Chemistry 1

Introduction to Quantum Chemistry
And Molecular Spectroscopy

Lecture 32

Diatomic Vibrational Spectra

Harmonic Model

Prof. Mangala Sunder Krishnan,

Department of Chemistry,

India Institute of Technology Madras

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 . Here we shall

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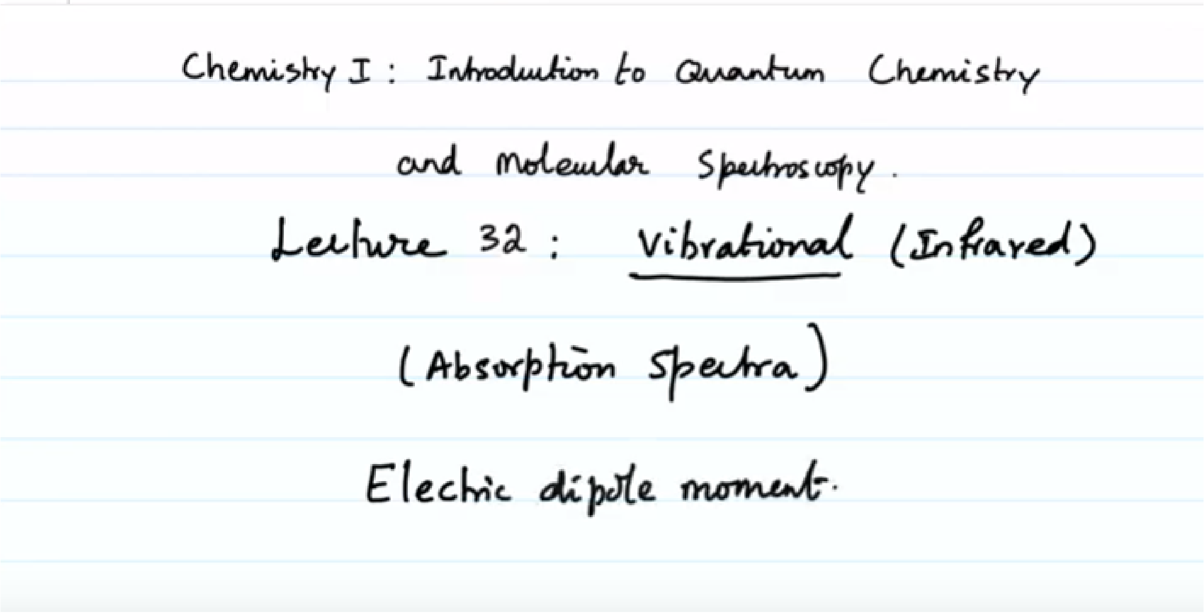

Chemistry I : Introduction to Quantum Chemistry
and Molecular Spectroscopy.
Lecture 32 : Vibrational (Infrared)
(Absorption Spectra)
Electric dipole moment.

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 electrical dipole moment. We shall start with a diatomic molecular system and then it is easier for us to understand dipole moment, as very simple concept coming as a result of the separation of the positive charge centre of the molecule, with the negative charge centre and in the case of diatomic molecule, we associate the atoms with

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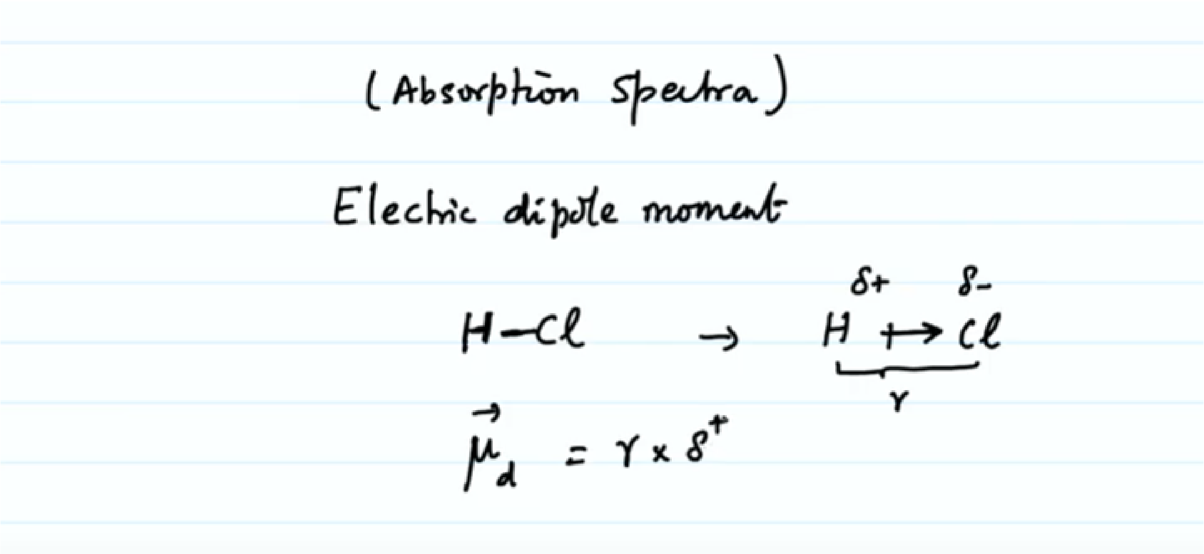

(Absorption Spectra)

Electric dipole moment

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

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

certain partial charges like in the case of HCL ,e bond distance and the fact that the hydrogen and chlorine have electro negativity 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 or so the µD 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 centre 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 diamtomic molecule, the oscillation of the atoms, about the equilibrium, positions of the atoms, results in the dipole moment, oscillating in values. For example

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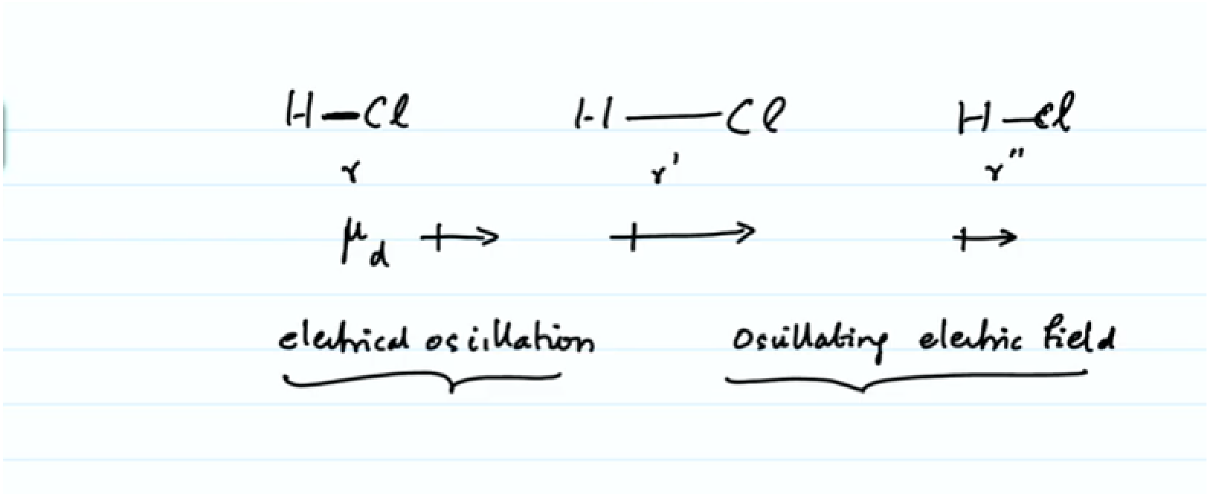

$H-Cl$ $\quad$ $H——Cl$ $\quad$ $H-Cl$

r $\quad$ r' $\quad$ r''

$\mu_d \mapsto \quad \longmapsto \quad \mapsto$

$\underbrace{\text{electrical oscillation}}$ $\quad$ $\underbrace{\text{Oscillating electric field}}$

if you think about HCl, undergoing molecular vibrations, to give a slightly larger distance and a shorter distance it is Cl and if you do that then the R, here it is R prime and some other value the dipole moment µ D, changes it oscillates from a small value, to a slightly larger value and back to a small value. This is an electric change oscillation, electrical oscillation and the electromagnetic field with the oscillating component, of the electric feild. If these oscillations are in resonance, then there is 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 process of spectroscopy become active and it is due to the fact that the electrical dipole moment

