Chemistry II: Introduction to Molecular Spectroscopy
Prof. Mangala Sunder
Department of Chemistry and Biochemistry
Indian Institute of Technology, Madras

Lecture – 10
Diatomic Vibration Spectra Harmonic Model

Welcome back to the lectures on chemistry and an introduction to molecular spectroscopy. In this and the next several lectures, we shall look at one of the important aspects of molecular motion namely, vibrational motion and the details of infrared spectroscopy. We will talk about absorption spectrum. And, when it comes to scattering, we shall discuss Raman spectroscopy at that point of time with vibrational motion as one of the motions to be studied under Raman spectra at that point of time.

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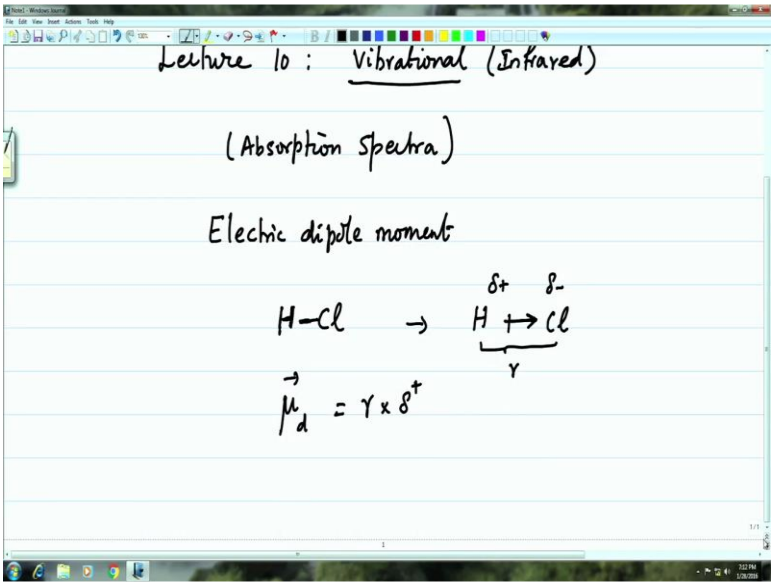

Lecture 10 : Vibrational (Infrared)

(Absorption Spectra)

Electric dipole moment

$$H-Cl \rightarrow \overset{\delta+}{H} \underbrace{\mapsto}_{r} \overset{\delta-}{Cl}$$

$$\vec{\mu}_d = r \times \delta^+$$

Here we shall look at the IR spectrum. What is important fundamentally for vibrational spectroscopy or for a molecule to show a vibrational spectrum is the presence of an electric dipole moment. We shall start with a diatomic molecular system and then it is easier for us to understand dipole moment as a very simple concept coming as a result of the separation of the positive charge center of the molecule with the negative charge center. And, in the case of diatomic molecule, we associate the atoms with certain partial charges like in the case of HCl – the bond distance and the fact that, the hydrogen and chlorine have electronegativity differences result in an electric moment which is given by the product of the charges either positive or negative – the charge separation times the distance r. So, the mu d as it is written with a vector notation; dipole moment is a vector; and, here the charge distribution is from the positive to the negative center of the charge direction. And, the dipole moment points in this direction and it is given by the bond distance times delta plus. Dipole moment is an extremely important quantity. And, in the case of a diatomic molecule, the oscillation of the molecule – the atoms about the equilibrium positions on the atoms, results in the dipole moment oscillating in values.

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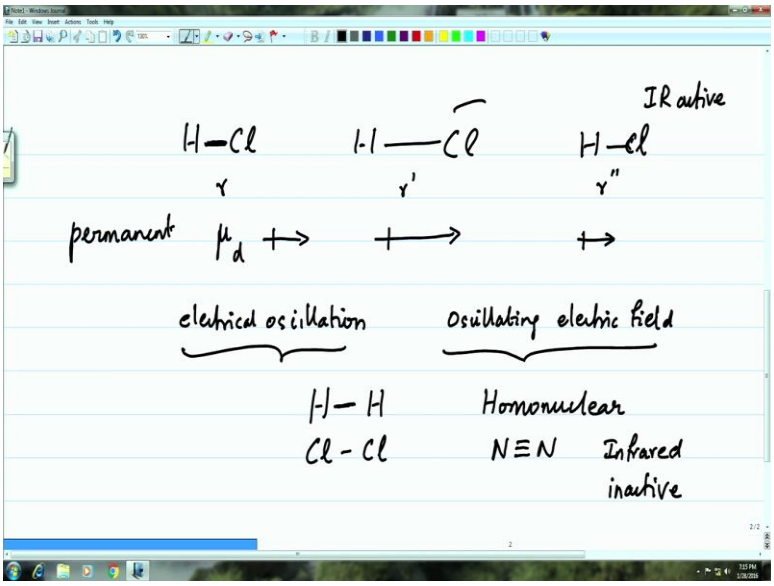

For example, if you think about HCl undergoing molecular vibrations to give a slightly larger distance and a shorter distance – HCl; if you do that, then the r here – it is r prime; and, some other value. The dipole moment mu d changes; it oscillates from a small value to a slightly larger value and back to a small value. This is an electric charge oscillation – electrical oscillation and the electromagnetic field with the oscillating component of electric field.

If these oscillations are in resonance; then, there is a resultant absorption of energy and the molecule undergoes molecular vibrational excitation; it goes to a higher energy level and then emits radiation and so on. Therefore all the processes of spectroscopy become active and it is due to the fact that, the electrical dipole moment – the permanent electrical dipole moment that is present in the molecule interacts with the oscillating electric field of the electro magnetic radiation. So, this is a fundamental requirement for the infrared intensity to be measurable.

If a molecule such as hydrogen, where both the atoms are identical, that is, homonuclear diatomic molecules do not show IR spectrum, do not reveal any – there the information through IR spectrum. On the other hand, they can be studied using Raman spectroscopy when we study scattering later. But, for the purpose of the vibrational infrared spectroscopy, homonuclear diatomic molecules like that or N triple bond N, whatever that you have molecules, which do not have a permanent dipole moment, because there is no charge separation between the positive charges and the negative charges.

