Chapter 17

SPECTROSCOPY

17.1 Introduction

Spectroscopy is the branch of science which deals with the study of the interaction of electromagnetic radiation with matter. It is the most powerful tool available for the study of structures of atoms and molecules. There are several spectroscopic techniques that help in investigating various aspects of atomic and molecular structure. In this chapter, we will discuss the common spectroscopic techniques like electronic spectroscopy (which includes UV–visible), infrared spectroscopy (IR), rotational, microwave, nuclear magnetic resonance (NMR) and Raman spectroscopy. The chapter deals with the principles, experimental techniques and applications of the various spectroscopic methods. However, before starting it is essential to discuss some basic fundamentals of spectroscopy.

17.2 Basic Terms and Principles of Spectroscopy

Electromagnetic radiations

Electromagnetic radiation is a form of radiant energy which has both particle as well as wave nature. In vacuum, it normally travels in a straight line with the speed of light (3×10^8 m/s). It has both electric and magnetic field components, which are coplanar and oscillate perpendicular to each other and perpendicular to the direction of wave propagation (Fig. 17.1).
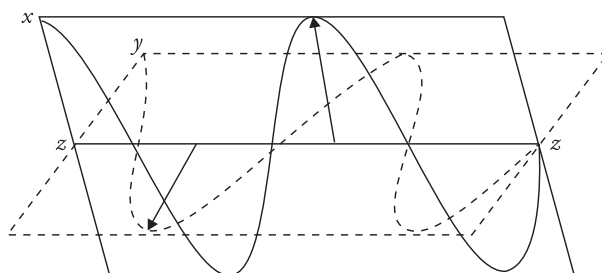

Figure 17.1   *Planes of electromagnetic waves*

Properties of electromagnetic radiations

The properties of electromagnetic radiation can be described easily by ascribing wave nature to these radiations.

(a) **Wavelength** It is denoted by λ (lambda) and is defined as the distance between two adjacent crests (C–C) or troughs (T–T) in a particular wave (Fig. 17.2). It can be expressed in centimeters. The other units for expressing wavelength are given below.

  (i) Angstrom (Å)   1 Å = 10^{-8} cm = 10^{-10} m

  (ii) Nanometer (nm) or millimicron (mμ)

   1 nm = 1 mμ = 10^{-7} cm = 10^{-9} m

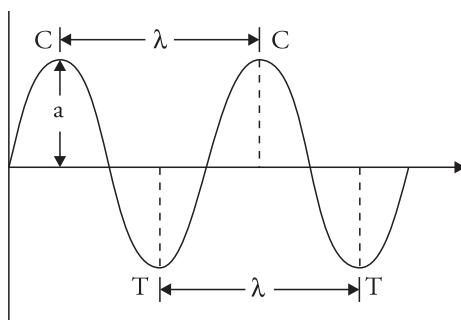 (iii) Micron (μ)   1μ = 10^{-4} cm = 10^{-6} m

Figure 17.2 *Properties of electromagnetic radiations*

The wavelength of visible light ranges from 3800 Å (violet end) to 7600 Å (red end).

(b) **Frequency** It is denoted by ν (nu) and is defined as the number of waves which can pass through a point in one second. Frequency is expressed in cycles per second or Hertz (Hz) where 1 Hz = 1 cycle/s.

$$\text{Frequency } (\nu) = \frac{c}{\lambda}$$

where c = velocity of electromagnetic radiation in cm/s = 2.998×10^{10} cm/s.

λ = wavelength.

We know that the wavelength of visible light is 3800–7600 Å. The corresponding frequency can be calculated as follows.

  (i) When λ = 3800 Å = 3800 × 10^{-8} cm,

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\, \text{cm s}^{-1}}{3800 \times 10^{-8}\, \text{cm}}$$

$$= 7.88 \times 10^{14}\, \text{s}^{-1} = 7.88 \times 10^{14}\, \text{Hz} = 7.88 \times 10^{8}\, \text{MHz}$$

(ii) When $\lambda = 7600$ Å $= 7600 \times 10^{-8}$ cm.

$$\nu = \frac{2.998 \times 10^{10}\,\text{cm s}^{-1}}{7600 \times 10^{-8}\,\text{cm}} = 3.94 \times 10^{14}\,\text{s}^{-1}$$

$$= 3.94 \times 10^8 \text{ MHz}$$

Thus, the frequency range of visible light is 7.88×10^8 MHz to 3.94×10^8 MHz.

(c) **Velocity**   Velocity of a wave is denoted by c and is defined as the distance travelled by a wave in one second. Electromagnetic radiations travel with the speed of light, hence the value of c is 2.998×10^8 cm/s or 18600 miles per second.

(d) **Wave number**   It is denoted by $\bar{\nu}$ (nu bar) and is defined as the total number of waves in a length of one centimetre. Wave number is the reciprocal of wavelength and is expressed in per centimetre or cm^{-1}.

$$\bar{\nu} = \frac{1}{\lambda \text{ in cm}}$$

(e) **Energy**   Energy of a wave can be calculated by applying the Planck relation.

$$E = h\nu = \frac{hc}{\lambda}$$

where h = Planck constant = 6.626×10^{-34} Joule seconds

ν = frequency of radiation in cycles/s

λ = wavelength in meters

It should be noted that the energy of a wave is directly proportional to its frequency and inversely proportional to its wavelength.

Solved Examples

1. Calculate the energy associated with a radiation having wavelength 3000 Å. Give the answer in kcal mol^{-1} and also in kJ mol^{-1}.

    Solution

    $\lambda = 3000$ Å $= 3000 \times 10^{-8}$ cm

    $$E = h. \frac{c}{\lambda}$$

    $$= \frac{6.628 \times 10^{-27}\,\text{erg s} \times 2.998 \times 10^{10}\,\text{cm s}^{-1}}{3000 \times 10^{-8}\,\text{cm}} = 6.6236 \times 10^{-12}\,\text{ergs}$$

$$= \frac{6.6236 \times 10^{-12} \times 6.023 \times 10^{23}}{4.18 \times 10^{10}} \quad \because \text{ 1 mole} = 6.023 \times 10^{23} \text{ and } 4.187 \times 10^{7} \times 10^{3} \text{ erg} = 1 \text{ kcal}$$

$$= 95.4 \text{ kcal mol}^{-1}$$

Also 1 kcal = 4.184 kJ

$\therefore$ E = 95.4 × 4.184 = 399.15 kJ mole^{-1}

2. Calculate the wave number of a radiation whose wavelength is 2.5 μ.

Solution

$$\lambda = 2.5\ \mu = 2.5 \times 10^{-4}\ \text{cm}$$

$$\bar{v} = \frac{1}{\lambda} = \frac{1}{2.5 \times 10^{-4}\ \text{cm}} = 4000\ \text{cm}^{-1}$$

3. Calculate the frequency of radiation whose wavelength is 400 nm. Express this wavelength in wave number.

Solution

$$\lambda = 400\ \text{nm} = 400 \times 10^{-7}\ \text{cm}$$

$$\text{Frequency }\ v = \frac{c}{\lambda} = \frac{3 \times 10^{10}\ \text{cm/s}}{400 \times 10^{-7}\ \text{cm}} = 7.5 \times 10^{14}\ \text{cycles/s}$$

$$\text{Wave number }\ \bar{v} = \frac{1}{\lambda(\text{cm})} = \frac{1}{400 \times 10^{-7}\ \text{cm}} = 25000\ \text{cm}^{-1}$$

Practice Problems

1. The frequency of a radiation is found to be 5.09 × 10^{14} s^{-1}. Calculate the wavelength in nanometres. (Given   c = 3 × 10^{8} m/s.)   [Ans   589.4 nm]
2. Calculate the wave number of the radiation if the frequency is 2.06 × 10^{14} Hertz.
    (Given   c = 3 × 10^{10} cm/s.)   [Ans   6866.6 cm^{-1}]

Electromagnetic spectrum

An electromagnetic spectrum is obtained when all types of electromagnetic radiations are arranged in the order of increasing wavelength or decreasing frequencies (Fig. 17.3).

Visible light lies in the wavelength range 3800–7600 Å. The region of 3800 Å corresponds to *violet colour* and that of 7600 Å corresponds to *red colour*. If the wavelength is less than 3800 Å, the radiation is called ultraviolet radiation and if it is greater than 7600 Å, it is called infrared radiations. Both infrared and ultraviolet radiations are not visible to the human eye. Beyond infrared region, on the side of increasing wavelength are microwaves. Beyond microwaves, lie the radio waves which have the highest wavelength.

The arrangement of different types of electromagnetic radiation in increasing order of their wavelength is

Cosmic rays < γ rays < X rays < Ultraviolet rays < Visible rays < Infrared rays < Microwaves < Radiowaves

Since $v = \dfrac{c}{\lambda}$, increasing wavelength means decreasing frequency. Thus, cosmic rays have the highest frequencies and radio waves, the least frequencies.

All types of electromagnetic radiations travel with the same speed, the velocity of light, but their wavelength (or frequency) differ from each other. Radio waves are least energetic (maximum wavelength, minimum frequency) and cosmic rays have maximum energy (minimum wavelength $E = \dfrac{hc}{\lambda}$)
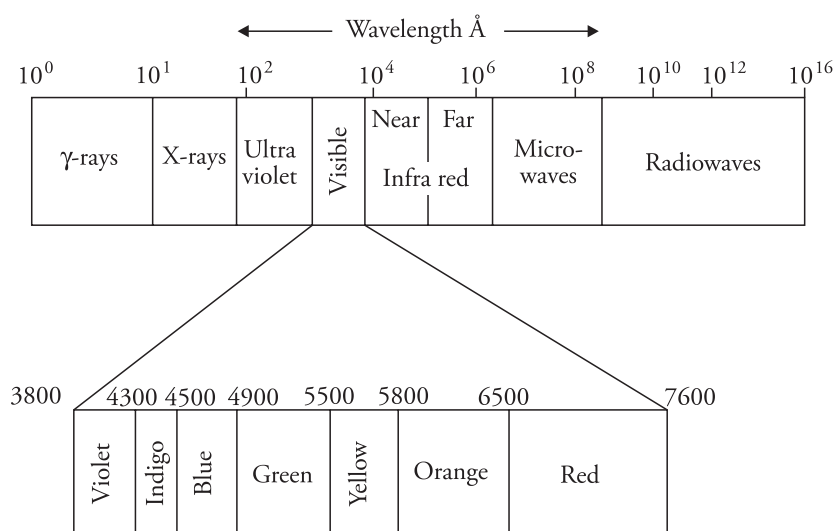

Figure 17.3 *Electromagnetic spectrum*

Origin of electronic spectra

When a sample of molecules is exposed to electromagnetic radiation, the electric field of the radiation interacts with the electrical charges (electrons and nuclei) of the molecule. Quantum mechanics deals with such interactions and the quantum mechanical treatment shows that when a molecule in state E_1 is irradiated, it may absorb a photon of frequency v and may get promoted to a higher energy state E_2 if the frequency of radiation satisfies the condition $E_2 - E_1 = hv$. Similarly, a photon will be emitted only if the above mentioned condition is satisfied.

$\Delta E\ \alpha\ \nu\ $ or $\ \Delta E = h\nu$

where h is the Planck constant. It has a value of 6.63×10^{-34} J s. The energy emitted or absorbed by a body will be some whole number multiple of a quantum, that is,

$E = nh\nu$

where n is an integer such as 1, 2, 3. Hence, a body can emit or absorb energy equal to $h\nu$, 2 $h\nu$, 3 $h\nu$ … but not 1.6 $h\nu$, 2.2 $h\nu$ … or any other fractional value.
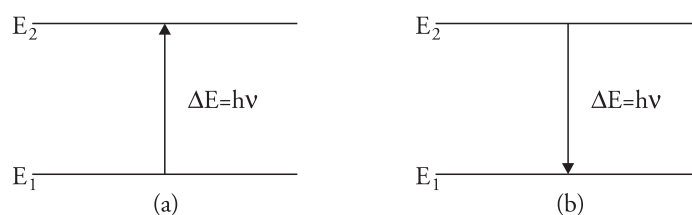

Figure 17.4   *Energy transition for (a) absorption (b) emission*

The frequency of absorbed or emitted radiation is given (Fig. 17.4) by

$$\nu = \frac{\Delta E}{h}\,\text{Hz}$$

The energy change or frequency of electromagnetic radiation emitted or absorbed can be recorded in the form of a spectrum with the help of an instrument called spectrophotometer. A spectrum is a plot of the absorbance or transmittance of radiation against energy.

There are different types of spectra. They are explained below.

(i) **Continuous spectrum**   When white light passes through a prism, it splits into different colours. These colours merge into one another without any discontinuity. Such a spectrum is called a continuous spectrum. A continuous spectrum can be obtained from light emitted by some incandescent substances.

(ii) **Emission spectrum**   When there is transition from a higher energy level to a lower energy level (Fig. 17.4b), energy is emitted out and the spectrum thus obtained is called an emission spectrum.

An emission spectra is obtained by heating the substance and then passing the emitted radiation through a prism.

(iii) **Absorption spectrum**

When there is transition from a lower energy state to a higher energy state, the energy absorbed will be equal to the energy difference ΔE. The spectrum thus obtained is called an absorption spectrum.

When a continuous electromagnetic radiation (say, white light) is allowed to pass through a gas or solution of some salt and then analysed, we obtain dark lines in the otherwise continuous

spectrum. The dark lines indicate that the radiations of corresponding wavelengths have been absorbed by the substance from white light. Such a spectrum containing dark lines due to the absorption of light is known as an absorption spectrum.

Emission or absorption spectrum can be of two types.

(i) Atomic spectra (ii) Molecular spectra

Atomic spectra

When atoms interact with electromagnetic radiation, the spectrum obtained is called an atomic spectrum. The transition of electrons takes place between the electronic energy levels of the atom. The spectra are obtained as sharp lines. These lines are characteristic of the atom, hence, line spectra are also regarded as finger prints of the atoms.

Molecular spectra

Molecular spectroscopy deals with the interaction of electromagnetic radiations with molecules. In the spectra of molecules, in addition to electronic levels, transitions also occur between rotational and vibrational levels.

In this chapter, we will discuss molecular spectroscopy.