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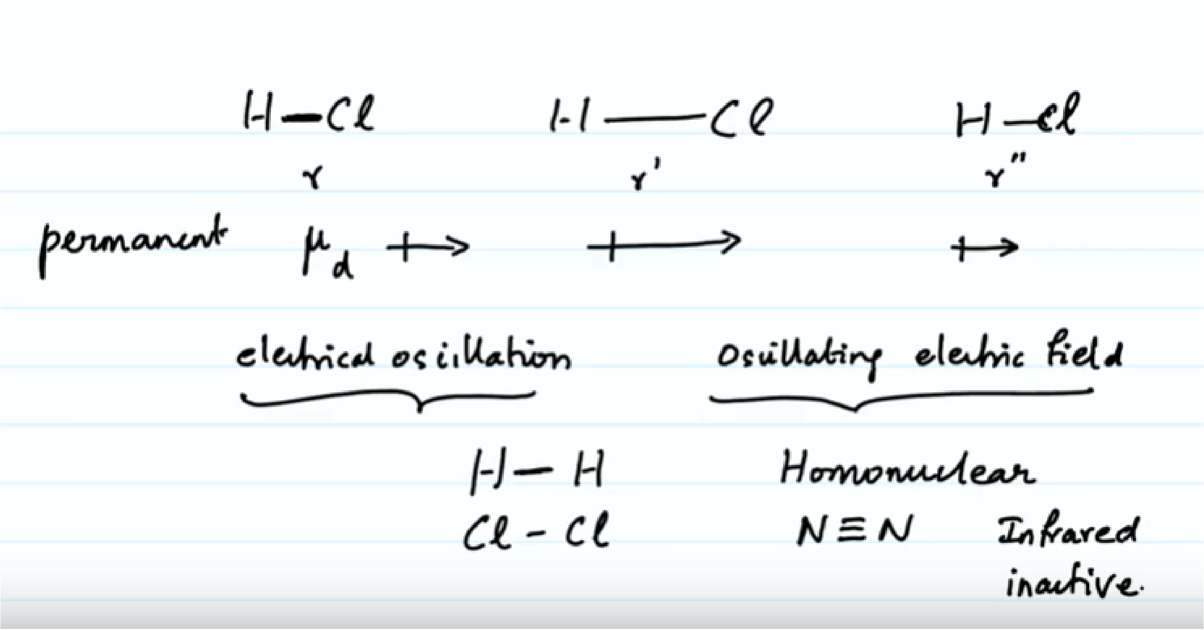

H—Cl H——Cl H—Cl

r r' r''

permanent μ_d +→ +——→ +→

electrical oscillation Oscillating electric field

H—H Homonuclear

Cl - Cl N≡N Infrared inactive.

the permanent electrical dipole moment, that is present in the molecule, interacts with the oscillating electric field of the electromagnetic radiation. So this is a fundamental requirement for the infrared intensity, to be measured. If a molecule such as hydrogen, where both the atoms are identical, that is homo nuclear diatomic molecules, do not show IR spectrum, do not reveal the 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, homo nuclear diatomic molecules like, that or N triple bond N. What about 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 it is one point and therefore there is no moment associated with that the first moment, there is 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. Polyatomoic molecules, that 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. But in the case of a diatomic molecule the vibrational motion, is one degree of freedom motion given the fact that

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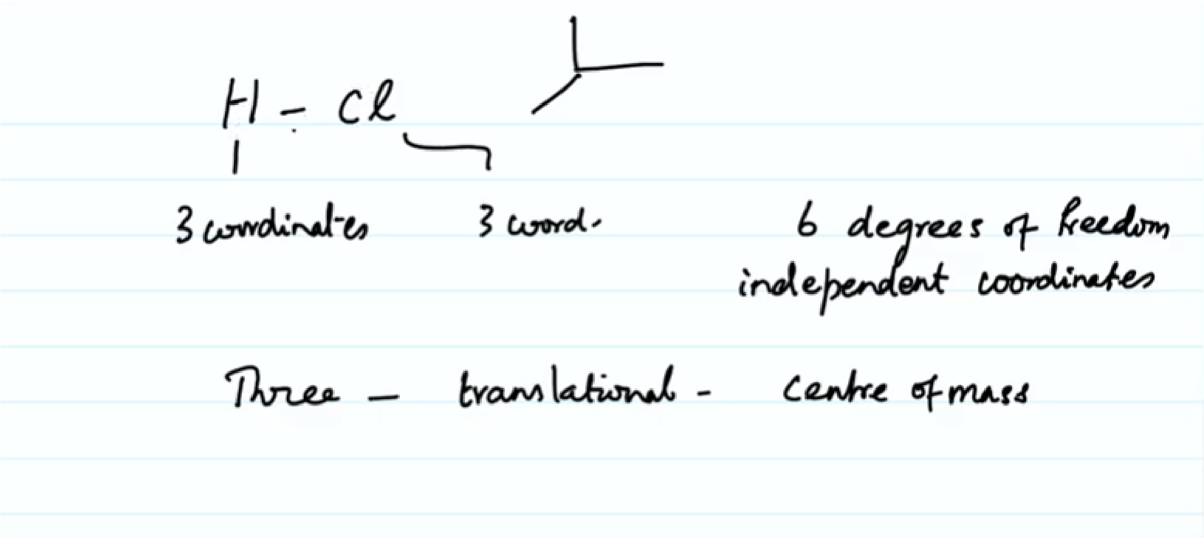

H - Cl

3 coordinates   3 coord.   6 degrees of freedom
independent coordinates

Three — translational - centre of mass

if you have again HCl, hydrogen has three coordinates, in any space, in any axis system. Hydrogen atom has three coordinates, that is three degrees of freedom, linear degrees and Chlorine has another three coordinates. Therefore the molecules has six degrees of freedom or 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 centre of mass. The centre 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 transitional 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 this molecule also rotates about two independent axis

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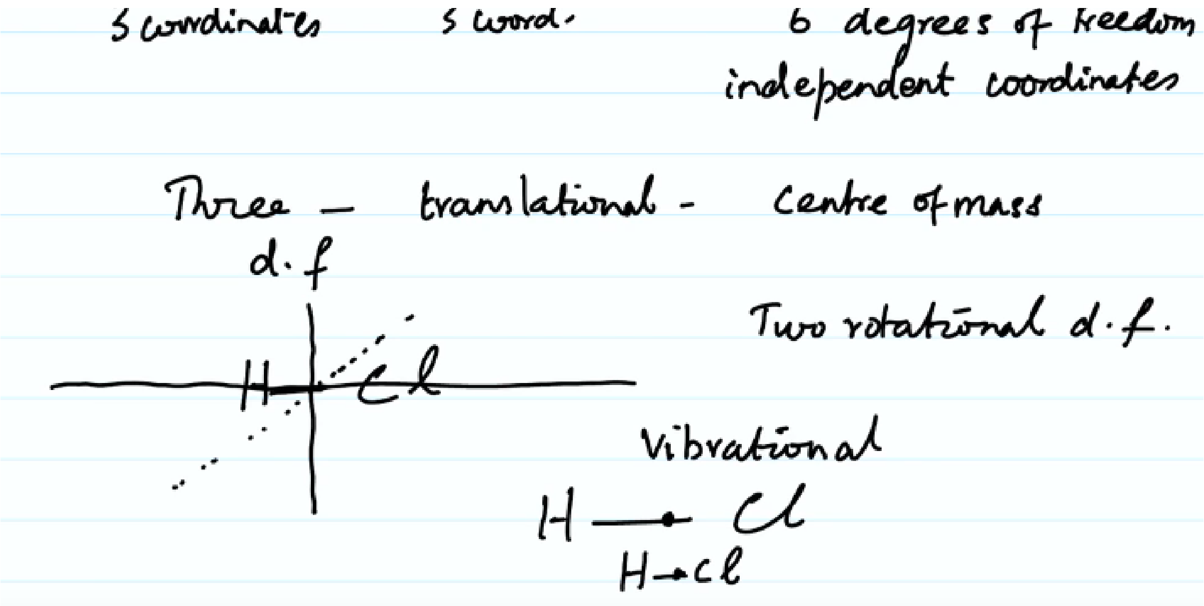

3 coordinates   3 coord.   6 degrees of freedom
independent coordinates

Three — translational - centre of mass
d.f

Two rotational d.f.