This is one point. And therefore, there is no moment associated with that; the first moment, there is no none. Therefore, such molecules are not infrared active. They are called infrared inactive. And, HCl is called infrared IR active. And, so is carbon monoxide, carbon dioxide, polyatomic molecules; polyatomic molecules – there is more than one vibrational motion as we will see. And therefore, it is possible for us to have infrared spectra for some of the motions.

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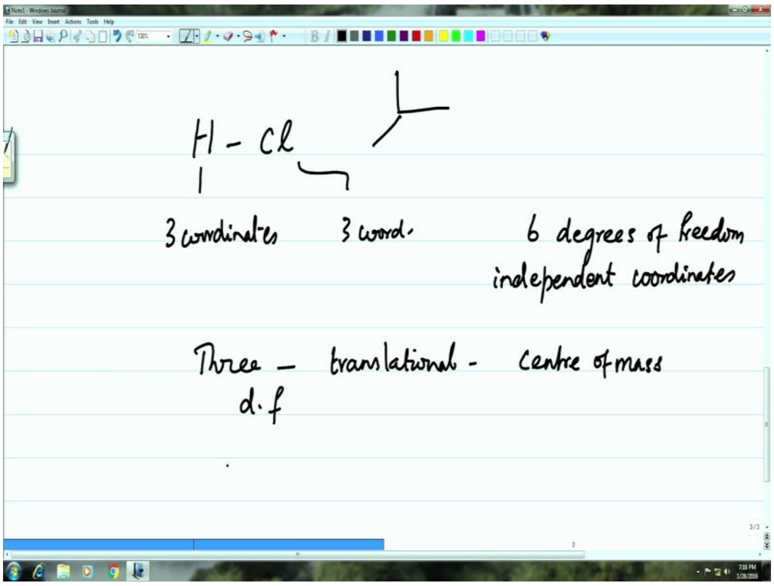

H - Cl

3 coordinates 3 coord. 6 degrees of freedom independent coordinates

Three – translational - Centre of mass
d.f

But, in the case of a diatomic molecule, the vibrational motion is one degree of freedom motion. Given the fact that, if you have again HCl, hydrogen has three coordinates in any space; any access system, hydrogen atom has three coordinates. There is three degrees of freedom – linear degrees. And, chlorine has another three coordinates. Therefore, the molecule has six degrees of freedom for six independent coordinates as we call them. And, of these six, it is possible for us to use three of them to describe the overall molecular motion; and, that motion is the translational motion of the center of mass. The center of mass is of course, is the point in the molecule, where we concentrate the entire mass of the molecule. And therefore, the motion of the molecule in space is the translational motion – rectilinear translational motion in any one of the three directions. Therefore, three degrees of freedom are due to – three degrees of freedom are due to translational motion.

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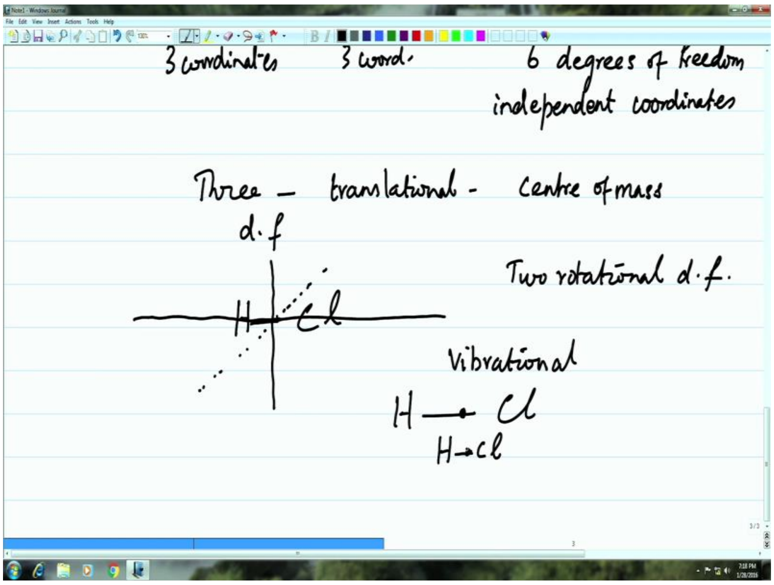

This molecule also rotates about two independent axes: the axis that is passing through the center of mass and an axis perpendicular to the center of mass. About these two axes, the molecule has a moment of inertia, because the atoms are away from the axis system. And, if you recall the moment of inertia as the m i r i square, hydrogen and chlorine both contribute to that. Therefore, the molecule has the moment of inertia. And, these are the two mutually perpendicular axis systems.

The molecular axis itself that you have right here, the atoms are on the axis; as point masses, they do not have a moment of inertia. And therefore, there is no rotational energy; there is no energy associated with molecular motion about the axis system. There are only two rotational degrees of freedom. And therefore, of the six coordinates – independent coordinates or independent degrees of freedom, three are translational, two are rotational; and, there is one more, which is the vibrational degree of freedom. And, that is the relative motion of the hydrogen, chlorine with respect to the center of mass, which is not moving, because center of mass motion is already been taken out into the translational part. Therefore, if you have that, the vibrational motion would be – the center of mass does not move. So, this is a genuine vibration and there is only one vibrational degree of freedom.

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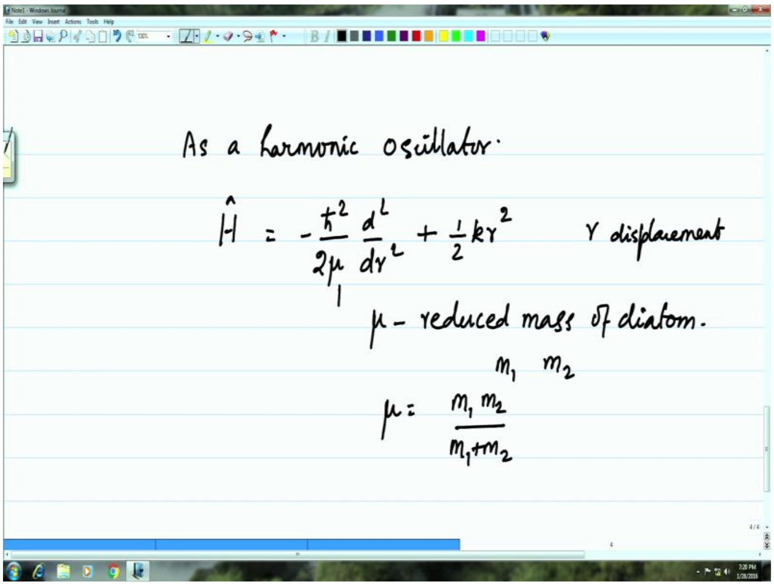

As a harmonic oscillator.

