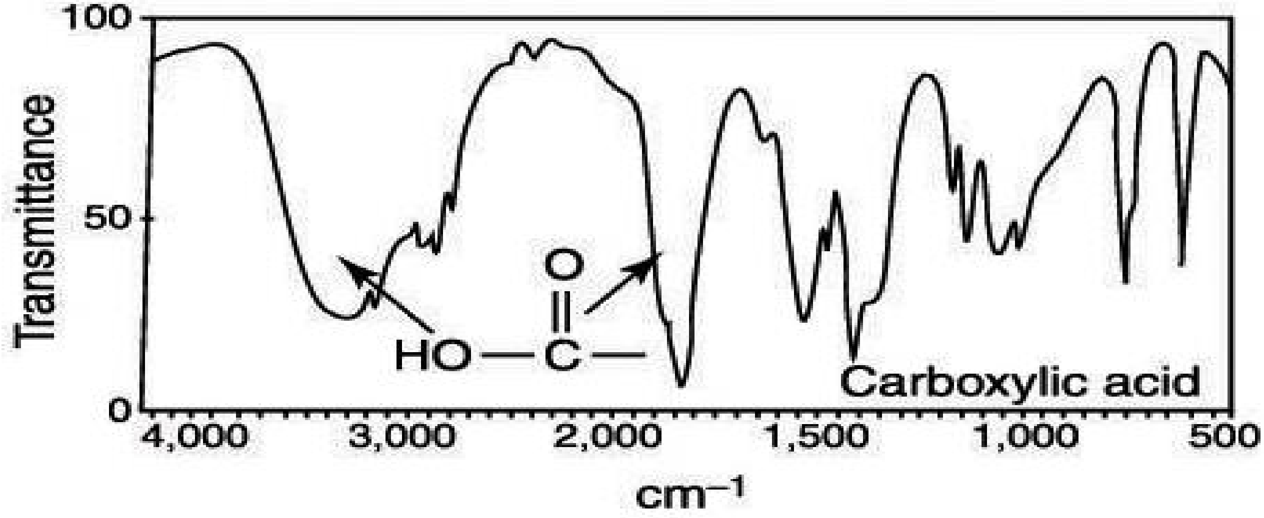


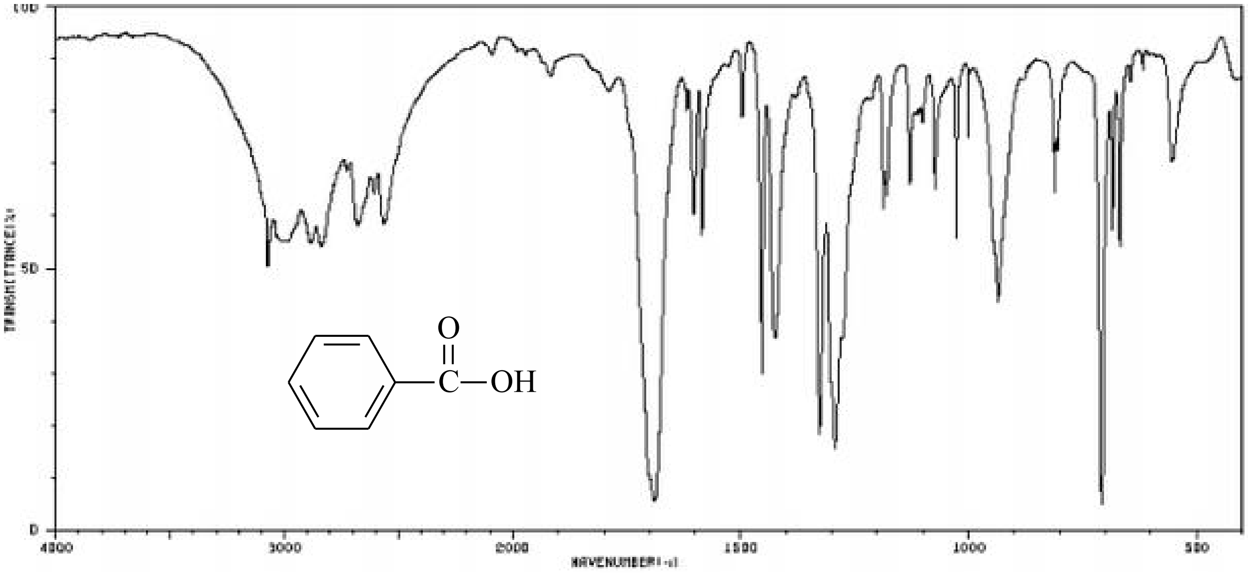


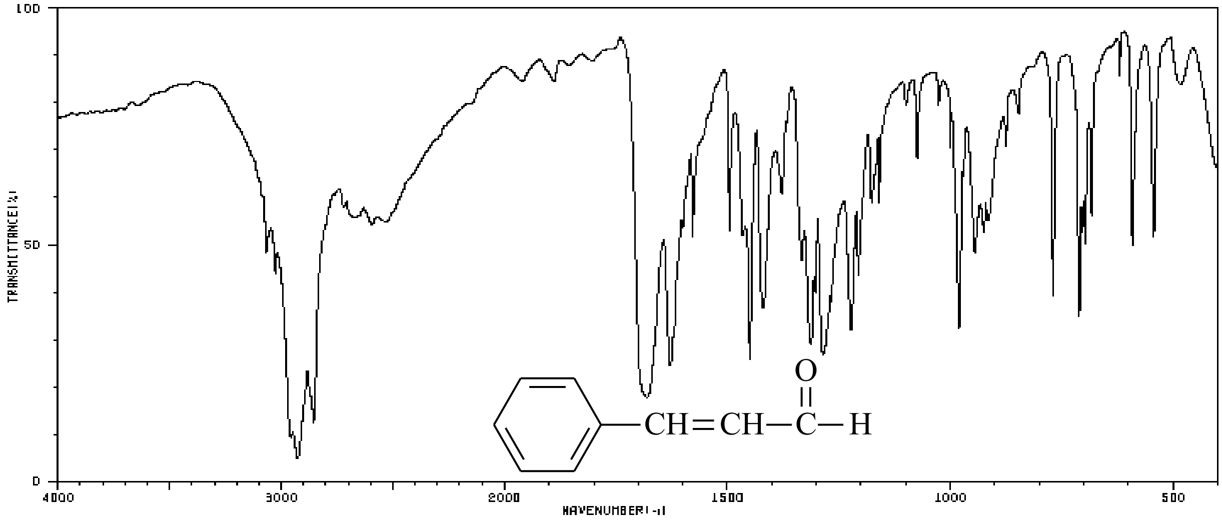


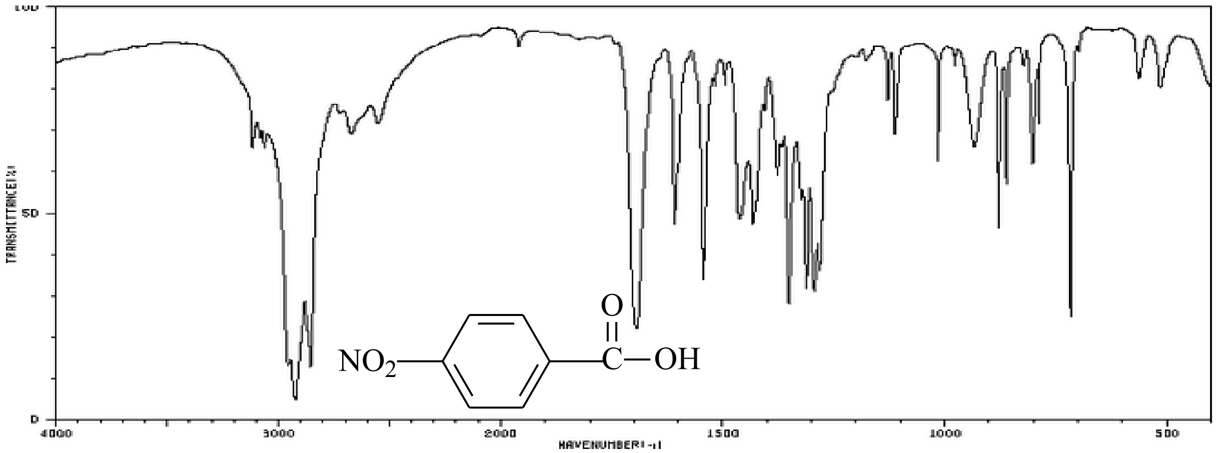
Carboxylic acids: Carboxylic acids give strong band for the C = O group in the range of 1730 – 1700 cm^{-1} for simple aliphatic acids in the *dimeric* form. Presence of with conjugation to a C = C or phenyl group shift it to lower frequencies. The O – H stretch gives broad band in the range of 3400 to 2400 cm^{-1}. If this very broad O – H stretch band is seen, along with a C = O peak, it almost certainly indicates the compound is a carboxylic acid.

O – H	Stretch, usually very broad (stronhly H-bonded), occurs at 3400-2400 cm^{-1} and often overlaps the C – H absorptions.
C = O	At 1730-1700 cm^{-1}. Conjugation shifts the absorption to a lower frequency.
C – O	Stretch occurs in the range 1320-1210 cm^{-1}, with medium intensity.

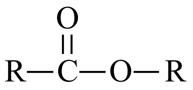
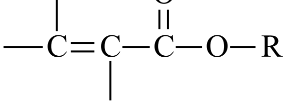


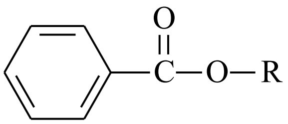
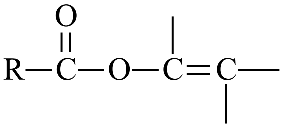
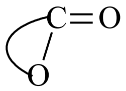




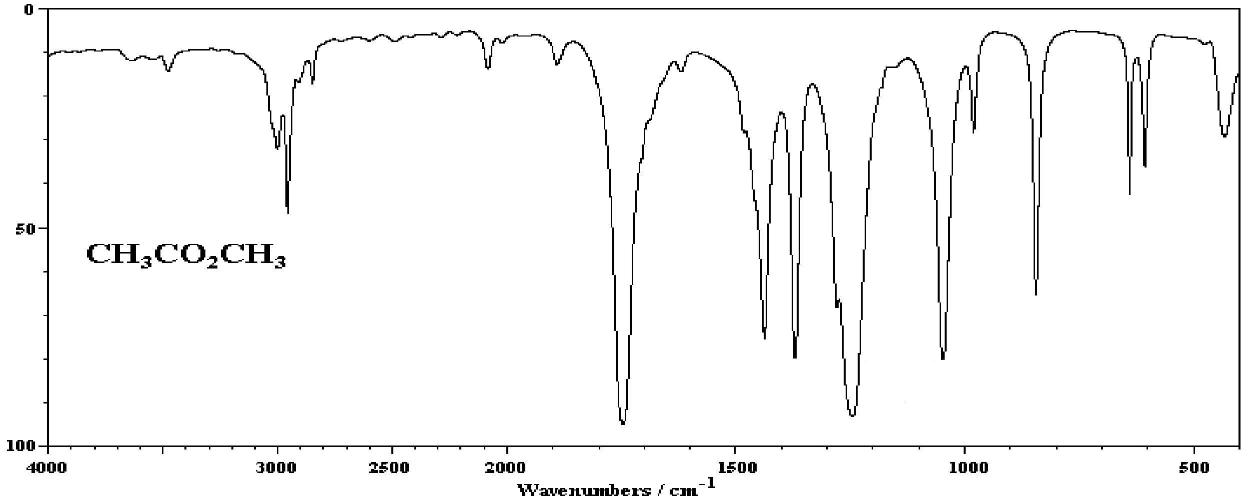


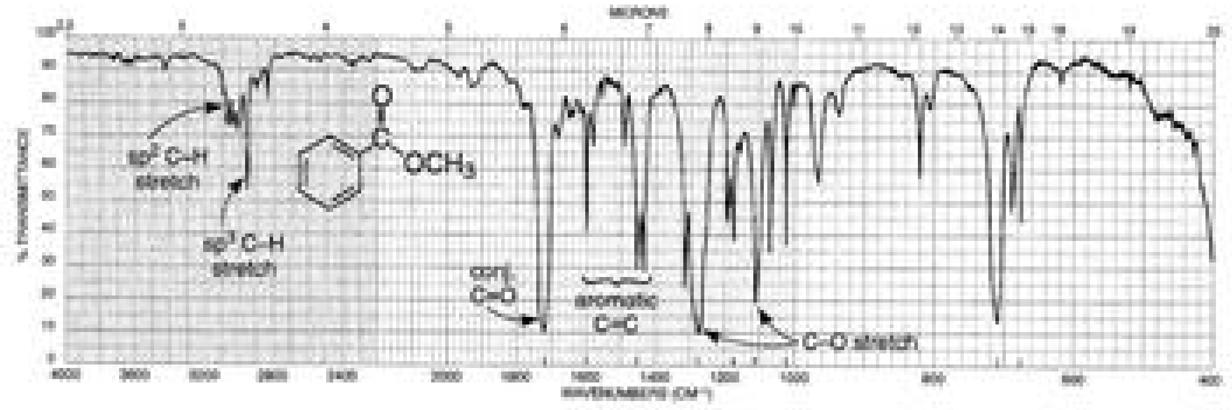
Esters: Esters show strong band for the C = O group which appears in the range of 1750-1735 cm^{-1} for aliphatic esters. The C = O band is shifted to lower frequencies when it is conjugated to a C = C or phenyl group. On the other hand, conjugation of a C = C or phenyl group with the single bonded oxygen of an ester leads to an increased frequency from the range given above. Ring strain moves the C = O absorption to a higher frequency in cyclic esters (lactones).

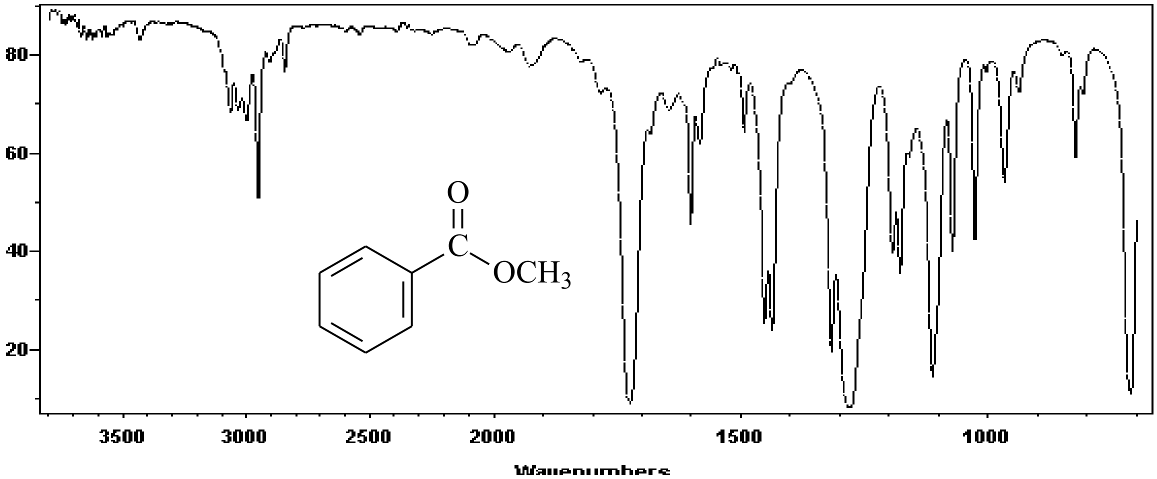
 $R-\overset{O}{\overset{\parallel}{C}}-O-R$	C = O stretch: 1750-1735 cm^{-1} for aliphatic esters.
 $-\overset{\vert}{C}=\underset{\vert}{C}-\overset{O}{\overset{\parallel}{C}}-O-R$	Conjugation of C = O with α,β C = C; 1740-1715 cm^{-1} for C = O and 1640-1625 cm^{-1} for C = C (two bands for some C = C, *cis* and *trans*)

	Conjugation of C = O with phenyl; 1740-1715 cm^{-1} for C = O and 1600-1450 cm^{-1} for ring.
 $R-\overset{\overset{O}{\|}}{C}-O-\overset{\vert}{C}=\underset{\vert}{C}-$	Conjugation through aingle-bonded oxygen atom with C = C or phenyl; 1765-1762 cm^{-1} for C = O
	Cyclic esters (lactones); C = O frequency increases with decreasing ring size.
C—O	Stretch in the range 1300-1000 cm^{-1}.

Some representative spectra are as follow:

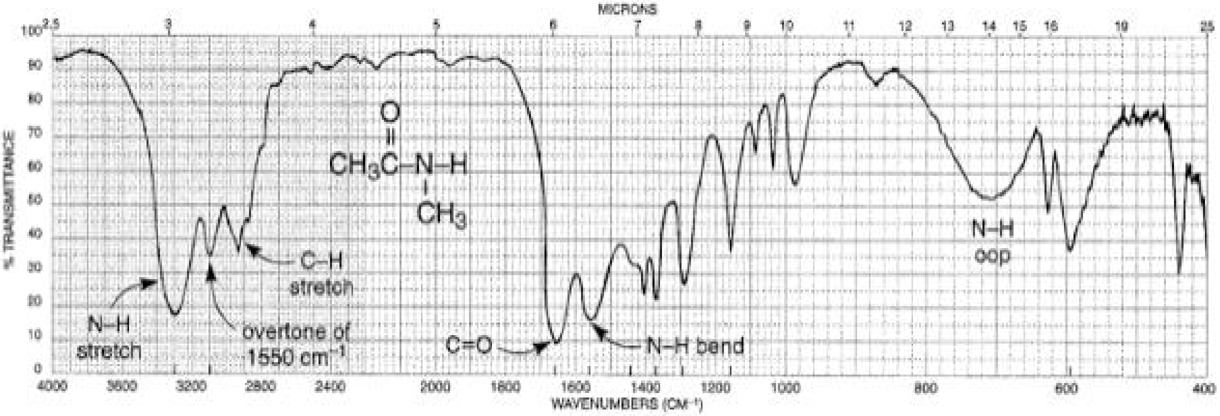




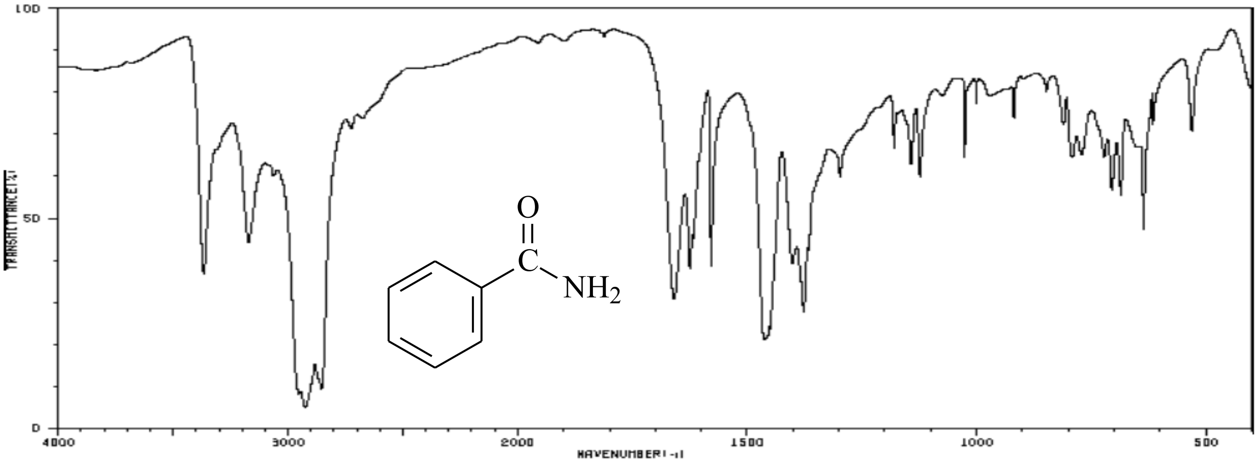


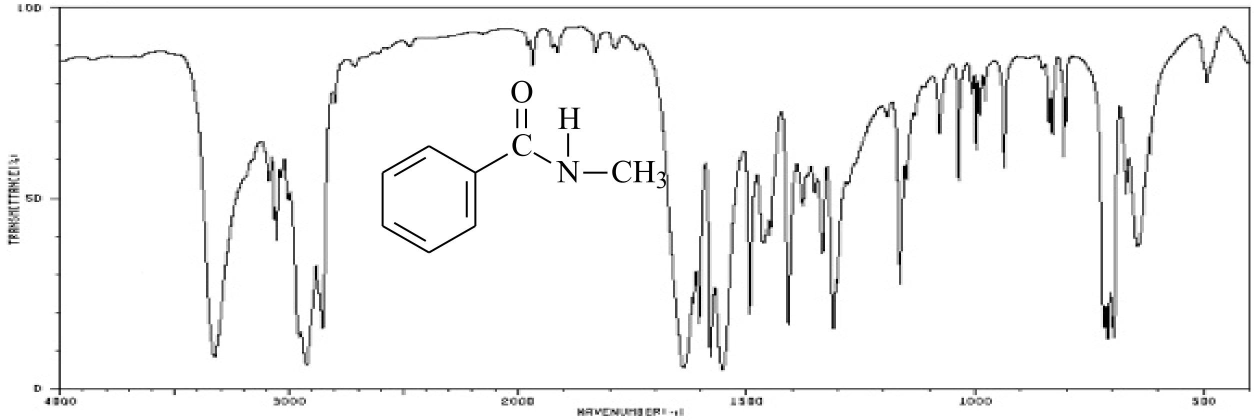
Amides: Amides show C = O stretchinh peak in the range of 1680-1630 cm^{-1}. However,the N – H stretch is observed in the range of 3475-3150 cm^{-1}. 1^{0} amides, R-CO-NH$_2$, show two bands in the N-H region while 2^{0} amides, R-CO-NH-R, show only one band. The presence of N-H bands plus an unusually low value for the C =O would suggest the presence of an amide functional group. 3^{0} amides, R-CO-NR$_2$, show the C = O in the range of 1680-1630 cm^{-1}, but are devoid of N-H stretch.

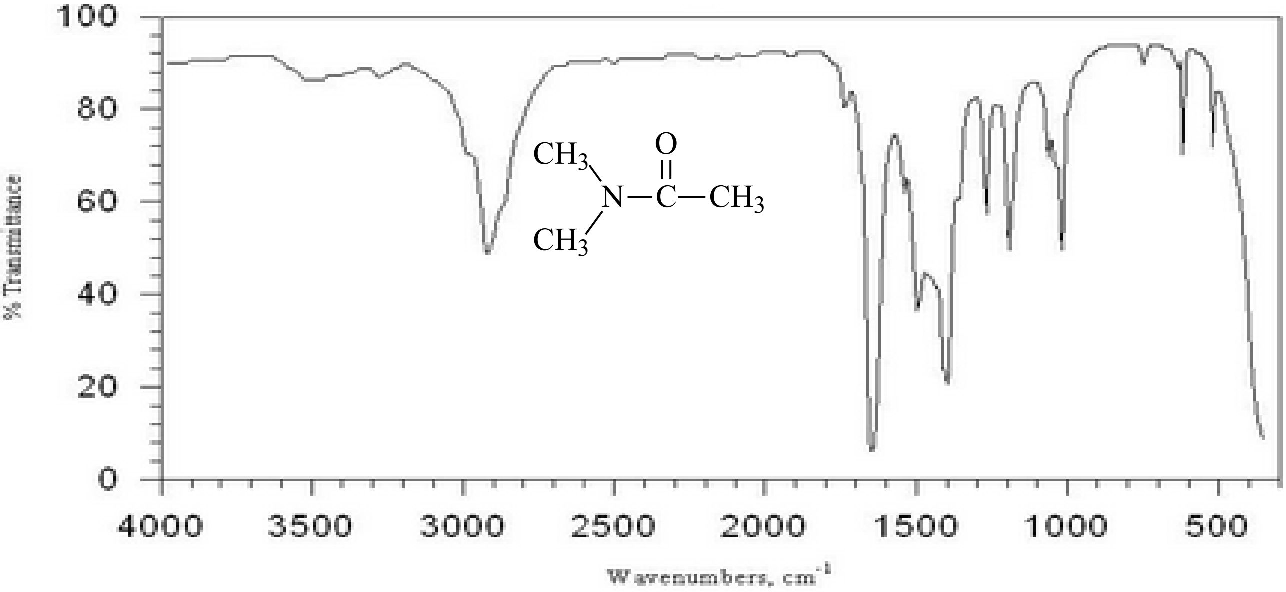
C = O	At 1680-1630 cm^{-1}
N – H	Two bands near 3350 and 3180 cm^{-1} for 1^{0} amides. 3300 cm^{-1} for Secondary amides
N – H	Bending at 1640-1550 cm^{-1} both for primary and secondary amides.



Some representative spectra of the amide molecules are as follow:


100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
O
C
NH$_2$

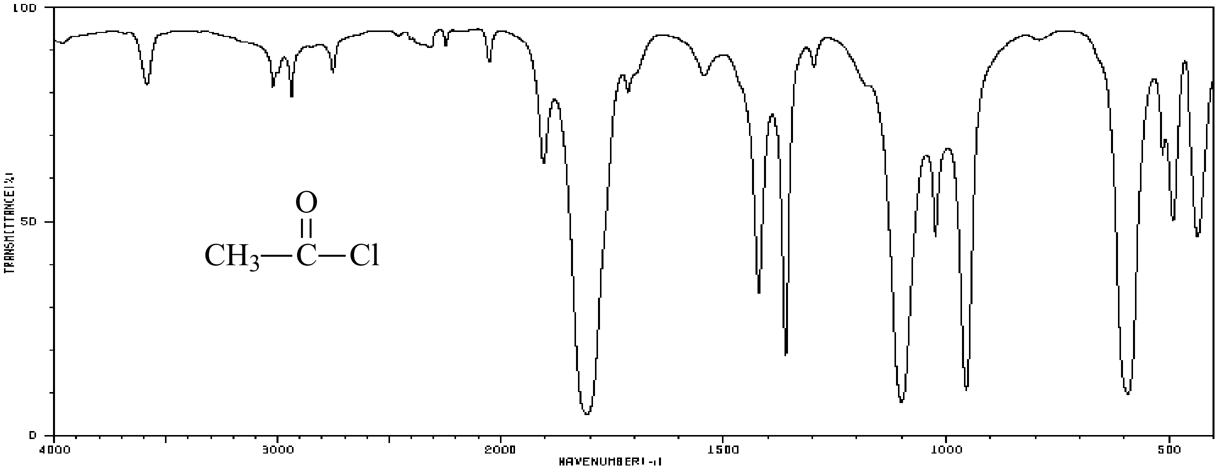

100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
O
H
C
N
CH$_3$

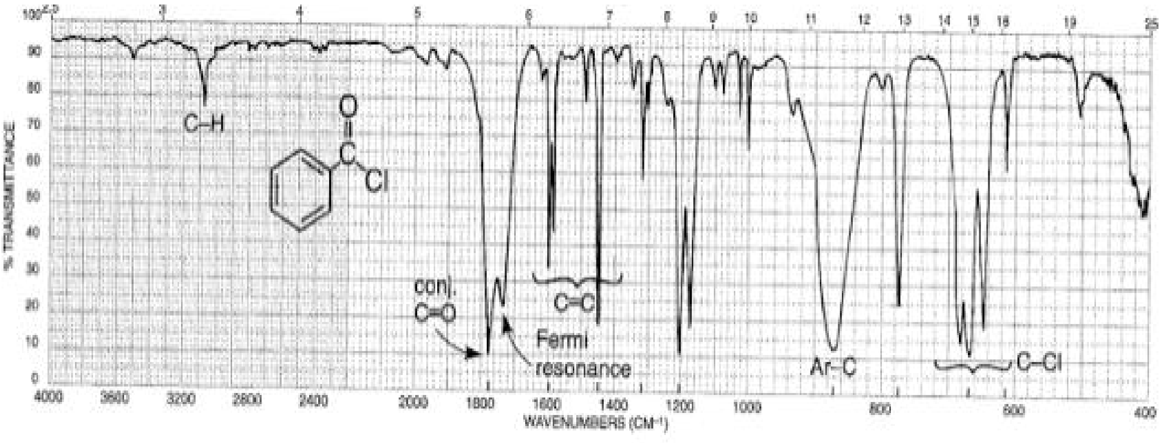

100
80
60
40
20
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers, cm^{-1}
CH$_3$
N
C
O
CH$_3$
CH$_3$

Acid Chlorides: Acid chlorides show strong intensity C = O stretching in the range of 1810-1775 cm^{-1} for aliphatic acid chlorides. Acid chloride and anhydrides are the most common functional groups that have a C = O appearing at such a high frequency. Conjugation lowers the frequency.

