

Lecture 28 Title: Diatomic Molecule : Vibrational and Rotational spectra

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In this lecture we will understand the molecular vibrational and rotational spectra of diatomic molecule

We will start with the Hamiltonian for the diatomic molecule that depends on the nuclear and electronic coordinate.

Then we will use the Born-Oppenheimer approximation, to separate the nuclear and electronic wavefunctions

We will derive the eigen energy values to understand the rotational and vibrational spectra of the ground electronic state of diatomic molecules.

At the end we will discuss the rotational and vibrational spectra of some diatomic molecules.

For a diatomic molecule A - B with n electrons as shown in figure-28.1, the Schrodinger equation can be written as

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 + V \right) \Psi = E \Psi \quad \dots\dots\dots(28.1)$$

Where, Ψ is the total electronic and nuclear wavefunction & E is the total energy.

1st term: K.E. of the relative motion of the nuclei with reduced mass $\mu = \frac{m_A m_B}{m_A + m_B}$

2nd term: K.E. of all electrons.

And the potential,

$$V = \sum_{i>j=1}^n \frac{e^2}{r_{ij}} - \sum_{i=1}^n \frac{Z_A e^2}{r_{iA}} - \sum_{i=1}^n \frac{Z_B e^2}{r_{iB}} + \frac{Z_A Z_B e^2}{R}$$

$$= V_{ee} - V_{en} + V_{nn}$$

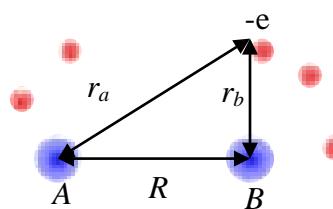


Figure-28.1

The molecular wavefunction, Ψ depends on both electron & nuclear coordinates,

$$\Psi = \Psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_n, y_n, z_n, X, Y, Z) = \Psi(r, R)$$

w.r.t. origin say nucleus A

Since the wavefunction depends on both electron and nucleus coordinates, it is difficult to solve this problem even for a simple molecule. We would like to separate electronic and nuclear motion.

Because of the different masses of the electrons and nuclei, we can consider the nuclei to be stationary to solve the electronic problem (Born-Oppenheimer approximation).

The essence of the Born-Oppenheimer approximation is to decompose nuclear and electronic motions based on the large disparity of the masses of nuclei and mass of electron.

If we need to solve the Schrodinger equation given in equation-28.1 using Born-Oppenheimer approximation, we have to follow five steps.

Step-1

Let us assume that the nuclei are clamped in fixed positions. This approximation is almost close to the reality because the electronic motion is so fast that it will see the nuclear motions almost stationary. This will eliminate the nuclear kinetic energy term in the Hamiltonian in equation 28.1

Step-2

Under the assumption in step-1, we can write equation 28.1 as

$$\left\{ -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 + V(r, R) \right\} \phi(r, R) = E_e(R) \phi(r, R) \dots\dots\dots(28.2)$$

Here nuclear K.E. is zero, and R appears only as a parameter and $\phi(r, R)$ is the electronic wavefunction.

We can follow the procedure to fix $R = R_1$

$$\text{Solve } \left\{ -\frac{\hbar^2}{2m} \sum \nabla_i^2 + V(r, R_1) \right\} \phi(r, R_1) = E_e(R_1) \phi(r, R_1)$$

Then, fix $R = R_2$

$$\text{Solve } \left\{ -\frac{\hbar^2}{2m} \sum \nabla_i^2 + V(r, R_2) \right\} \phi(r, R_2) = E_e(R_2) \phi(r, R_2)$$

and do it for the entire range of R .

Step-3

Having obtained the electronic wavefunction $\phi(r, R)$, and $E(R)$ we can write the total molecular wavefunction,

$$\Psi(r, R) = \phi(r, R) \chi(R) \dots\dots\dots(28.3)$$

where, $\chi(R) \Rightarrow$ Nuclear wavefunction

Step-4

Now we can substitute equation 28.3 in equation 28.1 and we get,

$$\begin{aligned} & \left\{ -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + V(r, R) \right\} \phi(r, R) \chi(R) \\ &= \left(-\frac{\hbar^2}{2\mu} \nabla^2 \right) \phi(r, R) \chi(R) + \left\{ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + V(r, R) \right\} \phi(r, R) \chi(R) \\ &= E \phi(r, R) \chi(R) \end{aligned}$$

Step-5

Since, ∇_i^2 operates only on $\phi(r, R)$. We can write,

$$= \left(-\frac{\hbar^2}{2\mu} \nabla^2 \right) \phi(r, R) \chi(R) + E_e(R) \chi(R) = E \phi(r, R) \chi(R)$$

Now, ∇^2 is the difference w.r.t. R , so can operate on both $\phi(r, R)$ and $\chi(R)$.

