ANSWERS

1) less 2) $\log \frac{I_o}{I}$ 3) N 4) uv 5) quartz
6) chromophore 7) azo 8) - OH 9) donors
10) hyperchromic.

III. State the following are TRUE or FALSE

1) Atomic spectrum is a band spectrum.
2) $\nu = c\lambda$
3) The S.I. unit for energy is erg.
4) 1 Einstein = Nh $\bar{\nu}$
5) Energy is inversely proportional to wave number.
6) The wave length of ultraviolet region is 400 nm.
7) The energy of visible region is about 300 kJ.
8) Rotational transitions require more energy.
9) Beer's law is deviated in concentrated solutions.
10) Tungsten lamp is used in visible spectra
11) The monochromator used in infra red region is quartz prism.
12) Quartz cells are used in ultra violet region.
13) The energy of $\sigma - \sigma^*$ transition is higher than for a $\pi - \pi^*$ transition.
14) NO_2 is an auxochrome.
15) $\in_{max}$ depends an λ_{max}
16) Methanol is used as a solvent in electronic spectra
17) The enhancement of $\in_{max}$ is called blue shift.
18) During a red shift, λ_{max} is shifted to higher wave length.
19) An auxochrome changes a molecule into a dye.
20) Compound with one chromophone is usually colourless.

ANSWERS

1) False 2) False 3) False 4) False 5) False
6) True 7) True 8) False 9) True 10) True
11) False 12) True 13) True 14) False 15) False
16) True 17) False 18) True 19) True 20) False.

CHAPTER - 9

INFRA RED SPECTROSCOPY

Infra red spectroscopy is an important tool in the hands of organic chemists. Using this, the structure of all compounds, especially, organic compounds can be identified. Compounds absorb energy in the infra red region and exhibit infra red spectra.

In the previous chapter we have seen among, uv, visible and infra red regions, infra red region has the lowest energy. The region of electromagnetic spectrum in between the visible and microwave region is called infra red region. In the infra red spectra, we obtain usually vibrational modes accompanied by rotational transitions. The important informations about infra red spectra are given below –

(i)	Wave number, $\bar{\nu}$	10^2 to 10^4 cm^{-1}
(ii)	Wave length, λ	0.01 to 0.0001 cm (or) 100 μ to 1 μ $(\because 1\mu = 1 \times 10^{-4}$ cm)
(iii)	frequency, ν	3×10^{12} to 3×10^{14} Hz
(iv)	Energy, E	10^3 to 10^5 J mol^{-1}

The infra red region may be divided into the following three sections for convenience –

(i) The very near Infra red region : This is known as *overtone region* and ranges from 1.2 to 2.5 μ.

(ii) The near Infra red region : This is also known as *vibration rotation region* and ranges from 2.5 to 25 μ

(iii) The far Infra red region : This is known as rotation region. This ranges from 25 to 300 μ.

Note : When an analytical chemist speaks of infra red spectroscopy, he usually means the region from 2.5 to 25 μ or 4000 to 400 cm^{-1}.

This range gives him the valid informations about the vibrations of molecules and hence about the structure of molecules.

Principle : The absorption of radiation by a sample requires that –

(i) the energy content of radiation should correspond to the energy difference between the two vibrational states.

(ii) there should be strong coupling interaction between the sample and the radiation.

This coupling interaction takes place only if there is a change in dipole moment during the absorption process. If there is no change in dipole moment during the vibration process, there will be no coupling interaction between the sample molecule and radiation and therefore no absorption is possible, even if the first condition is satisfied.

The essential condition for a molecule to have infrared spectrum is that ***it must have change in dipole moment during vibration or rotation.*** Thus,

(i) Molecules like H_2O, NH_3 which have permanent dipole moment exhibit infra red spectra.

(ii) Molecules which absorb infra red radiation alone will have infra red spectra. Homonuclear molecules like H_2, N_2, X_2 can not absorb infra red radiation and they do not have infra red spectra.

(iii) Heteronuclear molecules like HD, HX, CO, NO are able to exhibit infra red spectra as they absorb infra red radiation.

(iv) Though carbon dioxide molecule does not have permanent dipole moment, yet it gives infra red spectra. The reason is that the asymmetric stretching and bending modes of vibrations of carbon dioxide creates some changes in dipole moment. Hence, infra red spectrum is possible for carbon dioxide.

Vibration Transitions : *In a polyatomic molecule, each atom is having three degrees of freedom in three (x, y and z) directions which are perpendicular to one another. Consequently, a poly atomic molecule is requiring three times as many degrees of freedom as the number of atoms. Thus, a molecule of n atoms has $3n$ degrees of freedom. This total degrees of freedom is composed of the following:*

(i) Translational degrees of freedom

(ii) Rotational degrees of freedom

(iii) Vibrational degrees of freedom

i.e., 3n = trans. deg. free. + rot. deg. free. + vib. deg. free

The translational degrees of freedom for any molecule will be always three.

∴ rot. deg. free. + vib. deg. free = (3n – 3)

For a non – linear molecule, three of the degrees of freedom describe rotation. Hence, for a non – linear molecule, the number of vibrational degrees of freedom = (3n – 3) – 3

= (3n – 6)

(3n – 6) is called the **fundamental vibrations** for a non – linear molecule.

In a linear molecule, only two degrees of freedom are required to describe rotation.

Thus, a linear molecule has (3n – 3) – 2 = (3n – 5) vibrational degrees of freedom.

Types of stretching and bending vibrations

According to the characteristic of vibration, normal vibrations can be divided into the following two principal groups –

(i) Stretching vibrations

(ii) Bending vibrations

Stretching Vibrations : In this type of vibrations, the atoms move essentially along the bond axis, so that the bond length increases or decreases periodically. As this type of vibrations correspond to one dimensional motion, it means that there will be (n – 1) stretching vibrations for non – cyclic systems.

During stretching vibrations, bond angles change only if it is required to do so by the centre of gravity resisting displacement.

Stretching vibrations are of two types –

(i) Symmetric stretching

(ii) Asymmetric stretching

These are denoted by ν. These are given for a AB_2 molecule in the figures 1 and 2

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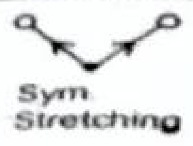


Fig. 1

Fig. 2

Stretching vibrations appear in the region 5000 – 500 cm^{-1}. The frequency of asymmetric stretching mode is always greater than that of symmetric stretching mode.

Bending vibrations : In this type, there occurs a change in bond angles between bonds with a common atom.

