

UNIT 7 MOLECULAR SPECTROSCOPY – I

Structure

- 7.1 Introduction
 - Objectives
 - 7.2 Energy Levels in Molecules
 - 7.3 Types of Molecular Spectra
 - 7.4 The Intensity of Spectral Lines or Bands
 - 7.5 General Features of Absorption Spectrometer
 - 7.6 Requisite for Microwave Absorption
 - 7.7 Theory of Rotational Spectra
 - 7.8 Rotational Spectra of HCl Molecule
 - 7.9 Summary
 - 7.10 Terminal Questions
 - 7.11 Answers
-

7.1 INTRODUCTION

In Unit 6, we studied the correlation between some of the molecular properties and molecular structure. Presently, we take up the study of molecular spectra with a view to obtain more direct information about molecular structure. It is worth recollecting that in Unit 1, we have seen how atomic spectra are useful in the understanding of the electronic arrangement in atoms. The transitions of the electrons between the various energy levels of the atom result in emission or absorption of electromagnetic radiations. Corresponding to energy difference between the levels, the spectral lines occur in different regions, and this gives rise to atomic spectra. Just as atomic spectra give information about the structure of the atom, molecular spectra give information regarding the molecular structure. We may define molecular spectroscopy as the study of the interaction of electromagnetic radiation with molecules.

In this unit, first of all we explain different types of energy levels in molecules and the conditions under which transitions occur among these levels. Then we describe various types of absorption spectra and general features of a spectrometer used in obtaining absorption spectra. We then explain how rotational spectra can be used to calculate simple molecular parameters like bond length and moment of inertia. In the next unit, we shall study how infrared, visible and ultraviolet spectra can be used to obtain some more molecular parameters.

Objectives

After studying this unit, you should be able to :

- define different types of energy levels in molecules,
 - state various types of molecular spectra,
 - explain the reason for the difference in the intensity of spectral lines,
 - describe the general features of an absorption spectrometer,
 - state the pre-requisite for exhibiting rotational spectra,
 - explain the theory of rotational spectra, and
 - calculate the parameters like bond length and moment of inertia of a heteronuclear diatomic molecule using microwave spectra.
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7.2 ENERGY LEVELS IN MOLECULES

We have already discussed in Unit 1 the energy changes in an atom, accompanying the transfer of electrons from lower energy levels to high energy levels and *vice versa*. The electronic transitions in an atom are due to absorption or emission of electromagnetic radiation. We have further stated that electronic transitions in an atom are quantised and the resulting line emission spectra correlate with the difference between the electronic energy levels.

The round about arrow in fig. 7.1a indicates the rotation of the molecule about an axis (indicated as dotted line) passing through its centre of gravity. The arrows attached to each atom in figure 7.1b-d show the direction of its motion during half of the vibration.



Fig. 7.1 : Rotation and vibration within molecules: (a) shows rotation about two different axes; (b), (c), and (d) show vibrations. (b) and (c) are referred to as stretching and (d) as bending.

Now, if E is the energy of a molecule, it can be expressed as the sum of translational, rotational, vibrational and electronic contributions.

$$E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \quad \dots(7.1)$$

Molecular energies in increasing order of their magnitude : $E_{\text{rot}} < E_{\text{vib}} < E_{\text{elec}}$

The translational energy levels of a molecule in a container are so close that they can be considered as continuous. The other three forms of energy are considered to be quantised in a manner similar to the electronic energy in atoms. The magnitude of the various forms of energy and the difference between adjacent levels vary considerably. Calculations indicate that the difference between the energy levels for electronic energy change is about 100 to 10^4 kJ mol⁻¹, for vibrational energy changes, it is generally between 1 and 100 kJ mol⁻¹, and for rotational changes, it is between 0.01 and 1 kJ mol⁻¹. On the other hand, at room temperature, the average translational energy of gas molecule is about 10^{-21} J molecule⁻¹.

We may use two different conventions to illustrate molecular energies further. The first shows a plot of energy of the molecule versus internuclear distance, as illustrated in Fig. 7.2. This figure shows how the energy of the molecule changes with the internuclear distance.

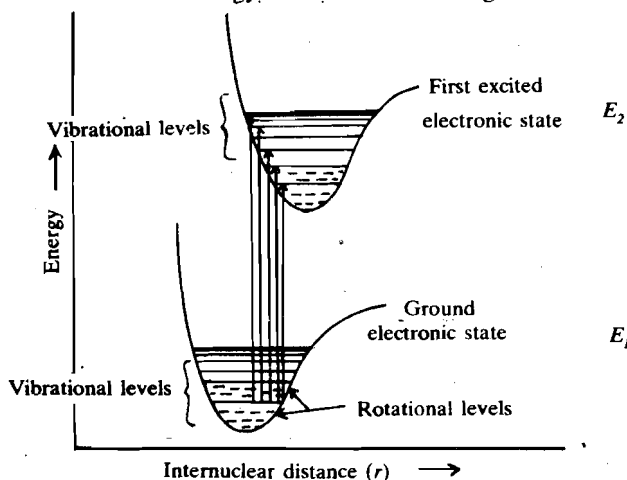


Fig. 7.2 : Representative plot for the potential energy of a diatomic molecule.

The two curves represent the ground and the first excited electronic state or electronic energy level. The individual, narrow lines indicate the allowed quantum vibrational and rotational levels. The molecule can reside in any one of the quantised rotational, vibrational and electronic energy levels that are indicated in this figure. A diagram such as this is usually used only for diatomic molecules because, for polyatomic molecules, there are too many different interatomic distances to be represented.

The second convention is to represent the energies of molecules as exemplified in Fig. 7.3. We show comparative spacing of energy levels of different types of energy. It is clear that electronic levels are much more widely spaced than vibrational levels, which in turn are more widely spaced than rotational levels.

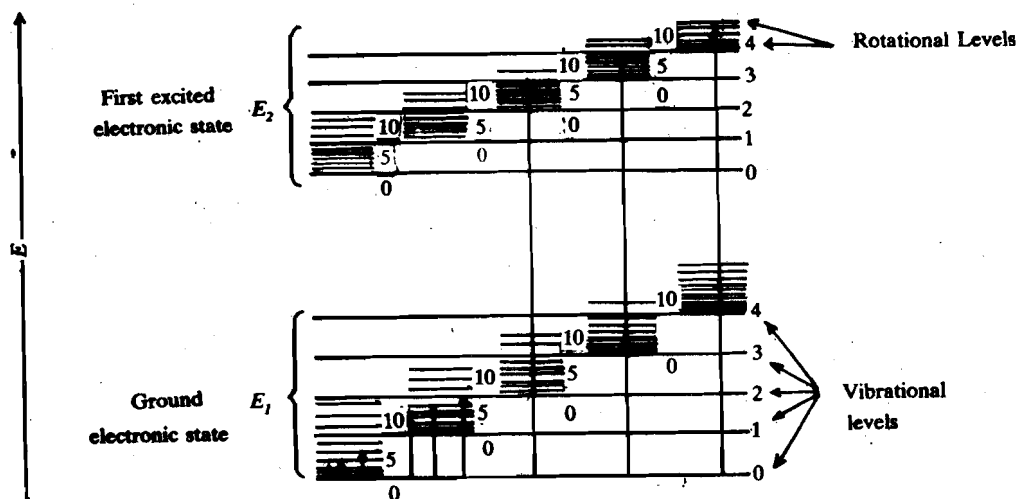


Fig. 7.3 : Diagrammatic representation of possible quantised energy levels and energy changes within a molecule.