C = O	Stretch between 1810-1775 cm^{-1} in unconjugated chlorides. Conjugation lowers the frequency to 1780-1760 cm^{-1}.
C – Cl	Stretch in the range 730-550 cm^{-1}.

IR of some compounds belonging to acyl halids/aryl halides are as follow:

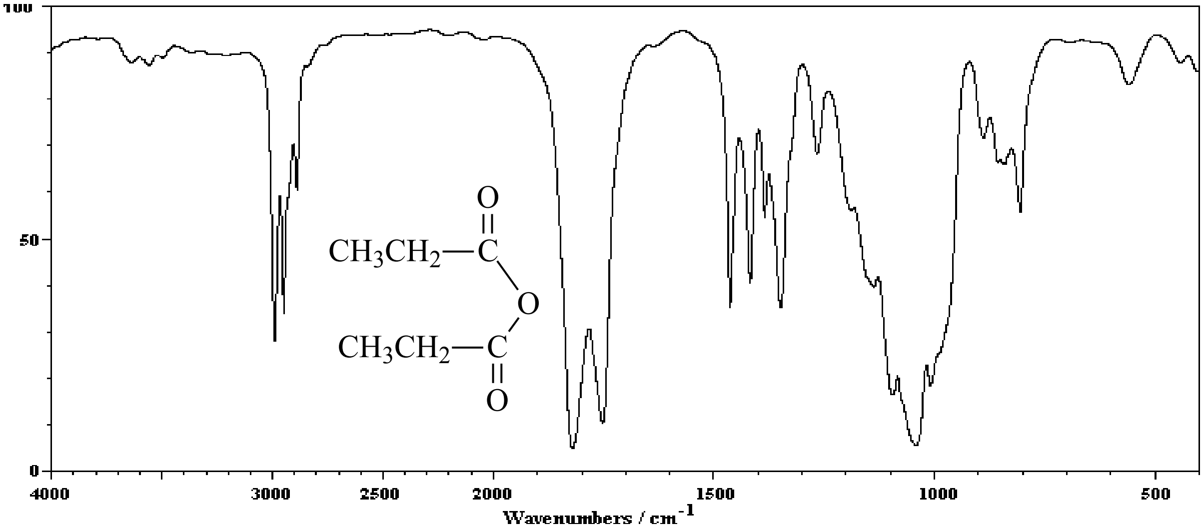


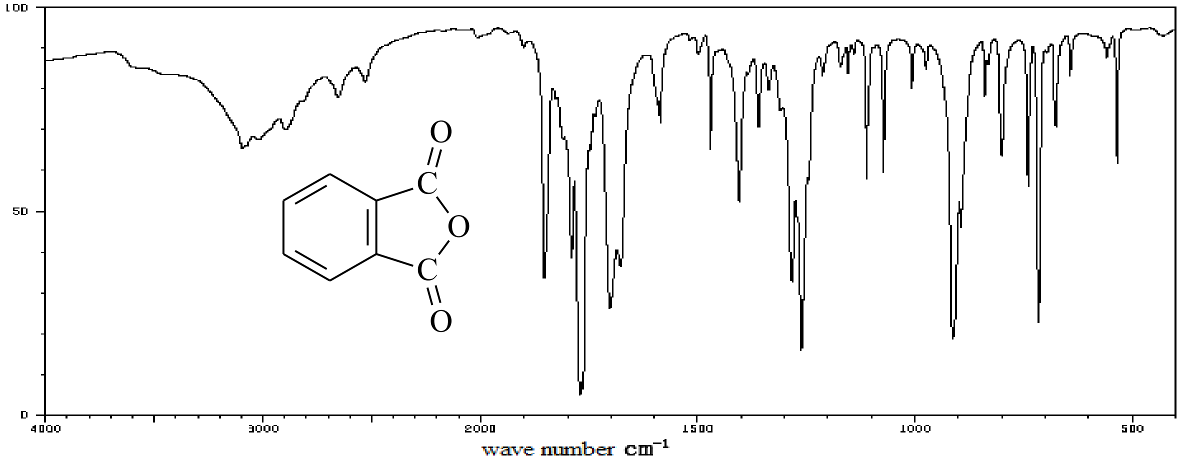


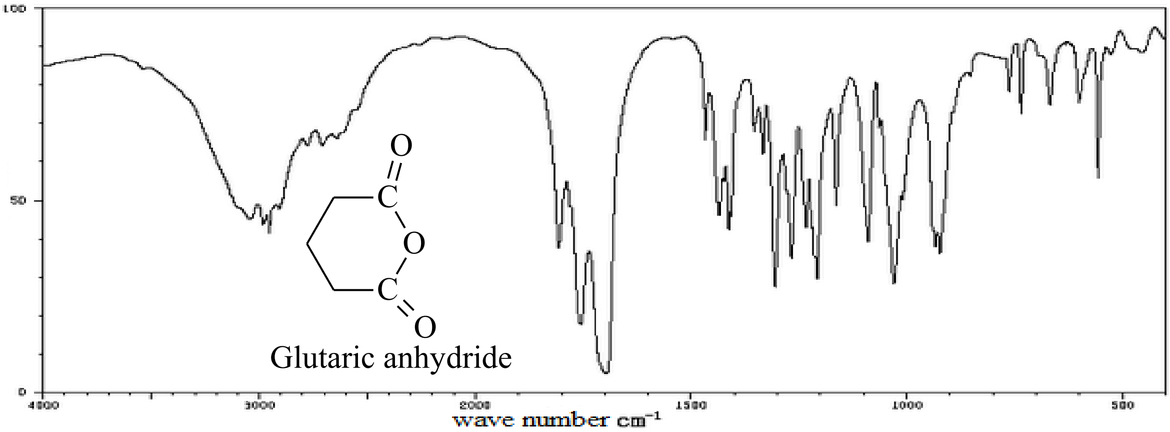
Anhydrides: Anhydrides exhibit two strong bands for the C = O groups near 1820 and 1750 cm^{-1}. Anhydrides and acid chlorides are the most common functional groups that have a C = O peak appearing at such a high frequency. Conjugation shifts each of the bands to lower frequencies (about 30 cm^{-1} each). Simple five-membered ring anhydrides have bands at near 1860 and 1780 cm^{-1}.

C = O	Stretch two bands, 1830-1800 cm^{-1} and 1775-1740 cm^{-1}, with variable relative intensity. Conjugation moves the absorption to a lower frequency. Cyclic anhydrides move the absorption to a higher frequency.
C – O	Stretch in the range 1300-900 cm^{-1}

The IR of some anhydride molecules are as follow:



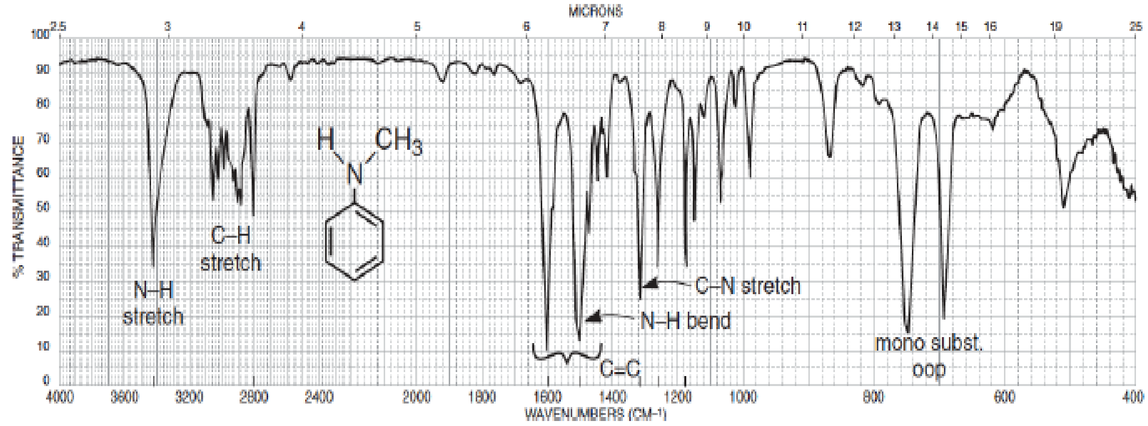


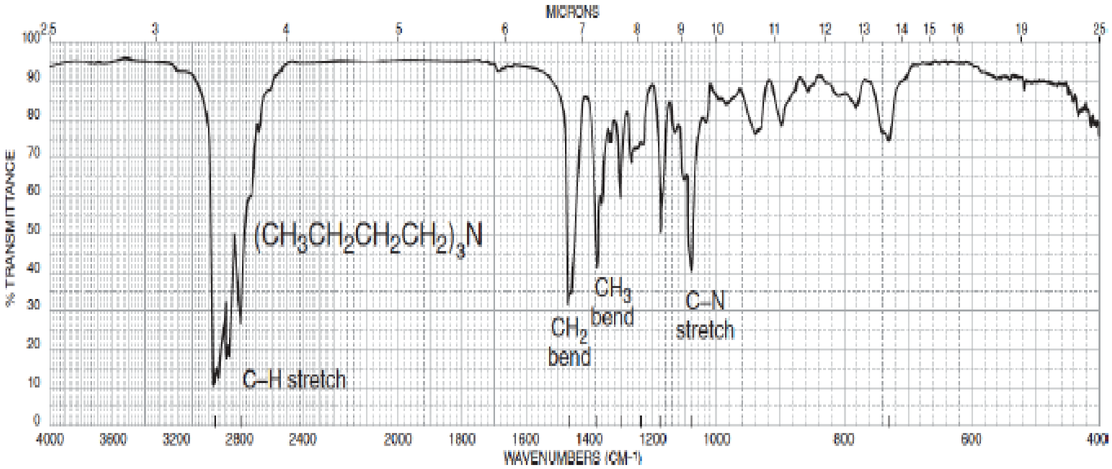


Amines: 1^0 amines, R-NH_2, show two N-H stretching bands in the range 3500-3300 cm^{-1}, whereas 2^0 amines, R_2N-H, show only one band in that region. 3^0 amines will not show an N-H stretch. Because of these features, it is easy to differentiate among primary, secondary and tertiary amines by inspection of the N-H stretch region.

N – H	3500-3300 cm^{-1}. 1^0 amines have two bands. 2^0 amines have one band: a vanishingly weak one for aliphatic compounds and a stronger one for aromatic secondary amines. Tertiary amines have no N – H stretch.
N – H	Bend in 1^0 amines results in a broad band in the range 1640-1560 cm^{-1}. 2^0 amines absorb near 1500 cm^{-1}
N – H	Bending absorption can sometimes be observed near 800 cm^{-1}.
C – N	In the range 1350-1000 cm^{-1}.

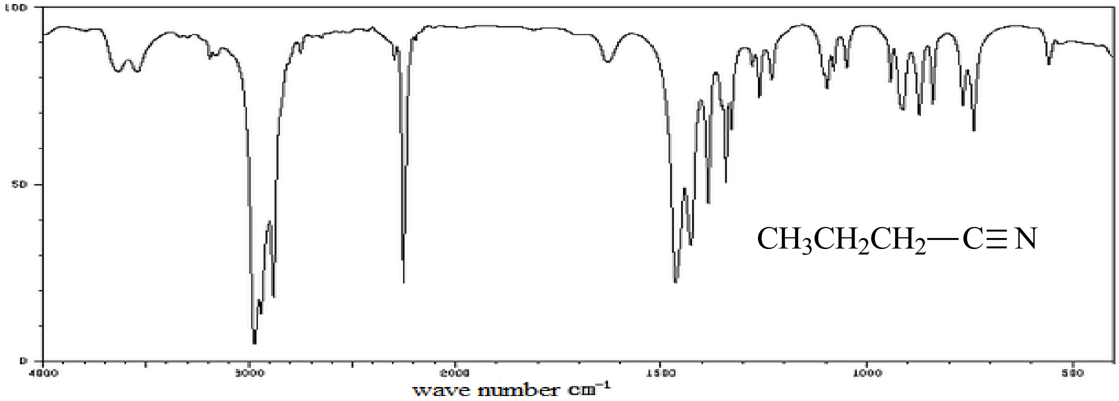
Examples:

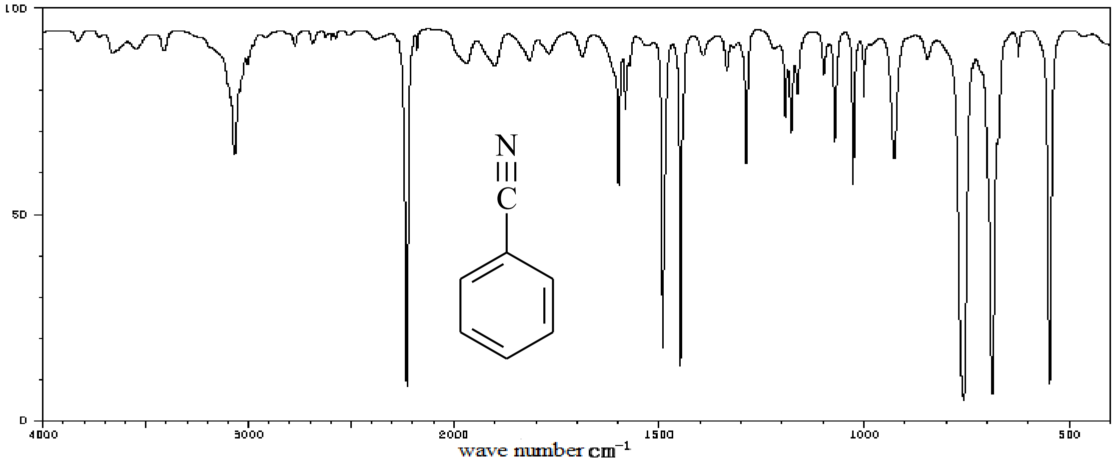


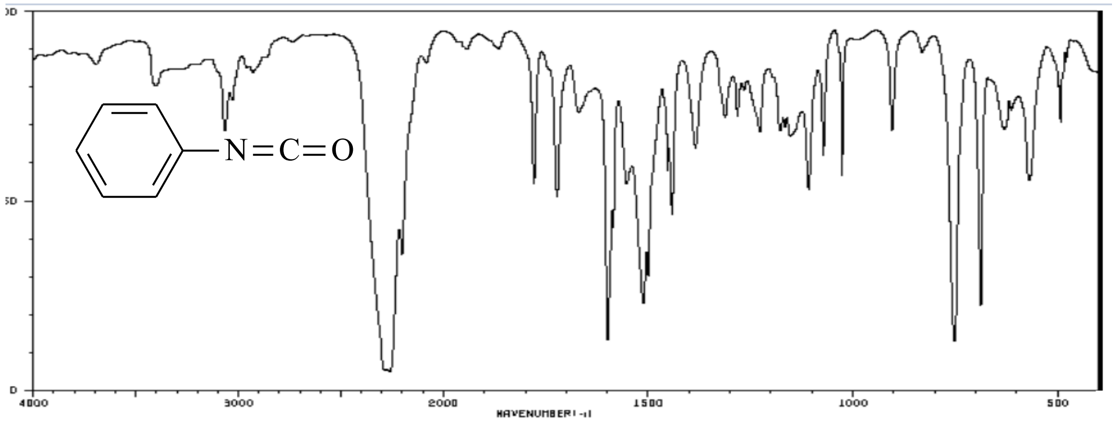


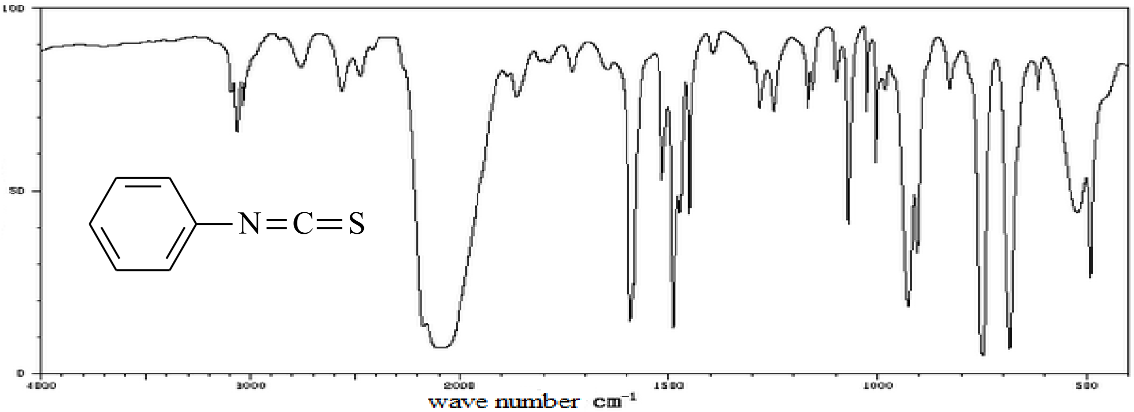
Nitriles, isocyanates, isothiocyanates and imines: Nitriles, isocyanates and isothiocyanates all have *sp*-hydridized carbon atoms similar to the C ≡ C bond. They absorb in the region 2100-2270 cm^{-1}. On the other hand the C = N bond of an imine has an sp^2 carbon atom. Imines and similar compounds absorb near where double bonds appear, 1690-1640 cm^{-1}

- C ≡ N	Strong and sharp absorption near 2250 cm^{-1}. Conjugation with double bonds or aromatic rings moves the absorption to a lower frequency.
- N=C=O	Stretch in an isocyanate gives a broad, intense absorption near 2270 cm^{-1}.
-N=C=S	Stretch in an isothiocyanate gives one or two broad, intense absorption centering near 2125 cm^{-1}.
R_2-C=N-R	Stretch in an imine, oxime, and so on gives a variable-intensity absorption in the range 1690-1640 cm^{-1}.

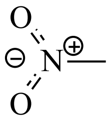


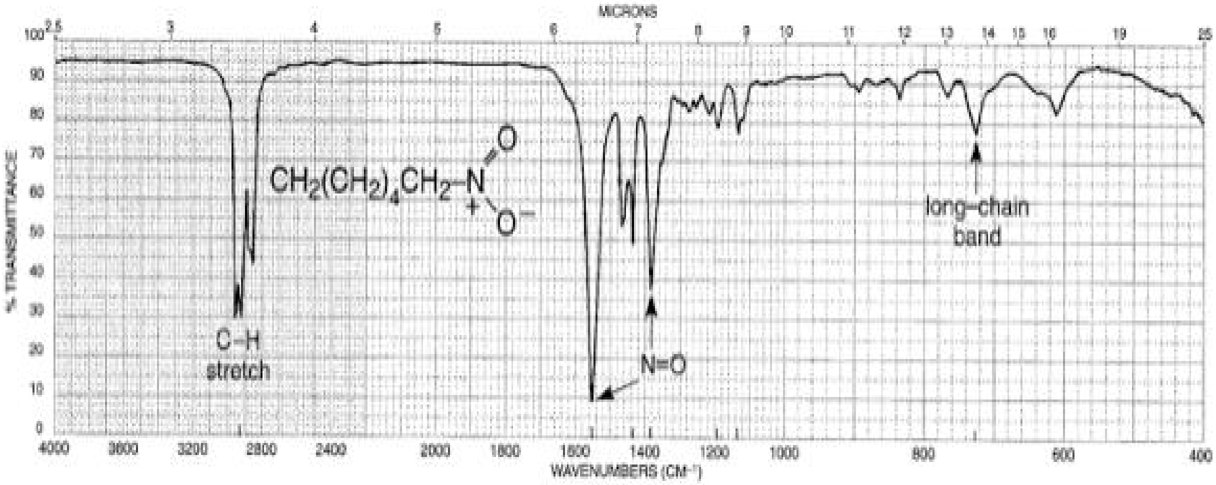


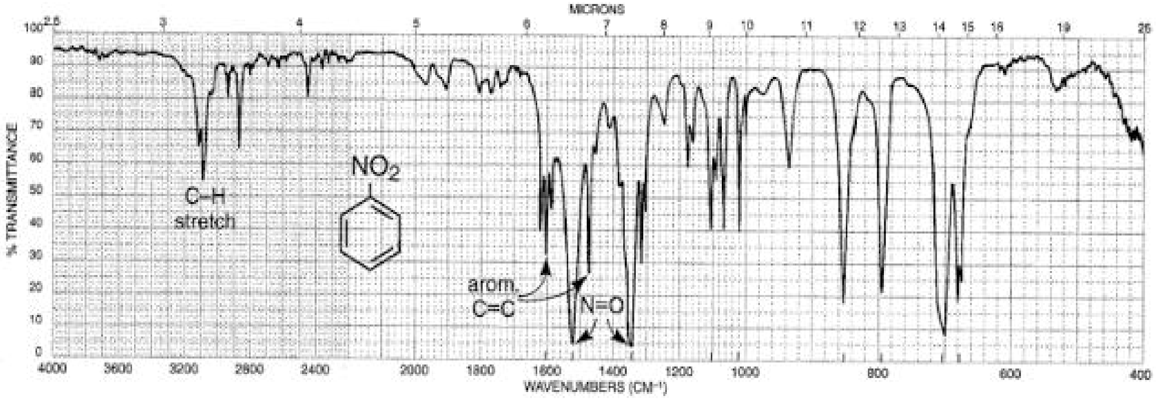




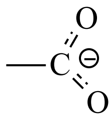
Nitro Compounds: Nitro compounds show two strong bands in the infrared sectrum. One appears near 1550 cm^{-1} and the other near 1350 cm^{-1}. Although these two bands may partially overlap the aromatic ring region, 1600-1450 cm^{-1}, it is usually easy to see the NO_2 peaks.

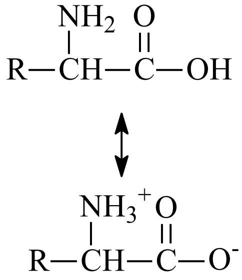
	Aliphatic nitro compounds: asymmetric stretch (strong), 1600-1530 cm^{-1}; symmetric stretch (medium), 1390-1300 cm^{-1}. Aromatic nitro compounds (conjugated): asymmetric stretch (strong), 1550-1490 cm^{-1}; symmetric stretch (strong), 1355-1315 cm^{-1}.

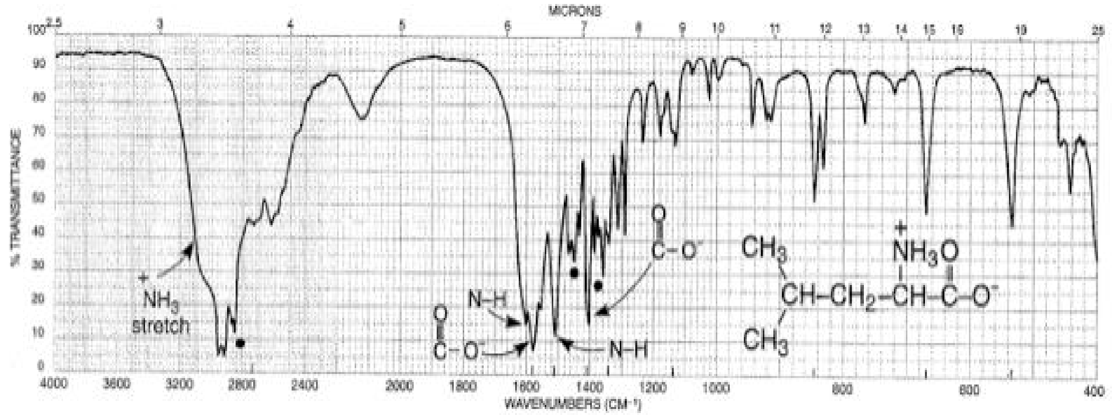




Carboxylate salts, amine salts and amino Acids: This section covers compounds with ionic bonds. Included here are carboxylate salts, amine salts and amino acids. Amino acids are included in this section because of their zwitterionic nature.

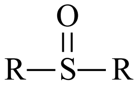
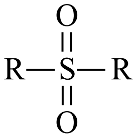
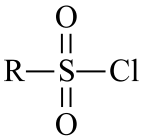
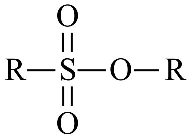
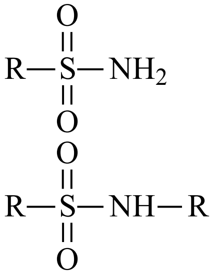
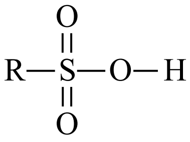
	Strong asymmetric stretch 1600 cm^{-1}; symmetric stretch near 1400 cm^{-1}. Frequency of C = O absorption is lowered from the value found for the parent carboxylic acid because of resonance (more single-bond character).

N-H	At 3300-2600 cm^{-1}. The ammonium ion absorbs to the left in this range, while the 3^0 amine salt absorbs to the right. 1^0 and 2^0 amine salts absorb in the middle of the range, 3100-2700 cm^{-1}. A broad band often appears near 2100 cm^{-1}.
N-H	Bending occurs at 1610-1500 cm^{-1}. 1^0 (two bands) is asymmetric at 1610 cm^{-1}, symmetric at 1500 cm^{-1}. 2^0 absorbs in the range 1610-1550 cm^{-1}. 3^0 absorbs only weakly.
 $R-\overset{NH_2}{CH}-\overset{O}{\overset{\Vert}{C}}-OH \longleftrightarrow R-\overset{NH_3^+}{CH}-\overset{O}{\overset{\Vert}{C}}-O^-$	These compounds exist as zwitterions (internal salts) and exhibit spectra that are combinations of carboxylate and primary amine salts. Amino acids show NH_3^+ stretch (very broad), N – H bend (asymmetric/symmetric), and COO^- stretch (asymmetric/symmetric).