The bending vibrations are also called **deformation vibrations**. As these vibrations are describing two dimensional motions, there will be (2n – 5) bending vibrational modes for non cyclic molecules. These appear at lower frequencies, whereas stretching vibrations appear at higher frequencies.

The force constants of deformation vibrations are generally less than those of the stretching vibrations. Due to the smaller force constants, the deformation vibrations are more sensitive to environmental influence. Bending vibrations are more in number as compared to stretching vibrations.

Deformation vibrations are of the following two types –

(i) in plane deformation vibrations

(ii) out of plane deformation vibrations.

In plane deformation vibrations include –

a) scissoring

b) rocking vibrations

Out of plane deformation vibrations include –

a) twisting

d) wagging vibrations

This may also comprise (i) symmetric and (ii) asymmetric vibrations.

Few deformation vibrations are shown in fig 3 to 6

Fig 3

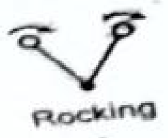


Fig. 4

Fig 5

Fig. 6

The number of possible bending modes of vibrations of molecules can be calculated as below :

(i) Linear molecule : (3n – 5) – (n – 1)=(2n – 4)

(ii) Non linear molecule : (3n – 6) – (n – 1)=(2n – 5)

We can explain them by taking suitable examples.

1) Diatomic molecules

All diatomic molecules will be linear. Hence, the number of vibrational modes for them will be

$$(3n - 5) = (3 \times 2 - 5) = 6 - 5 = 1$$

Thus, all diatomic molecules exhibit only one vibrational frequency in the infra red region. This vibrational mode will be a stretching mode as per (n – 1) = (2 – 1) = 1

The stretching frequencies of few diatomic molecules are as follows –

HF (3958 cm^{-1}) HCl (2886 cm^{-1})

HBr (2559 cm^{-1} HI(2230 cm^{-1})

NO (1780 cm^{-1} CO(2140 cm^{-1})

2) Triatomic molecules

Based on their structure, triatomic molecules can be classified into the following two types –

a) Linear triatomic molecules

b) Non linear triatomic molecules

We can explain them with suitable example.

Linear triatomic molecule, CO_2

The number of possible modes of vibration is

$$(3n - 5) = (3 \times 3 - 5) = 9 - 5 = 4$$

The number of stretching modes of vibration is

$(n - 1) = (3 - 1) = 2$ and these two are (i) symmetric stretching and (ii) asymmetric stretching vibrations. Hence, the number of bending vibration $= 4 - 2 = 2$

These are shown in the figures 7 to 10

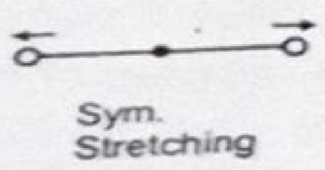


Fig 7

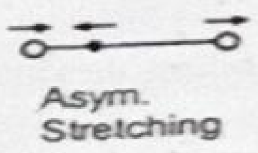


Fig. 8

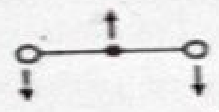


Fig. 9

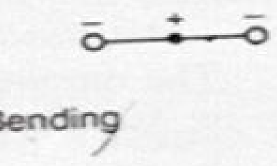


Fig. 10

The bending vibrations (figures 9 and 10) have the same energy, so they are called **degenerate**. Thus, there are only three different normal vibrations in the case of CO_2 or any linear triatomic molecule as follows –

(i) One symmetric stretching vibration.
(ii) One asymmetric stretching vibration
(iii) two degenerate bending vibrations at two perpendicular directions.

The first selection rule for vibrational spectra is that the molecule should have a change in the dipole moment. If we consider CO_2, the symmetric stretching vibration (figure 7) is inactive in the infra red because the dipole moment is not altered by symmetrical displacements of the two outer atoms. Thus, CO_2 will exhibit two infra red absorption bands corresponding to –

(i) asymmetric stretching at 2350 cm^{-1}
(ii) degenerate bending at 667 cm^{-1}

Non linear triatomic molecules H_2O, SO_2 and NO_2

The number of possible vibrational modes is,

$$(3n - 6) = (3 \times 3 - 6) = 9 - 6 = 3$$

Among them, the number of stretching modes are

$(n - 1) = (3 - 1) = 2$. These are (i) symmetric stretching and (ii) asymmetric stretching

The remaining $(3 - 2) = 1$ is the bending vibration.

Three vibrations for water molecule are given in figures 11, 12 and 13

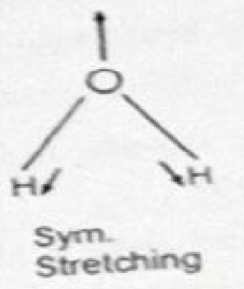


Fig. 11

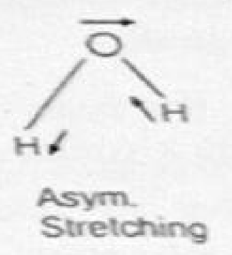


Fig. 12

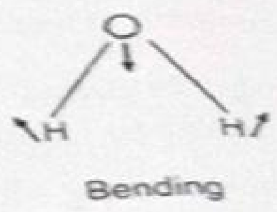


Fig. 13

All the three vibrations involve change in dipole moment. These vibrations are infra red active and can be noticed in the infra red spectrum of water.

Similarly, it is possible to calculate the number of possible vibrational degrees of freedom for higher atomic molecules and their vibrational modes can be identified without much difficulty from their infra red spectra.

Vibrational frequencies and force constant

It is possible to calculate the frequency of a bond using Hooke's law as below –

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \ sec^{-1} \qquad \text{......} \quad (1)$$

Here, k = force constant; ν = frequency

$$\mu = \text{reduced mass} = \frac{m_1 m_2}{(m_1 + m_2) N}$$

m_1 and m_2 are the atomic mass of two atoms connected by a bond and are given in atomic mass unit, amu.

N = Avogadro number $= 6.023 \times 10^{23}$

We know that, $\nu = c\bar{\nu}$ ..... (2)

Using (2), equation (1) can be written as,

$$c\bar{\nu} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ \text{sec}^{-1} \qquad \ldots\ (3)$$

$$\text{or}\quad \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ \text{cm}^{-1} \qquad \ldots\ (4)$$

Here, c is the velocity of light $= 3 \times 10^{10}$ cm sec^{-1}

From equation (1), the force constant,

$$k = 4\pi^2 \nu^2 \mu \text{ dyne cm}^{-1} \qquad \ldots\ (5)$$

From equation (4), the force constant,

$$k = 4\pi^2 \bar{\nu}^2 c^2 \mu \text{ dyne cm}^{-1} \qquad \ldots\ (6)$$

Force constant is regarded as a measure of the stiffness (strength) of the bond.