As in the atomic spectra, quantised energy changes within a molecule are associated with the emission or absorption of electromagnetic radiation and these can be detected in the form of spectra using an instrument, known as **spectrometer**. The energy changes in a molecule are specified in terms of frequency (ν), wavelength (λ) and wave number ($\bar{\nu}$) as per Eq. 7.2.

$$\text{Energy change } (\Delta E) = h\nu = hc/\lambda = hc\bar{\nu} \quad \dots(7.2)$$

where h is the Planck's constant and c is the velocity of light.

You can find a list of units normally used in representing these quantities in Table 7.1. We use these quantities to express the position of a line or band in the absorption or emission spectrum.

Table 7.1 : Parameters Commonly Used for Representing Wavelength, Frequency and Wave Number

Parameter	Symbol	Unit
Wavelength	λ	nm(10^{-9} m)
Frequency	ν	Hz or s^{-1}
Wave number	$\bar{\nu}$	m^{-1} (or more commonly cm^{-1})

Further, the choice of the unit of a particular quantity depends on how far it can be expressed as a convenient small number. For example, 'nm' unit for wavelength is chosen to represent absorptions in ultraviolet and visible regions of electromagnetic spectrum since values of wavelength in this region lie between 200 – 800 nm. We have already discussed electromagnetic spectrum and its regions in Unit 1,

You should try the following SAQ to be convinced that $\bar{\nu}$, ν or ΔE values are not quite convenient in expressing absorptions in ultraviolet region.

SAQ 1

Calculate the following corresponding to $\lambda = 200 \text{ nm}$:

- ΔE (in kJ mol^{-1})
- ν
- $\bar{\nu}$

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7.3 TYPES OF MOLECULAR SPECTRA

As you know, the molecules can exist in specific molecular energy levels. The rotational, vibrational and electronic energies are quantised in a manner similar to quantisation of electronic energy of an atom. As a result, spectra from even simple molecules exhibit large number of lines. To illustrate this, the emission spectrum of N_2 in the ultraviolet region is given in Fig. 7.4.

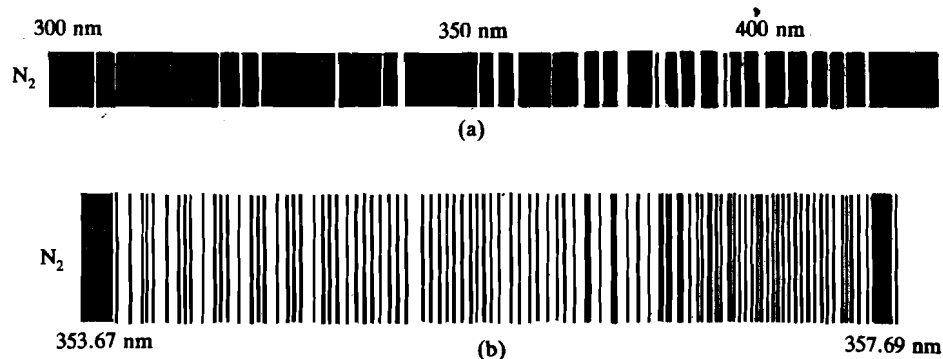


Fig. 7.4 : Spectra of nitrogen molecule : (a) bands of N_2 at low resolution; (b) bands of N_2 resolved into individual lines corresponding to transitions between rotational-vibrational sublevels of the electronic states.

Spectra can be recorded in two ways. The first method is to depict photographically the areas of greater and lesser exposure indicating the light intensity at each wavelength or wave number or frequency (See spectrum of N_2 in Fig. 7.4). The other method is to plot a graph with λ or ν or $\bar{\nu}$ in the x-axis and absorbance/transmittance in the y-axis. (See the spectrum of benzene given in Fig. 7.5).

In this case, unlike atomic spectra, molecular spectra appear as **bands** at low resolution (see Fig. 7.4a). At high resolution, one finds that instead of the bands, the spectrum is composed of sharp lines. These lines arise from the presence of vibrational and rotational energy levels. Since there are many such levels, a large number of individual lines are possible for a single electronic transition. Such a high resolution spectrum is shown in Fig. 7.4b. This figure can give you an idea as to how complex the whole spectrum would look, with many electronic energy transitions, interspersed with vibrational and rotational changes.

In solid or in liquid phase, even at high resolution, these individual lines are broad and are known as **unresolved bands**. All the spectra that we use for analysis of condensed media (liquids and solids) have bands due to large number of unresolved spectral transitions. This is illustrated in Fig. 7.5. Notice that the absorption bands are more sharp for benzene vapour rather than for its solution in ethanol.

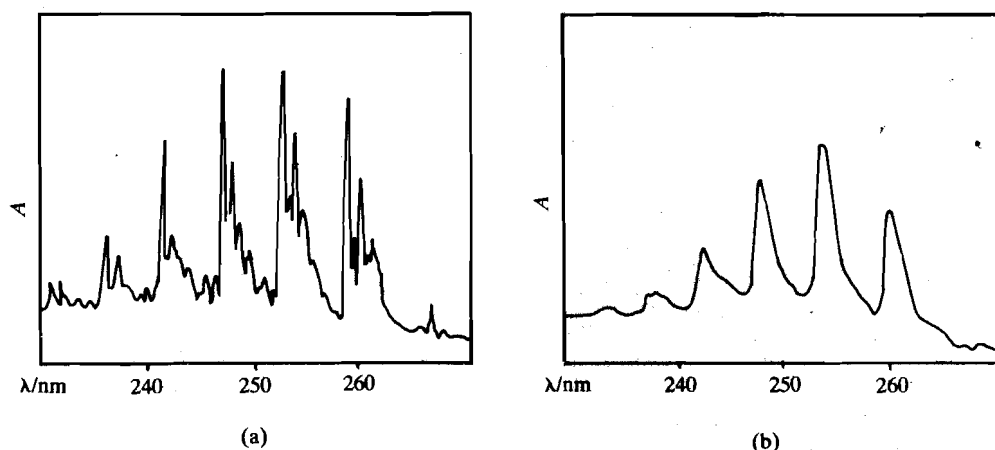


Fig. 7.5 : Absorption spectrum of benzene in ultraviolet region : (a) benzene vapour ; (b) benzene in ethanol.