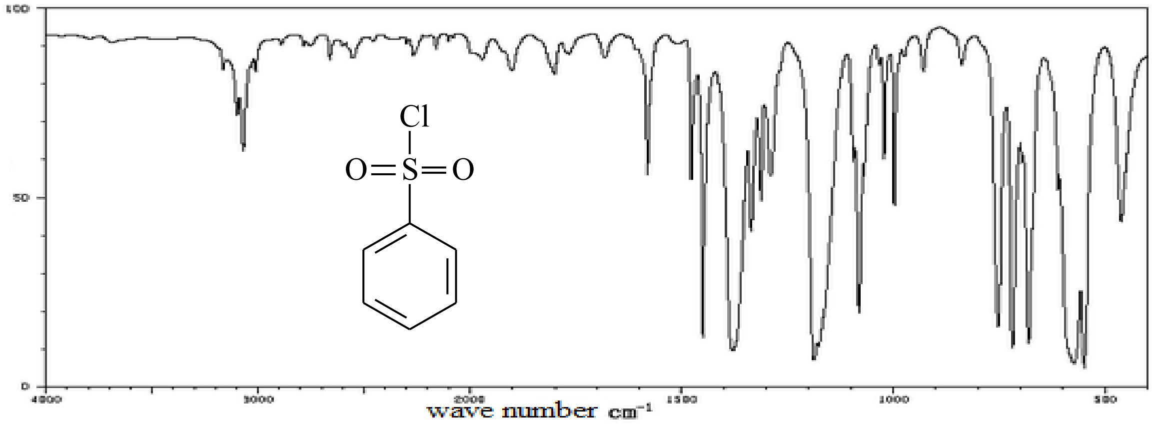


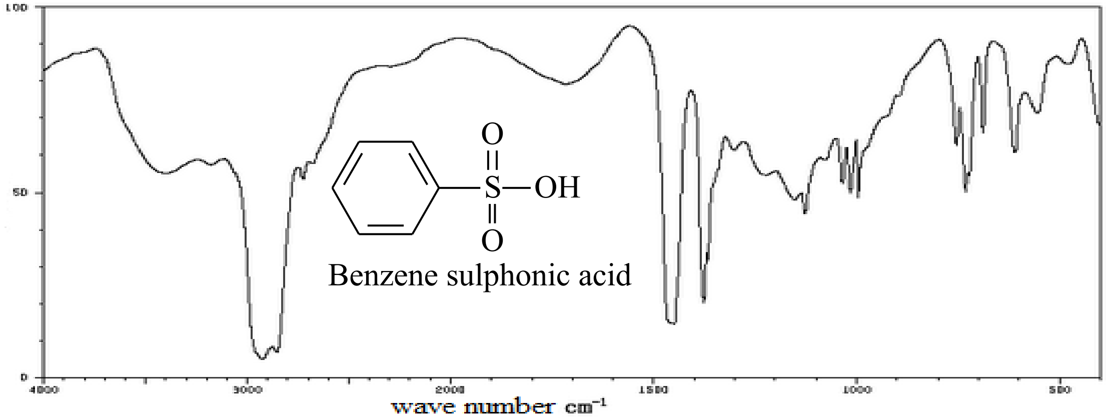
Sulfur Compounds: IR spectral data for sulfur-containing compounds are covered in this section. Inlcluded her are single-bonded compounds (mercaptans or thiols and sulfides). Double-bonded S = O compounds are also included in this section.

Mercaptans S – H	Stretch, near 2550 cm^{-1} and virtually confirms the presence of this group.
Sulphide R-S-R	Little useful information is obtained from the infrared spectrum.

Sulfoxides  $R-\overset{O}{\overset{\|}{S}}-R$	S = O Stretch, near 1050 cm^{-1}.
 $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-R$ Sulphones	S = O Stretching Strong asymmetric stretch at 1300 cm^{-1}, symmetric at 1150 cm^{-1}.
 $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Cl$ Sulphonyl chloride	S = O str. strong asymmetric at 1375 cm^{-1}, symmetric at 1185 cm^{-1}.
 $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-R$ Sulphonates	S = O str. strong asymmetric stretch at 1350 cm^{-1}, symmetric stretch at 1175 cm^{-1} S – O Stretch, in the range 1000-750 cm^{-1}
N  $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-NH_2$ $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-NH-R$ Sulphonamide	S=O str. strong asymmetric stretch at 1325 cm^{-1}, symmetric at 1140 cm^{-1} 1^0 N-H stretch at 3350 and 3250 cm^{-1}, 2^0 stretch at 3250 cm^{-1}; bend occurs at 1550 cm^{-1}.
 $R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H$ Sulphonic acid	S = O strong asymmetric stretch at 1350 cm^{-1}, symmetric stretch at 1150 cm^{-1} S-O Stretch (strong) occurs at 650 cm^{-1}

Examples of sulphur compounds:





Benzene sulphonic acid

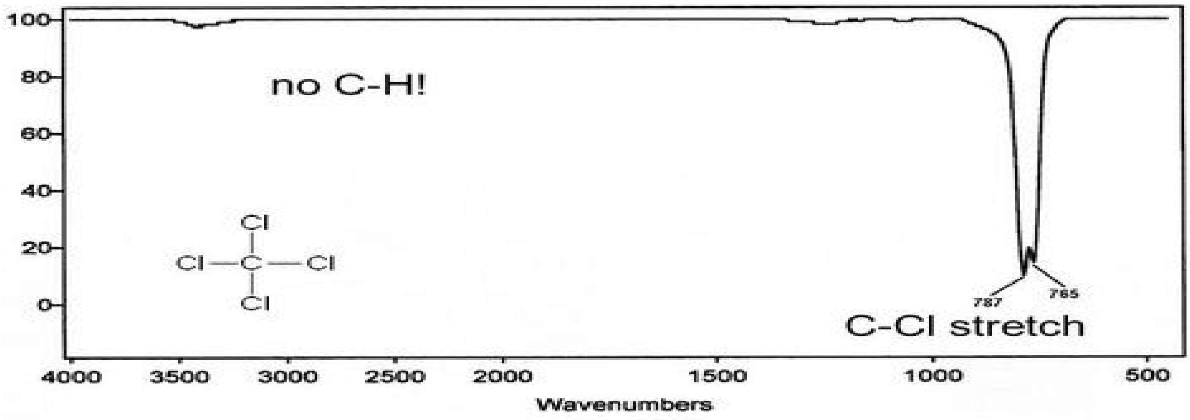
Phosphorus Compounds: Infrared spectral data for phosphorus-containing compounds are covered in this section. Included here are single-bonded compounds (P-H, P-R, and P-O-R). Double bonded P = O compounds are also included in this section.

P – H	Stretch, one strong, sharp band, at 2320-2270 cm^{-1}
PH_2	Bend, medium bands, at 1090-1075 cm^{-1} and 840-810 cm^{-1}
P-H	Bend, medium band, at 990-885 cm^{-1}
P-CH_3	Bend, Medium bands, at 1450-1395 cm^{-1} and 1346-1255 cm^{-1}
P-CH_2	Bend, medium band, at 1440-1400 cm^{-1}

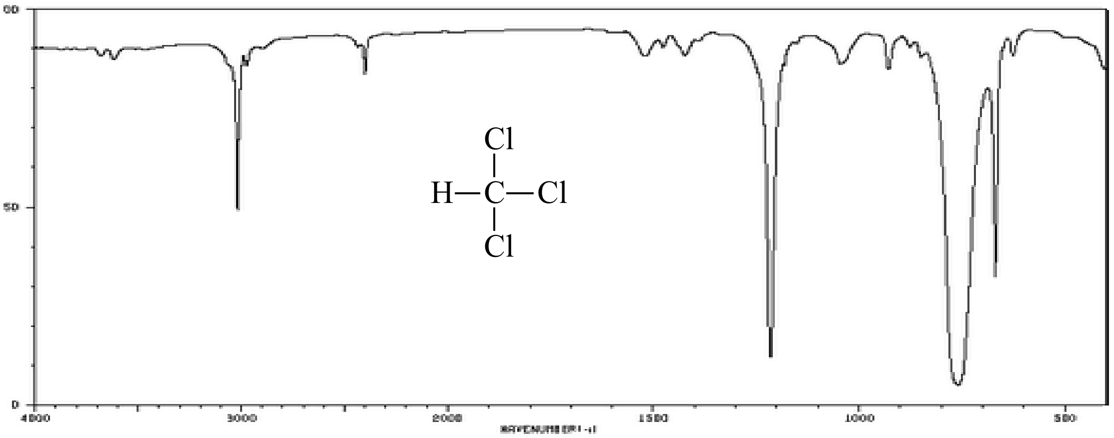
P = O	Stretch, one very strong band, at 1210-1140 cm^{-1}
P=O	Stretch, one very strong band, at 1300-1240 cm^{-1}
R-O	Stretch, one or two strong bands, at 1088-920 cm^{-1}
P-O	Stretch, medium band, at 845-725 cm^{-1}

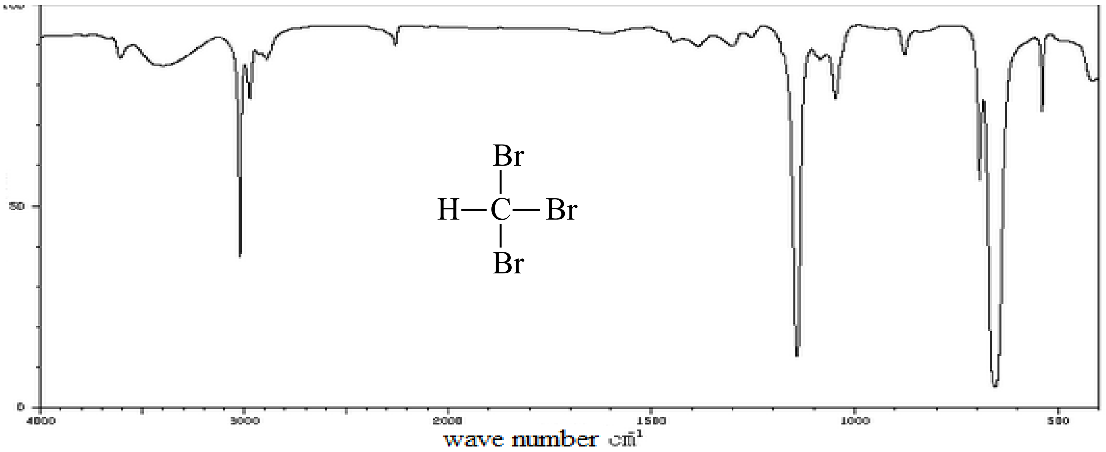
Alkyl and aryl halides

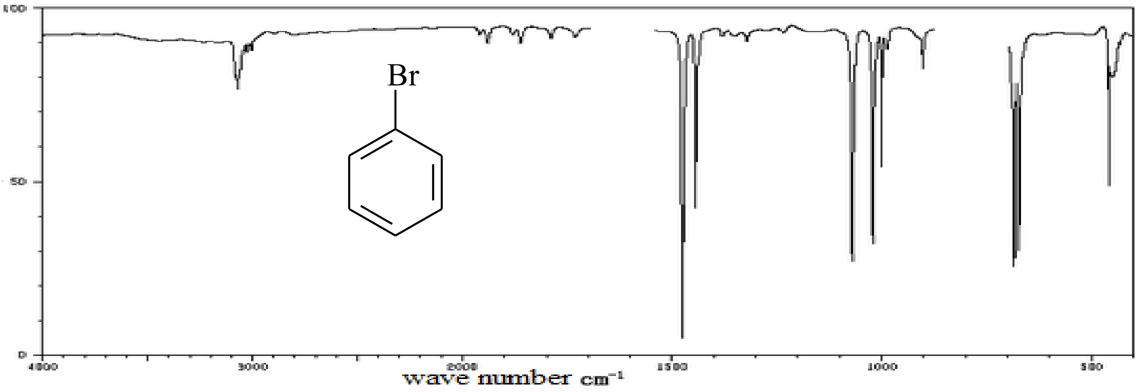
C –F	Stretch (strong) at 1400-1000 cm^{-1}.
C – Cl	Stretch (strong) in aliphatic chlorides occurs in the range 785-540 cm^{-1}.
CH_2-Cl	Bend (wagging) at 1300-1230 cm^{-1}.
C –Br	Stretch (strong) in aliphatic bromides occurs at 650-510 cm^{-1}.
CH_2-Br	Bend (wagging) at 1250-1190 cm^{-1}.
C –I	Stretch (strong) in aliphatic iodides occurs at 600-485 cm^{-1}.
CH_2-I	Bend (wagging) at 1200-1150 cm^{-1}.

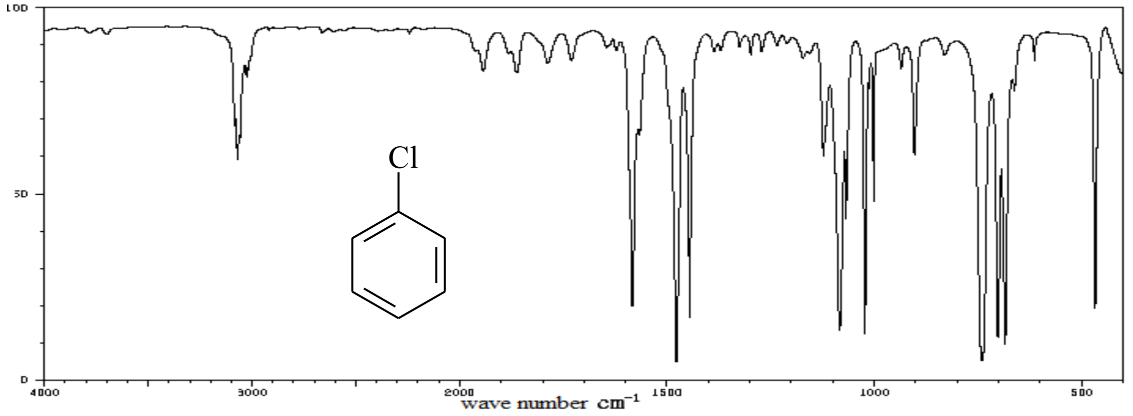


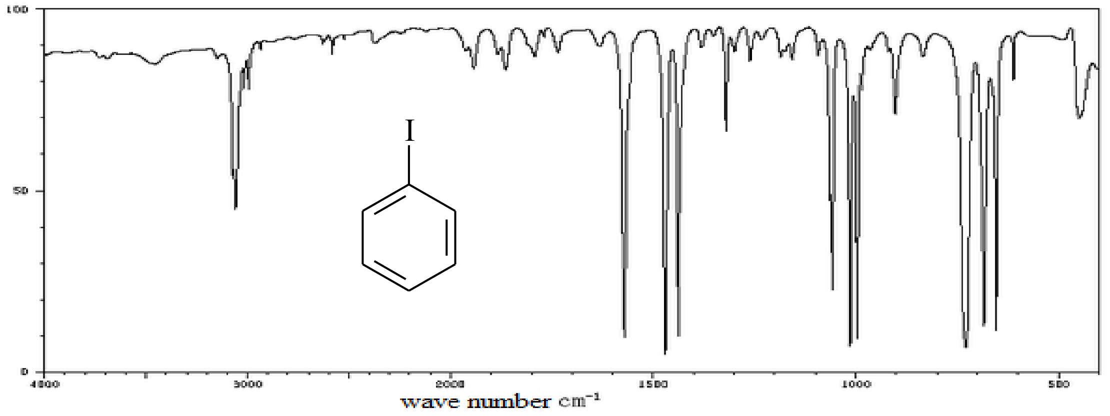
Examples:


100
50
0
4000
3000
2000
1500
1000
500
WAVENUMBER
Cl
H—C—Cl
Cl


50
0
4000
3000
2000
1500
1000
500
wave number cm⁻¹
Br
H—C—Br
Br


100
50
0
4000
3000
2000
1500
1000
500
wave number cm⁻¹
Br





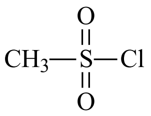
5.14 SUMMARY

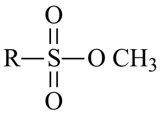
This unit describes the basic knowledge of vibrational/rotational spectroscopy,extension to polyatomic molecules, fingerprint region, Group frequencies, Interpretation of IR spectra Differenr regions of IR spectrum viz; functional group and fingerprint region. Impact of IR radiation and molecular vibrations, its type, the molecule spring analogy, Hookes law. Bond stretching frequencies effect of increasing atomic weight and bond energy, IR active and inactive frequencies, Selection rule. About instrumentation this unit describe dispersive and FTIR,its working etc. This unit also explain that how to approach the analysis of an IR-spectrum at aglance its general survey for the detection of different functional groups. Factors influencing vibrational frequencies like conjugation electronic effects (inductive and mesmeric effects), hydrogen bonding, Ring strain etc has also been described with examples.Frequencies of different functional groups hve been listed and some of the IR spectra of different class of compounds have intrepeted.This unit will be very helpful for the readers to study the functional groups

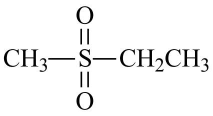
5.15 TERMINAL QUESTIONS

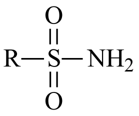
Q.1 Tick the correct option (MCQ)

i. Which one have the highest value of S=O stretching frequency?

A.

$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}Cl}$

B.

$\mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O\,CH_3}$

C.

$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}CH_2CH_3}$

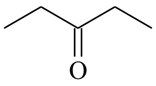
D.

$\mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}NH_2}$

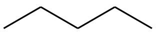
ii. Infrared spectroscopy provides valuable information about

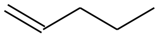
A. Molecular mass B. Functional group

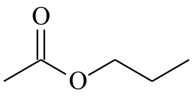
B. Conjugation D. Melting point

iii. Which of the following compounds has IR absorption at 1640 cm^{-1}?

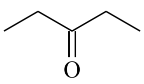
A.


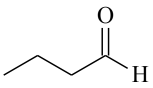
B.


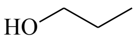
C.


D.


iv. Which of the following compound has an IR absorption at 3300 cm^{-1}?

A.


B.


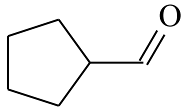
C.


D.

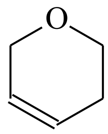

v. Deduce the structure of an unknown compound with molecular formula $C_9H_{10}O$ using information given by its infrared spectrum.

Intensity (peak):	Frequency (cm^{-1}):
s	3100
m	2900
m	2800
s	1710
m-w	1600
m-w	1475
m	1465
m	1450
m	1375

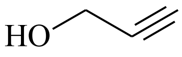
A.



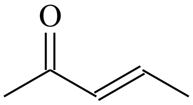
B.



C.



D.



vi. Which of the following bonds would be expected to have the lowest frequency stretch?

A. C-I

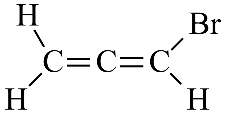
B. C-Cl

C. C- Br

D. C- F

vii. Deduce the structure of an unknown compound with molecular formula C_3H_3Br using information given by an infrared spectrum. As wave numbers(cm^{-1}): 3300(m),2225(m),2800(m),1450(m),1375(m) 667(s)

A.



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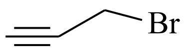
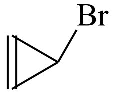


C.



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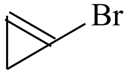
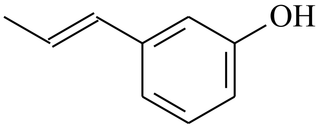
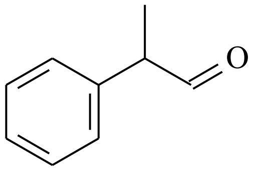


viii. Deduce the structure of an unknown compound with molecular formula $C_9H_{10}O$ using information given by its infrared spectrum. As wave numbers (cm^{-1}):3100(s), 2900(m), 2800(m), 1710(s), 1600(m-w), 1475(m-w) 1465(m), 1450(m), 1375(m).

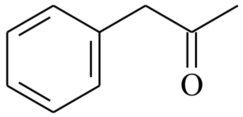
A.



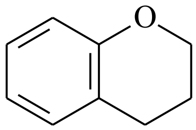
B.



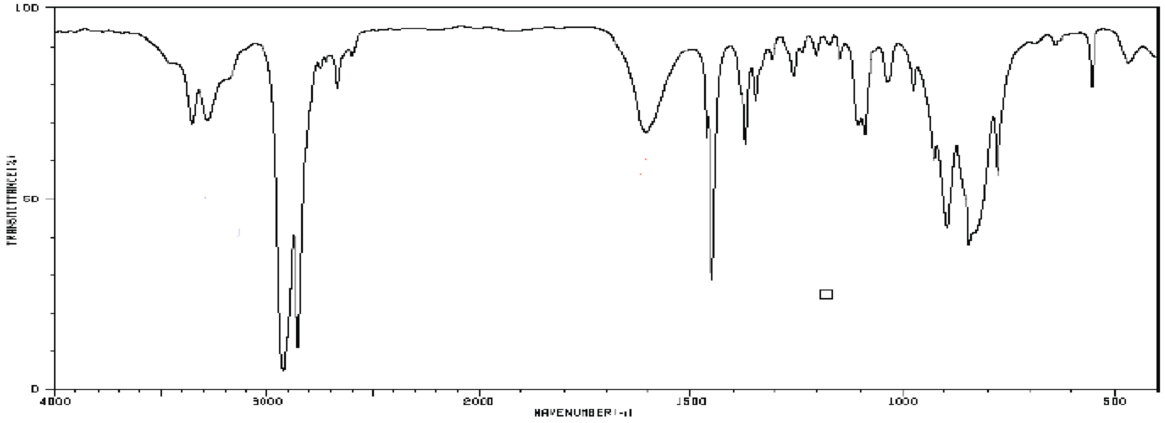
C.

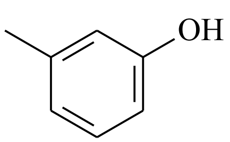


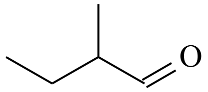
D.

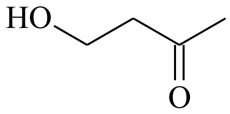


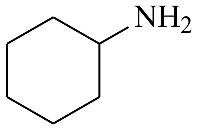
ix. The IR- spectrum is probably indicates the molecule:



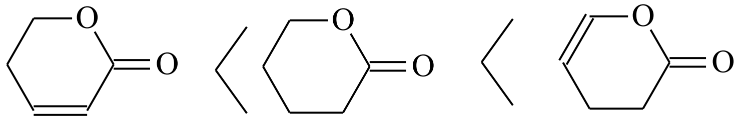
A. 

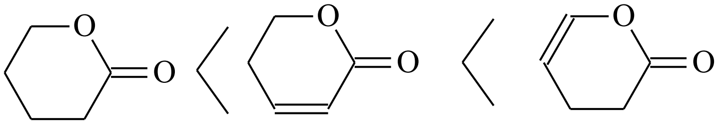
B. 

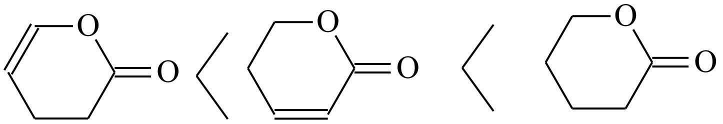
C. 

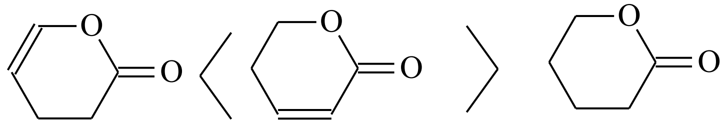
D. 

x. The correct order of carbonyl stretching frequency (1720 cm^{-1}< 1745 cm^{-1} < 1760 cm^{-1}) in the following lactones will be.

A. 

B. 

C. 

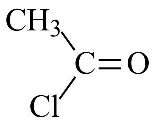
D. 

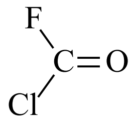
Q.2. Write and discuss the equation used to calculate the vibrational frequency of a diatomic molecule

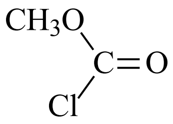
Q.3. What is Michelson interferometer discuss the difference between dispersive and FT-IR spectrophotometer.

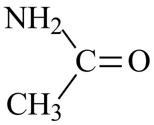
Q.4. How will you distinguish 1^{0,} 2^{0} and3^{0} amines with the help of Ir-spectroscopy? Discuss with example.

Q.5.Giving reason arrange the carbonyl frequency in the following compounds.

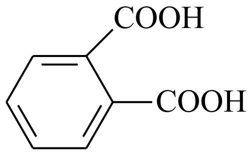
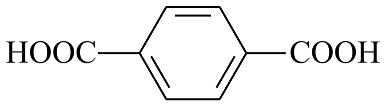




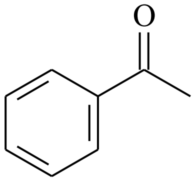
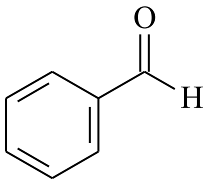


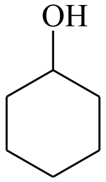
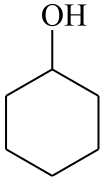


Q.6.How will you distinguish the following pairs of organic compounds? Name the vibration and appropriate position of absorption in each case.

1.  and 

2. $CH_3CH_2C{\equiv}CCH_2CH_3$ and $H{\equiv}C{-}CH_2CH_2CH_2CH_2CH_3$

3.  and 

4.  and 

In neat

In CCl_4

Q.7. Discuss the effect of conjugation on carbonyl group.

Q.8. How bond angle and ring strain influence the vibrational frequeny? Discuss with example

Q.9. Discuss molecular vibrations with schematic representation.

Q.10. Write short note on:

A. Light source in IR-spectroscopy

B. Classification of IR-bands

C. Applications of IR-spectroscopy

5.16 ANSWERS (MCQ) TERMINAL QUESTIONS

i-A	ii-B	iii-C	iv – D	v – D
vi –A	vii – B	viii – C	ix – D	x - A

5.17 REFERENCES

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Pavia, D.L., Lampman, G. M. and Kriz, G.S. Introduction to Spectroscopy (A guide for students of organic chemistry) 2001; Thomson Asia Pte Ltd., Singapore IInd reprent Thomson Information India Pvt. Ltd., India.

Kemp W., Organic Spectroscopy.1991Macmillan Press Ltd. London.