Vibrational

H — Cl

H→Cl

the axis that is passing through the centre of mass and an axis perpendicular to the centre of mass. Above these two axis 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 DMI as RI squared, hydrogen and chlorine both contribute to that, therefore the molecule has the moment of the 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 the molecular motion. About the axis system, there are only two rotational degrees of freedom and therefore of the six coordinated are independent degrees of freedom three our translational, two are rotational and there is only one more, which is the vibrational degree of freedom and that is the relative motion of the Hydrogen Chlorine, with respect to the centre of mass which is not moving, because centre mass motion has already been taken out, into the translational part. Therefore if you have that, the vibrational motion would be the centre-of –mass does not move. So this is a genuine vibration and there is only one vibrational degree of freedom. What is the process of measurement and what is the

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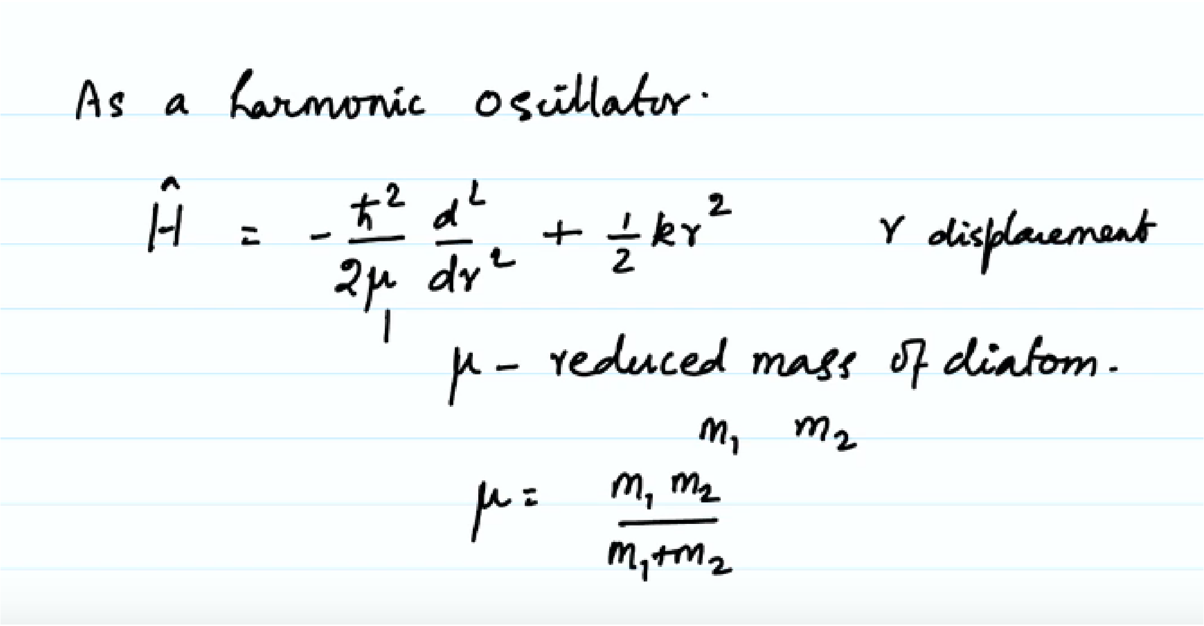

As a harmonic oscillator·

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

r displacement

μ - reduced mass of diatom.

$m_1 \quad m_2$

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

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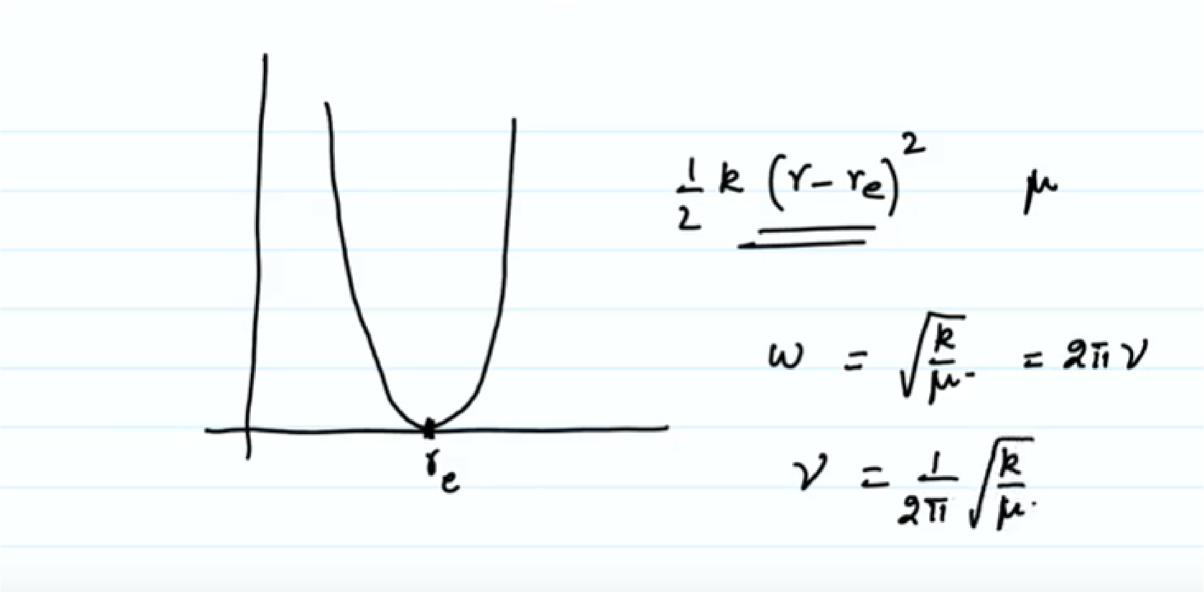

process of understanding the vibrational motion in the elementary form, as a harmonic oscillator. The of course we started with a little bit of an introductory harmonic oscillator, in an earlier lecture, remember that the Hamiltonian for the harmonic oscillator, is the kinetic energy term minus H bar square by 2 μ d square by D R squared her μ, is the reduced mass of the diatomic molecule and so if you have em 1 and em 2, then μ is m 1 plus m 2, by m1 plus m2. This is a kinetic energy and the potential energy for the harmonic oscillator comes from the Hookes law and it is expressed in terms of the force constants K or square, where R is the displacement from equilibrium. Because at equilibrium, we assume that the potential energy is a minimum 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 re and any displacement from the equilibrium, will result in the force and therefore a potential energy ½ KR minus re squared which contributes to the vibrational energy and what you have is of course the vibrational frequency associated with such motion, for a diatomic molecule, with the reduced mass, is the angular frequency if you write it, or make up is square root of K by μ.

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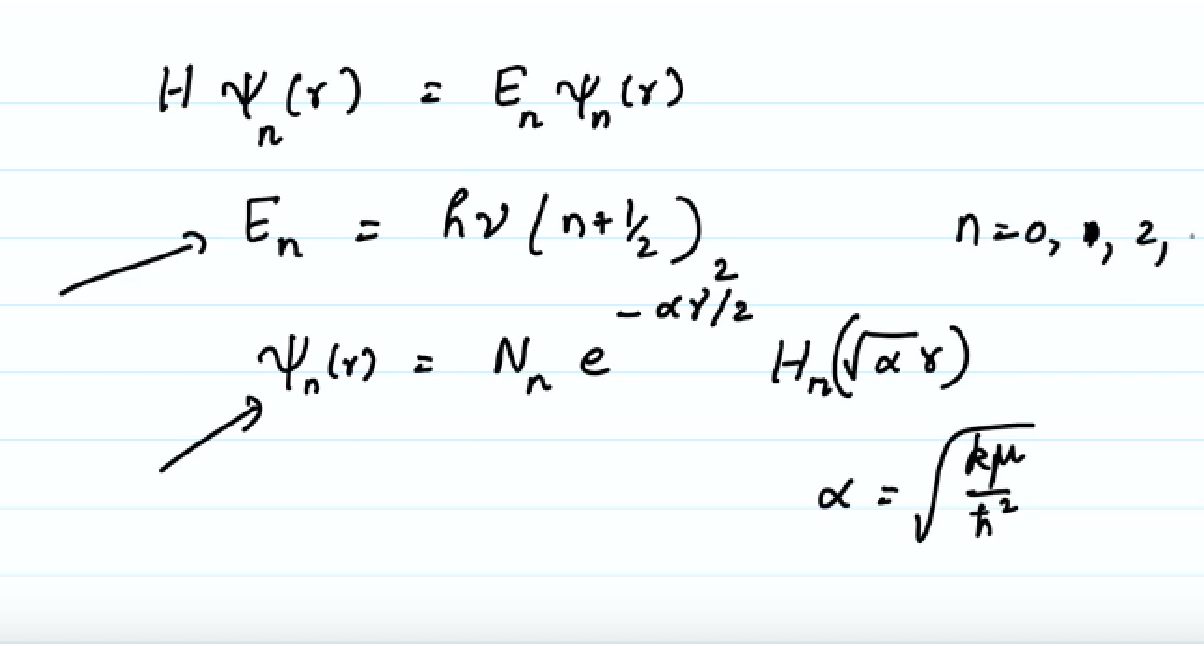

$$H\psi_n(r) = E_n\psi_n(r)$$

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

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

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

The angular frequency is expressed terms of the normal experimental frequency, that we measure 2 p nu and for the natural frequency for a harmonic oscillator is 1 by 2 pi square root of K by µ. Harmonic oscillator model gives us energies when you solve the Schrodnger equation. H sine of r is equal to e sy en en sy n of R and the energies are given as you know from H nu times n plus ½ and the vibrational wave functions sy en of r are given by the Gaussian and they have made polynomials with the 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 the R minus re that I have written down. This is the vibrational displacement and what is alpha? Alpha is square root of K µ by H bar square that you have been told earlier in one of the lectures. So these are the vibrational wave functions sine of r and these are the vibrational energies, quantized with n equal to 0, n equal to 1 2 3 etc., as the possible energy levels and therefore when you write this in the harmonic oscillator, potential energy model.