Now we will consider molecular spectra in detail. Depending on the method of obtaining molecular spectra, it can be classified into three types, viz.,

- i) Emission spectra
- ii) Absorption spectra
- iii) Spectra through scattering, such as, Raman spectra.

Let us study each of these types in a brief manner.

i) Emission Spectra

Molecules give emission spectra when subjected to intense heat or electric discharge. By this process, the molecules obtain the necessary energy to become excited. On returning to their lower energy state, molecules may emit radiation. Such emission is the result of a transition of a molecule from an excited state to one of lower energy, usually the ground state. This excess energy is emitted as a photon and the corresponding frequency is recorded as the **emission spectrum**. If the transition is from upper energy level E_2 to lower energy level E_1 , the frequency (ν) of the emission spectrum is given by,

$$\nu = \frac{E_2 - E_1}{h} = \frac{\Delta E}{h} \quad \dots(7.3)$$

As an illustration, a portion of the emission spectrum of N_2 molecule is given in Fig. 7.4. The different spectral series in the atomic spectra of hydrogen discussed in Unit 1 are examples for atomic emission spectra.

ii) Absorption Spectra

When a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to the molecules, raising them from the ground state to an excited state. This process is known as **absorption** and the resultant spectrum is known as **absorption spectrum**. Energy absorption occurs only when the energy difference between the ground state and higher energy level is exactly matched by the energy of the incident electromagnetic radiation. The frequency of the absorption spectrum is also given by the Eq. 7.3.

The difference between emission and absorption spectra is that in emission spectra, the molecule passes on from higher energy level to lower energy level ; in absorption spectra, it is raised from lower energy level to higher energy level. The energy absorbed, ΔE , by a molecule may bring about changes in one or more of its energy levels such as rotational, vibrational and electronic.

In an absorption spectrum, it can be seen that molecule absorbs some of the wavelengths (or frequencies or wave numbers) of electromagnetic radiation while the rest of it is transmitted. We can plot either absorbance (A) or percent transmittance ($\%T$) vs. wavelength or frequency or wave number to get the absorption spectrum. The plot of absorbance (A) vs. wavelength or frequency or wave number is illustrated in Fig. 7.6a. In this figure you can see that two maxima occur, corresponding to the points (i) and (ii), denoting intense absorptions at the corresponding wavelengths, frequencies and wave numbers. If the

Relationship between absorbance and % transmittance can be expressed by the relation:

$$A = \log \left(\frac{100}{\%T} \right) = 2 - \log (\%T)$$

absorptions are to be represented as % transmittance (%T) vs. wavelength or frequency or wave number, the plot will look like Fig. 7.6b. Minima appear in Fig. 7.6b corresponding to the maxima of Fig. 7.6a. We will discuss absorbance and transmittance in detail in Unit 8.

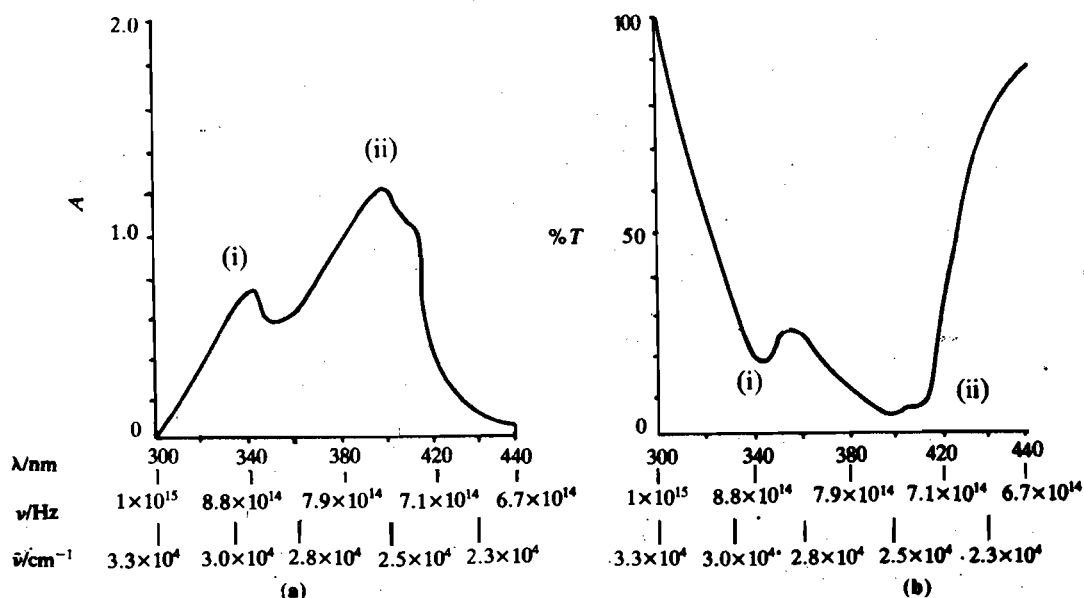


Fig. 7.6 : Presentation of absorption spectral data.

iii) Raman Spectra

Besides the above two types of spectra, another variety is also observed. When a substance is irradiated with electromagnetic radiation, some of the radiation may be scattered as shown in Fig. 7.7.

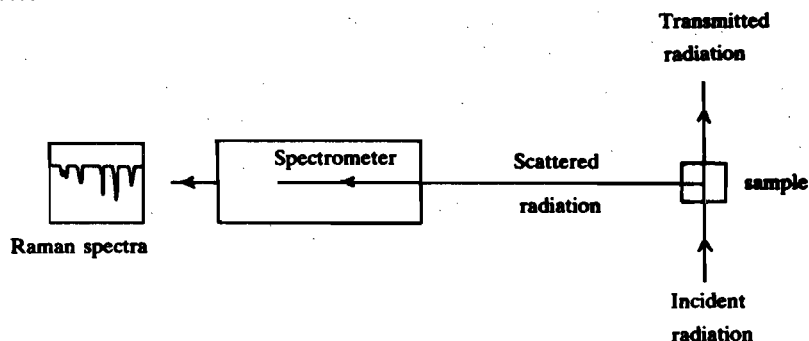


Fig. 7.7: Origin of Raman Spectra in scattered light.