Silverstein R. M. and Webster, F. X. Spectrometric Identification of Organic Compounds Sixth Ed. 2008. Printed at: Pashupati Printers P. Ltd., Delhi, Authorized reprint by Wiley India(P.) Ltd. New Delhi.

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UNIT 6: RAMAN SPECTROSCOPY

CONTENTS:

6.1 INTRODUCTION

In undergraduate classes we have studied that within a molecule, there are certain energy levels which are associated with rotation, vibration or electronic level. When a radiation of a particular wavelength falls on a molecule, there is absorption of radiation which results in transition between these energy levels. This technique is known as spectroscopy. Now a days, spectroscopy is a very vast topic in chemistry and constitute one of the subject in chemistry. It involve several spectra depending on the type of radiation absorbed. For example, if a molecule absorbs radiations falling in microwave region, there is a transition between rotational energy levels. This spectroscopy is known as pure rotational spectroscopy or microwave spectroscopy.Likewise, when a molecule absorbs radiations falling in infra-red region, the spectroscopy is known as vibrational spectroscopy in which there is transition between vibrational energy level of a molecule.

The present unit deals with Raman spectroscopy which was observed by C. V. Raman (Physicist) and for this he was awarded by Nobel Prize. This spectroscopy includes the concept of polarizability that changes on exposure to the radiations. Polarizability is defined as the ability of a non-polar molecule to acquire dipole moment in presence of an electric field.Further in this unit, we will discuss about the mechanism of Raman excitation, polarizability ellipsoids, selection rule (on the basis of which we decide whether the transition between energy levels are allowed or forbidden). In order to understand the unit more clearly, we will consider Raman spectra of a diatomic molecule which includes pure rotational and pure vibrational Raman spectra along with the law of mutual exclusion which play an important role in determining the structure of a molecule. Raman spectra is different from all the other type of spectra, as all other spectra involves absorption of radiation while in Raman spectra, there is scattering of radiation instead of absorption. The scattering is a two photon process. Therefore much focus has been given in order to make the unit more interesting.

6.2 OBJECTIVES

After reading this unit, you will be able to:

- Define Raman spectroscopy.
- Understand the mechanism of Raman excitation.

- To know the region of radiation in which molecule shows Raman spectroscopy.
- Explain the selection rule involved during the transition between different energy levels.
- Define polarizability of a molecule.
- Explain pure rotational Raman spectra of a diatomic molecule.
- Explain pure vibrational Raman spectra of a diatomic molecule
- Have knowledge of Raman shift.
- Explain depolarization factor.
- Define Stokes and anti-Stokes Raman lines.

6.3 MECHANISM OF RAMAN EXCITATIONS

As we have discussed earlier that there is scattering of radiation in Raman spectroscopy instead of absorption. We can obtain Raman spectra for solid, liquid and gaseous sample. Homo - diatomic molecules or molecules without permanent dipole moment like N_2, O_2, H_2etc also show Raman spectra whereas for a molecule to be infra- red active, molecule must possess permanent dipole moment.In Raman spectroscopy, an intense beam of monochromatic light of visible region is allowed to pass through the molecule and the scattered light which is observed at right angle to the incident beam is observed. It has been seen that some of the scattered light have same frequency as that of the incident light while some scattered light have frequencies different (less or more) from the incident light. This is known as Raman effect or Raman shift.There are two theories that explain Raman scattering, one is classical theory of Raman scattering while other is a quantum theory of Raman scattering. The classical theory is known as the theory of polarizability. The quantum theory explains the mechanism of Raman excitation. According to the quantum theory of Raman scattering, there is a collision between the incident photon or radiation and the molecule. Let us consider a molecule having energy E_1. If an incident light of energy $h\upsilon_i$(υ_i = frequency of the incident radiation) falls on a molecule, its energy is raised to E_3. Thus the energy (E_3) of the molecule after absorbing incident photon is equal to the sum of E_1 and $h\upsilon_i$ ($E_3 = E_1 + h\upsilon_i$). The molecule then emit or scatter a radiation of frequency(υ_s) resulting in the lowering of energy of a molecule say E_2 (this energy is intermediate between E_1 and E_3.

$$\text{Thus } E_2 = E_3 - h\upsilon_s$$

Putting the value of E_3 in above equation we obtain: $E_2 = E_1 + h\upsilon_i - h\upsilon_s$

$$E_2 - E_1 = h\upsilon_i - h\upsilon_s = h(\upsilon_i - \upsilon_s) = h\Delta\upsilon$$

Where $\Delta\upsilon$ is Raman shift which is the difference in the frequency of the incident light and the scattered light. Therefore:$\Delta\upsilon = \upsilon_i - \upsilon_s$. When the frequency of the scattered light is less than the frequency of the incident light ($\upsilon_i > \upsilon_s$), Stokes Raman lines are produced. Here Raman shift is positive. When the frequency of the scattered light is more than the frequency of the incident light i.e. $\upsilon_i < \upsilon_s$, we obtain anti-Stokes Raman lines. Here Raman shift is negative. When the frequency of the scattered light is equal to the frequency of the incident light ($\upsilon_i = \upsilon_s$), Rayleigh Raman lines are obtained. All these scattered Raman lines are shown in Fig. 6.1. It is important to remember that Raman shift ($\Delta\upsilon$) is independent of the frequency of the incident radiation but it depends on the characteristic of the molecule showing Raman effect. Raman shift lies in the region of near and far infra- red radiation. Finally it is concluded that for a molecule to show Raman effect, there must be at least three different energy levels within the molecule. Here in this case discussed above, E_1 and E_3 represents the energy of the initial and final state respectively while E_2 represents the energy of the intermediate state.

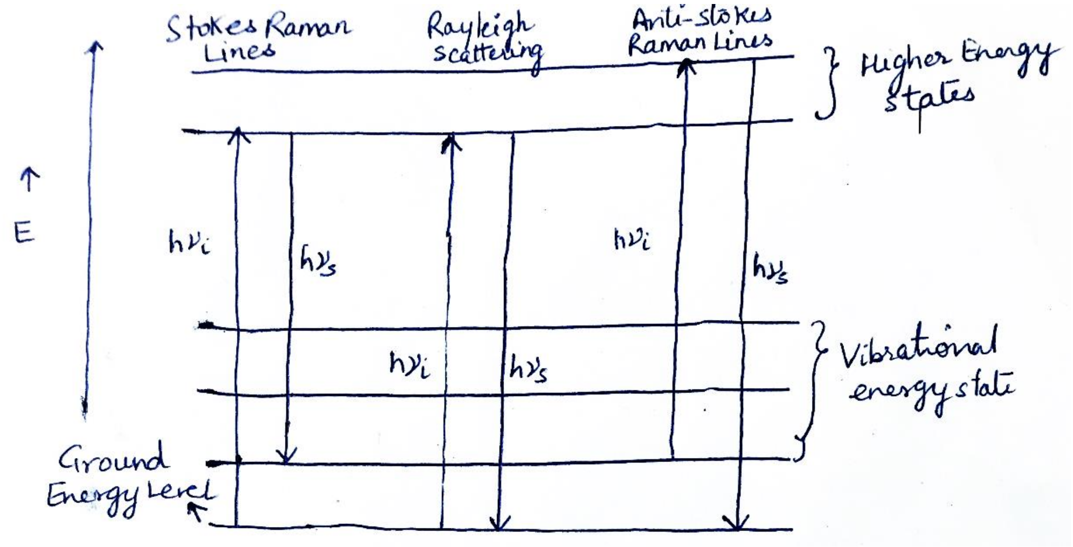

Fig. 6.1. Diagram of scattered Raman lines

The experimental setup consist of a cell into which a sample is taken. One end of a cell is horn like while the other end is provided with optically glass plate. A beam of monochromatic radiation is allowed to fall on the cell containing the sample. Sample must be colorless, pure and clean solid, liquid or gas molecule. Concentrated samples are taken so that the Raman lines produced possess high intensity. The source of a monochromatic radiation is helium tube which was used in previous time but now a day's mercury arc is used. This mercury arc is placed close to the cell so that the cell receive radiations of high intensity. The scattered radiations emerges through the optically plane glass plate. There is a lens that direct the scattered radiations on the spectrograph. Spectrograph possess short focus camera, prism having high resolving power and large light gathering power. The complete experimental setup for Raman spectra is shown in Fig. 6.2.

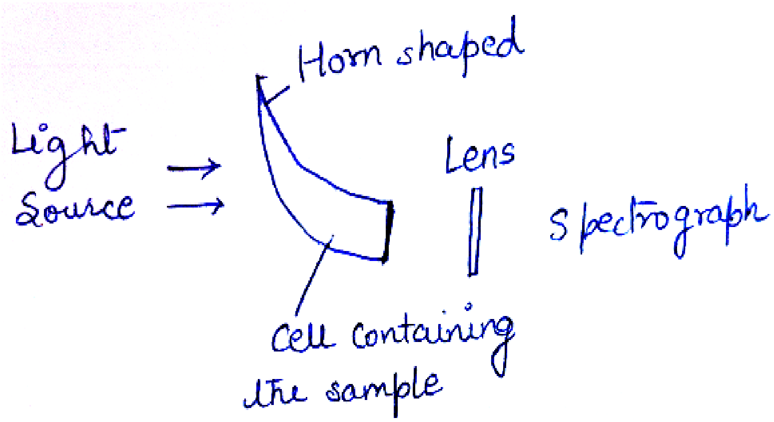

Fig. 6.2. Experimental setup for Raman spectroscopy

6.4 STOKES AND ANTI-STOKES LINES

As we have discussed above that when monochromatic light is scattered by a molecules, the scattered light having frequency equal to the frequency of the incident light is known as Rayleigh line or Rayleigh scattering. Some of the scattered light possess frequency lower than the frequency of the incident light, this give rise to Stokes lines in Raman spectra. This decrease in frequency is due to the transfer of some amount of energy of incident light to the molecule. As a result there is decrease in energy causing decrease in frequency. The part of energy absorbed by the molecule is used in the transition to higher energy states. For Stokes lines, Raman shift or Raman effect which is represented by $\Delta\upsilon$ is positive. Out of three types of lines (Stokes, anti-Stokes and Rayleigh) obtained after scattering of light in infra-red and far infra-red region, Stokes lines possess intensity more than the intensity of anti- Stokes lines but less than that of Rayleigh line. The wavelength of Stokes lines is more than that of the wavelength of the incident light.

Some of the scattered light possesses frequency higher than the frequency of the incident light, this give rise to anti-Stokes lines in Raman spectra. This increase in frequency is due to the transfer of molecular energy to the incident photon which results in the increase of energy or frequency of the scattered light. The part of energy lost by the molecule results intransition from higher energy or excited vibrational state to lower energy or ground state. For these lines, Raman shift or Raman effect ($\Delta\upsilon$) is negative. The intensity of anti-Stokes lines are lower than that of Stokes lines. This can be explained on the basis of Boltzmann distribution law. According to which the intensity depends on the number of molecules present in the lower energy state or ground state before irradiation. As it is clear from above that in case of Stokes lines, there is transition of molecule from lower energy level to higher energy level whereas in case of anti-Stokes lines, there is transition from higher energy state to lower energy state. Therefore, the number of molecules is more in the ground state prior to irradiation in case of Stokes lines in comparison to anti- Stokes lines. Hence more is the number of molecules or atoms in the ground sate, more is the intensity of the scattered line. Thus Stokes lines are more intense than anti-Stokes lines. The wavelength of these lines is less than the wavelength of the incident light. These Raman lines are shown in Figure 6.1.

6.5 POLARIZABILITY ELLIPSOIDS

The classical theory of Raman scattering is also known as theory of polarizability. According to this theory, in the presence of an electric field, the electrons of a molecule (neutral) are attracted to the positive pole while nuclei of a molecule are attracted towards the negative pole. As a result, a dipole moment is induced or produced in the molecule. In this state, a molecule is said to be polarized. In this way electron cloud get distorted in the presence of an electric field. This ability of a molecule to gain dipole moment is called polarizability. The induced dipole moment (μ) is related to electric field (E) by an expression:

$$\mu = P\,E$$

where P is polarizability of the molecule. The value of μ (induced dipole moment) depends on the direction of the electric field. When the direction of the electric field is along the inter-nuclear axis then the value of induced dipole moment is high. When the direction of electric field is perpendicular to the inter-nuclear axis then the value of induced dipole moment is low. In case of spherically symmetrical molecule, the direction of electric field is independent of the value of the induced dipole moment. For non- isotropic molecule for principle axis:

$$\mu'_x = P_{x'x'}E_{x'}; \mu'_y = P_{y'y'}E_{y'}; \mu'_z = P_{z'z'}E_{z'}$$

Here x′, y′ and z′ are three principle axis. If from the origin of the principle axis coordinate system, we draw lines of length proportional to the inverse of the square root of polarizability in any direction, then the locus of the points of lines form a surface. This surface is known as polarizability ellipsoid which is shown in Fig. 6.3. The equation of an ellipsoid is:

$$P_{x'x'}\, x'^2 + P_{y'y'}\, y'^2 + P_{z'z'}\, z'^2 = 1$$

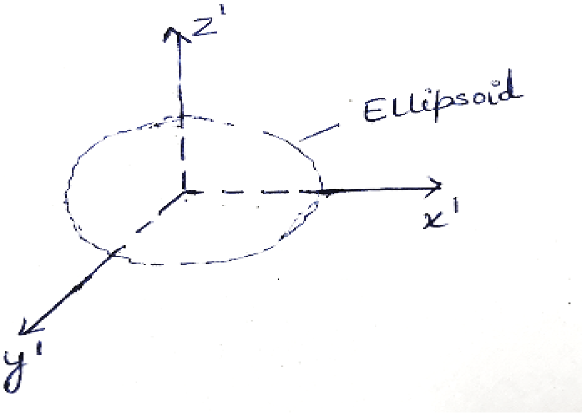

Fig. 6.3. Polarizability ellipsoid

If the vibration in the molecule does not change the polarizability of the molecule than we will observe Rayleigh lines. There must be change in polarizability of the molecule to be Raman active (Stokes and anti- stokes lines). Homo-nuclear diatomic molecule such as O_2, N_2 , show Raman spectra as there is change in polarizability of the molecule due to vibration. One of the principle axis of the polarizability ellipsoid is the axis of the molecule. When a molecule rotates about an axis which is perpendicular to the molecular axis, then the polarizability ellipsoid acquire the same position after half a rotation and again after one complete rotation. During one complete rotation of a molecule, there exist two maxima and two minima of polarizability.

6.6 ROTATIONAL AND VIBRATIONAL RAMAN SPECTRA

Here under this heading we will discuss pure rotational and pure vibrational Raman spectra of a diatomic molecules. Let us discuss these spectra one by one.

6.6.1 Pure rotational Raman spectra

Diatomic molecule as we know consist of two atoms. When two atoms are same, the molecule is called homo-nuclear diatomic molecule like H_2, N_2whereas when two atoms are different, the molecule is called hetero-diatomic molecule like HCl, HCN. When homo-nuclear diatomic molecule undergoes rotation, there is change in the orientation of the molecule with respect to the electric field of rotation. If molecule possess different polarizabilities in different direction or we can say that if the molecule is optically anisotropic then there is variation in the polarization with time. If α is the change in polarizability of a molecule then:

$$P = P_o + \beta \sin 2\Pi (2\upsilon_r) t \qquad (1)$$

Where $\upsilon_r$is the rotational frequency. The induced dipole moment (μ) is related to electric field (E) by an expression:

$$\mu = P E$$

where P is polarizability of the molecule.

$$E = E_o \text{ Sin } 2\Pi\upsilon t$$

where υ is the frequency of the incident light, $E_o$is the vibrating electric field's amplitude

$$\mu = PE_o \text{ Sin } 2\Pi\upsilon t$$

On putting the value of P from equation 1 in the above equation, we obtain:

$$\mu = P_o + \beta \sin 2\Pi (2\upsilon_r) t (E_o \text{ Sin } 2\Pi\upsilon t)$$

$$\mu = P_oE_o \text{ Sin } 2\Pi\upsilon t + \beta E_o \text{ Sin } 2\Pi\upsilon t \sin 4\Pi \upsilon_r t$$

$$\mu = P_oE_o \text{ Sin } 2\Pi\upsilon t + \tfrac{1}{2} \beta E_o [\text{Cos } 2\Pi (\upsilon - 2\upsilon_r) t - \text{Cos } 2\Pi (\upsilon + 2\upsilon_r) t]$$

It is clear from the above equation that Raman lines have frequencies $(\upsilon - 2\upsilon_r)$ and$(\upsilon + 2\upsilon_r)$. Raman shift (Δυ) is therefore equals to twice the frequency of rotation of a molecule.

$\Delta\upsilon = (\upsilon + 2\upsilon_r) - \upsilon = 2\upsilon_r$

The pure rotational Raman spectra contain a series of equidistant lines on both side of a Rayleigh line as shown in Fig. 6.4. On the right of the Rayleigh line, anti-stokes lines are present. The separation between Rayleigh line and first anti-stokes line is 6B followed with the separation of 4B between two successive anti-stokes lines. Here B is rotational constant. On the left of the Rayleigh line, Stokes lines are present. The separation between Rayleigh line and first stokes line is 6B followed with the separation of 4B between two successive stokes lines. It has been observed that greater is the anisotropy of the molecule, more will be the intensity of the rotational Raman lines. The intensity of Raman lines depends on the frequency of the incident radiation and concentration of the sample used. Intensity is directly proportional to the frequency of the incident light raise to the power four. Rayleigh line possess more intensity than the Sokes lines whereas Stokes lines possess more intensity than the anti-Stokes lines.

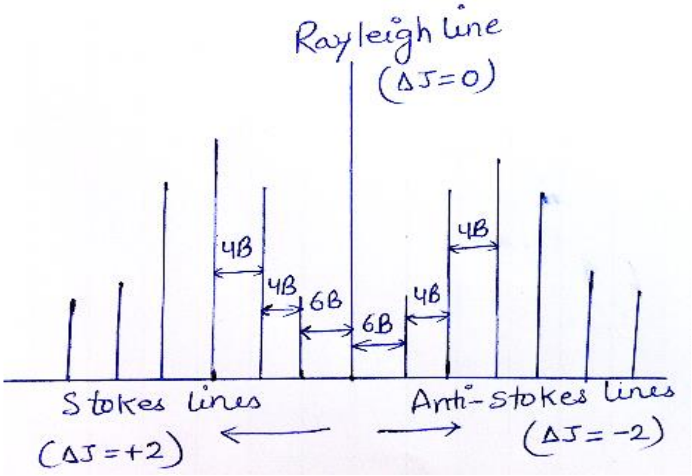

Fig. 6.4. Diagram showingpure rotational Raman spectra

6.6.2 Pure vibrational Raman spectra

This type of Raman spectra results from the change in polarizability of a molecule that results when a photon strikes a molecule. As we have studied that in case of rotational Raman spectra, more is the anisotropy, more is the intensity of Raman line. Similarly. In case of pure vibrational Raman spectra, more is the change in polarizability of the molecule, more is the intensity of vibrational Raman line produced. Examples of molecules that show pure vibrational Raman spectra are CO_2, NO_2. Let us consider a diatomic molecule, when light falls on a molecule, there is vibration in the molecule that results in the change in polarizability of the molecule. If d represents the change in the displacement due to vibration, the change in polarizability of a molecule (P) is given by expression:

$$P = P^o + \beta\ d/A$$

Where P^orepresent the polarizability when there is no vibration or P^orepresent equilibrium polarizability, A is the amplitude while β is the rate of vibration of the polarizability with displacement. Assuming that molecule undergoes simple harmonic motion, then the displacement (d) is written as:

$$d = A \sin 2\Pi\upsilon_v t$$

where$\upsilon_v$is the frequency of vibration of a molecule. We know that:

$$\mu = PE_o \sin 2\Pi\upsilon t$$

$$\mu = (P^o + \beta\ d/A)\ E_o \sin 2\Pi\upsilon t$$

$$\mu = P^oE_o \sin 2\Pi\upsilon t + \beta\ E_o \sin 2\Pi\upsilon t \sin 2\Pi\upsilon_v t$$

$$\mu = P^oE_o \sin 2\Pi\upsilon t + 1/2\beta\ E_o [\cos 2\Pi (\upsilon - \upsilon_v)t - \cos 2\Pi (\upsilon + \upsilon_v)t]$$

In the above equation, $(\upsilon - \upsilon_v)$ and $(\upsilon + \upsilon_v)$ terms are present, which indicates that there are certain lines in the vibrational Raman spectra that have frequency more than that of the frequency of the incident radiation while other have frequency less than that of the frequency of the incident radiation. Thus Raman shift ($\Delta\upsilon$) is given by expression:

$\Delta\upsilon = (\upsilon - \upsilon_v) - \upsilon = \upsilon_v$

It is therefore concluded that Raman shift in case of pure vibrational Raman spectra of a diatomic molecule is equal to the frequency of vibration.

6.7 SELECTION RULES

There are certain rules on the basis of which we decide whether the transition between energy level is allowed or forbidden.

- For rotational Raman spectra, the selection rule is:$\Delta J = 0, \pm 2$;Where J is rotational quantum number.

Case 1: If $\Delta J = 0$; This shows that there is no change in the rotational quantum number. In this case, the frequency of the incident and scattered radiation is same i.e. the scattering is Rayleigh scattering.

Case 2: $\Delta J = -2$; This corresponds to anti-Stokes Raman lines. Here the scattered radiations has more frequency than the incident radiation.

Case 3: $\Delta J = +2$; This corresponds to Stokes Raman lines. Here the scattered radiations has less frequency than the incident radiation.

- For vibrational Raman spectra, the selection rule is:$\Delta v = \pm 1$;Where v is vibrational quantum number. Two case arises:

Case 1: $\Delta v = +1$; This corresponds to Stokes Raman lines when there is transition from v to v + 1.

Case 2: $\Delta v = -1$; This corresponds to anti- Stokes Raman lines when there is transition from v + 1 to v.

- For rotational- vibratonal Raman spectra: the selection rule is: $\Delta J = 0, \pm 2$; $\Delta v = \pm 1$

This type of Raman spectra involves both rotation and vibration of a diatomic molecule when a monochromatic light falls on the molecule. Therefore there is change both in the vibrational and rotational quantum number. For rotational- vibrational Raman spectra, three branches are observed named as O branch, Q branch and S branch. The O branch refers to $\Delta J = -2$; Q branch refers to $\Delta J = 0$ while S branch refers to $\Delta J = +2$.

6.8 POLARIZATION OF RAMAN LINES

As we have discussed above that intensity of Raman lines depends on the frequency of the incident radiation and concentration of the solution. Therefore in order to have intense Raman lines, an incident radiation or light of lower wavelength or higher frequency is used. The polarization of Raman lines is measured by a ratio known as depolarization ratio. This depolarization ratio is an intensity ratio between the perpendicular component and parallel component of the scattered Raman lines. It has been seen that the direction of vibration of the electric field of the incident light and that of the scattered light may be same or vary to some extent. When there is variation in the direction of vibration of the electric field, two component of Raman scattered light is produced. One component is called parallel component and another component is called perpendicular component. When the direction of vibration of the electric field of Raman scattered light is perpendicular to the vibrational direction of the incident light, the perpendicular component is produced. When the vibrational direction of the electric field of Raman scattered light is parallel to the vibrational direction of the incident light, we obtain parallel component.Thus Raman scattered light consist of both the components parallel as well as perpendicular. The depolarization factor or ratio is given by ρ. Thus

ρ = Intensity of the perpendicular component/ Intensity of the parallel component

The value of depolarization factor depends on the normal vibration mode and on the molecular symmetry. For vibrational Raman lines, the value of ρ varies from 0.0 to 0.86 whereas for rotational Raman lines,ρ possess a single value i.e. 0.86. The large value of ρ shows diffuse Raman spectra which consist of weak Raman lines while the low value of ρ shows sharp Raman spectra that consist of strong lines. Raman lines having same value of depolarization factor shows that molecule possess same structure.

6.9 RULE OF MUTUAL EXCLUSION

According to mutual exclusion principle, those molecules which possess centre of symmetry i.e. they are centrosymmetric, the vibrations which are active in infra –red spectroscopy are inactive in Raman spectroscopy whereas the vibrations which are inactive in infra-red are active in Raman spectra. Those molecules which do not have centre of symmetry, some or all vibrations may be active in both infra-red and Raman spectra. For example, CO_2 symmetric stretching vibrations are inactive in infra-red but are active in Raman spectra. Similarly, H_2, O_2 (homonuclear diatomic molecule) are infra-red inactive but are Raman active. This principle provide information about the structure of a molecule. If Raman spectra and infra –red (IR) spectra do not show common lines, then according to the rule of mutual exclusion, the molecule must possess centre of symmetry. As mutual exclusion rule talk about Raman and IR spectra, therefore this rule is helpful in providing information about the structure of a molecule.

Let us consider a triatomic molecule having general formula of type AB_2. Let us consider a triatomic molecule say carbon dioxide (CO_2). Raman and IR spectra of CO_2 shows symmetrical stretching vibration, asymmetrical stretching vibration and bending vibration as shown in Fig. 6.5.

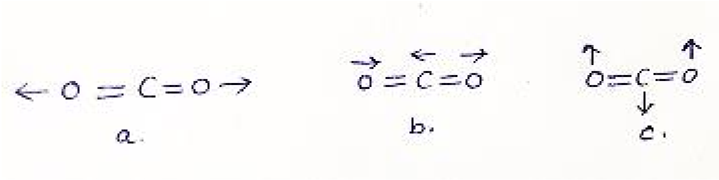

Fig. 6.5. Vibration of carbon dioxide

a. Symmetrical stretching vibration; b.Asymmetrical stretching vibration; c. Bending vibration

In symmetrical stretching vibration, as the name indicates that the symmetry is retained during the vibration. Here the dipole moment of the molecule do not undergoes any change while the polarizability of the molecule changes. This vibration is Raman active and IR inactive. In asymmetrical stretching vibration, as the name indicates that the symmetry is destroyed during the vibration. Here the dipole moment of the molecule undergoes a change while the polarizability of the molecule remains unchanged. This vibration is Raman inactive and IR active. In bending vibration, as the name indicates that there is bending of a molecule due to which symmetry is lost. There is change in the dipole moment of a molecule but the polarizability of the molecule do not change. This vibration is Raman inactive and IR active. Thus according to the rule of mutual exclusion, the molecules which are IR active and Raman active or vice versa must possess centre of symmetry. These vibrations shows that CO_2 possess centre of symmetry and is linear.

Let us consider an example say nitrous oxide (N_2O). Like carbon dioxide, nitrous oxide also have twenty two electrons. IR and Raman date of N_2O shows that out of three bands of N_2O, two bands at 2224 cm^{-1} (asymmetrical stretching) and 1285 cm^{-1} (symmetrical stretching) are active in both Raman and IR spectra while one band at 589 cm^{-1} is active only in IR. Form this data it is concluded that N_2Omolecule do not possess centre of symmetry considering the rule of mutual exclusion. Though N_2O is linear but do not possess centre of symmetry. Hence from this rule we can predict the information of a molecule. From this above discussion it is concluded that from Raman and IR spectra of a triatomic molecule whether the molecule is linear or not and if it is linear then symmetrical of not (asymmetric).