WORKED EXAMPLES

1. The fundamental vibrational frequency of HBr is 2559 cm^{-1}. Calculate the force constant. Given that the amu of H and Br are 1 and 80 respectively.

Use : $k = 4\pi^2 \bar{\nu}^2 c^2 \mu$ dyne cm^{-1}

Given : $\bar{\nu} = 2559$ cm^{-1}; $c = 3 \times 10^{10}$ cm sec^{-1}

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)N} = \frac{1 \times 80}{(1 + 80) \times 6.023 \times 10^{23}}$$

$$= \frac{80}{81 \times 6.023 \times 10^{23}} = 1.64 \times 10^{-24}\ \text{g}$$

$$\therefore k = 4 \times \frac{22}{7} \times \frac{22}{7} \times (2559)^2 \times (3 \times 10^{10})^2 \times 1.64 \times 10^{-24} \text{ dyne cm}^{-}$$

Force constant, $k = \mathbf{3.82 \times 10^5}$ **dyne cm^{-1}.**

2. HBr molecule absorbs infra red radiation at the wave length of 3.77 × 10^{-6}m. Calculate the force constant of HBr. Given that, c = 2.998 × 10^8 ms $^{-1}$; H = 1 amu and Br = 80 amu

Note : The wave length and the velocity of light are given in S.I. units. Hence, we have to calculate the force constant, k in S.I. unit namely, Nm^{-1}.

Use : $k = 4\pi^2 \nu^2 \mu$ Nm^{-1}

$$\text{But,}\quad \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8}{3.77 \times 10^{-6}}\ \text{s}^{-1} = 7.952 \times 10^{13}\ \text{s}^{-1}$$

5.721×10^{-24}s

$$\mu = \frac{m_1\, m_2}{(m_1 + m_2)\,N}$$

$$\frac{1 \times 19 \times 10^{-3}}{20 \times 6.023 \times 10^{23}}$$

Here, m_1 = atomic mass of H $= 1 \times 10^{-3}$ kg

m_2 = atomic mass of Br $= 80 \times 10^{-3}$ kg

$$\therefore \mu = \frac{1 \times 80 \times 10^{-3}}{(1 + 80) \times 6.023 \times 10^{23}}\ \text{kg} = 1.64 \times 10^{-27}\ \text{kg}$$

$$\therefore k = 4 \times \frac{22}{7} \times \frac{22}{7} \times (7.952 \times 10^{13})^2 \times 1.64 \times 10^{-27}\ \text{Nm}^{-1}$$

Force constant, $k = \mathbf{410}$ **Nm^{-1}**

3. Calculate the fundamental vibrational frequency of C = C stretching in cm^{-1}. You are given that the force constant, k = 9.8 × 10^5 dyne cm^{-1} and velocity of light, c = 3 × 10^{10} cm s^{-1}.

Use : $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ cm^{-1}

Given : $c = 3 \times 10^{10}$ cm s^{-1}; $k = 9.8 \times 10^5$ dyne cm^{-1}

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)N} = \frac{12 \times 12}{(12 + 12)\, 6.023 \times 10^{23}} = \frac{144}{24 \times 6.023 \times 10^{23}}$$

$$= 9.96 \times 10^{-24}\ \text{g}$$

$$\bar{\nu} = \frac{1}{2 \times \frac{22}{7} \times 3 \times 10^{10}}\sqrt{\frac{9.8 \times 10^5}{9.96 \times 10^{-24}}}\ \text{cm}^{-1}$$

$$\bar{\nu} = 1663\ \text{cm}^{-1}$$

The fundamental vibrational frequency of C = C is 1663 cm^{-1}

PROBLEMS FOR EXERCISE

1. Calculate the stretching frequency of C – H bond, given that, force constant, $k = 5 \times 10^5\ g\,s^{-2}$

   the atomic mass of $C = 20 \times 10^{-24}$ g

   the atomic mass of $H = 1.6 \times 10^{-24}$ g **(Ans : 3086 cm^{-1})**
2. Calculate the force constant of CO molecule if it absorbs at 2140 cm^{-1} **(Ans : 1.86×10^6 dyne cm^{-1})**
3. Calculate the force constant of HI molecule in S.I. unit. HI has an absorbtion band at $6.6 \times 10^{13}\ sec^{-1}$ **(Ans : 290 Nm^{-1})**

Factors influencing vibrational frequencies

It has been found that many factors influence the vibrational frequencies. In this chapter we will confine our discussion with the following two factors –

(i) changes in the molecular structure

(ii) interaction of functional groups

(i) Bond strength

(i) When bond strength increases – the frequency (ν) and the force constant, (k) also increase as $\nu \propto \sqrt{k}$.

(ii) The strength of bonds depends on the bond order. It increases in the following way –

triple bond > double bond > single bond

This is reported in the following table.

TABLE 9.1

S.No.	Bond	Frequency (cm^{-1})	Nature of compound
1	C – C	1300 – 800	alkanes
2	C = C	1670 – 1640	alkenes
3	C ≡ C	2260 – 2100	alkynes
4	C – O	1050	alcohols
5	C = O	1740 – 1720	aldehydes
6	C ≡ O	2140	carbonyl complexes

2) Reduced mass,μ : As the reduced mass of the system decreases – (i) the frequency and (ii) the force constant increase because, $\bar{\nu} \propto \frac{1}{\sqrt{\mu}}$. For example, the stretching vibrational frequencies of C – H and O – H are higher than that of C – C and C – O, as their reduced mass increases in the reverse direction. The following table will substantiate this statement.

TABLE 9.2

S.No.	Molecule	Reduced mass $\mu \times 10^{-24}$ g	Frequency (cm^{-1})
1.	HF	1.56	3958
2.	HI	1.64	2230
3.	CO	11.38	2140
4.	NO	12.40	1780

There are few exceptions for this observation also. Few examples are discussed below :

(i) The stretching frequency of X – H must decrease in the following way on the basis of their reduced mass –

C – H > N – H > O – H > F – H

But, they increase actually. The reason for the increase is that t electronegativity of X increases in the above order which makes t bond stronger.

