# 13

## Physical Properties and Chemical Constitution

CHAPTER

P hysical properties of a substance depend on the intermolecular forces which originate in the internal structure or the constitution of the molecule. Thus the determination of properties such as surface tension, viscosity, refractive index etc., can give valuable information about the structure of molecules. In the modern times the molecular spectra of substances recorded by spectroscopic techniques have proved extremely helpful in elucidating the structure of organic molecules.

Physical properties may be classified into the following types :

### (1) Additive Property

**When a property of a substance is equal to the sum of the corresponding properties of the constituent atoms, it is called an additive property.** For example, molecular mass of a compound is given by the sum of the atomic masses of the constituent atoms.

### (2) Constitutive Property

**A property that depends on the arrangement of atoms and bond structure, in a molecule, is referred to as a constitutive**

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**property.** Surface tension and viscosity and optical activity are examples of constitutive property.

### (3) Additive and Constitutive Property

**An additive property which also depends on the intramolecular structure, is called additive and constitutive property.** Surface tension and viscosity are such properties.

In this chapter we will discuss the application of some important physical properties for elucidating the constitution of molecules.

## SURFACE TENSION AND CHEMICAL CONSTITUTION

### What are Parachors ?

From a study of a large number of liquids, Macleod (1923) showed that

$$\frac{\gamma^{1/4}}{D - d} = C \qquad \qquad ...(1)$$

where $\gamma$ is the surface tension, $D$ its density and $d$ the density of vapour at the same temperature, $C$ is a constant. Sugden (1924) modified this equation by multiplying both sides by $M$, the molecular weight of the liquid,

$$\frac{M\gamma^{1/4}}{D - d} = MC = [P] \qquad \qquad ...(2)$$

The quantity $[P]$, which was constant for a liquid, was given the name **Parachor.** As $d$ is negligible compared to $D$ the equation (2) reduces to

$$\frac{M}{D}\gamma^{1/4} = [P]$$

or $\qquad V_m\gamma^{1/4} = [P] \qquad \qquad ...(3)$

where $V_m$ is the molar volume of the liquid. If surface tension ($\gamma$) is unity, from equation (3), we may write

$$[P] = V_m$$

Thus, **the parachor $[P]$ may be defined as the molar volume of a liquid at a temperatures so that its surface tension is unity.**

### Use of Parachor in Elucidating Structure

Sugden examined the experimental parachor values of several organic compounds of known molecular structure. He showed that **the parachor is both an additive and constitutive property.** That is, the parachor of an individual compound can be expressed as a sum of :

(1) **Atomic Parachors** which are the contributions of each of the atoms present in the molecule.

(2) **Structural Parachors** which are the contributions of the various bonds and rings present in the molecule.

By correlating the experimental values of parachor with molecular structure, Sugden (1924) calculated the atomic and structural parachors listed in Table 13.1. These values were further revised by Vogel (1948) on the basis of more accurate measurements of surface tension.

| TABLE 13.1. SOME ATOMIC AND STRUCTURAL PARACHORS | | | | | |
|---|---|---|---|---|---|
| | **Parachor** | | | **Parachor** | |
| **Atom** | **Sugden** | **Vogel** | **Bond or Ring** | **Sugden** | **Vogel** |
| C | 4.8 | 8.6 | Single bond | 0 | 0 |
| H | 17.1 | 15.7 | Double bond | 23.2 | 19.9 |
| O | 20.0 | 19.8 | Coordinate bond | –1.6 | 0 |
| N | 12.5 | — | 3- membered ring | 17.0 | 12.3 |
| Cl | 54.3 | 55.2 | 6- membered ring | 6.1 | 1.4 |

We can now illustrate the usefulness of parachor studies in the elucidation of molecular structure.

### (1) Structure of Benzene (Vogel)

If the Kekule formula for benzene be accepted, the value of its parachor can be calculated by using Vogel's data.
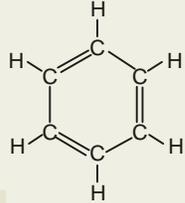


| | | |
|---|---|---|
| 6C | $6 \times 8.6$ | = 51.6 |
| 6H | $6 \times 15.7$ | = 94.2 |
| 3 (=) | $3 \times 19.9$ | = 59.7 |
| 6-membered ring | | = 1.4 |
| **Parachor of benzene** | | **= 206.9** |

Kekule formula

The experimental value of the parachor of benzene is 206.2. Since the calculated parachor tallys with that determined by experiment, the Kekule structure for benzene is supported.

### (2) Structure of Quinone (Sugden)

The two possible structural formulas proposed for quinone are :



A                    B
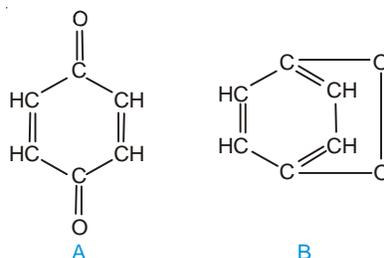
The parachors calculated for the two structures are :

| Structure A | | Structure B | |
|---|---|---|---|
| 6 C | $6 \times 4.8 = 28.8$ | 6 C | $6 \times 4.8 = 28.8$ |
| 4 H | $4 \times 17.1 = 68.4$ | 4 H | $4 \times 17.1 = 68.4$ |
| 2 O | $2 \times 20.0 = 40.0$ | 2 O | $2 \times 20.0 = 40.0$ |
| 4 (=) | $4 \times 23.2 = 92.8$ | 3 (=) | $3 \times 23.2 = 69.6$ |
| 1 six-membered ring | $1 \times 6.1 = 6.1$ | 2 six-membered rings | $2 \times 6.1 = 12.2$ |
| **Total = 236.1** | | **Total = 219.0** | |

The experimental value of parachor for quinone is 236.8. This corresponds to the parachor calculated from structure $A$. Therefore, the structure $A$ represents quinone correctly.

### (3) Structure of Nitro group (Sugden)

The parachor has also been found useful in providing information regarding the nature of bonds present in certain groups. The nitro group ($-NO_2$), for example, may be represented in three ways :



I                    II                    III
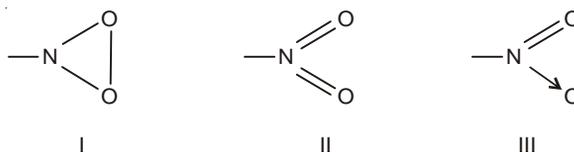
The calculated parachors are :

|  | Structure I | | Structure II | | Structure III | |
|---|---|---|---|---|---|---|
| 1 N | $1 \times 12.5 = 12.5$ | 1 N | $1 \times 12.5 = 12.5$ | 1 N | $1 \times 12.5$ | $= 12.5$ |
| 2 O | $2 \times 20.0 = 40.0$ | 2 O | $2 \times 20.0 = 40.0$ | 2 O | $2 \times 20.0$ | $= 40.0$ |
| 3-membered ring | $1 \times 17.0 = 17.0$ | 2 (=) | $2 \times 23.2 = 46.4$ | 1 (=) | $1 \times 23.2$ | $= 23.2$ |
|  |  |  |  | 1 ($\rightarrow$) | $1 \times (-1.6)$ | $= -1.6$ |
|  | **Total = 69.5** |  | **Total = 98.9** |  | **Total = 74.1** | |

The experimental value of parachor for $-NO_2$ group has been found to be 73.0. This approximates to the calculated parachor for structure III which is, therefore, the appropriate structure of $-NO_2$ group.

## VISCOSITY AND CHEMICAL CONSTITUTION

**Viscosity is largely due to the intermolecular attractions which resist the flow of a liquid.** Therefore, some sort of relationship between viscosity and molecular structure is to be expected. Viscosity is also dependent on the shape, size and mass of the liquid molecules. The following general rules have been discovered.

### (1) Dunstan Rule

Dunstan (1909) showed that viscosity coefficient ($\eta$) and molecular volume ($d/M$) were related as:

$$\frac{d}{M} \times \eta \times 10^6 = 40 \; to \; 60$$

This expression holds only for normal (unassociated) liquids. For associated liquids this number is much higher than 60. For example, the number for benzene ($C_6H_6$) is 73, while for ethanol ($C_2H_5OH$) it is 189. This shows that benzene is a normal liquid, while ethanol is an associated one. Thus Dunstan rule can be employed to know whether a given liquid is normal or associated.

### (2) Molar Viscosity

The molar surface of a liquid is $(M/d)^{2/3}$. **The product of molar surface and viscosity is termed molar viscosity.** That is,

$$\text{Molar Viscosity} = \text{Molar surface} \times \text{Viscosity}$$
$$= \left(\frac{M}{d}\right)^{2/3} \times \eta$$

Thorpe and Rodger (1894) found that molar viscosity is an additive property at the boiling point. They worked out the molar viscosity contributions of several atoms (C, H, O, S, etc) and groups. From these, they calculate the molar viscosity of a liquid from its proposed structure. By comparing this value with the experimental one, they were able to ascertain the structure.

### (3) Rheochor

Newton Friend (1943) showed that if molecular volume ($M/d$) be multiplied by the eighth root of the coefficient of viscosity, it gives a constant value [R]. The quantity [R] is termed *Rheochor*.

$$\frac{M}{d} \times \eta^{1/8} = [R]$$

**The Rheochor may be defined as the molar volume of the liquid at the temperature at which its viscosity is unity.** Like parachor, rheochor is both additive and constitutive. However it has not proved of much use in solving structural problems.

## DIPOLE MOMENT

In a molecule such as HCl, the bonding electron pair is not shared equally between the hydrogen atom and the chlorine atom. The chlorine atom with its greater electronegativity, pulls the electron pair closer to it. This gives a slight positive charge ($+q$) to the hydrogen atom and a slight negative charge ($-q$) to the chlorine atom.

$$\overset{}{\text{H}}\!\!\!\xrightarrow{\ \ \ \ }\!\!\!\overset{..}{\text{Cl}} \qquad \text{or} \qquad \overset{+q}{\text{H}}\!\!\!\xrightarrow{\ \ \ \ }\!\!\!\overset{-q}{\text{Cl}}$$
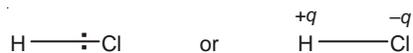
Such a molecule with a positive charge at one end and a negative charge at the other end is referred to as an **electric dipole** or simply **dipole.** The degree of polarity of a polar molecule is measured by its dipole moment, $\mu$ (Greek *mu*).
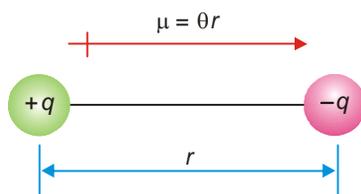


■ **Figure 13.1**
**An electric dipole of the magnitude $\mu = \theta r$.**

The dipole moment of a polar molecule is given by the product of the charge at one end and the distance between the opposite charges. Thus,

$$\mu = q \times r$$

The dipole moment ($\mu$) is a vector quantity. **It is represented by an arrow with a crossed tail.** The arrow points to the negative charge and its length indicates the magnitude of the dipole moment. Thus a molecule of HCl may be represented as

$$\text{H}\!\!\!\xrightarrow{\ +\ }\!\!\!\text{Cl}$$

### Unit of Dipole Moment

The CGS unit for dipole moment is the **debye,** symbolised by **D,** named after the physical chemist Peter Debye (1884-1966). A debye is the magnitude of the dipole moment ($\mu$) when the charge ($q$) is $1 \times 10^{-10}$ esu (electrostatic units) and distance ($r$) is $1\text{Å}$ ($10^{-8}$ cm).

$$\mu = q \times r = 1 \times 10^{-10} \times 10^{-8} = 1 \times 10^{-18} \text{ esu cm}$$

Thus $\qquad\qquad\qquad\qquad 1\,\text{D} = 1 \times 10^{-18}$ esu cm

In SI system, the charge is stated in Coulombs ($C$) and distance in metres ($m$). Thus dipole moment is expressed in Coulomb metres ($Cm$). The relation of debye to SI units is given by the expression coulomb:

$$1\,\text{D} = 3.336 \times 10^{-30}\,\text{Cm}$$

### Determination of Dipole Moment

**Electric condenser.** The dipole moment of a substance can be experimentally determined with the help of an electric condenser (Fig. 13.2). The parallel plates of the condenser can be charged by connecting them to a storage battery. When the condenser is charged, an electric field is set up with field strength equal to the applied voltage ($V$) divided by the distance ($d$) between the plates.

Polar molecules are electric dipoles. The net charge of a dipole is zero. When placed between the charged plates, it will neither move toward the positive plate nor the negative plate. On the other hand, it will rotate and align with its negative end toward the positive plate and positive end toward the negative plate. Thus all the polar molecules align themselves in the electric field. This orientation of dipoles affects the electric field between the two plates as the field due to the dipoles is opposed to that due to the charge on the plates.
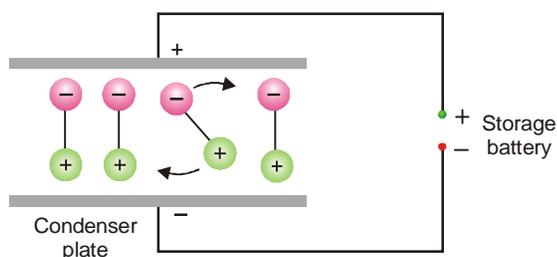
**Figure 13.2**
**Polar molecules rotate and align in electric field.**

The plates are charged to a voltage, say $V$, prior to the introduction of the polar substance. These are then disconnected from the battery. On introducing the polar substance between the plates, the voltage will change to a lower value, $V'$. Just how much the voltage changes depends on the nature of the substance. The ratio $\varepsilon = V/V'$ is a characteristic property of a substance called the **dielectric constant.** The experimentally determined value of dielectric constant is used to calculate the dipole moment.

## Use of Rotational Spectra

The rotational spectrum of a polar molecule is examined in the gas phase. It is found that the spectral lines shift when the sample is exposed to a strong electric field. From the magnitude of this effect (**Stark effect**), the dipole moment can be determined very accurately. The dipole moments of some simple molecules are listed in Table 13.2.

| TABLE 13.2. DIPOLE MOMENTS OF SOME SIMPLE MOLECULES IN THE VAPOUR PHASE | | | |
|---|---|---|---|
| **Formula** | **$\mu(D)$** | **Formula** | **$\mu(D)$** |
| $H_2$ | 0 | $CO_2$ | 0 |
| $Cl_2$ | 0 | $CH_4$ | 0 |
| HF | 1.91 | $CH_3Cl$ | 1.87 |
| HCl | 1.08 | $CH_2Cl_2$ | 1.55 |
| HBr | 1.80 | $CCl_4$ | 0 |
| HI | 0.42 | $NH_3$ | 1.47 |
| $BF_3$ | 0 | $H_2O$ | 1.85 |

## BOND MOMENT

Any bond which has a degree of polarity has a dipole moment. This is called **Bond moment.** The dipole moment of H—H bond is zero because it is nonpolar. The dipole moment of the H—Cl bond is 1.08 D because it is polar.

In a diatomic molecule, the bond moment corresponds to the dipole moment of the molecule. The dipole moments of the halogen halides shown below also indicate their bond moments.

| 1.91D | 1.08 D | 1.80 D | 0.42 D |
|---|---|---|---|
| H————F | H————Cl | H————Br | H————I |

The bond moment decreases with decreasing electronegativity of the halogen atom.

When a molecule contains three or more atoms, each bond has a dipole moment. For example,



The net dipole moment of the molecule is the vector resultant of all the individual bond moments. If a molecule is symmetrical having identical bonds, its dipole moment is zero. That is so because the individual bond moments cancel each other out.

## DIPOLE MOMENT AND MOLECULAR STRUCTURE

Dipole moment can provide important information about the geometry of molecular structure. If there are two or more possible structures for a molecule, the correct one can be identified from a study of its dipole moment.

### (1) $H_2O$ has a Bent Structure

Water molecule ($H_2O$) can have a linear or bent structure.



(a)                                                    (b)
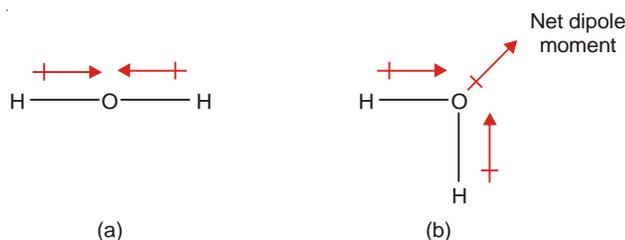
The dipole moments of the two O—H bonds in structure (a) being equal in magnitude and opposite in direction will cancel out. The net dipole moment ($\mu$) would be zero. In structure (b) the bond moment will add vectorially to give a definite net dipole moment. Since water actually has a dipole moment (1.85 D); its linear structure is ruled out. Thus water has a bent structure as shown in (b).

### (2) $CO_2$ has a Linear Structure and $SO_2$ a Bent Structure

Carbon dioxide has no dipole moment ($\mu = 0$). This is possible only if the molecule has a linear structure and the bond moments of the two C = O units cancel each other.
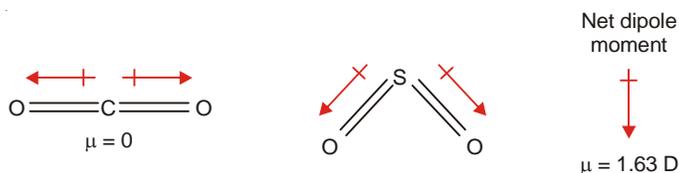


On the other hand, $SO_2$ has a dipole moment ($\mu = 1.63$). Evidently, here the individual dipole moments of the two S = 0 bonds are not cancelled. Thus the molecule has a bent structure. The vector addition of the bond moments of the two S = 0 units gives the net dipole moment 1.63 D.