A laser is a device that produces an intense beam of monochromatic coherent light. A laser beam remains a narrow pencil of light even after travelling a long distance. The word 'laser' stands for light amplification by the stimulated emission of radiation.

The scattered radiation shows some lines of higher and some of lower frequency than that of incident radiation. This arises because incident radiation can lose energy in exciting the molecules or can alternatively gain energy from molecules already excited. The resulting spectrum so obtained is known as **Raman Spectrum**. The lines of lower frequency are called Stokes lines; those of higher frequency are known as anti-Stokes lines. The experimental method of obtaining Raman spectra is different because the lines are very weak; but the use of lasers for the incident radiation has made the technique easier and of wider application.

Absorption spectra are studied extensively in order to elucidate the structure of molecules. We shall concentrate only on absorption spectroscopy in this and the next unit. The molecular spectra are more complicated than atomic spectra; they range over wider regions of the electromagnetic spectrum and their interpretation is often more difficult. We divide absorption spectra into different types on the basis of the radiation absorbed. In this and the next unit, we are concerned with three types of molecular absorption spectra as given below:

Microwave Spectra: Region of electromagnetic spectrum (3×10^{10} to 3×10^{12} Hz or 1 cm⁻¹ to 100 cm⁻¹) is concerned with the energy change of rotational levels which are of the order of 0.01 to 1 kJ mol⁻¹. Microwave radiation does not affect vibrational and electronic energy levels as it changes only the rotational energy and the resulting molecular spectra is called **rotational spectra**. The principles and the information given by rotational spectra will be dealt in sections 7.6 to 7.8.

Infrared Spectra: Electromagnetic radiation in the infrared region of the spectrum (3×10^{12} to 3×10^{14} Hz or 100 cm^{-1} to 10^6 cm^{-1}) results in changes of the vibrational energy of molecules. The energy change required for molecular vibrations is of the order of 1 to 100 kJ mol^{-1} , and changes in vibrational energy levels are accompanied by transitions between rotational levels too. So, in a vibrational spectrum, each line is accompanied by the rotational fine structures. Such a spectrum is evidently known as **vibrational-rotational spectrum**. If we do not consider the rotational fine structure, absorption spectrum is called **vibrational spectrum**.

Ultraviolet and Visible Spectra: Electromagnetic radiation in the ultraviolet and visible regions (3×10^{14} – 3×10^{16} Hz or 1000 – 10 nm) of the spectrum results in changes in the electronic structure of molecules. The energy change observed in this region is of the order of 100 – 10^4 kJ mol^{-1} . This type of absorption spectra is also called **electronic spectra**. The vibrational and rotational transitions also accompany electronic transitions and these transitions appear as **broad band absorption spectra**. In practice, the region 200 – 800 nm is generally used by chemists to observe electronic spectra. In Table 7.2, we summarise the types of absorption spectra and information available from each type.

Table 7.2: Types of Absorption Spectra and the Information Obtained from these

Radiation absorbed	Effect on the molecule	Information deduced
Microwave $\nu = 3 \times 10^{10}$ – 3×10^{12} Hz $\bar{\nu} = 1$ – 100 cm^{-1} $\lambda = 1 \text{ cm}$ – 0.01 cm $E = 0.01$ – 1 kJ mol^{-1}	Change in rotational energy levels of the molecule	Calculation of bond length, bond angle, etc.
Infrared $\nu = 3 \times 10^{12}$ – 3×10^{14} Hz $\bar{\nu} = 100$ – 10^4 cm^{-1} $\lambda = 0.01 \text{ cm}$ – 1000 nm $E = 1$ – 100 kJ mol^{-1}	Change in the vibrational and rotational energy levels in the molecule	Detection of functional groups in compounds, calculation of force constant, bond length and bond angle, etc., and in quantitative analysis.
Ultraviolet and Visible $\nu = 3 \times 10^{14}$ – 3×10^{16} Hz $\bar{\nu} = 10^4$ – 10^6 cm^{-1} $\lambda = 1000 \text{ nm}$ – 10 nm $E = 100$ – 10^4 kJ mol^{-1}	Change in electronic energy levels within the molecule. Vibrational and rotational transitions are also brought about; but their resolution is not possible in solid and liquid states.	In qualitative and quantitative analysis.

You try the following SAQ, which is based on the above discussion.

SAQ 2

Indicate the type of energy change brought about, when a gaseous molecule is exposed to the following radiation. Write your answer in the space provided.

a) Infrared

.....

b) Ultraviolet

.....

c) Microwave

.....

d) Visible

.....

7.4 THE INTENSITY OF SPECTRAL LINES OR BANDS

In the previous section, we have discussed the origin of spectral lines or bands in a spectrum. Now, in this section we are going to focus our attention on the factors which are responsible for the number and intensities of spectral lines or bands.

The number and the intensities of lines or bands which may appear in a spectrum are determined by the factors such as population of the energy levels and quantum mechanical selection rules.

The number of molecules present at each energy level is known as the population at that energy level. A large population at a particular level indicates that a large number of molecules may undergo a particular transition giving rise to an intense absorption band.

Quantum mechanical selection rules help us in deciding whether a particular transition is allowed or not. Again, the molecules, undergoing a transition which is permitted by the selection rules, give rise to an intense absorption line or a band. Forbidden transitions are those which are not permitted by the selection rules and give rise to weak absorption pattern. In our study of molecular spectroscopy, we will not go into the detailed reasoning for intensity pattern of spectral transitions; instead we will pay more attention to the applications of different types of spectra. Before taking up the details of the microwave spectra, let us first consider some features of an absorption spectrometer.

7.5 GENERAL FEATURES OF ABSORPTION SPECTROMETER

Let us now study the instruments used for obtaining molecular spectra. The instrument which we use to record the spectra of molecules, is called a **spectrometer**. The exact design of the instrument varies according to the spectral region being examined. But the basic features of all spectrometers are similar. A generalised schematic representation is shown in Fig. 7.8.

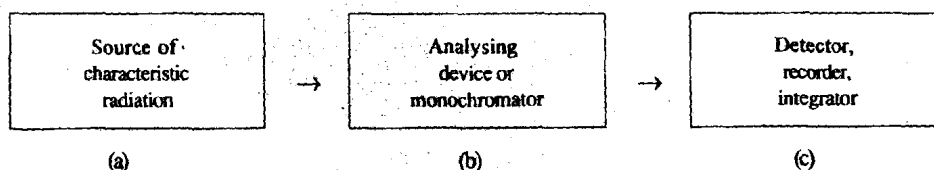


Fig. 7.8 : Schematic layout of spectrometer.