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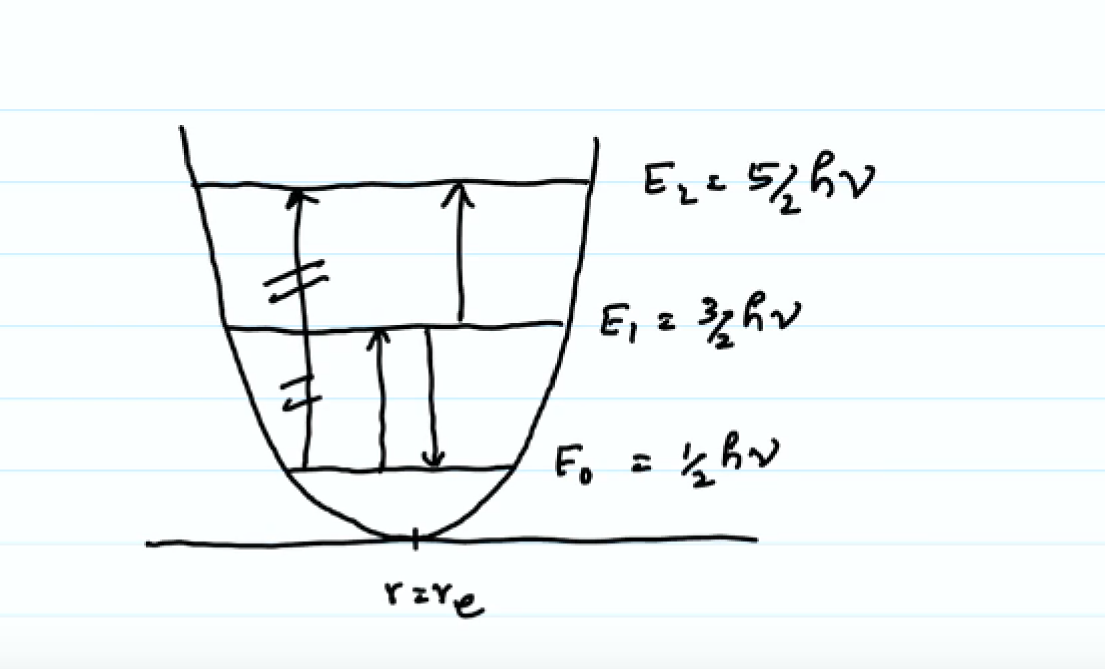

And if you write the r is equal to re, as this point r is equal to re, the potential is minimum at this point. Therefore if you write the harmonic oscillator potential energy with the parabolic form, if you do that, then the energy levels are e zero, which is half hu and then you have E1 which is 3 halves H nu and then you have E2, which is 5 halves hu and so on. In the harmonic oscillator model that we have, the vibrational transitions that we can see, are only transitions corresponding to the nearby energy levels. You will not be able to see a transition from 0 to 2 in the harmonic oscillator model this is not allowed, this is not seen.

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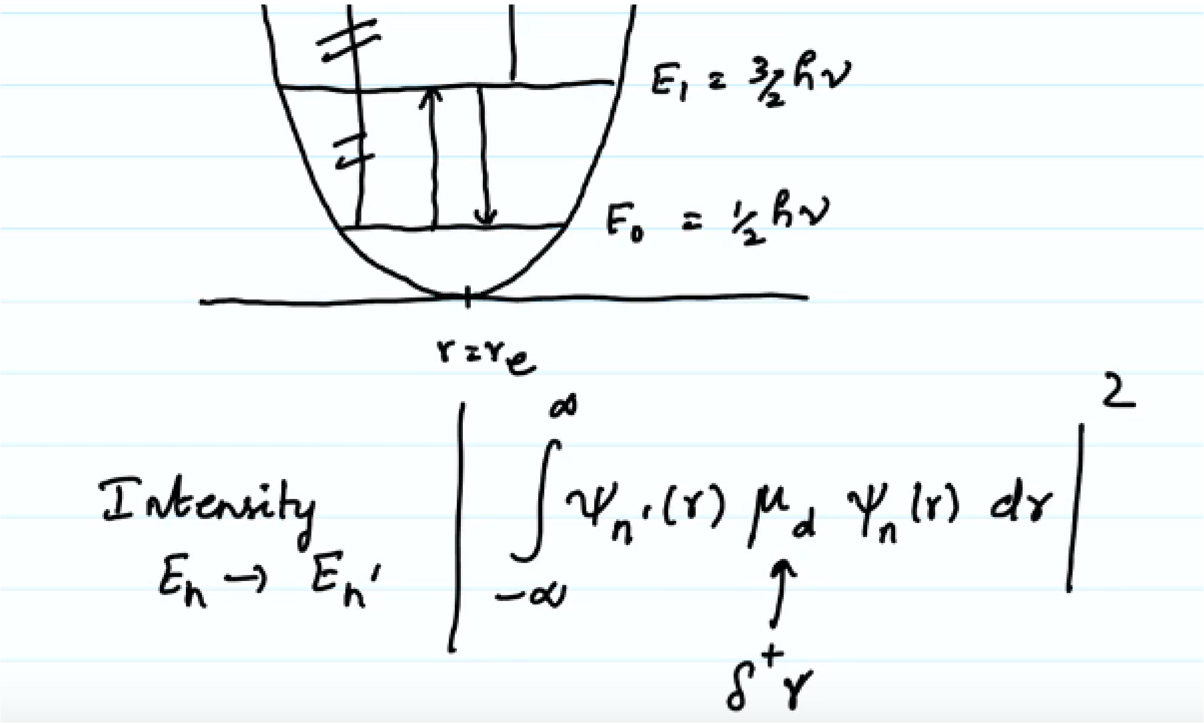

$$\text{Intensity} \quad E_n \rightarrow E_{n'} \quad \left| \int_{-\infty}^{\infty} \psi_{n'}(r)\, \underset{\substack{\uparrow \\ \delta^+ r}}{\mu_d}\, \psi_n(r)\, dr \right|^2$$

The reason for that, is the fact that the dipole moment is a function, is a linear function, of the displacement part itself and it is the electric dipole moment which interacts with the electric field and therefore the intensity is given by the quantity, the integral of the wave function intensity of transition from say En to En prime, ¥n if we mark two different energy levels then the integral corresponding to this form minus infinity ¥n prime of r µ of D that is a dipole moment, ¥n of r dr all the way from minus infinity to the plus infinity. The absolute square of this is proportional to the intensity and here you have µ D µ. D is a delta plus or minus whatever the charges times the inter nuclear distance are and therefore you see that this wave function intergral that you get for the

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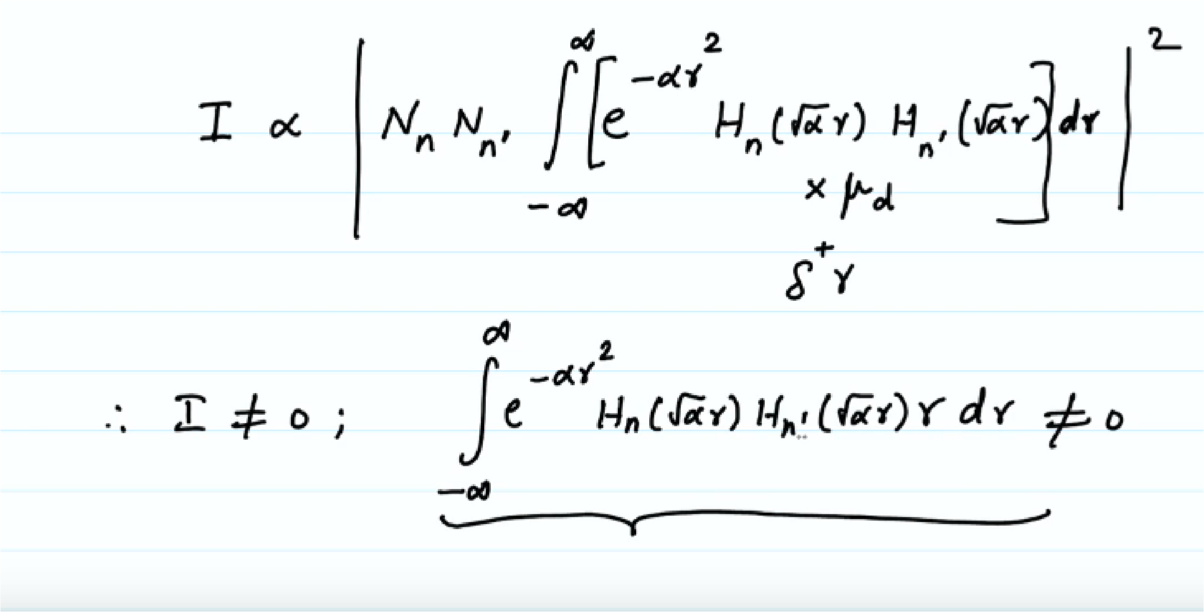

$$I \propto \left| N_n N_{n'} \int_{-\infty}^{\infty} \left[e^{-\alpha r^2} H_n(\sqrt{\alpha} r)\, H_{n'}(\sqrt{\alpha} r) \times \underset{\delta^{+} r}{\mu_d} \right] dr \right|^2$$

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

intensity is proportional to the absolute square of the normalization constants that you have here, sorry to do it again. The intensity is proportional to the normalization constant Nn Nn prime integral from minus infinity to plus infinity e to the minus alpha R square H n root alpha of all H n prime root alpha of r, dr and the absolute square of this integral times µ d. all of this is integrated with respect to D r. Now µD is delta plus times r, therefore for I to be Non zero this integral namely the integral E to the minus alpha r square H n root alpha or H nprime root alpha or r D r from minus infinity to plus infinity.