As a consequence, the electronic wavefunction is relatively insensitive to changes in the nuclear positions and momenta, and is therefore capable of adjusting itself quasi-statically to the nuclear motion. This is known as the adiabatic approximation.

Assumption: Electronic wavefunction varies slowly with the inter-nuclear distance,

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So we get,

$$\nabla^2 \phi(r, R) \chi(R) \approx \phi(r, R) \nabla^2 \chi(R)$$

$$\text{So, } \left[-\frac{\hbar^2}{2\mu} \nabla^2 + E_e(R) \right] \chi(R) = E \chi(R) \dots\dots\dots(28.4)$$

This is the Schrödinger equation of nuclear motion of diatomic molecule. It is independent of electronic motion whose effect appears only through $E_e(R)$, which is electronic energy as a function of R and act as a potential energy for the motion of the nuclei.

This is the central approximation of the Born-Oppenheimer approach. Its justification stems from the fact that nuclear velocities are small compared to electronic velocities.

Now we are ready to solve the equation-28.4. This is simple as we have solved it for hydrogen atom.

Let us introduce spherical polar coordinate (R, θ, ϕ) of one nucleus with respect to other as origin in equation 28.4, and we get

$$\left\{ -\frac{\hbar^2}{2\mu R^2} \left[\frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + E_e(R) \right\} \chi(R, \theta, \phi) = E \chi(R, \theta, \phi)$$

$$\text{Now, } \chi(R, \theta, \phi) = \mathfrak{R}(R) S(\theta, \phi) \dots\dots\dots(28.5)$$

Where, $S(\theta, \phi) = S_{JM}(\theta, \phi)$ are specified by the molecular total angular momentum quantum number J and Z - component M , analogous to H - atom quantum no. ℓ & m .

The angular part,

$$\begin{aligned}
 & -\frac{\hbar^2}{2\mu R^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) S_{JM}(\theta, \phi) = \frac{J(J+1)\hbar^2}{2\mu R^2} S_{JM}(\theta, \phi) \\
 \Rightarrow & -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) S_{JM}(\theta, \phi) = J(J+1)\hbar^2 S_{JM}(\theta, \phi) \\
 \Rightarrow & M^2 S_{JM}(\theta, \phi) = J(J+1)\hbar^2 S_{JM}(\theta, \phi) \quad \dots\dots(28.6)
 \end{aligned}$$

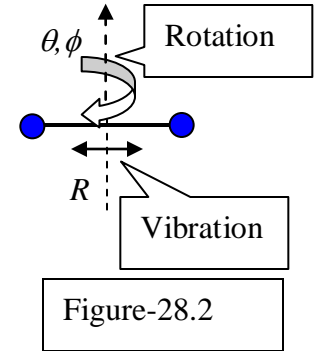
This is nothing but the rotational motion as shown in figure-28.2

Putting it in the equation,

$$\begin{aligned}
 & \left\{ -\frac{\hbar^2}{2\mu R^2} \left(\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) + E(R) \right\} \mathfrak{R}(R) S_{JM}(\theta, \phi) \\
 = & \left\{ -\frac{\hbar^2}{2\mu R^2} \left(\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} - J(J+1) \right) + E(R) \right\} \mathfrak{R}(R) S_{JM}(\theta, \phi) \\
 = & E_{v,J} \mathfrak{R}(R) S_{JM}(\theta, \phi)
 \end{aligned}$$

where, $v \Rightarrow$ Vibrational quantum number

$J \Rightarrow$ Rotational quantum number



$$-\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{J(J+1)\hbar^2}{2\mu R^2} \mathfrak{R}(R) + E(R) \mathfrak{R}(R) = E_{v,R} \mathfrak{R}(R) \quad \dots\dots\dots(28.7)$$

This depends only on inter-nuclear distance R and is called the radial equation for the nuclear motion.