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{1}{2}kr^2 \qquad r \text{ displacement}$$

μ – reduced mass of diatom.

$m_1 \quad m_2$

$$\mu = \frac{m_1 m_2}{m_1+m_2}$$

What is the process of measurement? And, what is the process of understanding the vibrational motion in the elementary form? As a harmonic oscillator; of course, we started with a little bit of an introductory harmonic oscillator in an earlier lecture. Remember that, the Hamiltonian for the harmonic oscillator is the kinetic energy term minus H bar square by 2 mu d square by d r square.

Here mu is the reduced mass of the diatomic molecule. And so, if you have m 1 and m 2; then, mu is m 1 m 2 by m 1 plus m 2. This is the kinetic energy. And, the potential energy for the harmonic oscillator comes from the Hooke’s law and is expressed in terms of the force constants k r square; where, r is the displacement from equilibrium, because at equilibrium, we assume that, the potential energy is a minimum.

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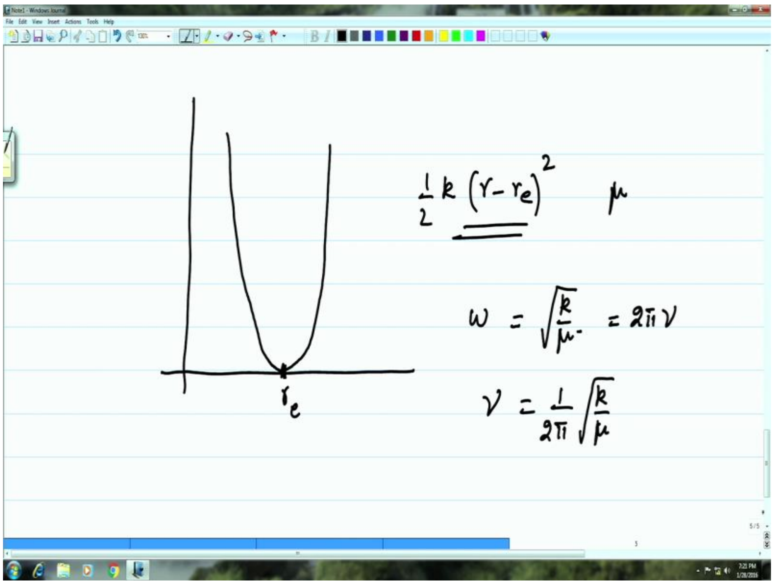

$\frac{1}{2} k \underline{\underline{(r - r_e)^2}}$ $\quad \mu$

$\omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu$

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

And therefore, if you plot the harmonic oscillator potential energy surface for a vibrating molecule; then, if you call, this is a parabolic and let us put the r. This is the equilibrium distance called r e. And, any displacement from the equilibrium will result in the force. And therefore, a potential energy – half k r minus r e square, which contributes to the vibrational energy.

And, what you have is of course, vibrational frequency associated with such motion for a diatomic molecule with the reduced mass, is the angular frequency. If you write it, omega is square root of k by mu. The angular frequency is expressed in terms of the normal experimental frequency that we measure 2 pi nu. And therefore, the natural frequency for harmonic oscillator is 1 by 2 pi square root of k by mu.

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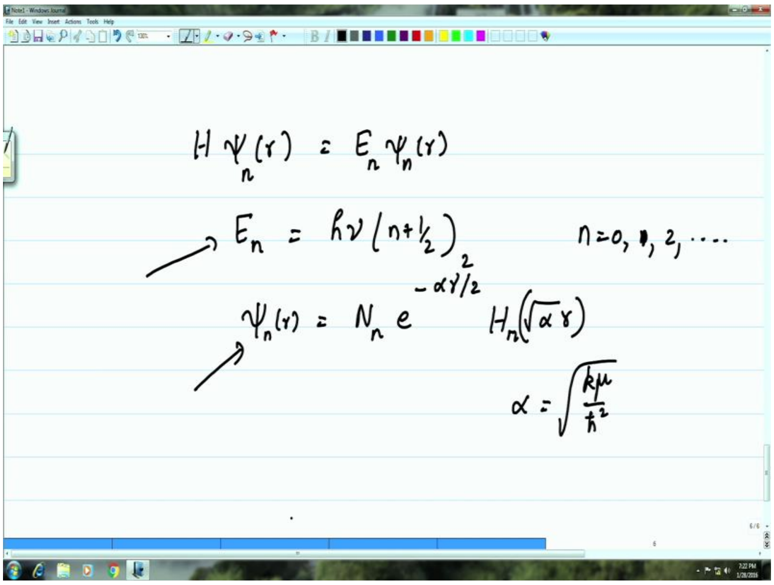

$$H\psi_n(r) = E_n\psi_n(r)$$

$$E_n = h\nu\left(n+\tfrac{1}{2}\right) \qquad n = 0, 1, 2, \ldots$$

$$\psi_n(r) = N_n\, e^{-\alpha r^2/2}\, H_n(\sqrt{\alpha}\, r)$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

Harmonic oscillator model gives us energies when you solve the Schrodinger equation h psi of r is equal to E psi n E n psi n of r. And, the energies are given as you know from h nu times n plus half. And, the vibrational wave functions – psi n of r are given by the Gaussian and the Hermite polynomial with a normalization constant – e to the minus alpha r square by 2 times H n square root of alpha times r. So, this r is the actual displacement away from the equilibrium. It is actually v r minus r e; that I have written down. This is the vibrational displacement.