Types of energy changes

A number of energy states are possible in molecules. The total energy is the sum of the translational, rotational, vibrational and electronic energy.

$$E_{total} = E_{translational} + E_{rotational} + E_{vibrational} + E_{electronic}$$

Moreover $E_{electronic} \gg E_{vibrational} \gg E_{rotational} \gg E_{translational}$

Since translational energy is negligibly small, and is not involved in molecular spectra, hence we can write the Born–Oppenheimer approximation as $E_{total} = E_{rotational} + E_{vibrational} + E_{electronic}$.

When the molecule is excited, it absorbs energy and electrons transit from an orbit of lower energy to an orbit of higher energy. The frequency of spectral lines is determined by the difference in the two energy levels. Now if electronic transition was the only mode in which a molecule would absorb or emit energy, then molecular spectra would have been a line spectrum similar to that of atoms. However, molecular spectrum is a band spectrum. This is because apart from electronic transition, rotational and vibrational changes also occur within the molecule. These rotational and vibrational motions are also quantised and are superimposed on the kinetic motion of the molecule. Thus, there are three types of changes in a molecule (Fig. 17.5).

1. Energy change due to transition of an electron from one orbit to another.
2. Energy change due to rotation of the molecule.
3. Energy change due to vibration of atoms of the molecule relative to one another.
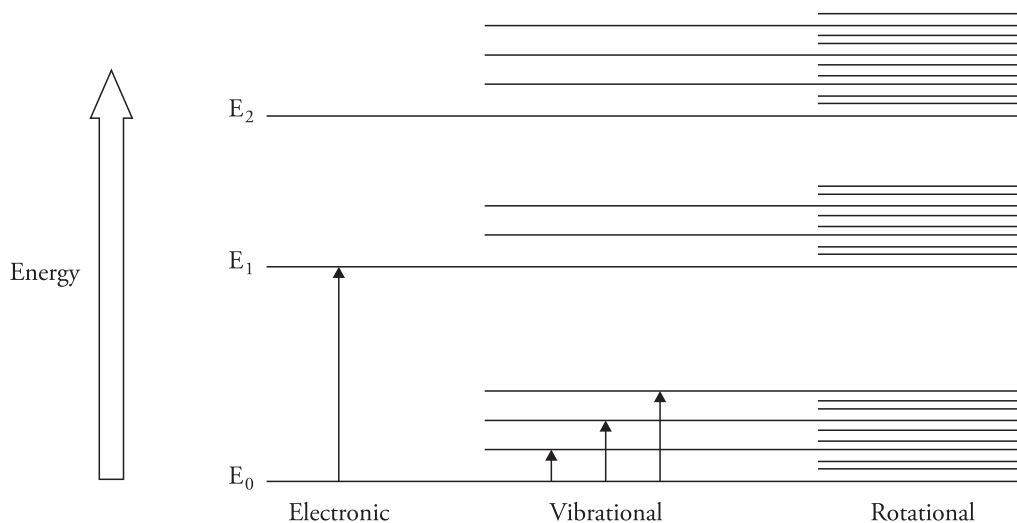
Figure 17.5 *Different types of transitions in molecules*

Types of molecular spectra

Different regions of the electromagnetic spectrum have different effects on interaction with matter. Molecular spectra are classified on the basis of the region of electromagnetic spectrum in which the transitions or changes take place. They are summarized in Table 17.1.

Table 17.1 Various types of molecular spectra and their origin

S. No.	Spectral region	Wavelength	Type of transition	Spectroscopy
1	Microwave	$1 - 100$ cm^{-1}	Between rotational energy levels	Microwave spectroscopy (rotational spectroscopy)
2	Infrared	$667 - 4000$ cm^{-1}	Between vibrational energy levels	Infrared spectroscopy (vibrational and vibrational–rotational spectroscopy)
3	Visible and ultraviolet	$12500 - 25000$ cm^{-1} (visible) $25000 - 70,000$ cm^{-1} (UV)	Between electronic energy levels	Ultraviolet–visible spectroscopy (electronic spectroscopy)
4	Radio frequency	< 1 cm^{-1} region	Between the nuclear spin energy of the molecules in the applied magnetic field	Nuclear magnetic resonance spectroscopy
5	Microwave region	$1 - 100$ cm^{-1} ($2 - 9.6$ GHz)	Between the electron spin energy of the molecules in the applied magnetic field	Electron spin resonance spectroscopy

General instrumentation

The instrument used to measure the absorption or emission of electromagnetic radiation by the sample under examination is called spectrometer. Spectrometers are of different types but the basic

design is similar. The individual components of the instrument might be different according to the optical region to be studied. For example, sample containers in ultraviolet spectroscopy are made of glass or quartz, whereas sample containers used in infrared spectroscopy are made up of NaCl and KBr.

There are five basic components.

1.   Source of electromagnetic radiation.

2.   Monochromator

3.   Sample containers for sample and solvent

4.   Detector unit

5.   Signal indicator or recording unit.

1.   **Source of electromagnetic radiation**   Incident light of required wavelength is provided by different sources for different spectroscopic techniques. The light sources used are summarized in Table 17.2.

Table 17.2 Various light sources

Spectral region	Light source
Visible spectroscopy	Incandescent tungsten filament lamp
Ultraviolet spectroscopy	Hydrogen discharge lamps and deuterium discharge lamps
Infrared spectroscopy	Electrically heated (~ 1500 °C) rods of • Nernst glower (sintered mixture of oxides of Zr, Y, Er, etc.) • Globar (silicon carbide) • Ceramic element For near infrared, a tungsten filament lamp is satisfactory.
Microwave spectroscopy	Klystron tube which is a specially developed electron tube in which electrons generate electromagnetic radiations

2.   **Monochromator**   A monochromator is used to convert polychromatic radiation into monochromatic radiations. It is a device that resolves radiations into its component wavelengths and then isolates the desired portion of the spectrum.

A monochromator unit consists of an entrance slit, focussing lens, dispersing device (prisms and gratings), filters and an exit slit.

3.   **Sample containers**   The sample is placed in sample containers called cuvettes or cells. A cuvette or cell must be transparent in the spectral region of interest. For ultraviolet region, the cell is made up of quartz or fused silica. If glass is used, the cell is useful only in the visible region.

The sample containers used in infrared spectroscopy are generally made up of NaCl or KBr.

4.   **Detector unit**   The function of the detector is to absorb the energy of the photons and convert it into a measurable quantity such as an electric current. A detector will be useful if

○   it responds to radiant energy over a broad wavelength range

○   it responds rapidly to radiation and is sensitive to low levels of radiant power.

The detectors generally produce an electric signal that can be readily amplified and the signal produced is proportional to the power of the beam striking it.

In UV–visible spectroscopy, photocells or photomutipliers are used as detectors (they detect photons). In the infrared region, thermocouples are used (they detect heat), whereas in the microwave region, the detector is a crystal rectifier.

5. **Amplification and recording unit**   The function of the amplifier is to amplify a signal so that it can be measured. An amplifier takes an input signal from the circuit and through electronic operations produces an amplified output signal which is recorded on a graph or on the computer monitor. Most recording spectrophotometers record wavelength versus absorbance. The absorbance A or optical density is given by

$$A = \log \frac{I_0}{I}$$

where I_o is the intensity of incident light and I is the intensity of transmitted light. A schematic representation of a spectrometer is given in Fig. 17.6.
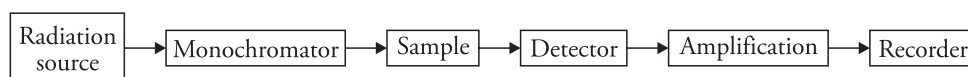
Radiation source → Monochromator → Sample → Detector → Amplification → Recorder

Figure 17.6   *Block diagram of a spectrometer*

17.3 Electronic (UV–Visible) Spectroscopy

Introduction

Electronic spectroscopy is the branch of spectroscopy that deals with the transitions of electrons between the electronic energy levels. The energy difference between the energy levels is such that the electronic spectra are observed in the UV–visible region of the electromagnetic spectrum extending from 200 to 760 nm (UV region 200–380 nm and visible region 380–760 nm).Hence electronic spectroscopy is termed as the UV–visible spectroscopy.

UV–visible spectroscopy is also called electronic spectroscopy as it involves the promotion of electrons (σ, π, n) from the ground state to higher energy states. Ultraviolet spectroscopy is used to measure the number of conjugated double bonds, differentiate between conjugated and non-conjugated systems. It also measures aromatic conjugation within the molecules.

Since energy levels in the molecule are quantised, when radiation of a fixed frequency falls on a molecule, it absorbs energy and the electrons are promoted to higher energy states. Thus, the intensity of the light ray decreases after passing through the sample. A record of the amount of light absorbed by the sample as a function of the wavelength of light in mμ or nm units is called the absorption spectrum, which generally consists of absorption bands.

Laws of absorption

Two fundamental laws govern the absorption of light by molecules. These are

1. Lambert's law   2. Beer's law

Lambert's law   It states that when a beam of monochromatic light passes through a homogenous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation. Mathematically,

$$\frac{-dI}{dx} \propto I \quad \text{or} \quad \frac{-dI}{dx} = kI \tag{1}$$

where   k = proportionality constant

       I = intensity of incident radiation

dI = infinitesimally small decrease in the intensity of radiation on passing through an infinitesimally small thickness, dx of the absorbing medium. The negative sign on the left-hand side indicates that I decreases as x increases. Equation (1) can be written as

$$\frac{-dI}{I} = k\,dx \tag{2}$$

Equation (2) can be integrated with the boundary condition that $I = I_o$ at $x = 0$ and $I = I$ at $x = x$, as,

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

$$\log_e \frac{I_0}{I} = kx$$

$$\text{or,} \quad 2.303 \; \log_{10} \frac{I_0}{I} = kx$$

$$\text{or} \quad \log_{10} \frac{I_0}{I} = \frac{kx}{2.303}$$

$$\text{or,} \quad \log_{10} \frac{I_0}{I} = \varepsilon x \qquad \varepsilon = \text{Absorption coefficient}$$

$$\text{or,} \quad \log_{10} \frac{I_0}{I} = A \qquad A = \text{Absorbance or optical density}$$

I_o is the intensity of radiation before entering the absorbing medium (i.e., when $x = 0$) and I is the intensity when the beam has travelled the thickness x of the absorbing material. The term $\log_{10} \frac{I_0}{I}$ is known as absorbance or optical density and is denoted by A.

Alternatively, Lambert's law can be stated as

When a parallel beam of monochromatic light enters perpendicularly into a homogenous absorbing medium, the absorbance is directly proportional to the length of the path traversed by the beam.

Beer's law   If the absorbing material is in the form of a solution, then the relationship between the intensities of incident and transmitted light is given by Beer's law.

According to this law, *when a parallel beam of monochromatic light enters perpendicularly into a dilute solution, the absorbance is directly proportional to the concentration of the solution.* Mathematically,

$$A = \log_{10} \frac{I_0}{I} = k'c$$

where k′ is a constant and c is the concentration of the solution.

Beer–Lambert law   It is the combined form of Beer's law and Lambert's law. According to this law *when a beam of monochromatic light is passed through a solution, the decrease in intensity of radiation with thickness of the absorbing material is directly proportional to the intensity of incident radiation as well as to the concentration of the solution*

If a monochromatic light of intensity I passes through a solution of molar concentration c and the length of the path is x cm, then the mathematical form of Beer–Lambert's law is

$$A = \log \frac{I_0}{I} = \varepsilon \, cx$$

Units

$\varepsilon = dm^3 \ mol^{-1} \ cm^{-1}$

A = dimensionless

$c = mol \ dm^{-3}$

x = cm

where ε is a constant called the molar absorption coefficient or molar absorptivity. If c = 1 and x =1, then

Extinction $A = \varepsilon$

Thus, molar absorption coefficient (formally, the molar extinction coefficient) can be defined as the extinction due to a 1-cm-thick layer of solution whose molar concentration is unity. It is characteristic of a compound provided the wavelength of light and temperature are kept constant.

Transmittance   If T is the transmittance of a solution, then it is defined as

$$T = \log \frac{I}{I_0}$$

or $T = - \varepsilon \, cb$

Transmittance is the reciprocal of absorbance.

Instrumentation

A spectrophotometer (which is regarded as a combination of a spectrometer and a photometer) is used to detect the percentage transmittance or absorbance of light radiation when light of a certain intensity or frequency range is passed through the sample. The instrument compares the intensity of the transmitted light with that of the incident light. It consists of the following.

(i) **An intense source of radiant energy**   The most common source of visible radiation is an incandescent tungsten filament lamp. Hydrogen/deuterium discharge lamps are used for the ultraviolet region.

(ii) **A filter or monochromator** to isolate the desired wavelength region.

(iii) **Sample holder**   A pair of cuvettes, one for the sample and the other for the blank or reference solution is used. For work in the ultraviolet region, the cuvette must be made of quartz whereas glass cuvettes can be used for visible region. The thickness of the cuvette is generally 1, 2 and 5 cm.

(iv) **Radiation detectors**   These are photoelectric devices which convert radiant energy into electric signals.

Ordinary spectrometers cover a range 220–800 nm. Spectroscopic techniques are not very useful below 200 nm since oxygen is strongly absorbed at 200 nm and below. To study absorption below 200 nm, the instrument has to be evacuated—it is then termed as vacuum UV spectroscopy.

Spectrophotometers are of two types: single-beam and double-beam spectrophotometers.

Single beam spectrophotometer

A single-beam spectrophotometer consists of a single beam of light which passes through the sample (Fig. 17.7). Since there is only one light path, it is necessary to manually interchange the sample and reference solutions for each wavelength.

Double beam spectrophotometer

Double-beam instruments split the beam into two light beams of equal intensity. One beam passes through the reference solvent and the other passes through the sample solution (Fig. 17.8).