(ii) Similarly, $\nu_{O-H} > \nu_{O-D}$ But, it is actually $\nu_{O-D} > \nu_{O-H}$

3. Hydrogen bonding : When hydrogen bonding is present an molecule, it decreases the vibrational frequency considerably an decrease depends on the strength and nature of hydrogen bo It is possible to ascertain the hydrogen bonding as –

(i) intermolecular (ii) intramolecular

from their infra red spectra. The difference between the two hydrogen bonding are given in the table.

TABLE 9.3

S.No.	Intermolecular hydrogen bonding	Intramolecular hydrogen bonding
1.	It exhibits broad bands	It exhibits sharp bands.
2.	It depends on the concentration. i.e., On diluting the solution, the intensity of the band decreases band finally vanishes.	It does not depend on the concentration.
3.	The difference in absorption frequencies between discrete and associated molecules is high.	Low.

The hydrogen bonding present in amines usually shows small difference in vibrational frequencies than in alcohols. The reason is that oxygen is more electronegative than nitrogen and thereby the hydrogen bonding present in alcohols is more stronger than in amines.

4) Electronic effects : When we change a substituent near to a functional group, the frequency also changes. The change in frequency may be due to –

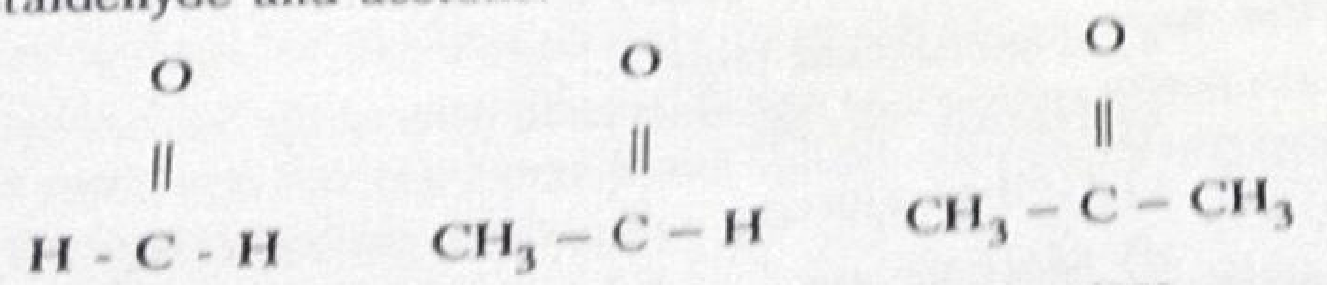
(i) inductive effect

(ii) measomeric effect or resonance effect

(iii) field effect.

These are explained below with suitable examples.

a) When an alkyl group is substituted in the molecule, due to its +I effect, the bond length increases and the bond strength decreases. The force constant as well as the absorption frequency also decrease. This is illustrated with formaldehyde, acetaldehyde and acetone.



Formula	$H-\overset{\overset{O}{\parallel}}{C}-H$	$CH_3-\overset{\overset{O}{\parallel}}{C}-H$	$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$
Compound	formaldehyde	acetaldehyde	acetone
$\nu_{C=O}$	1750 cm^{-1}	1745 cm^{-1}	1715 cm^{-1}
No. methyl groups	zero	one	two

b) On the otherhand, if we introduce electronegative atom or group in the molecule, due its – I effect, the following are increasing –

(i) strength of bond

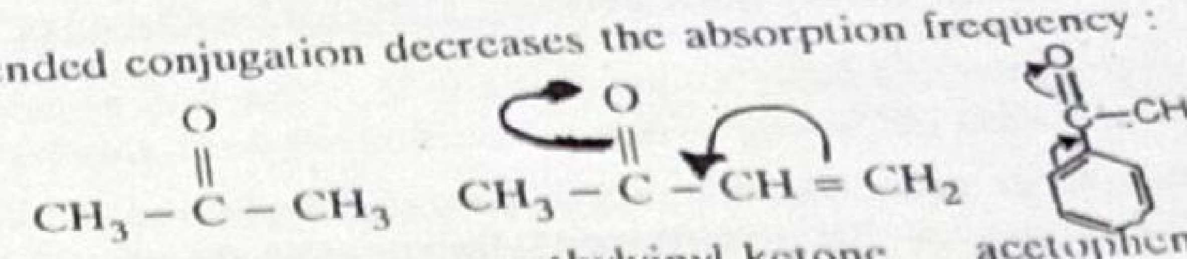
(ii) force constant

(iii) absorption frequency

This is explained with the following examples :

Formula	CH_3COCH_3	$ClCH_2COCH_2Cl$	$Cl_2CHCOCHCl_2$
Compound	acetone	dichloroacetone	tetrachloroacetone
$\nu_C = O\ (cm^{-1})$	1715	1740	1750
No. chlorine atoms	zero	two	four

c) Extended conjugation decreases the absorption frequency :

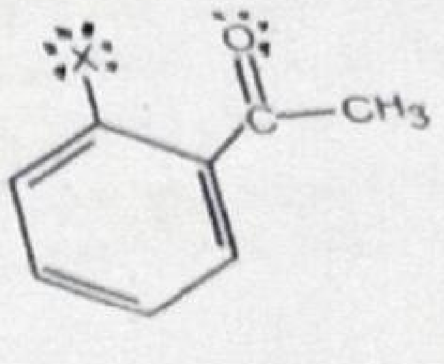


Formula	$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$	$CH_3-\overset{\overset{O}{\parallel}}{C}-CH=CH_2$	
Compound	acetone	methylvinyl ketone	acetophenone
$\nu_{C=O}\ (cm^{-1})$	1715	1705	1695

In methylvinyl ketone, the conjugation is due to α, β unsaturation whereas in acetophenone the extended conjugation is due to an aromatic ring.

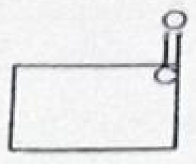
It can be noted that the inductive effect is of less important in these compounds. The mesomeric effect plays vital role in these compounds.

d) Field effect : In the ortho compounds, the lone pair of electrons present on the atoms interact with neighbouring groups and cause considerable changes in the absorption frequencies.

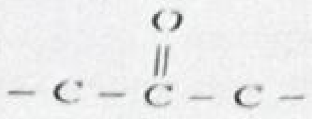


Example : o – haloacetophenone

5) Bond angles : In cyclobutanones, the $\nu_{C=O}$ values are maximum. The strain is high in these molecules. This can be explained in the following way.