$\mathfrak{R}(R) \Rightarrow$ Vibrational Wavefunction

$S_{JM}(\theta, \phi) \Rightarrow$ Rotational Wavefunction

Rotational Spectra of Diatomic Molecule

Simple model is rigid rotor i.e. R is fixed as R_e at equilibrium. In classical mechanics, the magnitude of angular momentum $|J|$ of such a molecule rotating about center of mass with angular velocity ω .

$$|J| = \mu R_e v = I_e \omega^2$$

From 28.6, rotational energy:

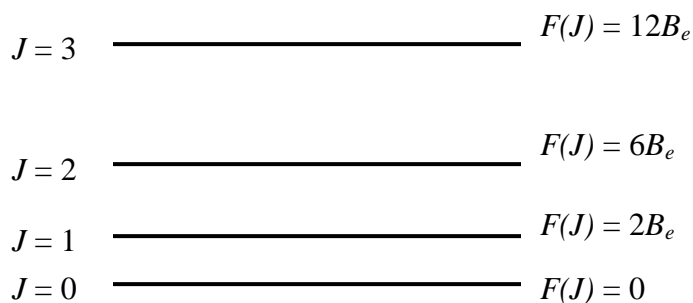
$$E_J = \frac{\hbar^2}{2\mu R^2} J(J+1) \quad \text{putting, } \begin{matrix} R = R_e \\ \mu R_e^2 = I_e \end{matrix}$$

$$E_J = \frac{\hbar^2}{2I_e} J(J+1) \quad \text{This is in energy unit joule. We will convert it to cm}^{-1}.$$

$$F(J) = \frac{E_J}{hc} \text{ cm}^{-1} = \frac{\hbar^2}{2hcI_e} J(J+1) = \frac{h}{8\pi^2 c \mu R_e^2} \dots\dots\dots (28.8) \\ = B_e J(J+1)$$

Energy Levels as shown in figure 28.3

$$\left. \begin{array}{ll} J=0 & ; \quad F(0)=0 \\ J=1 & ; \quad F(0)=2B_e \\ J=2 & ; \quad F(0)=6B_e \\ J=3 & ; \quad F(0)=12B_e \end{array} \right\} \quad S_{JM} = P_J^M (\cos \theta) e^{iM\phi}$$



Rotational energy levels

Figure-28.3

Now we will derive the selection rule for the transitions.

We know that we have to calculate the electric dipole transition moment integrals to derive the selection rule. We take μ_{el} as dipole moment of the molecule. So the transition moment integral R is

$$R = \int S_{JM} \mu_{el} S_{JM'} d\tau$$

The components of the dipole moment μ_{el}

$$(\mu_{el})_x = \mu_0 \sin \theta \cos \phi$$

$$(\mu_{el})_y = \mu_0 \sin \theta \sin \phi \quad d\tau = \sin \theta d\theta d\phi$$

$$(\mu_{el})_z = \mu_0 \cos \theta$$

$$R_z = \mu_0 \int_0^\pi P_J^M \cos \theta P_{J'}^{M'} \sin \theta d\theta \int_0^{2\pi} e^{iM\phi} e^{-iM'\phi} d\phi$$

$$\Downarrow$$

$$M = M'$$

Spherical Harmonics

$$\cos \theta P_J^{|M|}(\cos \theta) = \left(\frac{J+|M|}{2J+1} \right) P_{J-1}^{|M|} + \left[\frac{J-|M|+1}{2J+1} P_{J+1}^{|M|} \right]$$

$$R_z = 2\pi\mu_0 \left[\frac{J+|M|}{2J+1} \int P_{J-1}^{|M|} P_{J'}^{M'} \sin \theta d\theta + \frac{J-|M|+1}{2J+1} \int P_{J+1}^{|M|} P_{J'}^M \sin \theta d\theta \right]$$

$$\int P_{J_1}^{|M|} P_{J_2}^{|M|} \sin \theta d\theta = 0 \quad \text{if } J_1 \neq J_2$$

$$\left. \begin{array}{l} J-1 = J' \\ J+1 = J' \end{array} \right\} \Delta J = \pm 1 ; \Delta M = 0 \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} = \pm 1$$

.....(28.9)

Using the selection rule derived in equation 28.9, the transitions are shown in the following figure-28.4.