And, what is alpha? Alpha is square root of k mu by h bar square that you have been told earlier in one of the lectures. So, these are the vibrational wave functions – psi n r. And, these are the vibrational energies quantized with n equal to 0, n equal to 1, 2, 3, etcetera as the possible energy levels, and therefore when you write this in the harmonic oscillator, potential energy model.

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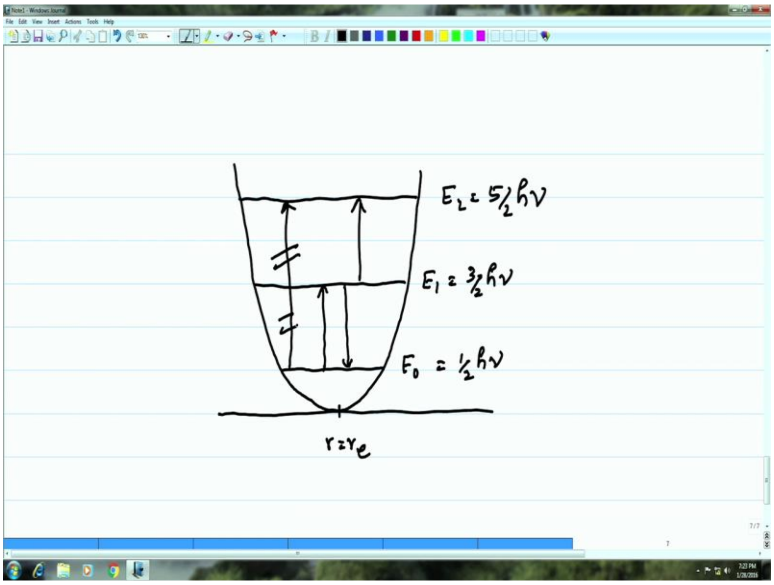

And, if you write the r is equal to r e as this point r is equal to r e; the potential is minimum at this point. Therefore, if you write the harmonic oscillator, potential energy with the parabolic form; if you do that, then the energy levels are E 0, which is half h nu. And then, you have E 1, which is 3 half h nu.

And then, you have E 2, which is 5 halves h nu and so on. In the harmonic oscillator model that we have, the vibrational transitions that we can see or only transitions corresponding to the nearby energy levels, you will not be able see a transition from 0 to 2 in the harmonic oscillator model; this is not allowed; this is not seen. The reason for that is the fact that, the dipole moment is a function – is a linear function of the displacement or itself. And, it is the electric dipole moment, which interacts with the electric field.

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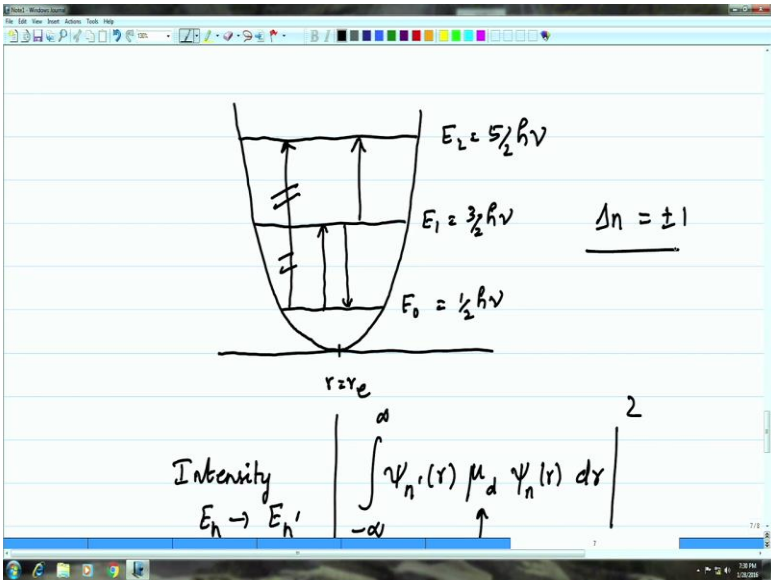

$$\Delta n = \pm 1$$

$$\text{Intensity } E_n \rightarrow E_{n'} \quad \left| \int_{-\infty}^{\infty} \psi_{n'}(r)\, \mu_d\, \psi_n(r)\, dr \right|^2$$

And therefore, the intensity is given by the quantity the integral of the wave function; intensity of transition from says E n to E n prime. If we mark two different energy levels, then the integral corresponding to this form minus infinity to plus infinity psi n prime of r mu of d, that is a dipole moment psi n of r d r all the way from minus infinity to plus infinity. The absolute square of this is proportional to the intensity. And, here you have mu d. The mu d is a delta plus or minus, whatever the charge is – times the inter nuclear distance r.

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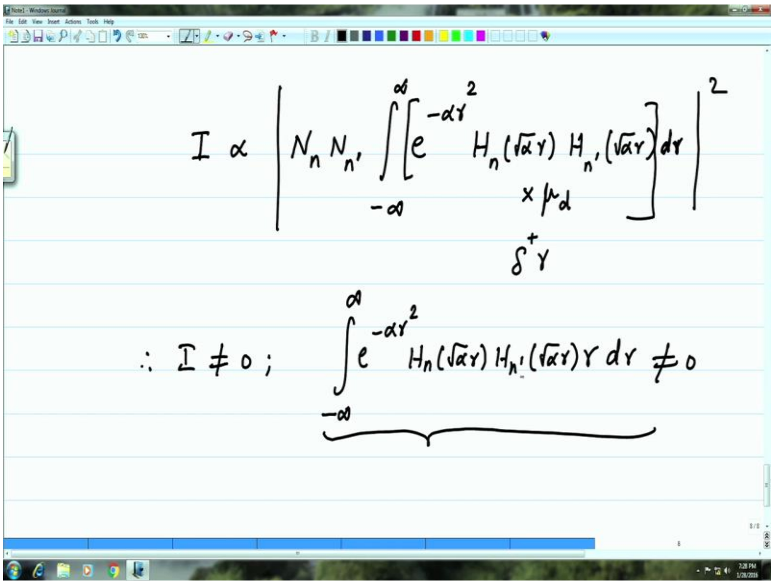

$$I \propto \left| N_n N_{n'} \int_{-\infty}^{\infty} \left[e^{-\alpha r^2} H_n(\sqrt{\alpha} r)\, H_{n'}(\sqrt{\alpha} r) \times \mu_d \right] dr \right|^2$$

$$\delta^+ r$$

$$\therefore I \neq 0; \quad \underbrace{\int_{-\infty}^{\infty} e^{-\alpha r^2} H_n(\sqrt{\alpha} r)\, H_{n'}(\sqrt{\alpha} r)\, r\, dr \neq 0}$$