Mutual exclusion rule is also responsible for deciding the structure of BF_3which is symmetrical planar molecule as well as the structure of NH_3 which is symmetrical pyramidal molecule. Form mutual exclusion rule, it is concluded that for tetratomic symmetrical molecules like BF_3, NH_3, there are four vibrational frequencies and for asymmetric or non- symmetric molecules like ClF_3, there are more than four vibrational frequencies.

6.10 APPLICATIONS OF RAMAN SPECTROSCOPY

There are several applications of Raman spectroscopy. These are:

1. Identification of unknown compound: It is one of the most important application of Raman spectroscopy. This can be done by comparing the spectra of unknown compound with the spectra of the known compound. Each compound possess a unique spectrum as there is a finger print region which is the characteristic of a particular molecule or a compound.

2. By using Raman spectra, we can determine whether a substance possess crystalline form or an amorphous form. Raman spectra of the crystalline form of a substance consist of fine lines whereas Raman spectra of an amorphous form of a substance consist of broad and closely packed lines.

3. Using Raman spectra, we can determine whether the dissociation of an electrolyte is partial, incomplete or complete. We can obtain Raman spectra of pure substance (electrolyte) as well as Raman spectra of ions into which an electrolyte dissociates. By comparing the intensity and position of Raman lines, we can detect the number of ions produced.

4. Raman spectra is also used in order to produce whether the compound is covalent or ionic. It has been found that Raman lines in case of covalent compounds possess high intensity whereas ionic compounds which are also known as electrovalent compounds possess low intensity Raman lines. For example, NaCl do not show Raman lines as it is ionic whereas on the other hand $HgCl_2$ which is a covalent in nature show sharp Raman lines.

5. By using Raman spectra, we can determine whether a given organic compound is aliphatic or aromatic.

6.11 SELF- ASSESSMENT QUESTIONS (SAQs)

Fill in the blanks:

1. Raman spectra involves ………. of radiations.

2. In Raman spectra, there is ………. In polarizability.

3. In Raman spectra, when the scattered radiation have frequency same as the incident radiation, ………. line is produced.

4. In Raman spectroscopy, when the scattered radiation have frequency less than the frequency of the incident radiation, the line produced is called ………. line.

5. In Raman spectroscopy, when the scattered radiation have frequency more than the frequency of the incident radiation, the line produced is called ………. line.

6. The sample taken for Raman spectra may be ………., ………. and ………..

7. Homo-nuclear diatomic molecule can even undergoes ………. effect.

8. Ionic compounds possess Raman spectra that are ………. in intensity.

9. The selection rule for pure vibrational Raman effect of a diatomic molecule is ……….

10. The selection rule for pure rotational Raman effect of a diatomic molecule is given by ……

11. Law of mutual exclusion principle is applied to those molecules that possess …………

12. The radiation used for studying Raman effect is ……….

13. The selection rule for rotational- vibrational Raman spectra of a diatomic molecule is ………

14. The sample used for Raman scattering should be ………. and ……….

15. The depolarization factor is the ratio of ……….

True and False:

1. We can observe Raman effect only for solid samples.

2. According to mutual exclusion principle, Raman active vibrations are infra-red inactive while infra-red active vibrations are Raman inactive in case of molecules that contains centre of symmetry.

3. We can determine the structure of a molecule by using Raman spectroscopy.

4. Covalent compounds possess Raman lines of higher intensity than the ionic compounds.

5. The selection rule for pure rotational Raman spectra is $\Delta v = \pm 1$.

6. Selection rule predicts whether the transition within the energy level is allowed or not.

7. Molecules must possess centre of symmetry in order to obey law of mutual exclusion principle.

8. Intensity of Raman line is directly proportional to the forth power of the frequency of the incident radiation.

9. The frequency of Raman lines or Raman shift depends on the frequency of the incident radiation.

10. The polarizability of a molecule remains unchanged in Raman spectroscopy.

Multiple choice Questions:

1. Raman spectroscopy occurs in

a. Infra- red region

b. Microwave region

c. Visible region

d. Ultra violet region

2. In Raman spectroscopy, which condition of frequency is satisfied for anti-stokes lines provided that $\upsilon_i$is the frequency of the incident light, $\upsilon_s$is the frequency of the scattered light.

a. $\upsilon_i=\upsilon_s$

b. $\upsilon_i>\upsilon_s$

c. $\upsilon_i<\upsilon_s$

d. No relation between $\upsilon_i$and υ_s

3. In Raman spectroscopy, which condition is satisfied for stokes lines provided that $\upsilon_i$is the frequency of the incident light, $\upsilon_s$is the frequency of the scattered light.

a. $\upsilon_i=\upsilon_s$

b. $\upsilon_i>\upsilon_s$

c. $\upsilon_i<\upsilon_s$

d. No relation between $\upsilon_i$and υ_s

4. For pure vibrational Raman spectra of diatomic molecule, selection rule is

a. $\Delta v = 0$

b. $\Delta v = \pm 1$

c. $\Delta v = \pm 2$

d. $\Delta v = \pm 3$

5. For pure rotational Raman spectra of diatomic molecule, selection rule is

a. $\Delta J = 0, +1$

b. $\Delta J = 0, \pm 1$

c. $\Delta J = 0, \pm 2$

d. $\Delta J = \pm 1$

6. Raman shift ($\Delta\upsilon$) is zero for which of the following scattered line:

a. Stokes line

b. Anti-stokes line

c. Rayleigh line

d. None of the above

7. By using Raman spectroscopy, we can determine whether a substance possess crystalline form or amorphous form. Which of the following statement is correct.

a. Crystalline form show Raman spectra with fine lines.

b. Amorphous form show Raman spectra with fine lines.

c. Crystalline form and amorphous form do not show Raman spectra.

d. All the above statement are false.

8. Raman spectra can be obtained for

a. Solids only

b. Liquids only

c. Gases only

d. All of the above

9. Which is the correct statement:

a. Covalent compounds possess less intensity than the ionic compounds.

b. Covalent compounds possess more intensity than the ionic compounds.

c. Both covalent compounds as well as ionic compounds possess same intensity.

d. Covalent compounds do not show Raman spectra.

10. Raman shift ($\Delta\upsilon$) is positive for

a. Stokes lines

b. Rayleigh lines

c. Anti-stokes lines

d. None of the above

11. For rotational- vibrational Raman spectra of diatomic molecule, selection rule is

a. $\Delta J = 0, \pm 2$

b. $\Delta v = \pm 1$

c. Both a and b

d. None of the above

12. In Raman spectroscopy, the spectrograph must possess

a. High light gathering power

b. High resolving power

c. Short focus camera

d. All of the above

6.12 SUMMARY

In this unit, we have discussed Raman spectroscopy which includes mechanism of Raman excitation, Stokes and anti- Stokes lines, polarizability ellipsoid, rotational Raman spectra of diatomic molecules, vibrational Raman spectra of a diatomic molecules, selection rules, polarization of Raman lines and mutual exclusion principle. By using mutual exclusion principle, one can predict whether a molecule contains centre of symmetry or not. In addition to this, we have also discussed the application of Raman spectroscopy as applied for the identification of the unknown compounds.

6.13 GLOSSARY

- **Polarizability**: Ability of a non-polar molecule or atom to acquire dipole moment in presence of an electric field.
- **Selection rule**: Rules that decides whether the transition between energy levels are allowed or not.
- **Homo- nuclear diatomic molecule:** Molecule in whichboth atoms possess same nuclei like O_2, N_2.
- **Hetero-nuclear diatomic molecule**: Molecule in which atom possess different nuclei like HCl, NO_2.
- **Stokes lines**: Raman lines that possess frequency less than the frequency of the incident radiations.
- **Anti- stokes lines**: Raman lines that possess frequency more than the frequency of the incident radiations.
- **Depolarization factor**: Intensity ratio of perpendicular and parallel component.

6.14 POSSIBLE ANSWERS TO SAQ

Fill in the blanks:

1. Scattering; 2. Change; 3. Rayleigh; 4. Stokes; 5. Anti- stokes; 6. Solid, liquid and gas; 7. Raman effect; 8. Low; 9. $\Delta v = \pm1$; 10. $\Delta J = 0, \pm2$; 11. Centre of symmetry; 12. Visible radiation; 13. $\Delta J = 0, \pm 2$;$\Delta v = \pm 1$; 14. Pure and colorless; 15. Intensity

True and False:

1. False; 2. True; 3. True; 4. True; 5. False; 6. True; 7. True; 8. True; 9. False; 10. False

Multiple choice Questions:

1. c. Visible region; 2. c. $\upsilon_i<\upsilon_s$; 3. b. $\upsilon_i>\upsilon_s$ 4. b. $\Delta v = \pm1$; 5. c. $\Delta J = 0, \pm2$; 6. c. Rayleigh line; 7. a. Crystalline form show Raman spectra with fine lines; 8. d. All of the above; 9. b. Covalent compounds possess more intensity than the ionic compounds; 10. a. Stokes lines; 11. c. Both a and b; 12. d. All of the above

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6.16 TERMINAL QUESTIONS

1. Explain Raman scattering in detail with respect to pure vibrational and pure rotational Raman spectra of a diatomic molecule.
2. Explain the applications of Raman spectroscopy.
3. Explain the mechanism of Raman excitation.
4. Describe the concept of polarizability in Raman scattering.
5. Discuss mutual exclusion rule along with its applications.

UNIT 7: ELECTRONIC SPECTROSCOPY: APPLICATIONS OF UV-VIS SPECTROMETRY

CONTENTS:

7.1 INTRODUCTION

Electron spectroscopy is an analytical technique to study the electronic structure and its dynamics in atoms and molecules. The electron in a molecule can be excited from an occupied molecular orbital to an empty or partially filled molecular orbital. This constituted what is known as electronic transition. The radiation required for the electronic transition lies in the visible or ultraviolet region. A molecule in each stable electronic level can execute vibrational and rotational motions. The total energy of the molecule is given as :

$$E_{\text{total}} = E_e + E_v + E_r$$

This spectroscopy gives the information about the molecule under investigation are obtained from the various types electronic transitions taking place. Depending on the types of electrons present i.e. bondingσ , π electronsa nd *n* nonbonding electrons, different types of electronic transitions occur. The electronic transitions are accompanied by changes in vibrational and rotational energy levels. The vibrational transitions appear as the coarse structure where as rotational transition as the fine structure. In cases of the molecules containing more than one type of electrons, several transitions may occur resulting in the formation of several bands.

The electronic spectra of molecules are found in the wavelength range 100-800 nm of the electromagnetic spectrum. The visible region corresponds to the range of wavelength between 400 - 800 nm. The ultraviolet region is subdivided into two spectral regions. The region between 200 and 400 nm is known as near ultraviolet region and region below 200 nm is called the far or vacuum ultraviolet region.

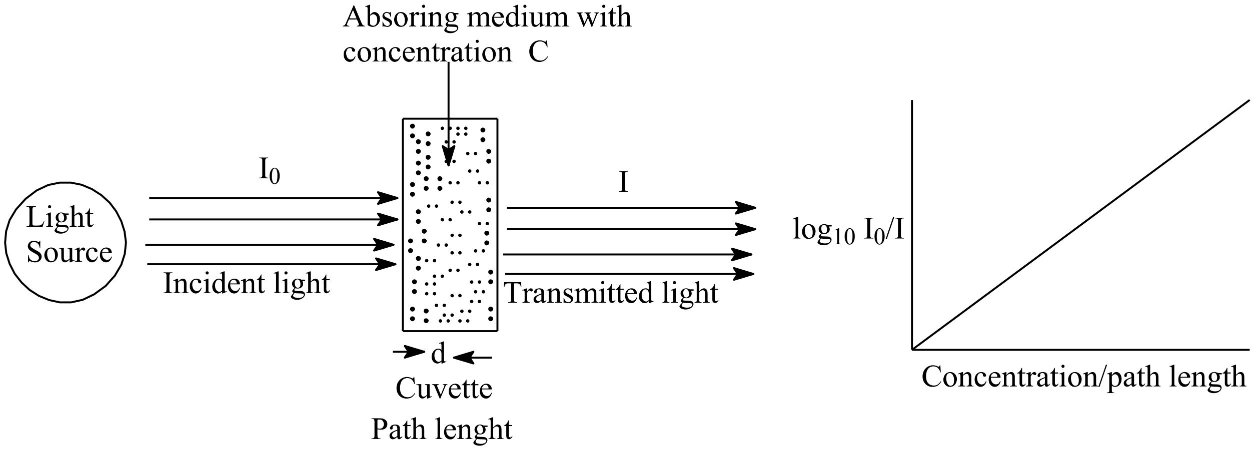
7.2 OBJECTIVES

The objective of this unit are to make aware the readers particularly students about bsorption of UV- Visible radiation and change in internal energy of the molecules in term of electronic excitation.To study different electronic transitions and energy level; To aware about chromophores and auxochromes, Law of absorption (Beer-Lambert law); Uv-Vis spectra, effect of conjugation and solvent on UV spectra; Terminology used in UV spectroscopy; The selection rules (allowed and for forbidden transitions). To study about the measurement of UV spectra, general application of spectroscopy (extent of conjugation, comparison of different compounds with the same chromophore, study of strain, study of geometrical isomerism and steric effects, study of tautomerism, effect of S-cis and S-trans conformations, effect of alkyl substitution and exocyclic double bond, Woodward Fieser rules for conjugated dienes and enones, identification of aromatic systems. Tran's annular conjugation and to study about the influence of constituents ring size and strain on UV Spectra.

7.3 PRINCIPLE

UV spectroscopy is an important tool in analytical chemistry. The other name of UV (Ultra-Violet) spectroscopy is Electronic spectroscopy as it involves the promotion of the electrons from the ground state to the higher energy or excited state. It is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm.) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra-violet radiation that is absorbed is equal to the energy difference between the ground state and higher energy states. The most favoured transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).

UV spectroscopy obeys the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.



The expression of Beer-Lambert law is:

$$A = \log (I_0/I) = \varepsilon.\ c.l$$

Where, A = absorbance

I_0 = intensity of light incident upon sample cell

I = intensity of light leaving sample cell

C = molar concentration of solute

L = length of sample cell (cm.)

E = molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

Working of UV spectroscopy

Most of the modern UV spectrometers consist of the following parts (fig 7.1)-

Light Source- Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm. Now day’s xenon lamps are being used.

Monochromator- Monochromators generally composed of prisms and slits. The most of the spectrophotometers are **double beam spectrophotometers**. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

Sample and reference cells- One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

Detector- Generally two photocells serve the **purpose of detector in UV spectroscopy**. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Amplifier- The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many times so we can get clear and recordable signals.

Recording devices- Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

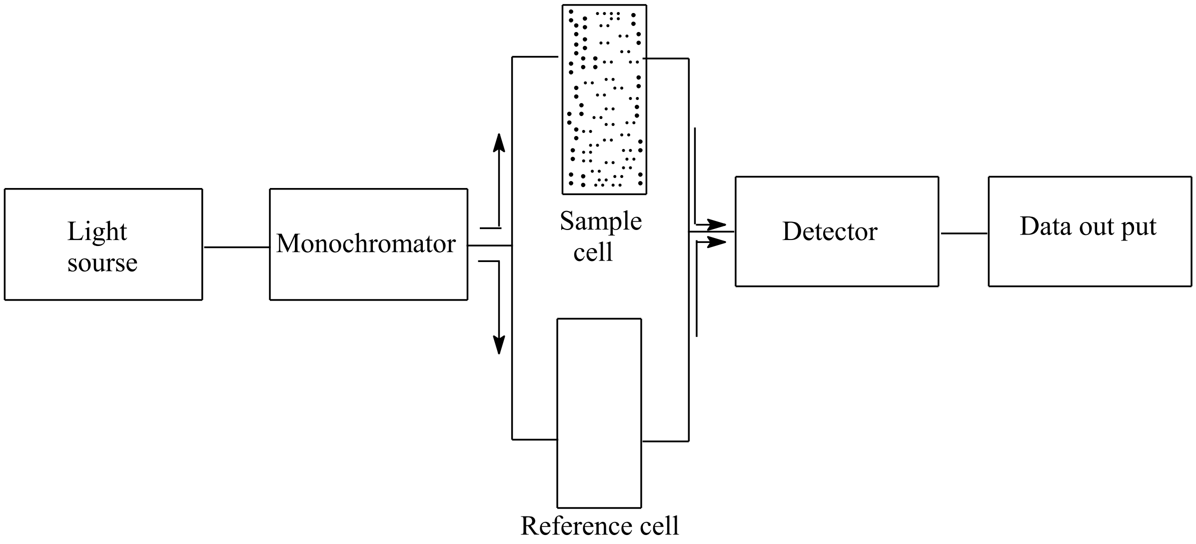


Fig: 7.1. Double beam UV-Vis spectrophotometer

7.4 ELECTROMAGNETIC RADIATION

Electromagnetic (EMR) waves can be thought of as stream of particles, where each particle is moving with the speed of light. Each particle contains a bundle of energy. This bundle of energy is called a photon. EMR consists of electromagnetic waves, which are synchronized oscillations of electric and magnetic fields that propagate at the speed of light through a vacuum. The oscillations of the two fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation, forming a transverse wave.

The effects of EMR upon chemical compounds and biological organisms depend both upon the radiation's power and its frequency. EMR of visible or lower frequencies (i.e., visible light, infrared, microwaves, and radio waves) is called non-ionizing radiation, because its photons do not individually have enough energy to ionize atoms or molecules.

The effects of these radiations on chemical systems and living tissue are caused primarily by heating effects from the combined energy transfer of many photons.In contrast, high ultraviolet, X-rays and gamma rays are called ionizing radiation, since individual photons of such high frequency have enough energy to ionize molecules or break chemical bonds. These radiations have the ability to cause chemical reactions and damage living cells beyond that resulting from simple heating, and can be a health hazard.

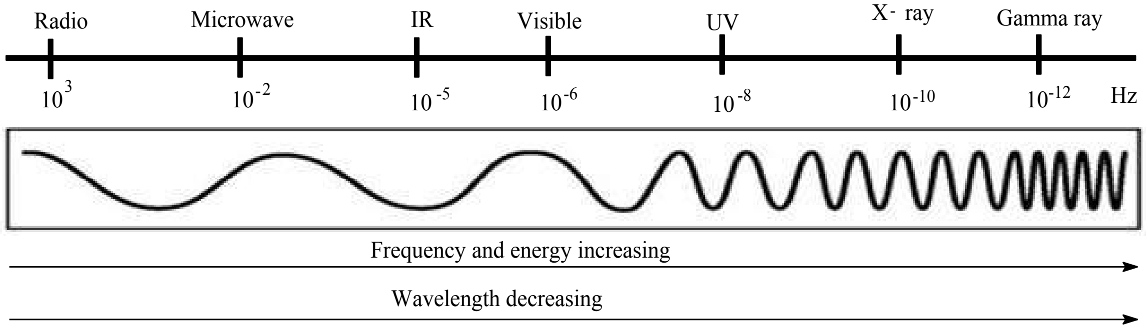


Fig.7.2. various frequency regions of electromagnetic radiation

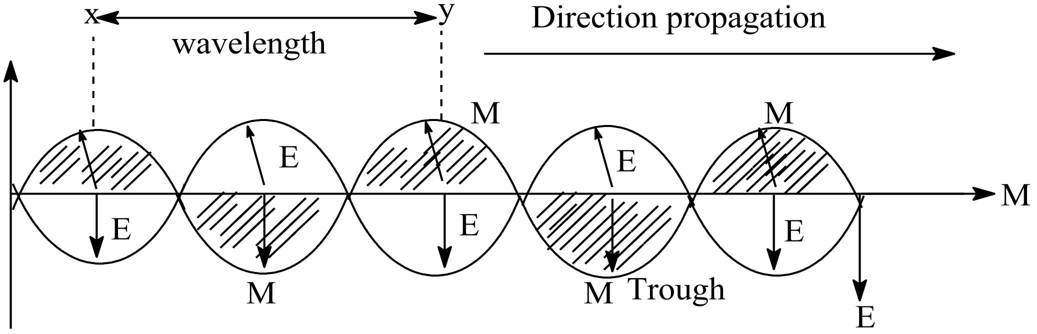


Fig.7.3. A beam of EMR showing electric (E) and magnetic (M) components

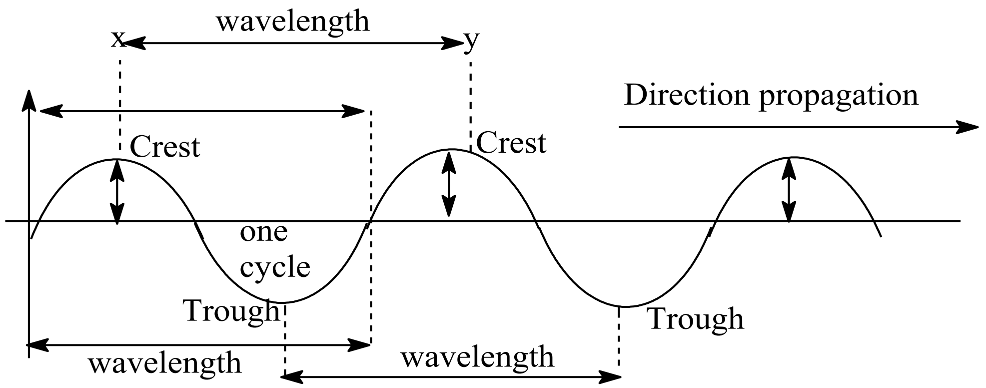


Fig.7.4. Electric (E) component of a propogating light wave

Fig 7.2 illustrated above represent the various energy/frequency/wavelength region of an electromagnetic radation. The EMR is composed of electric and magnatic components as also described above. These two components moves perpendicularly to each other as represented in fig.7.3. The electric components have been represented in fig.7.4. The EMR is described by particle as well as wave theory. According to particle nature EMR travel in the form of small energy packets known as photon with energy:

$$\Delta E= hv$$

Where ΔE is energy, h= Plank's constant (6.625×10^{-34} Js) and v= frequency

According to wave nature a wave can be described by using following important wave parameters

1. **Wavelength**: The wavelength, λ, of a wave is the distance from any point on one wave to the same point on the next wave along. Wavelength is also measured in metres (m) - it is a length after all.

The other commonly used units of wavelength are nm, µm, A^0 etc.

1nm = 10^{-9}m, = 10^{-3} µm = $10A^0$ (1A0 = 10^{-10}m; 1 µm = 10^{-6} m =10^{-3}m; 1cm =10^{-2} m)

2. **Frequency:** Frequency is the number of waves repeating per unit of time. It is represented by v and measured in Hz, MHz, cylces/sec. The term frequency is directly proportional to energy.

1 cycle/second = 1Hz

Bigger units are kHz (1 kHz = 103 Hz); MHz (1MHz = 10^6Hz or cps)

$$\Delta v = \Delta E$$

3. **Wave number:** wavenumber is inversely proportional to wavelength, it is directly proportional to frequency and energy which makes it more convenient to use. Its unit is cm^{-1} and represented as v^{-}.

$$v^{-} = E \text{ , } v^{-} = v \text{ as } E = v$$

$$v^{-} = 1/\lambda$$

7.5 ELECTRONIC TRANSITIONS AND ENERGY LEVEL

When a molecule absorb radiation in UV-Visible region the electronic excitation takes place i.e. the electron from their ground state (low energy state) pass to excited state (high energy state). Fig .7.5 illustrates the process of excitation, which is quantized. The EMR absorbed is equal to the energy difference between excited and ground states $\Delta E = hv$.

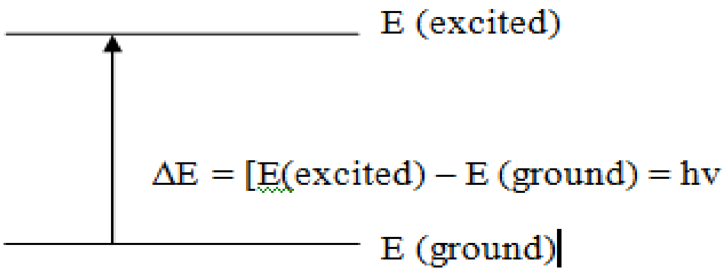


Fig. 7.5. The excitation process

The electronic transitions generally occur in between a bonding or lone- pair orbital and unoccupied non – bonding or anti – bonding orbital. The difference of energy between these levels in most organic compounds varies from 30 to 150 kcal/mole. The σ orbitals, involved in forming σ bonds, are the lowest energy occupied molecular orbitals. The π orbitals lie at somewhat hugher energy and ortbitals holding the lone pair of electron pair (non- bonding orbitals) lie above the π- bonding molecular orbitals. The anti- bonding orbitals (π^* and σ^*) are the higher energy orbitals. The electronic transitions of σ,π and n electrons as a result of UV-Visible light absorption has been presented in fig 7.6.

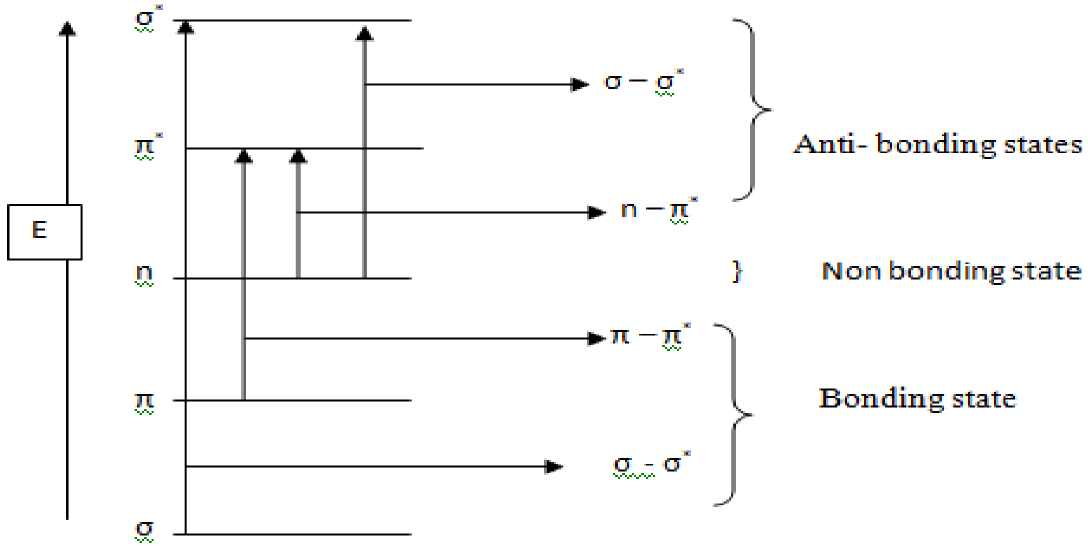


Fig. 7.6. Electronic energy levels and electronic transitions

Generally the most probable transition is found from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The energy required to bring about transitions from the HOMO in the ground state to the LUMO is less than the energy required to bring about atransition from lower occupied energy level. In fig 6 an n – π^* transition would have alower energy than a π- π^* transition. For many purposes, the transition of lowest energy is the most important.