### (3) $BF_3$ has a Planar and $NH_3$ a Pyramid Structure

The dipole moment of boron trifluoride molecule is zero. This is possible if the three B—F bonds are arranged symmetrically around the boron atom in the same plane. The bond moments of the three B—F bonds cancel each others effect and the net $\mu = 0$.

Boron trifluoride, $BF_3$
($\mu = 0$)

Ammonia, $NH_3$
($\mu = 1.47$ D)
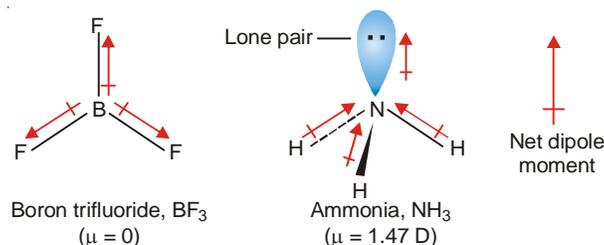
Ammonia molecule ($NH_3$) has a dipole moment ($\mu = 1.47$ D). This is explained by its pyramidal structure. The three H atoms lie in one plane symmetrically with N atom at the apex of the regular pyramid. The dipole moments of the three N—H bonds on vector addition contribute to the net dipole moment. In addition, there is a lone pair of electrons on the N atom. Since it has no atom attached to it to neutralise its negative charge, **the lone pair makes a large contribution to the net dipole moment.** Thus the overall dipole moment of ammonia molecule is the resultant of the bond moments of three N—H bonds and that due to lone-pair.

It may be recalled that the high dipole moment of water ($H_2O$) can also be explained by the presence of two lone-pairs of electrons on the oxygen atom.



(a)

(b)
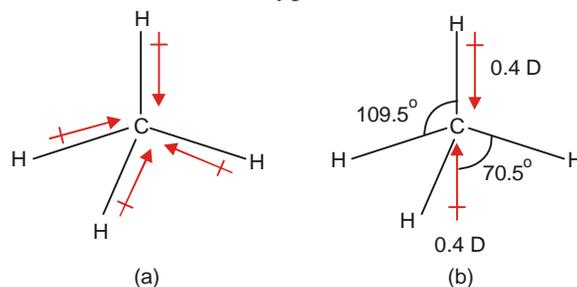
■ **Figure 13.3**
**Dipole moment of methane molecule.**

## (4)  $CH_4$ **has Tetrahedral Structure**

Methane ($CH_4$) has zero dipole moment, despite the fact that each C—H bond possesses a dipole moment of 0.4 D. This can be explained if the molecule has a symmetrical tetrahedral structure (Fig. 13.3).

Each C—H bond in the pyramidal $CH_3$ group contributes $\frac{1}{3}\mu$ ($\mu \cos 70.5$) to the resultant dipole moment. Thus the net dipole moment of $CH_3$ group is equal to $\mu$. This acts in a direction opposite to that of the fourth C—H bond moment, thereby cancelling each other.

## (5)  **Identification of** *cis* **and** *trans* **Isomers**

The dipole moment can be used to distinguish between the *cis* and *trans* isomers. The *cis* isomer has a definite dipole moment, while the *trans* isomer has no dipole moment ($\mu = 0$). For example,



*cis*-Dichloroethylene
($\mu = 2.96$ D)

*trans*-Dichloroethylene
($\mu = 0$)
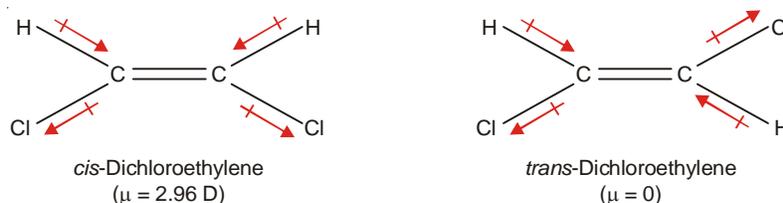
In the *cis* isomer, the bond moments add vectorially to give a net dipole moment. The *trans* isomer is symmetrical and the effects of opposite bond moments cancel so that $\mu = 0$.

**(6) Identification of *ortho*, *meta* and *para* Isomers**

Benzene has a dipole moment zero. Thus it is a planar regular hexagon. Let us examine the dipole moments of the three isomeric dichlorobenzenes ($C_6H_4Cl_2$). Since the benzene ring is flat, the angle between the bond moments of the two C—Cl bonds is 60° for ortho, 120° for *meta* and 180° for *para*. On vector addition of the bond moments in each case, the calculated dipole moments are *ortho* 2.6 D, *meta* 1.5 D and *para* 0 D. These calculated values tally with the experimental values. Thus the above structures of o-, m - and p-isomers stand confirmed. In general, **a para disubstituted benzene has zero dipole moment, while that of the ortho isomer is higher than of meta isomer.** This provides a method for distinguishing between the isomeric *ortho*, *meta* and *para* disubstituted benzene derivatives.



μ = 2.6 D            μ = 1.5 D            μ = 0
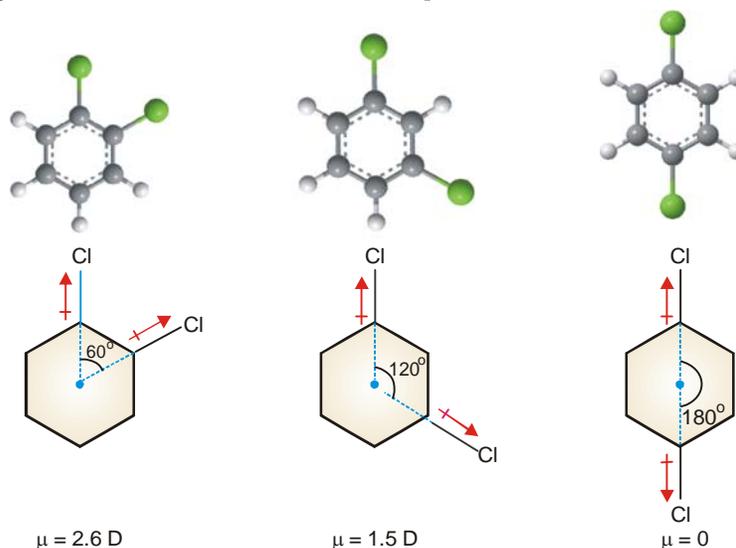
■ **Figure 13.4**
**Dipole moments of *ortho*, *meta* and *para* dichlorobenzenes.**

**Dipole Moment and Ionic Character**

The magnitude of the dipole moment of a diatomic molecule determines its ionic character. Let us consider an HBr molecule whose measured dipole moment ($\mu_{exp}$) is 0.79 D and bond distance $(r) = 1.41 \text{Å}$.

If the molecule were completely ionic ($H^+Br^-$), each of the ions will bear a unit electronic charge, $e$ ($4.8 \times 10^{-10}$ esu). Thus the dipole moment of the ionic molecule ($\mu_{ionic}$) can be calculated.

$$\mu_{ionic} = e \times r = (4.8 \times 10^{-10} \text{ esu}) (1.41 \times 10^{-8} \text{ cm})$$
$$= 6.77 \text{ D}$$

But the experimental dipole moment ($\mu_{exp}$) of $H^{\delta+}$—$Br^{\delta-}$, which determines its actual fractional ionic character, is 0.79 D. Therefore,

$$\% \text{ ionic character of HBr} = \frac{\mu_{expt}}{\mu_{ionic}} \times 100$$

$$= \frac{0.79 D}{6.77 D} \times 100 = 11.6$$

Hence HBr is 12% ionic in character.

## MOLAR REFRACTION AND CONSTITUTION

The molar refraction ($R_M$) is an additive and constitutive property. **The molar refraction of a molecule is thus a sum of the contributions of the atoms (atomic refractions) and bonds (bond**

**refractions) present.** From the observed values of $R_M$ of appropriate known compounds, the atomic refractions of different elements and bonds have been worked out. Some of these are listed in Table 13.3.

**TABLE 13.3. SOME ATOMIC AND BOND REFRACTIONS IN cm³ mol⁻¹ FOR D LINE (VOGEL 1948)**

| Atom | $R_{atomic}$ | Bond | $R_{bond}$ |
|---|---|---|---|
| C | 2.591 | C–H | 1.676 |
| H | 1.028 | C=C | 4.166 |
| O (in C=O) | 2.010 | C ≡ C | 1.977 |
| O (in –O–) | 1.643 | 6C ring | –0.15 |
| O (in –O–H) | 1.518 | 5C ring | –0.10 |
| Cl | 5.844 | 4C ring | 0.317 |
| Br | 8.741 | | |

The molar refraction of the proposed structure of a molecule can be computed from the known atomic and bond refractions. If this value comes out to be the same as the experimental value, the structure stands confirmed. Some examples are given below for illustrating the use of molar refractions in elucidating molecular structure.

(1) **Acetic acid.** The accepted structural formula of acetic acid is
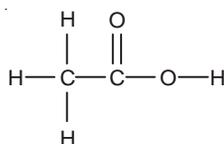


The molar refraction ($R_M$) may be computed from the atomic refractions of the constituent atoms as

| 2C | $2 \times 2.591$ | = | 5.182 |
|---|---|---|---|
| 4H | $4 \times 1.028$ | = | 4.112 |
| 1O (in OH) | $1 \times 1.518$ | = | 1.518 |
| 1O (in C=O) | $1 \times 2.010$ | = | 2.010 |
| | **Total $R_M$** | **=** | **12.822 cm³ mol⁻¹** |

The value of molar refraction of acetic acid found by determination of its refractive index is 13.3 cm³ mol⁻¹. There is a fairly good agreement between the calculated and experimental values. It confirms the accepted formula of acetic acid.

(2) **Benzene.** The molar refraction of benzene ($C_6H_6$) on the basis of the much disputed Kekule formula may be calculated as :



Kekule formula for benzene
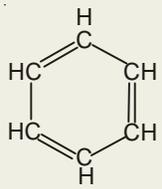
| 6C | $6 \times 2.591$ | = | 15.546 |
|---|---|---|---|
| 6H | $6 \times 1.028$ | = | 6.168 |
| 3C=C | $3 \times 1.575$ | = | 4.725 |
| 16 C ring | | = | –0.150 |
| **Total $R_M$** | | **=** | **26.289 cm³ mol⁻¹** |

The observed values of $R_M$ for benzene is 25.93. This is in good agreement with the calculated value. Hence the Kekule formula for benzene is supported.

(3) **Optical Exaltation.** A compound containing conjugated double bonds (C=C—C=C) has a higher observed $R_M$ than that calculated from atomic and bond refractions. The molar refraction is thus said to be exalted (raised) by the presence of a conjugated double bond and the phenomenon is called **optical exaltation.** For example, for **hexatriene,**

$$CH_2=CH—CH=CH—CH=CH_2$$
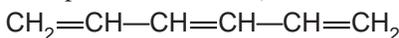
the observed value of $R_M$ is 30.58 cm$^3$ mol$^{-1}$ as against the calculated value 28.28 cm$^3$ mol$^{-1}$.

If present in a closed structure as benzene, the conjugated double bonds do not cause exaltation.

## OPTICAL ACTIVITY AND CHEMICAL CONSTITUTION

Optical activity is a purely constitutive property. This is shown by a molecule which is **dissymmetric or chiral** (pronounced ky-ral). A chiral molecule has no plane of symmetry and cannot be superimposed on its mirror image. One such molecule is lactic acid, $CH_3CHOHCOOH$. Assuming that carbon has a tetrahedral structure, lactic acid can be represented by two models I and II.



Model I
(+)-Lactic acid

Mirror

Model II
(−)-Lactic acid
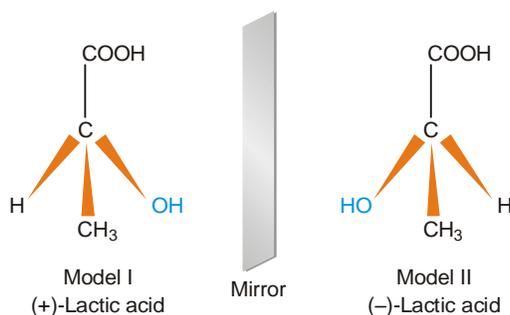
■ **Figure 13.5**
**Two chiral models of lactic acid.**

If you try to place model II on model I so that any two similar groups coincide, the remaining two will clash. Suppose you try to coincide COOH and H by rotating model II, the groups OH and $CH_3$ will go in opposite positions. The fact that model II cannot be superimposed on model I shows that they represent different molecules. **The molecules that are nonsuperimposable mirror images, are called enantiomers.**

Lactic acid is actually known to exist in two enantiomeric forms (optical isomers). They have the same specific rotation but with sign changed.

(+)-Lactic acid $\qquad [\alpha]_D^{25} = +3.8°$

(−)-Lactic acid $\qquad [\alpha]_D^{25} = -3.8°$
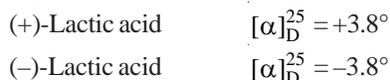
A third variety of lactic acid is obtained by laboratory synthesis. It is, in fact, a mixture of equimolar amounts of (+)- and (−)-lactic acid. It is represented as (±)-lactic acid and is termed **racemate** or **racemic mixture.** Evidently, a racemic mixture has zero optical rotation.
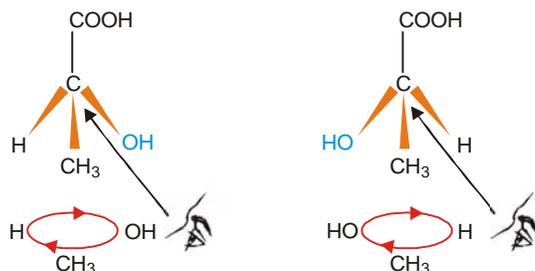


■ **Figure 13.6**
**The interaction of polarized light with the opposite orientation of groups produces opposite rotatory powers in two enantiomers of lactic acid.**

## What Makes a Molecule Optically Active ?

Lactic acid molecule is chiral because it contains a carbon joined to four different groups H, OH, $CH_3$, COOH. A carbon bearing four different groups is called an **asymmetric** or **chiral carbon.** It may be noticed that the arrangement of groups about the asymmetric carbon is either clockwise or anticlockwise. It is the interaction of polarized light with these opposite arrangements of groups which is responsible for the opposite rotatory powers of (+)- and (−)-lactic acids.

## Presence of Chiral Carbons, Not a Necessary Condition for Optical Activity

A molecule containing two or more chiral (or asymmetric) carbons may not be optically active. **It is, in fact, the chirality of a molecule that makes it optically active.**

Let us consider the example of tartaric acid which contains two chiral carbon atoms. It exists in three stereoisomeric forms.
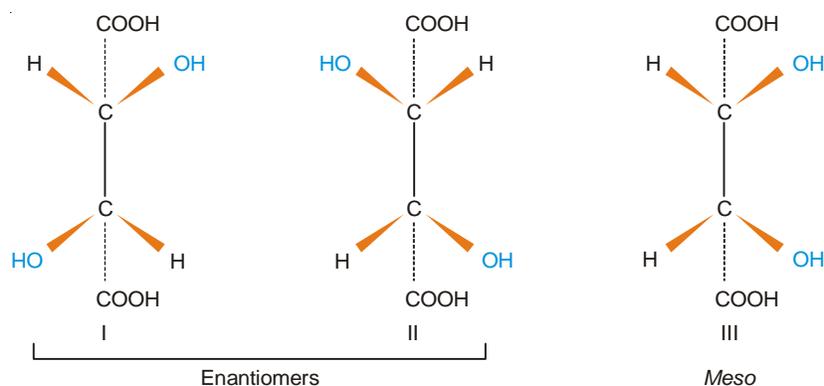


The forms I and II are nonsuperimposable mirror images. They represent an enantiomeric pair. The form III has a plane of symmetry and divides the molecule into two identical halves. The arrangement of groups about the two chiral carbons is opposite to each other. The optical rotation due to the upper half of the molecule is cancelled by the rotation of the lower half. **Thus the form III although containing two chiral carbons, is optically inactive.** This is called the **meso form.**

Tartaric acid is actually known to exist in three stereoisomeric forms :

$$(+)\text{-Tartaric acid} \qquad [\alpha]_D^{20} = +12.7°$$
$$(-)\text{-Tartaric acid} \qquad [\alpha]_D^{20} = -12.7°$$
$$\textit{meso}\text{-Tartaric acid} \qquad [\alpha]_D^{20} = 0°$$
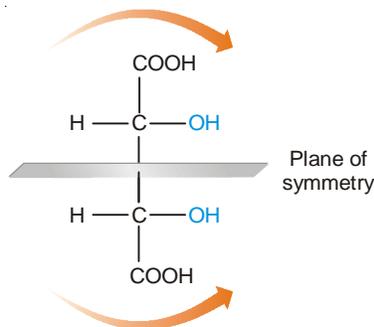


An equimolar mixture of (+)-tartaric acid and (−)-tartaric acid is referred to as **racemic tartaric acid** or ( ± )-tartaric acid.

## MAGNETIC PROPERTIES

On the basis of their behaviour in a magnetic field, substances can be divided into two classes.

(1) **Diamagnetic substances** which are slightly repelled or pushed out of the magnetic field. Most substances belong to this class.