The essential features of an absorption spectrometer are fairly simple. It consists of a suitable source of electromagnetic radiation, a system to analyse the radiation or a monochromator and an appropriate detector to detect the intensity of the radiation absorbed. Depending on the technique, the sample may be positioned between (a) and (b) or between (b) and (c). These features are summarised in Table 7.3 for the different spectral types.

The final absorption spectrum is displayed either on a video screen or, more generally, recorded on a chart paper. In this manner, we can measure the extent to which a substance absorbs radiation at each wavelength (or frequency or wave number).

Table 7.3 : General Features of Absorption Spectrometer

	Ultraviolet	Visible	Infrared	Microwave
Source (a)	Hydrogen discharge lamp	Tungsten filament lamp	Electrically heated rod of rare earth oxides	Klystron valve
System of Analysis (b)	System of mirrors and rotating grating to select appropriate wavelength.		System of mirrors and rotating grating	Frequency varied electronically

A high frequency radio valve is called a klystron valve which can be turned to emit monochromatic radiation over a limited range of frequency in the microwave region.

The fourteen elements from Ce to Lu are known as rare earth elements.

Sample	Generally dilute solutions but gases can be used. Quartz cell used in ultraviolet region.	Gases, liquids dilute solutions, solids ground with KBr and pressed into discs.	Gases or Vapours
Dete. (c)	Photographic device or more generally, a p. multiplier tube.	Heat sensor or photo conductivity device.	Crystal detector for radio frequencies

With this background, we take up the study of microwave spectra in this unit. We shall study infrared, visible and ultraviolet spectra in the next unit.

7.6 REQUISITE FOR MICROWAVE ABSORPTION

We have mentioned earlier that absorption in the microwave region of electromagnetic spectrum can cause transition of the absorbing molecule from one rotational level to another. Therefore, the microwave spectra is also known as rotational spectra. The condition for a molecule to exhibit rotational spectra is that a molecule must possess permanent dipole moment. When a molecule having permanent dipole moment rotates, it generates an electric field which can interact with the electric component of the microwave radiation. During this interaction, energy can be absorbed or emitted and thus the rotation of the molecule gives rise to a spectrum. If molecules do not have permanent dipole moment, interaction is not quite prominent and these molecules are said to be "microwave inactive". Examples of microwave inactive molecules are H_2 , Cl_2 , etc. On the other hand, the molecules like HCl , CH_3Cl , etc., which possess permanent dipole moment are "microwave active".

Let us now see how microwave spectra can be utilised to derive information regarding bond length. Before that, answer the following SAQ.

SAQ 3

Which of the following molecules can absorb in the microwave region? Write YES or NO in the space given.

- a) CO
- b) SO_2
- c) N_2
- d) Cl_2
- e) HCl

7.7 THEORY OF ROTATIONAL SPECTRA

We have already mentioned that rotational energy, like other forms of molecular energy, is quantised. The permitted energy values (energy levels) may be calculated for any molecule by solving the Schrödinger equation for the molecule. For simple molecules, the derivations involved are somewhat simple while for large systems, it is more complicated and requires gross approximations. We are not concerned with tedious derivations of the expressions like Eq. 7.4, but we will only apply the same to simple cases such as heteronuclear diatomic molecules. For such a system, the rotational energy levels, as obtained by solving the Schrödinger equation, are given by the expression,

$$E_{rot} = \frac{h^2}{8\pi^2 I} J(J+1) \quad \dots(7.4)$$

Molecules that have no dipole moment can also have rotational spectra, although these are often weak. In this unit, we shall consider only the spectra of molecules which have permanent dipole moment.

$$\begin{aligned}
 & \text{Unit of } E_{\text{rot}} \\
 &= \text{Unit of } \frac{h^2}{8\pi^2 I} J(J+1) \\
 &= \frac{\text{J}^2 \text{s}^2}{\text{kg m}^2}
 \end{aligned}$$

Note that J (italicised) stands for the rotational quantum number whereas J (roman) stands for the energy unit, joule. Here J stands for the energy unit, joule only. Also the rotational quantum number J is a mere number without a unit.

Hence, the unit of

$$\begin{aligned}
 E_{\text{rot}} &= \frac{\text{J}^2 \text{s}^2}{\text{kg m}^2} \\
 &= \frac{\text{J.J s}^2}{\text{kg m}^2} \\
 &= \frac{\text{J kg m}^2 \text{s}^{-2} \text{s}^2}{\text{kg m}^2} \\
 \therefore 1 \text{ J} &= 1 \text{ kg m}^2 \text{ s}^{-2} \\
 &= \text{J}
 \end{aligned}$$

where,

h = Planck's constant (6.626×10^{-34} J s),

I = Moment of inertia (kg m^2),

J = Rotational quantum number which has values 0, 1, 2, 3, etc. It is **dimensionless**.

By the application of simple mechanics, we can define moment of inertia. Consider a diatomic molecule AB, in which atomic masses of the atoms A and B are m_1 and m_2 , respectively. Suppose that these two atoms are joined by a rigid bond of length r . Let the two atoms A and B be at distances r_1 and r_2 , respectively, from the centre of gravity G of the molecule about which the molecule rotates end-over as shown in Fig. 7.9.

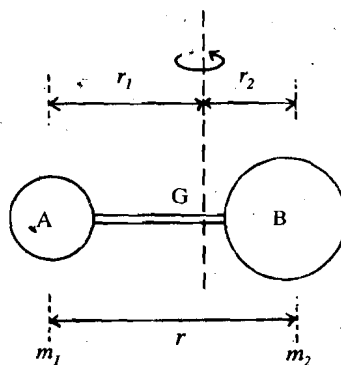


Fig. 7.9 : Simple model for rotational motion of a diatomic molecule.

It is evident that the bond length r must be equal to the sum of r_1 and r_2 .

$$r = r_1 + r_2 \quad \dots(7.5)$$

In this case, the moment of inertia, I , about the axis of rotation is defined by,

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots(7.6)$$

Since G is the centre of gravity, moments $m_1 r_1$ and $m_2 r_2$, must be equal.

$$\text{i.e., } m_1 r_1 = m_2 r_2 \quad \dots(7.7)$$

On rearranging this expression, we get,

$$\frac{r_1}{r_2} = \frac{m_2}{m_1}$$

using the characteristics of proportions, we can write,

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

i.e.,

$$r_1 = \frac{m_2}{(m_1 + m_2)} (r_1 + r_2) = \frac{m_2}{(m_1 + m_2)} r \quad \dots(7.8)$$

Similarly, rearranging Eq.7.7 as,

$$\frac{r_2}{r_1} = \frac{m_1}{m_2}$$

we get,

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

i.e.,

$$r_2 = \frac{m_1}{(m_1 + m_2)} (r_1 + r_2) = \frac{m_1}{(m_1 + m_2)} r \quad \dots(7.9)$$

On substituting Eqs. 7.8 and 7.9 in Eq. 7.6, we obtain the following expression,

$$I = m_1 \left(\frac{m_2}{m_1 + m_2} \right)^2 r^2 + m_2 \left(\frac{m_1}{m_1 + m_2} \right)^2 r^2 \quad \dots(7.10)$$

Rearranging, we get,

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

$$= \mu r^2 \quad \dots(7.11)$$

where μ is the **reduced mass** of the diatomic molecule and its value is $\mu = m_1 m_2 / (m_1 + m_2)$. The unit of reduced mass is kg. Eq. 7.11 defines the moment of inertia in terms of atomic masses and bond length.