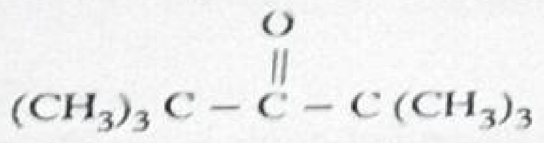
The bond angle of



$$-C-\overset{\overset{O}{||}}{C}-C-$$

should be 120°. If there is any decrease in this value, then the s–character increases. This in turn increases the bond strength and absorption frequency by decreasing the bond distance. On the other hand, if the band angle is higher than 120°, the absorption frequency decreases.

Example :



ditertiary butyl ketone, $(CH_3)_3C-\overset{\overset{O}{||}}{C}-C(CH_3)_3$

Instrumentation – Block diagram

The important components of an infra red spectrometer are

- (i) Source of radiation
- (ii) Monochromators
- (iii) Cell
- (iv) Detectors
- (v) Recorders

The infra red spectrophotometers are of two types –

- (i) Single beam spectrophotometer
- (ii) Double beam spectrophotometer

The block diagram of a double beam spectrophotometer is given in the fig. 9.14

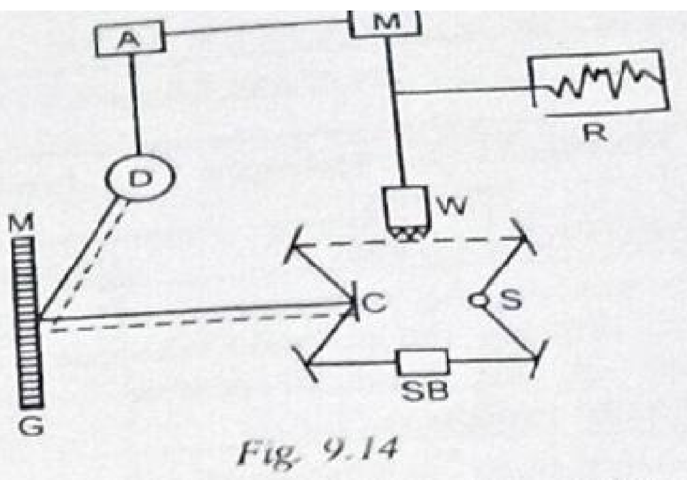


Fig. 9.14

The light emerging from source *S* is divided into two beams. One beam of light is passing through the sample cell (SB). The other is passing through the reference. The two beams are reflected on a frequency reflector. This reflects the beam of light of the sample and reference alternatively to a monochromator MG. From the monochromator, light rays go to the frequency detector D. There, infra red energy is converted into electrical energy. The detector receives the high intense reference beam and less intense sample beam alternatively from the frequency reflector. The detector arranges for the flow of alternating current in the amplifier A. When the sample does not absorb light, the intensity of both beams will be the same. The signal obtained from the detector is fed into a motor, *M*. This sends an optical wedge (W) to the reference beam so as to get same intensity of light from both beams.The oscillation of optical wedge operates the recorder, R which has a pen on a printed chart paper. The movement of pen on the chart paper gives the infra red spectra.

We shall now discuss the important components of infra red spectrophotometer in detail.

1) Radiation Source : The various radiation sources used in infra red spectrosphotometer are –

- a) Incandescent lamp
- b) Nernst Glower
- c) Globar source
- d) Mercury arc

a) Incandescent lamp : In the near infra red instruments, an ordinary incandescent lamp is generally used.

However, this fails in the far infra red region because it is glass enclosed and has a low spectral emissivity.

b) Nernst Glower : It consists of a hollow rod which is about 2 mm in diameter and 30 mm in length. The glower is composed of rare earth oxides such as zinconia, yttria and thoria.

It emits infra red radiation over wide wave length range. The intensity of radiation remains steady and constant over long periods of time.

c) Globar source : It is a rod of sintered silicon carbide which is about 50 mm in length and 4 mm in diameter. When it is heated to a temperature between 1300 and 1700°C, it strongly emits infrared radiation.

It works at wavelengths longer than 650 cm^{-1}.

d) Mercury arc : In the far infra red instruments, high pressure mercury arc is generally employed.

2) Monochromators : The radiation source emits radiations of various frequencies. As the sample in the infra red spectroscopy absorbs only at certain frequencies, it becomes necessary to select desired frequencies from the radiation source. This selection has been achieved by means of monochromators which are mainly of two types –

a) prism monochromators

b) grating monochromators

a) Prism monochromators : In both mono - pass and double pass monochromators, sodium chloride (rock salt) prism is employed for the entire region from 4000 – 650 cm^{-1}. Prism of LiF or CaF_2 give more resolution in the region where the significant stretching vibrations are located.

b) Grating monochromators : If a prism in a prism monochromator is replaced by a grating, higher dispersion can be achieved. The grating is essentially a series of parallel straight lines cut into a plane surface.

Grating can be made with materials like aluminium which are not attacked by moisture. On the other hand, metal salt prisms are subject to etching from atmosphere moisture.

3) Sample cells : As infra red spectroscopy has been used for the characterisation of solid, liquid or gas samples, it is evident that samples of different phases have to be handled. But the samples must be treated differently. However, the only common point to the sampling of different phases is that the material containing the sample must be transparent to the infra red radiation.

This condition restricts our selection to only certain salts like NaCl or KBr. However, a final choice of salt will depend on the wave length range to be studied.

4) Sampling Techniques : As infra red spectroscopy has been used for the study of solid, liquid or gas samples, it is evident that different techniques have to be used for different phases. We shall discuss sampling techniques for solid, liquid and gaseous samples.

a) Sampling of solids : The following four techniques are generally employed for solid samples –

(i) solids run in solution

(ii) solid films

(iii) mull technique

(iv) pressed pellet technique

(i) Solids run in solution : If the solution of solid can be prepared in a suitable solvent, then the solution is run in one of the cells for liquids.

When the investigating solids are in solutions, the absorption due to solvent has to be compensated by keeping the solvent in a cell of same thickness as that containing the sample, in the path of the reference beam of double beam spectrophotometer.

(ii) Solid films : If a solid is amorphous in nature, the sample is deposited on the surface of the KBr or NaCl cell by evaporation of a solution of the solid.

This technique is useful for rapid qualitative analysis but becomes useless for carrying out quantitative analysis.

(iii) Mull technique : In this technique, the finely ground solid sample is mixed with **Nujol** (mineral oil) to make a thick paste which is then made to spread between infra red transmitting windows. This is then mounted in a path of infra red beam and the spectrum is run.