(2) **Paramagnetic substances** which are slightly attracted or pulled into the magnetic field. Some substances belong to this class.

A few substances are intensely paramagnetic and retain their magnetic property when removed from the magnetic field. These are known as **ferromagnetic substances.** Examples are iron, cobalt and nickel.

### Measurement of Magnetic Properties

The magnetic properties of substances can be measured with the help of a **magnetic balance** or **Gouy balance** (Fig. 13.7). The sample under investigation is first weighed without the magnetic field.
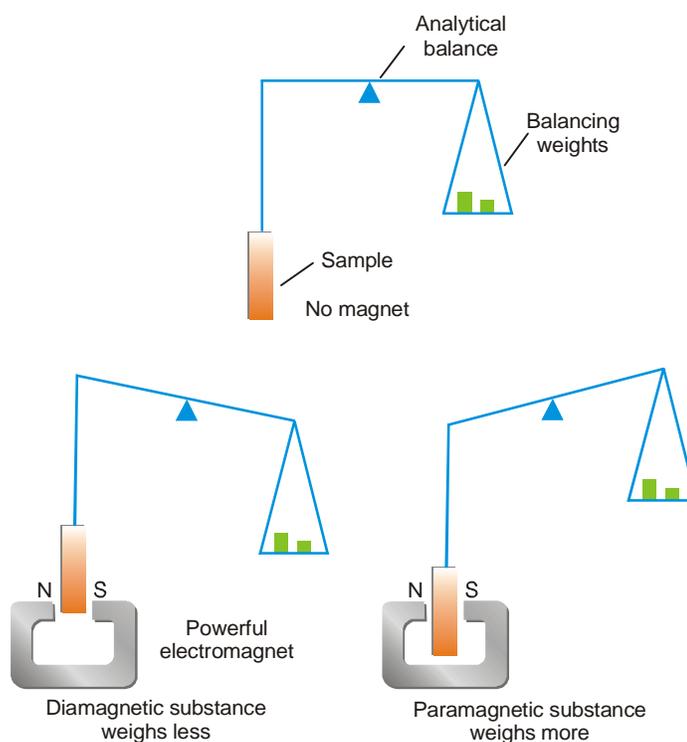


■ **Figure 13.7**
**Whether a substance is diamagnetic or paramagnetic can be determined by a Gouy balance.**

Then it is suspended between the poles of a strong electromagnet. A diamagnetic substances is pushed out of the field and weighs less. On the other hand, a paramagnetic substance is pulled into the field and weighs more. **The difference in the sample weight when there is no magnetic field and the weight on the application of the field, determines the magnetic susceptibility of the substance.**

### Why a Substance is Paramagnetic or Diamagnetic ?

A single electron spinning on its own axis generates a magnetic field and behaves like a small magnet. Therefore a substance with an orbital containing an unpaired electron will be attracted into the poles of an electromagnet. It follows that **any atom, ion or molecule that contains one or more**

**unpaired electrons will be paramagnetic.** When an orbital contains two electrons (↑↓), their spins are opposed so that their magnetic fields cancel each other. Thus an atom, ion or molecule in which all electrons are paired will not be paramagnetic.



(a)                    (b)
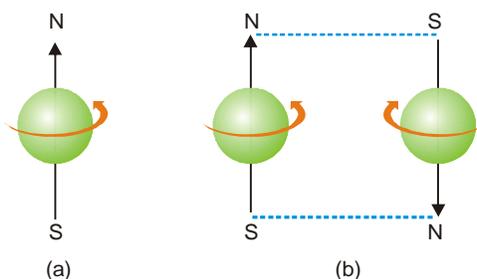
**■ Figure 13.8**
**(*a*) An electron spinning on its axis behaves like a tiny magnet; (*b*) Two electrons with opposite spins cancel the magnetic field of each other.**

Most atoms or molecules have all their electrons paired (↑↓). These are repelled by a magnetic field and are said to be **diamagnetic.** This can be explained in a simple way. When an external magnetic field is applied to such a substance, it sets up tiny currents in individual atoms as if in a wire. These electric currents create new electric field in the opposite direction to the applied one. This causes the repulsion of the substance when placed in a magnetic field.

The fact that an atom, ion or molecule is paramagnetic if it contains one or more unpaired electrons and diamagnetic if it contains all paired electrons, can be illustrated by taking simple examples. The configuration of sodium shows that it has one unpaired electron and it is paramagnetic. Magnesium having all paired electrons is diamagnetic.



Iron has four incompleted *d* orbitals having single electrons with spins aligned. The magnetic field due to these four unpaired electrons adds up to make iron strongly paramagnetic or **ferromagnetic.**



3d orbitals of Fe
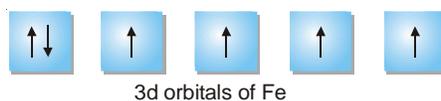
## Magnetic Properties and Molecular Structure

A paramagnetic molecule or ion contains one or more unpaired electrons. **Each spinning electrons behaves like a magnet and has a magnetic moment.** The magnetic moment ($\mu$) of a molecule or ion due to the spin of the unpaired electrons is expressed by the formula

$$\mu = \sqrt{n(n+2)}$$

where $\mu$ is the magnetic moment in **magnetons** and $n$ the number of unpaired electrons. The number of unpaired electrons can be determined by measuring magnetic moment with the help of **Gouy balance.** This has proved of great use in establishing the structure of certain molecules and complex ions.

### (1) Oxygen Molecule

The Lewis structure of oxygen molecule postulates the presence of a double bond between the two oxygen atoms.

$$:\ddot{O}::\ddot{O}: \qquad or \qquad :\ddot{O}=\ddot{O}:$$
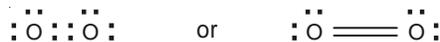
Such a structure would predict oxygen to be diamagnetic. Actually, oxygen is found to be slightly, paramagnetic showing the presence of two unpaired electrons. Thus the correct structure of oxygen molecule is written as

$$:\ddot{O}:\ddot{O}: \qquad or \qquad :\ddot{O}—\ddot{O}:$$

Unpaired electrons
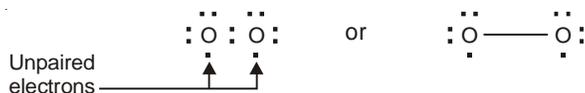
### (2) Complex Ions

The geometrical structures of complex ions can be inferred from a study of their magnetic moments. For example, the complex $K_2NiCl_4$ is paramagnetic with a magnetic moment corresponding to two unpaired electrons. Thus the complex ion $NiCl_4{}^{2-}$ must have the same configuration of the $3d$ electrons as in nickel.

3d                    4s          4p

↑↓  ↑↓  ↑↓  ↑  ↑

The $4s$ and three $4p$ orbitals could be involved in $sp^3$ hybridization, giving a tetrahedral structure for $NiCl_4^{2-}$ ion. This has been confirmed experimentally.
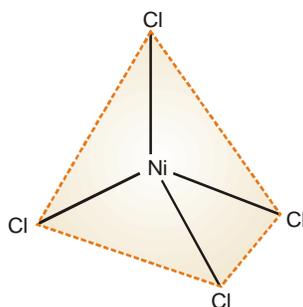


■ **Figure 13.9**
**Tetrahedral structure of $NiCl_4^{2-}$ as predicted by a study of its dipole moment.**

## MOLECULAR SPECTRA

We have studied previously (Chapter 1) how hydrogen atom exhibits an **atomic spectrum** by interaction with electromagnetic radiation. This was explained in terms of energy levels in the atom. An electron can pass from one energy level to another by emission or absorption of energy from the incident radiation. When an electron drops from a higher energy level $E_2$ to another of lower energy $E_1$, the surplus energy is emitted as radiation of frequency $v$. That is

$$E_2 - E_1 = hv$$

where $h$ is Planck's constant. Each frequency of emitted radiation records a bright line in the spectrum. On the other hand, if the transition of an electron occurs from a lower energy level $E_1$, to another of higher energy $E_2$, energy $(hv)$ is absorbed. This records a dark line in the spectrum.

A spectrum which consists of lines of different frequencies is characteristic of atoms and is termed **Line Spectrum or Atomic Spectrum.**

A spectrum which consists of bright lines produced by emission of electromagnetic radiation is termed **Emission Spectrum.**

A spectrum which consists of dark lines produced by absorption of incident radiation, is termed **Absorption Spectrum.**

Similar to atoms, molecules also have energy levels. Thus molecules exhibit **Molecular spectra** by interaction with electromagnetic radiations. These spectra may consist of bright or dark bands composed of groups of lines packed together. Such spectra are termed **Band spectra.** Molecules generally exhibit spectra made of dark bands caused by absorption of incident radiation. These are referred to as **Absorption Band spectra** and provide valuable information about the chemical structure of molecules. However, molecular spectra are relatively complex. Before taking up their systematic study, it is necessary to acquaint the student with the Electromagnetic spectrum as also the Molecular energy levels.

## ELECTROMAGNETIC SPECTRUM

Visible light, X-rays, microwaves, radio waves, etc., are all electromagnetic radiations. Collectively, they make up the **Electromagnetic spectrum** (Fig. 13.10).
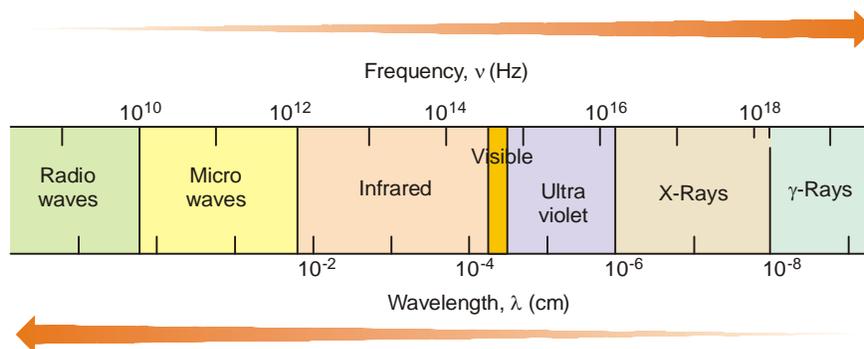


■ **Figure 13.100**
**The Electromagnetic Spectrum.**
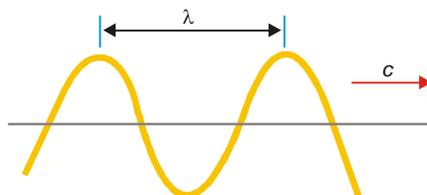


■ **Figure 13.11**
**A single electromagnetic wave.**

Electromagnetic radiations consist of electrical and magnetic waves oscillating at right angles to each other. They travel away from the source with the velocity of light (C) in vacuum. Electromagnetic waves are characterised by :

(1) **Frequency ($v$) :** It is the number of successive crests (or troughs) which pass a stationary point in one second. The unit is **hertz;** $1\text{Hz} = 1\text{s}^{-1}$.

(2) **Wavelength ($\lambda$) :** It is the distance between successive crests (or troughs). $\lambda$ is expressed in centimetres (cm), metres (m), or nanometres ($1\text{nm} = 10^{-9}\,\text{m}$).

(3) **Wave number $\bar{v}$ :** It is the reciprocal of wavelength, Its unit is $\text{cm}^{-1}$.

$$\bar{v} = \frac{1}{\lambda}$$

**Relation Between Frequency, Wavelength and Wave Number**

Frequency and wavelength of an electromagnetic radiation are related by the equation

$$\nu\lambda = c \qquad \qquad ...(1)$$

or
$$\nu = \frac{c}{\lambda} \qquad \qquad ...(2)$$

where $c$ is the velocity of light. It may be noted that wavelength and frequency are inversely proportional. That is, **higher the wavelength lower is the frequency;** lower the wavelength higher is the frequency.

Further
$$\bar{\nu} = \frac{1}{\lambda} \; cm^{-1} \qquad \qquad ...(3)$$

From (2) and (3)
$$\nu = c\bar{\nu}$$

## Energy of Electromagnetic Radiation

Electromagnetic radiation behaves as consisting of discrete wave-like particles called **Quanta** or **Photons.** Photons possess the characteristics of a wave and travel with the velocity of light in the direction of the beam. The amount of energy corresponding to 1 photon is expressed by **Planck's equation.**

$$E = h\nu = h\,c/\lambda$$

where $E$ is the energy of 1 photon (or quantum), $h$ is Planck's constant ($6.62 \times 10^{-27}$ ergs-sec); $\nu$ is frequency in hertz; and $\lambda$ is wavelength in centimetres.

If $N$ is the Avogadro number, the energy of 1 mole photons can be expressed as

$$E = \frac{Nhc}{\lambda} = \frac{2.85 \times 10^{-3}}{\lambda} \; kcal/mol$$

This shows that per photon, **electromagnetic radiation of longer wavelength has lower energy. Radiation of higher frequency has higher energy.**

## MOLECULAR ENERGY LEVELS

The internal energy of a molecule is of three types : (*a*) Rotational energy; (*b*) Vibrational energy; and (*c*) Electronic energy.

## Rotational Energy

It involves the rotation of molecules about the centre of gravity or of parts of molecules.



Axis of          Axis of
rotation         rotation
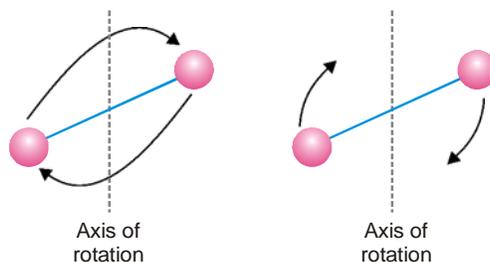
■ **Figure 13.12**
**Molecular rotations in a linear molecule.**

## Vibrational Energy

It is associated with stretching, contracting or bending of covalent bonds in molecules. The bonds behave as spirals made of wire.

## Electronic Energy

It involves changes in the distribution of electrons by splitting of bonds or the promotion of electrons into higher energy levels.



Stretching          Contracting          Bending
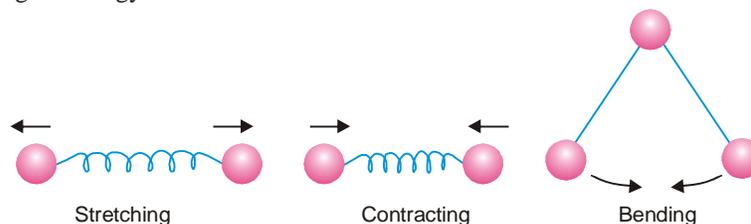
■ **Figure 13.13**
**Vibrations within molecules.**
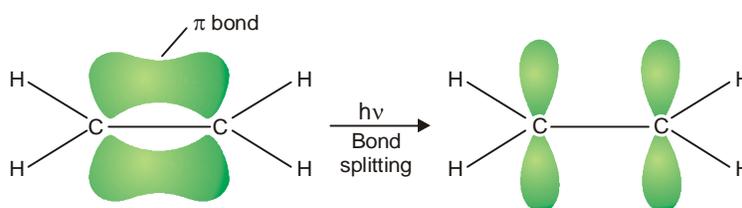


■ **Figure 13.14**
**Splitting of pi bond by absorption of energy.**

## The Three types of Molecular energy Quantized

The three types of molecular energy *viz.*, rotational, vibrational and electronic are quantized. Thus there are quantum levels for each of the three kinds of energy. A change in rotational level, in vibrational level, or electronic energy level will occur by absorption or emission of one or more quanta of energy. The difference between the successive energy levels (the quantum) of electronic changes is 450 kJ mol$^{-1}$; for vibrational changes 5 to 40 kJ mol$^{-1}$; and for rotational changes, about 0.02 kJ mol$^{-1}$.The three types of energy levels are illustrated in Fig. 13.15. It may be noted that electronic energy levels are relatively far apart. For each electronic level there exist a number of closely spaced vibrational energy levels. Likewise each vibrational level contains a large number of rotational energy levels.