And therefore, you see that, this wave function integral that you get for the intensity is proportional to the absolute square of the normalization constants that you have here. We have to do it again; intensity is proportional to the normalization constant N n N n prime integral from minus infinity to plus infinity e to the minus alpha r square H n root alpha of r H n prime root alpha of r d r; and, the absolute square of this integral times mu d. Whole of this is integrated with respect to d r. Now, mu d is delta plus times r. Therefore, for I to be nonzero, this integral namely, the integral e to the minus alpha r square H n root alpha r H n prime root alpha r r dr from minus infinity to plus infinity. This integral should be finite – should be greater than 0.

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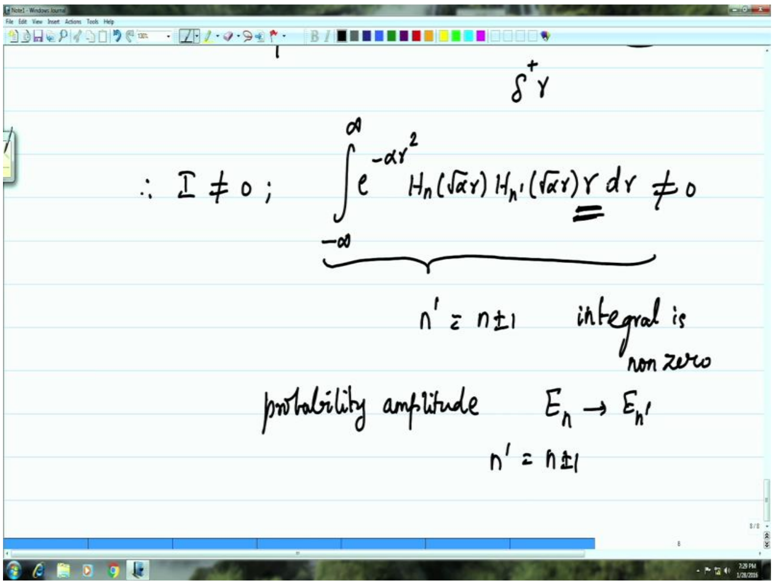

$\delta^{+} r$

$$\therefore\ I \neq 0 ; \quad \underbrace{\int_{-\infty}^{\infty} e^{-\alpha r^2} H_n(\sqrt{\alpha} r)\, H_{n'}(\sqrt{\alpha} r)\, \underline{\underline{r}}\, dr}_{n' = n \pm 1 \quad \text{integral is non zero}} \neq 0$$

probability amplitude $E_n \to E_{n'}$

$n' = n \pm 1$

Therefore, calculation of this integral tells you that, if n and n prime are near to each other; they are adjacent to each other; namely if n prime is n plus or minus 1, this integral is nonzero. This is called the probability amplitude for transition between the level E n to E n prime. And, this particular integral is nonzero only when n prime is n plus or minus 1, because of the fact that, it is the dipole moment which is proportional to the bond length; the linear displacement connects Hermite polynomials of any n with only the Hermite polynomial next to it – n plus or minus 1.

Therefore, this tells you that, the vibrational selection rule is precisely what we have here namely, delta n is always plus or minus 1; plus 1 is absorption, minus 1 is emission. That is when the radiation is emitted for molecules sitting from a higher energy level jumping to a lower energy level. Of course, you get the addition – the radiation emitted. Therefore, it is absorption or emission. But, the point is selection rule is the change in the quantum number is plus or minus 1.

Now, in this, the remaining lecture, we shall just do a small calculation with some numbers and then continue with the molecular system for slightly anharmonic potential energies.

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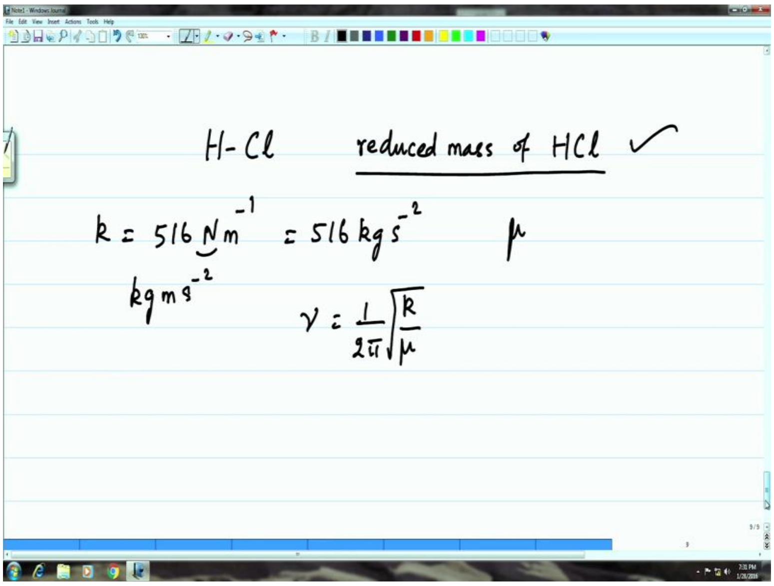

H-Cl   reduced mass of HCl ✓

$k = 516 \underbrace{N}_{kg\,m\,s^{-2}} m^{-1} = 516\, kg\, s^{-2}$ μ

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

So, let us consider a simple example of say HCl. Some data are known to us namely, the mass of the reduced mass of HCl we know. If we are given the force constant k as, 516 Newton per meter; please remember – newton is kilogram meter per second square. Therefore, newton meter is the same as 516 kilogram per second square. If we are given this, we also know how to calculate mu from the atomic masses of hydrogen and chlorine. Therefore, we can calculate the harmonic oscillator frequency as 1 by 2 pi – pi – square root of k over mu – the reduced mass.

