
UNIT 4 VIBRATIONAL SPECTRA OF DIATOMIC MOLECULES

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4.1 INTRODUCTION

While going through Unit 7 of the course "Atoms and Molecules" (CHE-01), you might have appreciated the use of vibrational spectroscopy as an analytical technique for the determination of molecular structure. In the last block of this course, two units viz. Units 1 and 3 have been devoted to atomic spectra and rotational spectra, respectively. In this unit and Unit 5, we will discuss vibrational spectroscopy which is another kind of spectroscopy dealing with molecules.

In this unit, the theory and applications of vibrational spectra of diatomic molecules will be described. The vibrational spectra of polyatomic molecules is discussed in Unit 5.

In this unit, we will start our discussion with the classical example of the vibration of a single particle supported by a spring. The similarity of the vibration in a diatomic molecule with the vibration of a single particle is then brought about and possible transitions for the harmonic oscillator model of diatomic molecules are discussed. This is followed by the explanation of observed vibrational spectra of diatomic molecules, the introduction of anharmonicity and the rotational-vibrational spectra of diatomic molecules.

Objectives

After studying this unit, you should be able to:

- discuss Hooke's law and motion of a harmonic oscillator,
- explain observed infrared spectra of diatomic molecules,
- evaluate harmonic frequency of diatomic oscillator, force constant and anharmonicity constant from the observed infrared spectra,
- predict vibrational frequencies of isotopically substituted molecules if the vibrational frequencies of unsubstituted molecules are known,
- evaluate zero point energies, and
- explain rotational-vibrational spectra of diatomic molecules.

4.2 HARMONIC OSCILLATOR

Consider a particle of mass m held by a rigid support through a spring as shown in Fig. 4.1(a). When this particle is displaced from its equilibrium position (a) see Fig. 4.1

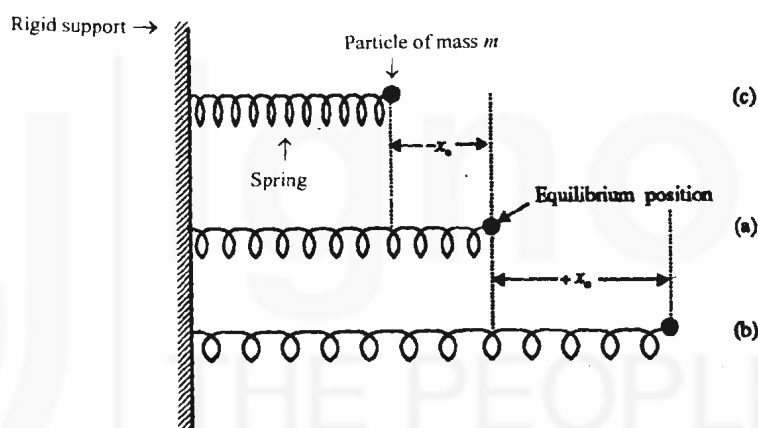


Fig. 4.1: Contraction (c) and expansion (b) of the spring showing displacement of the particle from its equilibrium position (a). The restoring force F acts in a direction opposite to the direction of displacement.

using some external force (like pushing or pulling by hand), it is observed that the particle tends to go back to its equilibrium position after the force is withdrawn. As it will be explained in sub-Sec.4.2.2, the particle not only goes back to its equilibrium position but goes still further on the opposite side till the distance is equal to the initial displacement and if there is no frictional loss or gravitational pull, the particle keeps moving between the two extremes in a periodic motion. Such oscillations are referred to as **Simple Harmonic Motion (SHM)** and the particle is referred as a **Harmonic Oscillator**.

4.2.1 Hooke's Law

The motion of the particle referred above towards its equilibrium position after the external force is withdrawn can be explained as follows. On giving a displacement (x) to the particle, a force called **restoring force (F)** arises in the spring in the direction opposite to that of the displacement and acts to bring it back to its equilibrium position. A spring which behaves in this manner is said to obey *Hooke's law*. Hooke's law states that *the restoring force (F) is proportional to the displacement (x) and acts in a direction opposite to the direction of the displacement*. This can be represented mathematically as:

$$F \propto -x$$

or

$$F = -kx$$

...(4.1)

Note that the negative sign in Eq. 4.1 indicates that if the displacement is positive, the restoring force is negative and vice versa.

The proportionality constant, k is called the **force constant** of the spring. The force constant k is a measure of the strength of the spring. Hence, a large value of k means a stronger and less flexible spring. From Eq. 4.1, it may be further noticed that for a given value of x , a larger value of k will result into a larger restoring force.

4.2.2 Equation of Motion

It is experimentally observed that if the particle is displaced from its equilibrium position by a distance $+x_0$ (Fig. 4.1b) and the external force is withdrawn, the particle returns to the equilibrium position (Fig. 4.1a) and then continues to move to a position, $-x_0$, away from the equilibrium position (Fig. 4.1c). The state of the spring in Fig. 4.1(b) and 4.1(c) corresponds to the stretched and the compressed states, respectively. And as mentioned above, if there is no frictional loss or gravitational pull, the particle continues to move between these two extremes passing through the equilibrium position. If the value of the maximum displacements (also called **amplitude**) on the two extremes is denoted by $-x_0$ and $+x_0$, then the value of the displacement (or amplitude) x after time t sec is given by a cosine function (Fig. 4.2) as shown below:

$$x = x_0 \cos 2\pi \nu_{\text{osc}} t \quad \dots(4.2)$$

where ν_{osc} is the oscillation frequency in sec^{-1} . Equation 4.2 represents the equation of motion of the particle.

Similar to Eq. 4.2,
 x can also be given as

$$x = x_0 \sin 2\pi \nu_{\text{osc}} t$$

You must also remember that the sin function is 90° out of phase with respect to the cos function

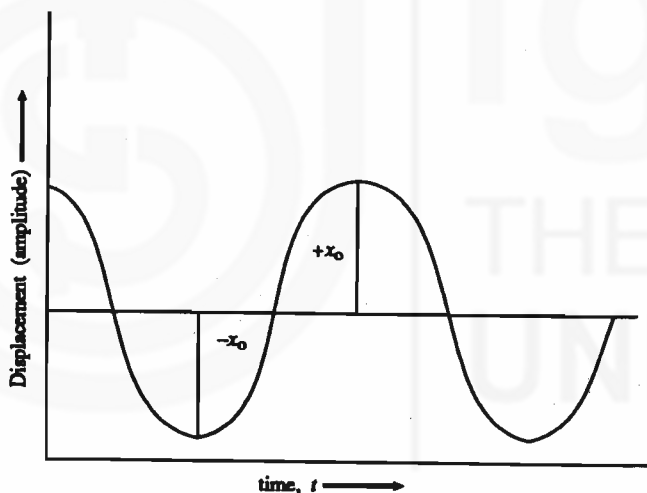


Fig. 4.2: A cosine function represents the equation of motion of the harmonic oscillator.

4.2.3 Expressions for Force Constant and Characteristic Frequency

Now, the restoring force F in Eq. 4.1 can be represented in terms of Newton's second law of motion as:

$$F = ma \quad \dots(4.3)$$

where a is the acceleration of motion which is denoted by second differential of x with respect to time, i.e. $a = \frac{d^2x}{dt^2}$. This on combination with Eq. 4.1 gives

$$m \frac{d^2x}{dt^2} = -kx \quad \dots(4.4)$$

Using Eq. 4.2 for x , we find

$$\frac{d^2 x}{dt^2} = -4\pi^2 \nu_{osc}^2 x_0 \cos 2\pi \nu_{osc} t = -4\pi^2 \nu_{osc}^2 x \quad \dots(4.5)$$

$$\therefore x = x_0 \cos 2\pi \nu_{osc} t$$

$$\frac{dx}{dt} = -x_0 2\pi \nu_{osc} \sin 2\pi \nu_{osc} t$$

$$\begin{aligned} \frac{d^2 x}{dt^2} &= -x_0 (2\pi \nu_{osc})^2 \cos 2\pi \nu_{osc} t \\ &= -4\pi^2 \nu_{osc}^2 x_0 \cos 2\pi \nu_{osc} t \end{aligned}$$

The results of Eqs. 4.4 and 4.5 on combination give

$$-kx = -4\pi^2 \nu_{osc}^2 x m$$

From the above equation, we can get the expression for the force constant, k as

$$k = 4\pi^2 \nu_{osc}^2 m \quad \dots(4.6)$$

and that for the oscillation frequency, ν_{osc} as

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \dots(4.7)$$

Thus, for a given spring with force constant, k and a particle of mass, m there is only one oscillation frequency possible, ν_{osc} , which is independent of the maximum displacement of the particle. This is called **characteristic frequency** of the harmonic oscillator.