Selection Rule: There are certain transitions, that would at first sight seems to be possible but are generally not observed in the UV-Visible spectrum, because of some restrictions called selection rules.The selections rules for electronic excitations in UV-Visible spectroscopy are as follow.

- First rule says that allowed transitions must involve the promotion of electrons without a change in their spin.
- Second rule is related to multiplicity i.e. singlet to teiplet or vice versa are not aloowed.
- Third rule sayse that transitions arising from symmetry stateare forbidden. Viz due to local symmetry a non-bonding electron to pie-antibonding aorbital (n – π^*) in HCHO is not allowed.

Frank Codon rule and forbidden transitions: Frank Codon has stated an important rule for understanding the nature of electronic transition. According to him electronic transitions will take place only when the internuclear distances are not significantly different in the two states and where the nuclei have little or no velocity.The forbidden transitions htus may arise when the internuclear distances are significantly different in the two states and where the nuclei have significant velocity (fig. 7.7).

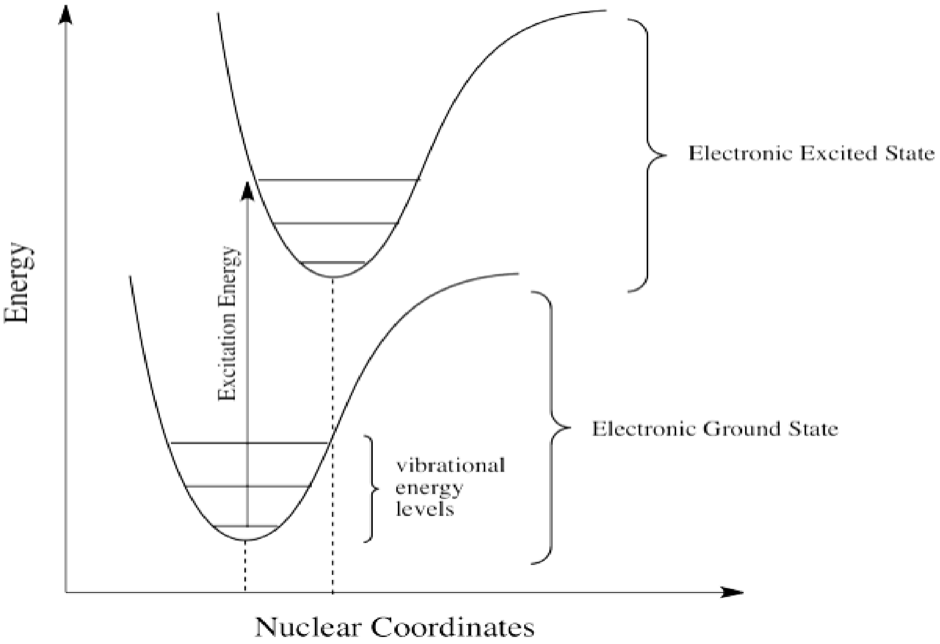


Fig. 7.7. Frank-Codon diagram

7.6 UV-VISIBLE SPECTRUM AND DESIGNATION OF BANDS

The UV-Visible spectrum is simply record of wavelength (λ) against absorption. The λ corresponding maximum absorptium in the spectrum indicate the λ_{max} value (fig 7.8 a). The ultraviolet spectrum may be divided into the following regions (fig. 7.8 b):

1. Far or vacuum region: (10 – 200 nm): This region is studied in evacuated system and known as “vacuum ultraviolet” region. The atmospheric absorptions below 200 nm is a blessing to all, including the spectroscopists, since it prevents the hazardous (high energy) ultraviolet radiation in the sunlight from striking the earth’s surface. In organic molecules, the maximum energy separation occurs when electrons in σ bonds are excited giving rise to

absorption in the range 120-200 nm. The range is difficult to measure and is of little diagnostic value.

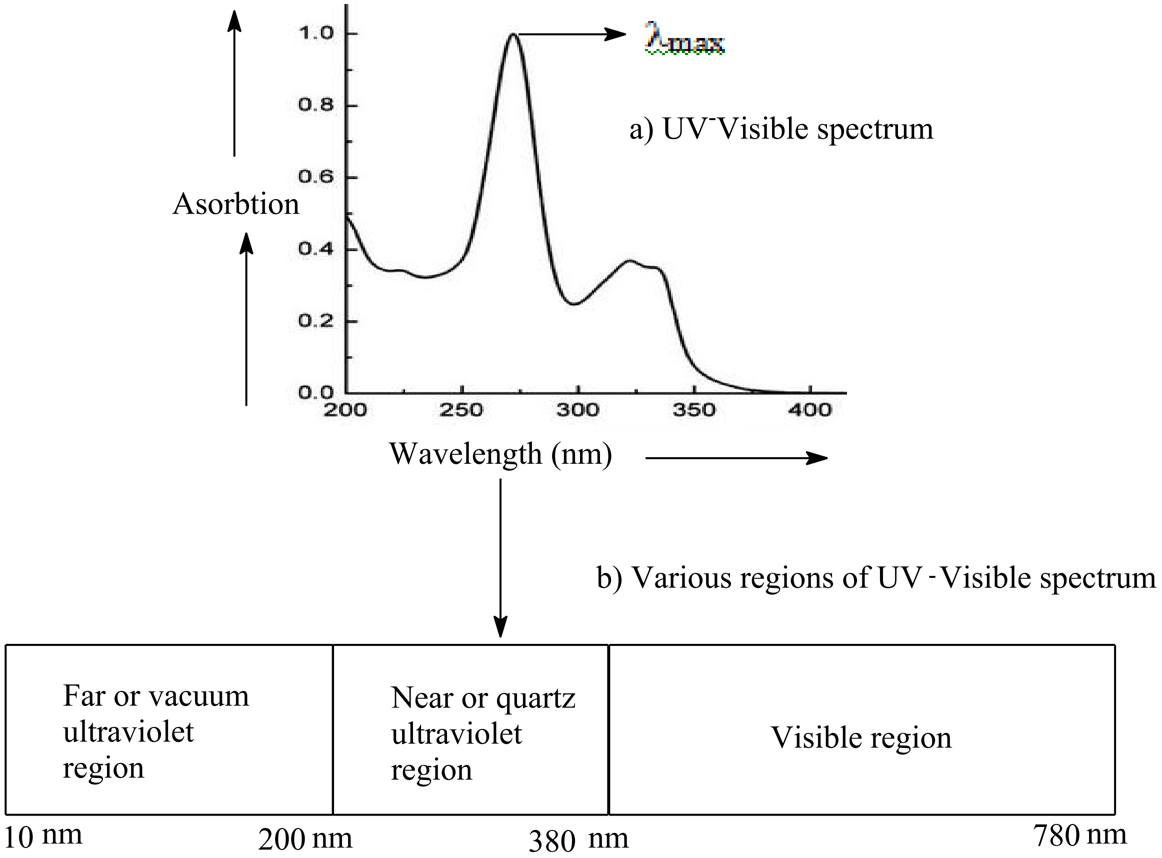
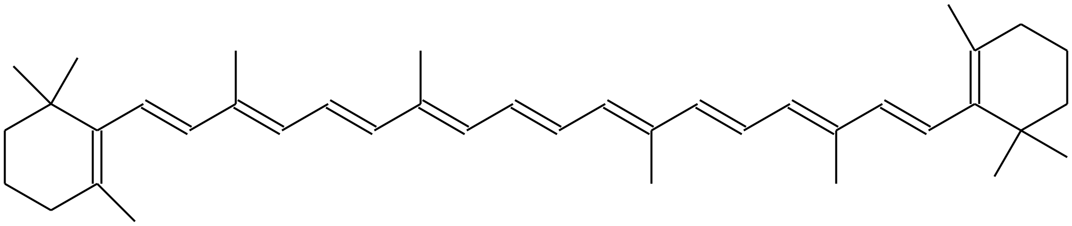


Fig 7.8. a). UV-Visible spectrum b) different regions of UV-visible spectrum.

2. Near or Quartz ultraviolet (200-380nm): The range from 200-380 nm is the portion of the spectrum normally covered by the term ultraviolet. The atmosphere is transparent in this region and quartz optics may be used to scan from 200-380 nm. The excitation of electrons from p & d orbital, π-orbitals and particularly π conjugated systems occurs above 200nm and gives rise to readily accessible and informative spectra.
3. Visible region (380 nm 780 nm): The spectral range which is accessible with most instruments is from 200 nm to 800 nm and this entire region is often referred to as ultraviolet spectrum although it includes the visible region (380 to 780 nm). A tungsten filament lamp is generally used for the visible region of the spectrum. Conjugation of double bonds lowers the energy required for the transition and absorption moves to longer

wavelength. When there are enough double bonds in conjugation, absorption will move into the visible region and the compound will be coloured. B-carotene as follow, for example, contains eleven carbon-carbon double bonds in conjugation and owes its colour to absorption in the visible region of the spectrum (λ_{max} = 451 nm.)



beta carotene

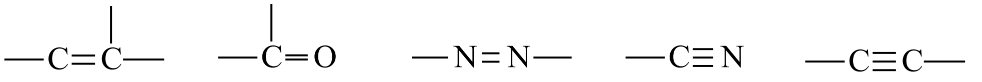
DESIGNATION OF UV BANDS: Electronic spectra arise from transitions between electronic energy levels accompanied by changes in both vibrational and rotational states. Since the wavelength of absorption is a measure of the separation of the energy levels of the orbitals concerned, a transition between these levels, when gaseous sample is irradiated, gives rise to fine structure consisting of a number of closely spaced lines which, very often, merge (due to solvent-solute interaction) to give a broad absorption band, when spectral measurement are carried out in solution. Electronic absorption bands are, therefore, usually broad as compared to infrared or NMR bands. The absorption bands in the UV spectrum may be designated either by using electronic transitions or by the letter designation, as illustrated below:

1. ***R- Bands (German, radikalartig)***: The bands attributed to n →π* transitions of single chromophoric groups, such as the carbonyl or nitro group, are referred to as the R-bands (German, radikalartig). They are characterized by low molar absorptivities (ε_{max} < 100) and undergo hypsochromic shift with an increase in solvent polarity.
2. ***K-bands (German, konjugierte):*** The bands pertaining to π→π* transitions in molecules containing conjugated π-systems, such as butadiene or mesityl oxide, are referred to as (K-bands, German, konjugierte). They are characterized by high molar absorptivity (ε_{max} < 10,000).
3. ***B (benzenoid) and E (ethylenic) bands:*** The B and E bands are characteristic of the spectra of aromatic or heteroaromatic molecules. All benzenoid compounds exhibit E

and B bands representing π→π* transitions. For example E_1 and E_2 bands of benzene occur near 180 and 200 nm respectively and their molar absortivity varies between 2000 and 14000. The B-band occurs in the region from 250 to 255 nm as a broad band containing multiple fine structures and represents a symmetry-forbidden transition which has finite but low probability due to forbidden transitions in the highly symmetrical benzene molecule. The vibrational fine structure appears only in the B-band and disappears frequently in the more polar solvents.

7.7 TERMINOLOGY OF UV-VISIBLE SPECTROSCOPY

A. Chromophore: The multiple bonded groups in the organic molecules due to which they owe their color are called chromophore (Chrom = colour, phore = bearing/possessing). The examples of chromophores are as follow:

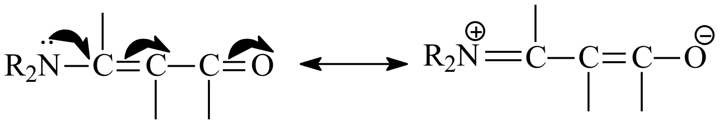


$-C{=}\overset{|}{C}-$ $\quad -\overset{|}{C}{=}O$ $\quad -N{=}N-$ $\quad -C{\equiv}N$ $\quad -C{\equiv}C-$ etc.

B. Auxochrome: An auxochrome are auxillary groups which intracts with the chromphore and cause a bathochromic shift i.e. they do not posses their own colour but intensify the colo bearing capacity of chromphore if attached with it. Viz;

NH_2, NHR, NR_2, -OH, $-OCH_3$ –R, -SH etc.

The unique property of auxochrome grouping is its ability to provide additional opportunity for charge delocalization and provide smaller energy increments for transition to excited states. The delocalization in molecules is increased due to lone pair of electrns in most of the auxochrome or due to other electronic displace ments lke hyperconjuction.



$R_2\ddot{N}-\overset{|}{C}{=}\underset{|}{C}-\underset{|}{C}{=}O \longleftrightarrow R_2\overset{\oplus}{N}{=}\overset{|}{C}-\underset{|}{C}{=}\underset{|}{C}-\overset{\ominus}{O}$

Attachement of auxochrome to chromphore always acuse bathochromic shift i.e. absorption takes place towards longer wavelength region.Some examples of auxochromic effects are as follow (table 7.1):

Table 7.1: Chromophoric effect of auxochrome

Auxochrome	Unsubstituted Chromophores	λmax (nm)	Substituted Chromophore	λmax (nm)
$-CH_3$	$H_2C=CH-CH=CH_2$	217	$H_2C=CH-CH=CHCH_3$	224
$-NCH_2CH_3$	$CH_3(CH_2)_2CH=CHCOOCH_3$	228	$Et_2NCH=CHCOCH_3$	307
-OR	$CH_3CH=CHCOOH$	204	$CH_3C(OCH_3)=CHCOOH$	234
-Cl	$CH_2=CH_2$	175	$CH_2=CHCl$	185

C. Bathochromic shift (Red-shift): Shift of absorption of EMR towards longer wavelength (λ) or low energy (low frequency) region in UV-Visible spectroscopy is known as bathochromic shift or Red-shift. The shift of absorption of of peak position is due to

1. Attachment of auxochrome to chromophore
2. Increased conjugation
3. Change in polarity of solvent

D. Hypsochromic shift (Blue-shift): A shift of absorption of EMR towards shorter wavelength (λ) or high energy (high frequency) region in UV-Visible spectroscopy is known as hypsochromic shift or blue-shift. This may be caused by

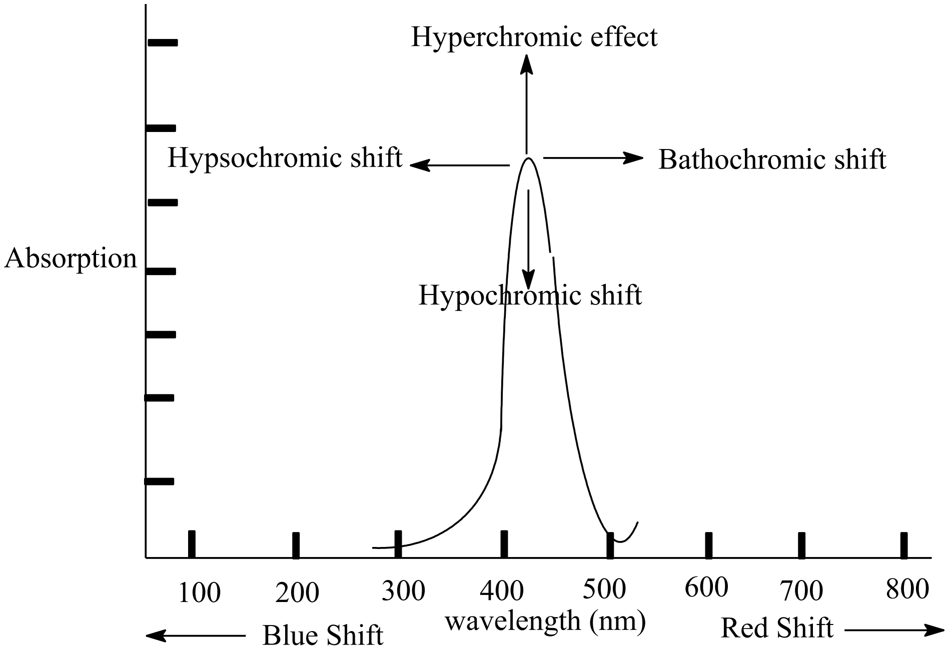
1. Deattachement of auxochrome
2. Decreased conjugation
3. Change in solvent polarityviz acetone absorb ar 279 nm in hexane while in water the λ_{max} value of acetone is 265 nm. This shift results from H….. bonding which lowers the energy of n-orbital. This can also be produced whe auxochrome is attached to double bonds where n-electrons are available viz; C=O.

E. Hyperchromic effect: It is effect leading to uncreased absorption intensity.It is related to bathochromic shift and molar absorbtivity coefficient (ε_{max} increases)

F. Hypochromic effect: It is effect leading to decreased absorption intensity. It is related to hypsochromic shift (ε_{max} decreases)

G. Isobestic point: A point common to all curves produced in the spectra of a compound taken at various pH values is called isobestic point.

The different term as discussed above can be well understood by using following diagram



7.8 FACTORS AFFECTING THE POSITION OF UV BANDS

1. **Conjugation:** a conjugated system always require lower energy for the $\pi - \pi^*$ transition than an unconjugated system. This can be explained by using the example of $CH_2=CH_2$ and $CH_2=CH-CH=CH_2$ as follow.

   Ethylene($CH_2=CH_2$) has only two orbitals; one ground state π bonding orbital and one excited state π^* anti-bonding orbital. The energy difference between them is about 176 kcal/mole. Butadiene ($CH_2=CH-CH=CH_2$) hoever with four π-orbitals has four available π-orbitals, two bonding (π_1 and π_2) and two anti-bonding (π^*_3 and π^*_4). The π_2 is designated as highly occupied molecular orbital (HOMO) and is more stable than π^*_3 which is designated as Least unoccupied molecular orbital (LUMO). The energy difference between HOMO and LUMO of butadiene is 136 kcal/mole, which is lower than π (HOMO) and π^* (LUMO) of ethylene(176 kcal/mole). For excitation of electron from HOMO to LUMO orbital longer wavelength is required while for HOMO-LUMO excitation of electron in ethylene shorter wavelength will be required. It is clear from tjis example that in $CH_2=CH_2$ there is only one double bond and require more energy for electronic excitation while in $CH_2=CH-CH=CH_2$ there are two double bonds and require low energy for electronic excitation. Hence as the conjugation is increasing from ethylene to butadiene the energy gap between HOMO and LUMO is decreasing and ultimately leading to bathochromic shift. Schematically it has been illustrated as follow fig.7.9:

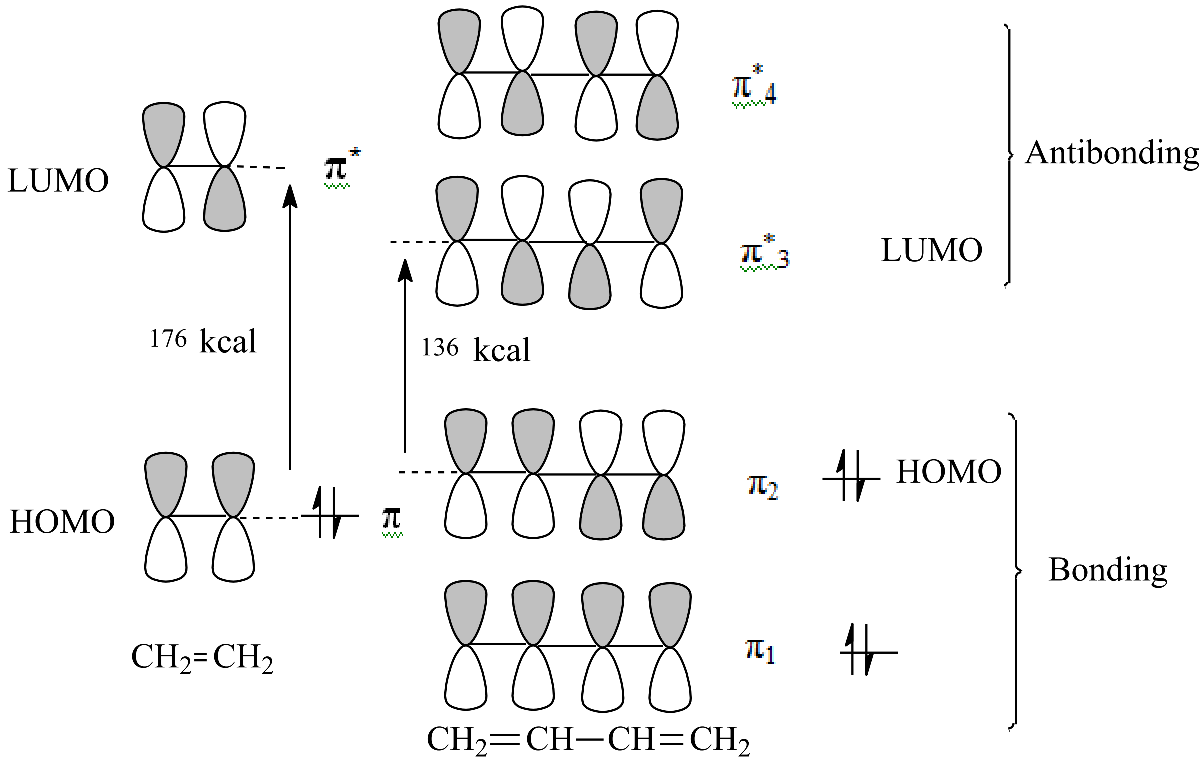


Fig 7.9. MO energy levels of ethylene and 1,3-butadiene

From above concept it is concluded that as the conjugation increases the HOMO- LUMO gap decreases, hence require low energy for electronic excitation and leading higher value of $\lambda_{max.}$

2 .Effect of steric hinderance on co-planarity: Conjugation is always supported by planarity, any type of distortion to planarity in the molecule decrease the possibility of conjugation as $\pi - \pi$ overlapping is possible in planar system only. Schamatically the planar and distorted planarity conjugation can be seen as follow.

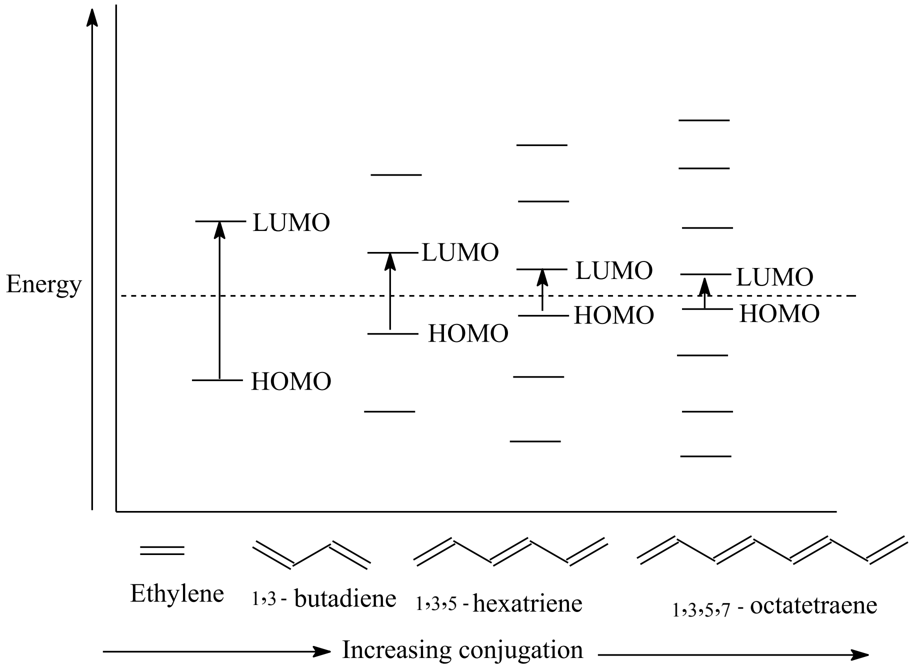
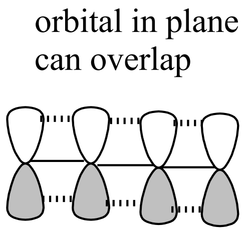
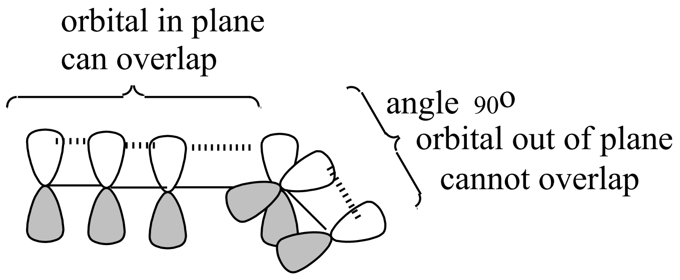


Fig.7.10. A comparasion of HOMO-LUMO energy gap in aseries of polyenes of increasing chain length

2 .Effect of steric hinderance on co-planarity: Conjugation is always supported by planarity, any type of distortion to planarity in the molecule decrease the possibility of conjugation as $\pi - \pi$ overlapping is possible in planar system only. Schamatically the planar and distorted planarity conjugation can be seen as follow.



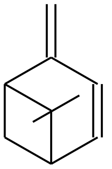
Planar system



Distorted palanarity

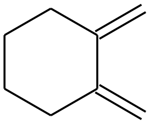
The distortion of the chromophore may lead to red or blue shifts depending upon the nature of distortion viz; molecule A as below show its λ_{max} at 245 nm, however the usual calculation shows at at 229 nm. The molecule B is expected to have λ_{max} 273 nm but distortion of the chromophore is out of planarity as a ruselt the conjugation is lost and cause the λ_{max} value as low as 220 nm with similar loss in intensity

A



verbenene

B

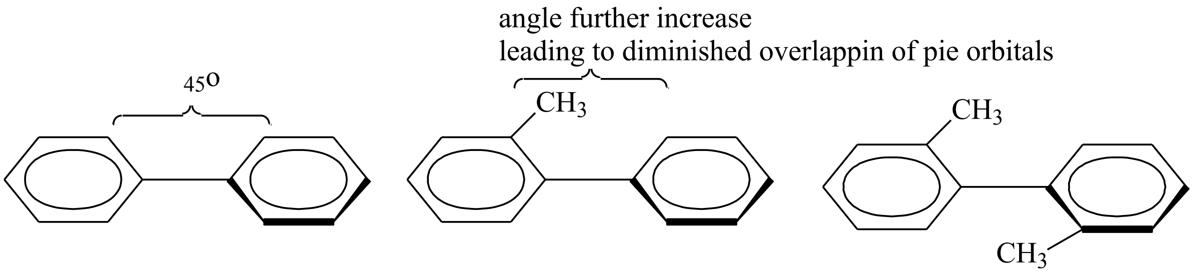


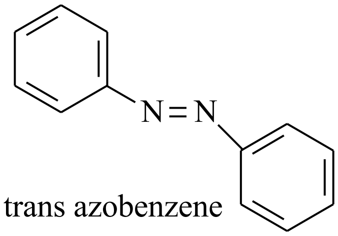
diene

λ_{max} observed = 245nm λ_{max} observed = 220 nm

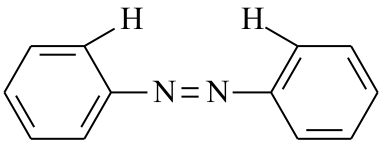
λ_{max} calculated =229 nm λ_{max} calculated =273 nm

Similar pattern can be ovserved in biphenyls in which the two two phenyl rings are not coplanar but are situated at about 45^0 of angle. Incercetion of steric group futher fush the phenyl rings to out of plane and diminish the conjugation.Similarly in cis and trans azobenzene the conjugation related to planarity effect the absorption and intensity of UV bands as shown below.