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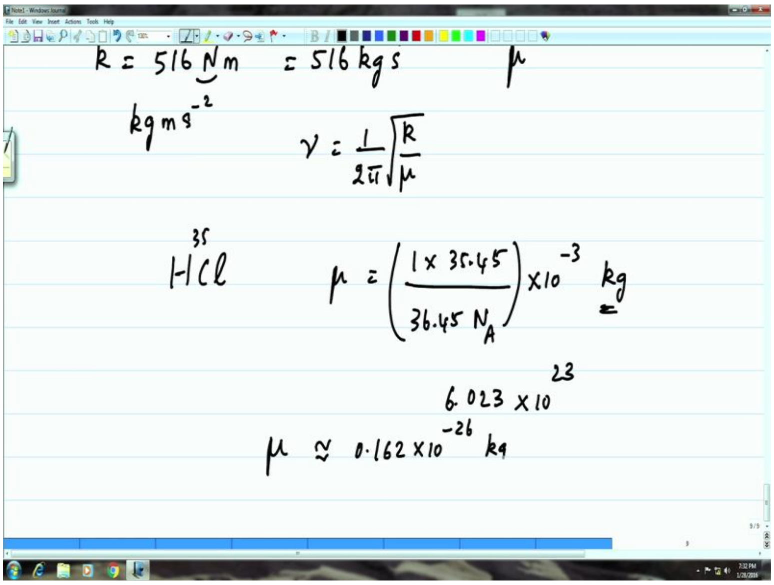

$k = 516\ \underbrace{N}\,m \quad = 516\ kg\,s \qquad \mu$

$kg\,m\,s^{-2}$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$H\,^{35}Cl$

$$\mu = \left(\frac{1 \times 35.45}{36.45\ N_A}\right) \times 10^{-3}\ \underline{kg}$$

6.023×10^{23}

$$\mu \simeq 0.162 \times 10^{-26}\ kg$$

In a simple experiment, for us into calculation, you assume 35.45 for the atomic mass. So, we will call it as the chlorine 35 isotope and H is 1. Therefore, you are talking about the reduced mass as one times 35.45 divided by m 1 plus m 2, which is 36.45. Of course, the masses are to be divided by the Avogadro number in order to get the atomic mass. And so, if you divide this by Avogadro number square and you have Avogadro number, therefore, you will get N A; and, this is in gram units.

Therefore, you multiply by 10 raised to minus 3 to get you kilograms, so that we use the SI units. And, N A is 6.03 into 10 raised to 23. So, with this number, it is easy to calculate that, the reduced mass is approximately 0.162 times 10 to the minus 26 kilograms. The force constant is 516.

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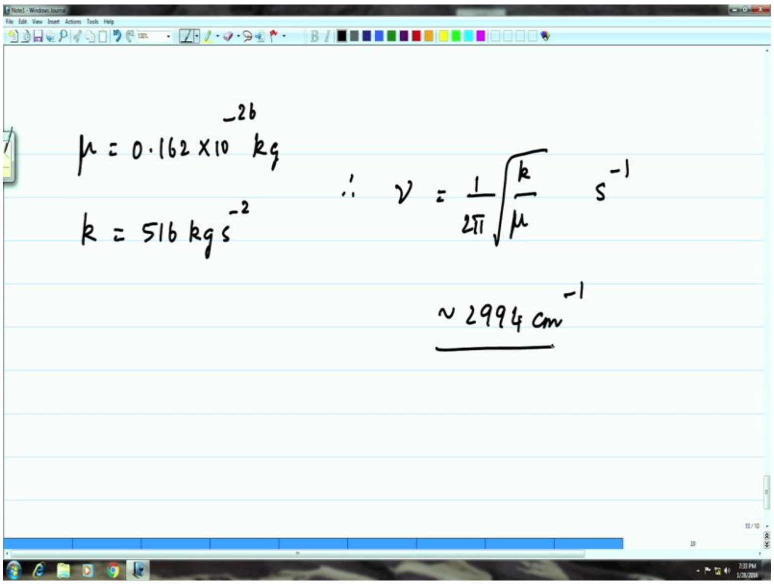

$\mu = 0.162 \times 10^{-26}$ kg

$k = 516$ kg s^{-2}

$\therefore \ \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \ s^{-1}$

$\underline{\sim 2994 \text{ cm}^{-1}}$

So, let me write mu here as 0.162 times 10 to the minus 26 kg. And, the force constant is 516 kilogram per second square. Therefore, you know immediately the frequency nu, which is 1 by 2 pi times square root of k by mu is per second, because the kilograms cancel out and the per second square becomes per second under the square root. Therefore, what the number do you get? You get approximately 2 9 9 4 centimeter inverse. You can do it very accurately, but I am just telling you how to do the simple calculations. This is the fundamental frequency for the hydrogen chloride molecule under the harmonic oscillator approximation.

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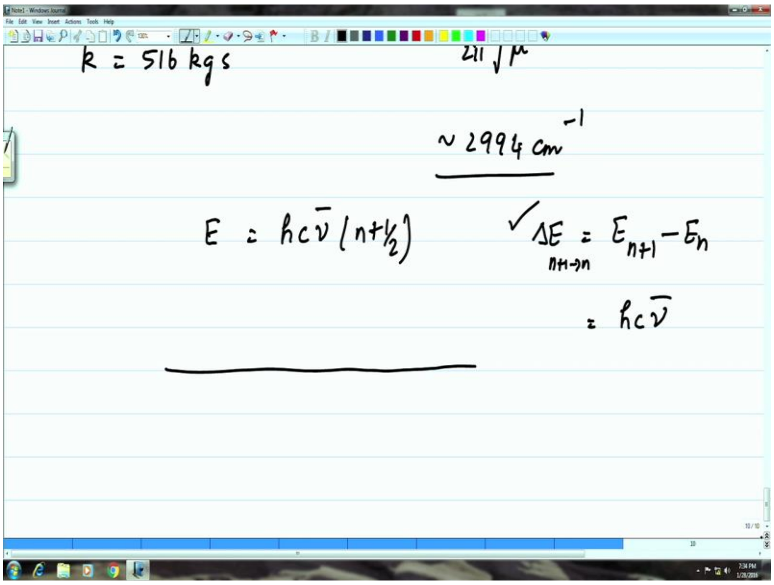