Although Nujol is transparent throughout infra red region, yet it has the disadvantage that it has the absorption maxima at 2915, 1462, 1376 and 719 cm^{-1}

(iv) Pressed pellet technique : In this technique, a small amount of finely ground solid sample is intimately mixed with about 100 times its weight of powdered potassium bromide. The finely ground mixture is

then pressed under very high pressure in a press to form a small pellet. The resulting pellet is transparent to infrared radiation and is run as such.

b) Sampling of liquids : Samples that are liquids at room temperature are usually put frequently with no preparation, into the rectangular cell made of NaCl or KBr and their infra red spectra are obtained directly.

c) Sampling of gases : The gas sample is put into a special cell generally about 10 cm long, which is then kept across the path of the infra red beam. The end walls of the cell are generally made up of NaCl. For measuring very dilute gases, long path cells are to be employed.

4) Detectors : The various types of detectors used in infrared spectroscopy are discussed.

a) Bolometers : A bolometer usually consists of a thin metal conductor. When radiation such as infra red falls on this conductor, its temperature changes. As the resistance of a metallic conductor changes with temperature, the degree of change in resistance is regarded as a measure of the amount of radiation that has fallen on the bolometer.

b) Thermomcouples : These are used as detectors in modern infra red spectrophotometers. A thermocouple is made by welding together at each end of two wires of different semiconductor materials of high thermo electric efficiency. If two welded joints are kept at different temperatures, a small electrical potential is developed between the joints. A thermocouple is enclosed in an evacuated steel casing with a KBr or CsI window to avoid losses of energy by convection.

In the infra red spectroscopy, one welded joint (called **cold junction**) is kept at a constant temperature and is not exposed to infra red radiation, but the other welded joint (called **hot junction**) is exposed to the infra red radiation which increases the temperature of the junction. The temperature difference between the two junction generates potential difference which depends on how much infra red

radiation falls on the hot junction. The response time of a thermocouple is about 60 milli sec.

c) Thermistors : These consist of a fused mixture of metal oxides which show a negative thermal coefficient of electrical resistance. This enables use of thermistors in the same way as bolometers.

d) Golay cell : It is generally used in several commercial spectrophotometers. It consists of a small metal cylinder which is closed by a blackened metal plate at one end and by a flexible metallized diaphragm at the other. After filling the cylinder with xenon, it is sealed. When infra red radiation is allowed to fall on the blackened metal plate, it heats the gas which causes it to expand. The resulting pressure increase in the gas deforms the metallized diaphragm which separates two chambers. Light from a lamp is made to fall on the diaphragm which reflects the light on to a photocell. Motion of the diaphragm changes the out put of the cell. The signal seen by the phototube is modulated in accordance with the power of the radiant beam incident on the gas cell.

Golay cell is best suited when working at wave lengths greater than about 15μ. It is more expensive and bulky.

e) Photoconductivity cell : This is a non – thermal detector of greater sensitivity. It consists of a thin layer of PbS or PbTe supported on glass and enclosed into an evacuated glass envelope. When infra red radiation is focussed on PbS, its conductance increases and causes more current to flow. Response time is 0.5 milli second.

5) Recorders : The electrical energy obtained from the detector is amplified with the help of an amplifier which is connected with a motor. The motor operates an optical wedge. The movement of the wedge is recorded on a printed chart paper with the help of a pen. Thus, we obtain infra red spectrum. The spectrum can be calibrated using polystyrene film. Usually the transmittance values are taken in the y–axis and frequency of radiation in cm^{-1} is taken in the x axis. The infrared spectrum of acetic acid is shown in fig. 9.15