This integral should be finite, should be greater than 0,

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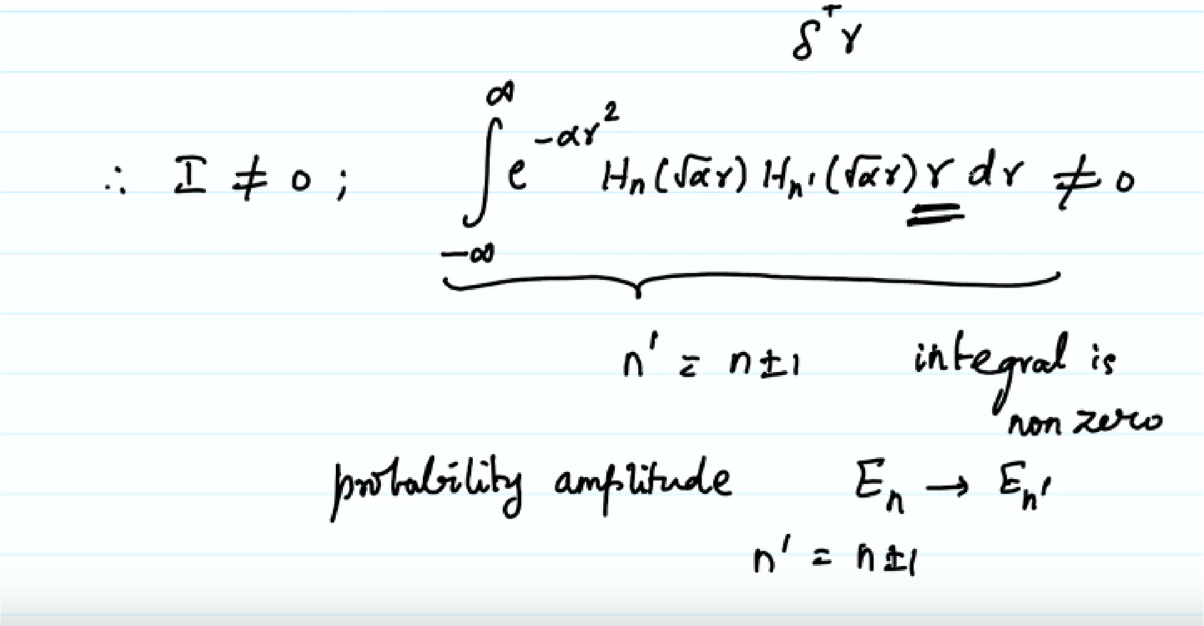

$\delta^+ r$

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

integral is non zero

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 the n prime is n plus or minus 1, this integral is nonzero. This is called the probability amplitude for transition between the level En to En prime and this particular integral is non zero Only when En prime is in plus or minus 1 because of the fact that it is the dipole moment. Dipole moment which is proportional to the bond length the linear displacement connects hermit polynomials of any n with only the hermit polynomial next to it and plus or minus 1.

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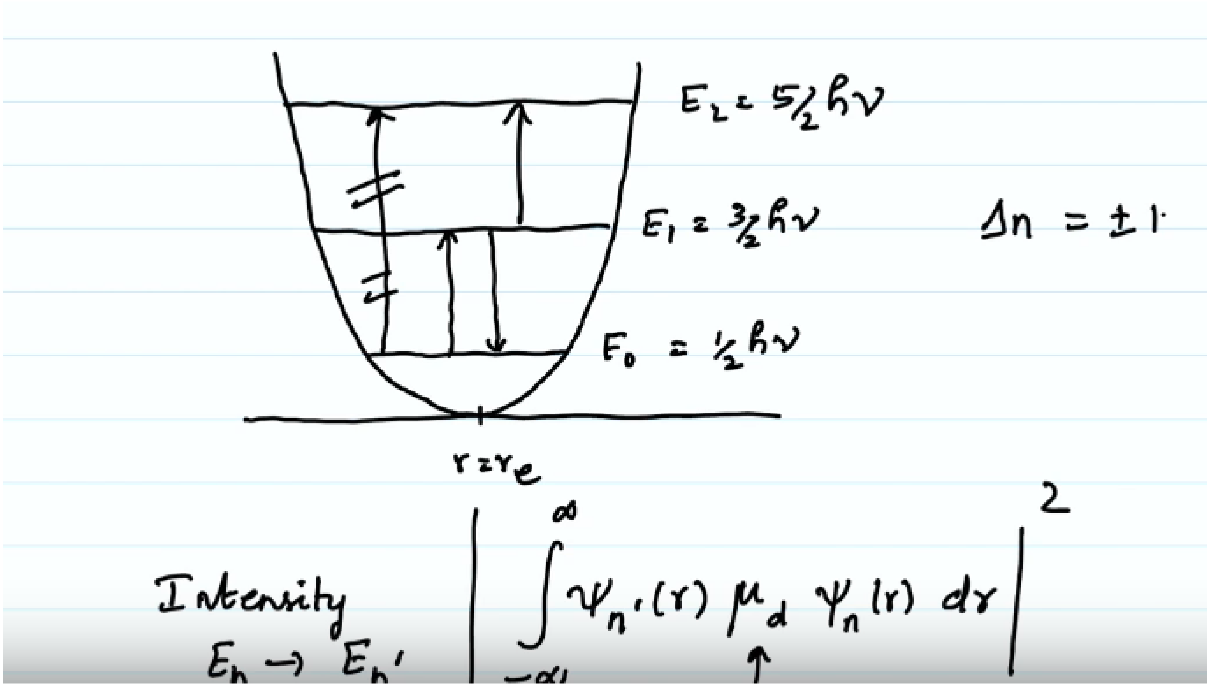

$\Delta n = \pm 1$

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

Therefore this tells you that the vibrational selection role is precisely what we have here namely delta En is always plus or minus, 1 plus 1 is absorption minus 1 is the 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. know 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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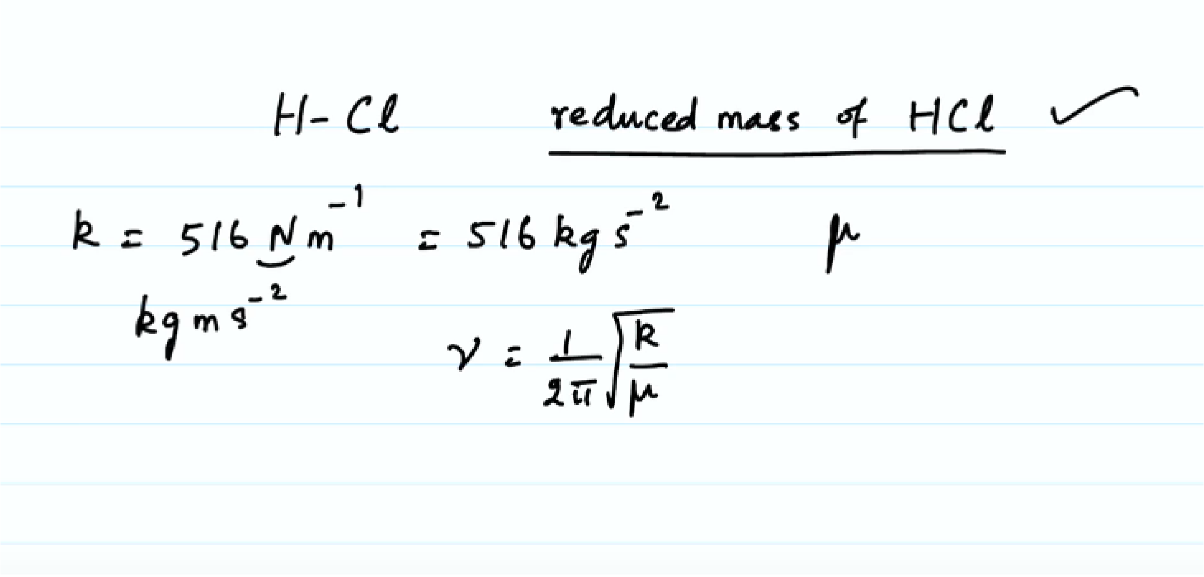