Now consider again Eq. 7.4, which expresses the allowed energies in joules; we, however, generally express rotational energies, in terms of wave number. Since $E = hc\bar{\nu}$, Eq. 7.4 can be written as:

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

$$= \frac{h}{8\pi^2 I c} J(J+1) \quad \dots(7.12)$$

where c is the velocity of light expressed in m s^{-1} and the unit of wave number is reciprocal meter or m^{-1} .

Further, we generally write B for $h/8\pi^2 I c$; so, Eq. 7.12 can be expressed as,

$$\bar{\nu} = B J(J+1) \quad \dots(7.13)$$

where B is called the **rotational constant**. The literature values for B are in cm^{-1} unit. You can convert the values in cm^{-1} unit into m^{-1} unit, if you remember the relationship, $1 \text{ m}^{-1} = (10^2 \text{ cm})^{-1} = 10^{-2} \text{ cm}^{-1}$

We shall illustrate this conversion in Sec. 7.8.

From Eq. 7.13, by using integral values 0, 1, 2, 3, 4, 5, etc. for J we can show the allowed rotational energy levels diagrammatically, as in Fig. 7.10.

Rotational quantum number (J)	Allowed rotational energy value in $\bar{\nu}$ unit
5	30B
4	20B
3	12B
2	6B
1	2B
0	0

Fig. 7.10 : The allowed rotational energy levels of a rigid diatomic molecule.

In order to predict the rotational spectrum, we now need to consider the difference between the rotational energy levels. The energy difference between two levels will be given by,

$$\Delta E_{\text{rot}} = E_{J'} - E_J = \frac{h^2}{8\pi^2 I} J'(J'+1) - \frac{h^2}{8\pi^2 I} J(J+1) \quad \dots(7.14)$$

where J = lower quantum number, J' = higher quantum number.

When a molecule moves from one energy level to another, ΔE gives the amount of energy absorbed or emitted. This energy is detected by the spectrometer in the form of spectral lines. Since, we prefer mentioning the rotational transitions in wave number units, we can rewrite Eq. 7.14 as,

the purpose of introducing the term, reduce mass, is to simplify the rotation of a two partical system (of masses m_1 and m_2) into that of a one partical system (of mass μ)

$$\text{Unit of } \bar{\nu} = \text{unit of } \frac{h}{8\pi^2 I c} J(J+1)$$

$$= \frac{\text{J s}}{\text{kg m}^2 \text{ m s}^{-1}}$$

Remember, the rotational quantum number, J , has no unit.

$$\text{Unit of } \bar{\nu} = \frac{\text{J s}}{\text{kg m}^3 \text{ s}^{-1}}$$

$$= \frac{\text{kg m}^2 \text{ s}^{-2} \text{ s}}{\text{kg m}^3 \text{ s}^{-1}}$$

$$= \text{m}^{-1}$$

$$\begin{aligned} \bar{\nu}_{J \rightarrow J'} &= \frac{\Delta E_{\text{rot}}}{hc} = \frac{h^2}{8\pi^2 I hc} [J'(J'+1) - J(J+1)] \\ &= \frac{h}{8\pi^2 I c} [J'(J'+1) - J(J+1)] \\ &= B [J'(J'+1) - J(J+1)] \quad \dots(7.15) \\ (\because B &= \frac{h}{8\pi^2 I c}) \end{aligned}$$

When $J = 0$ and $J' = 1$, Eq. 7.15 becomes :

$$\bar{\nu}_{0 \rightarrow 1} = B [1(1+1) - 0(0+1)] = 2B$$

Thus, for $J = 0$ to $J' = 1$ transition, an absorption line will appear at $2B$. If the molecule is raised from $J = 1$ to $J' = 2$ level by the absorption of more energy in the microwave region, then the wave number corresponding to this transition is given by,

$$\begin{aligned} \bar{\nu}_{1 \rightarrow 2} &= B [2(2+1) - 1(1+1)] \\ &= 4B \end{aligned}$$

It means that corresponding to the transition, $J = 1$ to $J' = 2$, an absorption line will appear at $4B$. In general, when the molecule is raised from the level J to $J + 1$, the wave number for the transition is,

$$\begin{aligned} \bar{\nu}_{J \rightarrow J+1} &= B [(J+1)(J+2) - J(J+1)] \\ &= B (J+1)(J+2 - J) \end{aligned}$$

$$\bar{\nu}_{J \rightarrow J+1} = 2B (J+1) \quad \dots(7.16)$$

From Eq. 7.16, it is clear that stepwise, raising of rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B$, etc. The allowed energy transitions, the general pattern of rotational spectrum and rotational lines in the absorption spectrum of hydrogen chloride are shown in Fig. 7.11.