Electronic          Vibrational          Rotational
levels              levels               levels
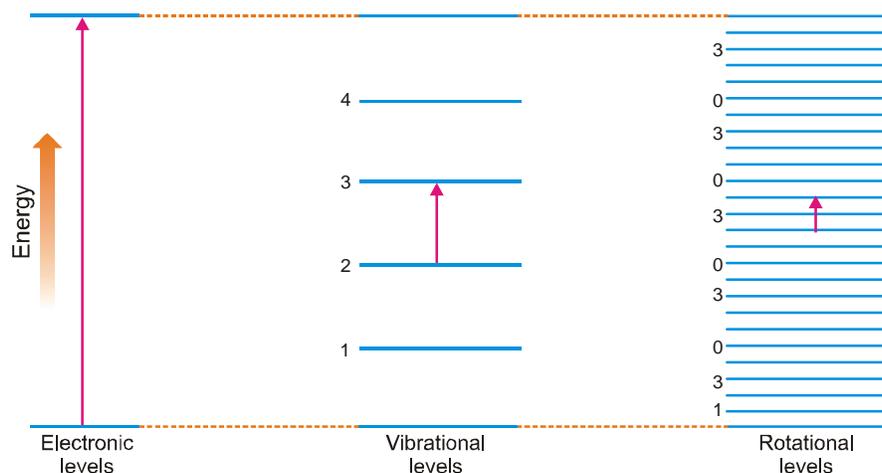
■ **Figure 13.15**
**An illustration of the electronic, vibrational and rotational energy levels.**

## ABSORPTION SPECTROPHOTOMETER

Absorption spectrum of a given sample is obtained experimentally with the help of an apparatus called **absorption spectrophotometer.** It is shown in Fig. 13.16. Light of a range of wavelengths from the source is passed through the sample. The wavelengths corresponding to allowed molecular transitions are absorbed. The transmitted light passes through a prism which resolves it into various wavelengths. It is then reflected from the mirror onto a detector. The prism is rotated so that light of each given wavelength is focussed on the detector. The response of the detector is recorded on a chart by means of a motor-driven pen synchronized with the prism movement. The pen recorder records the intensity of radiation as a function of frequency and gives the absorption spectrum of the sample.
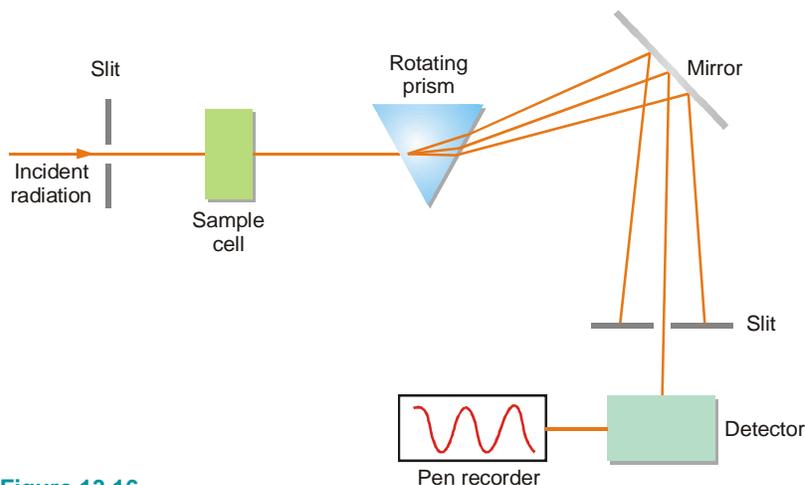
■ **Figure 13.16**
**Schematic diagram of an Absorption Spectrophotometer.**

## TYPES OF MOLECULAR SPECTRA

To obtain a molecular spectrum, the substance under examination is exposed to electromagnetic radiations of a series of wavelengths. Molecules of the substance absorb certain wavelengths in order to be excited to higher electronic, vibrational or rotational energy levels. **The series of wavelengths absorbed in each case gives a distinct molecular spectrum.** Thus there are three main types of molecular spectra.

**(1) Electronic Spectra**

These are caused by absorption of high energy photons which can send electrons to higher energy levels. The *electronic spectra* are within the visible or ultraviolet regions of the electromagnetic spectrum.

**(2) Vibrational Spectra**

Lower energy photons cause changes in vibrational energy levels. The spectra thus obtained are referred to as *vibrational spectra*. These are in the near infrared region (near to the visible region).

**(3) Rotational Spectra**

Still lower energy photons cause changes in the rotational levels in the molecules. These spectra are called the *rotational spectra*. These spectra are in the far infrared or microwave region.

In order to use numbers of reasonable size, different units are used for different types of spectra. In ultraviolet and visible spectra the radiation is stated as a wavelength in nm or as a wave-number in $cm^{-1}$. In infrared spectra, wave-numbers in $cm^{-1}$ are often used. In microwave or NMR spectra, frequencies are expressed in Hz (or MHz).
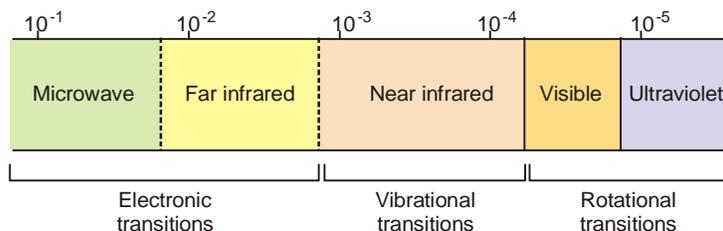
**■ Figure 13.17**
**The regions of the electromagnetic spectrum and associated energy transitions in molecules.**

When energy of the incident photon is large enough to produce changes in electronic levels, it can also bring, about changes in vibrational and rotational levels. Therefore some spectra are **electronic-vibrational-rotational spectra.** Similarly, the photon that is capable of bringing about changes in vibrational levels can also cause rotational energy changes. Thus vibrational -rotational spectra result. Pure **rotational spectra** involve only small energy changes which cannot bring about vibrational or electronic changes.

## ROTATIONAL SPECTRA

**Rotational spectra are used to determine the bond lengths in heteronuclear molecules, A–B.** Such molecules have a permanent dipole moment and while rotating produce electric field. Thus electromagnetic radiations interact with these molecules and produce rotational spectra. The rotational spectra are observed in the far infrared and microwave regions.

We have shown in Fig. 13.15 that the rotational energy levels are spaced equally. For a molecule A–B, the energies of the rotational levels are given by the formula

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

where $J$ is the rotational quantum number and $I$ the moment of inertia.

As a rule, a **molecule can be excited to only the next higher rotational level by absorption of energy.** If the molecule is raised from quantum number $J = 0$ to $J = 1$, the energy difference $\Delta E$ is given by

$$\Delta E = E_{J=1} - E_{J=0} \qquad \text{...(2)}$$

Using equation (1), we can write

$$\Delta E = \frac{h^2}{8\pi^2 I} 1(1+1) - 0 = \frac{h^2}{4\pi^2 I} \qquad \text{...(3)}$$

From (2) it follows

$$hv = \Delta E = \frac{h^2}{4\pi^2 I}$$

or

$$v = \frac{h}{4\pi^2 I}$$

In terms of the wave numbers,

$$\bar{v} = \frac{v}{c} = \frac{h}{4\pi^2 I c} \qquad \text{...(4)}$$

The **moment of inertia** of the molecule $A - B$ is defined as

$$I = \left(\frac{m_A m_B}{m_A + m_B}\right) r^2$$

where $m_A$ and $m_B$ are the masses of the respective atoms and $r$ is the bond length. The term inside the bracket is called **reduced mass** and is denoted by $\mu$. Thus,

$$I = \mu r^2$$

Substituting the value of $I$ in equation (4),

$$\bar{v} = \frac{h}{4\pi^2 c \mu r^2}$$

Hence

$$r = \sqrt{\frac{h}{4\pi^2 c \mu \bar{v}}}$$

$\bar{v}$ is measured from the experimental spectrum and all other quantities under the square root are known for a given molecule. Hence $r$ can be calculated.

**SOLVED PROBLEM.** The spacing between the lines in the rotational spectrum of HCl is 20.68 cm$^{-1}$. Calculate the bond length.

**SOLUTION**

Applying the equation

$$\bar{v} = \frac{h}{4\pi^2 Ic}$$

$$20.68 \text{ cm}^{-1} = \frac{h}{4\pi^2 Ic} = \frac{55.96 \times 10^{-40} \text{g cm}}{I}$$

$$I = 2.71 \times 10^{-40} \text{ g cm}^2$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Since $m_A$ and $m_B$ are atomic masses in grams divided by the Avogadro number, we have

$$\mu = \frac{(1.008)\,(35.457)\,/\,(6.02 \times 10^{23})}{(1.008 + 35.457)\,/\,(6.02 \times 10^{23})} = 0.980 \text{ g}$$

Hence

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.71 \times 10^{-40} \text{ g cm}^2}{0.980 \text{ g}}} = 1.663 \times 10^{-20} \text{ cm}$$

$$= \mathbf{1.663 \times 10^{-12}} \text{ Å}$$

## VIBRATIONAL SPECTRA

Atoms in a molecule are in constant vibrational motion about mean or equilibrium positions. The modes of vibration may be bond stretching, bond bending, rocking motions and the like. The vibratory motion in a diatomic molecule is illustrated in Fig. 13.18.
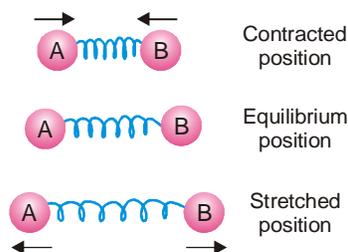


■ **Figure 13.18**
**Vibratory motion in a diatomic molecule, A–B.**

The energy involved in each mode of vibration is quantized and any change in the energy levels produces absorption at particular wavelengths in the infrared spectrum. Thus we can state that : **the vibrational spectra are those caused in the infrared region by the transitions in the vibrational levels in different modes of vibrations.**

The vibrational energy levels of a molecule are given by the relation

$$E_v = \left( v + \frac{1}{2} \right) h v_0 \qquad \qquad ...(1)$$

where $v$ is the vibrating quantum number and $v_0$ is the frequency of the vibration. Thus the energy absorbed in promoting a molecule from its lowest energy level to the next highest, that is from $v_0$ to $v_1$ is given by the relation

$$\Delta E = \frac{3}{2} h v_0 - \frac{1}{2} h v_0 = h v_0 \qquad \qquad ...(2)$$

Also for a diatomic system as shown in Fig. 13.18. executing a harmonic motion, we have

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \qquad \qquad ...(3)$$

where $\mu$ is reduced mass and $k$ is stretching **force constant.** The force constant is a measure of the strength of the bond between two atoms. Knowing the value of $v_0$ from the absorption spectrum, the value of $k$ can be calculated.

Combining equations (3) and (1), the energy difference, $\Delta E$, between two adjacent vibrational levels for a diatomic molecule is given by the equation

$$\Delta E = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

A molecule whose vibration can cause a change in its dipole moment, absorbs energy in the infrared region. Such a molecule is called **infrared active.** Thus H – Cl molecule possesses a dipole moment (atomic charge × bond distance). Its stretching vibration alter the bond distance and its dipole moment alters. Therefore H – Cl molecule is infrared active. On the other hand, a molecule of hydrogen, H – H, has no dipole moment, nor produces one on vibration. It is infrared inactive.



(STRETCHING)    (CONTRACTION)

Most molecules containing three or more atoms have several modes of vibration. Some of these modes are infrared active, while others are not. The infrared active modes only show prominent peaks in the infrared spectrum. For example, $CO_2$ molecule has four modes of vibration which can be represented as in Fig. 13.19. The mode (1) is called a **symmetrical stretch** which does not involve a dipole moment change. It is IR inactive. The **asymmetric stretch** in mode (2) does involve a dipole moment change and is IR active. The modes (3) and (4) involve bending in the same plane and out of plane respectively. These modes are degenerate (same energy) and cause only one characteristic absorption in the IR spectrum. Actually, the IR spectrum of $CO_2$ shows prominent absorption frequencies of 667 $cm^{-1}$ (bending motion) and 2349 $cm^{-1}$ (asymmetric stretch).
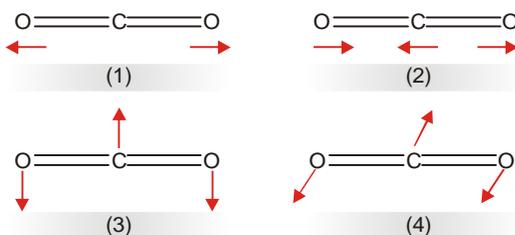


**■ Figure 13.19**
**The vibrational modes of carbon dioxide molecule.**

## INFRARED SPECTROSCOPY

An infrared (IR) spectrometer subjects a compound to infrared radiation in the 5000-667 cm$^{-1}$ (2µm) range. Although this radiation is weak, it does supply sufficient energy for bonds in the molecule to vibrate by **Stretching** or **Bending** (Fig. 13.20). The atoms of a molecule can be considered as linked by springs that are set in motion by the application of energy. As the molecule is subjected to the individual wavelengths in the 5000-667 cm$^{-1}$ range, it absorbs only those possessing exactly the energy required to cause a particular vibration. Energy absorptions are recorded as bands (peaks) on chart paper.



Stretching vibrations          Bending vibrations
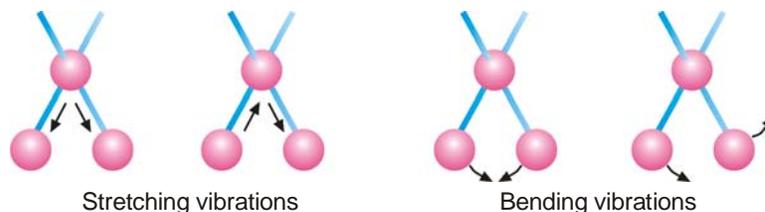
■ **Figure 13.20**
**Molecular vibrations caused by infrared radiation.**

Since different bonds and functional groups absorb at different wavelengths, an infrared spectrum is used to determine the structure of organic molecules. For example, carbon-carbon triple-bond is stronger than a carbon-carbon double bond and requires a shorter wavelength (greater energy) to stretch. The same considerations apply to carbon-oxygen and carbon-nitrogen bonds.

| $C \equiv C$ | $C = O$ | $C \equiv N$ |
|---|---|---|
| 2100–2200 cm$^{-1}$ | 1690–1750 cm$^{-1}$ | 2210–2260 cm$^{-1}$ |
| $C = C$ | $C - O$ | $C - N$ |
| 1620–1680 cm$^{-1}$ | 1050–1400 cm$^{-1}$ | 1050–1400 cm$^{-1}$ |

Thus, from the position of an absorption peak, one can identify the group that caused it. Fig. 13.21 shows the general areas in which various bonds absorb in the infrared.
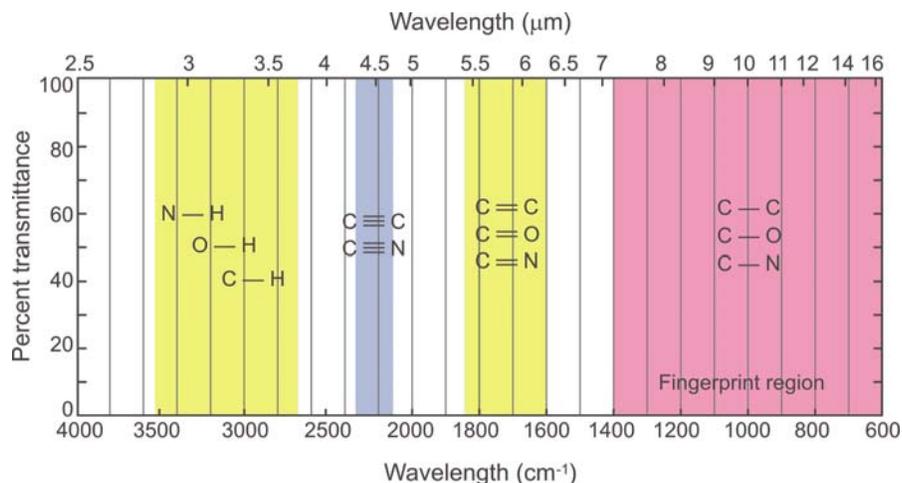


■ **Figure 13.21**
**Area of absorption for various bonds in the infrared.**

An infrared spectrum is usually studied in two sections :

(1) **Functional Group Region.** The area from 5000 cm$^{-1}$ to 1300 cm$^{-1}$ is called the functional group region. The bands in this region are particularly useful in determining the type of functional groups present in the molecule.