4.2.4 Potential Energy Curve

If F_{ext} is the external force applied to displace the particle by a distance dx , the work done in doing so is stored as potential energy (P.E.), dV . Thus

$$dV = F_{ext} dx \quad \dots(4.8)$$

Note that work is given as follows:
work = force \times distance

Since the external force is equal and opposite of the restoring force ($-F$) exerted by the spring, we can write

$$dV = -F dx \quad \dots(4.9)$$

or
$$\frac{dV}{dx} = -F = kx \quad \text{or} \quad dV = kx dx \quad \dots(4.10)$$

If equilibrium position is taken as that of zero potential energy, integration of above equation gives

$$V = \frac{1}{2} kx^2 \quad \dots(4.11)$$

Since potential energy varies linearly with the square of the displacement, a plot of V vs. x gives a parabola as shown in Fig. 4.3.

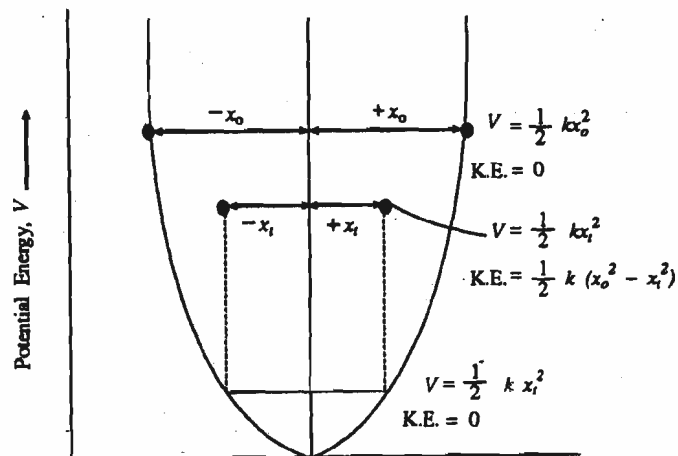


Fig. 4.3: Potential energy curve of the harmonic oscillator.

Now let us imagine that the particle has been displaced by a distance x_0 and released. When it is displaced by a distance x_0 , at that point it has gained a potential energy of $\frac{1}{2} k x_0^2$. After its release, say at a time t if the displacement is x_t , then its potential energy will be $\frac{1}{2} k x_t^2$. The difference, $\frac{1}{2} k x_0^2 - \frac{1}{2} k x_t^2$ represents the kinetic energy of the particle which is given by $\frac{1}{2} m v^2$ where v is the velocity of the particle at a displacement x_t . Thus, one can determine the velocity of the particle at a displacement x_t if one knows the values of m, k, x_0 and x_t .

Thus,

$$\text{K.E.} = \frac{1}{2} k (x_0^2 - x_t^2) = \frac{1}{2} m v^2 \quad \dots(4.12)$$

Using $v = \frac{dx}{dt}$, we can write

$$\text{K.E.} = \frac{1}{2} m \left(\frac{dx}{dt} \right)^2 = 2 m \pi^2 v_{\text{osc}}^2 x_0^2 \sin^2 (2\pi v_{\text{osc}} t) \quad \dots(4.13)$$

$$\text{P.E.} = \frac{1}{2} k x_t^2 = 2 m \pi^2 v_{\text{osc}}^2 \cos^2 (2\pi v_{\text{osc}} t) \quad \dots(4.14)$$

$$\text{Total energy} = \frac{1}{2} k x_0^2 = 2 m \pi^2 v_{\text{osc}}^2 x_0^2 \quad \dots(4.15)$$

$$\begin{aligned} \because x &= x_0 \cos 2\pi v_{\text{osc}} t \\ \frac{dx}{dt} &= -x_0 2\pi v_{\text{osc}} \sin 2\pi v_{\text{osc}} t \\ \left(\frac{dx}{dt} \right)^2 &= x_0^2 4\pi^2 v_{\text{osc}}^2 \sin^2 2\pi v_{\text{osc}} t \end{aligned}$$

4.2.5 Quantisation and Energy Levels

As you have been introduced in Unit 2 of the "Atoms and Molecules" Course (CHE-01), the motion of a microscopic particle can be described in quantum mechanics by Schrödinger's wave equation. Similarly, the motion of a harmonic oscillator, if the particle involved is microscopic in nature, can be discussed by solving Schrödinger wave equation. We shall not go into the details of the solution, however, we shall use the results obtained which are very interesting.

The wave equation of this system is given as

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} \left(E - \frac{1}{2} k x^2 \right) \psi = 0 \quad \dots(4.16)$$

where ψ is the wave function of the oscillator, h is Planck's constant and E is the total energy of the oscillator. The solution of this equation gives the energy, E as given below:

$$E = \frac{h}{2\pi} \sqrt{\frac{k}{m}} \left(v + \frac{1}{2} \right) \quad \dots(4.17)$$

where v is an integer and can take values 0, 1, 2,etc. and is known as **vibrational quantum number**.

Using Eq. 4.7, we can write Eq. 4.17 as given below:

$$E = h \nu_0 \left(v + \frac{1}{2} \right) \quad \dots(4.18)$$

The expression for E given in Eq. 4.18 deserves some further analysis. It shows that E has different values for different values of v . Increasing v by one integer increases the

You may remember from Unit 2 of 'Atoms and Molecules' (CHE-01) course that Schrödinger Equation for a particle in one - dimension can be given as follows:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

Thus, for $V = \frac{1}{2} k x^2$, we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} \left(E - \frac{1}{2} k x^2 \right) \psi = 0$$

value of E by a quantity $h\nu_{osc}$ where ν_{osc} is the characteristic frequency of the oscillator. This shows that the energy of the oscillator cannot be changed at will but it can be only changed by a multiple of $h\nu_{osc}$. This is referred to as **quantisation of energy**. By showing the values of E for varying values of ν we can build up energy levels as shown in Fig. 4.4.

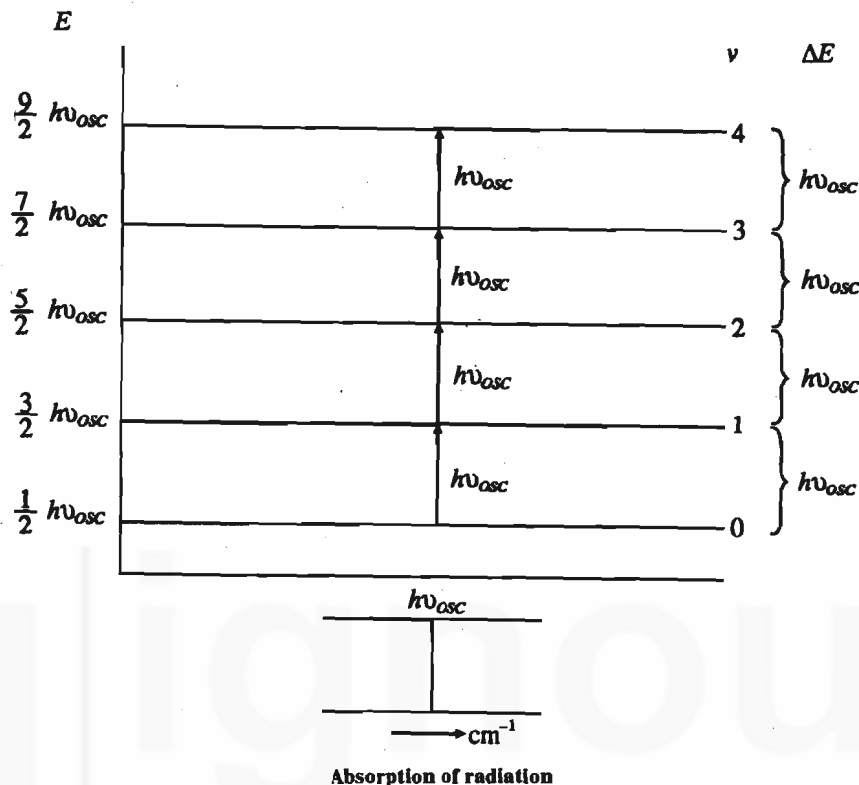


Fig. 4.4: Energy levels of a harmonic oscillator.