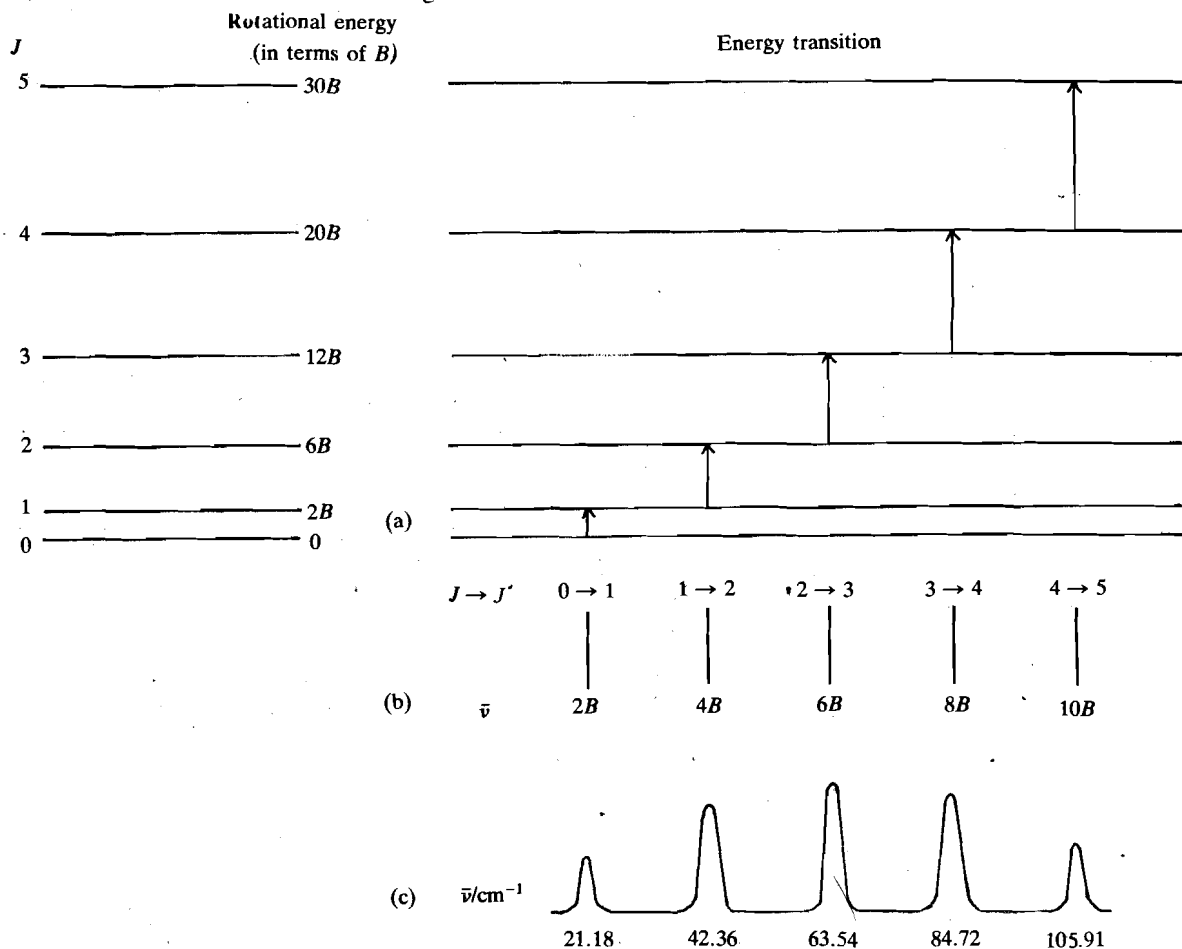


Fig. 7.11 : Rotational spectrum: (a) Allowed rotational transitions; (b) rotational lines in the absorption spectrum ; (c) rotational spectrum of hydrogen chloride.

Note a constant difference of $2B$ between adjacent lines; this value, $2B$, is called rotational spacing. In the case of the spectra of $^1\text{H}^{35}\text{Cl}$ molecule, the rotational spacing is equal to 2118 m^{-1} or 21.18 cm^{-1} . It is assumed here that the molecule is rigid. Such a system is also called rigid rotator.

Selection rule for rotational spectra :

In the above discussion, we have not considered the sequence of transitions, $J = 0 \rightarrow J' = 2$, $J = 2 \rightarrow J' = 4$, etc. We considered transitions only to the immediate neighbouring energy level. It can be shown using quantum mechanics that only those transitions are possible in which J changes by one unit, all other transitions being spectroscopically forbidden. Such a result is called selection rule. Therefore, for rigid diatomic rotator, selection rule is:

$$\Delta J = \pm 1$$

For absorption spectra, $\Delta J = +1$; similarly, for emission, $\Delta J = -1$. That is, the allowed transition for absorption is $J \rightarrow J + 1$.

So far, we have discussed the theory of microwave spectra. In the next section, we shall consider the application of rotational spectra taking HCl molecule, as an example.

7.8 ROTATIONAL SPECTRA OF HCl MOLECULE

The rotational spectra of HCl molecule is shown in Fig. 7.11c. Let us now apply Eq. 7.16 to this spectrum to calculate the rotational constant, moment of inertia and bond length of the molecule.

The first line corresponding to $J = 0$ to $J' = 1$ appears in the rotational spectrum of HCl at 21.18 cm^{-1} . Hence, from Eq. 7.16,

$$\bar{\nu}_{0 \rightarrow 1} = 21.18 \text{ cm}^{-1} = 2B \text{ cm}^{-1}$$

or $B = 10.59 \text{ cm}^{-1}$. Since the literature values of B are given in cm^{-1} , whereas we use SI units throughout, it is better to convert B also into SI units.

$$B = 1059 \text{ m}^{-1} \quad (\because 1 \text{ cm}^{-1} = 10^2 \text{ m}^{-1})$$

$$\text{Since, } B = \frac{h}{8\pi^2 I c}, \quad I = h / 8\pi^2 B c,$$

substituting the values of h , π , B and c ,

$$\begin{aligned} I(\text{HCl}) &= \frac{6.626 \times 10^{-34} \text{ (J s)}}{8 \times 3.142^2 \times 1059 \text{ (m}^{-1}) \times 2.998 \times 10^8 \text{ (m s}^{-1})} \\ &= 2.646 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

Since the moment of inertia of HCl is known, we can calculate its bond length using the steps described below :

$$I = \mu r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2$$

$$\text{Mass of an H atom} = \frac{1.008 \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$

$$\text{Mass of a Cl atom} = \frac{35.45 \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$

Thus, the reduced mass,

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{1.008 \text{ (kg)} \times 35.45 \text{ (kg)}}{(1.008 + 35.45) \text{ (kg)}} \times \frac{10^{-3}}{6.022 \times 10^{23}} = 1.627 \times 10^{-27} \text{ kg}$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.646 \times 10^{-47} \text{ (kg m}^2\text{)}}{1.627 \times 10^{-27} \text{ (kg)}}$$

$$r = 127.5 \text{ pm.}$$

From the above discussion, it follows that rotational spectra can be used to calculate simple molecular parameters such as moment of inertia and bond length. Besides this, we can also obtain information regarding molecular symmetry and bond angle.

To test your understanding of the above discussion, try the following SAQ.

SAQ 4

The lowest wave number absorption line in the rotational spectrum of $^1\text{H}^{19}\text{F}$ is at 41.11 cm^{-1} . Answer the following questions.

- What is the value of the lowest frequency of absorption in the rotational spectrum of HF?
- Which are the two energy levels involved in this transition?
- What is the value of the rotational constant (B) for HF?
- Calculate the moment of inertia for HF molecule.
- Calculate the bond length of HF molecule.