(2)  **Fingerprint Region.** The area from $1300\ cm^{-1}$ to $667\ cm^{-1}$ is called the fingerprint region. A peak-by-peak match of an unknown spectrum with the spectrum of the suspected compound in this region can be used, much like a fingerprint, to confirm its identity. Table 9.1 shows some characteristic infrared absorption bands. Fig. 13.22 shows some examples of infrared spectra.
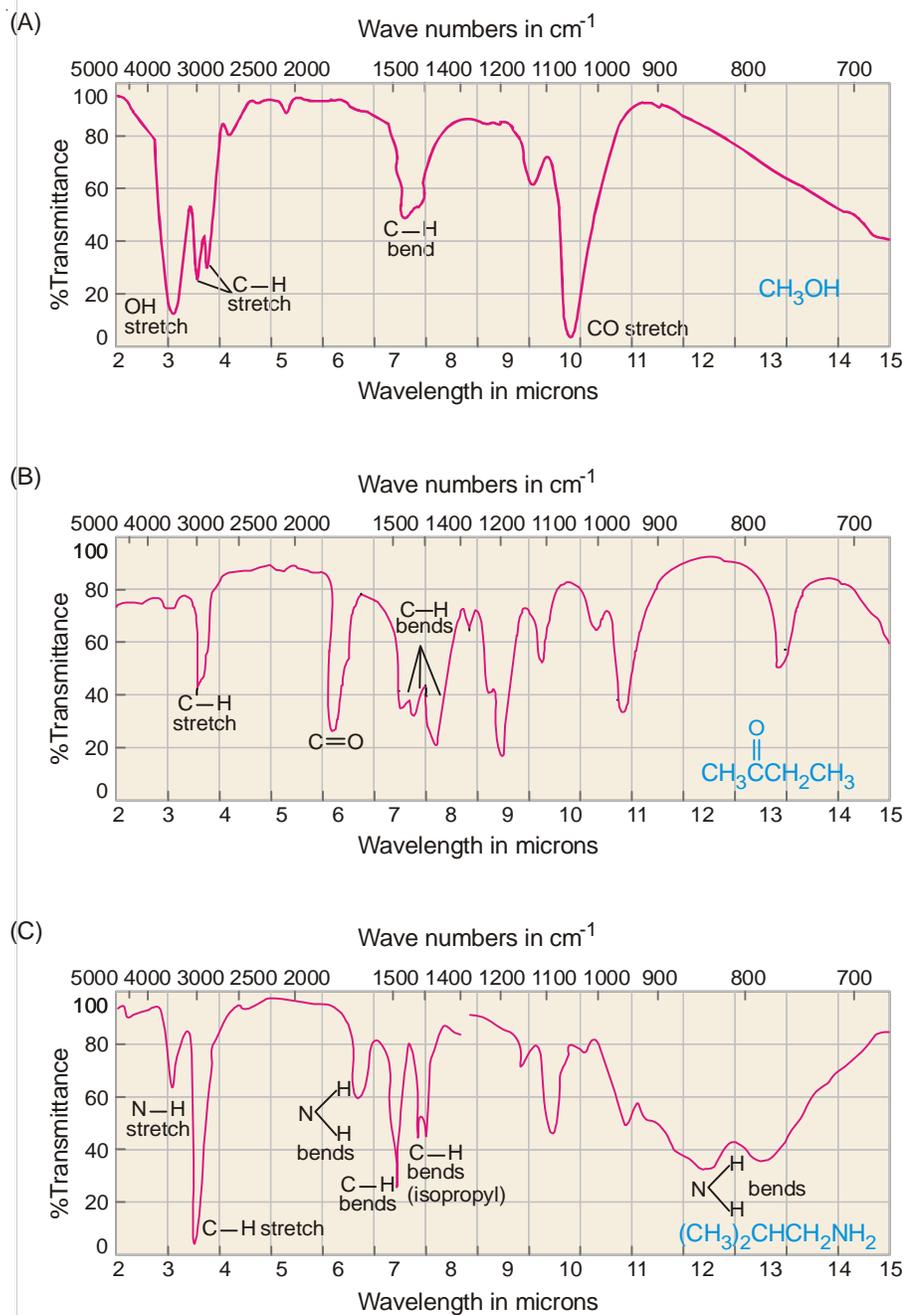


**Figure 13.22**

**Some examples of IR spectra. (A) is Methanol. (B) is Butanone. (C) is  Isobutylamine.**

| Range in cm⁻¹ | Bond (Remarks) |
|---|---|

**TABLE 13.4 : SOME CHARACTERISTIC IR ABSORPTION BANDS**

| Range in cm⁻¹ | Bond (Remarks) |
|---|---|
| 1050-1400 | C–O   (in ethers, alcohols, esters) |
| 1050-1400 | C–N   (in amines) |
| 1315-1475 | C–H   (in alkanes) |
| 1340-1500 | $NO_2$   (two peaks) |
| 1450-1600 | C=C   (in aromatic rings ; several peaks) |
| 1620-1680 | C=C   (in alkenes) |
| 1630-1690 | C=O   (in amides) |
| 1690-1750 | C=O   aldehydes, ketones, esters) |
| 1700-1725 | C=O   (in carboxylic acids) |
| 1770-1820 | C=O   (in acid chlorides) |
| 2100-2200 | C≡C |
| 2210-2260 | C≡N |
| 2500 | S–H |
| 2700-2800 | C–H   (of aldehyde group) |
| 2500-3000 | O–H   (of COOH group) |
| 3000-3100 | C–H   (C is part of aromatic ring) |
| 3330 | C–H   (C is part of C≡C) |
| 3020-3080 | C–H   (C is part of C=C) |
| 2800-3000 | C–H   (in alkanes) |
| 3300-3500 | N–H   (in amines, amides) |
| 3200-3600 | O–H   (in H-bonded ROH) |
| 3600-3650 | O–H |

## SUMMARY OF IR SPECTROSCOPY

(1) Absorption of infrared radiation causes covalent bonds within the molecule to be promoted from one vibrational energy level to a higher vibrational energy level.

(2) Stronger bonds require greater energy to vibrate (stretch or bend). Therefore, such bonds absorb infrared radiation of shorter wavelengths.

(3) Different functional groups absorb infrared radiation at different wavelengths, and their presence or absence in a molecule can be determined by examination of an IR spectrum.

(4) No two compounds have exactly identical infrared spectra.

## ULTRAVIOLET–VISIBLE    SPECTROSCOPY

In ultraviolet-visible (UV-Vis) spectroscopy, the 200-750 nm region of the ultraviolet spectrum is used. This includes both the visible region (400-750 nm) and near ultraviolet region (200-400 nm). Radiation of these wavelengths is sufficiently energetic to cause the promotion of loosely held electrons, such as nonbonding electrons or electrons involved in a π-bond to higher energy levels. For absorption in this particular region of ultraviolet spectrum, the molecule must contain conjugated double bonds. If the conjugation is extensive, the molecule will absorb in the visible region.

The ultraviolet-visible spectrum is composed of only a few broad bands of absorption (Fig. 13.23). The wavelength of maximum absorbance is referred to as $\lambda_{max}$. The following points should be kept in mind while interpreting a UV-Vis spectrum.

(1) Nonconjugated alkenes show an intense absorption below 200 nm and is therefore inaccessible to most commonly used UV spectrometers. For example, ethylene has $\lambda_{max}$=171 nm. This absorption comes from the light-induced promotion of a $\pi$-electron to the next higher energy level.
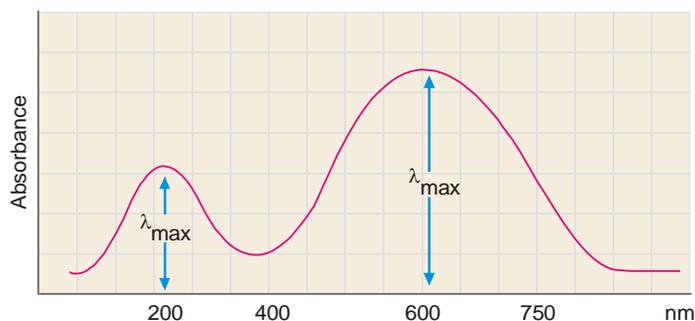


**Figure 13.23**
**A sample UV-Vis spectrum.**

(2) Nonconjugated carbonyl compounds have a very weak absorption band in the 200-300 nm region. This band arises from excitation of one of the nonbonding electrons (from an unshared pair) to the next higher energy level. For example,

Acetone
279 nm

Cyclohexanone
291 nm
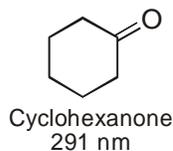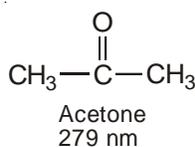
(3) When a molecule contains two or more nonconjugated carbon-carbon double bonds, the UV spectrum is that expected of a simple alkene. However, when the double bonds are conjugated, $\lambda_{max}$ is shifted to longer wavelengths. For example,

$CH_2$=CH—$CH_2$—$CH_2$—CH=$CH_2$

1,5-Hexadiene
178 nm

$CH_3CH$=CH—CH=$CHCH_3$

2,4-Hexadiene
227 nm
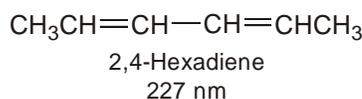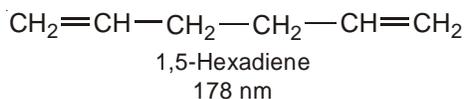
(4) Conjugation of a carbon-carbon double bond and a carbonyl group shifts the $\lambda_{max}$ of both groups to longer wavelengths. For example,

$(CH_3)_2C$=CH—$CH_2CH_3$        180 nm

$(CH_3)_2CH$—$CH_2$—C—$CH_3$   283 nm

$(CH_3)_2C$=CH—C—$CH_3$   230 nm (for C=C)
327 nm (for C=O)
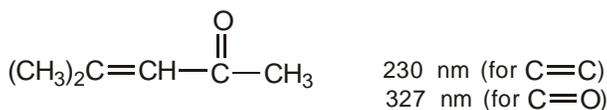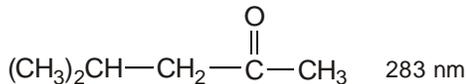
(5) As the number of double bonds in conjugation increases, $\lambda_{max}$ also increases. For example,

$CH_2$=CH—CH=$CH_2$

1,3-Butadiene
215 nm

Benzene
257 nm
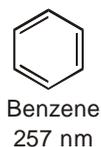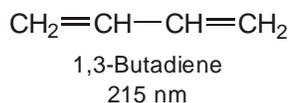
**SUMMARY OF UV-VIS SPECTROSCOPY**

(1)  Absorption of ultraviolet-visible radiation (200-700 nm) causes electrons within molecules to be promoted from one energy level to a higher electronic energy level.

(2)  If an organic compound does not absorb UV-Vis radiation, it means that the compound does not contain conjugated double bonds.

(3)  If an organic compound absorbs UV-Vis radiation, it means that the compound contains a carbonyl group or conjugated double bonds. For example, conjugated dienes, carbonyl compounds, and aromatic compounds all absorb in the UV-Vis region.

## NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Nuclear magnetic resonance spectroscopy involves absorption of electromagnetic radiation in the radio frequency region. Absorption of radiowaves in the presence of magnetic field is accompanied by a special type of nuclear transition, and for this reason we call this type of spectroscopy nuclear magnetic resonance (NMR) spectroscopy.

The nuclei of certain atoms behave as if they are spinning charges. Any spinning charge creates a magnetic field and behaves as if it were a tiny bar magnet. Of the three nuclei most common in organic compounds ($^1$H, $^{12}$C, and $^{16}$O)only the hydrogen nucleus proton behaves in this manner.

When a proton in an organic molecule is placed in a strong magnetic field, it can align with the field or against it. In the more stable low-energy state, it is aligned *with* the magnetic field (Fig. 13.24). If energy is supplied in the form of radiowaves of exactly the right frequency, radiation will be absorbed and the nucleus will "flip" and align *against* the applied magnetic field in the higher energy state. For example, a proton in an applied field of 14000 gauss requires a frequency of 60 million hertz (cycles per second) for this particular transition. When this exact frequency is applied, it is absorbed, and the absorption recorded on a chart paper. In practice, either the magnetic field can be held constant and the radio frequency varied, or more commonly, the radio frequency can be held constant and the magnetic field varied. Fig. 13.25 shows the various components of a NMR spectrometer.
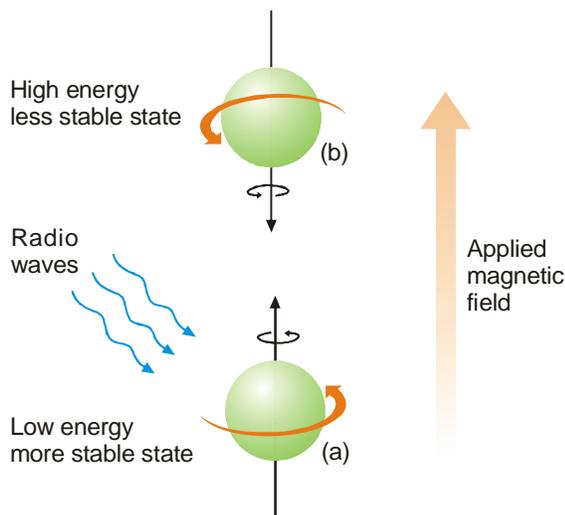


■ **Figure 13.24**

**Orientation of a spinning hydrogen nucleus in an applied magnetic field.**
**(*a*) shows the nucleus in more stable low-energy state. (*b*) shows the nucleus in less stable high-energy state. Applying radiowaves *flips* the nucleus from the more stable 'aligned' state (*a*) to less stable 'nonaligned' state (*b*).**

**Position of Signals ; Chemical Shifts.** The main purpose of NMR is not to detect the presence of

protons in a molecule. It can distinguish between protons in different chemical environments within the molecule. Protons on benzene ring, or on a carbon bearing a chlorine, or on a carbon adjacent to a carbonyl group absorb radio frequency energies at different applied magnetic fields, and appear at different locations (chemical shifts) on the recording paper. Also, the position of absorption is relatively constant for protons in a particular chemical or structural environment. Hence, *the number of signals recorded on the NMR chart paper indicates the number of different types of protons in a molecule.* The position of the peak can give information about the molecular structure in the vicinity of the proton.

To understand the application of NMR, we should know what are **Equivalent** and **Non-equivalent protons**. Equivalent protons are protons in the same molecule that are chemically indistinguishable. In other words, equivalent protons are positioned in structurally and chemically equivalent areas in the molecule. As an example, let us consider the following compounds.
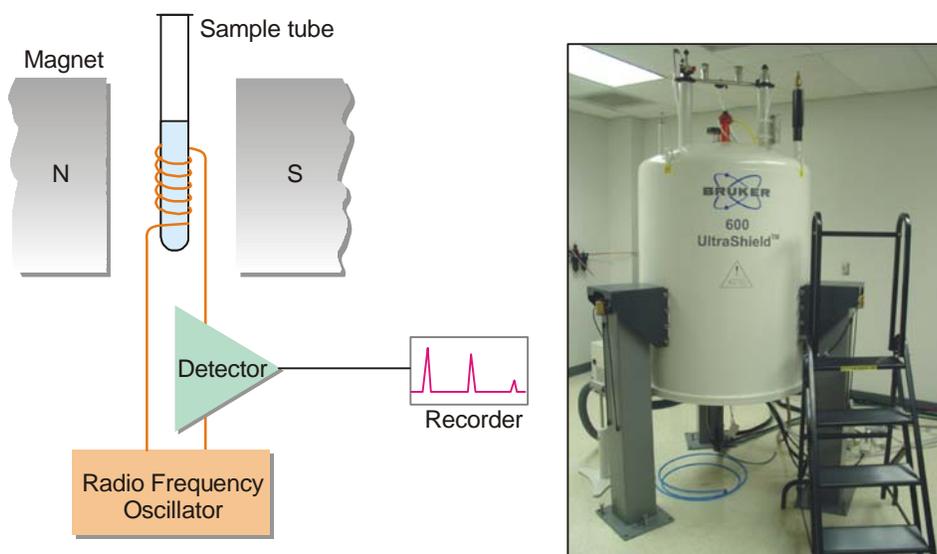


■ **Figure 13.25**
**Schematic diagrams of a NMR spectrometer.**

$$CH_3 \underset{a}{-} CH_2 \underset{b}{-} Cl$$

Ethyl chloride
(2 Signals)

$$CH_3 \underset{a}{-} CH_2 \underset{b}{-} CH_2 \underset{c}{-} Cl$$

*n*-Propyl chloride
(3 Signals)

$$CH_3 \underset{a}{-} \underset{b}{\overset{\overset{\displaystyle Cl}{|}}{CH}} \underset{c}{-} CH_3$$

Isopropyl chloride
(2 Signals)
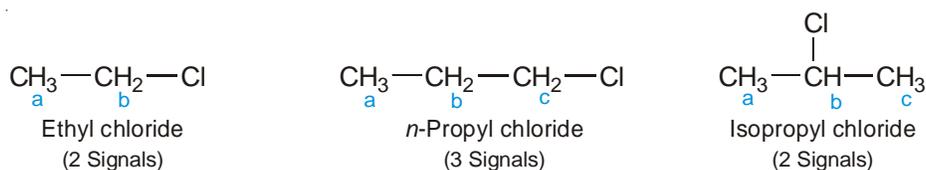
Equivalent protons are indicated by the same letter, non-equivalent protons by different letters. Notice that *n*-propyl chloride can be easily distinguished from its isomer isopropyl chloride, by simply examining the NMR spectra of the two compounds. *n*-propyl chloride gives three NMR signals and has three non-equivalent sets of protons, whereas isopropyl chloride gives two NMR signals and has two sets of equivalent protons and one non-equivalent proton.

**Delta and Tau Scales.** Nuclear magnetic resonance chart paper is rectangular with a linear scale of $\delta$ (*delta*) units across the bottom. Most chart papers have scales from $\delta = 0$ to $\delta = 8$ or 9 ppm (parts per million). To every sample a small amount of **Tetramethylsilane** (TMS), $(CH_3)_4Si$, is added as a reference (the TMS signal is at $\delta = 0$). All other signals are relative to TMS. Sometimes $\tau$ (*tau*) scale is used where the TMS signal is at 10.0 ppm. Hence $\tau = 10 - \delta$.

Table 13.5 lists some characteristic chemical shifts (from TMS) of different types of protons.

| Table 13.5 : SOME  TYPICAL  NMR  CHEMICAL  SHIFTS  OF  PROTONS | | |
|---|---|---|
| Type of Proton | Type of Compound | $\delta$  Value |
| $R–CH_3$ | Alkane | 0.8–1.2 |
| $Ar–CH_3$ | Arene | 2.2–2.5 |
| $C=C–CH_3$ | Alkene | 1.6–1.9 |
| $R–O–CH_3$ | Ether | 3.2–3.3 |
| $Ar–O–CH_3$ | Ether | 3.7–4.0 |
| $R–CO–CH_3$ | Ketone | 2.1–2.4 |
| $Ar–CO–CH_3$ | Ketone | 2.4–2.6 |
| $CH_3–COOR$ | Ester | 1.9–2.2 |
| $R–COOCH_3$ | Ester | 3.0–3.9 |
| $CH_3–N<$ | Amine | 2.2–2.6 |
| $R–CH_2–R$ | Alkane | 1.1–1.5 |
| $R–CH_2–Ar$ | Arene | 2.5–2.9 |
| $R–CH_2–X$ | Alkyl halide | 2.7–4.5 |
| $R–CH_2–NO_2$ | Nitroalkane | 4.4–4.6 |
| $R–CH_2–OH$ | Alcohol | 3.4–4.0 |
| $Ar–CH_2–OH$ | Alcohol | 4.0–5.0 |
| $R–CH_2–COOH$ | Acid | 2.0–2.6 |
| $R_3C–H$ | Alkane | 1.4–1.6 |
| $Ar–H$ | Arene | 6.0–7.5 |
| $C=C–H$ | Alkene | 4.5–6.0 |
| $C\equiv C–H$ | Alkyne | 1.7–1.9 |
| $R–CHO$ | Aldehyde | 9.0–10.0 |
| $R–COOH$ | Acid | 10–12 |
| $R–OH$ | Alcohol | 2–6 |
| $Ar–OH$ | Phenol | 6–8 |
| $R–NH_2$ | Amine | 1–5 |

As an example, let us consider the NMR spectrum of benzyl alcohol (Fig. 13.26A). Notice that there are four signals in this spectrum.