Double-beam instruments measure the absorbance of the solvent and solution simultaneously. The spectrophotometer electronically subtracts the absorption of the solvent in a reference beam from the absorption of the solution and measures the absorbance or transmittance characteristic of the compound alone. The intensity of absorbance versus the corresponding wavelength is recorded automatically on the graph. The spectrum is usually plotted as absorbance $A = \left(\log_{10} \dfrac{I_0}{I} \right)$ against wavelength λ (abcissa). The plot is often represented as ε_{max} (extinction coefficient or molar absorptivity) against wavelength.
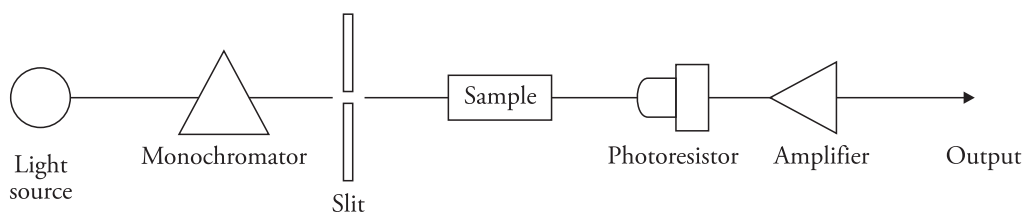

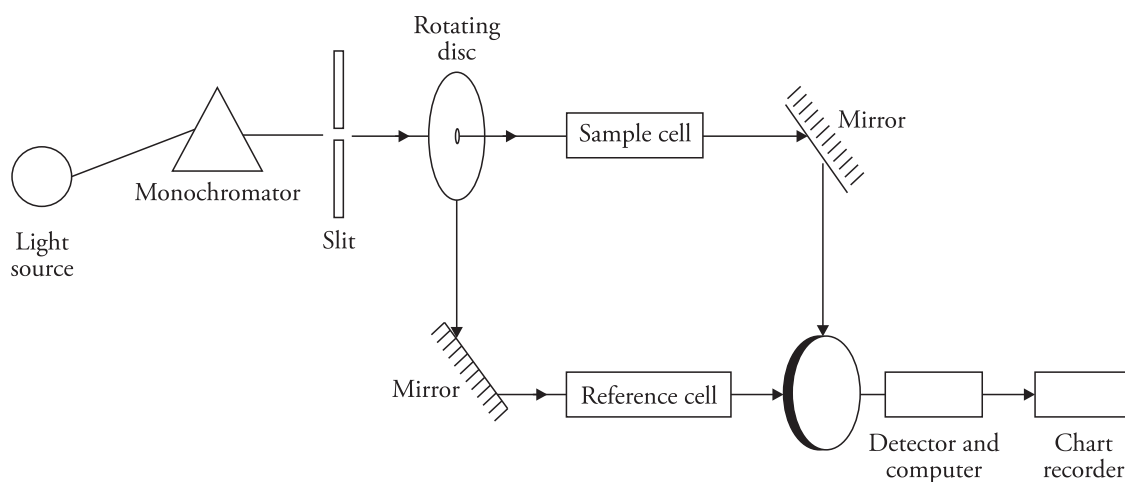**Figure 17.7**   *Single-beam spectrophotometer*

Figure 17.8 *Double-beam spectrophotometer*

Theory of electronic spectroscopy

When a molecule absorbs ultraviolet or visible light, its electrons are promoted from the ground state to a higher energy state. The electrons in the bonding molecular orbitals, for example, σ orbital, π orbital or non-bonding orbitals are promoted to anti-bonding molecular orbitals like σ^* and π^* (asterick * designates the anti-bonding orbital).

The following types of electronic transitions are possible.

$\sigma \rightarrow \sigma^*$ **transitions**   The σ bonded electrons are held firmly in the molecule. Hence, the transitions from σ to σ^* require large amount of energy. These transitions require high energy radiations and therefore, occur in the far ultraviolet region (~150 nm; high energy). Since oxygen of air absorbs strongly in this region, air has to be evacuated (vacuum ultraviolet spectroscopy). $\sigma \rightarrow \sigma^*$ transitions occur in hydrocarbons like methane, propane and are less informative.

n $\rightarrow \sigma^*$ **transitions**   This type of transitions occur in saturated compounds with one hetero atom having unshared pairs of electrons (*n* electrons) like alcohols, ethers, amines, ketones, aldehydes, etc. The energy required for these transitions is lesser than the energy required for $\sigma \rightarrow \sigma^*$ transitions, for example, water absorbs at 167 nm, methyl alcohol at 174 nm and methyl chloride absorbs at 169 nm.

$\pi \rightarrow \pi^*$ **transitions**   These transitions take place in compounds containing double and triple bonds. The excitation of π electrons requires lesser energy; hence they occur at longer wavelength. In unconjugated alkenes, absorption bands appear around 170–190 nm.

n $\rightarrow \pi^*$ **transitions**   In these transitions, the electrons of the unshared electron pair on the hetero atom is excited to π^* anti-bonding orbital. As non-bonding electrons are loosely held, these require least energy and occur at larger wavelengths. They occur in unsaturated compounds with hetero atoms having unshared pairs of electrons like C = O, C = S.

Saturated aldehydes show both the transitions n $\rightarrow \pi^*$ transition occurring around 280 nm and $\pi \rightarrow \pi^*$ transition at around 180 nm. n $\rightarrow \pi^*$ transitions are less intense because the electrons in the *n* orbital are situated perpendicular to the plane of the π bond and hence the probability of electrons jumping from *n* to π^* is low.

The relative energies required for the various transitions follow the order.

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$
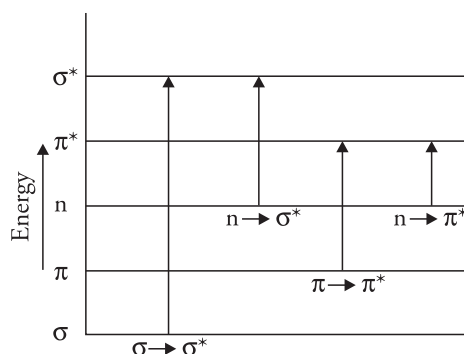
The order is illustrated in Figure 17.9.

Figure 17.9 ● *Energy of various electronic transitions*

Transition probability

Depending upon the value of the extinction coefficient, transitions are classified as

(a)   Allowed transitions

(b)   Forbidden transitions

Allowed transitions are transitions with values of extinction coefficient ε_{max} more than 10^4. They generally arise due to $\pi \rightarrow \pi^*$ transitions.

The value of ε_{max} for forbidden transitions is below 10^4. Forbidden transitions are generally due to $n \rightarrow \pi^*$ transitions.

Benzophenone shows both types of transitions

(i) $\pi \rightarrow \pi^*$ 252 nm ε_{max} 20,000 (allowed)

(ii) $n \rightarrow \pi^*$ 325 nm ε_{max} 180 (forbidden)

Designation of bands

Absorption bands in UV spectroscopy may be designated by using electronic transitions such as ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, etc) or by using letters as described below.

(i)   **K-bands**   They arise due to $\pi \rightarrow \pi^*$ transitions in conjugated π systems (from the German word *Konjugierte*). These bands are found in dienes, polyenes, enones, etc. They are allowed transitions and are intense ($\varepsilon_{max} > 10^4$).

(ii)   **R-bands**   They arise due to $n \rightarrow \pi^*$ transitions (from the German word *Radikal*). They have low molar absorptivities ($\varepsilon_{max} < 100$) and are forbidden transitions. They are observed in compounds with single chromophoric groups, that is, carbonyl or nitro.

(iii) **B-bands**   These are benzenoid bands and are characteristic of aromatic and heteroaromatic compounds. They represent $\pi \rightarrow \pi^*$ transitions. In benzene, the B-band appears at 256 nm and displays fine structure, that is, the band contains multiple peaks.

(iv) **E-bands**   These are ethylenic bands and are also characteristic of aromatic systems like B-bands. The E_1 and E_2 bands of benzene occur near 180 nm and 200 nm, respectively, with ε value between 2000 and 1,4000.

Franck–Condon Principle

The Franck–Condon principle helps in interpreting the intensity distribution in an absorption spectrum. There is no selection rule and no quantum mechanical restrictions for vibrational quantum number v during an electronic transition, hence when a molecule undergoes electronic transition every transition from lower state represented by a double prime (v″) to higher state represented by a single prime (v′) is possible. Hence many vibrational spectral lines are expected, all of which are not of the same intensity. The intensity of these spectra are explained by the Franck–Condon principle which states that *compared to the vibrational motion of the nuclei, the electronic transitions in a molecule take place so rapidly that the instantaneous internuclear distance is considered as unchanged during the electronic transition*. According to the Franck–Condon principle, the electronic transition is represented by a vertical line on a plot of potential energy versus the internuclear distance, and conventionally labelled according to the (v′, v″) numbers where the upper state is written first (0, 0), (1, 0), (2, 0) and so on. Generally all the molecules exist in the lowest vibrational state, that is, v″ = 0, hence all the transitions take place from the ground electronic state.

Figure 17.10 depicts the absorption transitions between the two electronic states in a diatomic molecule. Three situations arise, which are as follows:

1. The equilibrium internuclear distance between the lower and upper electronic states is equal. The most probable transition is v″ = 0 → v′ = 0 as it connects configurations of high probability and appears as a vertical line in accordance with the Franck–Condon principle. In this case 'r' does not change during the electronic transition. This transition (0, 0) appears with maximum intensity. Transition to level v′ = 1, 2, 3….(1, 0 and 2, 0) also occur but these involve a change in 'r', thus deviating from the Franck–Condon principle and hence they lead to weak absorption bands.

   Thus the absorption band (0, 0) appears with maximum intensity and the intensity decreases rapidly for higher bands (Fig. 17.10 a).

2. Figure 17.10 b shows the case when the internuclear distance in excited electronic state is slightly greater than the ground state. In this situation the most probable transition that satisfies the Franck Condon principle and connects to the configurations of maximum probability is v″= 0 → v′ = 2. This band will be most intense and the bands corresponding to transitions to levels v′ = 0, 1, 3, 4…. will have lesser intensity (Figure 17.10 b).

3. Figure 17.10 c shows that the internuclear distance in upper electronic state is considerably greater than the lower electronic state. In such a case, a vertical electronic transition from the mid point of v′ = 0 level is most likely to terminate in the continuum of the upper electronic state, thus dissociating the molecule. The spectrum is complex and is expected to consist of a progression of weak bands joined by a continuum of maximum absorption intensity.
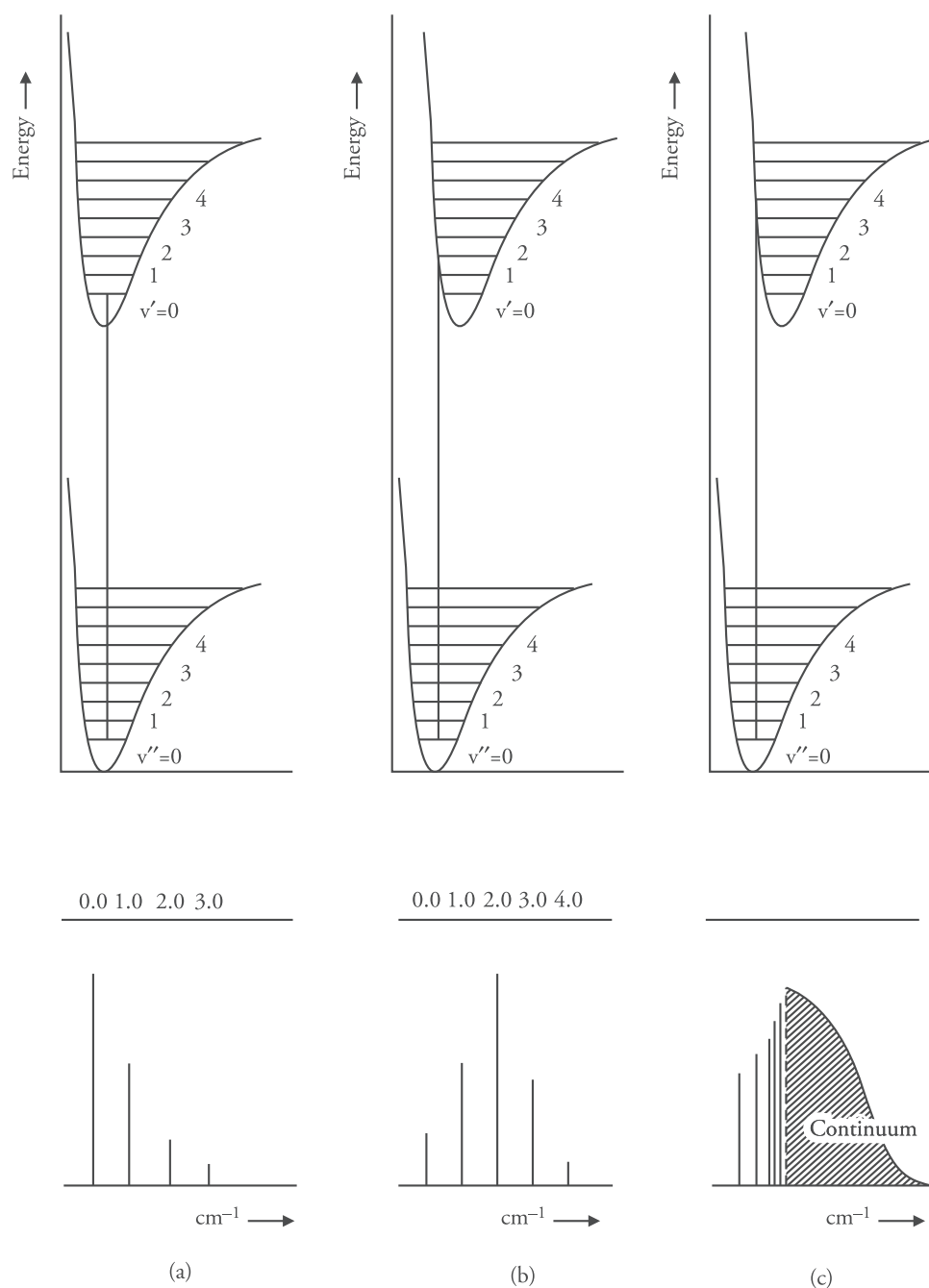
Figure 17.10 *Franck–Condon Principle (a) internuclear distances are equal in the upper and lower states, (b) internuclear distance in upper state is greater than in the lower state and (c) internuclear distance in the upper state is considerably larger.*

Chromophores and auxochromes

Chromophore Originally, a chromophore was considered as any system responsible for imparting colour to a compound.

For example, nitro compounds are generally yellow in colour. Hence, a nitro group is a chromophore which imparts yellow colour.

The term 'chromophore' has now been extended and redefined as *an isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region.* Chromophores can be two types.

(i) Those which contain π electrons and undergo $\pi \rightarrow \pi^*$ transitions. Example C=C, –C≡C–, etc.

(ii) Those which contain both π electrons and non-bonding electrons. They undergo $\pi \rightarrow \pi^*$ and n → π^* transitions. Example : $\rangle$C=O, –C≡N, –N=N–, etc.