H-Cl reduced mass of HCl ✓

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

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

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

so let's 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 one by 2π by square root of K over μ,

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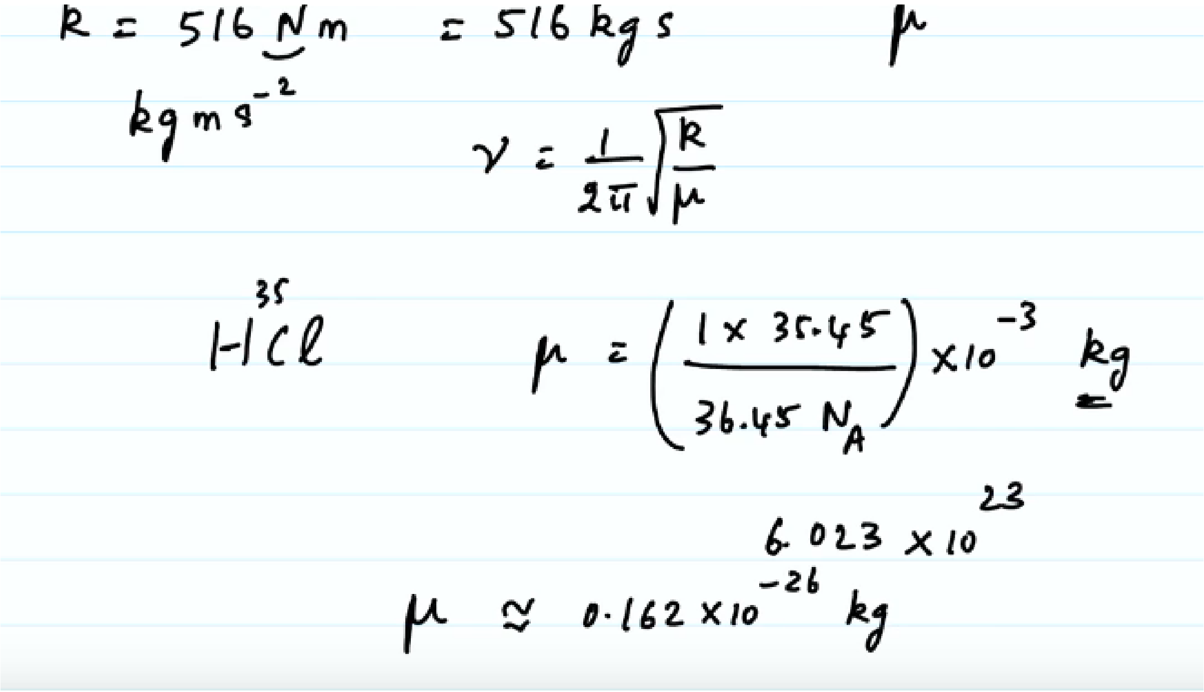

$$K = 516\,\underbrace{N}_{kg\,m\,s^{-2}}\,m \quad = 516\,kg\,s \qquad \mu$$

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

$$H^{35}Cl \qquad \mu = \left(\frac{1 \times 35.45}{36.45\,N_A}\right) \times 10^{-3}\ \underline{kg}$$

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

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

The reduce to mass in a simple experiment or a simple calculation you assume thirty five point four five for the atomic mass so we will call it as the chlorine-35 isotope and HS one therefore you are talking about the reduced mass one times thirty five point four five divided by m1 plus m2 which is

thirty six point four five 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 that what you will get Na and this is in gram units therefore you multiply it by 10 raised to minus three to get new kilograms. so that we use the SI units and Na is six point zero two three into 10 raised to 23 so with this number it is easy to calculate that the reduced mass is approximately 0.16 two times ten to the minus twenty six kilograms, the force constant is five hundred and sixteen so let me write μ here

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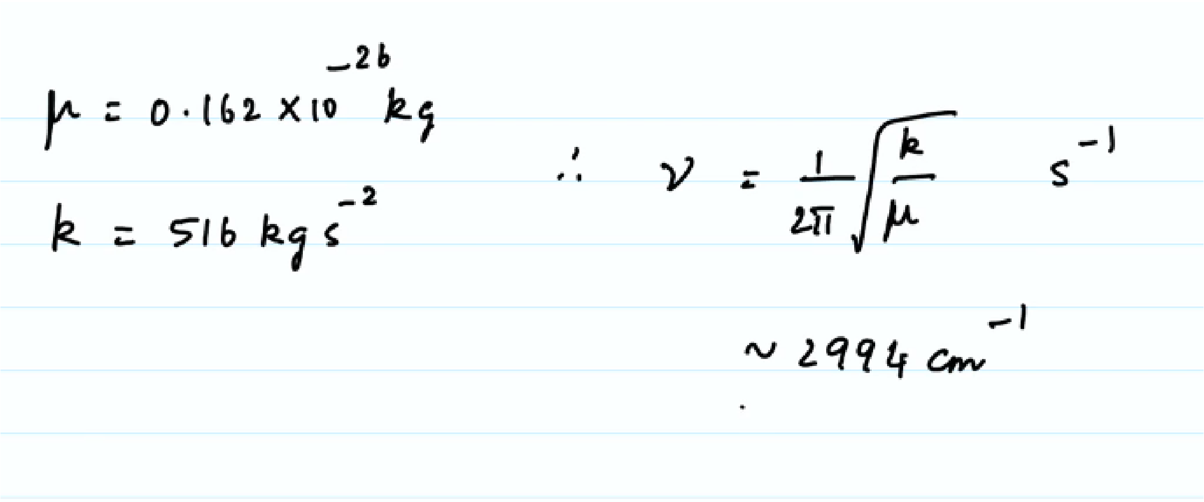

$\mu = 0.162 \times 10^{-26}$ kg

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

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

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

as 0.16 two times ten to the minus twenty six kg and the force constant is five hundred and sixteen kilogram per second square, therefore do you know immediately the frequency nu which is 1 by 2 pi times square root of K by μ is per second because the kilograms cancel out and the per second square becomes per second under the square root for what number do you get you get approximately - 2994 centimeter inverse. you can do it very accurately but I'm just telling you how to do these simple calculations this is the fundamental frequency for the hydrogen chloride molecule under the harmonic oscillator approximation and

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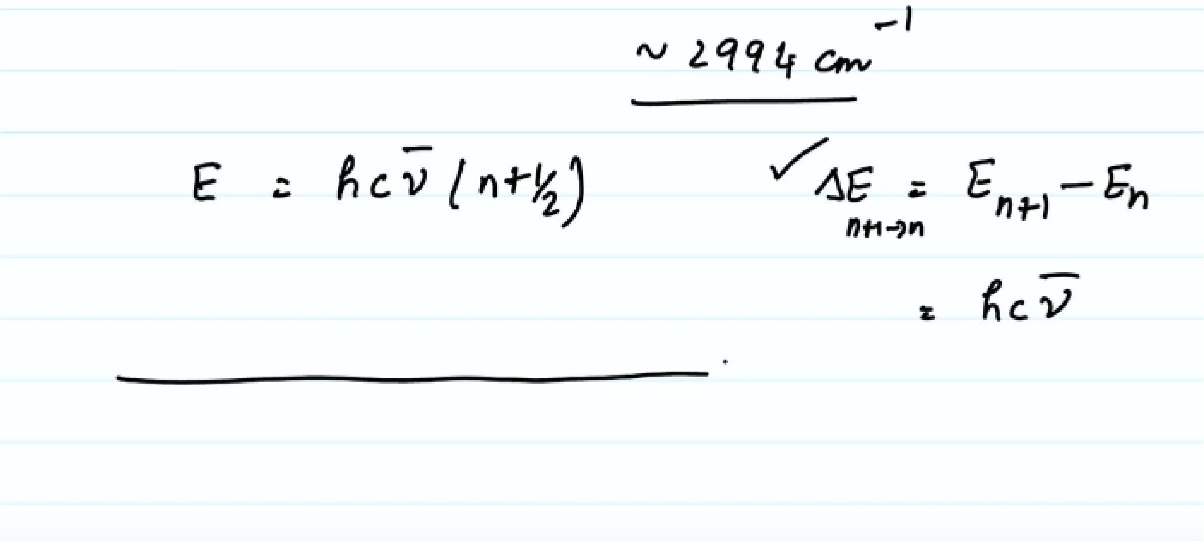

$$\underline{\sim 2994 \text{ cm}^{-1}}$$

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

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

$$= hc\bar{\nu}$$

therefore it is easy for you to calculate the energies E as h c new bar because this is in the numbers and you know that this is the n plus 1/2 so you can calculate the delta E as nothing other than E n plus 1 En nearest level n plus 1 to n, if you look at it then this is hc new bar and so the new bar law therefore we know the frequency of the transition energies and another important quantity that we have to calculate before we close this part of the lecture