(1)  The signal on the far right at $\delta = 0$ is that of the TMS reference.

(2)  The signal at $\delta = 7.3$ is a single sharp peak due to the five chemically equivalent phenyl protons.

(3)  The signal at $\delta = 4.6$ is a single sharp peak due to the two chemically equivalent methylene ($–CH_2–$) protons.

(4)  The signal at $\delta = 2.4$ is a single sharp peak due to the hydroxy (–OH) proton.
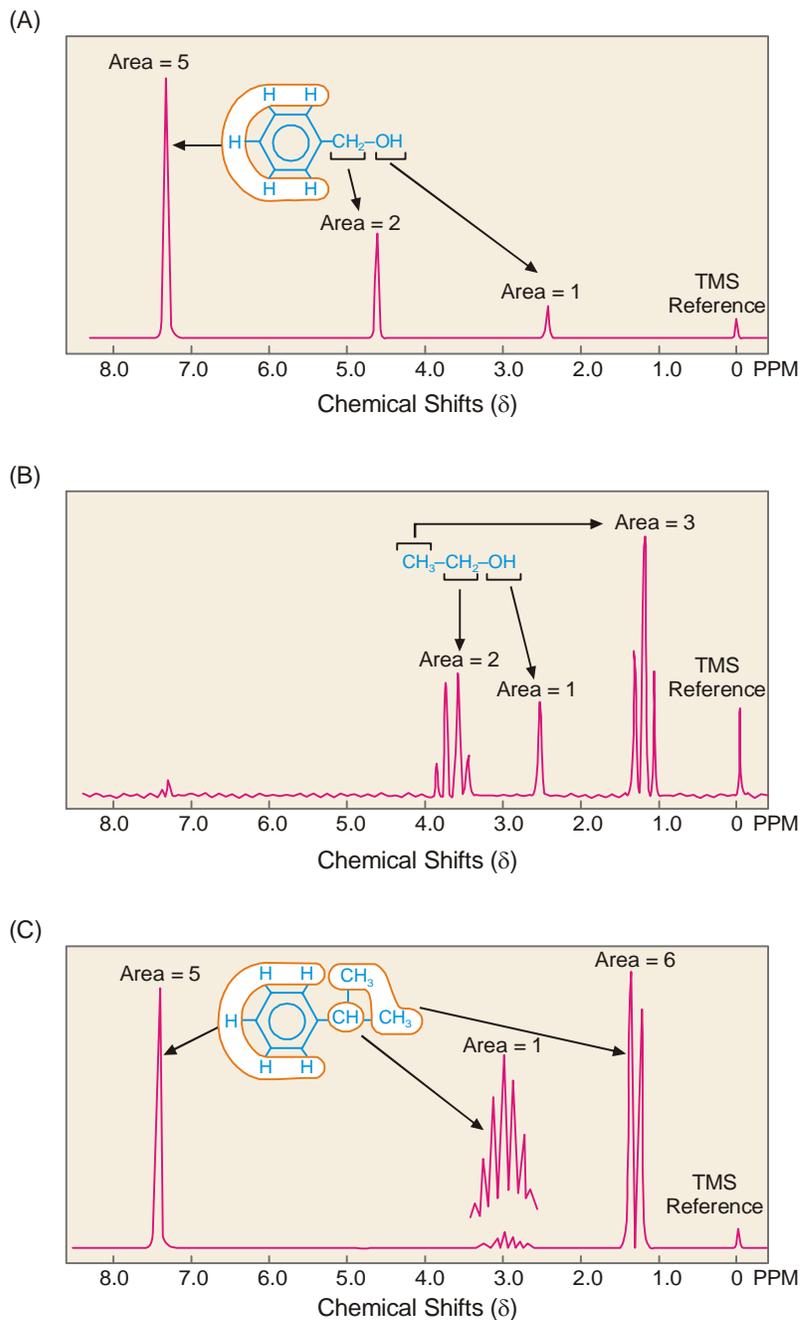
**Figure 13.26**
Some examples of NMR spectra. **(A) is Benzyl alcohol. (B) is Ethyl alcohol. (C) is Isopropylbenzene.**

**Peak Area ; Integration.** The relative areas under the various peaks of a NMR spectrum are in proportion to the number of protons contributing to each signal. These areas can be electronically integrated by a NMR spectrometer. Comparison of the areas provides the ratio among the various

kinds of protons in the molecule. For example, consider the NMR spectrum of benzyl alcohol (Fig. 13.26A). The hydrogens in the molecule are in a 1 : 2 : 5 ratio, like the corresponding areas in the spectrum.

**Peak Splitting ; Splitting Pattern.** Hydrogens on adjacent carbons, each with a different chemical shift, can influence the signal of the other. This influence appears as peak splitting. We can generalise the phenomenon by saying that *the number of peaks into which a particular proton's signal is split, equals one more than the total number of protons on directly adjacent carbons*. The split peaks are not of equal height. Fig. 13.27 shows the splitting pattern for various types of non-equivalent protons.
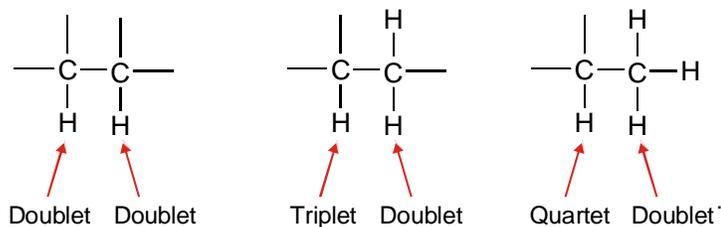


■ **Figure 13.27**
**Splitting pattern for various types of non-equivalent protons.**

In the NMR spectrum of ethyl alcohol (Fig. 13.26 B), notice that the ethyl group is indicated by a quartet and a triplet.

In the NMR spectrum of isopropyl benzene (Fig.13.26C), notice that the isopropyl group is indicated by a heptet and a doublet.

**SUMMARY OF NMR SPECTROSCOPY**

(1) Absorption of radiowaves in the presence of a magnetic field causes nuclei within molecules to be promoted from one spin energy level to a higher spin energy level.

(2) The number of signals in the NMR spectrum corresponds to the number of different types of protons in the molecule.

(3) The position (chemical shift) of each signal gives information about the structural environment of the protons.

(4) The relative areas (Integration) under the signals give the ratio of the numbers of each type of proton in the molecule. If the molecular formula is known, the actual number of each type of proton can be determined.

(5) The splitting pattern of each signal gives us the number of protons on neighboring carbons. The number of peaks into which a signal is split is one more than the total number of protons on directly adjacent carbons.

**IMPORTANT TERMS USED IN NMR SPECTROSCOPY**

**Chemical shift :** The separation between the peak of the reference standard (TMS) and any other peak in an nmr spectrum.

**δ scale :** An nmr scale in which the TMS peak is set at zero and peaks to the left of it (downfield) have increasingly positive values, in parts per million (ppm).

**TMS :** Abbreviation for tetramethylsilane, $(CH_3)_4Si$, the reference standard in nmr spectrometry.

**Downfield shift :** The protons of most organic compounds are less shielded than those of TMS and therefore require less energy for resonance to take place. The peaks appear therefore at lower fields, or *downfield* of the TMS reference peak.

**Spin-spin coupling :** The splitting of a signal into two or more peaks because of magnetic interactions between neighboring protons.

## MAGNETIC RESONANCE IMAGING (MRI)



MRI is a diagnostic technique that generates images of the internal body. It specializes in creating a thin-section image of any part of the body – especially the heart, veins, arteries, brain and central nervous system – from any angle or direction.
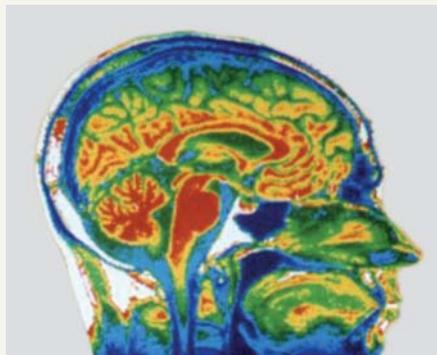


This MRI scan of a normal adult head shows the brain, airways, and soft tissues of the face. The large cerebral cortex, appearing in yellow and green, forms the bulk of the brain tissue; the circular cerebellum, *center left*, in red, and the elongated brainstem, *center*, in red, are also prominently shown.

Magnetic Resonance Imaging (MRI), medical diagnostic technique that combines strong magnetic fields, radio waves, and computer technology to create images of the body using the principles of *nuclear magnetic resonance*. A versatile, powerful, and sensitive tool, MRI can generate thin-section computerized images of any part of the body–including the heart, arteries, and veins–from any angle and direction, without surgical invasion and in a relatively short period of time. MRI also creates "maps" of biochemical compounds within any cross section of the human body. These maps give basic biomedical and anatomical information that provides new knowledge and may allow early diagnosis of many diseases. In 2003 Paul Lauterbur of the United States and Sir Peter Mansfield of the United Kingdom shared the Nobel Prize in physiology or medicine for their contributions to MRI technology.

MRI is possible in the human body because the body is filled with small biological "magnets," the most abundant and responsive of which is the proton, the nucleus of the hydrogen atom. The principles of MRI take advantage of the random distribution of protons, which possess fundamental magnetic properties. Once the patient is placed in the cylindrical magnet, the diagnostic process follows three basic steps. First, MRI creates a steady state within the body by placing the body in a steady magnetic field that is 30,000 times stronger than Earth's magnetic field. Then MRI stimulates the body with radio waves to change the steady-state orientation of protons. It then stops the radio waves and "listens" to the body's electromagnetic transmissions at a selected frequency. The transmitted signal is used to construct internal images of the body using principles similar to those developed for computerized axial tomography, or CAT scanners.

In current medical practice, MRI is preferred for diagnosing most diseases of the brain and central nervous system. MRI scanners provide equivalent resolution and superior contrast resolution to that of X-Ray CAT scanners. MRI scanners also provide imaging complementary to X-Ray images because MRI can distinguish soft tissue in both normal and diseased states.

**(n + 1) rule :** A rule that allows us to predict into how many smaller peaks a given signal is split by neighbouring protons. The rule states that a signal is split into (n + 1) peaks, where n represents the number of equivalent *next-door protons*.
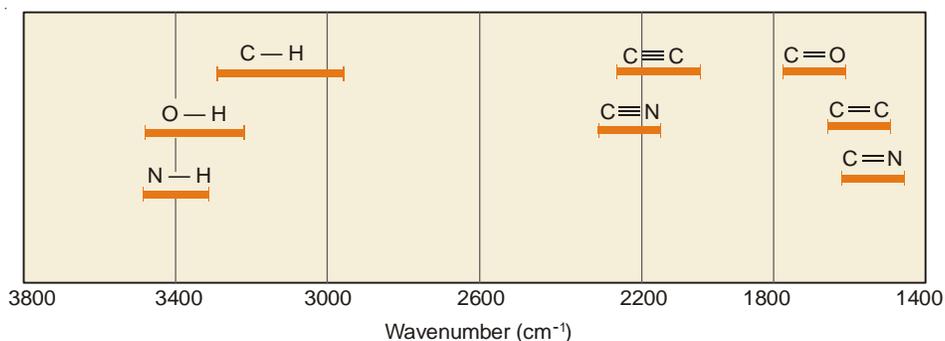


Group Assignments in Infrared Spectra
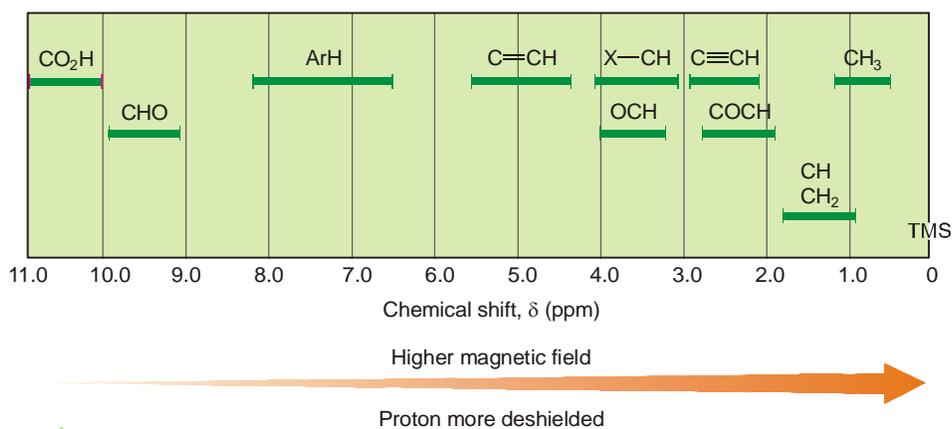


Group Assignments in NMR Spectra

## MASS SPECTROSCOPY

In a mass spectrometer, organic molecules are vapourised and bombarded with a beam of very high-energy electrons (Fig. 13.28). The resulting collisions impart considerable energy to the molecule, which in turn emit electrons to produce positively charged ions. These ions possess so much energy that they often fragment through various bond cleavages to produce new positively charged ions.

$$ABC^+ \quad \text{(Molecular ion)}$$
$$ABC \xrightarrow[\text{beam}]{\text{electron}} AB^+ \quad C^+$$
$$A^+ \quad BC^+$$
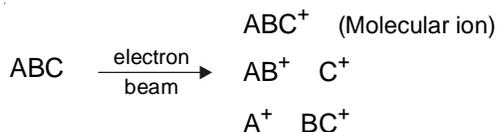
The positive ions are accelerated toward a negatively charged plate by passing them through a magnetic field, which deflects the ions. The ions of lighter mass are deflected more than heavier ions. Each kind of ion has a particular mass to charge (m/e) ratio. For most ions produced in the fragmentation of the molecule, the charge is +1 so, that m/e usually represents the mass of the ion.

**Base Peak.** The set of ions produced from a molecule can be analysed since each has its own m/e ratio, and produces a signal whose intensity is due to the relative abundance of that ion. *The largest peak found in a mass spectrum (that of highest intensity) is called the base peak,* and is given

the numerical value of 100. The intensities of all other peaks are expressed relative to the height of the base peak. A mass spectrum is highly characteristic of a particular compound.