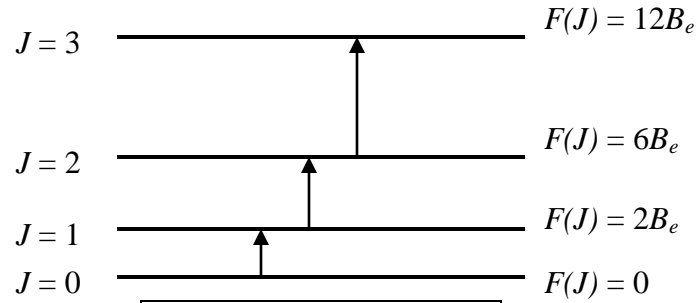


Figure-28.4

The transition energies are

$$J = \pm 1$$

$$F(J+1) = B_e (J+1)(J+2)$$

$$F(J) = B_e J(J+1)$$

$$\bar{\nu}(J) = F(J+1) - F(J)$$

$$= B_e (J+1)[J+2-J]$$

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

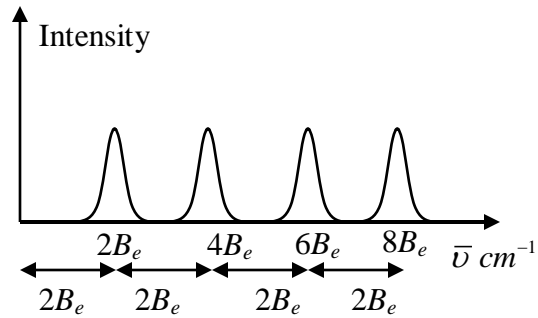


Figure-28.5

Where $J = 0, 1, 2, \dots$

The expected rotational spectrum is shown in figure-28.5

So we see that under non-rigid approximation, the transition are equidistant with value $2B_e$ and depends on the value of B_e .

Example:

Rotational Spectrum of HCl molecule shown in figure-28.6

$$2B_e = 21.18 \text{ cm}^{-1}$$

$$B_e = 10.59 \text{ cm}^{-1} = \frac{\hbar^2}{2I_e hc} = \frac{h^2}{8\pi^2 \mu R_e^2 hc}$$

$$= \frac{h}{8\pi^2 \mu c R_e^2}$$

$$H = 1.0079 \text{ amu}$$

$$Cl = 35.453 \text{ amu}$$

$$1 \text{ amu} = 1.66 \times 10^{-24} \text{ gm}$$

$$\mu = 1.63 \times 10^{-24} \text{ gm}$$

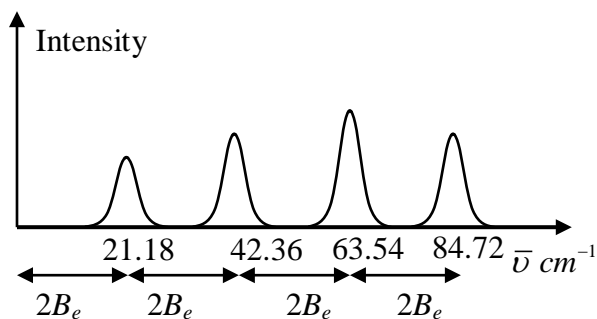


Figure-28.6

$$R_e^2 = \frac{6.6256 \times 10^{-27} \text{ erg. sec. cm.}}{8 \times 3.14^2 \times 1.63 \times 10^{-24} \text{ gm} \times 10.59 \times 3 \times 10^{10} \text{ cm/sec}}$$

$$= 1.622 \times 10^{-16} \text{ cm}$$

$$R_e = 1.27 \times 10^{-8} \text{ cm} = 1.27 \text{ \AA}$$

So the equilibrium bond length of the HCl molecule is 1.27 \AA .

Thus from the rotational spectrum of a molecule, we can derive the bond length and structure.

Note: For molecules without permanent dipole moments such as H_2 , the electric dipole pure rotation transition probability is zero. In that system the moment of inertia & internuclear distance can be found out from analysis of rotational structure of electronic absorption bands or rotational Raman Spectra. We will discuss these two spectra in later.