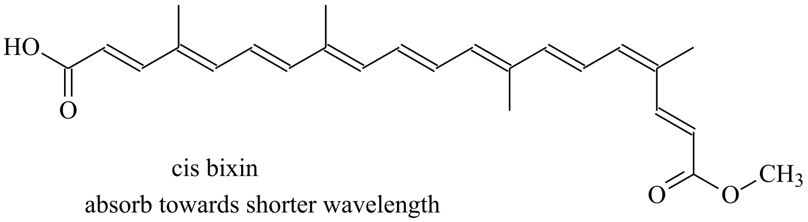
trans azobenzene



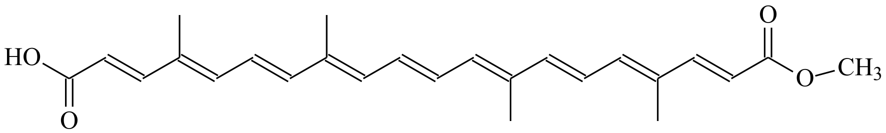
cis azobenzene

Molecule	π-π*(λ_{max})	ε_{max}	n-π*(λ_{max})	ε_{max}
trans azobenzene	320	21300	443	510
cis -azobenzene	281	5260	433	1520

3. **Conformation and geometry in polyene systems:** In long chain conjugated polyenes steric hinderance to coplanarity can arise when cis-bonds are present. Viz in naturally occurring bixin (all trans methyl carotenoid) and its isomer with central cis double bond. The longwacelength band is weakened and a digonistically useful cis- band probably due to a partial chromophore appears at shorter wavelength.



cis bixin
absorb towards shorter wavelength



trans bixin
Absorb towards longer wavelength

4. Effect of solvents: Solvents play important role in shifting absorbtion maxima of compounds in UV-visible spectroscopy. Both position and intensity of UV bands hve been observed by changing the solvents. Generally the following shifts are observed for change to solvents of increased polarity:-

A. Conjugated dienes/polyenes and aromatic hydrocarbons exhibit very little solvent shift.

B. α, β- unsaturated carbonyl compounds display two different types of shifts. (1) $\pi - \pi^*$ band shifts towards longer wavelength (bathochromic shift or red shift) while (2) $n - \pi^*$ band shifts to shorter wavelength (Hypsochromic shift or blue shift).

The solvent effect in α, β- unsaturated carbonyl compounds may be because of salvation on the relative energies of π, n and π^* orbitals. The salvation can be described as follow.

a) Solvation by polar solvent stabilize π, n and π^* orbitals

b) The stabilization n orbital is particularly pronounced with H…. bonding solvends like H_2O or CH_2CH_3OH. The non – bonded electrons on oxygen co-ordinate with hydoxylic solvents and thermodynamically decrease the net energy of the n-electrons.

c) π^* orbitals are more stabilized by salvation as compared to π-orbitals because $\pi - \pi^*$ transition has a polar excited state which would naturally be stabilized by H…bonding in more polar solvents. The final inference of salvation is that the energy of $\pi - \pi^*$ transition becomes less with salvation (red shift), while the energy of $n - \pi^*$ transition become higher (hypsochromic shift). Schematically the effect of solvent can be illustrated as follow Fig.7.11.

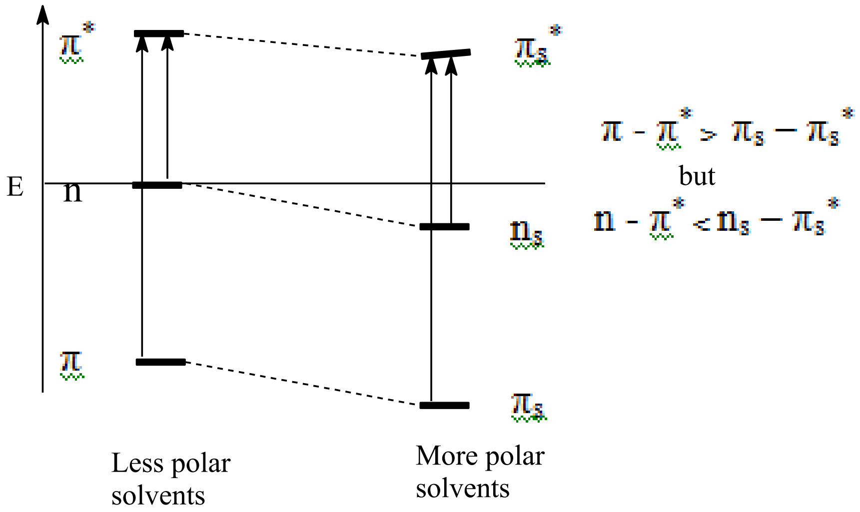
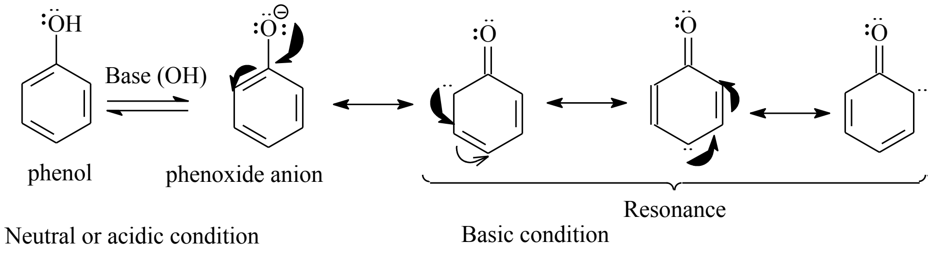


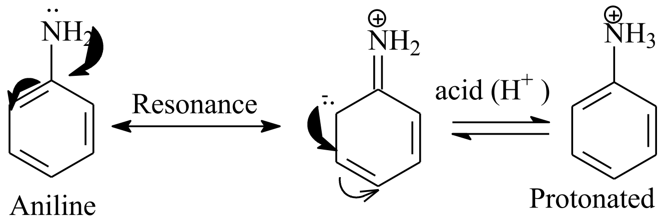
Fig.7.11. Effect of sovation on the relative energies of n, π and π^* orbitals.

5. Effect of pH: Dramatic changes to the UV-Vis spectra of some compounds, especially certain substituted aromatic compounds, occur with a change in the pH of the solvent. Phenols and substituted phenols are acidic and display striking changes to their absorptions upon the addition of base. Removal of the acidic phenolic proton increases the conjugation of the lone pairs on the oxygen with the π-system of the aromatic ring, as shown below leading to a decrease in the energy difference between the HOMO and LUMO orbitals, and an associated red or bathochromic shift (to longer wavelength), along with an increase in the intensity of the absorption.



λ_{max} (H_2O) 210 (6000) 270 (1500) λ_{max} (H_2O) 235 (9400) 284 (2600)

Treatment of an aromatic amine with acid, on the other hand, causes protonation of the amine as given below, leads to a loss of the overlap between the amine lone pair and the aromatic π-system. The result is a blue hypsochromic shift (to shorter wavelength) along with a decrease in intensity



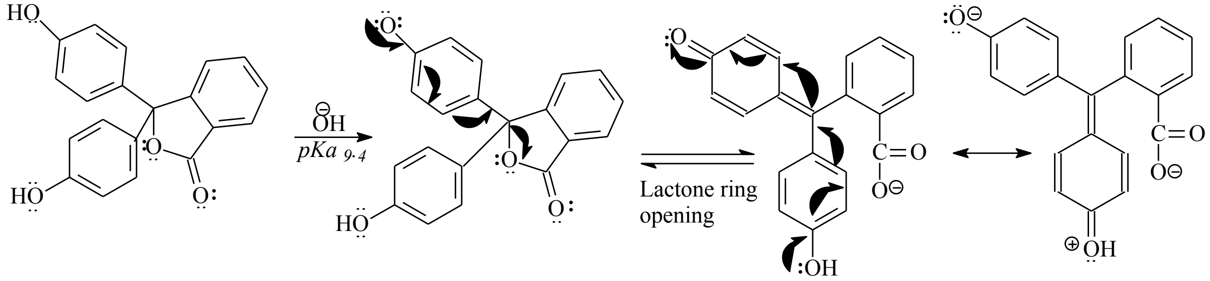
Neutral or basic condition

λ_{max} (H_2O) 235 (14800)
285 (2800)

Acidic condition

λ_{max} (H_2O) 203 (7500)
254 (180)

Many pH indicators owe their utility to their absorptions in the visible region of the UV-Vis spectrum. Changes to the pH lead to changes in the indicator chromophore, and result in reliable colour changes at predictable pH values. One such example is that of phenolphthalein which is a phenol and can be deprotonated at elevated pH to give the anion as follow, extending the chromophore and leading to a substantial bathochromic shift (to longer wavelength).



Phenolphthalein (colourless) λ_{max} 231 nm
275 nm

Acidic medium → basic medium

Phenolphthalein (deep magenta) λ_{max} 230 nm
553 nm

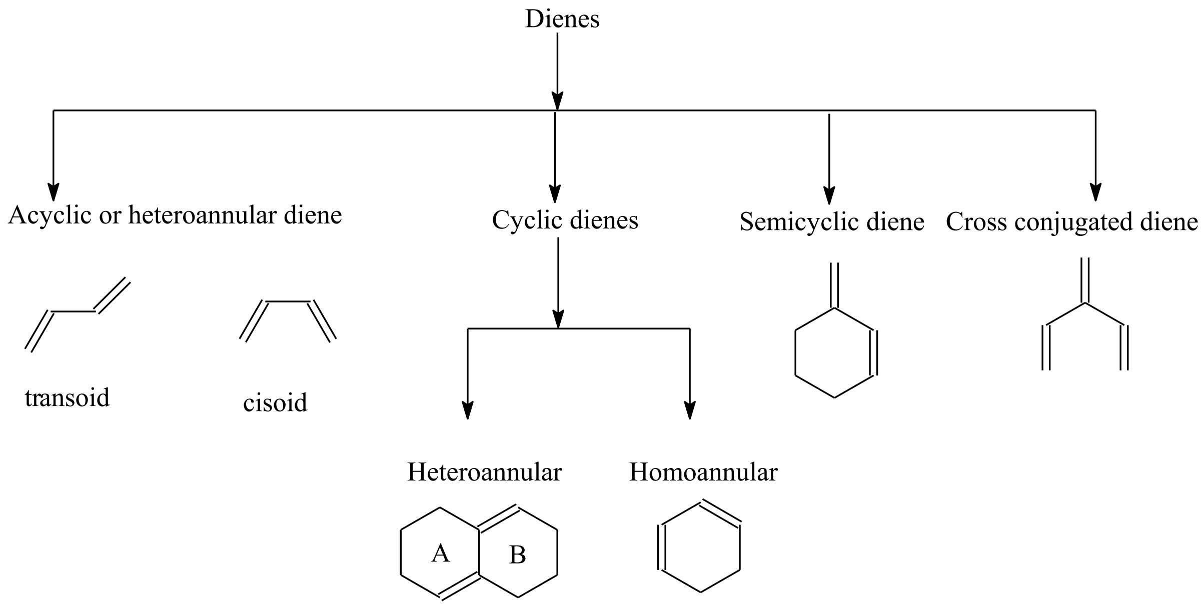
Thus the anion of phenolphthalein is deep magenta in colour, while un-ionized phenolphthalein is colourless The pK_a of this acid-base equilibrium is 9.4: at acidic and neutral pH there is insufficient anion to detect the colour by eye, and it appears colourless.

As the pH approaches the pK_a, the concentration of anion increases and, at pH 8.2, the colour becomes visible to the eye. As pH 8.2 is close to neutrality, phenolphthalein is widely used to show the end-point in weak acid strong base titrations.

7.9 THE WOODWARD – FIESER RULES FOR DIENES

As we have already seen, delocalization of electrons by conjugation decreases the energy difference between the HOMO and LUMO energy levels, and this leads to a red shift. Alkyl substitution on a conjugated system also leads to a (smaller) red shift, due to the small interaction between the σ-bonded electrons of the alkyl group with the π-bond system. These effects are additive, and the empitical Woodward-Fieser rules were developed to predict the λ_{max} values for dienes (and trienes). Similar sets of rules can be used to predict the λ_{max} values for α, β-unsaturated aldehydes and ketones (enones) and the λ_{max} values for aromatic carbonyl compounds. These rules are summarized as follow for dienes and enones.

Dienes and their types: Compounds containing two carbon-carbon double bonds are known as dienes. Based on their position/orientation in molecules dienes can be caterogised as follow:-

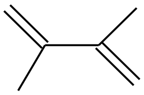
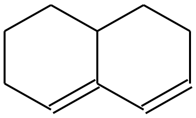


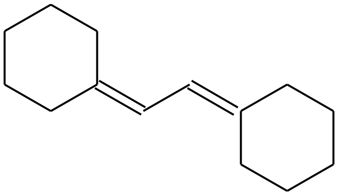
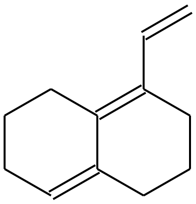
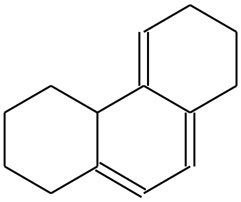
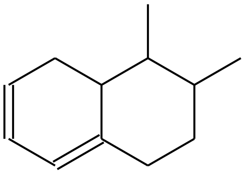
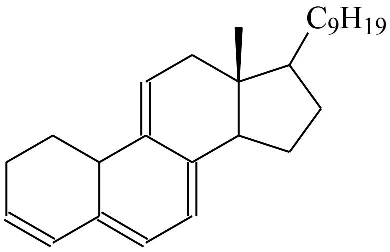
Using the Woodward-Fieser rules, we can predict the absorption maximum of an unsaturated compound with pleasing accuracy, generally to within ±5 nm of the observed value as per the table-7.2 given below

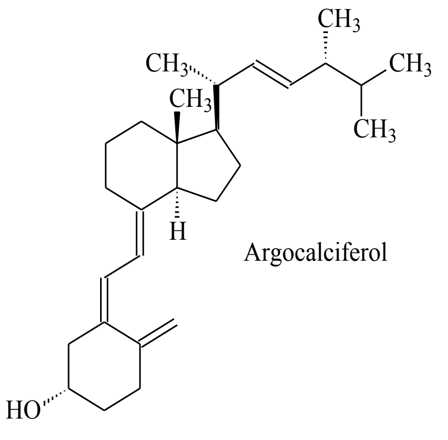
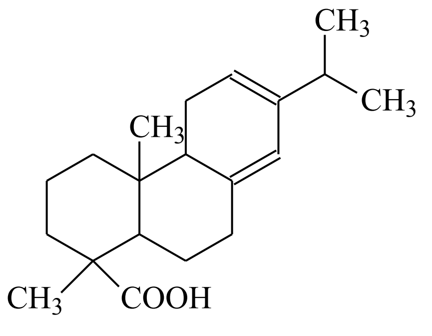
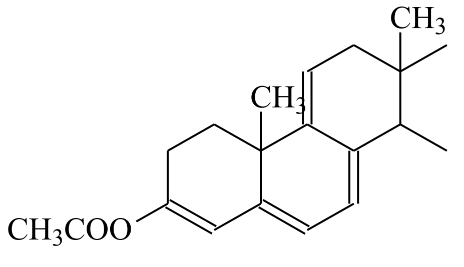
Table 7.2: Woodward Fieser's rules for calculating ultraviolet absorption maxima of substituted dient (C_2H_5OH solution)

S.N.	**Diene system**	**Base values**
1	Parent acyclic diene	217 nm
2.	Parent heteroannular diene	214 nm
3.	Parent homoannular diene	253 nm
INCREMENTS FOR SUBSTITUENTS		
i	Alkyl group or ring residue (if the alkyl group is attached to two double bonds, count it twice)	+ 5 nm
ii	Exocyclic double bond (effect is two fold if bind is exocyclic to two rings)	+ 5 nm
iii	Double bond extending conjugation	+30 nm
iv	Halogen (-Cl, -Br)	+ 5 nm
v	O- (alkyl) (-OR), O- (acyl) (-O-COR)	+ 5 nm
vi	S-(alkyl) (-S-R)	+ 0 nm
vii	N-(alkyl)$_2$, (-NRR')	+60 nm

Some important examples as given as follow for calculating λ_{max} values of dienes.

Compounds	**λ_{max} values**
	Parent acyclic diene (base value) = 217nm Ring residues(substituents) 2×5 = 10nm λ_{max} Calculated =227nm λ_{max} Observed =226nm
	Parent heteroannular diene (base value) = 214nm Ring residues(substituents) 3×5 = 15nm Exocyclic double bond 1×5 =5nm λ_{max} Calculated =234nm

	Parent acyclic diene (base value) = 217nm Ring residues(substituents) 4×5 = 20 nm Exocyclic double bond 2×5 =10 nm λ_{max} Calculated =247nm λ_{max} Observed =247nm
	Parent heteroannular (base value) = 214nm Ring residues(substituents) 4×5 = 20 nm Exocyclic double bond 2×5 =10 nm Double bond extending conjugation 1×30 = 30nm λ_{max} Calculated =274nm
	Parent homoannular(base value) = 253nm Ring residues(substituents) 5×5 = 25 nm Exocyclic double bond 3×5 =15 nm Double bond extending conjugation 1×30 = 30nm λ_{max} Calculated =323nm
	Parent homoannular(base value) = 253nm Ring residues(substituents) 3×5 = 15 nm Exocyclic double bond 1×5 = 5 nm λ_{max} Calculated =373nm
	Parent homoannular(base value) = 253nm Ring residues(substituents) 5×5 = 25 nm Exocyclic double bond 3×5 = 15 nm Double bond extending conjugation 2×30 = 60nm λ_{max} Calculated =353nm

 Argocalciferol	Parent acyclic diene (base value) = 217nm Ring residues(substituents) 3×5 = 15 nm Exocyclic double bond 1×5 = 5 nm Double bond extending conjugation 1×30 = 30nm λ_{max} Calculated =267nm
	Parent homocyclic diene (base value) = 253nm Ring residues(substituents) 4×5 = 20 nm Exocyclic double bond 1×5 = 5 nm λ_{max} Calculated =278nm λ_{max}Observed =275nm
	Parent homocyclic diene (base value) = 253nm Ring residues(substituents) 5×5 = 25 nm Exocyclic double bond 3×5 = 15 nm Double bond extending conjugation 2×30 = 60nm λ_{max} Calculated =353nm λ_{max} Observed = 355nm

The rules described above holds well for unsaturated compounds containing up to four double bonds. However, for conjugated systems contaibibg more than four double bonds the following equation for the prediction of λ_{max} and ε_{max} has been predicted.

$$\lambda_{max}\,(nm) = 114 = 5M + n(48.0 - 1.7n) - 16.5R_{endo} - 10R_{exo}$$

Where n = number of conjugated double bonds

M = Number of alkyl substituents/ring residues on the conjugated system.

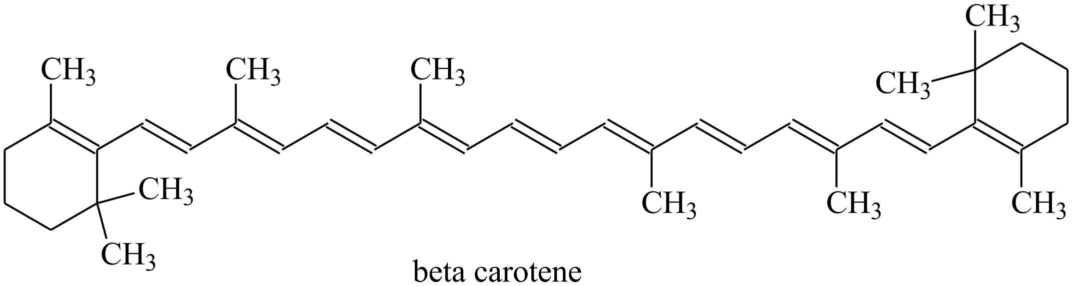
R_{endo} = Number of rings with endocyclic double bonds in the conjugated system

R_{exo} = Number of rings with exocyclic double bonds

ε_{max} value can similarly be calculated with the help of the following equation:

$\varepsilon_{max} = (1.74 \times 10^4)_n$

The λ_{max} value of *β*- carotene can be calculated as described follow



beta carotene

Basic λ_{max} value =114 nm

M = Number of ring residues =10

N = Number of conjugated double bonds =11

R_{endo} = Number of rings with endocyclic double bonds =2

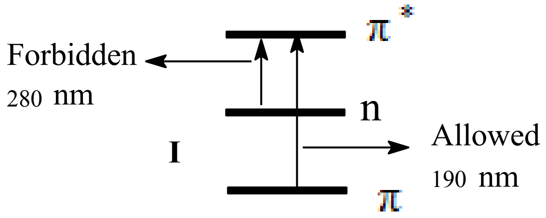
R_{exo} = Number of rings with exocyclic double bonds =0

λ_{max} Cal. = 114 +5×10 +11[48.0 – (1.7 ×11)] – 16.5×2 - 10×0 = 453.3 nm, λ_{max} Obs. 452 nm

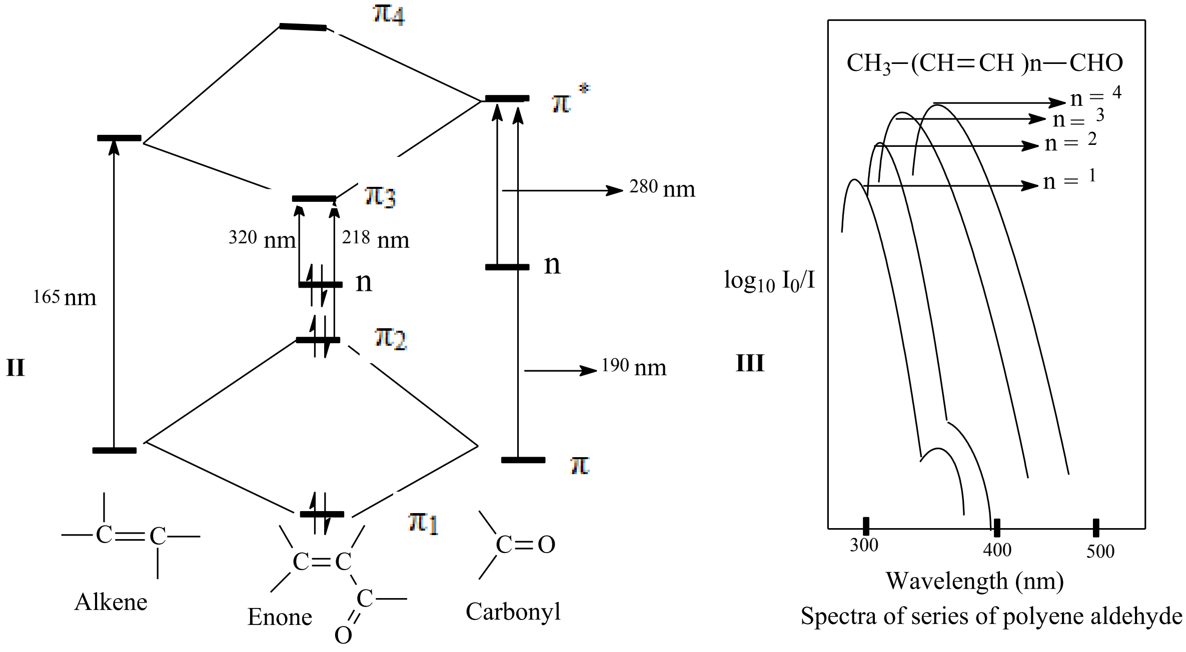
ε_{max} Cal. = $(1.74 \times 10^4)_n$ = $(1.74 \times 11 \times 10^4 = 19.4 \times 10^4$

ε_{max} Obs. = 15.2×10^4

α, β Unsaturated aldehydes, ketones and their derivatives: Carbonyl compounds have two principal UV transitions, the allowed $\pi - \pi^*$ transition and the $n - \pi^*$ transitions.In these transitions $n - \pi^*$ transition is weak and generally forbidden, commonly observed above the cut-off limit of solvent. Attaxhment of auxocgromes like $-NR_2$, -OH, -OR, $-NH_2$ or amide, acids,esters or acid chlorides produce bathochromic shift on $n - \pi^*$, however lesser bathochromic shift is observed in $\pi - \pi^*$ transition. The bathochromic shift is caused because of resonance interaction of lone pair of electrons on auxochromes. If carbonyl group is part of conjugation system then both $n - \pi^*$ and $\pi- \pi^*$ bands are shifted to longer wavelengths. However the energy of the $n - \pi^*$ transition does not decrease as rapidly as that of $\pi - \pi^*$ band, which is more intense.If the conjugation increases in a long chain, the n – π^* band is buried under the more intense π – π^* band. The transition in carbonyl group, transition in α,β-unsaturated carbonyl (enone) and polycongugated carbonyl compounds has been illustrated in fig. 7.12 as follow.



Electronic transitions in carbonyl compounds



Spectra of series of polyene aldehyde

Orbitals of enone system compared to those of the non interacting chromophores.

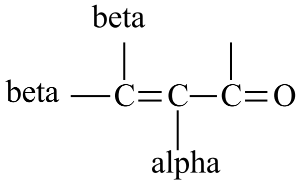
Fig.7.12 I. Electronic transition in carbonyl group.**II** Effect of α,β- unsaturation on carbonyl group **III** Effect of conjugation on n – π^*transition

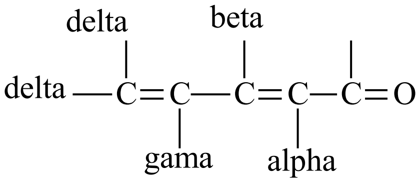
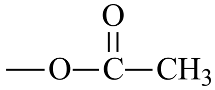
7.10 THE WOODWARD – FIESER RULES FOR ENONES

The conjugated carbonyl group leads to intense absorption (ε = 8,000 to 20,000) which corresponds to a π – π^* transition of the carbonyl moiety. The absorption is found between 220 and 250nm in simple enones. The $n - \pi^*$ transition in much less intense (ε =50 to 100) and appear at 310 to 330nm. The $\pi - \pi^*$ transition is affected by structural modification of the chromophore, however the $n - \pi^*$ transition doed not exhibit such predictable behavior. Woodward examined the UV spectra of numerous enones and predicted a set of empirical rule which enable us to predict the wavelength at wich the $\pi - \pi^*$ transition occurs in unknown enones table 3.