4.3 DIATOMIC MOLECULE AS HARMONIC OSCILLATOR

Let us now consider two particles of masses m_1 and m_2 joined together by a spring having a force constant k (Fig. 4.5a). The distance of separation between the particles is r_e . The spring can be stretched and compressed by pulling the two particles apart (Fig. 4.5b) or by pushing them to come closer (Fig. 4.5c).

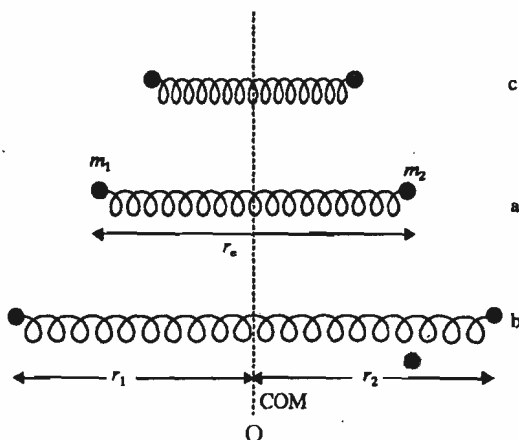


Fig. 4.5: Stretching and compression of two particles joined together by a spring.

particles 1 and 2, respectively, from the centre of mass O. If the new distance of separation of the two particles in Fig. 4.5 (b or c) is referred to as r , the displacement of m_1 with respect to m_2 given by $r - r_e$ (while keeping the centre of mass at O) can be employed in the equations of motion (similar to Eq. 4.4) as follows:

$$\frac{m_1 d^2 r_1}{dt^2} = -k(r - r_e) \quad \dots(4.19)$$

and

$$\frac{m_2 d^2 r_2}{dt^2} = -k(r - r_e) \quad \dots(4.20)$$

Since $r = r_1 + r_2$ and $m_1 r_1 = m_2 r_2$, we get

$$r_1 = \frac{m_2}{m_1 + m_2} r \text{ and } r_2 = \frac{m_1}{m_1 + m_2} r \quad \dots(4.21)$$

Using these expressions for r_1 and r_2 , Eqs. 4.19 and 4.20 reduce to

$$\frac{m_1 d^2 \left(\frac{m_2 r}{m_1 + m_2} \right)}{dt^2} = -k(r - r_e)$$

We can take out m_2 and $(m_1 + m_2)$ out of differentiation because they are constant.

$$\text{Thus, } \frac{m_1 m_2}{(m_1 + m_2)} \frac{d^2 r}{dt^2} = -k(r - r_e) \quad \dots(4.22)$$

Here $m_1 m_2 / (m_1 + m_2)$ can be denoted by μ which is called the **reduced mass**.

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots (4.23)$$

Thus, Eq. 4.22 can be rewritten as

$$\mu \frac{d^2 r}{dt^2} = -k(r - r_e) \quad \dots(4.24)$$

Since $\frac{d^2(r - r_e)}{dt^2} = \frac{d^2 r}{dt^2}$ because r_e is a constant, we substitute $\frac{d^2(r - r_e)}{dt^2}$ for $\frac{d^2 r}{dt^2}$ in Eq. 4.24 for having similarity in the variable on the two sides of the equation. Thus,

$$\mu \frac{d^2(r - r_e)}{dt^2} = -k(r - r_e) \quad \dots (4.25)$$

A comparison of Eqs. 4.4 and 4.25 shows that the two expressions are similar if m of Eq. 4.4 is identified with μ of Eq. 4.25 and x of Eq. 4.4 is identified with $r - r_e$ of Eq. 4.25. This leads us to conclude that the oscillational motion for two particles joined together can be identified to the **simple harmonic vibration** of a particle of mass equal to μ and a displacement equal to $r - r_e$ (called Δr) in the above case. Going on similar analogy, therefore, we can write equations similar to Eqs. 4.2, 4.6, 4.7, 4.11 and 4.12 for oscillations of the two particles joined by a spring viz.

$$\Delta r = \Delta r_0 \cos 2\pi \nu_{\text{osc}} t \quad \dots (4.26)$$

$$k = 4\pi^2 \nu_{\text{osc}}^2 \mu \quad \dots (4.27)$$

Note that the potential energy is proportional to the square of relative displacement of the particle and is given by

$$V = \frac{1}{2} k (r - r_e)^2$$

and the restoring force is given as

$$F = -k(r - r_e).$$

Thus, the equations of motion for the two particles m_1 and m_2 are as given by Eqs 4.19 and 4.20, respectively.

From $m_1 r_1 = m_2 r_2$, we can write

$$r_1 = \frac{m_2 r_2}{m_1} \quad \dots (A)$$

$$\text{and } r_2 = \frac{m_1 r_1}{m_2} \quad \dots (B)$$

$$\therefore r = r_1 + r_2$$

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

$$r = \frac{r_2 m_2^2 + r_1 m_1^2}{m_1 m_2}$$

From $r_1 + r_2 = r$, we can say that

$$r_1 = r - r_2$$

Using this value of r_1 in Eq. A above, we get

$$r - r_2 = \frac{m_2 r_2}{m_1}$$

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

or

$$m_1 r - m_1 r_2 = m_2 r_2$$

or

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

or

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

Similarly, from the Eq. B above, we can derive

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

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots (4.28)$$

$$V = \frac{1}{2} k(r - r_e)^2 \quad \dots (4.29)$$

$$\text{K.E.} = \frac{1}{2} \mu v^2 \quad \dots (4.30)$$

where ν_{osc} is the characteristic oscillational frequency of the system under consideration, and $v = d(\Delta r)/dt$.

The vibrations in diatomic molecule can be treated in a similar way. Instead of the spring with force constant k , we have in the case of diatomic molecules binding of the two nuclei through a bond with a force constant k and these nuclei oscillate with a characteristic oscillational frequency, ν_{osc} .

Extending the similarity further the wave equation for oscillation in diatomic molecule can be given similar to Eq 4.16 viz.

$$\frac{d^2 \psi}{d(\Delta r)^2} + \frac{8\pi^2 \mu}{h^2} \left[E - \frac{1}{2} k(\Delta r)^2 \right] \psi = 0 \quad \dots (4.31)$$

and the expression for energy similar to Eq. 4.17 can be given as

$$E = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2} \right) \quad \dots (4.32)$$

4.3.1 Zero Point Energy

Let us study the above equation more carefully. You will realise that even for $v = 0$, the energy E is not zero and the molecule oscillates with a definite value of frequency.

The energy at $v = 0$ is given by $E_0 = \frac{1}{2} h \nu_{\text{osc}}$ and is referred to as zero point energy.

The zero point energy corresponds to the energy of the molecule in the vibrational ground state.

4.3.2 Infrared Spectra and Selection Rules

If infrared radiations are passed through a sample of diatomic molecules in the gas phase and the transmitted radiations are analysed through the monochromator and detector of a spectrometer (for details of working see - Unit 9) an infrared spectrum is obtained. The infrared spectrum results from the absorption of radiation causing transition from one energy level to another. The observed line position in the spectrum gives information about the difference between the energy levels. However, the intensity of the spectral lines gives information about the population of levels involved in the transition. The spectrum so obtained is characteristic of the diatomic molecule under investigation. The spectrum is employed to get information about the vibrations of the molecule and interactions between the vibrational and rotational motions.

The infrared spectral bands observed for HCl are shown schematically in Fig. 4.6. Notice a signal with a strong intensity followed by two more of weak intensity (Fig. 4.6 a). The positions of the signals are given in terms of frequency of radiation absorbed, $\bar{\nu}$ (cm^{-1}).

The frequency, ν (sec^{-1}) = $c \bar{\nu}$ (cm^{-1}), where c is the velocity of light.

Because of various broadening mechanisms as well as rotational fine structure, these signals do not appear as single lines but appear as bands. Depending on the resolution of the equipment used, the bands show different type of features and fine structure as shown in Fig. 4.6 (c). We shall try to understand salient points of this spectrum in the following sections.