Vibrational Spectra of Diatomic Molecule

Radial equation 28.7,

$$-\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d\mathfrak{R}}{dR} \right) + E_{ROT} \mathfrak{R}(R) + E_e(R) \mathfrak{R}(R) = E_{v,J} \mathfrak{R}(R)$$

Where $\frac{J(J+1)\hbar^2}{2\mu R^2} \simeq \frac{J(J+1)\hbar^2}{2\mu R_e^2} = E_{ROT}$

The total energy, $E_{v,J} = E_{ROT} + E_{vib} = E_{nucl}$

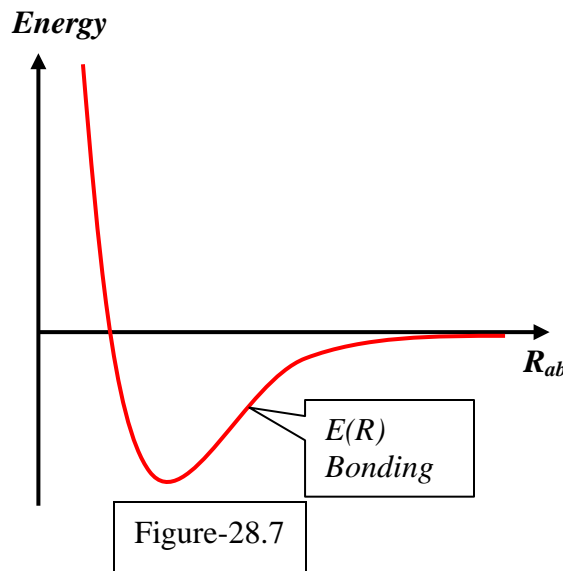
$$-\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d\mathfrak{R}}{dR} \right) + E_{ROT} \mathfrak{R}(R) + E_e(R) \mathfrak{R}(R) = (E_{ROT} + E_{vib}) \mathfrak{R}(R)$$

$$\Rightarrow -\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d\mathfrak{R}}{dR} \right) + E_e(R) \mathfrak{R}(R) = E_{vib} \mathfrak{R}(R)$$

Putting $\mathfrak{R}(R) = \frac{1}{R} \xi(R)$

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \xi(R) + E(R) \xi(R) = E_{vib} \xi(R)$$

$E_e(R)$ is the electronic energy as shown in the following figure-28.7 which behaves as the potential energy of the nuclear motion.



Expand this function in power series about $R = R_e$,

$$E_e(R) = E(R_e) + \left(\frac{dE}{dR} \right)_{R_e} (R - R_e) + \frac{1}{2} \left(\frac{d^2E}{dR^2} \right)_{R_e} (R - R_e)^2 + \dots$$

Choose zero of the energy at $E(R_e) = 0$ minimum because this point is minimum

$$\left(\frac{dE}{dR} \right)_{R_e} = 0.$$

$$\text{So, } E_e(R) = \frac{1}{2} \left(\frac{d^2E}{dR^2} \right)_{R_e} (R - R_e)^2 + \frac{1}{3!} \left(\frac{d^3E}{dR^3} \right)_{R_e} (R - R_e)^3 + \dots$$

Putting $R - R_e = \rho$

$$E(\rho) = \frac{1}{2} K_e \rho^2 + \dots$$

$$\text{Where } K_e = \left(\frac{d^2E}{dR^2} \right)_{R_e}$$

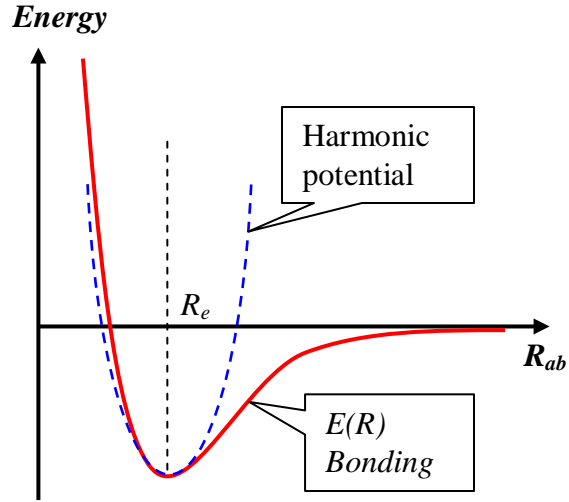


Figure-28.8

If neglect the higher power

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{d\rho^2} \xi(\rho) + \frac{1}{2} K_e \rho^2 \xi(\rho) = E_{vib} \xi(\rho)$$

Harmonic oscillator equation with potential as shown in figure-28.8, so the energy value

$$E_{vib} = E_v = \left(v + \frac{1}{2} \right) \hbar \omega_e \quad v = \text{vibrational quantum number} = 0, 1, 2, 3, \dots$$

$$\nu_e \Rightarrow \text{Classical frequency} = \frac{1}{2\pi} \left(\frac{K_e}{\mu} \right)^{1/2}$$