$k = 516$ kg s

$2\pi \sqrt{\mu}$

$\underline{\sim 2994 \text{ cm}^{-1}}$

$E = hc\bar{\nu}(n+\frac{1}{2})$

$\checkmark \ \Delta E_{n+1 \to n} = E_{n+1} - E_n$

$= hc\bar{\nu}$

And therefore, it is easy for you to calculate the energies E as h c nu bar because this is in wave numbers and you know that this is n plus half. So, you can calculate the delta E as nothing other than E n plus 1 to E n – nearest level – n plus 1 to n. If you look at it, then this is h c nu bar. And so, the nu bar is known. Therefore, we know the frequency of the transition energies.

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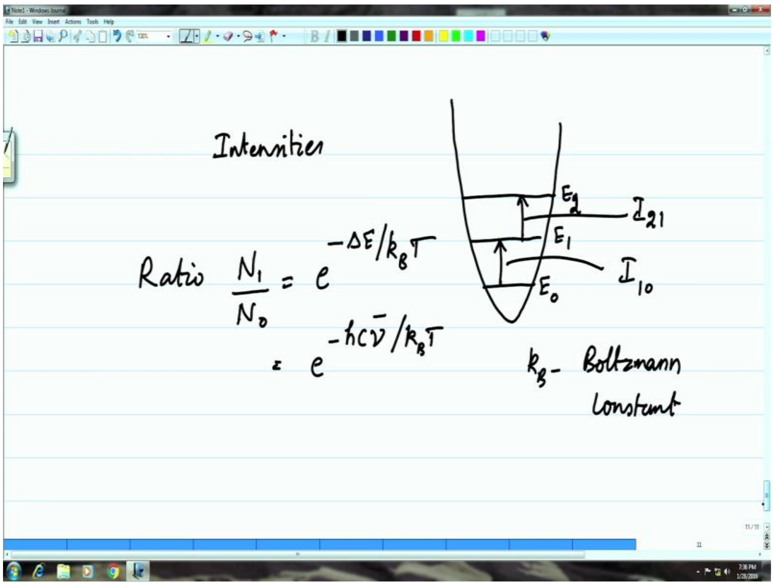

Intensities

$$\text{Ratio } \frac{N_1}{N_0} = e^{-\Delta E/k_B T}$$

$$= e^{-hc\bar{\nu}/k_B T}$$

k_B - Boltzmann Constant

And, another important quantity that we have to calculate before we close this part of the lecture is the intensities or relatively smaller as you go from an energy level, for example, E 1 – E 0 to E 1, if you calculate that. And, E 1 to E 2, if you calculate this; suppose you call this as E 0, E 1 and E 2. And, this intensity is I 1 0; this is E 2. And, this intensity you call it as I 2 1. Then, what is the ratio of what is the ratio of these intensities? That is approximately proportional to the number of molecules, which are here; which will jump up to the second level versus the number of molecules, which are here.

Therefore, you have to also calculate the ratio N 1 by N 0 in order to understand that, the intensities of the energy level transitions that you see are also progressively weaker as we go from the zero energy level to the first level energy level or first to second or second to third and so on. This ratio in this case of a simple diatomic molecule is given by the very elementary, that is, quantity known as the Maxwell-Boltzmann distribution.

So, you have minus delta E by k B T. And, the delta E is of course, h c nu bar at the temperature T. And, k B is the Boltzmann constant.

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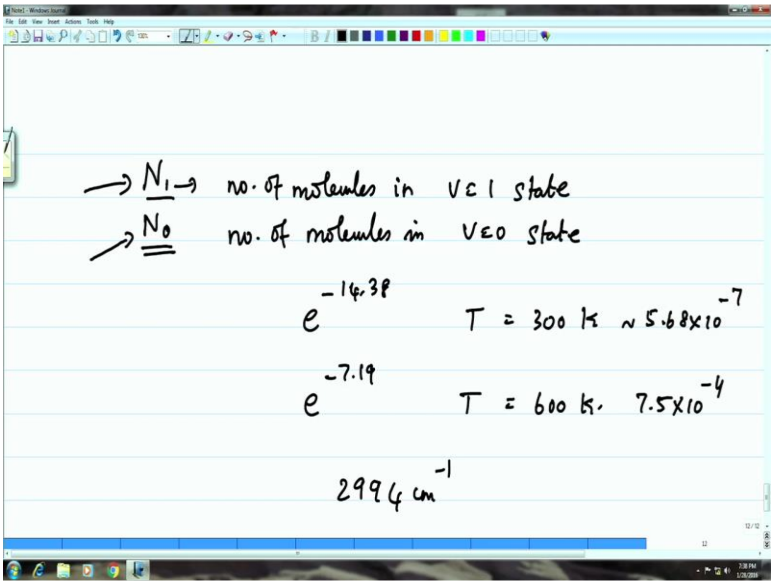

$\rightarrow \underline{N_1} \rightarrow$ no. of molecules in v = 1 state

$\rightarrow \underline{\underline{N_0}}$ no. of molecules in v = 0 state

$e^{-14.38}$ T = 300 K $\sim 5.68\times10^{-7}$

$e^{-7.19}$ T = 600 K. 7.5×10^{-4}

2994 cm^{-1}

So, if you have to calculate these values, the N 1 by N 0, the number of molecules in the first excited states in v is equal to 1 state versus the number of molecules in the ground state in v is equal to 0 state. If you calculate that, the number turns out to be approximately e to the minus 14.38 for T is equal to 300 kelvin; and, it is e to the minus 7.19 for T is equal to 600 kelvin; so, very small number. This is about 7.5 times 10 raised to minus 4. And, this number is about 5.68 times 10 to the minus 7.