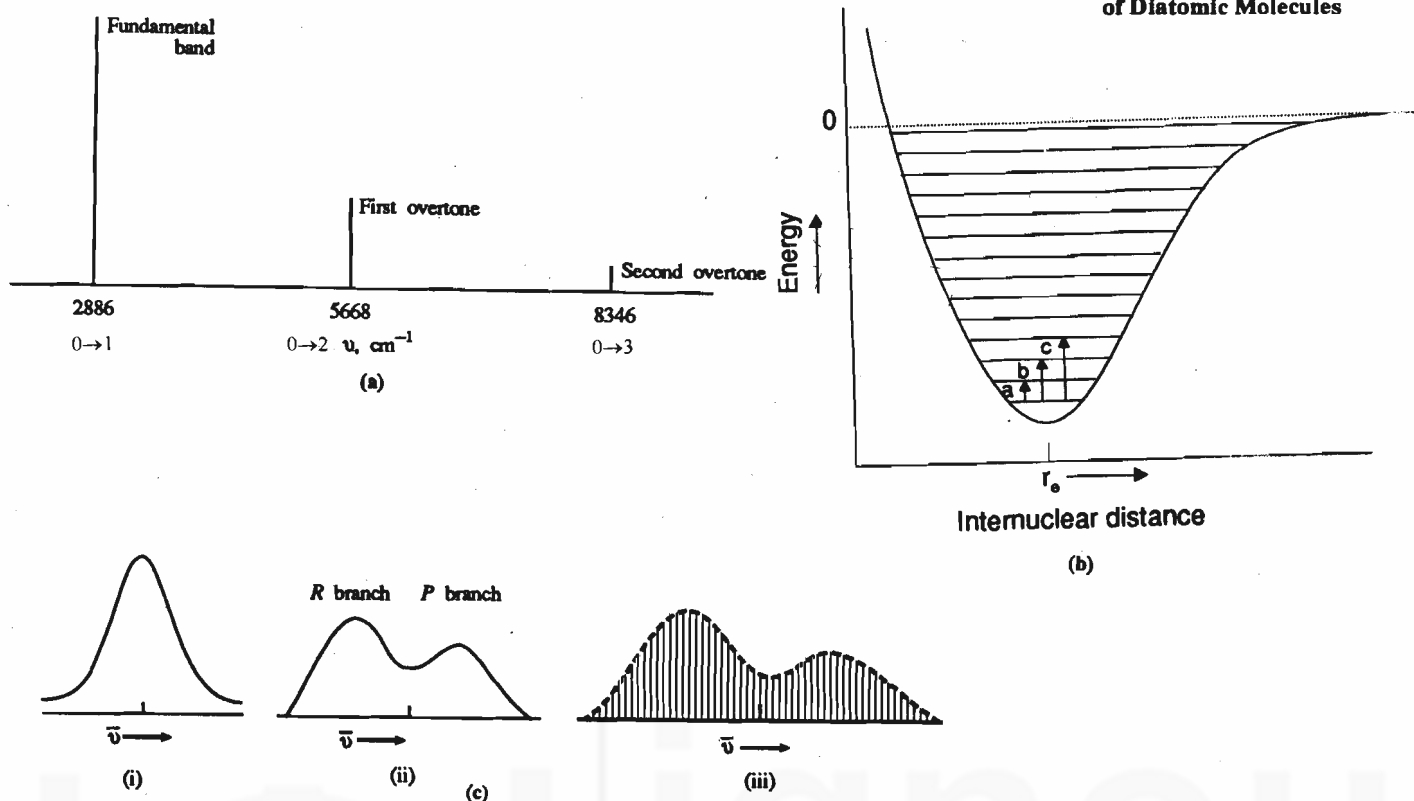


Fig. 4.6 (a): Schematic representation of the positions and intensities of first three bands of HCl. The numbers in notation $0 \rightarrow 1$, $0 \rightarrow 2$ and $0 \rightarrow 3$ indicate the initial and final levels of each transition.

- (b) A typical potential energy curve for a diatomic molecule. The minimum in the curve r_e corresponds to the equilibrium distance between the atoms. Horizontal lines represent vibrational levels. Transitions shown by a, b and c are the fundamental, first overtone and second overtone, respectively. The deviation from equal spacing between energy levels is due to anharmonicity, as you will study in Sec 4.4.
- (c) Fundamental band of HCl under (i) low, (ii) moderate and (iii) high resolutions.

As given in Fig. 4.4, the energy levels for diatomic molecules, when considered similar to those of harmonic oscillator, are equidistant with an energy gap equal to $h \nu_{\text{osc}}$

where ν_{osc} is the vibrational frequency of the diatomic molecule in sec^{-1} and h is Planck's constant. A promotion of the diatomic oscillator from a lower level to an upper level can take place if an external energy, equal to the energy gap between the two levels, is supplied. If the energy supplied is in the form of an electromagnetic radiation with frequency $\nu \text{ sec}^{-1}$, a transition will occur if $E = E_2 - E_1 = h \nu$ where E_2 and E_1 denote energies of the final and the initial levels. Note the difference between ν and ν_{osc} ; the former denotes the frequency of electromagnetic radiation whereas the latter denotes the oscillational frequency of the diatomic molecule. If the quantum numbers, ν for final and initial levels are given by ν_f and ν_i , respectively, then

$$h\nu = h \nu_{\text{osc}} (\nu_f - \nu_i) \quad \dots(4.33)$$

An absorption of radiation takes place and the oscillator flips from energy level with quantum number ν_i to that with ν_f as shown in Fig. 4.7. The transitions for which $\Delta \nu = 1$ are called **fundamental transitions** and those with $\Delta \nu = 2, 3, 4$ etc. are called **first, second, third etc. overtones** respectively.

Eq. 4.33 shows that a *fundamental transition takes place if the frequency of electromagnetic radiation is equal to the oscillational frequency of the diatomic molecule. The overtone transitions take place if the frequency of electromagnetic radiation is an integral multiple of the oscillational frequency.*

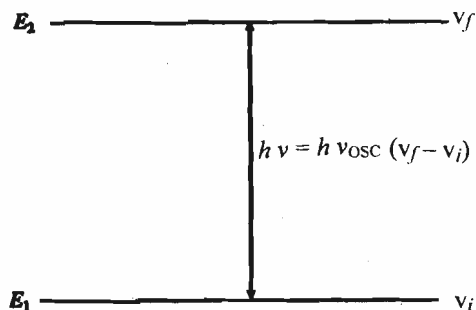


Fig. 4.7: Absorption of radiation and vibrational transition.

As you have noticed in Eq. 4.33, the harmonic oscillator with different energy levels defined by different values of v , has different wave functions. As mentioned in the appendix of Unit 2, an electric dipolar transition from energy level v_i to v_f is only allowed in case the transition moment integral given below is non-zero, i.e.

$$\int_{-\infty}^{+\infty} \psi_{v_f} M \psi_{v_i} d\tau_v \quad \dots (4.34)$$

where ψ_{v_f} and ψ_{v_i} are wave functions for v_f and v_i levels, $d\tau_v$ is volume element and M is dipole moment operator. Without giving any further derivation, it can be stated that if dipole moment is a linear function of internuclear distance of the diatomic molecule, the above integral is nonzero only if $\Delta v = \pm 1$ and if the dipole moment is a non linear function of internuclear distance, the above integral is nonzero for all integral values of Δv . However, in practice only transitions with $\Delta v = \pm 1$ are allowed for harmonic oscillator model of diatomic molecules where the dipole moment is known to be a linear function of the internuclear distance. The "+" sign for Δv above refers to transitions from lower energy levels to higher levels whereas the "-" sign refers to transitions from higher energy levels to lower energy levels. The absorption of radiations thus corresponds to "+" sign and emission of radiations to "-" sign of the v values given above. Further, expansion of dipole moment operator M in Eq. 4.34 shows that fundamental transitions are allowed only if $d\mu/d(\Delta r)$ is non zero, i.e. the vibration should be accompanied by a change in the dipole moment to show a fundamental transition. Thus, the homonuclear diatomic molecules do not show any absorption in the fundamental vibrational spectrum. These rules regarding which transitions are allowed and which are forbidden, are referred to as Selection Rules.