Auxochromes

An auxochrome is a colour enhancer. *It is defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength).*

It is a saturated group which when attached to a chromophore changes its intensity as well as wavelength of maximum absorption, for example OH, NH_2 and Cl. The effect of NH_2 on benzene is as follows.

Benzene absorbs at 255 nm with ε_{max} = 203, whereas aniline absorbs at 280 nm with ε_{max} = 1430. Hence amino group (–NH_2) is an auxochrome.

Absorption and intensity shifts

(a) **Bathochromic shift (red shift)** A bathochromic shift is one in which the absorption maximum shifts towards a longer wavelength either due to the presence of an auxochrome or due to the effect of the solvent. Example n → π^* transitions of carbonyl compounds experience bathochromic shift when the polarity of the solvent is decreased.

(b) **Hypsochromic shift (blue shift)** The shift of absorption maximum towards a shorter wavelength. It occurs due to the removal of conjugation or effect of solvent. For example, aniline absorbs at 280 nm because the pair of electrons on the nitrogen atom is in conjugation with the π bond system of the benzene ring. In acidic solutions, a blue shift is observed and absorption occurs at shorter wavelength (~203 nm). The $\langle\bigcirc\rangle$–$\overset{\oplus}{N}H_3$ ion formed in acidic solutions does not have an electron pair and hence the conjugation is removed.

(c) **Hyperchromic shift** Due to this effect, the intensity of absorption maximum increases, that is, ε_{max} increases. It generally occurs due to the introduction of an auxochrome. For example, the B-bands of pyridine at 257 nm with ε_{max} = 2750 is shifted to 262 nm with ε_{max} = 3560 for methyl pyridine.

(d) **Hypochromic shift** The intensity of absorption (ε_{max}) maximum decreases due to this effect. Groups which distort the geometry of a molecule cause hypochromic shift. For example, biphenyl absorbs at 250 nm with ε_{max} = 19,000, whereas 2-methyl biphenyl absorbs at 237 nm with ε_{max} = 10,250. The introduction of the methyl group distorts the geometry of biphenyl.

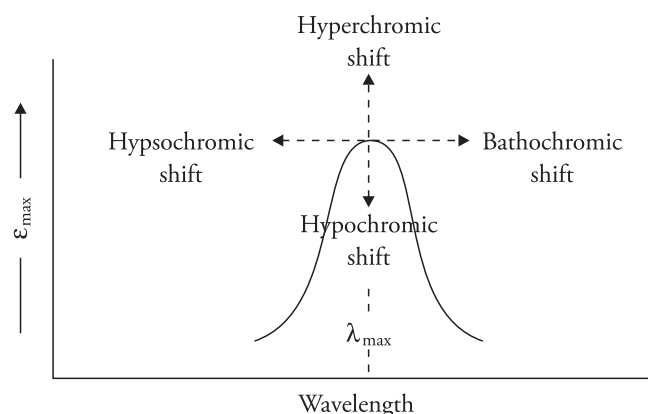The various shifts are shown in Figure 17.11.

Figure 17.11   *Absorption and intensity shifts*

Solvent effects

The solvent used for preparing solutions should not absorb in the region under investigation. The most commonly used solvents in UV spectroscopy are ethanol, hexane, methanol, cyclohexane, etc.

The polarity of the solvent greatly affects the position and intensity of the absorption maximum. The following shifts are observed on changing the solvent polarity.

*   Non-polar compounds like ethylene, butadiene, aromatic hydrocarbons and conjugated hydrocarbons experience very little shift on changing the polarity of the solvent. The absorption maximum of non-polar compounds like ethylene is the same in alcohol (polar solvent) as well as in hexane (non-polar solvent).

*   Polar compounds like α, β -unsaturated carbonyl compounds show two different shifts on changing the polarity of the solvent.

$n \rightarrow \pi^*$ **transition (less intense)**   On increasing the polarity of the solvent, the $n \rightarrow \pi^*$ band moves to the shorter wavelength (blue shift). This is because the polar solvent stabilises n orbitals more than π^* orbitals. The energy of n orbital is thus lowered, increasing the energy gap between the ground state and the excited state. Hence, the absorption band moves to the shorter wavelength (Fig. 17.12). For example, absorption maximum of acetone is at 279 nm in hexane and 264 nm in water (polar solvent).
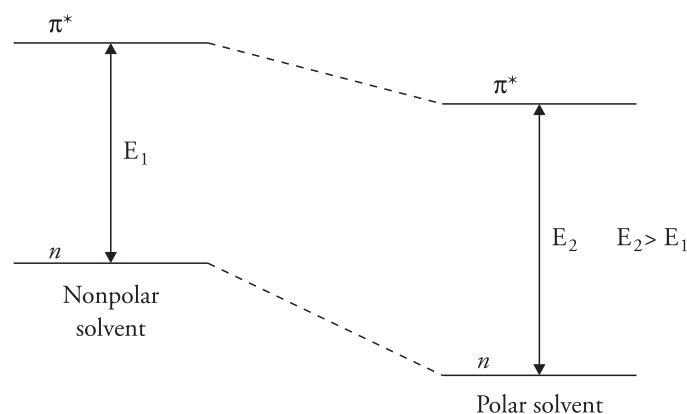

Figure 17.12   *Absorption shift n $\rightarrow$ π* band with change in solvent polarity*

$\pi \rightarrow \pi^*$ **transition (intense)**   On increasing the polarity of the solvent, the absorption band moves to the longer wavelength (red shift). This is because the dipole–dipole interactions with the solvent molecules lower the energy of the excited state more than that of the ground state (Fig. 17.13). In other words, hydrogen bonding with a polar solvent stabilises the π^* orbital because of greater polarity of π^* compared to π orbitals. Thus, the energy required for $\pi \rightarrow \pi^*$ transition is less and the absorption moves towards the red end of the spectrum (longer wavelength side). The value of the absorption maximum is greater in ethanol than that observed in hexane.
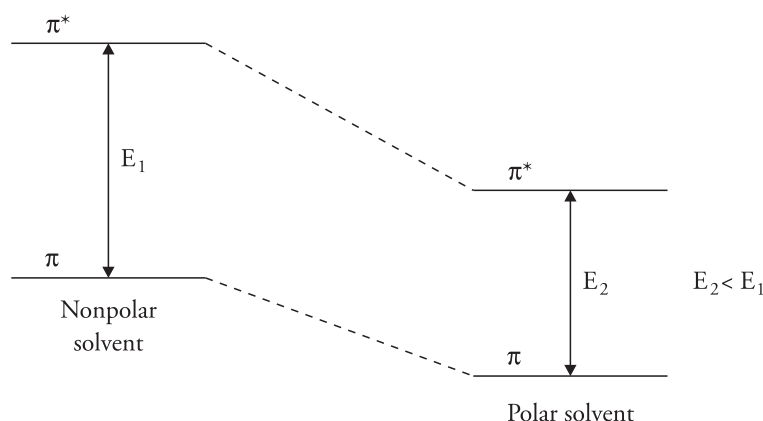
**Figure 17.13** ● *Absorption shift $\pi \rightarrow \pi^*$ transition with change in solvent polarity*

$n \rightarrow \sigma^*$ transitions in alcohols and amines experience blue shift (shift towards shorter wavelength) due to greater stabilisation of non-bonding electrons. Hence, the transition requires greater energy.

Applications of ultraviolet spectroscopy

Ultraviolet spectroscopy finds extensive use in the determination of structures of organic compounds. Some important applications of ultraviolet spectroscopy are as follows.

1. **Extent of conjugation**   Conjugation lowers the energy required for $\pi \rightarrow \pi^*$ transition. The greater the extent of conjugation, the longer is the absorption wavelength. For example, ethylene absorbs at 170 nm due to $\pi \rightarrow \pi^*$ transitions whereas butadiene having two double bonds absorbs at 217 nm, and a polyene with eight conjugated double bonds absorbs at about 420 nm, that is, in the visible region and they appear coloured to the human eye. Similarly, lycopene with eleven conjugated double bonds absorbs at 454 nm and imparts red colour to tomatoes.

2. **Determination of geometrical isomers**   Effective $\pi \rightarrow \pi^*$ transitions take place when the molecule is coplanar. The steric strain in cis-isomer prevents coplanarity. Thus, cis isomers absorb at a shorter wavelength when compared to the trans-isomer, for example, cis-stilbene absorbs at 280 nm and trans-stilbene absorbs at 295 nm.

3. **Identification of unknown compounds**   Unknown compounds can be identified by comparing its spectra with the spectra of known compounds. Identical spectra reveal identical structure and if the spectra is different, then the structure is different.

4. **Distinction between conjugated and non-conjugated compounds** Consider the following compounds.

$$(CH_3)_2C=CH-\underset{\underset{O}{\|}}{C}-CH_3 \qquad CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

(a)   (b)
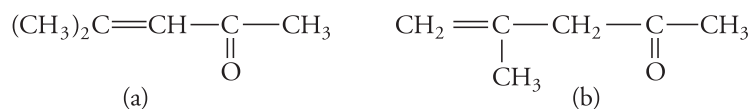
Compound (a) has longer λ_{max} values because C = O group is in conjugation with the double bond.

5. **Detection of impurities** Ethanol contains benzene as an impurity. Since benzene is toxic in nature, it is essential to detect its presence. The presence of benzene can be detected through the UV spectrum of the sample at 280 nm (Fig. 17.14). Ethanol is transparent at this wavelength but benzene shows an absorption band with $\varepsilon_{max} = 230$.

6. **Detection of hydrogen bonding** Hydrogen bonding can be detected on the basis of the shift absorbed in polar solvents.

7. **Quantitative analysis** This is based on Beer–Lambert's law

$$A = \varepsilon c l$$

where A = absorbance at a particular wavelength

c = concentration of the sample

ε = constant termed as molar absorptivity or extinction coefficient.

The absorbance of the standard solution (A_1) and the unknown solution (A_2) are measured in a sample cell. If the concentration (c_1) of the standard solution is known, the concentration (c_2) of the sample can be determined as follows

$$\frac{A_1}{A_2} = \frac{c_1}{c_2}$$

Example For a solution of camphor in hexane in a 5-cm cell, the absorbance A was found to be 2.52 at 295 nm with $\varepsilon_{max} = 14$. What is the concentration of camphor?

Solution

$$A = \varepsilon c \ell$$

$$A = 2.52 \quad c = ? \quad \varepsilon = 14 \quad \ell = 5 \text{ cm}$$

$$\therefore 2.52 = 14 \times c \times 5$$

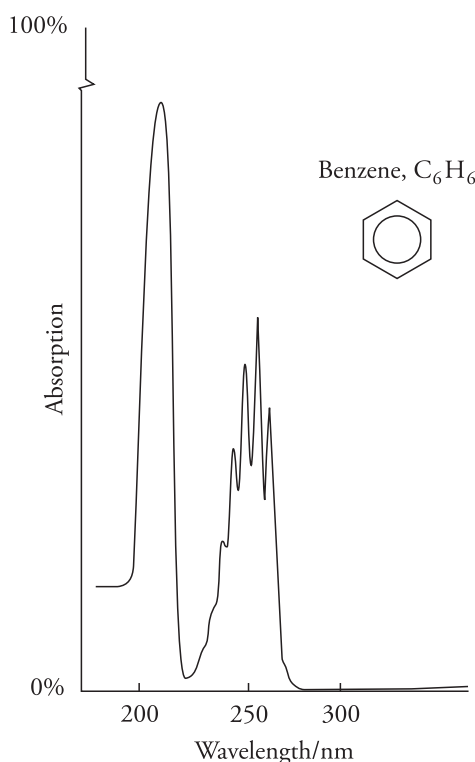$$c = \frac{2.52}{14 \times 6} = 3.6 \times 10^{-2} \text{ mol/L}$$

Figure 17.14 *UV absorption spectra of benzene in ethanol*

17.4 IR Spectroscopy

Introduction

Infrared spectroscopy is a very important tool for the determination of the structure of a compound. It is also called vibrational spectroscopy as it involves the transition between vibrational energy levels. Infrared radiations do not have sufficient energy to bring about electronic excitation; however, it causes atoms and groups to vibrate about the covalent bond connecting them. As these vibrations are quantised, the compound absorbs the infrared energy in different regions of the spectrum. An infrared spectrum is obtained when the frequency of molecular vibration corresponds to the frequency of the infrared radiation absorbed. Apart from vibrational changes, rotational changes also occur in the molecule, hence some fine structures are obtained on the vibrational band.

The IR region of electromagnetic spectrum extends from 0.8 μ to 200 μ (12,500 cm^{-1} to 50 cm^{-1}) but the most important region for the purpose of study is 2.5 μ to 15 μ (4000 cm^{-1} to 667 cm^{-1}). Molecular vibrations are detected and measured in this region. The region from 0.8 μm to 2.5 μm is called near infrared and that from 15 μm to 200 μm is called far infrared region.