Therefore, you see there is very little population in the first excited state compared to molecular population in the ground state. Therefore, for a molecule such as HCl for whom the vibrational frequency is reasonably large, please remember – it is 2994 centimeter from elementary calculation. That is a large vibrational frequency for such a molecule. Most molecules are in the ground state and fewer in the first excited state, and even less in the second. But, the molecule does not have a vibrational spectrum, it has only one line; because all intensities that you talk about from 0 to 1 or 1 to 2 or 2 to 3 – all these intensities happen at the same energy.

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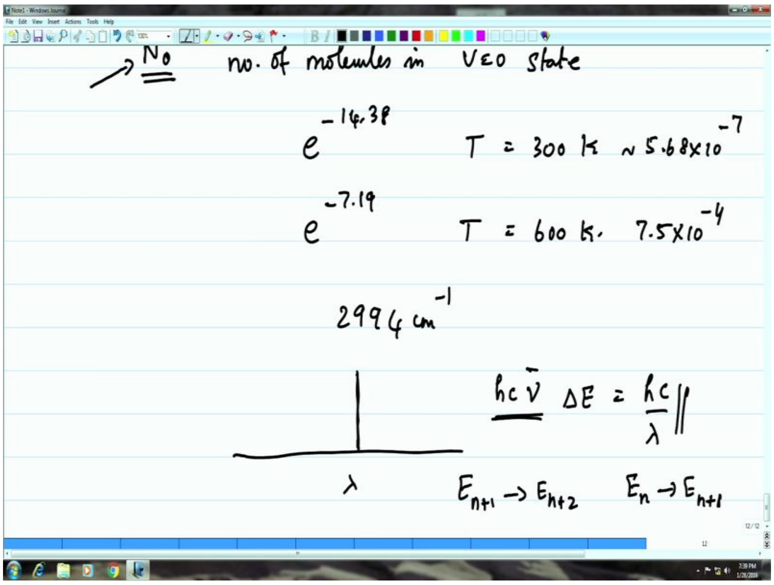

$\underline{\underline{N_0}}$ no. of molecules in $v = 0$ state

$e^{-14.38}$ $T = 300\ K$ $\sim 5.68 \times 10^{-7}$

$e^{-7.19}$ $T = 600\ K.$ 7.5×10^{-4}

$2994\ cm^{-1}$

$\underline{hc\bar{\nu}}$ $\Delta E = \frac{hc}{\lambda} \|$

λ

$E_{n+1} \rightarrow E_{n+2}$ $E_n \rightarrow E_{n+1}$

So, if you plot the spectrum as a function of lambda, please remember – the energy at which the transition appears is h c nu bar or lambda given by – you can write that. So, if you write this as h c by lambda; if the energy of the transition E is given; it is h c by lambda. It is a same thing whether E – the delta E that you talk about is from n plus 1 to n plus 2 or n to n plus 1.

All these vibrational transitions; all of them happen at the same energy of absorption corresponding to the wavelength lambda given by this h c nu bar or h c by lambda; therefore, these is no spectrum for a diatomic molecule in the harmonic oscillator approximation. So, how do we correct for this? This is not what you see.

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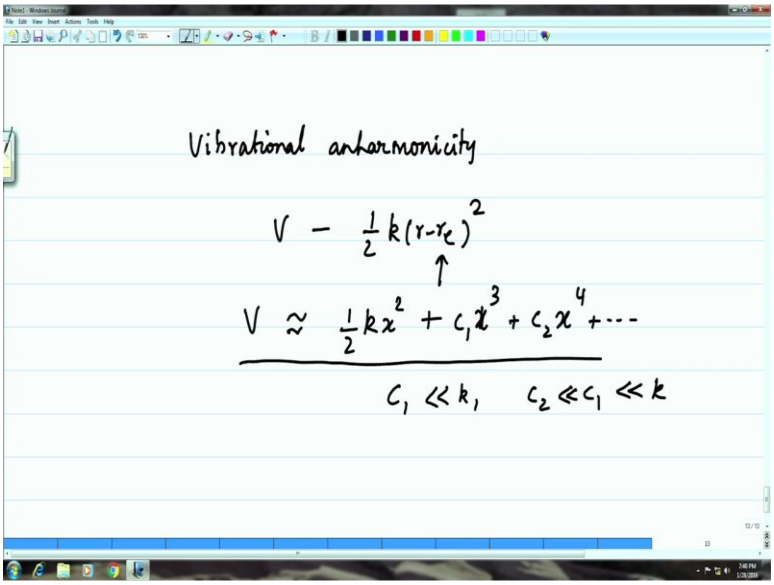

Vibrational anharmonicity

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

$$\uparrow$$

$$\underline{V \approx \frac{1}{2}kx^2 + c_1 x^3 + c_2 x^4 + \cdots}$$

$$c_1 \ll k, \quad c_2 \ll c_1 \ll k$$

When you see even diatomic molecules at room temperature, you may see more than one line. And, how do you correct for that? That we will consider in the next lecture by way of considering what are called the vibrational anharmonicity; that is, the vibrational motion is not given by half k r minus r e square from displacement from equilibrium, but it is actually given. Suppose we call this as x square half k x square; then, anharmonic motion essentially means that the potential energy v is approximately given by contributions, which are other than the squares. So, you can call it as c 1 x cube c 2 x to the power 4 and so on.

And, of course, we hope that, c 1 is much less than k; c 2 is much less than c 1; and therefore, much less than k and so on in order for us to approximately calculate the vibrational frequencies and vibrational energies. When you use such an anharmonic oscillator model different from the Hooke’s law, which led to the harmonic oscillator model; you will see that, the energy levels are not equidistant; they are not h nu into n plus half. But, the energy levels are not of – they – they differ by different bounds when you go from 1 to 2, 2 to 3 and so on. Therefore, it is possible for you to see vibrational satellites as you call them the satellites are essentially translationary; the transitions from the higher energies say b is equal to – n equal to 1 to n equal to 2 or n equal 2 to n equal to 3 and so on. Such transitions you can see them only as a result of vibrational anharmonicity.

And, vibrational anharmonicity can be modeled by many different processes. We will see one important vibrational unharmonic model called the Morse oscillator in the next part of this lecture.

Until then, thank you very much.