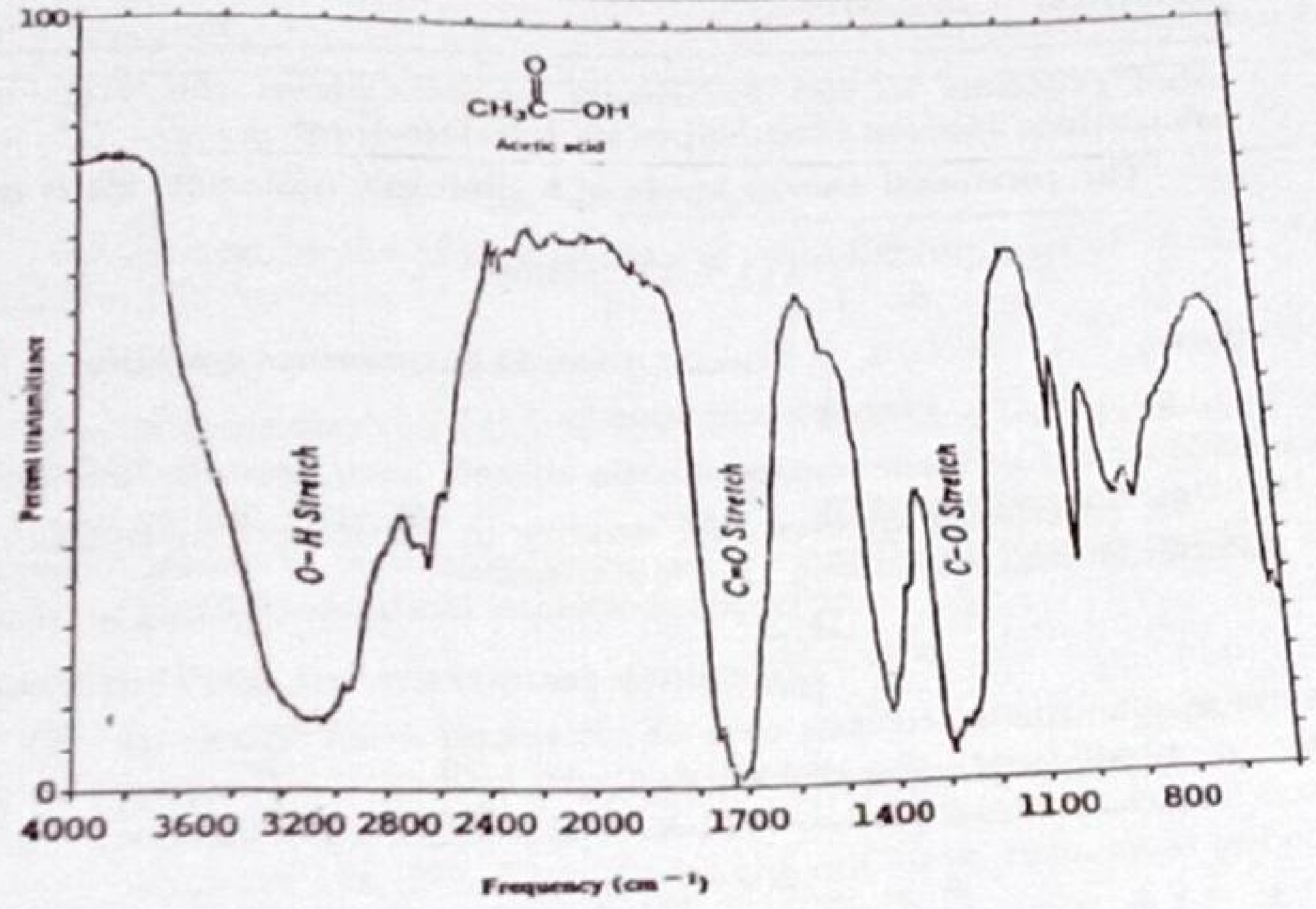


Fig. 9.15

Identification of organic compounds from characteristic absorption bands

The number of possible infra red absorption bands of diatomic and triatomic molecules have been calculated using $(3n - 5)$ and / or $(3n - 6)$ formula. We can use this formula for polyatomic molecules also. But, in poly atomic molecules, the actual number of modes of vibrations will be altogether different from those calculated theoretically. The main reasons for this are –

(i) The over tones (multiples of fundamental frequency) and combination of over tones may increase the number of modes of vibrations.

(ii) Some other phenomenon may reduce the number of bands.

However, each molecule in the infra red region exhibits its characteristic peaks. The nature of the absorption bands and its position serve as finger print of the molecule in the region 1400 – 900 cm^{-1}. This is called **finger print region.** We know that the finger print of any two persons will not be identical. In the same way, no two organic compounds will have the identical infra red spectra. In the finger print region C–C, C–O and C–N stretching vibrations along with many bending vibrations take place. Using this finger print region along with far and near infrared regions, it becomes possible to identify the compound. The absorption frequencies of important functional groups are accurately determined and are available in the form of tables (as below) in the literature. Comparing the experimental value with the literature value, we can easily identity the compound. In the following table the details of absorption frequencies of few important functional groups are given.

TABLE 9.4

The vibrational frequencies of few functional groups

S.No.	Bond	Type of Compounds	Wave number (cm^{-1})
1.	C–H	Alkanes, $-CH_3$ $-CH_2$ Ring Alkenes Alkynes Aromatic	2960 and 2870 2925 and 2855 3100 - 2990 > 3000 3333 - 3267 3100 - 3000
2.	C–C	Alkanes	1300–800
3.	C=C	Alkenes Conjugated dienes Aromatic	1670 – 1640 1650 – 1600 1600 – 1500
4.	C≡C	Alkynes	2260 –2100
5.	C–O	1° - alcohols 2° – alcohols 3° – alcohols Phenol Acid Ether	1050 1100 1200 1200 1315 – 1280 1150 – 1070
6.	C = O	Acid Aldehydes Ketones Esters	1720 – 1665 1740 – 1720 1725 –1705 1750 – 1735

7.	O – H	Alcohols/Phenols Without H – bond Acid	3650 – 3585 3550 – 3200 3300 – 2500
8.	N – H	Amines	3500 – 3300
9.	C – Cl	Chloro compounds	800 – 600

Selection rules for Infrared spectra

1) The molecule must have a permanent dipole moment ie., H_2, N_2, O_2, X_2 are infrared inactive whereas H_2O, NH_3, HX, CO are infra red active.
2) During transition, change in vibrational quantum number can be ±1, i.e., $\Delta v = \pm 1$

Applications of infra red spectroscopy

i) This is useful to identify the compounds, particularly organic compounds.
ii) It is useful in the detection of impurities. Extra absorption bands will appear if impurities are present.
iii) It is useful to ascertain the presence of hydrogen bonding in a molecule as hydrogen bond causes broadening and shifting to lower wave numbers.
iv) Dipole moment can be measured using this spectra.
v) It is used to calculate the force constants, bond lengths and bond angles of molecules.
vi) It can be used to study the structure of coordination compounds.
vii) Quantitative determination of compounds in a mixture can be done.

Microwave
Introduction

~~Note on rotational spectra~~

Pure rotational absorption spectra are observed in the far infra red and microwave region. It is also called **microwave spectroscopy**. It is proving in recent years a great asset in the studies of various problems in physics, chemistry, electronics and even astronomy. Particularly, this has been found to be very useful in the determination of the structures of those molecules which do not give good results by using other spectroscopic methods. The ability to measure frequencies

H — X

more precisely in the microwave region allows the very accurate calculations than in other types of spectroscopy.

The rotational energy levels of a diatomic molecule, E_J is given as

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

where, J = 0, 1, 2 ...., rotational quantum number
h = Planck's constant
I = moment of inertia

H – H
O – O
N – N
H – Cl

In rotational spectra, the energy is expressed in terms of wave number, $\bar{\nu}$ and we know, $E = h\nu = hc\bar{\nu}$

$$\therefore \bar{\nu} = \frac{E_J}{hc} \quad \text{..... (2)}$$

Using equation (2) we have $\bar{\nu} = \frac{E_J}{hc} = \frac{h^2}{8\pi^2 I h c} J(J+1) \text{ cm}^{-1}$

$$\bar{\nu} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \quad \text{..... (3)}$$

where, c = velocity of light. It is common to write B for $\frac{h}{8\pi^2 Ic}$ so that the equation (3) becomes,

$$\bar{\nu} = BJ(J+1) \text{ cm}^{-1} \quad \text{..... (4)}$$

where, B is the rotational constant and is given as,

$$B = \frac{h}{8\pi^2 Ic} \quad \text{..... (5)}$$

when J = 0, the equation (4) becomes,

$$\bar{\nu}_0 = B \times 0(0+1) = 0 \quad \text{..... (6)}$$

when J = 1, the equation (4) becomes,

$$\bar{\nu}_1 = B \times 1(1+1) = 2B \text{ cm}^{-1} \quad \text{..... (7)}$$

when J = 1 and J' = 0 using equation (6) and (7) we have

$$\bar{\nu}_{0 \to 1} = 2B - 0 = 2B \text{ cm}^{-1} \quad \text{..... (8)}$$

From equation (8) it follows that an absorption line will appear at $2B \text{ cm}^{-1}$

If the molecule is raised from $J^1 = 1$ to $J = 2$ level by the absorption of more energy and the equation (8) becomes.

$$\bar{\nu}_{1 \to 2} = B \times 2(2 + 1) - B(1 + 1)\ cm^{-1}$$

$$= 6B - 2B = 4B\ cm^{-1} \qquad \text{..... (9)}$$

In general, when the molecule is raised from J to (J + 1), the equation (8) becomes

$$\bar{\nu}_{J \to J+1} = 2B\,(J + 1)\,J\ cm^{-1} \qquad \text{..... (10)}$$

From the equation (10), it is clear that a step wise raising of the rotational energy gives rise to an absorption spectrum which consists of lines at 2B, 4B, 6B .... cm^{-1} with a constant interval of 2B cm^{-1} whereas a similar lowering of rotational energy would give rise to a similar identical emission spectrum.