Infrared spectrum

When a beam of IR radiation of varying frequency passes through a sample, it absorbs energy when the energy matches the difference between the vibrational energy levels of its bonds. Absorption

bands are thus obtained. Infrared spectrum is usually plotted with the percentage transmittance rather than the absorbance as ordinate. This makes the absorption bands appear as dips or troughs rather than as maxima as in the case of ultraviolet and visible spectra. These dips or troughs are called bands and they represent absorption of infrared radiation at that frequency of the sample. The bands can be strong, medium or weak depending upon the absorption.
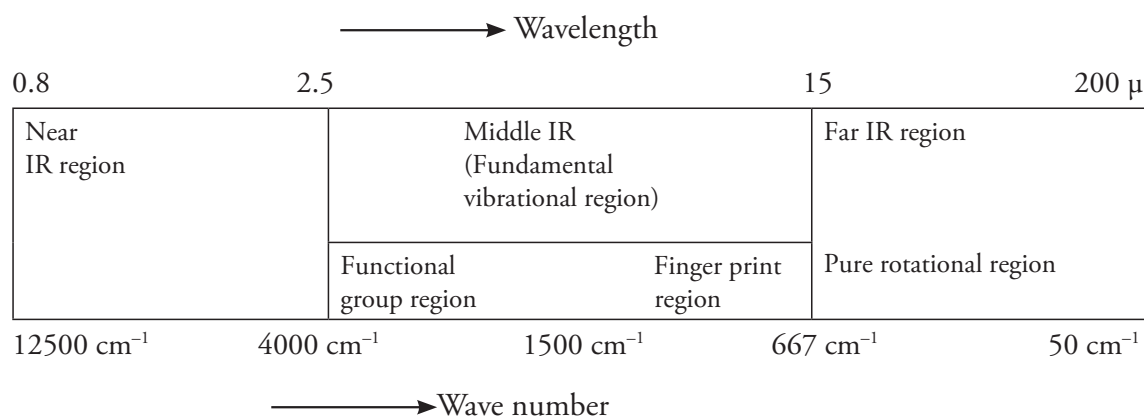
The position of the infrared absorption band is specified in frequency units expressed not in hertz but in wave numbers, cm^{-1} or by its wavelength λ measured in micrometers (μm).

$$\overline{v} = \frac{1}{\lambda(\text{in cm})} \quad \text{or} \quad \overline{v} = \frac{10,000}{\lambda(\text{in } \mu\text{m})}$$

Band intensity is expressed either in terms of absorbance (A) or transmittance (T)

$$A = \log_{10}(1/T)$$

IR spectroscopy is divided into three regions:

$\longrightarrow$ Wavelength

0.8		2.5		15	200 μ
Near IR region		Middle IR (Fundamental vibrational region)		Far IR region	
		Functional group region	Finger print region	Pure rotational region	

12500 cm^{-1} 4000 cm^{-1} 1500 cm^{-1} 667 cm^{-1} 50 cm^{-1}

$\longrightarrow$ Wave number

- The near IR region extends from 12500 cm^{-1} to 4000 cm^{-1} wave number. It is of little significance as there are few absorptions in this range.

- The most important and useful region extends from 4000 cm^{-1} to 667 cm^{-1}. Most absorptions occur in this region.

- The far infrared region deals with the pure rotational motion of the molecule. Very few absorptions appear in this region. It extends from 667 cm^{-1} to 50 cm^{-1}.

Instrumentation

The instrument consists of the following.

(i) **Light source** Infrared radiations are produced by electrically heating Globar or a Nernst filament to 1000–1800 °C. Globar is a rod of silicon carbide, whereas the Nernst filament is a high resistance element composed of sintered oxides of zirconium, cerium and thorium.

(ii) **Filter or monochromator** Optical prisms or gratings are used to obtain monochromatic light. Glass or quartz cannot be used as the prism material because they absorb in the infrared region. Prisms are made of sodium chloride or alkali metal halides.

(iii) **Sample holder** Cells are made of NaCl or alkali metal halides as they do not absorb IR radiations. Solid samples are ground with KBr and made into a disc. The sample should be absolutely dry as water absorbs strongly in the IR region. Solvents used for IR are chloroform, carbon tetrachloride, carbon disulphide, etc.

(iv) **Detectors** Thermocouple based detectors are used. Light from the source is split into beams, one of which passes through the sample and the other through the reference. The beam on passing through the sample becomes less intense. There is a difference in intensity of the two beams. This is detected and recorded and an IR spectrum is obtained.

The schematic diagram of an IR spectrophotometer is shown in Figure 17.15.
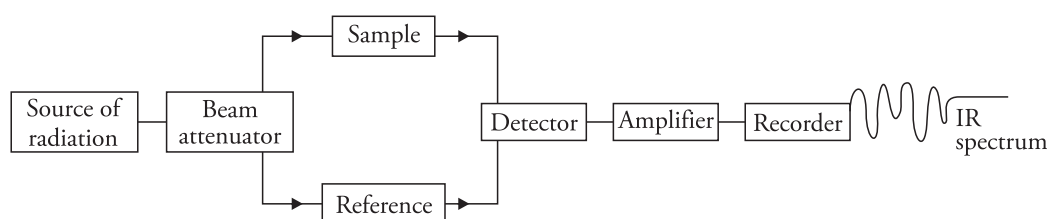
Figure 17.15 *Schematic diagram of IR spectrophotometer*

Theory: Absorption of infrared radiation and molecular vibrations

Covalent bonds behave like tiny springs connecting the atoms. The atoms in the molecules do not remain in a fixed position but vibrate. This vibrational motion is quantised. At room temperature, the molecules of a sample are in their lowest vibrational state. When infrared radiation is passed through the sample, the molecule absorbs radiation of appropriate energy and gets excited to a higher vibrational level (Fig. 17.16). It is important to note here that IR light is absorbed only when the dipole moment of the molecule is different in the two vibrational levels and the oscillating dipole moment due to molecular vibrations interacts with the oscillating electric vector of the infrared beam.
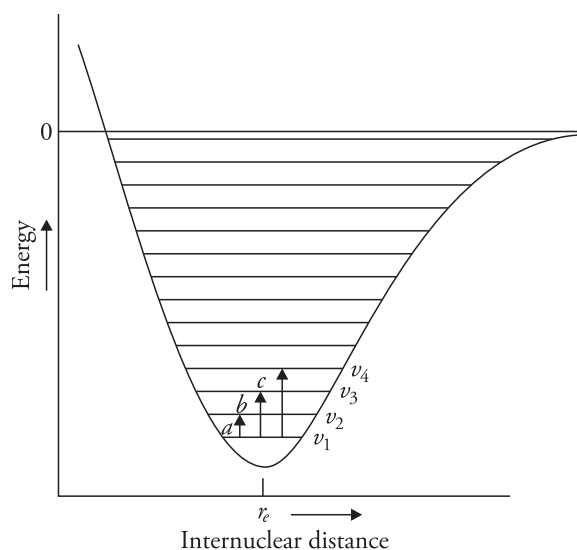

Figure 17.16 *Vibrational spectra of diatomic molecules*

Types of vibrations

There are two types of vibrations.

(a) **Stretching**   In this type of vibrations, the distance between the atoms increases or decreases but the atoms remain in the same bond axis. Stretching can be of two types:

  (i) Symmetric   (ii) Asymmetric

  (i) **Symmetric stretching**   In symmetric stretching, the movement of the atoms with respect to a particular atom is in the same direction (Fig. 17.17).
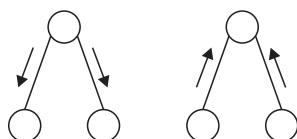

Figure 17.17   *Symmetric stretching*

  (ii) **Asymmetric stretching**   In these vibrations, one atom approaches the central atom and the other departs from it (Fig. 17.18).
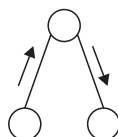
Figure 17.18   *Asymmetric stretching*

(b) **Bending vibrations**   In these types of vibrations, the position of the atom changes with respect to the original bond axis but the distance between the atoms remains constant.

 Bending vibrations are of two types.

  (i) **In-plane bending vibrations**   In this type, the atoms remain in the same plane as the nodal plane of the system. These, also, are of two types.

  Scissoring   In this type, the two atoms approach each other and move away like the two arms of a scissors (Fig. 17.19 a).

  Rocking   In this type, both the atoms move in the same direction (Fig. 17.19 b).
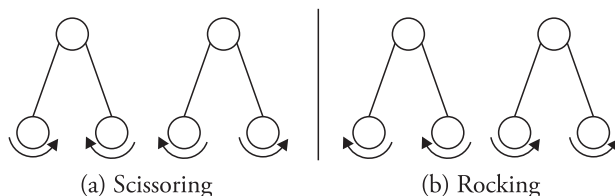

(a) Scissoring   (b) Rocking

Figure 17.19   *In-plane bending vibrations*

(ii) **Out-of-plane bending vibrations** The atoms move out of the nodal plane with respect to the central atom. These are again of two types.

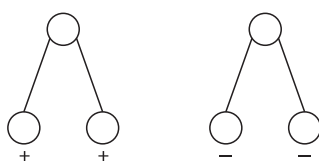**Wagging** In this type, both the atoms swing up and down with respect to the central atom (Fig. 17.20).

Figure 17.20 *Out-of-plane bending-wagging*

Twisting In this type, one atom moves up the plane and the other moves down the plane with respect to the central atom (Fig. 17.21).
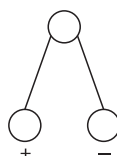

Figure 17.21 *Out-of-plane bending-twisting (the signs + and − indicate movement towards and away from the reader)*

Remember that it takes more energy to stretch a spring then to bend it; hence, stretching vibrations appear at a higher frequency as compared to the bending vibrations.
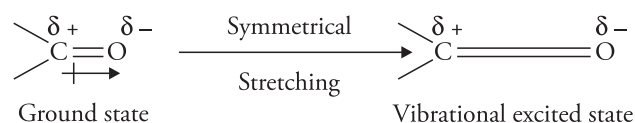
Dipole moment and infrared spectrum

All types of molecules cannot interact with IR radiation. Only those molecules which undergo a net change in dipole moment because of its vibrational or rotational motion absorb in the IR region. Homonuclear diatomic molecules like H_2, O_2, N_2 or Cl_2 do not show change in dipole moment during vibration and hence they do not absorb in the infrared region. Such molecules are termed as *infrared inactive.*

As stated earlier, infrared radiation is absorbed when the oscillating dipole moment interacts with the oscillating electric vector of the infrared beam. For such an interaction to occur, the dipole moment of the molecule in the ground state and the vibrational excited state should be different. The greater the difference in these dipole moments, the more intense is the absorption. For example, the symmetrical stretching vibration of the C–C bond in ethylene can be represented as
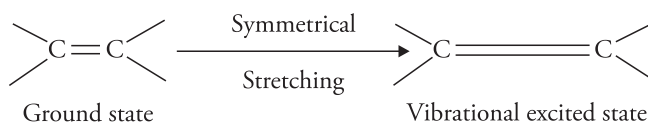
Symmetrical stretching of a carbonyl group can be expressed as

Ground state — Symmetrical Stretching — Vibrational excited state

 is non-polar, hence, on symmetrical stretching, there is little or no change in dipole moment and hence, the infrared absorption is either absent or very weak. However, the carbonyl group $\left(\!\!\!\begin{array}{c}\diagdown\\\diagup\end{array}\!\!\!C\!=\!O\right)$ is polar due to the different electronegativities of the atoms. On stretching, the dipole moment increases considerably. This change in dipole moment leads to the generation of an oscillating electric field. If the frequency of this oscillating electric field is equal to the frequency of the fluctuating electric field of the infrared radiation, the energy is absorbed or emitted resulting in an infrared spectrum. Hence $\left(\!\!\!\begin{array}{c}\diagdown\\\diagup\end{array}\!\!\!C\!=\!O\right)$ is *infrared active* and will show an intense absorption. Similarly, the trans-isomer is non-polar having zero dipole moment. On stretching, the
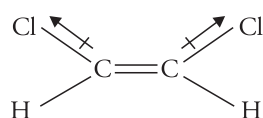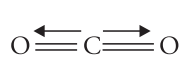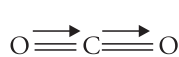

Dipole moment
μ = 2.95 D
cis - 1, 2 dichloroethene
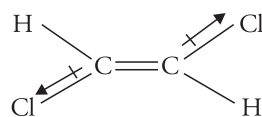
μ = O
trans - 1, 2 dichloroethene

dipole moment does not change; hence, it is infrared inactive. On the other hand, the cis-isomer undergoes change in dipole moment and hence, it is infrared active.

Some molecules do not have a permanent dipole moment but some of their vibrational modes are accompanied by change in dipole moment making them infrared active. For example, the symmetrical stretching of C=O in CO_2 is infrared inactive while asymmetrical stretching and bending vibrations are infrared active.

(a) Symmetrical stretching (IR inactive)

(b) Asymmetrical stretching (IR active)
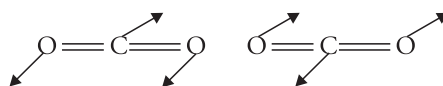
(c) Bending vibrations (IR active)

Vibrational Spectra

Simple harmonic oscillator model: Consider a diatomic molecule associated with a dipole moment. The vibrational motion of atoms of a diatomic molecule may be similar to the vibration of a simple harmonic oscillator. In such an oscillator the force required to restore an atom to its original state is proportional to the displacement of the vibratory atom from its original position in accordance with the Hooke's law. If Δx is the displacement in the vibratory atom from its original position then according to Hooke's law, restoring force

$$F \propto \Delta x$$

$$F = -kx \qquad (1)$$

k is the force constant (units of k are N m^{-1}, that is, force per unit distance), $x = r - r_e$, where r is the distance to which the atoms have been stretched and r_e is the equilibrium distance between the two atoms. The potential energy of a simple harmonic oscillator as a function of displacement from equilibrium configuration is given by the Hooke's law equation

$$V_{(x)} = \frac{1}{2}kx^2 \qquad (2)$$

This is the equation for a parabola. Hence a parabolic potential energy curve is obtained
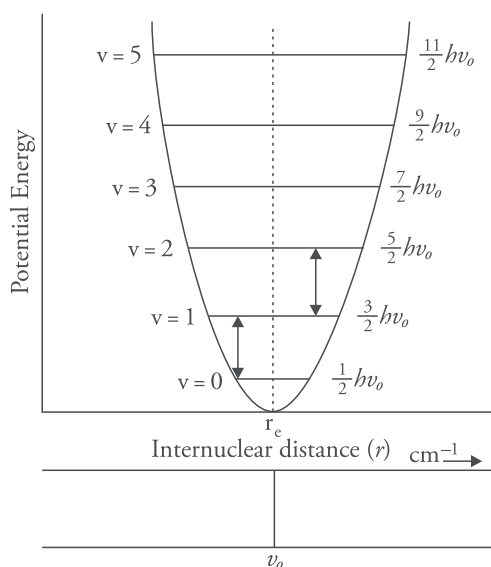

Figure 17.22 *Potential energy diagram for a harmonic oscillator*

The vibrational frequency of a point mass m connected by a spring of force constant k is given by

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (3)$$

where μ is the reduced mass. If m_1 and m_2 are the masses of the two atoms then

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

The solution of Schrodinger wave equation for a simple harmonic oscillator gives quantised vibrational energy levels

$$E_v = (v + \frac{1}{2})\, h\upsilon \qquad (E_v \text{ in joules}) \ldots(4)$$

v is the vibrational quantum number with the allowed values 0, 1, 2, 3 …… and v is the frequency of vibration given by Eq. (3). On solving equation 4 for v = 0, 1, 2, 3, the values of E_v work out to be $\frac{1}{2}hv$, $\frac{3}{2}hv$, $\frac{5}{2}hv$, $\frac{7}{2}hv$, respectively, which shows that the quantised energy levels are equally spaced as shown in Figure 17.22. It is also clear that the lowest energy level at v = 0 is not zero but E_v for v = 0 is $\frac{1}{2}hv$ and this is termed as the *zero point energy* of the molecule.