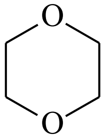
Table.7.3Woodward Fiser's emperical rule to predict the λmax value for enones

<table>
<tr><th>S.N</th><th>Enone

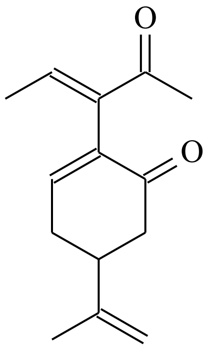
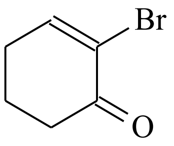
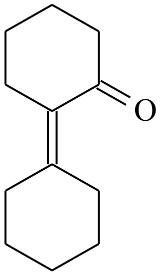
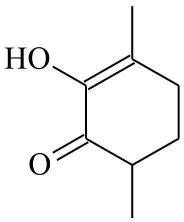
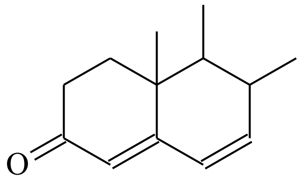


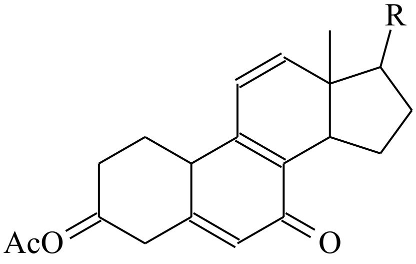
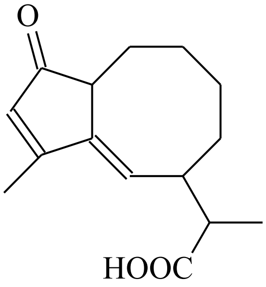
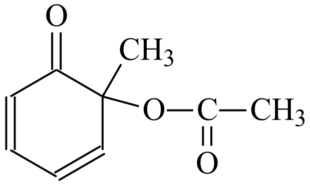

</th><th>Base value
(Wavelength)</th></tr>
<tr><td>1.</td><td>Six membered ring or acyclic parent enone</td><td>215nm</td></tr>
<tr><td>2.</td><td>Five membered ring oarent enone</td><td>202nm</td></tr>
<tr><td>3.</td><td>Acyclic dienone</td><td>245nm</td></tr>
<tr><td>4.</td><td>Parent α, β –unsaturated aldehyde</td><td>207nm</td></tr>
<tr><td>5.</td><td>Parent α, β –unsaturated carboxylic acids and esters</td><td>195nm</td></tr>
<tr><td colspan="3">INCREMENTS FOR SUBSTITUENTS</td></tr>
<tr><td>i</td><td>Double bond extending conjugation</td><td>+30nm</td></tr>
<tr><td>ii</td><td>Alkyl group or ring residue</td><td>α = +10nm
γ and higher +18nm</td></tr>
<tr><td rowspan="2">iii</td><td>Polar groups (-OH)</td><td>α = +35nm, β= +30nm δ =+50nm</td></tr>
<tr><td>

$—O—\overset{\overset{O}{||}}{C}—CH_3$</td><td>α, β, δ =+6nm</td></tr>
</table>

	$-OCH_3$	α =+35nm, β =+30nm, γ =+17nm, δ= +31nm
	Thioalkyl	β =+85nm
	Dialkylamino	β =+95nm
iv	-Cl	α =15nm, β= +12nm
v	-Br	α =25nm, β= +30nm
vi	$-NR_2$	β = +95nm
vii	Exocyclic double bond	+5nm
viii	Homocyclic diene component	+39nm
ix	Solvent correction (relative to C_2H_5OH)	variable
1	H_2O	-8nm
2	CH_3OH	+0nm
3	$CHCl_3$	+ 1nm
4		+5nm
5	$C_2H_5OC_2H_5$	+7nm
6	$CH_3CH_2CH_2CH_2CH_2CH_3$	+11nm

Some important examples as given as follow for calculating λ_{max} values of enones.

Compounds	**λ_{max} values**
	Parent α,β unsaturated ketone = 215nm One α- subatituent =+ 10nm One β- subatituent =+ 12nm λ_{max} Calculated = 237nm
	Parent ketone = 215nm α-bromo subatituent =+ 25nm Ring residue β (one) =+ 12nm λ_{max} Calculated = 252nm
	Parent ketone = 215nm α- subatituent =+ 10nm β – substituent (2×12) =+24nm Exocyclic double bond(2×5) =+ 10nm λ_{max} Calculated = 259nm
	Parent ketone = 215nm α- subatituent (OH) =+ 35nm Ring residue β (2×12) =+24nm λ_{max} Calculated = 274nm
	Parent ketone = 215nm Double bond extending conjugation = +30nm One β- substituents =12 nm One δ-substituents = 18nm Exocyclic double bond =+ 5nm

	λ_{max} Calculated = 280nm
	Parent ketone = 215nm Double bond extending conjugation = +30nm Homoannular diene components =+39nm One α- substituents =+10 nm One β-substituents =+ 12nm One δ-substituents =+18nm Exocyclic double bond =+ 5nm λ_{max} Calculated = 329nm
	Parent ketone = 202nm Double bond extending conjugation = +30nm One β- substituents =+12 nm One γ & one β-substituents =+ 36nm Exocyclic double bond =+ 5nm λ_{max} Calculated = 285nm
	Six –membered enone = 215nm Double bond extending conjugation =+30nm Homocyclic diene = +39nm δ – Ring residue =+18nm λ_{max} Calculated = 3 02nm

7.11 IDENTIFICATION OF AROMATIC COMPOUNDS

The UV spectrum of most aromatic compounds consists of three absorption bands. These bands are obtained due to $\pi - \pi^*$ transitions. In case of benzene an intense band, without any vibrational structure occur at 184nm ($\varepsilon = 60000$) and results from an allowed transition. The weaker bands at 204 ($\varepsilon = 7900$) and 256nm ($\varepsilon = 200$) result from forbidden transitions in the highly symmetrical benzene molecule, the latter band exhibiting characteristic vibrational structure as follow fig.7.13

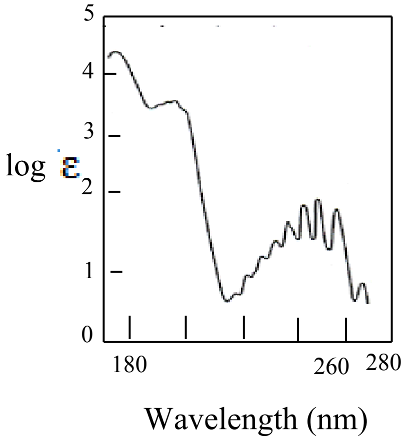
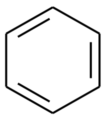
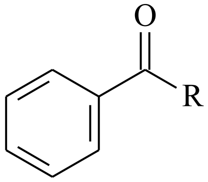


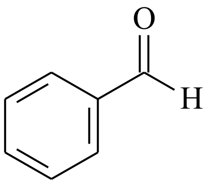
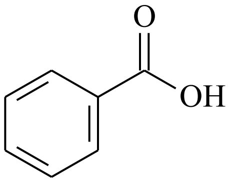
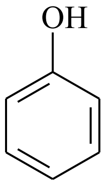
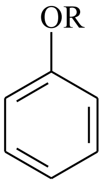
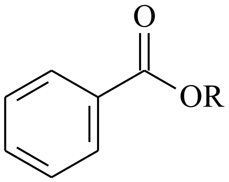
Fig.7.13. The UV spectrum of benzene in hexzne

The band 256 nm also called benzenoid band, is usually easily recognizable. It has about same intensity (ε =250 – 300) and similar vibrational structure (up to six vibrational bands) in benzene and its simple derivatives. The vibrational structure is less evident in polar solvents and more sharply defined in vapour spetra or in non polar solvents

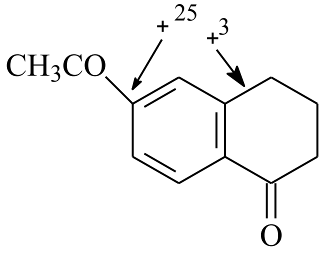
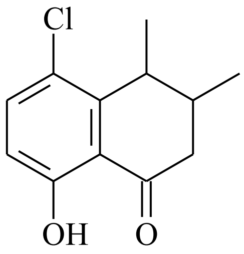
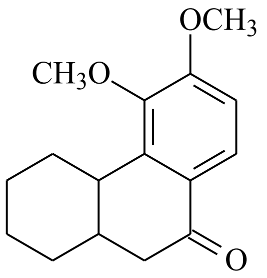
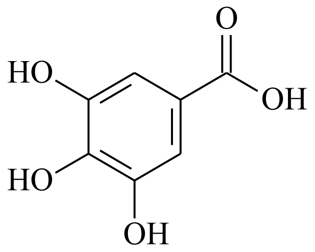
The λ_{max} pertaining to the principal band ($\pi - \pi^*$ transition) of substituted benzene derivatives can be predicted by using the data given in table as under (table 4).

Table 7.4: Red shift induced by various substituents in the principal band ($\pi - \pi^*$ transition) of benzene derivative.

Aromatic compounds/derivative	Position of substituents	Ethanol λ_{max} (nm)
Parent chromophore 		246
		250

    		230
INCREMENTS FOR SUBSTITUENTS		
Alkyl or ring residue	o, m	+ 3nm
	p	+10nm
-Cl	o,m	+0 nm
	p	+10nm
-Br	o,m	+2nm
-OH,-OCH$_3$ –OR	o,m	+7nm
	p	+25nm
-O$^-$ (oxy anion)	o	+11nm
	m	+20nm
	p	+78 May be decreased by Steric Hinderance to planrity
-NH$_{2=}$	o, m	+13nm
	p	+58nm
-NHCOCH$_3$	o, m	+20nm
	p	+45nm
-NHCH$_3$	p	+73nm
-N(CH$_3$)$_3$	o,m	+20nm
	p	+85nm

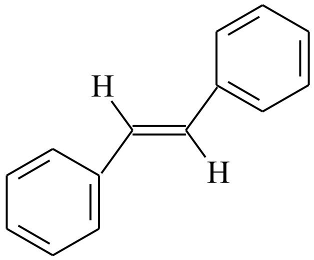
Few examples are as follow:

Aromatic compound	λ_{max} values
	Parent chromophore =Ar = 246nm (o- ring residue) + 3nm (p-methoxy) +25nm λ_{max}Calculated =274nm λ_{max} Observed = 276nm
	Parent chromophore =Ar = 246nm (o- ring residue) + 3nm (o-OH) +7nm λ_{max}Calculated =256nm λ_{max} Observed = 257nm
	Parent chromophore =Ar = 246nm (o- ring residue) + 3nm (m-OCH_3) +7nm (p-OCH_3) +25nm λ_{max}Calculated =281nm λ_{max} Observed = 278nm
	Parent chromophore =230nm (m-OH) 2×7 =14nm (p-OH) +25nm λ_{max}Calculated =269nm λ_{max} Observed = 270nm

7.12 STUDY OF ISOMERISM

It is an important analytical tool It is helpful both for qualitative and quantitative analysis:

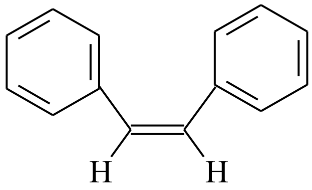
Geometrical Isomerism (Steric Effects) When an alkene chromophore is capable of exhibiting geometrical isomerism, it has been established that the *trans* isomer displays longer wavelength absorption and higher intensity than the corresponding *cis* isomer. 1,2-diphenylethylene (stilbene) is a good example of comparison of spectra *cis* and *trans* isomers.



trans stilbene

λ_{max} = 295 nm

ε_{max} = 27000



cis stilbene

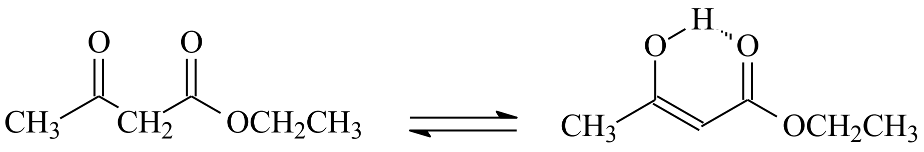
λ_{max} = 280 nm

ε_{max} = 13500

This is ascribed to the more effective π-orbital overlap possible in the *trans* isomer whereas in the cis-isomer, the coplanarity is lost bt steric effects.

Keto-Enol Tautomerism β-diketones and β-keto-esters are known to exist as tautomeric mixtures and their ultraviolet spectra will exhibit absorptions characteristic of both keto and enol forms, i.e., in addition to a weak n →π* absorption due to the keto-carbonyl group, a strong π→π* absorption due to conjugated double bond (characteristic of the enol) is also observed.

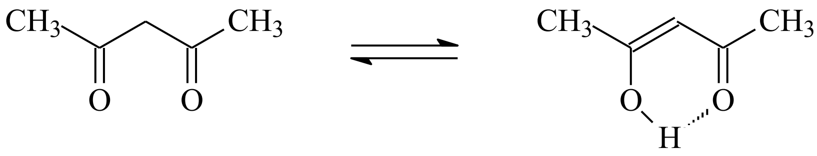
In the classical example of ethylacetoacetate; the keto-form, I, exhibits a low intensity (ε~20) band around 275 nm characteristic of an isolated keto-carbonyl group, the enol form, II, displays a high intensity band around 245 nm (ε ~18000) ascribed to conjugated double bond.



Keto form (I)

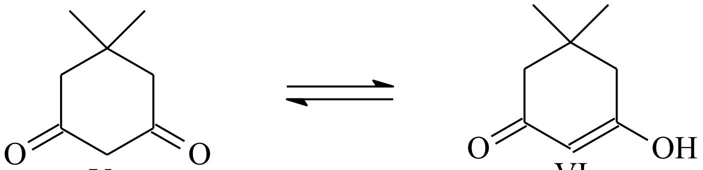
Enol form (II)

In similar pattern, acetylacetone (β-diketone) III enolizes (84%) in ethanol and consequently absorbs strongly at 273 nm (ε ~10500). The usually high value of λ_{max} is probably a consequence of the chelation in the enol form (IV). The enol form (VI) a dimedon (V) which is transoid and in which chelation is impossible shows λ_{max} 255 nm (ε = 17000) in acid medium, which agrees very well with the value predicted from the Woodward-Fieser rules.



III

IV



V

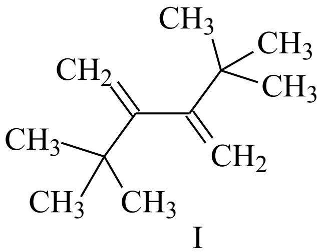
VI

7.13 CONFORMATIONAL ANALYSIS AND DTERMINATION OF CONFIGURATIONAL CORRELATION

The ultraviolet spectroscopy may be used for conformational analysis of organic compounds provided the compound under consideration contains a chromophore capable of interacting electronically with a adjacent group in a particular conformation. For example, cyclohexanone derivatives with a α-substituted halogen (or a similar electron acceptor group) in axial disposition leads to a bathochromic shift because of the overlapping of the antibonding π* carbon orbital of the carbonyl group with a vacant orbital (usually 3s) of the electronegative group. Ultraviolet spectroscopy has been used extensively for the determination of configurational correlation. This is illustrated by the following examples:

A. In conjugated systems such as biphenyls and analogues, both the absorption maxima and extinction co-efficients are affected in a predictable manner as the molecules are twisted around the pivotal bonds form a planar to a non-planar conformation. Thus, the UV spectra of simple biphenyl and 2,2-demethylbiphenyl exhibit λ_{max} 240 nm (ε_{max} = 19000) and 224 nm (ε_{max} = 700), respectively. The hypsochromic shift and lower of extinction coefficient in the latter are due to steric inhibition of resonance indicating non-planar configuration.

B. Any non-plannar arrangement of double bonds will result in a reduction of orbital overlap with a corresponding shift of λ_{max} to lower wavelength and decreased intensity. This is illustrated by taking the example of 2,3-di-tert-butyl-1,3-butadiene (I) in which tere is little conjugation between the double bonds, due to the bulk of the tert-butyl groups. This compound exhibits λ_{max} = 180 nm and a shoulder at 220 nm whereas a typical dialkyl-1, 3-butadiene exhibits λ_{max} = 227 nm.



I

7.14 APPLICATIONS OF UV-VISIBLE SPECTROSCOPY

Before NMR spectroscopy and mass spectroscopy revolutionized the structural elucidation of organic molecules, UV spectroscopy was an important technique and was used to identify the key chromophore of an unknown molecule. The importance of UV is much diminished now a days, but it still retains its place in certain applications, such as the determination of kinetic parameters, K_M(the Michaelis constant) and k_{cat} (the turnover rate of an enzyme, in molecules per second), for a number of enzymic reactions and in the analysis of pharmaceuticals.It is is an important analytical tool It is helpful both for qualitative and quantitative analysis:

1. UV in the Analysis of Pharmaceutical Preparations:

The molar absorptivity (ε) of a known is constant under identical conditions of solvent, concentration and path length, and can be used to quantity the amount of a particular pharmaceutical in a tablet. Such assays form the basis of many quality assurance procedures in the pharmaceutical industry, and have been extensively used by the British Pharmacopoeia (B.P.). More recently, however, high-performance liquid chromatography (HPLC) has replaced UV analysis in many B.P. assays, as most industrial analysis routinely use HPLC.

In the pharmaceutical industry, medicines are standardized to a particular weight of active pharmaceutical per unit (for example, mg of substance per tablet), so the weight of a substance in a tablet, or volume of medicine, is of more interest than the number of moles. For most pharmaceutical preparations, then we use the specific absorbance, A (1%, 1 cm), which is the absorbance ($\log_{10}I_0/I$) of a 1% w/v solution (i.e. 1g of substance in 100 cm^3 solvent) in a 1 cm path length cell, in place of the molar absorptivity, ε. This is the absolute method of substance identification, and the absorbance, A, can be related to A (1%, 1 cm) by equation

$$A = A\ (1\%,\ 1\ \text{cm}) \times \text{concentration} \times \text{path length}$$

The absolute method relies on the UV spectrophotometer being accurate in the measurement of wavelength and intensity, and the B.P. specifies methods for the calibration of both. However, UV-Vis spectra are not specific for any one particular substance, as many UV absorbing molecules have similar UV spectra, and this method is used in conjunction with several identification tests, as described in the B.P.

A number of B.P. tests require derivatization of the substance under investigation before the UV absorbance is recorded. In these cases, in order to take account of the possibility of the reaction not proceeding to completion, the comparative method is employed, which makes use of a reference (defined in the B.P.). The concentrations and absorbances of the reference and substance under investigation are related by equation:

$$C_1/C_2 = A_1/A_2$$

2. UV Detection in Chromatography:

UV spectroscopy is exploited for the detection of analytes in a number of separative analytical techniques, such as thin layer chromatography (TLC) and HPLC.

Thin Layer Chromatography

TLC is a simple technique that is commonly used for the rapid qualitative analysis of reaction mixtures. Many organic compounds used in chemical and pharmaceutical manufacture, and in organic and medicinal chemistry research, contain an aromatic ring or other UV-absorbing system which can be visualized on the TLC plate under a UV lamp. The whole procedure takes about 5 minutes and is a much-valued technique in the laboratory.

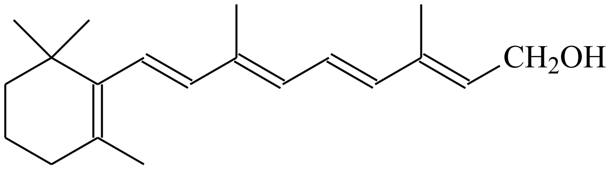
3. UV Detector in HPLC

HPLC has transformed quality control in the pharmaceutical and chemical industries, as it provides a rapid means of checking the purity of samples and even allows for the purification of small amounts of samples by preparative HPLC. The majority of such systems use UV to detect and quantify substances as they elute from the separative column. UV detectors are usually variable wavelength abd can be used to detect molecules with absorption maxima above 210 nm by measuring the absorbance of the eluent. When a UV-absorbing substance is eluted from the

HPLC column, it absorbs UV radiation at the appropriate wavelength for its chromophore. The amount of UV absorbed is proportional to the quantity of substance being eluted, and is converted into a peak on a chart recorder. Integration of each peak allows the relative quantities of the components of the solute to be determined.

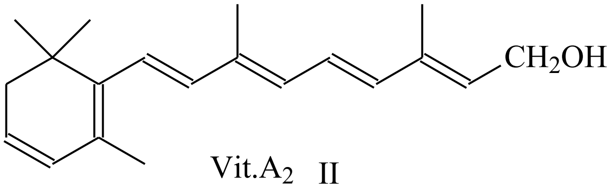
4. Quantitative application:

Uv-visible spectroscopy has been used extensively in industrial analytical organic chemistry. Viz; th % content of Vit. A (I) and Vit. A_2 (II) in natural fats and oils is concentiently estimated by measurement of intensities of peals at 325nm (five conjugated double bonds) and 351 nm(six conjugated double bonds) respectively. Comparasion of these intensities with those of solutions of the vitamins of known concentration enables the concentrations to be calculated. Similar method may be adopted for the estimstion of ergosterol (provitamin D) in fats, anthracene in benzene, carbon disulphide in carbontetrachloride, chlorophyll in plant material etc.



Vit. A I

λ_{max} 325 nm



Vit.A_2 II

λ_{max} 351 nm

Uvi-visible spectroscopy is useful for quantitative estimation of coloured solutions by using Beer-Lamber law (Colorimetry)

7.15 SUMMARY

This unit describes in simplified way the introduction of electromagnetic radiation, electronic transitions and energy level. The chromophores (C=C and C=O), auxochromes have been well presented with examples. The designation of UV-bands corresponding to different electronic transitions has been explained very well.The law of absorption (Beer-Lambert law) has bben described well to make the students aware about it. The concept of HOMO-LUMO orbitals in order to exaplain the ffect of conjugation on UV Spectra has been described well.The terminology of UV Spectroscopy along with selection rules has been narrated in this unit. Effect of solvent on absorption maxima has also been described. Woodward-Fieser rule for predicting absorption maxima in dienes, enones gives an idea to the learners that, how the substituents effect the position and intensity of UV bands.This part has been well discussed with suitable examples. The absorption maxima of aromatic compounds and their derivatives have been explained in this unit. This unit also describes the study of isomers like geometrical isomers and conformers by UV-Visible spectroscopy. Applications of UV-Vis. Spectroscopy in various field both for qualitative and quantitative analysis has been discussed in this unit.

7.16 TERMINAL QUESTIONS

Q1. Tick the appropriate option (MEQs):

i. What is the principle of UV-Visible spectroscopy?

1. Electronic transition 2. Molecular vibration

3. Nuclear flipping 4. Ionization of molecule

ii. The range of UV-Visible spectrum is:-

1.200nm – 400nm 2.200nm-700nm

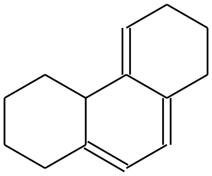
2.10 nm-200nm 190nm – 400nm

iii. Which of the following compounds does not absorb light in the UV/visible spectrum?

1. Paracetamol 2.Chloral hydrate

3. Aspirin 4.Phenobarbitone

iv. What is the λ_{max} value of following compound?



1. 323nm
2.318nm
3.325nm
4.330nm

v. UV spectroscopy in chromatographic technique is used as

1. Detector
2.Developer
3. Column part
4. Injector

vi. The correct order of λ_{max} among CH_3Cl, CH_3Br and CH_3I is:

1. $CH_3Cl < CH_3Br < CH_3I$
2. $CH_3I < CH_3Br < CH_3Cl$
3. $CH_3Cl < CH_3I < CH_3Br$
4. $CH_3Br < CH_3Cl < CH_3I$

vii. Beer's Law states that:

1. Absorbance is proportional to both the path length and concentration of the absorbing species
2. Absorbance is proportional to the log of the concentration of the absorbing species
3. Absorbance is equal to P_0 / P
4. Absorption is independent to concentration and pathlength

viii. Which of the following is the principal chromophore in an azo-dye?

1. $N\equiv N$
2. $N=N$
3. $C=N$
4. $C\equiv N$

ix. What is a chromophore?

1. A group of atoms in a compound responsible for electromagnetic radiation.
2. A group of atoms in a compound responsible for the absorption of electromagnetic radiation.

3. A group of atoms in a coloured compound.

4. A coloured compound.

x. How do values of λ_{max} for the $\pi^* \leftarrow \pi$ transitions vary among a series of conjugated polyenes?

1. Values vary very little.

2. Values vary but in no particular pattern.

3. Values shift to shorter wavelength as the number of C=C double bonds increases.

4. Values shift to longer wavelength as the number of C=C double bonds increases

Q. 2. What is an ultraviolet spectrum? Give various regions associated with ultraviolet spectrum.

Q.3.How will you account for the variation in UV absorption for the following compounds ?

A. λ_{max} for methane =125nm

B. λ_{max} for ethane =135nm

C. λ_{max} for cyclopropane =190nm

Q.4.Predict the various electronic transitions possible in the following compound.

1.CH_4

2.CH_3Cl

3.$H_2C=O$

4.Cl_2

Q.5.Discuss the reason for bathochromic shift in polyconjugated compounds.

Q.6. Write short note on:-

1. Bathochromic shift

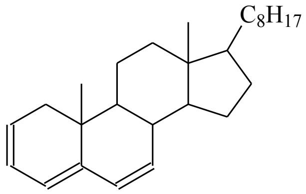
2. Isobestic point

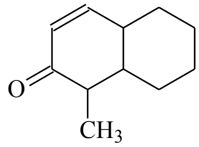
3. Beer-Lambert law

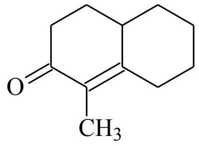
4. Effect of polar solvent in $n - \pi^*$ and $\pi - \pi^*$ transition

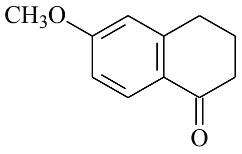
5. Effect of planarity on λ_{max}

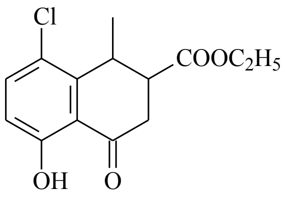
Q.7 Determine λ_{max} of the following molecules.

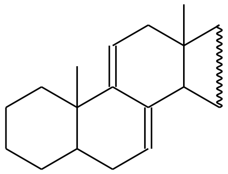












7.17 ANSWER TERMINAL QUESTIONS (MCQs)

i-1	ii -2	iii -2	iv -1	v -1
vi -1	vii -1	viii-2	ix -2	x-4

7.18 REFERENCES

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