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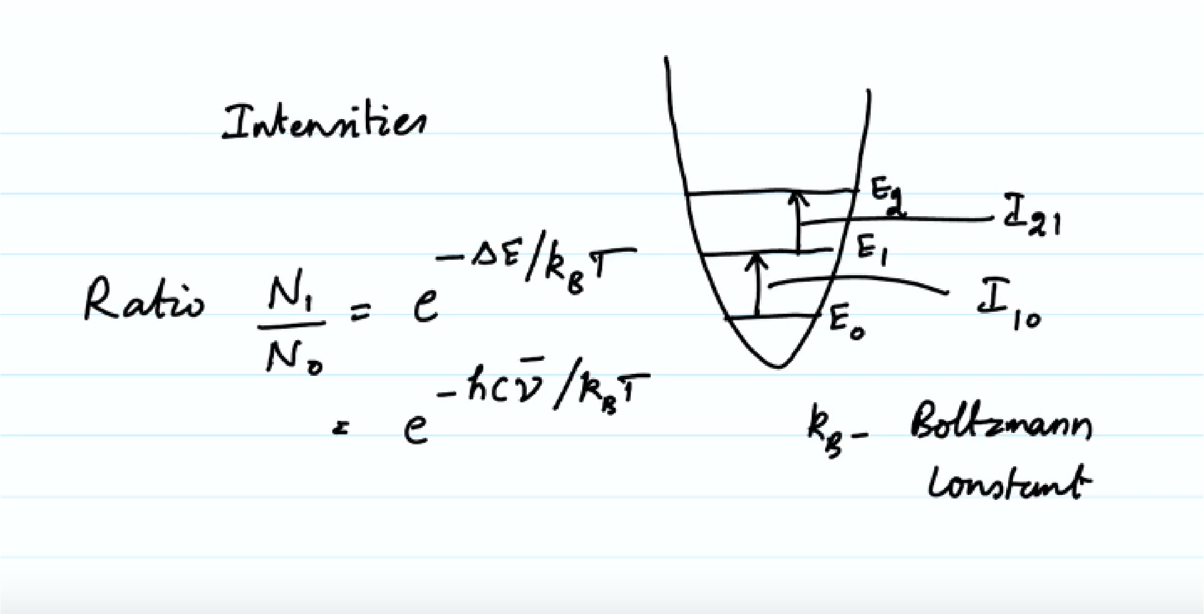

Intensities

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

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

k_B - Boltzmann Constant

is the intensities or relatively smaller as you go from an energy level for example, E1 E0 to E1 if you calculate that and E1 to E2 if you calculate to this suppose you call this as E0 E1 and E 2 and this intensity is I1 0 this is E2 and this intensity you call it as I2 1 then what's the ratio of what's what's the ratio of these intensities that's 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 N1 by N0 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 energy level 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 KBT and the Delta e is of course H C nu bar at the temperature T and KB is the Boltzmann constant.

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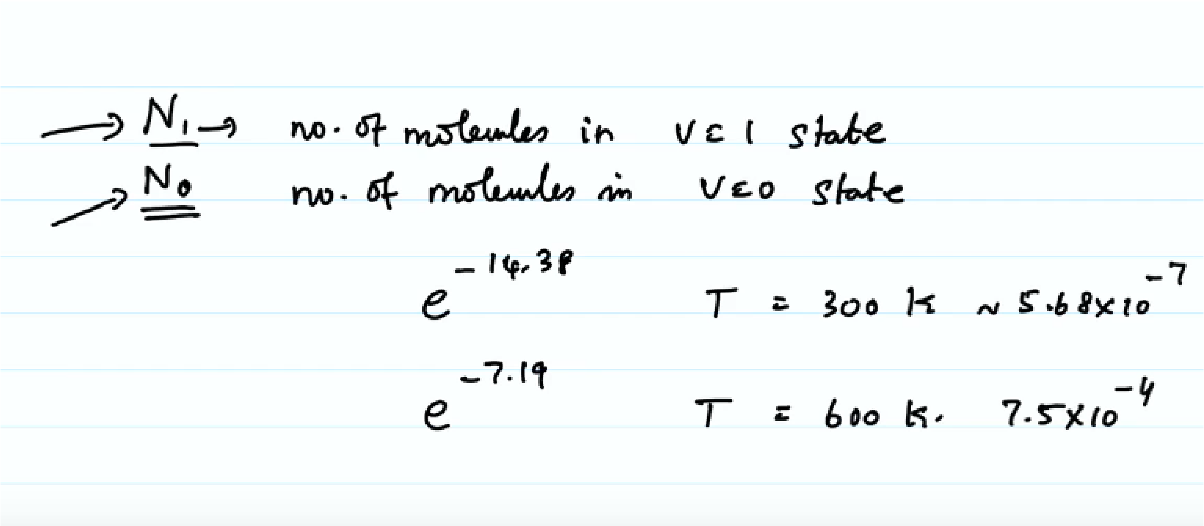

$\rightarrow \underline{N_1} \rightarrow$ no. of molecules in $v = 1$ state

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

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

$e^{-7.19}$ $T = 600\ K.$ 7.5×10^{-4}

So if you have to calculate these values the N1 by N0 the number of molecules in the first excited states in V is equal to one state versus the number of molecules in the ground state in V is equal to zero state if you calculate that the number turns out to be approximately e to the minus fourteen point three eight for T is equal to 300 Kelvin and it is e to the minus seven point one nine for T is equal to 600 Kelvin okay it is a very small number this is about seven point five times 10 raised to minus four and this number is about five point six eight times ten to the minus seven 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 two thousand nine hundred and ninety four centimetre

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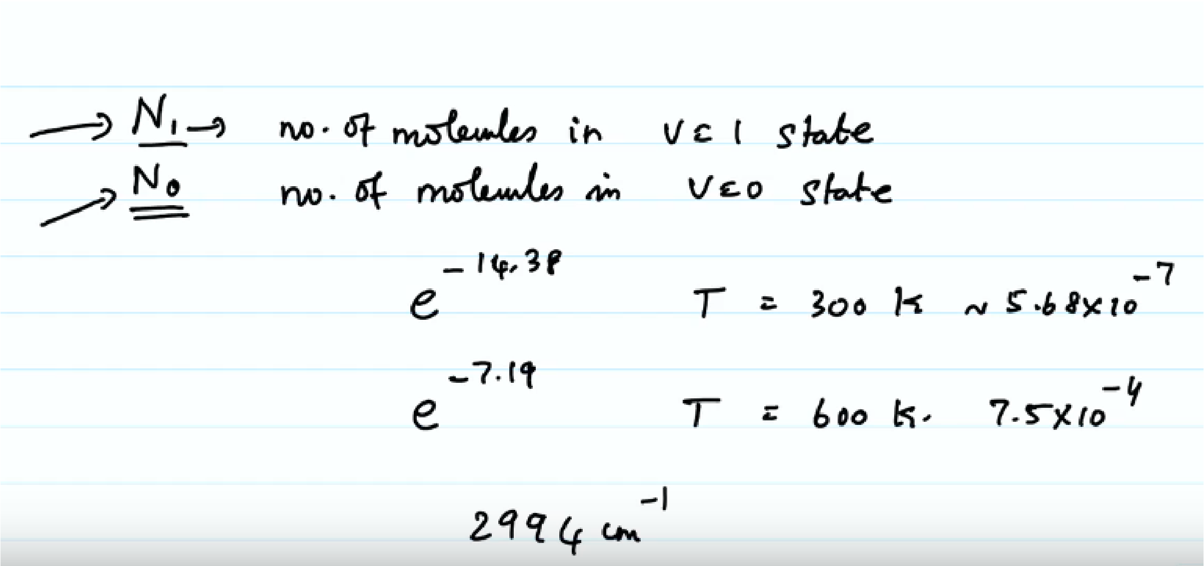

→ N_1 → no. of molecules in $v = 1$ state

→ $\underline{\underline{N_0}}$ 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}