Vibrational Spectrum for Simple Harmonic Oscillator

Energy levels of harmonic oscillator: If a diatomic molecule undergoes transitions from upper vibrational level v+1 to lower vibrational level v, the change in vibrational frequency is given by

$$\Delta E_v = \left[(v+1) + \frac{1}{2} \right] hv - (v + \frac{1}{2})hv$$

$$\Delta E_v = hv = \frac{hc}{\lambda} = hc\bar{v}$$

where $\bar{v}$ is the wave number

Thus for a diatomic molecule two consecutive energy levels are equally spaced and they are equal to $hc\bar{v}$.

Selection rule

The selection rule for vibration transition in a simple harmonic oscillator is

$$\Delta v = \pm 1 \tag{6}$$

The positive sign indicates absorption spectra and the negative sign indicates emission spectra. Hence transition from any v to v + 1 level will give the same energy change and hence only one line is expected. Moreover at room temperature most of the molecules are in ground vibrational state (v = 0) hence the transitions will occur only from v = 0 to v = 1 and the vibrational frequency corresponding to this is the *fundamental vibrational frequency.*

Anharmonic Vibrations

In a harmonic oscillator model the restoring force is proportional to displacement and the energy of harmonic oscillator is given by

$$E_v = (v + \frac{1}{2}) hc\bar{v} \tag{7}$$

where v is the vibrational quantum number. In harmonic oscillator model the diatomic molecule reaches equilibrium state and it can never dissociate, but for a real molecule this is not true. The movement of a real oscillator is not perfectly harmonic because as displacement increases the

restoring force becomes weaker and for large amplitude of vibration, the atoms must fall apart, that is, the molecule must dissociate into atoms. Such a real oscillator is said to be an *anharmonic oscillator*. P.M. Morse in 1929 suggested an empirical expression for the potential energy of an anharmonic diatomic oscillator, given by

$$V(r) = D_e \left[1 - e^{\alpha(r - r_e)} \right]^2 \tag{8}$$

where α is a constant, D_e is the dissociation energy of the molecule. If V(r) is plotted as a function of r we obtain a sketch, as shown in Figure 17.23.
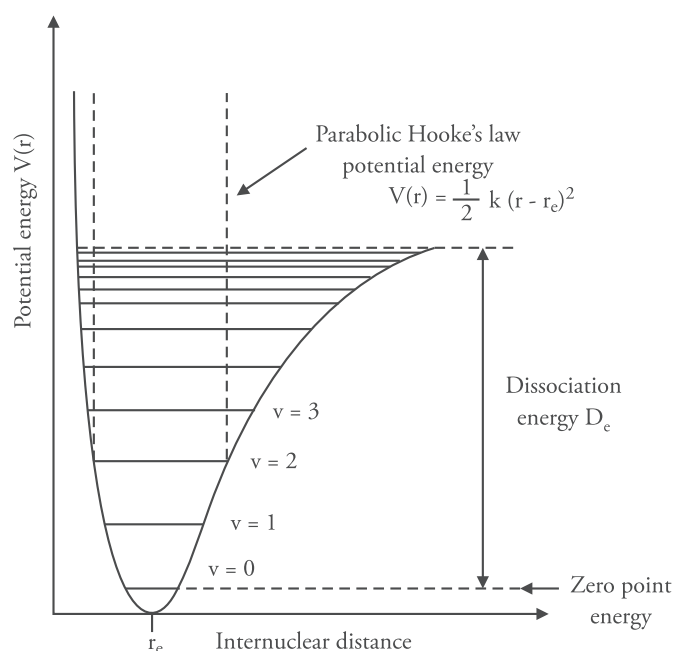

Figure 17.23 *Morse potential energy for an anharmonic diatomic oscillator*

On solving the Schrodinger wave equation for an anharmonic oscillator using the Morse potential energy, the energy levels are given by

$$E_v = \left(v + \frac{1}{2} \right) h \bar{v}_e - \left(v + \frac{1}{2} \right)^2 h x_e \bar{v}_e \qquad (E_v \text{ in joules}) \tag{9}$$

where $\bar{v}_e$ is the equilibrium oscillation frequency and x_e is the anharmonicity constant (a small positive number) and v = 0, 1, 2, 3 ….

As expected $v_e x_e <<< v_e$; the consequence of this is that the vibrational energy levels of SHO are slightly lowered and the successive energy levels are not equally spaced, they come closer and closer as the quantum number increases (remember in harmonic oscillator model the energy levels were equally spaced). Moreover for anharmonicity the selection rule is no longer $\Delta v = \pm 1$ but transitions corresponding to $\Delta v = \pm 2, \pm 3, \ldots$ are also observed. Hence the selection rule for anharmonic oscillator is

$\Delta v = \pm 1, \pm 2, \pm 3$ and so on.

Transitions from $v = 0$ to $v = 1$ is most intense as the ground energy level is populated and is called the fundamental absorption or fundamental band. The transition from $v = 0$ to $v = 2$ has a weak intensity and is the first overtone; $v = 0$ to $v = 3$ is the second overtone with still lesser intensity.

Solved Examples

(i)   Of the following, which one is expected to absorb at higher frequency for stretching vibration?

(a) $C \equiv C$ and $C = C$ (b) C–H and C–C

(c) O–H and C–C   (b) C = C and C–C

Ans (a) $C \equiv C$ (b) C–H   (c) O–H   (d) C = C

Solution   This is because the bond strength of $C \equiv C$, C –H, O–H and C = C are greater than that of C = C, C – C, C – C and C – C, respectively.

(ii) Calculate the vibrational absorption frequency of the carbonyl, $>C=O$ group, if the force constant for the double bond is 1×10^6 dynes cm^{-1}

Solution

$$\text{Mass of oxygen atom} = \frac{16}{6.023 \times 10^{23}} \approx 2.65 \times 10^{-23}\, \text{g (approx)}$$

$$\text{Mass of carbon atom} = \frac{12}{6.023 \times 10^{23}} \approx 2.00 \times 10^{-23}\, \text{g (approx)}$$

$$\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\bar{v} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}}\sqrt{\frac{1 \times 10^6}{\dfrac{2.65 \times 10^{-23} \times 2.00 \times 10^{-23}}{2.65 \times 10^{-23} + 2.00 \times 10^{-23}}}} = 1581\ \text{cm}^{-1}$$

Practice problems

1.   Calculate the approximate frequency of the C–H stretching vibration from the following data.

$k = 5 \times 10^5\, \text{g s}^{-2}$

Mass of carbon atom $(m_1) = 20 \times 10^{-24}\, \text{g}$

Mass of hydrogen atom $(m_2) = 1.6 \times 10^{-24}\, \text{g}$ [Ans   3100 cm^{-1}]

2. Calculate the approximate wavelength of absorption associated with the C–H bond in the stretching vibration of the methyl group. The force constant for the single bond is 5×10^5 dynes cm^{-1}. The masses of carbon and hydrogen are 20×10^{-24} g and 1.6×10^{-24} g, respectively.

$$[\text{Ans} \quad \bar{\nu} = 3023 \text{ cm}^{-1} \; \lambda = 3.31 \times 10^{-4} \text{ cm} = 3.31 \text{ μm}]$$

Number of fundamental vibrations for polyatomic molecules Polyatomic molecules show more than one fundamental band. The number of fundamental bands of a polyatomic molecule depends upon the degrees of freedom in a molecule. The number of degrees of freedom is equal to the sum of the coordinates necessary to locate all the position of the atoms in space. The position of an atom is specified by the three cartesian coordinates (x, y, z). Hence, its degree of freedom is three. The degree of freedom of an atom and molecule are given in Table 17.3.

Table 17.3 Degrees of freedom

	Types of degree of freedom	Total degree of freedom
Isolated atom	Only translational degree of freedom (it does not have rotational and vibrational degree of freedom)	3
Molecule	Translational + rotational + vibrational degree of freedom	$3n$ where n is the number of atoms in a molecule

We are concerned only with the vibrational degree of freedom which gives the number of fundamental bands. Therefore, let us calculate the vibrational degree of freedom for different types of molecules.

(a) **For linear molecules of n atoms**

Total degrees of freedom = $3n$

Translational degree of freedom = 3

Rotational degree of freedom = 2

∴   Vibrational degree of freedom = $3n - 3 - 2 = 3n - 5$

∴   Number of fundamental bands for a linear molecule = $3n - 5$.

Rotation about the axis of linearity does not bring about any change in the position of atoms while rotation about the other two axes, changes the position of the atoms. Hence, linear molecule has two degrees of rotation.

(b) **For non-linear molecules of n atoms**

Total degrees of freedom = $3n$

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degree of freedom = $3n - 3 - 3 = 3n - 6$

Hence, number of fundamental bands = $3n - 6$

Combination bands and Fermi resonance

Combination bands, difference bands or overtones are produced due to the interaction of the vibrational states in polyatomic molecules. If there are two fundamental bands at *a* and *b*, then the additional bands that can be expected are

(i)   2a, 2b (overtones)

(ii)   a + b, a + 2b, 2a + b, etc. (combination bands)

(iii)   a – b, a – 2b, 2a – b, etc. (difference bands)

The intensity of these bands is 10–100 times less than the intensity of the fundamental bands. When an overtone or combination band falls near the fundamental band, there is resonance and the molecule transfers its energy from the fundamental to the overtone band and back. Due to this resonance, both the bands share their intensity and appear as a pair of equally intense bands in the IR spectrum. Such type of resonance is known as *fermi resonance*.

Solved Examples

(i)   Calculate the theoretical number of vibrational degrees of freedom in
   - (a) Carbon dioxide
   - (b) Benzene
   - (c) Water
   - (d) Sulphur dioxide
   - (e) N_2O

Solution

(a) CO_2 is a linear triatomic molecule

Vibrational degree of freedom = $3n - 5$ where $n = 3$

$$= 3 \times 3 - 5 = 4$$

(b) C_6H_6 is a non-linear molecule where $n = 12$ (6C + 6H)

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 12 - 6 = 30$$

30 fundamental bands are expected in benzene but the number is less as the bands may fall outside the region under investigation or may be too weak to be observed as bands.

(c) H_2O is a non-linear molecule with $n = 3$

Vibrational degree of freedom = $3 \times 3 - 6 = 3$

(d) SO_2 is a non-linear molecule with $n = 3$

Vibrational degree of freedom $= 3n - 6$

$$= 3 \times 3 - 6 = 3$$

(e) N_2O is a non-linear molecule with $n = 3$

Vibrational degree of freedom $\qquad = 3n - 6$

$$= 3 \times 3 - 6 = 3$$

Practice Problems

(i) Calculate the theoretical number of vibrational degrees of freedom in

(a) HCN   (b) $C_6H_5CH_3$ (c) CH_4 [Ans   (a) 4 (b) 39 (c) 9]

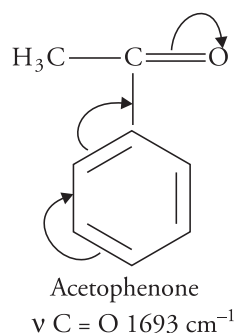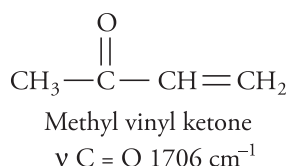## Factors influencing vibrational frequencies

The vibrational frequency as calculated by Hook's law and that obtained experimentally usually differs due to various factors which influence the vibrational frequencies. The factors are explained below.

1. **Physical state**   A compound absorbs at a higher frequency in vapour state than when it is in solid or liquid state. For example, cyclopentanone shows carbonyl absorption in the vapour phase at 1772 cm^{-1} and in the liquid phase at 1746 cm^{-1}. Carbonyl stretching frequency of acetone in vapour phase is 1742 cm^{-1} and in liquid phase, it lowers to 1718 cm^{-1}.

2. **Electronic effects**   Inductive effects, mesomeric effects change the force constant or bond strength and affect vibrational frequency. Some examples are given below.

Compound	HCHO	CH_3CHO	CH_3COCH_3
Absorption (cm^{-1})	1750	1745	1715

Introduction of alkyl group (+ I effect) causes lengthening or weakening of the bond, hence the force constant is lowered and the wave number of absorption decreases.

Similarly,

CH$_3$—C—CH=CH$_2$ (with O double bonded to C)
Methyl vinyl ketone
ν C = O 1706 cm^{-1}

Acetophenone
ν C = O 1693 cm^{-1}

In the above case, the mesomeric effect dominates over the –I effects of $-CH = CH_2$ and C_6H_5- group. Thus, the absorption frequency of $-C = O$ group falls.

3. **Hydrogen bonding**   Hydrogen bonding brings about downward frequency shifts. The stronger the hydrogen bonding, the greater is the absorption shift towards the lower wave number. Infrared spectroscopy helps in differentiating between inter- and intramolecular hydrogen bonding. Intermolecular hydrogen bonding gives rise to broad absorption bands which are concentration-dependent. Bands arising from intramolecular hydrogen bonding are sharp and independent of concentration. For example, in aliphatic alcohols, a sharp band appears at 3650 cm^{-1} in dilute solutions due to free O–H group while a broad band appears at 3350 cm^{-1} due to hydrogen bonded OH group.

4. **Effect of solvent**   Change in solvent shifts the IR band. For example, the carbonyl stretching frequency of acetone is different in different solvents.

Solvent	Hexane	Chloroform	Ethanol
Absorption band	1726 cm^{-1}	1713 cm^{-1}	1709 cm^{-1}

5. **Coupled vibrations and Fermi resonance**

   Vibrational frequency changes due to interaction between fundamental vibration and overtones (Fermi resonance). For example, in aldehydes C–H stretching absorption usually appears as a doublet (~2820 cm^{-1} and 2720 cm^{-1}) due to interaction between C–H stretching (fundamental band) and the overtone of C–H deformation (bending vibration).

Applications of infrared spectroscopy

Infrared spectroscopy is a very important tool used to determine the structures of organic compounds. A great advantage of IR spectroscopy is that it can study virtually any sample state from liquids to solutions, pastes, powders, films, fibres, and so on; all can be examined by the judicious use of sampling techniques.