**Molecular Ion.** *The ion formed by removing one electron from the parent molecule is called molecular ion or parent ion.* The molecular ion peak is usually represented as $M^+$. It may or may not be the peak of highest intensity. The molecular ion is the most important ion, since its mass is the **Molecular Weight** of the parent molecule.
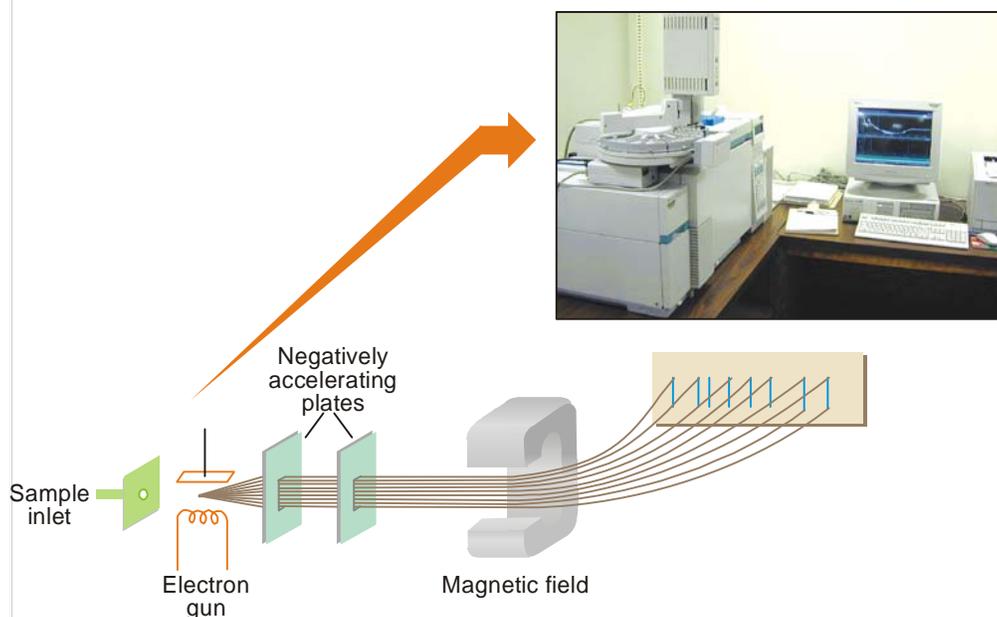


**Figure 13.28**
**Schematic diagram of a Mass spectrometer.**

The use of mass spectroscopy is not limited to the determination of the molecular weight of compounds. It also has great utility in the elucidation of the structure of a molecule. The fragmentation processes of organic molecules follow certain patterns in that the fragments broken off are related to bond strengths and the stability of the species formed. Since certain structural features in molecule produce definite characteristic fragmentation patterns, the identification of these fragments and their relative intensities in a mass spectrum can be used to determine the structure of organic compounds. The following examples illustrate how a mass spectrum can be used to determine the structure of organic molecules :

**Example 1.** Let us consider the following isomers.

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \quad n\text{-Octane}$$

$$\underset{\displaystyle CH_3CH_2CH_2CHCH_2CH_2CH_3}{\overset{\displaystyle CH_3 \atop |}{}} \quad \text{4-Methylheptane}$$
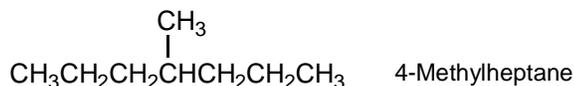
*n*-Octane can be easily distinguished from 4-methylheptane, since the methyl group branched at

C-4 in the latter compound, is easily broken off as $CH_3^+$ fragment and will give a peak of large intensity

at $m/e = 15$

**Example 2.** Consider the mass spectrum shown in Fig. 13.29. The fragmentation pattern and

relative abundance of peaks is as follows. A molecular weight of 32, which corresponds to $O_2$, is ruled out, since the only other possible fragment would be O with a peak of relatively *high* intensity at $m/e = 16$. An $m/e$ peak is present at a value of 16, but has a very *low* relative intensity, 0.21. The peak at $m/e = 15$ is due to a $CH_3^+$ fragment, and the overall spectrum indicates an elemental composition of $CH_4O$. Consideration of other peaks present leads to the conclusion that the molecule producing this spectrum is methyl alcohol ($CH_3OH$).

| m/e | Relative abundance |
|-----|--------------------|
| 12  | 0.32 |
| 13  | 0.72 |
| 14  | 2.4  |
| 15  | 1.3  |
| 16  | 0.21 |
| 17  | 1.0  |
| 28  | 6.3  |
| 29  | 64   |
| 30  | 3.8  |
| 31  | 100  |
| 32  | 66   |
| 33  | 0.98 |
| 34  | 0.14 |
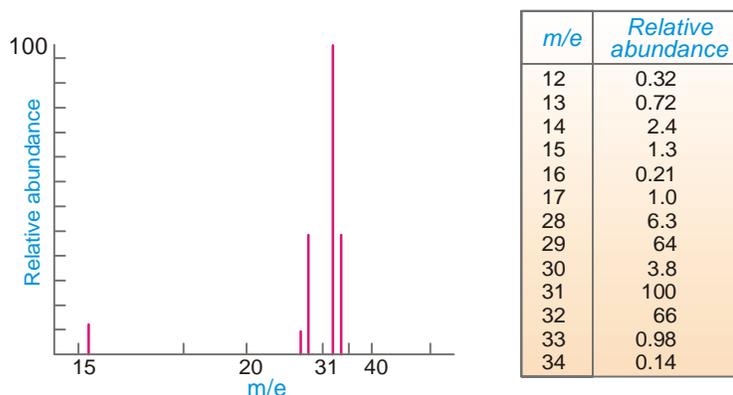
■ **Figure 13.29**
**Mass spectrum of Methyl alcohol, CH₃OH**

## SUMMARY OF MASS SPECTROSCOPY

(1) Mass spectroscopy involves organic molecules being bombarded by a very high-energy electron beam.

(2) The peak of highest intensity in a mass spectrum is referred to as the base peak.

(3) Fragmentation processes can produce numerous fragments, from which the structures of organic molecules can be deduced.

(4) When one electron is removed from a molecule, a molecular ion is produced. The $m/e$ value of the molecular ion peak is the molecular weight of the compound being investigated. The molecular weights obtained by mass spectroscopy are extremely accurate.

## RAMAN SPECTRA

When an intense beam of light is passed through a liquid or gas, some of the light is scattered by the molecules of the medium. Most of the scattered light has the same frequency as the incident light. This type of scattering which occurs without a change in the incident frequency is termed **Rayleigh scattering.** In 1928, Indian physicist Sir C.V. Raman discovered that a very small fraction of the scattered light has frequencies higher or lower than the incident frequency. The scattering which occurs with a change in the frequency of the incident radiation is called **Raman scattering.** The phenomenon is called **Raman effect.** The spectrum obtained from scattered radiations of a sample can be observed with the help of the apparatus shown in Fig. 13.30. Laser beam is now used as incident radiation. Raman originally used ultraviolet light which gave weak spectral lines.

The general pattern of spectrum recorded by scattered light is illustrated in Fig. 13.31. The sharp line in the middle corresponds to Rayleigh scattered light and is referred to as **Rayleigh line.** Raman scattered light records a series of lines on either side of the Rayleigh line. These are called **Raman lines** and constitute **Raman spectrum.**
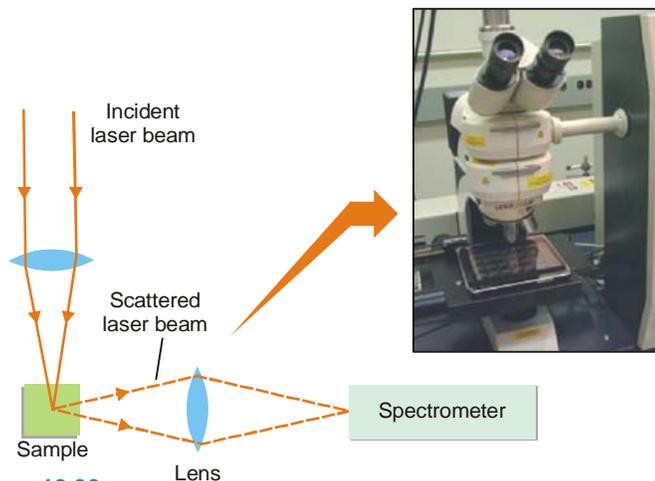
**Figure 13.30**
**Apparatus for obtaining Raman spectra.**
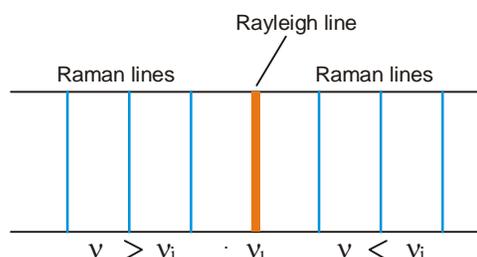


**Figure 13.31**
**Raman spectrum (an illustration).**

### Explanation of Raman Spectrum

**The change in frequency by scattering occurs due to the exchange of energy between the incident photon and the scattering molecule.** If the photon collides with an 'excited' molecule, it acquires energy from the molecule. Thus the scattered light emerges with a higher frequency. If the photon collides with a molecule in the 'ground state', it loses energy to the molecule. This lowers the frequency of the scattered light. It explains why Raman spectrum of a substance shows lines of higher frequency and others of lower frequency than the incident line. The frequency difference ($\Delta V$) between each Raman line and the incident line, is called the **Raman frequency** ($v_{Raman}$). The Raman frequencies shown by a substance are independent of the incident frequency and are characteristic of the substance.

### Raman Spectra and Molecular Structure

**Raman spectra provide valuable information about the shape and structure of molecules.** When studied together, Raman and *IR* spectra can tell us whether : (*i*) a molecule is linear or non-linear; (*ii*) a molecule is symmetrical or asymmetrical.

The most important application of Raman spectra is in the determination of structure of organic molecules. Definite frequencies are associated with different types of bonds. The Raman frequency for C–H bond is about 2800 cm$^{-1}$, for C ≡ C bond about 2100 cm$^{-1}$ and for C = C bond about 1600 cm$^{-1}$. Thus like infrared spectra; Raman spectra are useful in establishing the structure of organic molecules.

## EXAMINATION QUESTIONS

1. Define or explain the following terms :
   (a) Surface tension                    (b) Parachor
   (c) Viscosity                          (d) Rheochor
   (e) Dipole moment                      (f) Molar Refraction
   (g) Diamagnetic substances             (h) Paramagnetic substances
   (i) Electromagnetic spectrum           (j) Fingerprint region
   (k) Chemical shifts                    (l) TMS

2. Give an account of pure rotational spectra. How force constant and bond length can be calculated for simple diatomic molecule?                                    (*Jiwaji BSc, 2000*)

3. (a) Describe various normal modes of vibration pictorially for water molecules.
   (b) Define stretching force constant. How does it change from fluorine to iodine molecule?
   (c) Write briefly applications of NMR spectroscopy.           (*Jamia Millia BSc, 2001*)

4. (a) Define dipole moment. How can it be used in elucidation of molecular structure?
   (b) Discuss a method for determining magnetic susceptibility and discuss the magnetic behaviour of $K_3 [Fe(CN)_6]$                                            (*Jamia Millia BSc, 2002*)

5. (a) Calculate the normal modes of vibration in $CO_2$ and $CH_4$ molecules.
   (b) Differentiate between permanent and induced electric dipole moments.     (*Panjab BSc, 2002*)

6. Calculate the percentage ionic character of HBr from the following data :
   Dipole moment of HBr = $0.79 \times 10^{-18}$ esu
   Bond length of HBr = $1.42 \times 10^{-8}$ cm
   Theoretically expected dipole moment of HBr = $6.816 \times 10^{-18}$ cm
   **Answer.** 11.59%                                            (*Mizoram BSc, 2002*)

7. Define optical density and molar extinction coefficient. On which the magnitude of these quantities depend?                                                    (*Guru Nanak Dev BSc, 2002*)

8. (a) What is meant by molar volume, molar refraction, polarization and dipole moment?
   (b) Calculate the percent ionic character in HCl molecule, if the observed dipole moment is 1.08 D and bond length is 1.2746 Å.
   **Answer.** 17.64%                                            (*Allahabad BSc, 2002*)

9. (a) Explain the terms (i) Specific refractivity and (ii) Molar refractivity.
   (b) Discuss the use of dipole moment measurements in the study of structure of compounds.
                                                                 (*Mizoram BSc, 2002*)

10. Write the expression for the vibrational energy of a diatomic molecule. What are the selection rules for the vibrational transition in a diatomic molecule and what type of vibrational spectrum is expected for a diatomic molecule taking it as simple harmonic oscillator.      (*Panjab BSc, 2003*)

11. How many fundamental vibrational frequencies would you expect for $CO_2$? How do you represent these modes?                                               (*Sambalpur BSc, 2003*)

12. Calculate the molar refractivity of allyl chloride at a temperature at which its density is 0.938 g cm$^{-3}$. The experimentally observed value of refractive index at this temperature is 1.3715.
    **Answer.** 18.5133                                          (*Delhi BSc, 2004*)

13. Explain the role of molar refraction in determining the chemical constitution of a compound.

14. Name the two most common instruments used in measuring refractive index.

15. Define specific and molar refraction.                        (*Kerala BSc, 2004*)

16. Define molecular refraction. Briefly describe the principle, construction and working of the instrument used in determining the molecular refraction of a liquid.    (*Sri Venkateswara BSc, 2004*)

17. Discuss the principle and applications of NMR spectroscopy in structure determination of organic compounds.                                         (*HS Gaur BSc, 2004*)

18. What is meant by the term Chemical Shift of a particular proton in NMR spectroscopy ? Draw the splitting patterns of protons in NMR spectrum of ethyl alcohol.     (*Kalyani BSc, 2004*)

**19.** How will you distinguish between 1,3-pentadiene and 1,4-pentadiene by UV spectroscopy ?

(*Baroda BSc, 2004*)

**Answer.** 1,3-Pentadiene will have higher $l_{max}$ than 1,4-pentadiene. This is because 1,3-Pentadiene is conjugated ; whereas 1,4-pentadiene is not.

**20.** How will you distinguish between benzene and anthracene by UV spectroscopy ?

(*Bharathidasan BSc, 2004*)

**Answer.** Anthracene will have higher $\lambda_{max}$ than benzene. This is because anthracene is more conjugated than benzene.

**21.** Define dipole moment and discuss its ability in determining the molecular structure.

(*Allahabad BSc, 2005*)

**22.** What is meant by Chemical shift? On what factors does it depend?      (*Baroda BSc, 2005*)

**23.** Two isomeric dienes (A) and (B) having the molecular formula $C_5H_8$ absorb at $\lambda_{max}$ 223 nm and $\lambda_{max}$ 178 nm respectively. Write the structures of the two isomers.      (*Madras BSc, 2005*)

**Answer.** (A) is     $CH_2{=}CH{-}CH{=}CH{-}CH_3$  ; 1,3-Pentadiene

(B) is     $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$ ; 1,4-Pentadiene

**24.** Arrange the following compounds in the increasing order of their UV absorption maxima :

(a)   Ethylene                                           (b)   Naphthalene
(c)   Anthracene                                       (d)   1,3-Butadiene

**Answer.** (a) < (d) < (c) < (b)

**25.** Discuss the principle of IR spectroscopy. How will you distinguish between the following pairs of compounds on the basis of IR spectroscopy :

(a)   Ethyl alcohol and diethyl ether

(b)   Acetic acid and ethyl acetate      (*Jiwaji BSc, 2005*)

**Answer.** (a) Ethyl alcohol shows a strong/broad absorption at 3200-3500 cm$^{-1}$ (due to O–H bond) while diethyl ether does not ; and (b) Acetic acid shows a strong/broad absorption at 2500–3500 cm$^{-1}$ (due to O–H bond) while ethyl acetate does not.

**26.** Two compounds, (A) and (B), have the same molecular formula $C_2H_6O$. They have different IR spectra. Compound (A) shows a strong/broad absorption at 3400 cm$^{-1}$, while compound (B) does not. Suggest formulas for (A) and (B) which account for the difference.(*Madras BSc, 2005*)

**Answer.** (A) is ethyl alcohol ($CH_3CH_2OH$) ; (B) is dimethyl ether ($CH_3OCH_3$). The strong absorption at 3400 cm$^{-1}$ in (A) is due to the O–H bond.

**27.** How many NMR signals do you expect from each of the following compounds. Indicate also the splitting pattern of the various signals.      (*Kalyani BSc, 2005*)

(a)   $CH_3OCH_3$                    (b)   $CH_3OCH_2CH_3$                    (c)   $CH_3CH_2OH$

**Answer.** (a) One signal (singlet) ;   (b) Three signals (singlet, quartet, triplet) ; and (c) Two signals (singlet, quartet).

**28.** How many signals (ignoring the splitting patterns) would you see in the NMR spectra of the following compounds ?      (*Mysore BSc, 2005*)

(a)   Butanone          (b)   Cyclobutane          (c)   p-xylene          (d)   2-Propanol

**Answer.** (a)Three signals ; (b) One signal ; (c) Two signals ; and (d) Three signals.

**29.** What type of information one can obtain from : (i) IR spectrum ; (ii) UV spectrum ; and (iii) NMR spectrum.      (*Kanpur BSc, 2006*)

**30.** What type of molecular transitions are brought about by absorption of :

(a)   Ultraviolet-visible radiation

(b)   Infrared radiation      (*Madurai BSc, 2006*)

**31.** Write notes on :

(a)   UV  spectroscopy      (*Banaras BSc, 2006*)

(b)   IR  spectroscopy      (*Agra BSc, 2006*)

(c)   NMR  spectroscopy      (*Jadavpur BSc, 2006*)

**32.** (*a*) Describe NMR spectroscopy.

(*b*) How is NMR method used to determine structure of ethyl alcohol? (*Panjab BSc, 2006*)

**33.** The NMR spectrum of a compound $C_4H_9Br$ consists of a single sharp line. What is the structure of the compound ? (*Delhi BSc, 2006*)

**Answer.** The compound is *tert*-Butyl bromide, $(CH_3)_3CBr$.

**34.** Suggest the structure of a compound each with the following NMR spectral features :

(a) An alcohol with two NMR peaks

(b) A compound $C_5H_{10}$ with a single NMR peak

(c) A compound $C_4H_6$ with a single NMR peak. (*Madras BSc, 2006*)

**Answer.** (a) Methyl alcohol ; (b) Cyclopentane ; (c) 2-Butyne

**35.** Calculate the percentage ionic character of H – Cl bond if the distance between the two atoms is 1.275 Å and its dipole moment is 1.03 D. (*Sambalpur BSc, 2006*)

**Answer.** 16.885%

**36.** The parachor equivalent for C is 4.8; for H, 17.1 ; and for 0, 20.0 Calculate the parachor for methanol.

(*Andhra BSc, 2006*)

**Answer.** 93.2

**37.** The parachor equivalents for C is 4.8 ; for H, 17.1 ; and for O, 20.0. Calculate the parachor for ethyl alcohol. (*Indore BSc, 2006*)

**Answer.** 132.2

## MULTIPLE CHOICE QUESTIONS

**1.** The molecular mass of a compound is an example of

(*a*) additive property      (*b*) constitutive property

(*c*) additive as well as constitutive property      (*d*) none of these

**Answer.** (*a*)

**2.** The molar volume of a liquid at a temperature where its surface tension is unity is called

(*a*) molar volume      (*b*) molar surface tension

(*c*) molar viscosity      (*d*) parachor

**Answer.** (*d*)

**3.** The parachor is

(*a*) an additive property      (*b*) a constitutive property

(*c*) both an additive and constitutive property (*d*) none of these

**Answer.** (*c*)

**4.** The molar viscosity is the

(*a*) product of molar surface and viscosity      (*b*) sum of molar surface and viscosity