7.9 SUMMARY

In this unit, we have briefly described the principles of molecular spectroscopy with special reference to rotational spectra. We are summarising below what we have studied so far :

- Molecules have different types of quantised energy ; e.g., rotational, vibrational and electronic.
- Molecular spectra are more complex than atomic spectra ; the former can be classified into three types on the basis of the method to obtain them, namely, emission spectra, absorption spectra and Raman spectra.
- Different regions of electromagnetic radiations are used for different types of absorption spectra.
- The condition for a molecule to exhibit rotational spectra is that it must possess permanent dipole moment.
- The rotational spectra of a diatomic molecule is a series of equally spaced lines of wave numbers $2B, 4B, 6B$, etc. The wave numbers of the line can be used to provide accurate value of bond length.

7.10 TERMINAL QUESTIONS

- Calculate ΔE , ν and $\bar{\nu}$ for visible radiation of wavelength 800 nm.
- CO absorbs electromagnetic radiation at about 6.4×10^{13} Hz.
 - In which region of the electromagnetic spectrum does this frequency lie?
 - Which type of molecular energy is likely to be affected?
- What is the selection rule for the microwave absorption spectra?
- Complete the Table given below:

Rotational quantum number	Energy	Energy transition
0		
1		
2		
3		
4		
5		

- The bond length of $^1\text{H}^{80}\text{Br}$ molecule is 141 pm. Calculate the wave numbers in cm^{-1} for the following rotational transitions :

$$J = 0 \rightarrow J' = 1 ;$$

$$J = 1 \rightarrow J' = 2; \text{ and}$$

$$J = 2 \rightarrow J' = 3.$$

SAQs

1. a) To calculate the energy per mole, multiply hc/λ by Avogadro constant (N_A)

$$\text{Thus, } \Delta E = \frac{N_A hc}{\lambda}$$

$$= \frac{6.022 \times 10^{23} (\text{mol}^{-1}) \times 6.626 \times 10^{-34} (\text{J s}) \times 2.998 \times 10^8 (\text{m s}^{-1})}{200 \times 10^{-9} (\text{m})}$$

$$= 5.981 \times 10^5 \text{ J mol}^{-1}$$

$$= 598.1 \text{ kJ mol}^{-1}$$

$$\text{b) } \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 (\text{m s}^{-1})}{200 \times 10^{-9} (\text{m})} = 1.499 \times 10^{15} \text{ s}^{-1} \text{ or Hz}$$

$$\text{c) } \bar{\nu} = \frac{1}{\lambda} = \frac{1}{200 \times 10^{-9} (\text{m})} = 5 \times 10^6 \text{ m}^{-1}$$

$$= 5 \times 10^4 \text{ cm}^{-1}$$

2. **Radiation** **Molecular energy changes**

- | | |
|----------------|--|
| a) Infrared | Vibrational and rotational |
| b) Ultraviolet | Electronic, vibrational and rotational |
| c) Microwave | Rotational |
| d) Visible | Electronic, vibrational and rotational |

3. a) Yes b) Yes c) No d) No e) Yes

4. a) First convert the unit of $\bar{\nu}$ into m^{-1} ; then substitute this value in the equation,
 $\nu = \bar{\nu} c$.

$$\text{Hence, } \nu = 1.232 \times 10^{12} \text{ Hz.}$$

- b) The lowest frequency absorption arises due to the transition from $J = 0$ level to $J = 1$ level.

$$\text{c) } 2B = 41.11 \text{ cm}^{-1}, \text{ therefore } B = 20.56 \text{ cm}^{-1}$$

$$= 2056 \text{ m}^{-1}$$

$$\text{d) Since } B = \frac{h}{8\pi^2 I c},$$

$$I = \frac{h}{8\pi^2 B c} = \frac{6.626 \times 10^{-34} (\text{J s})}{8 \times (3.142)^2 \times 2056 (\text{m}^{-1}) \times 2.998 \times 10^8 (\text{m s}^{-1})}$$

$$= 1.363 \times 10^{-47} \text{ kg m}^2$$

- e) To calculate the bond length of HF molecule, first calculate reduced mass, μ ;

$$\mu = \frac{m_H \times m_F}{(m_H + m_F)} \times \frac{10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$

$$= \frac{1 \times 19 \times 10^{-3}}{(1 + 19) \times 6.022 \times 10^{23}} \text{ kg}$$

$$= 1.578 \times 10^{-27} \text{ kg}$$

From Eq. 7.11, bond length can be calculated as follows:

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

$$= \sqrt{\frac{1.363 \times 10^{-47} \text{ (kg m}^2\text{)}}{1.578 \times 10^{-27} \text{ (kg)}}}$$

$$= 92.94 \text{ pm}$$

Terminal Questions

1. $\Delta E = 149.5 \text{ kJ mol}^{-1}$; $\nu = 3.748 \times 10^{14} \text{ Hz}$;

$$\bar{\nu} = 1.25 \times 10^6 \text{ m}^{-1} = 1.25 \times 10^4 \text{ cm}^{-1}$$

2. a) Infrared
b) Vibrational and rotational.
3. $\Delta J = \pm 1$.

4.

Rotational quantum number	Energy	Energy transition
0	0	
1	2B	J = 0 to J = 1, 2B
2	6B	J = 1 to J = 2, 4B
3	12B	J = 2 to J = 3, 6B
4	20B	J = 3 to J = 4, 8B
5	30B	J = 4 to J = 5, 10B

5. Use Eq. 7.11 to calculate the moment of inertia.

$$I = \mu r^2$$

$$\mu = \frac{m_{\text{H}} m_{\text{Br}}}{m_{\text{H}} + m_{\text{Br}}} \times \frac{10^{-3}}{6.022 \times 10^{23}} \text{ kg} \quad (\text{Atomic mass of hydrogen is 1 and that of bromine is 80})$$

$$= 1.640 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2 = 1.640 \times 10^{-27} \text{ (kg)} \times (141 \times 10^{-12})^2 \text{ (m)}^2$$

$$= 3.260 \times 10^{-47} \text{ kg m}^2$$

Once I is known, we can calculate B using the equation,

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

$$= \frac{6.626 \times 10^{-34} \text{ (J s)}}{8 \times (3.142)^2 \times 3.260 \times 10^{-47} \text{ (kg m}^2\text{)} \times 2.998 \times 10^8 \text{ (m s}^{-1}\text{)}}$$

$$= 858.4 \text{ m}^{-1}$$

$$= 8.584 \text{ cm}^{-1}$$

For the transition $J = 0$ to $J' = 1$, $\bar{\nu} = 2B = 17.17 \text{ cm}^{-1}$;

For the transition $J = 1$ to $J' = 2$, $\bar{\nu} = 4B = 34.34 \text{ cm}^{-1}$;

For the transition $J = 2$ to $J' = 3$, $\bar{\nu} = 6B = 51.50 \text{ cm}^{-1}$.