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Wave Function

$$\xi_v = N_v e^{-\frac{1}{2}\beta x^2} H_v(\sqrt{\beta}x)$$

$$\beta = \frac{4\pi^2 \mu \nu_{ose}}{h}$$

where, $H_v(\sqrt{\beta}x) \Rightarrow$ Hermite polynomial

The wavefunctions are shown in the figure-28.9 with dashed curves. The solid curves are the $|\xi_v|^2$

Dipole moment

$$\mu = \mu_0 + \mu_1 x$$

where, $\mu_0 \Rightarrow$ Permanent

$\mu_1 \Rightarrow$ Induced due to vibration

Selection rule :

$$R_x = \mu_0 \int \xi_{v'}^* \xi_{v''} dx + \mu_1 \int x \xi_{v'}^* \xi_{v''} dx$$

$$\begin{array}{ccc} \uparrow & \downarrow & \downarrow \\ v' \neq v''; 0 & v' = v'' + 1 & v' = v'' - 1 \end{array}$$

$$E(0) = \frac{1}{2} \hbar \omega_e$$

$$E(1) = \frac{3}{2} \hbar \omega_e$$

$$\therefore E(1) - E(0) = \hbar \omega_e$$

So only one transition is predicted under harmonic oscillator approximation Figure-28.9). However, many transitions are seen in the infra red vibrational spectra of diatomic molecule. So harmonic approximation is not the good approximation.

Note: Dipole moment of molecule with equal nucleus is always zero. So for N_2, O_2, \dots no infrared spectrum.

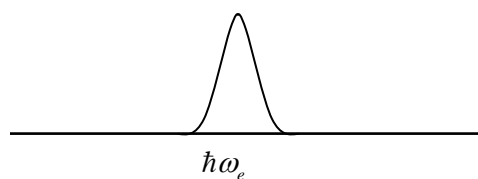
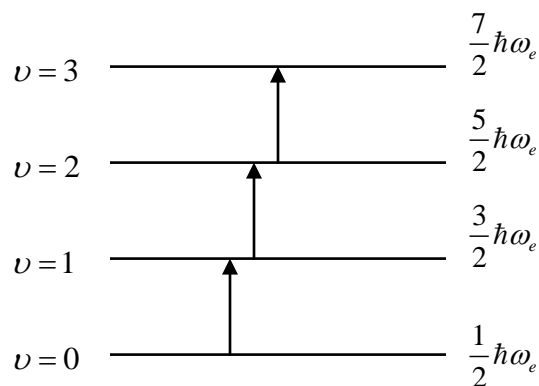
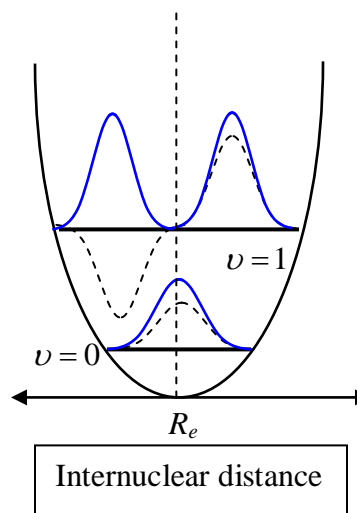


Figure-28.9

Anharmonic Oscillator

Introducing anharmonicity

$$E_e(R) = f(r - r_e)^2 - g(r - r_e)^3 + \dots \quad \text{Condition: } g \ll f$$

Morse Potential as shown in the figure-28.10 : $E(R) = D_e \left(1 - e^{-\beta(r - r_e)^2} \right)$

$$\text{Energy levels: } E_v = \hbar \omega_e \left(v + \frac{1}{2} \right) - \hbar \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \hbar \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \dots$$

Convert in cm^{-1}

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3$$

where $\omega_e, \omega_e x_e, \omega_e y_e$ in terms of cm^{-1} .