Remember that according to the Boltzman distribution, the number of molecules present in the excited state (N_2) are related to the number of molecules in the ground state (N_1) by the following expression:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}}$$

Since the frequency of the electromagnetic radiation which satisfies the condition given in Eq. 4.33 falls in the infrared region, these transitions are referred to as infrared transitions and are observed in the infrared region of the spectrum. The intensity of the band corresponds to the amount of radiation absorbed and is related to the square of the transition moment integral (Eq. 4.34). The frequency at which the maximum absorption is observed corresponds to the frequency of electromagnetic radiation responsible for transition as defined by Eq. 4.33. According to the Boltzman distribution, the number of oscillators in $v > 0$ level are expected to be very small at room temperature; hence only transitions from $v = 0 \longrightarrow v = 1$ are observed where the ν_{osc} for the oscillator is equal to the frequency of the electromagnetic radiation absorbed to give the fundamental transition. At higher temperatures $v = 1 \longrightarrow v = 2$ etc. transitions may also be observed. Such transitions are referred to as hot transitions (or hot bands in the spectrum).

4.3.3 Evaluation of Force Constant and Maximum Displacement

As we have noticed above, the frequency of electromagnetic radiation at which absorption takes place can give the value of oscillational frequency of the diatomic molecule, e.g. for a transition $v_i = 0$ to $v_f = 1$.

$$\Delta E = h\nu = h\nu_{osc}, \quad \nu = \nu_{osc} \quad \dots (4.35)$$

and if we know the reduced mass of the diatomic molecule, we can calculate the value of force constant, k by using Eq. 4.27 and 4.28. Eqs. similar to 4.15 and 4.17 for diatomic molecule can be employed to evaluate maximum displacement Δr_0 for various values of v as follows:

$$\begin{aligned} \text{Total energy} &= \frac{1}{2} k \Delta r_0^2 = 2 \mu \pi^2 \nu_{\text{osc}}^2 \Delta r_0^2 \\ &= \left(v + \frac{1}{2} \right) h \nu_{\text{osc}} \end{aligned} \quad \dots (4.36)$$

$$\text{giving } \Delta r_0 = \pm \sqrt{\frac{(v + \frac{1}{2}) h}{2 \mu \pi^2 \nu_{\text{osc}}}} \quad \dots (4.37)$$

SAQ 1

HCl molecule shows an absorption at 2886 cm^{-1} . Determine its force constant and maximum displacements (changes in internuclear distance) for $v = 0, 1, 2, 3$.

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$$\begin{aligned} \Delta E &= E_f - E_i \\ &= h \nu_{\text{osc}} \left(v_f + \frac{1}{2} \right) - h \nu_{\text{osc}} \left(v_i + \frac{1}{2} \right) \\ &= h \nu_{\text{osc}} \left(1 + \frac{1}{2} \right) - h \nu_{\text{osc}} \left(0 + \frac{1}{2} \right) \\ &= h \nu_{\text{osc}} \left(\frac{3}{2} - \frac{1}{2} \right) \\ &= h \nu_{\text{osc}} \end{aligned}$$

4.3.4 Isotope Effect

We have noted above that the HCl molecule absorbs radiation of 2886 cm^{-1} frequency. Let us see what changes we expect in the infrared spectrum, if HCl is changed to DCl. This brings change in the reduced mass, i.e.

$$\begin{aligned} \mu_{\text{HCl}} &= \frac{1 \times 35.5}{36.5 \times 6.023 \times 10^{23}} = 1.63 \times 10^{-27} \text{ kg} \\ \mu_{\text{DCl}} &= \frac{2 \times 35.5}{37.5 \times 6.023 \times 10^{23}} = 3.14 \times 10^{-27} \text{ kg} \end{aligned}$$

Thus, we can say that

$$\mu_{\text{DCl}} \approx 2 \mu_{\text{HCl}} \quad \dots (4.38)$$

The force constant is a property of the bond which in turn depends on the number of electrons in H and D. Since number of electrons in H and D are equal it is assumed that to a good degree of approximation that the force constant for HCl and DCl are equal.

Using the above argument in Eq. 4.28, we can conclude that

$$\nu_{\text{osc}} \propto \frac{1}{\sqrt{\mu}}$$

Thus,

$$\frac{\nu_{\text{osc}}^{\text{HCl}}}{\nu_{\text{osc}}^{\text{DCl}}} = \sqrt{\frac{\mu_{\text{DCl}}}{\mu_{\text{HCl}}}} = \sqrt{\frac{\frac{m_{\text{D}} m_{\text{Cl}}}{m_{\text{D}} + m_{\text{Cl}}}}{\frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}}}} \cong \sqrt{\frac{m_{\text{D}}}{m_{\text{H}}}} = \sqrt{2} \quad \dots (4.39)$$

And since the fundamental transition takes place with electromagnetic radiation of frequency equal to oscillational frequency, we can write that

In general, we can say that

$$\frac{\nu^i}{\nu} = \sqrt{\frac{\mu}{\mu^i}}$$

where ν^i and μ^i denote the frequency and the reduced mass for the isotopically substituted molecule.

$$\frac{\nu_{\text{HCl}}}{\nu_{\text{DCl}}} = \frac{\bar{\nu}_{\text{HCl}}}{\bar{\nu}_{\text{DCl}}} = \sqrt{2} \quad \dots (4.40)$$

Thus, when HCl is changed to DCl, the fundamental transition in infrared spectrum is observed at a lower frequency of electromagnetic radiation than that for HCl and the ratio between these frequencies is given by Eq. 4.40.

SAQ 2

If the fundamental transition for O-H species is observed at 3735 cm⁻¹, find out the position of the corresponding transition for O-D species.

.....

SAQ 3

Calculate the ratio between the zero point energies of HCl and DCl.

.....

4.3.5 Vibrational Term Value

Eqs. 4.28 and 4.32 give expression for energy of diatomic oscillator as follows:

$$E = h\nu_{\text{osc}} \left(\nu + \frac{1}{2} \right) \quad \dots (4.41)$$

If we divide both sides of Eq 4.41 by hc , we get

$$\frac{E}{hc} = \frac{\nu_{\text{osc}}}{c} \left(\nu + \frac{1}{2} \right) \quad \dots (4.42)$$

The term E/hc is referred to as the **term value** $G(\nu)$ and the term ν_{osc}/c , the **harmonic frequency** $\bar{\nu}_{\text{osc}}$. Both $G(\nu)$ and $\bar{\nu}_{\text{osc}}$ have the units of wave number i.e. cm⁻¹, thus giving the new expression for energy of the vibrational levels in term values as follows.

$$G(\nu) = \bar{\nu}_{\text{osc}} \left(\nu + \frac{1}{2} \right) \quad (\text{in cm}^{-1}) \quad \dots (4.43)$$

This is a convenient expression for equating the frequency of the oscillator, $\bar{\nu}_{\text{osc}}$ with the frequency of the electromagnetic radiation absorbed for fundamental transition of the harmonic oscillator, $\bar{\nu}$ as given below:

For $\nu = 0, G(0) = \frac{1}{2} \bar{\nu}_{\text{osc}} \quad \dots (4.44)$

and for $\nu = 1, G(1) = \frac{3}{2} \bar{\nu}_{\text{osc}} \quad \dots (4.45)$

Thus, $G(1) - G(0) = \bar{\nu}_{0 \rightarrow 1} = \bar{\nu}_{\text{osc}} \quad \dots (4.46)$

It may be further noted that Eq. 4.44 represents the zero point energy in cm⁻¹

4.4 ANHARMONICITY

As was shown in Fig. 4.3, the potential energy curve of a harmonic oscillator is a parabola. Increase of displacement x_0 continuously shows an increase in the energy. In a diatomic molecule where change in the internuclear distance, Δr_0 is equated to the displacement, x_0 of harmonic oscillator, it is not realistically possible to expect higher and higher potential energy with increasing value of Δr_0 since after a certain increase in bond distance, dissociation takes place and the molecule breaks into the constituent atoms. The true variation of the potential energy with internuclear distance and the potential energy function for harmonic oscillator model of diatomic molecule are shown in Fig. 4.8.