Selection rule for rotational spectra

(i) In order for a molecule to give rise to rotational spectrum it becomes essential that the molecule must have a dipole moment. Thus, HX, CO and NO would have rotational spectra whereas H_2, N_2, O_2, X_2 would not have rotational spectra.

(ii) All transitions are not permitted and only $\Delta J = \pm 1$ are permitted. It is evident that only those transitions are permitted in which there is an increase or decrease by unity in J value.

Applications of rotational spectra

From the rotational spectra of a molecule, the following are determined –

(i) moment of inertia, I

(ii) bond length, r. This is explained with carbon monoxide molecule.

The first line corresponding to J = 0 appears in the rotational spectrum of CO at 3.84235 cm^{-1}

i.e., $2B = 3.84\,235\ cm^{-1}$

$\therefore B = 1.92118\ cm^{-1}$

But, $B = \dfrac{h}{8\pi^2 Ic}$

or, moment of inertia, $I = \dfrac{h}{8\pi^2 Bc}$

Substituting, $h = 6.625 \times 10^{-27}$ erg sec

$c = 3 \times 10^{10}$ cm sec^{-1}

$B = 1.92118\ cm^{-1}$

$$I = \frac{6.625 \times 10^{-27}}{8 \times \left(\frac{22}{7}\right)^2 \times 1.92118 \times 3 \times 10^{10}}\ g\ cm^2$$

$$I = 1.456 \times 10^{-39}\ g\ cm^2$$

$\sqrt{\frac{x}{\mu}} = I$

But, $I = \mu r^2$ and $r = \sqrt{\dfrac{I}{\mu}}$

where, μ = reduced mass $= \dfrac{m_1 m_2}{(m_1 + m_2) N}$

where m_1 and m_2 are the atomic mass of atoms. Here

$m_1 = 12$ amu; $m_2 = 16$ amu and $N = 6.023 \times 10^{23}$

$$\therefore \mu = \frac{12 \times 16}{(12 + 16) \times 6.023 \times 10^{23}} = 1.138 \times 10^{-23}\ g$$

$$\therefore \text{Bond length, } r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.456 \times 10^{-39}}{1.138 \times 10^{-23}}} = 1.13 \times 10^{-8}\ cm$$

$$r = 1.13\text{Å}\ (\because 1\text{Å} = 1 \times 10^{-8}\ cm)$$

WORKED EXAMPLES

1. Hydrogen iodide molecule exhibits rotational spectrum with an interval of 13 cm^{-1}. Calculate the moment of inertia and band length in S.I. units.

Use : $B = \dfrac{h}{8\pi^2 Ic}\ cm^{-1}$

$I = \dfrac{h}{8\pi^2 Bc}\ g\ cm^2$

and $r = \sqrt{\dfrac{I}{\mu}}$ cm

Given : $2B = 13\ cm^{-1}$; $B = 6.5\ cm^{-1}$; $h = 6.625 \times 10^{-34}$ J sec

$$c = 3 \times 10^8 \text{ m sec}^{-1}$$

$$\therefore I = \frac{6.625 \times 10^{-34}}{8 \times \left(\frac{22}{7}\right)^2 \times 6.5 \times 3 \times 10^8} = 4.30 \times 10^{-47} \text{ kg m}^2$$

Reduced mass, $\mu = \frac{m_1 m_2}{(m_1 + m_2) N}$ kg

$m_1 = 1 \times 10^{-3}$ kg mol^{-1}; $m^2 = 127 \times 10^{-3}$ kg mol^{-1}

$N = 6.023 \times 10^{23}$

$$\mu = \frac{1 \times 127 \times 10^{-3}}{(1 + 127) \times 6.023 \times 10^{23}} = 1.647 \times 10^{-27} \text{ kg}$$

$$\therefore \text{Bond length, } r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{4.30 \times 10^{-47}}{1.647 \times 10^{-27}}} = 1.615 \times 10^{-10} \text{ m}$$

---

2. The internuclear distance in sodium chloride is 2.36 Å. Calculate its reduced mass and moment of inertia.

Reduced mass, $\mu = \frac{m_1 m_2}{(m_1 + m_2) N}$ g

m_1 = atomic mass of sodium = 23 g mol^{-1}

m_2 = atomic mass of chlorine = 35.5 g mol^{-1}

$N = 6.023 \times 10^{23}$

$$\mu = \frac{23 \times 35.5}{(23 + 35.5) \times 6.023 \times 10^{23}} = 2.317 \times 10^{-23} \text{ g}$$

Moment of inertia, $I = \mu r^2$ g cm^2

Bond length, $r = 2.36\text{Å} = 2.36 \times 10^{-8}$ cm

$$\therefore I = 2.317 \times 10^{-23} \times (2.36 \times 10^{-8})^2$$

$$= \mathbf{1.29 \times 10^{-38} \text{ g cm}^2}$$

The vibrational – rotational spectral data of few diatomic molecules are given in CGS as well as S.I units in the following tables.

TABLE – I (CGS Unit)

Rotational and Vibrational data for few compounds

No.	Compound	m_1 amu	m_2 amu	$\mu \times 10^{-24}$ g	B cm^{-1}	1×10^{-40} g cm^2	r (Å)	$\bar{\nu} \times 10^3$ (cm^{-1})	k × 10^5 dyne cm^{-1}
1.	HF	1	19.0	1.56	21.00	1.33	0.92	3.958	8.7
2.	HCl	1	35.5	1.63	10.15	2.65	1.29	2.886	4.98
3.	HBr	1	80.0	1.64	8.89	3.31	1.41	2.559	4.1
4.	HI	1	127.0	1.64	6.50	4.29	1.60	2.230	2.9
5.	CO	12	16.0	11.38	1.93	14.5	1.13	2.140 1.700	18.5 11.7
6.	NO	14	16.0	12.40	1.70	16.5	1.15	1.780	13.95