Table 17.4 gives the characteristic IR absorption frequencies of important functional groups that help in their identification

Infrared spectrum is usually studied under two regions

(a)   Functional group region   (4000 – 1500 cm^{-1})

(b)   The finger print region   (1500 – 667 cm^{-1})

The higher frequency region 4000 – 1500 cm^{-1} is called the functional group region. The characteristic stretching frequencies of all the important functional groups such as OH, NH_2, C=O, etc., lie in this region. The region below 1500 cm^{-1} (1500–667 cm^{-1}) is rich in absorptions caused by bending vibrations and those resulting from the stretching vibrations of C—C, C—O and C—N bonds. These bands are unique to an organic compound just like finger prints are characteristic to an individual. Hence, this region is termed as the fingerprint region.

Table 17.4 Characteristic IR absorption frequencies of important functional groups that help in their identification

Group	Type of vibration	Region (in cm⁻¹) and intensity
alkane	C-H str C-C str C-H def	2960-2850(m, s) 1300-800(w) 1485-1440(m)
alkenes	>C=C-H str C=C str	3100-3000 (m) 3090-3075 (m) ~1675 (m)
non conjugate diene	C=C str	1650-1600 (v) variable
conjugate diene	C=C str	-1600 (w) ~1650 (w)
alkynes	C≡C-H str C-H def	3300 (s) 650-610 (s)
aromatic	Ar-H str C=C str C-H def	3050-3000 (v) variable 1600 (v) 1580 (v) 1500 (m_ 1450 (m) 900-700 (m)
mono substituted	C-H def	710-690 (s) 770-730 (s)
Disubstituted (meta)	C-H def	710-690 (m) 800-750 (m)
Disubstituted (ortho)	C-C def	770-735 (v, s)
Disubstituted (para)	C-H def	840-800 (m)
Alcohols Free O-H group	O-H str	3700-3500 (v, sh)
Intermolecular hydrogen bonded OH	O-H str	3400-3200 (v, b)
Intramolecular hydrogen bonded OH	O-H str	3570-3450 (v)
Primary alcohols	C-O str	1350-1260 (s) 1050 (s)
Secondary alcohols	C-O str	1350-1260 (s) 1100 (s)
Tertiary alcohols	C-O str	1400-1310 (s) 1150 (s)

| Phenols	C-O str	~1200 (s) 1410-1300 (s)
Saturated aldehydes	C=O str	1740-1720 (s)
HCHO	C=O str	1750 (s)
CH$_3$CHO	C=O str	1745 (s)
Carboxylic acids	O-H str (bonded)	3000-2500 (w, b)
Saturated aliphatic acids	C=O str	1725-1700 (s)
Primary amides	C=O str N-H str N-H str (hydrogen bonded) N-H (def)	~1690 (s) ~3500 (m) ~3400 (m) ~3350 (m) ~3180 (m) 1620-1590 (s)
Saturated esters	C=O str	1750-1735 (s)
α, β - unsaturated ester	C=O str	1730-1715 (s)
Primary amines	N-H str (sym and asym)	3500-3300 (m) (two sharp bands)
secondary	N-H str	3500-3300 (m) (one band)

Solved Problems

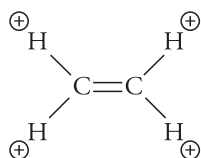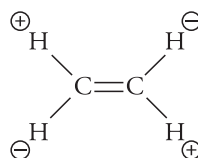1. Indicate whether the following vibrations will be IR active or inactive

Molecule		Motion
(a)	CH$_3$—CH$_3$	C—C stretching
(b)	CH$_3$—CCl$_3$	C—C stretching
(c)	SO$_2$	Symmetric stretching
(d)	CH$_2$=CH$_2$	C—H str (shown on next page)
(e)	CH$_2$=CH$_2$	C—H str (shown on next page)
(f)	CH$_2$=CH$_2$	CH$_2$ wagging (shown on next page)
(g)	CH$_2$=CH$_2$	CH$_2$ twisting (shown on next page)
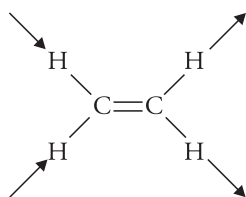
(d) C—H str
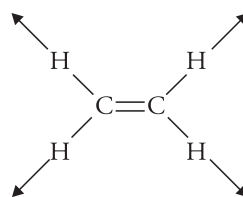
(e) C—H str

(f) CH$_2$ wagging

(g) CH$_2$ twisting

Answer (a) Inactive   **(b)** Active   **(c)** Active   **(d)** Active

         (e) Inactive   **(f)** Active   **(g)** Inactive

2. The following characteristic peaks were observed in the infrared spectrum of an organic compound having the formula C_2H_6O.

    (a) Strong band at 3300 cm^{-1} **(b)** Band at 2965 cm^{-1}

    (c) Band at 2920 cm^{-1} **(b)** Band at 1050 cm^{-1}

Name the compound.

    Solution

- Peak at 3300 cm^{-1} indicates the presence of –OH group.

- Strong band at 1050 cm^{-1} confirms the presence of primary alcoholic group.

- Band at 2965 and 2920 cm^{-1} may be due to C–H stretching.

  Hence the compound contains a primary alcoholic group. As the molecular formula is C_2H_6O, the structure of the given compound is CH_3CH_2OH (ethyl alcohol).

3. Give the characteristic absorption peaks of CH_3COOH.

    Solution

- CH_3COOH spectrum will have the following characteristic peaks.

- Broad band at 3030–3040 cm^{-1} due to hydrogen bonded O–H stretching of carboxylic acid.

- Band at 1720 cm^{-1} due to carbonyl (C=O) stretching of a saturated chain carboxylic acid.

- A band at 1280 cm^{-1} due to C–O stretching of –COOH group.

- A band at about 940 cm^{-1} due to O–H bending of –COOH group.

4. Give the characteristic absorption bands in the infrared spectrum of benzaldehyde.

Solution

- A band at 3080 cm^{-1} due to C–H stretching of benzene ring.
- Bands at 2680 cm^{-1} and 2780 cm^{-1} due to C–H str. of an aldehyde group
- A band at 1700 cm^{-1} due to C=O str. of an aromatic benzene ring.
- Bands at 745 cm^{-1} and 685 cm^{-1} due to C–H bending of monosubstituted benzene.

5. How will you differentiate between the following pairs using IR spectra?
    (a) CH_3CH_2CHO and $CH_2=CH\ CH_2OH$
    (b) CH_3CH_2OH and CH_3CHO

Solution

(a) CH_3CH_2CHO will show absorption band at 1740–1720 cm^{-1} for C=O group. $CH_2=CH\ CH_2OH$ will show the following absorption bands

- ~ 1050 cm^{-1} for primary alcohols (C–O stretching and bending)
- At 3100–3000 cm^{-1}, C=C str.
- At 905 cm^{-1} for vinyl group ($H_2C = C – C – H$) str.
- Band at 3200–3500 for OH group.

(b) CH_3CH_2OH will show the following bands.

- C – H str at 2960–2850 cm^{-1}
- Band at 3300–3400 cm^{-1} due to OH group.
- CH_3CHO shows the following absorption bands
- Band at 1745 cm^{-1} due to C=O str.

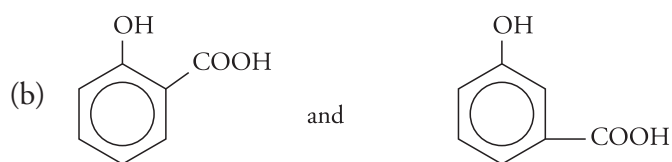**Practice problems**

1. Give the characteristic absorption bands of the infrared spectrum in the following compounds.

    (a) n-octane
    (b) $CH_3\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!CH_2\!-\!CH{=}CH_2$
    (c) CH_3CHO
    (d) $CH_3\ COCH_3$
    (e) $C_6H_5NH_2$
    (f) CH_3NH_2 (g) CH_3OH

2. Differentiate between the following compounds on the basis of their IR spectra.
    (a) CH_3COOH and CH_3COCH_3

    (b) and

3. Which of the following molecules will show IR spectrum and why?

    H_2, HCl, CH_4, CO_2, H_2O, N_2O

    [Ans   All except H_2 because it is homonuclear]

4. Where do the following absorb in the IR region?
    (i)   Primary aliphatic amine   (ii) Carbonyl in aliphatic aldehydes
    (iii) OH in phenols   (iv) OH in carboxylic acids

17.5 Rotational Spectroscopy of Diatomic Molecules

The rotational spectra results from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiations falling in the microwave region extending from 1 cm to 100 μm with an energy range of nearly 100 J/mol. The rotational energy is quantised which means that the rotational energy has certain permitted values known as rotational energy levels which may be calculated for any molecule.

Consider a diatomic molecule in which m_1 and m_2 are the masses of two atoms (assumed to be point masses) separated by a distance r, rotating about an axis passing through the centre of mass c. Let r_1 and r_2 be the distance of the two atoms from the centre of mass. The diatomic molecule is assumed to be a rigid rotor (i.e., it does not vibrate during rotation).

Although the point masses can rotate about three axes but for quantum (microscopic) objects rotation around the bond axis does not correspond to any change in the configuration of the molecule hence these point masses have two independent rotations with respect to the two axes passing through the centre of mass 'c' and perpendicular to the bond length.
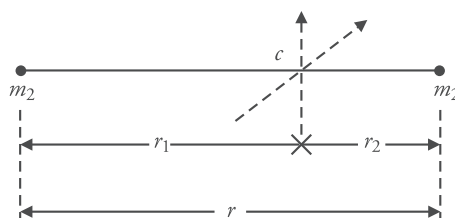

Figure 17.24   *A rigid diatomic molecule rotating about its centre of mass*

As the system is balanced about its centre of mass, we may write

$$m_1 r_1 = m_2 r_2 \tag{1}$$

Since the moment of inertia I is given by

$$I = \sum mr^2 \qquad \text{Units of I = kg m}^2$$

$$\therefore I = m_1 r_1^2 + m_2 r_2^2 \tag{2}$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \qquad \text{(Using equation 1)}$$

$$= r_1 r_2 (m_1 + m_2) \tag{3}$$

$$\because r = r_1 + r_2 \quad \text{(from the figure 1)} \tag{4}$$

$\therefore$ from eq (1) and eq (4)

$$m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$$

hence $r_1 = \dfrac{m_2 r}{m_1 + m_2}$ and $r_2 = \dfrac{m_1 r}{m_1 + m_2}$

Substituting the value of r_1 and r_2 in eq (2) we have

$$I = \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_1^2 m_2 r^2}{(m_1 + m_2)^2} \tag{6}$$

$$= \frac{m_1 m_2 (m_1 + m_2) r^2}{(m_1 + m_2)^2} = \frac{m_1 m_2 r^2}{m_1 + m_2} = \mu r^2 \tag{7}$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the molecule

Equation (7) gives the moment of inertia in terms of reduced mass μ at a distance r from the centre of mass c.

Rotational spectroscopy of linear rigid rotor molecules:

A diatomic molecule is assumed to be a linear rigid rotor, that is, its internuclear distance does not change during rotational motion.

The angular momentum L of a rotating molecule is given by $I\omega$ where ω is the angular (rotational) velocity in radians/s. Angular momentum is quantised and is given by

$$L = \sqrt{J(J + 1)} \frac{h}{2\pi} \tag{8}$$

where J = 0, 1, 2, 3 … termed as the rotational quantum numbers.

The energy E_J of a rotating molecule is given by

$$E_J = \frac{1}{2} I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \tag{9}$$

Substituting the value of L from Eq. (8)

$$E_J = J(J + 1) \frac{h^2}{8\pi^2 I} \tag{10}$$

E_J = energy in joules

h = Planck constant = 6.626×10^{-34} J s

I = moment of inertia in kg m^2

J = rotational quantum number

It is customary to express the energy difference between two rotational levels as wave number expressed in cm^{-1}. Wave number is the reciprocal of wavelength $\frac{1}{\lambda}$, hence on dividing Eq (10) by hc

$$\frac{E_J}{hc} = J(J+1)\frac{h}{8\pi^2 Ic} \tag{11}$$

The equation can be further simplified by writing it in terms of rotational constant B, which is defined as

$$B = \frac{h}{8\pi^2 Ic}$$

Units of B are wave number units, that is, cm^{-1}

Hence Eq. (11) reduces to

$$\frac{E_J}{hc} \text{ or } \bar{\upsilon} = BJ(J+1) \text{ cm}^{-1} \tag{12}$$

Putting the value of J = 0, 1, 2, 3 in Eq. (12), the wave numbers for different rotational levels will be 0, 2B, 6B, 12B, 20B, 30B, … and so on.
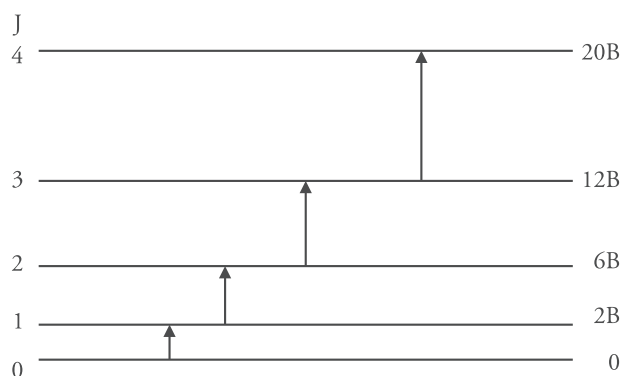

Figure 17.25   *Rotational energy levels of a rigid diatomic molecule and the allowed transitions.*

According to quantum mechanics the permissible transitions for a rigid rotator are those for which the difference in angular momentum is one. Hence the selection rule for a rotational transition is

Δ J = ± 1

This means that transitions can occur between rotational ground state (J = 0) and first excited state (J = 1) and vice versa or between levels J = 1 to J = 2 but transition cannot occur between J = 0 to J = 2.