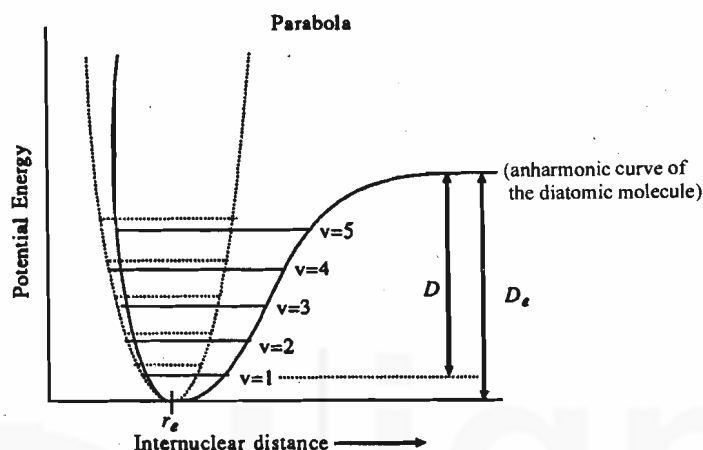


Figure 4.8 : The variation of potential energy with internuclear distance for a diatomic molecule is shown by solid line. The potential energy function for a harmonic oscillator is shown by broken line.

The deviation from harmonic oscillator behaviour is termed as **anharmonicity**. Note that the minimum in the curve occurs at r_e , the equilibrium internuclear distance. You can also see that in the vicinity of r_e , the curve very closely approximates the harmonic oscillator. However, at larger internuclear separation, the anharmonic curve shows significant deviation from the harmonic curve.

You will now study about the Morse Potential function which gives a better agreement with the real curve.

4.4.1 Morse Potential

A mathematical equation for expressing the potential energy of diatomic molecule was given by P.M. Morse and is called Morse potential. This can be written as follows.

$$V(\Delta r) = D_e \left[1 - e^{-\beta \Delta r} \right]^2 \quad \dots (4.47)$$

where $\Delta r = r - r_e$, D_e is dissociation energy of the molecule measured from the minimum of the curve and β a constant is given by

$$\beta = \nu_{\text{osc}} \sqrt{\frac{2\pi^2 c \mu}{D_e h}} \quad \dots (4.48)$$

where π , c , h have their usual meaning and μ , D_e and ν_{osc} are respectively the reduced mass, dissociation energy and oscillational frequency.

4.4.2 Energy Levels of Anharmonic Oscillator and Selection Rules

Since in our analysis of IR transitions, we are mainly concerned with bond distance

Also note that in an anharmonic oscillator, the energy levels are not equally spaced in contrast to the case of a harmonic oscillator shown in Fig. 4.4.

Unlike a parabola, Morse curve allows for dissociation at high energy.

The dissociation energy, D_e measured at the minimum of the P.E. curve is called the *equilibrium dissociation energy*. However, the *spectroscopic dissociation energy*, D_0 is energy of the lowest vibrational level ($v = 0$). Thus,

$$D_0 = D_e - \frac{1}{2} h \nu_{\text{osc}}$$

near the equilibrium value, r_e , therefore, instead of using Morse potential, the Maclaurian series expansion of potential energy is used for inclusion of anharmonicity in the oscillator as follows:

$$V(\Delta r) = \frac{1}{2!} \left[\frac{d^2 V}{d(\Delta r)^2} \right]_{\Delta r=0} (\Delta r)^2 + \frac{1}{3!} \left[\frac{d^3 V}{d(\Delta r)^3} \right]_{\Delta r=0} (\Delta r)^3 + \dots$$

$$= \frac{1}{2} k_2 (\Delta r)^2 + \frac{1}{6} k_3 (\Delta r)^3 + \dots \quad \dots (4.49)$$

Maclaurian series is given as follows

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

If we include higher terms like $\frac{1}{6} k_3 (\Delta r)^3$ etc. in the potential energy expression, the oscillator is referred to as **anharmonic oscillator** and such additional terms are referred to as **anharmonicity terms** of potential energy expression. Inclusion of anharmonicity terms leads to an improved version of energy levels, transition energies and selection rules.

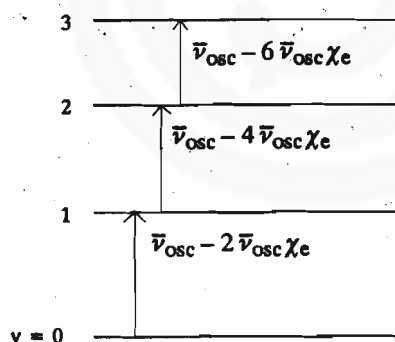
The vibrational energy levels of the anharmonic oscillator can be expressed as

$$G(v) = \bar{\nu}_{osc} \left(v + \frac{1}{2} \right) - X \left(v + \frac{1}{2} \right)^2 + Y \left(v + \frac{1}{2} \right)^3 + \dots \quad \dots (4.50 a)$$

X and Y are functions of constants k_2, k_3 etc. of Eq. 4.49 and are referred to as **anharmonicity constants**. Usually the expression is truncated after two terms as Y is far lesser in value than X . However, the equation of motion obtained by using a cubic potential energy function is not easy to handle. One approximate solution to the Schrodinger equation that may be formed expresses the energy in terms of the fundamental vibrational frequency, ν_{osc} and anharmonicity constant χ_e , as follows.

$$G(v) = \bar{\nu}_{osc} \left(v + \frac{1}{2} \right) - \bar{\nu}_{osc} \chi_e \left(v + \frac{1}{2} \right)^2 \quad \dots (4.50 b)$$

Note that X in Eq. 4.50 a is equal to $\bar{\nu}_{osc} \chi_e$ in Eq. 4.50 b.



Even with a linear dipole moment function, the anharmonic wave functions yield selection rules $\Delta v = \pm 1, \pm 2, \pm 3$ etc., thus overtone bands get allowed due to anharmonicity. The intensities of the overtone bands are, however, quite small in comparison to the intensity of the fundamental band (Fig. 4.6 a). Due to added terms in the energy expression (Eq. 4.50), the energy levels are no more equidistant and they are found to converge.

Thus, the anharmonic correction reduces the energy of every level. The reduction is greater for the higher energy levels. Thus, the spacing between the energy levels, $E_{(v+1)} - E_v$, gets smaller as v gets larger. This was shown in Fig. 4.8 and the extent of reduction is shown in the margin.

4.4.3 Evaluation of Anharmonicity Constants

The term values $G(v)$ for $v = 0, 1, 2, 3$ for anharmonic oscillator are given below:

$$G_0 = \frac{1}{2} \bar{\nu}_{osc} - \frac{1}{4} X + \frac{1}{8} Y \quad \dots (4.51)$$

$$G_1 = \frac{3}{2} \bar{\nu}_{osc} - \frac{9}{4} X + \frac{27}{8} Y \quad \dots (4.52)$$

$$G_2 = \frac{5}{2} \bar{\nu}_{osc} - \frac{25}{4} X + \frac{125}{8} Y \quad \dots (4.53)$$

$$G_3 = \frac{7}{2} \bar{\nu}_{osc} - \frac{49}{4} X + \frac{343}{8} Y \quad \dots (4.54)$$

Effect of anharmonicity on the vibrational energy levels of a diatomic molecule.

The energies of radiation in cm^{-1} for fundamental, first and second overtones can be given as

$$\bar{\nu}_{0 \rightarrow 1} = \bar{\nu}_{\text{osc}} - 2X + \frac{13}{4}Y \quad \dots (4.55)$$

$$\bar{\nu}_{0 \rightarrow 2} = 2\bar{\nu}_{\text{osc}} - 6X + \frac{31}{2}Y \quad \dots (4.56)$$

$$\bar{\nu}_{0 \rightarrow 3} = 3\bar{\nu}_{\text{osc}} - 12X + \frac{171}{4}Y \quad \dots (4.57)$$

Thus, by knowing the frequencies of electromagnetic radiation absorbed for fundamental and overtone transitions, one can evaluate the oscillational frequency and anharmonicity constants.

Also, the equilibrium dissociation energy, D_e of a molecule can be calculated from its spectroscopic dissociation energy, D_0 by using the following relation:

$$D_e = D_0 + \frac{\bar{\nu}_{\text{osc}}}{2} - \frac{\bar{\nu}_{\text{osc}}x_e}{4} + \frac{\bar{\nu}_{\text{osc}}y_e}{8} \quad \dots (4.58)$$

4.5 THE VIBRATING ROTATOR

In Unit 3, the pure rotations of diatomic molecules have been discussed and in the preceding sections of this unit we have discussed pure vibrations of diatomic molecule. The two motions have been discussed independent of each other. In reality, of course, the rotational and vibrational motions take place simultaneously. In this section, we now see how the spectrum gets modified because of this mixing.