$v \Rightarrow$ Vibrational quantum number

Here $\omega_e > \omega_e x_e > \omega_e y_e$

Selection rule,

$$\Delta v = \pm 1, \pm 2, \pm 3$$

$$\text{Zero point energy: } G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + \frac{1}{8} \omega_e y_e$$

If the energy referred to the lowest level,

$$G_0(v) = G(v) - G(0)$$

$$= \left\{ \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \dots \right\} - \left\{ \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + \frac{1}{8} \omega_e y_e + \dots \right\}$$

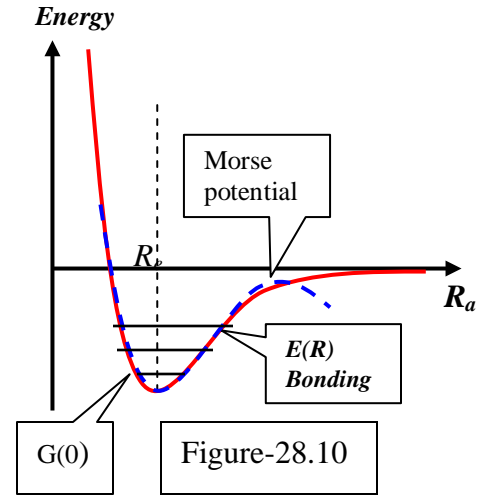
$$= \left(\omega_e - \omega_e x_e + \frac{3}{4} \omega_e y_e \right) v - \left(\omega_e x_e - \frac{3}{2} \omega_e y_e + \dots \right) v^2 + (\omega_e y_e + \dots) v^3$$

$$= \omega_0 v - \omega_0 x_0 v^2 + \omega_0 y_0 v^3$$

$$\omega_0 = \omega_e - \omega_e x_e + \frac{3}{4} \omega_e y_e$$

$$\text{where, } \omega_0 x_0 = \omega_e x_e - \frac{3}{2} \omega_e y_e + \dots$$

$$\omega_0 y_0 = \omega_e y_e + \dots$$



Transitions between the vibrational levels

$$\begin{aligned}\nu_{abs} &= G_0(\nu) - G(0) \\ &= G_0(\nu)\end{aligned}$$

Thus the observed absorption gives directly the positions of the energy levels.

Example: Observed Vibration Frequency of HCl

ν	$\nu_{abs} \text{ (cm}^{-1}\text{)}$	ΔG	$\Delta^2 G$	Cal.	Harmonic Approx.
0	0				
1	2885.9	2885.9	-103.7	2885.9	2885.9
2	5668.0	2782.1	-103.2	5668.2	5771.8
3	8346.9	2678.9	-102.7	8347.5	8657.7
4	10923.1	2576.2	-102.8	10923.6	11543.6
5	13396.5	2473.4		13396.5	14429.5

$$G_0(\nu) = \omega_0 \nu - \omega_0 x_0 \nu^2 + \dots$$

$$G_0(1) = \omega_0 - \omega_0 x_0 = 2885.9$$

$$G_0(2) = 2\omega_0 - 4\omega_0 x_0 = 5668.0$$

$$2\omega_0 - 4\omega_0 x_0 = 5668.0$$

$$2\omega_0 - 2\omega_0 x_0 = 5771.8$$

$$\begin{array}{ccc} (-) & (+) & (-) \\ \hline \end{array}$$

$$-2\omega_0 x_0 = -103.8 \Rightarrow \omega_0 x_0 = +51.6$$

$$\Delta G(\nu) = G_0(\nu+1) - G_0(\nu)$$

$$= \omega_0(\nu+1) - \omega_0 x_0(\nu+1)^2 - \omega_0 \nu + \omega_0 x_0 \nu^2$$

$$= \cancel{\omega_0 \nu} + \omega_0 - \cancel{\omega_0 x_0 \nu^2} - 2\omega_0 x_0 \nu - \omega_0 x_0 - \cancel{\omega_0 \nu} + \cancel{\omega_0 x_0 \nu^2}$$

$$= \omega_0 - \omega_0 x_0 - 2\omega_0 x_0 \nu$$

$$\Delta^2 G(\nu) = \Delta G(\nu+1) - \Delta G(\nu)$$

$$= \omega_0 - \omega_0 x_0 - 2\omega_0 x_0(\nu+1) - \omega_0 + \omega_0 x_0 + 2\omega_0 x_0 \nu$$

$$= -2\omega_0 x_0$$

which is directly the measured anharmonicity.

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Recap

In this lecture we have learnt the origin of vibrational and rotational spectra.

We started with the Schrodinger equation for the diatomic molecule.

Then we used the Born-Oppenheimer approximation, to separate the nuclear and electronic wavefunctions.

We derived the eigen energy values of the rotational and vibrational motions of the ground electronic state of diatomic molecules.

At the end we have discussed the rotational and vibrational spectra of some diatomic molecules.