(*c*) difference of molar surface and viscosity      (*d*) none of these

**Answer.** (*a*)

**5.** The Rhechor is the

(*a*) molar volume of the liquid at the temperature at which viscosity is zero

(*b*) molar volume of the liquid at the temperature at which viscosity is unity

(*c*) molar volume of the liquid at the temperature at which viscosity is infinite

(*d*) none of the above

**Answer.** (*b*)

6.  The quantity Rheochor [R] is given by the formula where $M$ is molar surface and $\eta$ is the viscosity

    (a)  $[R] = \dfrac{M}{d} \times \eta^{1/4}$

    (b)  $[R] = \dfrac{M}{d} \times \eta^{1/6}$

    (c)  $[R] = \dfrac{M}{d} \times \eta^{1/8}$

    (d)  $[R] = \dfrac{M}{d} \times \eta^{1/16}$

    **Answer.** (c)

7.  The Rheochor is

    (a)  an additive property

    (b)  a constitutive property

    (c)  both an additive and constitutive property  (d)  none of these

    **Answer.** (c)

8.  The dipole moment of a polar substance is given by the formula, where $q$ is charge at one end and $r$ is the distance between the opposite charges

    (a)  $\mu = q + r$

    (b)  $\mu = q - r$

    (c)  $\mu = q \times r$

    (d)  $\mu = q \div r$

    **Answer.** (c)

9.  The net dipole moment of the molecule is

    (a)  sum of all individual bond moments

    (b)  product of all individual bond moments

    (c)  vector resultant of all the individual bond moments

    (d)  none of the above

    **Answer.** (c)

10. Dichlorobenzene exists in three isomers-*ortho*, *meta* and *para* isomers. Out of these three isomers, one with highest dipole moment will be

    (a)  *ortho*-isomer

    (b)  *meta*-isomer

    (c)  *para*-isomer

    (d)  all will have the same dipole moment

    **Answer.** (a)

11. The molar refraction of a molecule is _____ of the contribution of atoms (atomic refraction) and bonds (bond refractions) present

    (a)  difference

    (b)  sum

    (c)  product

    (d)  none of these

    **Answer.** (b)

12. Optical activity is

    (a)  an additive property

    (b)  a constitutive property

    (c)  both an additive and constitutive property  (d)  none of these

    **Answer.** (b)

13. A Chiral molecule has

    (a)  no plane of symmetry

    (b)  one plane of symmetry

    (c)  infinite planes of symmetry

    (d)  none of these

    **Answer.** (b)

14. The molecules that are non-superimposable mirror images are called

    (a)  optical isomers

    (b)  racemic isomers

    (c)  enantiomers

    (d)  none of these

    **Answer.** (c)

15. A racemic mixture has

    (a)  zero optical rotation

    (b)  positive optical rotation

    (c)  negative optical rotation

    (d)  infinite optical rotation

    **Answer.** (a)

16. The necessary condition for a compound to be optically active is
    (a) the presence of no chiral atoms
    (b) the presence of at least one asymmetric atoms
    (c) the presence of chirality in the molecule
    (d) none of these
    **Answer.** (c)

17. An equimolar mixture of (+)-tartaric acid and (–)-tartaric acid is called
    (a) enantiomers
    (b) optically active mixture
    (c) racemic mixture
    (d) asymmetric mixture
    **Answer.** (c)

18. A diamagnetic substance is _____ by/in the magnetic field
    (a) attracted
    (b) repelled
    (c) rotated
    (d) revolved
    **Answer.** (b)

19. The substances which retain their magnetic field when removed from the magnetic field are called
    (a) paramagnetic
    (b) diamagnetic
    (c) ferrimagnetic
    (d) ferromagnetic
    **Answer.** (d)

20. The paramagnetism is due to the presence of
    (a) paired electrons
    (b) unpaired electrons
    (c) both paired as well as unpaired electrons
    (d) none of these
    **Answer.** (b)

21. Iron, cobalt and nickel are examples of
    (a) diamagnetic substances
    (b) paramagnetic substances
    (c) ferromagnetic substances
    (d) sometimes diamagnetic & sometimes paramagnetic substances
    **Answer.** (c)

22. The magnetic moment, $\mu$, is given by the formula in which $n$ is the number of unpaired electrons
    (a) $\mu = n \times (n + 2)$
    (b) $\mu = \sqrt{n \times (n+1)}$
    (c) $\mu = \sqrt{n \times (n+2)}$
    (d) $\mu = n \times (n + 1)$
    **Answer.** (c)

23. The frequency and wave length are related to each other by the formula
    (a) $\nu = c \, \bar{\nu}$
    (b) $\bar{\nu} = c \, \nu$
    (c) $\nu = \hbar \, \bar{\nu}$
    (d) $\bar{\nu} = \hbar \, \nu$
    **Answer.** (a)

24. The energy of one mole of photon is given by the relation
    (a) $E = \dfrac{N h c}{\lambda}$
    (b) $E = \dfrac{N h c}{\lambda^2}$
    (c) $E = \dfrac{N h c^2}{\lambda}$
    (d) $E = \dfrac{N h^2 c}{\lambda}$
    **Answer.** (a)

25. The internal energy of a molecule is its
    (a) rotational energy
    (b) vibrational energy
    (c) translational energy
    (d) all of these
    **Answer.** (d)

26. The electronic spectra are caused by
    (a) the absorption of light
    (b) the emission of light
    (c) the absorption of high energy photons
    (d) none of these
    **Answer.** (c)

27. The rotational spectra involve
    (a) a very high energy changes
    (b) small energy changes
    (c) no energy change
    (d) none of these
    **Answer.** (b)

28. A molecule can be excited to only the next higher rotational level by
    (a) absorption of energy
    (b) release of energy
    (c) the electric current
    (d) applying magnetic field
    **Answer.** (a)

29. The spectra caused in the infrared region by the transition in vibrational levels in different modes of vibrations are called
    (a) rotational spectra
    (b) electronic spectra
    (c) vibrational spectra
    (d) none of these
    **Answer.** (c)

30. The IR spectra of a compound helps in
    (a) proving the identity of compounds
    (b) showing the presence of certain functional groups in the molecule
    (c) neither of the above
    (d) both of the above
    **Answer.** (d)

31. The electronic spectra consists of
    (a) a large number of absorption bands
    (b) a large number of closely packed lines
    (c) a large number of peaks
    (d) none of these
    **Answer.** (b)

32. In the Raman spectrum, the middle line is called
    (a) Raman line
    (b) Rayleigh line
    (c) functional group line
    (d) none of these
    **Answer.** (b)

33. The change in frequency by scattering (Raman Effect) occurs due to _____ of energy between the incident photon and the scattering molecule.
    (a) release
    (b) absorption
    (c) exchange
    (d) none of these
    **Answer.** (c)

34. NMR spectroscopy is useful for determining the type and number of _____ atoms in organic molecules.
    (a) hydrogen
    (b) carbon
    (c) halogen
    (d) hetero atoms
    **Answer.** (a)

35. The magnetic moment of a molecule is expressed in
    (a) magnetic tons
    (b) magnetons
    (c) debye units
    (d) $g\,cm\,sec^{-1}$
    **Answer.** (b)

36. The electronic spectra lies within
    (a) infrared region
    (b) visible or ultraviolet regions
    (c) radio wave region
    (d) micro waves region
    **Answer.** (b)

37. The wave numbers are expressed in
    (a) $sec^{-1}$
    (b) $cm\,sec^{-1}$
    (c) $cm^{-1}$
    (d) $cm^2\,sec^{-1}$
    **Answer.** (c)

38. The magnetic moment of oxygen molecule is 2.8 magnetons. The number of unpaired electrons in its molecule is
    (*a*)  0                                         (*b*)  1
    (*c*)  2                                         (*d*)  3
    **Answer.** (*c*)
39. The magnetic moment of a molecule is 1.732 magnetons. The number of unpaired electrons is
    (*a*)  0                                         (*b*)  1
    (*c*)  2                                         (*d*)  3
    **Answer.** (*b*)
40. The electromagnetic radiations of higher wavelengths has _____ energy.
    (*a*)  higher                                    (*b*)  lower
    (*c*)  intermediate                              (*d*)  zero
    **Answer.** (*b*)
41. The Raman and IR spectra can tell us whether
    (*a*)  a molecule is linear or non-linear        (*b*)  a molecule is symmetrical or asymmetrical
    (*c*)  neither of the above                      (*d*)  both of the above
    **Answer.** (*d*)
42. Define "wavenumber."
    (*a*)  1/wavelength
    (*b*)  it is the same as wavelength
    (*c*)  wavelength  x  speed of light
    **Answer.** (*a*)
43. What does IR spectroscopy allow us to determine?
    (*a*)  the molecular formula of a compound       (*b*)  the kinds of bonds in a compound
    (*c*)  the molecular weight of a compound        (*d*)  the number of carbons in a compound
    **Answer.** (*b*)
44. Which of the following will show an absorption band at the greatest wavenumber?
    (*a*)  C=C                                       (*b*)  C≡C
    (*c*)  C=O                                       (*d*)  C–N
    **Answer.** (*b*)
45. What is a molecular ion?
    (*a*)  it is a compound that has gained an electron
    (*b*)  it is a compound that has lost an electron.
    (*c*)  it is a compound that has gained a pair of electrons.
    (*d*)  it is a compound that has lost a pair of electrons.
    **Answer.** (*b*)
46. What is plotted on the *x* and *y* axes in a mass spectrum?
    (*a*)  *y* axis = abundance of ion; *x* axis = charge/mass
    (*b*)  *y* axis = abundance of ion; *x* axis = mass/charge
    (*c*)  *y* axis = abundance of ion; *x* axis = charge
    (*d*)  *y* axis = abundance of ion; *x* axis = mass
    **Answer.** (*b*)
47. What is the "base peak" in a mass spectrum?
    (*a*)  the peak with the lowest intensity
    (*b*)  the peak with the highest *m/z* value
    (*c*)  the peak with the lowest *m/z* value
    (*d*)  the peak with the greatest intensity
    **Answer.** (*d*)

48. Where in an IR spectrum would you find an absorption band due to a carbon-oxygen double bond?
    (a) 1780-1650 cm$^{-1}$                          (b) 1250-1050 cm$^{-1}$
    (c) 1680-1600 cm$^{-1}$                          (d) 1600-1500 cm$^{-1}$
    **Answer.** (a)

49. Which of the following is not true about electromagnetic radiation?
    (a) frequency is directly proportional to wavelength
    (b) frequency is directly proportional to wavenumber
    (c) energy is inversely proportional to wavelength
    (d) energy is inversely proportional to wavenumber
    **Answer.** (a)

50. Which of the following bonds will show an absorption band at the greatest wavenumber?
    (a) C=O                                           (b) C=C
    (c) O–H                                           (d) C–H
    **Answer.** (c)

51. Which of the following compounds will show an absorption band at 2200 cm$^{-1}$?
    (a) $CH_3CH_2CH_2CH{=}O$                          (b) $CH_3CH_2CH_2C{\equiv}N$
    (c) $CH_3CH_2CH_2OH$                              (d) $CH_3CH_2CH_2COOH$
    **Answer.** (b)

52. An absorption band at 1600 cm$^{-1}$ indicates that a compound contains which of the following groups?
    (a) C=O                                           (b) C=C
    (c) O–H                                           (d) C–O
    **Answer.** (b)

53. What type of radiation is used in nuclear magnetic resonance (NMR) spectroscopy?
    (a) ultraviolet light                             (b) microwaves
    (c) radio waves                                   (d) infrared radiation
    **Answer.** (c)

54. Which of the following absorption bands could be used to distinguish between dimethylamine and trimethylamine?
    (a) 1750-1700 cm$^{-1}$                           (b) 2100 cm$^{-1}$
    (c) 3500-3300 cm$^{-1}$                           (d) 2950 cm$^{-1}$
    **Answer.** (c)

55. Which part of the IR spectrum is called the "fingerprint region"?
    (a) 3000-2000 cm$^{-1}$                           (b) 3000-1000 cm$^{-1}$
    (c) 2000-1000 cm$^{-1}$                           (d) 1000-600 cm$^{-1}$
    **Answer.** (d)

56. Which of the following bonds will show an absorption band at the greatest wavenumber?
    (a) N–H                                           (b) C=O
    (c) C–O                                           (d) C=C
    **Answer.** (a)

57. What part of an IR spectrum is called the functional group region?
    (a) 4000-3000 cm$^{-1}$                           (b) 4000-2000 cm$^{-1}$
    (c) 4000-1000 cm$^{-1}$                           (d) 3000-1000 cm$^{-1}$
    **Answer.** (c)

58. In what region of an IR spectrum would you find a C–H stretch?
    (a) 2100 cm$^{-1}$                                (b) 1600-1500 cm$^{-1}$
    (c) 3600-3400 cm$^{-1}$                           (d) 3300-2700 cm$^{-1}$
    **Answer.** (d)

59. What is the effect of hydrogen-bonding on the position and shape of an O–H stretch?
    (*a*) it is shifted to lower wavenumbers and remains sharp.
    (*b*) it stays at the same wavenumbers and broadens.
    (*c*) it is shifted to lower wavenumbers and broadens.
    (*d*) it is shifted to higher wavenumbers and broadens.
    **Answer.** (*c*)

60. Which of the following is required in order to obtain a mass spectrum?
    (*a*) the compound must lose an electron.
    (*b*) the compound must lose a pair of electrons.
    (*c*) the compound must be water soluble.
    (*d*) the compound must gain an electron
    **Answer.** (*a*)

61. Where in an IR spectrum does a carbon-carbon triple bond show a stretching vibration?
    (*a*) $3100 \text{ cm}^{-1}$                    (*b*) $2700 \text{ cm}^{-1}$
    (*c*) $2100 \text{ cm}^{-1}$                    (*d*) $3300 \text{ cm}^{-1}$
    **Answer.** (*c*)

62. How many kinds of chemically non-equivalent hydrogen nuclei are there in ethylbenzene?
    (*a*) 3                    (*b*) 4
    (*c*) 5                    (*d*) 6
    **Answer.** (*c*)

63. What is the multiplicity of the methylene hydrogens of a carbon that is attached to a methyl group and to a methyl group and to a methoxy group?
    (*a*) doublet                    (*b*) singlet
    (*c*) quartet                    (*d*) triplet
    **Answer.** (*c*)

64. Each of the following compounds has a singlet in its $^1$H NMR spectrum. Which compound would have its singlet at the highest frequency?
    (*a*) 1-bromo-2,2-dimethylpropane          (*b*) ethyl methyl ether
    (*c*) ethyl-*tert*-butyl ether                    (*d*) 1,2-dibromoethane
    **Answer.** (*b*)

65. Which of the following compounds would have the signal for its methylene hydrogens farthest downfield?
    (*a*) ethyl chloride                    (*b*) ethyl iodide
    (*c*) ethyl bromide                    (*d*) ethyl fluoride
    **Answer.** (*d*)

66. How many signals would you expect to see in the $^1$H NMR spectrum of chlorocyclobutane?
    (*a*) 1                    (*b*) 3
    (*c*) 4                    (*d*) 5
    **Answer.** (*d*)

67. What is the multiplicity of the OH group of an alcohol in a solution that contains a trace amount of acid?
    (*a*) doublet                    (*b*) quintet
    (*c*) quartet                    (*d*) singlet
    **Answer.** (*d*)

68. How many signals would you expect to see in the $^1$H NMR spectrum of butane?
    (*a*) 1                    (*b*) 2
    (*c*) 3                    (*d*) 4
    **Answer.** (*b*)

**69.** Which of the following will occur farthest downfield?

(*a*)  the hydrogens of benzene

(*b*)  the hydrogens of ethyne

(*c*)  the hydrogens of dimethyl ether

(*d*)  the hydrogens of $H-\overset{\overset{O}{\|}}{C}-H$

**Answer.** (*d*)

**70.** How many signals will vinyl chloride have in $^1H$ NMR spectrum?

(*a*)  1                                    (*b*)  2

(*c*)  3                                    (*d*)  4

**Answer.** (*c*)

**71.** How many signals does 2,2,4-trimethylpentane have in its $^1H$ NMR spectrum?

(*a*)  2                                    (*b*)  3

(*c*)  4                                    (*d*)  5

**Answer.** (*c*)

**72.** How many signals would you expect to see in the $^1H$ NMR spectrum of 2-methylpropene?

(*a*)  2                                    (*b*)  3

(*c*)  4                                    (*d*)  5

**Answer.** (*a*)

**73.** Which of the following compounds is frequently used as an internal reference in $^1H$ NMR spectroscopy?

(*a*)  TNS                                  (*b*)  DMF

(*c*)  TMS                                  (*d*)  DMSO

**Answer.** (*c*)

**74.** Which of the following describes the $^1H$ NMR spectrum of 1,2-dichloroethane?

(*a*)  one doublet                          (*b*)  two triplets

(*c*)  two doublets                         (*d*)  one singlet

**Answer.** (*d*)

**75.** What is the multiplicity of the $CH_2$, hydrogens in $CH_3OCH_2CH_2OCH_3$?

(*a*)  a singlet                            (*b*)  a triplet

(*c*)  a quartet                            (*d*)  a doublet

**Answer.** (*a*)

**76.** What would be the splitting of the protons on the $CH_2$ groups of butane?

(*a*)  doublet                              (*b*)  sextet

(*c*)  triplet                              (*d*)  singlet

**Answer.** (*c*)

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