4.5.1 Energy Levels

The total energy is given as a sum of the rotational and vibrational energies defined by the quantum numbers v and J .

$$E_{v,J} = G(v) + F(J) \\ = h\nu_{\text{osc}} \left(v + \frac{1}{2} \right) + BhcJ(J+1) \quad \dots (4.59)$$

or

$$E_{v,J} = h\nu_{\text{osc}} \left(v + \frac{1}{2} \right) + hcX \left(v + \frac{1}{2} \right)^2 + \dots \\ + BhcJ(J+1) - Dhc^2(J+1)^2 + \dots \quad \dots (4.60)$$

for $v = 0, 1, 2, \dots$ and $J = 0, 1, 2, \dots$ etc.

where Eq. 4.59 represents rotational vibrational energy for harmonic oscillator and rigid rotator whereas Eq. 4.60 represents the rotational vibrational energy for anharmonic oscillator and nonrigid rotator.

4.5.2 The IR Spectra and P,Q,R Branches

The selection rules for transitions in vibrating rotator are same as given for rotations and vibrations of diatomic molecules (Unit 3 and Sec.4.3.2) which state $\Delta v = \pm 1$ and $\Delta J = \pm 1$. Thus, for a fundamental vibrational transition $\Delta v = +1$, we shall have a series of transitions where $\Delta J = +1$ and another series where $\Delta J = -1$. The series with $\Delta v = +1$ and $\Delta J = +1$ defines the transitions (00) \rightarrow (11), (01) \rightarrow (12), (02) \rightarrow (13), (03) \rightarrow (14), ... etc; whereas the series with $\Delta v = +1$ and $\Delta J = -1$ defines the transitions (01) \rightarrow (10), (02) \rightarrow (11), (03) \rightarrow (12), (04) \rightarrow (13) etc. Here, the first number in the parenthesis denotes vibrational quantum number (v) and the second

number corresponds to the rotational quantum number (J). The transitions described above are shown in Fig. 4.9.

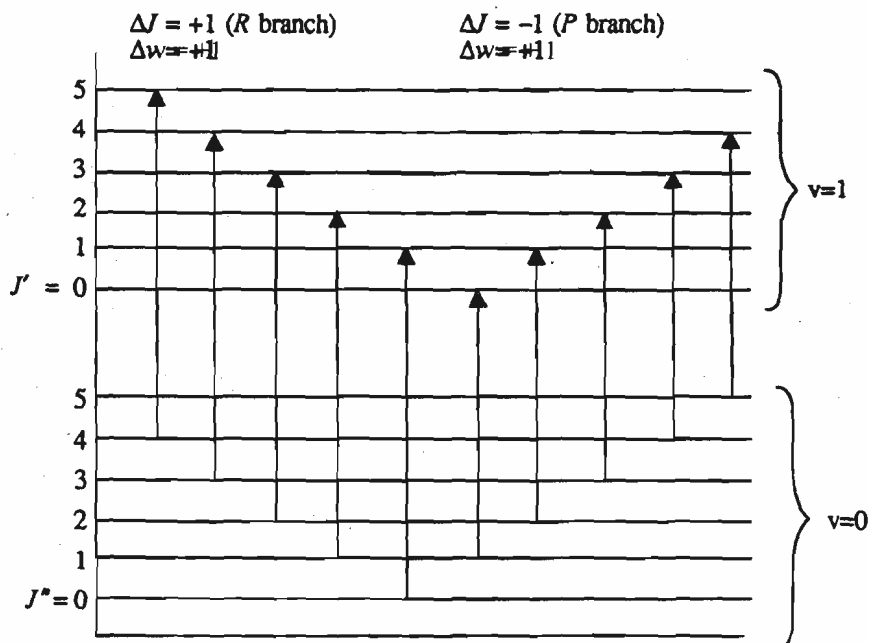


Fig. 4.9: The series of transitions with $\Delta v = +1$ and $\Delta J = \pm 1$.

For the vibrational transition $\Delta v = +1$, the series of transitions with $\Delta J = -1$ is called **P branch** and the series of transitions with $\Delta J = +1$ is called **R branch**. For harmonic oscillator and rigid rotator model

$$\begin{aligned} \Delta E_{v,J} &= E_{v',J'} - E_{v'',J''} \\ &= h\nu_{osc}(v' - v'') + Bhc[J'(J'+1) - J''(J''+1)] \end{aligned} \quad \dots (4.61)$$

For $v' = 1$ and $v'' = 0$, the **R branch** is represented by $J' = J'' + 1$ and **P branch** is represented by $J' = J'' - 1$. The energy expressions for the two branches are given below and they are shown schematically in Fig. 4.10.

$$\Delta E_{v,J} = h\nu_{osc} + 2Bhc(J'' + 1), \text{ R branch} \quad \dots (4.62)$$

where $J'' = 0, 1, 2, \dots$

$$\text{and } \Delta E_{v,J} = h\nu_{osc} - 2BhcJ'', \text{ P branch} \quad \dots (4.63)$$

where $J'' = 1, 2, 3, \dots$

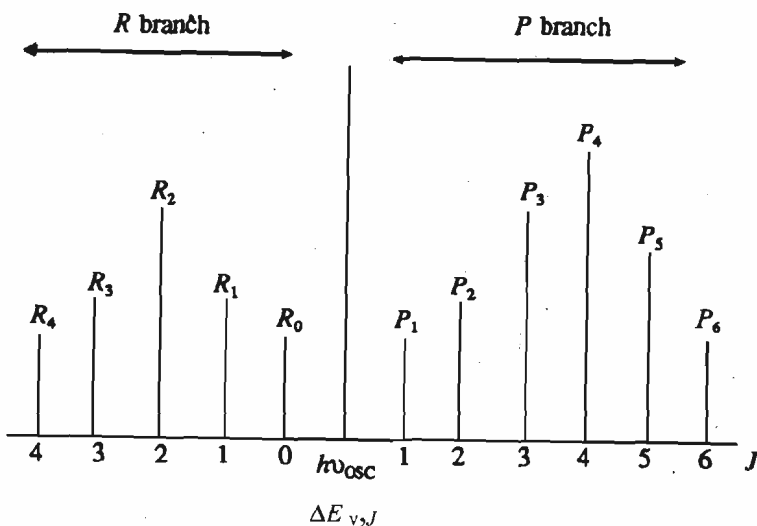


Fig. 4.10: P and R branches showing energies of transitions with varying J'' values.

Since $\Delta J = 0$ is not allowed, the transition with $\Delta E_{v,J} = h\nu_{\text{osc}}$ is not observed under these conditions. This is referred to as Q branch. The infrared spectrum of a diatomic molecule with this model will have two rotational vibrational bands with a dip in the centre corresponding to $\Delta J = 0$ as shown in Fig. 4.11. In working out the expressions for $\Delta E_{v,J}$ given by Eqs. 4.62 and 4.63, it is assumed that the diatomic molecule behaves like a rigid rotator and harmonic oscillator and also that the rotational constant B does not vary with the vibrational quantum number. In practice, however, these assumptions are not true and the expressions get slightly modified when these assumptions are taken into consideration.