Positive sign indicates absorption whereas negative sign indicates emission of radiation. In microwave spectroscopy usually absorption occurs; so $\Delta J = + 1$. Suppose the transition occurs from J to J + 1, then rotational frequency is given by the equation

$$\bar{v}_{[J \to (J+1)]} = B(J + 1)(J + 2) - BJ(J + 1)$$

$$= B[(J^2 + 3J + 2) - J^2 - J]$$

$$= B(2J + 2)$$

$$= 2B(J + 1)$$

$$\therefore \bar{v}_{[J \to (J+1)]} = 2B(J + 1) \text{ cm}^{-1} \tag{13}$$

$$J' = 0 \quad J'' = 1 \quad \bar{v}_{0 \to 1} = 2B \text{ cm}^{-1}$$
$$J' = 1 \quad J'' = 2 \quad \bar{v}_{1 \to 2} = 4B \text{ cm}^{-1}$$
$$J' = 2 \quad J'' = 3 \quad \bar{v}_{2 \to 3} = 6B \text{ cm}^{-1} \quad \text{etc.}$$

(where J' is the lower transitional level read as J prime and J'' is the upper transitional level read as J double prime)

It is obvious from the above expression that the difference between the two consecutive rotational spectral lines is 2B as shown in Figure 17.26
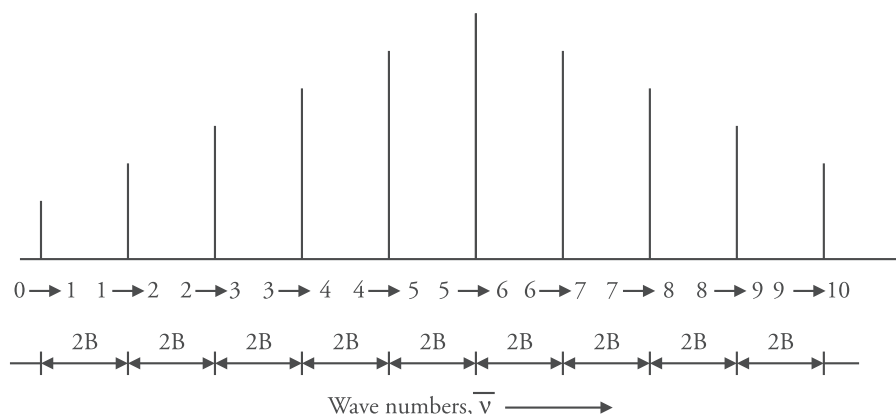

Figure 17.26 *Appearance of a rotational spectrum*

This is called the frequency separation or wave number separation. Thus the rotational spectral lines are equidistant.

Intensities of Rotational Spectral Lines

Although the rotational spectral lines are equally spaced but their intensities are not equal. The intensities increase with increasing J, pass through a maximum and then decreases as J increases further. The intensities of spectral lines depend upon the number of molecules in any energy level J. Greater the population of the energy level, greater is the number of molecules that can be promoted to the next higher level and hence greater is the intensity of absorption. Since the energy

level population is given by the Boltzmann distribution, the intensity of rotational spectral lines is also proportional to the Boltzmann distribution of molecules in the rotational energy levels, that is

$$\text{Intensity} \propto N_J / N_0 = e^{\frac{-E_J}{k_B T}}$$

where N_J and N_0 is the population of molecules in the higher and lower energy level and k_B is the Boltzman constant.

In the absence of external field all the energy levels are degenerate so the intensity of spectral lines depends upon the degeneracy factor g_J. For a diatomic molecule the degeneracy factor

$$g_J = 2J + 1 \tag{15}$$

Taking the degeneracy factor into account, Eq. (14) can be rewritten as

$$\frac{N_J}{N_0} = g_J e^{\frac{-E_J}{k_B T}} \tag{16}$$

From Eq. (15), this can be further be written as.

$$\frac{N_J}{N_0} = (2J + 1) \, e^{\frac{-E_J}{k_B T}}$$

$$\text{or Intensity} \propto \frac{N_J}{N_0} = (2J + 1) \, e^{\frac{-E_J}{k_B T}}$$

putting $E_J = \frac{hc}{\lambda} = hc\bar{\upsilon} = hcBJ(J+1)$ where $\bar{\upsilon} = BJ(J+1)$ (from Eq. 12)

hence, $\frac{N_J}{N_0} = (2J + 1) \, e^{\frac{-BJ(J+1)hc}{k_B T}}$ (17)

Figure 17.27 gives the plot of $\frac{N_J}{N_0}$ verses J for a diatomic molecule at room temperature.
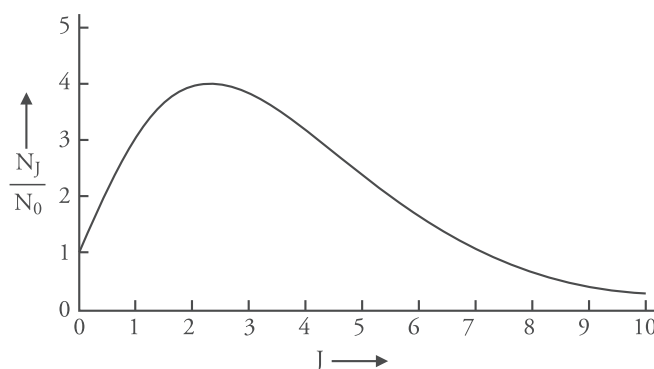

Figure 17.27   *Plot of the relative Boltzmann population verses J for a diatomic molecule*

The graph clearly shows that relative intensity passes through a maximum. The value of J corresponding to the maximum population is given by

$$J_{\max} = \left(\frac{k_B T}{2hcB} \right)^{\frac{1}{2}} - \frac{1}{2} \tag{18}$$

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

The Non-Rigid Rotor Model

When a molecule rotates with great speed, it cannot be treated as a rigid rotator because there are distortions due to centrifugal and other forces. Considering the centrifugal distortion alone the rotational energies are modified as

$$E_J \ (\text{in cm}^{-1}) \text{ or } \bar{v} = BJ(J+1) - DJ^2(J+1)^2 \tag{19}$$

D is the centrifugal distortion constant
When transition occurs from J to J+1, the wave number of the line produced is given by

$$\Delta \bar{v} = \Delta \bar{v}_{J+1} - \bar{v}_J$$

$$= \left[B(J+1)(J+2) - D(J+1)^2(J+2)^2 \right] - \left[BJ(J+1) - DJ^2(J+1)^2 \right]$$

$$= 2B(J+1) - 4D(J+1)^3$$

$$= 2(J+1)\left\{ B - 2D(J+1)^2 \right\}$$

As J increases, the factor $[B - 2D(J+1)^2]$ decreases; hence $\Delta \bar{v}$ decreases with increase in the value of J.

Applications of Microwave Spectroscopy

For a diatomic molecule, the moment of inertia I can be calculated with the knowledge of frequency separation Δv using the formula $B = h/8\pi^2 Ic$. If the masses of the two atoms in a diatomic molecule are known, then bond distance r can be calculated accurately using the formula

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

Solved Example

1. For CO molecule the rotational spectral lines appear at 3.8424 cm^{-1} for the transition J = 0 to J = 1. Calculate the moment of inertia and bond distance for the molecule.

Solution

We know that

$$\bar{v}_{J \to (J+1)} = \bar{v}_{0 \to 1} = 2B$$

Therefore 2B = 3.8424 cm⁻¹

or B = 1.9212 cm⁻¹

Moment of inertial I:

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.624 \times 10^{-27}}{8 \times 3.14 \times 3.14 \times 1.9212 \times 3 \times 10^{10}}$$

$$I = 1.4567 \times 10^{-39} \text{ g cm}^2$$

$$= 1.4567 \times 10^{-46} \text{ kg m}^2$$

reduced mass of CO ,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\frac{12}{N_A} \times \frac{16}{N_A}}{\frac{12}{N_A} + \frac{16}{N_A}} = \frac{12 \times 16}{N_A (12 + 16)}$$

where N_A = Avogadros number

$$\mu = \frac{12 \times 16}{6.023 \times 10^{23} \times 28} = 1.14 \times 10^{-23} \text{ g mol}^{-1} = 1.14 \times 10^{-26} \text{ kg mol}^{-1}$$

$$I = \mu r^2 \text{ or } r = \sqrt{\frac{I}{\mu}}$$

Bond distance $r = \sqrt{\frac{1.4567 \times 10^{-46}}{1.14 \times 10^{-26}}} = 1.13 \times 10^{-8} \text{ cm}$

$$= 1.13 \times 10^{-10} \text{ m} = 1.131 \text{Å} = 113 \text{ pm}$$

2. The internuclear distance (bond length) of carbon monoxide molecule is 1.13 Å. Calculate the energy (in joules and eV) of this molecule in the first excited rotational level. Also calculate the angular velocity of the molecule. Given atomic masses of $^{12}C = 1.99 \times 10^{-26}$ kg; $^{16}O = 2.66 \times 10^{-26}$ kg.

Solution

$r = 1.13 \text{ Å} = 1.13 \times 10^{-10}$ m

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.99 \times 10^{-26} \text{ kg} \times 2.66 \times 10^{-26} \text{ kg}}{1.99 \times 10^{-26} \text{ kg} + 2.66 \times 10^{-26} \text{ kg}} = 1.14 \times 10^{-26} \text{ kg}$$

moment of inertia $I = \mu r^2$

$$I = 1.14 \times 10^{-26} \text{ kg} \times (1.13 \times 10^{-10} \text{ m})^2 = 1.46 \times 10^{-46} \text{ kg m}^2$$

Energy of a rigid diatomic molecule is given by

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

For the first excited level, J=1; hence

$$E_1 = \frac{(6.626 \times 10^{-34})^2 \times 1(1+1)}{8 \times 3.14 \times 3.14 \times 1.46 \times 10^{-46} \text{ kg m}^2}$$

$$= 7.61 \times 10^{-23} \text{ Joule}$$

since $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

$$E_1 = \frac{7.61 \times 10^{-23}}{1.602 \times 10^{-19} \text{ J eV}^{-1}}$$

$$= 4.76 \times 10^{-4} \text{ eV}$$

angular velocity $\omega = \sqrt{\dfrac{2E_1}{I}} = \sqrt{\dfrac{2 \times 7.61 \times 10^{-23} \text{ J}}{1.46 \times 10^{-46} \text{ kg m}^2}} = 3.32 \times 10^{11} \text{ radians}^{-1}$

Practice Problems:

1. The pure rotational (microwave) spectrum of gaseous HCl consist of a series of equally spaced lines separated by 20.80 cm⁻¹. Calculate the bond distance of the molecule. The atomic masses are $^1\text{H} = 1.673 \times 10^{-27}$ kg; $^{35}\text{Cl} = 58.06 \times 10^{-27}$ kg   [Ans   129 pm]

2   For a rigid diatomic molecule the rotational constant at 300 K is 1.566 cm⁻¹, calculate the value of J_{max}.   [Ans   7.56 ≈ 8]

17.6 Vibrational–Rotational Spectra for a Diatomic Molecule

Since the rotational energy is lesser than the vibrational energy, hence vibrational motion is accompanied by rotational motion and we obtain a vibrational–rotational spectra where the transitions between rotational energy levels and vibrational energy levels occur simultaneously (i.e., both v and J change). Treating the molecule as an anharmonic oscillator the selection rules are

Δv = ± 1, ±2, ±3 and ΔJ = ± 1

ΔJ = 0 is not allowed.

Figure 17.28 gives the vibrational rotational spectrum of a diatomic molecule.
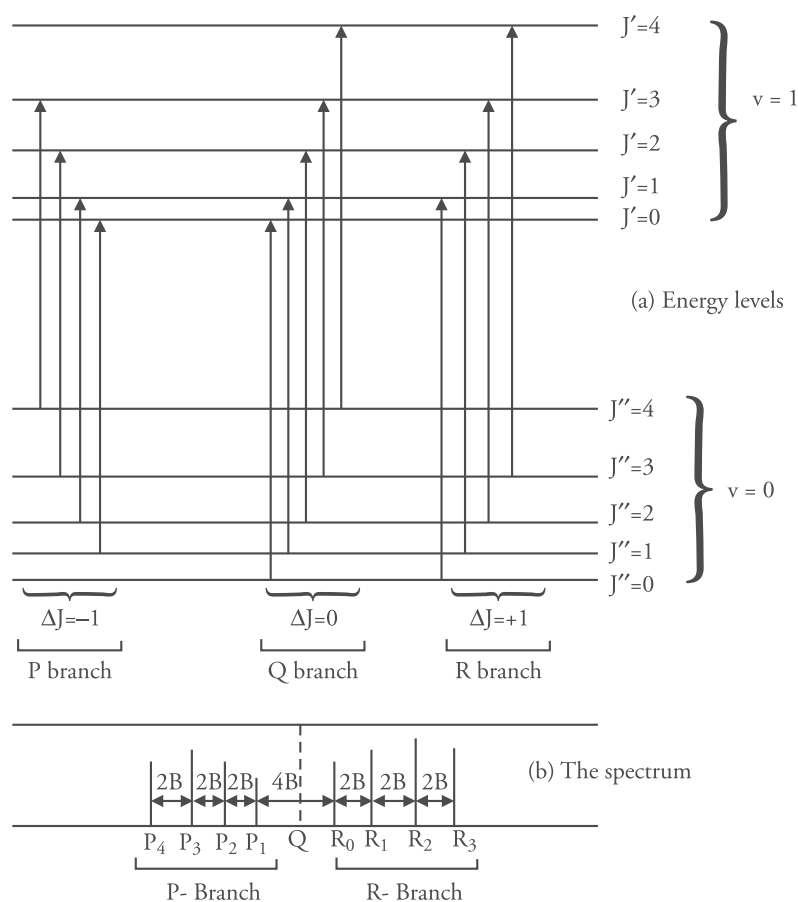
Figure 17.28   *The vibrational rotational spectrum of a diatomic molecule*

The spectra consists of equally spaced lines with spacing equal to 2B on each side of the band centre (Q). The spectral lines corresponding to $\Delta J = 0$ (forbidden) do not appear in the rotation vibration spectra (shown by dashed line Q in the spectra and termed as the band centre). The lines corresponding to $\Delta v = +1$ and $\Delta J = -1$ are called P branch are obtained at frequency lower than the fundamental frequency. Similarly lines corresponding to $\Delta v = 1$ and $\Delta J = +1$ are called R branch and appear at frequency higher than the fundamental frequency.

17.7 Nuclear Magnetic Resonance Spectroscopy

Introduction and theory

Like microwave, infrared and ultraviolet spectroscopy, nuclear magnetic resonance (NMR) spectroscopy is also a form of absorption spectroscopy. The sample absorbs electromagnetic radiations in the radiofrequency region. NMR spectrum is a plot of the frequencies of absorption peaks versus peak intensities.

To explain NMR spectroscopy, let us begin by describing the magnetic properties of the nuclei.