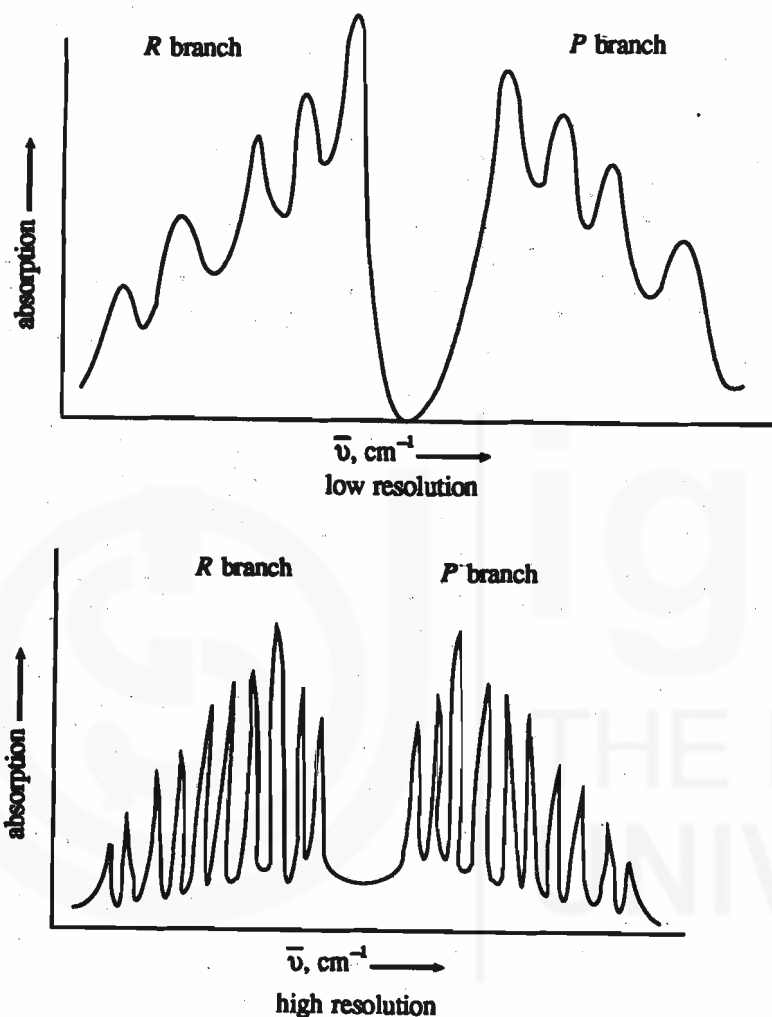


Fig. 4.11: The vibrational rotational infrared spectrum of a diatomic molecule with rigid rotator and harmonic oscillator model.

4.5.3 Symmetric Top Vibrating Rotator Model

As mentioned in Unit 3, a diatomic molecule can be considered as linear rotator if mass of electrons is ignored. The moment of inertia in the direction of the internuclear axis is zero and the moments of inertia in the other two directions (x, y) perpendicular to this axis are equal and nonzero. In case the mass of the electrons is also considered, the moment of inertia in the z -direction is small but finite and therefore, $I_x = I_y \gg I_z$. This is referred to a symmetric top model. The selection rules under these conditions for vibrational-rotational transitions get modified as $\Delta v = \pm 1$ and $\Delta J = 0, \pm 1$. The molecules belonging to this category thus will have all the three (P, Q, R) branches allowed and the infrared spectrum has a central branch (Q) surrounded by two branches P and R on the low and high energy side of the Q branch. It is found that for HCl molecule only P and R branches are observed in the vibrational rotational infrared spectrum whereas for NO molecule, all the three branches are observed.

SAQ 4

See Fig. 4.6 carefully now and note down the various features of the infrared spectrum you can explain.

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4.6 SUMMARY

In this unit, you have learnt the properties of the motion of a single particle joined by a spring fixed to a rigid wall. The motion follows Hooke's law which states that the restoring force is proportional to the displacement and acts in a direction opposite to the direction of the displacement. The displacement of the particle follows simple harmonic motion and is represented by a cosine function of time, t and characteristic frequency ν_{osc} . The expressions for the Hooke's law, Newton's second law of motion and simple harmonic motion are combined to obtain relationship between the oscillational frequency ν_{osc} and force constant of the spring, k (Eq. 4.7). The variation of the potential energy of the motion of the particle with the displacement is shown by a parabola. Expressions for the potential energy, kinetic energy and the total energy of the particle at a displacement x are then derived on the basis of the parabolic variation of the potential energy. It was shown how the use of Schrödinger wave equation for harmonic oscillator gives expression for energy of the motion which is *quantised* giving various energy levels with different values of quantum number $v = 0, 1, 2, 3 \dots$ etc. It is observed that the energy levels are equidistant with a consecutive gap of $h\nu_{osc}$. The motion of two particles joined by a spring was then dealt with. The mathematical derivation showed that the motion is equivalent to that of a harmonic oscillator mentioned above such that its displacement is equal to the change in internuclear distance and its mass is equal to the reduced mass of the two particles. The vibrations of the diatomic molecule were treated in a way similar to the vibrations of two particles joined by a spring, the internuclear bond made through the sharing of electrons replaces the spring. Energy levels and other expressions similar to those obtained for harmonic oscillator were used for studying the vibration of diatomic molecule.

Absorption of radiation in the infrared region led to transition of the diatomic oscillator from ground state energy level with ($v = 0$) to excited state. The frequency of the electromagnetic radiation at which absorption takes place is characteristic of the molecule, and is also equal to the frequency of oscillation of the diatomic harmonic oscillator. The selection rules for the vibrational transition shows that only transitions with $\Delta v = \pm 1$ are allowed. Also such transitions are allowed if there is a change in the dipole moment during the vibration. These rules restrict such transitions to be possible only for heteronuclear diatomic molecules from $v = 0$ to $v = 1$ levels. Due to Boltzman's distribution, population in $v > 0$ is found to be very small at room temperature for most of the common diatomic molecules; therefore, transitions for $v = 1$ to $v = 2$ etc. are not observed. Evaluation of force constant and maximum displacement, effect of isotopic substitution on oscillational frequency and expression for zero point energy were discussed.

The observed behaviour of diatomic molecules regarding their dissociation at higher internuclear distances is introduced in the form of anharmonicity in the potential energy expression. This led to some correction in the quantum mechanical energy leading to a convergence in energy levels. Selection rules allow the observation of overtones in the absorption spectrum of anharmonic oscillator which can be employed to evaluate anharmonicity constants. The last section on vibrating rotator showed that

simultaneous existance of vibrations and rotations in the diatomic molecules leads to observation of fine structure in the absorption bands of IR spectra in terms of P, Q, R branches.

4.7 TERMINAL QUESTIONS

1. What is the energy difference between energy levels of a harmonic oscillator?
2. Define zero point energy.
3. What are the selection rules for
 - (i) a harmonic oscillator to show vibrational spectrum and
 - (ii) an anharmonic oscillator to show vibrational spectrum ?
4. Calculate D_e for H_2^+ , if $D_0 = 21374.9 \text{ cm}^{-1}$

$$\nu_{\text{osc}} = 2321.7 \text{ cm}^{-1}$$

$$\nu_{\text{osc}} x_e = 66.2 \text{ cm}^{-1}$$

$$\nu_{\text{osc}} y_e = 0.6 \text{ cm}^{-1}$$

4.8 ANSWERS

Self Assessment Questions

$$1. \quad \mu = 1.627 \times 10^{-27} \text{ kg}$$

$$k = 4\pi^2 \nu_{\text{osc}}^2 \mu$$

Given $\nu = 2886 \text{ cm}^{-1}$. To get ν_{osc} from it, we have to multiply it by the velocity of light, c .

$$\text{Thus, } k = 4\pi^2 (\nu_{\text{osc}} c)^2 \mu$$

$$= 483 \text{ kg s}^{-2} = 483 \text{ N m}^{-1}$$

$\Delta r_0 = 1.08 \times 10^{-9}, 1.87 \times 10^{-9}, 2.42 \times 10^{-9}, 2.86 \times 10^{-9}$ for $v = 0, 1, 2, 3$, respectively.

$$2. \quad \text{O} - \text{D} = 2718 \text{ cm}^{-1}$$

By using $m_{\text{O}} = 15.9949 \times 10^{-3} \text{ kg}$

$$m_{\text{H}} = 1.007825 \times 10^{-3} \text{ kg}$$

$$m_{\text{D}} = 2.014101 \times 10^{-3} \text{ kg}$$

and then calculating μ and using Eq. 4.39.

$$3. \quad E_0 \text{ HCl} / E_0 \text{ DCI} = \sqrt{2}$$

$$4. \quad \text{Fundamental, I and II overtones at } 2886, 5668 \text{ and } 8346 \text{ cm}^{-1}$$

(i) Overtones are weaker than fundamentals.

(ii) Harmonic oscillators – only fundamental transitions are allowed, ($\Delta v = 0$).

Anharmonic oscillators – fundamental and overtones are allowed,

($\Delta v = 0, 1, 2$, etc).

- (iii) At high resolution, rotational fine structure shows *P* and *R* branches and a dip is observed in the place of *Q* branch since transitions with $\Delta J = 0$ are not allowed.

Terminal Questions

1. $h \nu_{\text{osc}}$
2. The energy of the molecule at $v = 0$, i.e. at vibrational ground level is called zero point energy.
3. $\Delta v = \pm 1$ for harmonic oscillator
 $\Delta v = \pm 1, \pm 2, \pm 3$ etc. for an anharmonic oscillator.
4. $\sim 22,540 \text{ cm}^{-1}$.