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

from elementary calculation that's a large vibrational frequency for such a molecule most molecules are in the ground state and few are in the first excited States 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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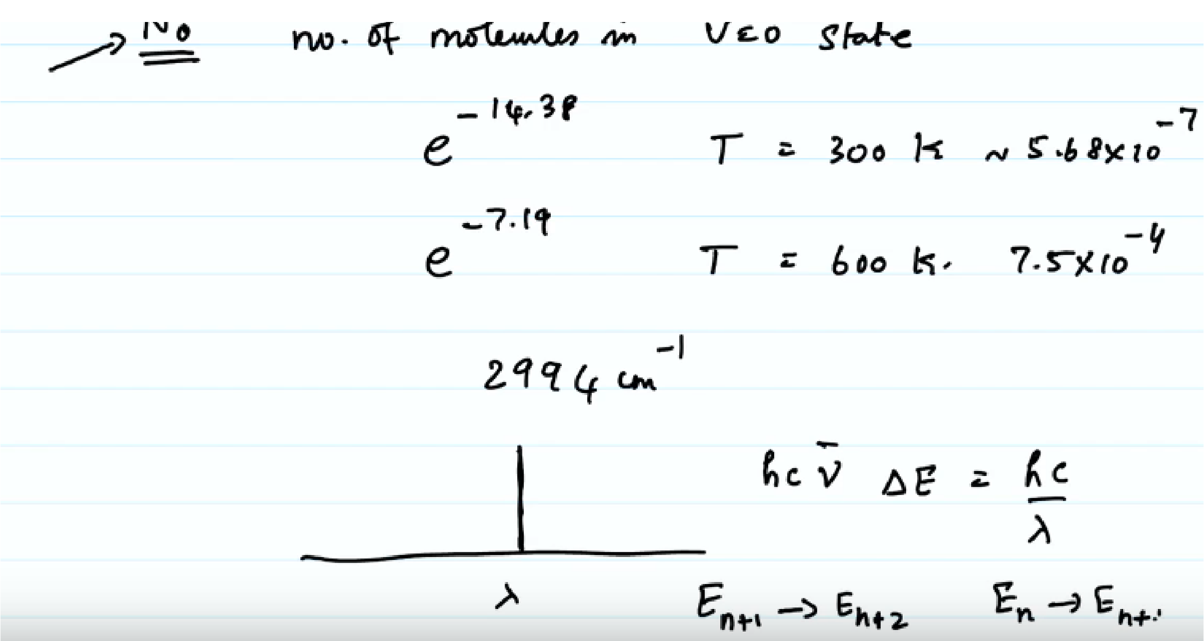

→ $\underline{\underline{N_0}}$ no. of molecules in $v = 0$ state

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

$e^{-7.19}$ $T = 600$ K. 7.5×10^{-4}

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

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

λ

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

So if you plot the spectrum as a function of lambda, please remember the energy at which the transition appears, is HC nu bar or lambda given by, you can write that, so if you write this as HC by lamda, okay in the energy of the transition E is given its hc by lamda. It is the same thing, whether 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 HC nu bar o HC by lambda therefore there's no spectrum for a diatomic molecule in the harmonic oscillator approximation.

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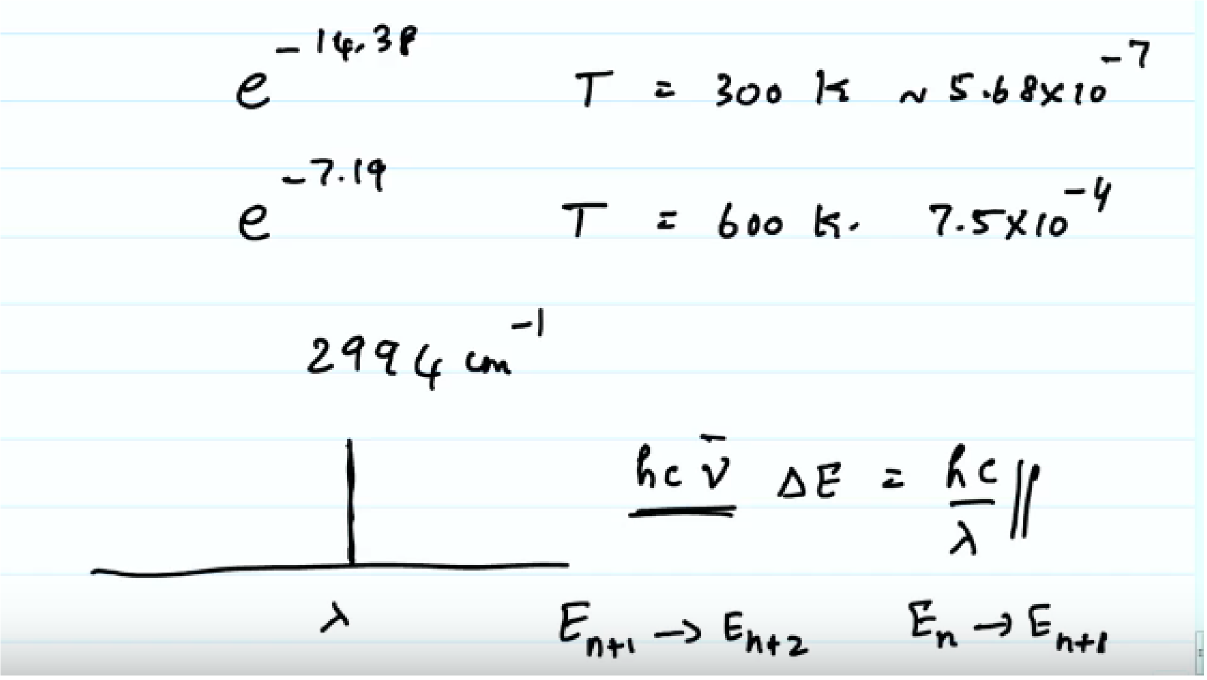

$e^{-14.38}$ $T = 300\ \text{K}$ $\sim 5.68\times10^{-7}$

$e^{-7.19}$ $T = 600\ \text{K}.$ 7.5×10^{-4}

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

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

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

so how do we correct for this this is not what you see 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 anharmonocity.

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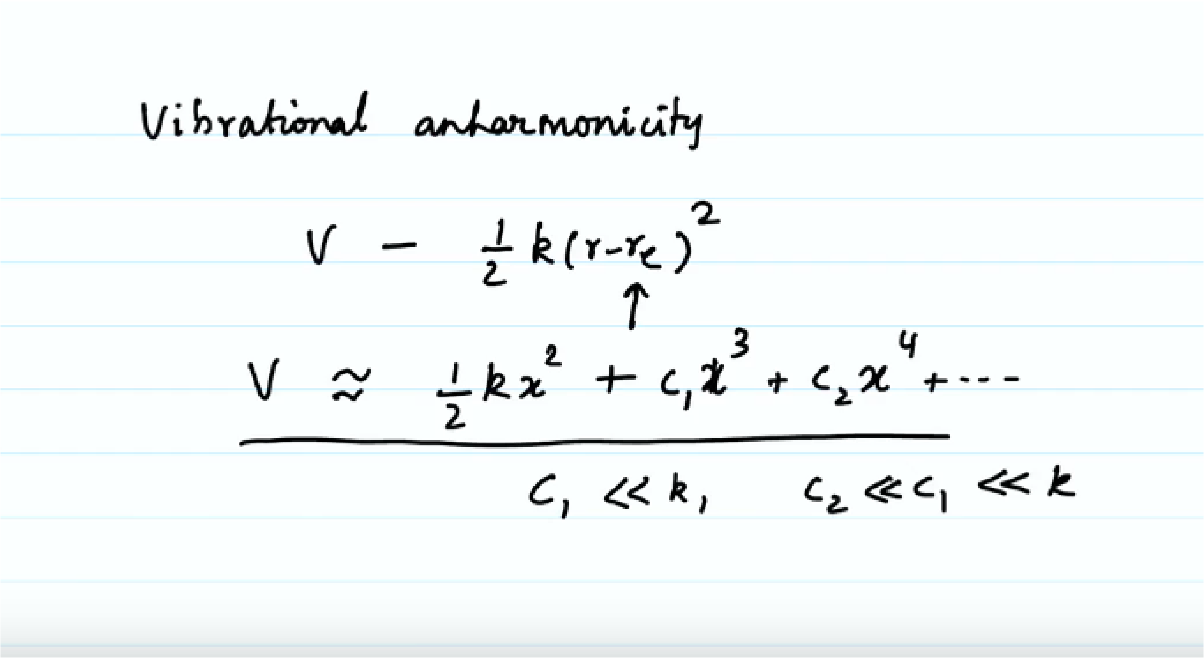

Vibrational anharmonicity

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

$$\uparrow$$

$$\underline{V \approx \frac{1}{2}kx^2 + c_1x^3 + c_2x^4 + \cdots}$$

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

that is the vibrational motion is not given by half K or - re square from displacement from equilibrium but it is actually given suppose we call this as X square half K X square then an harmonic motion essentially means that the potential energy V is approximately given by contributions which are other than the squares so you can call it a c1 X cube c2 X to the power 4 and so on and of course we hope that c1 is much less than K c2 is much less than c1 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 a none harmonic oscillator model different from the Hookes 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 1/2 but the energy levels are not they they differ by different amounts when you go from 1 to 2 to 2 to 3 and so on therefore it is possible for you to see vibrational satellites as you call them the satellites are essentially translation the transitions from the higher energy say V is equal to n equal to 1 to n equal to 2 or n equal to 2d and equal to 3 and so on such transitions you can see them only as a result of vibrational and harmonicity and vibrational and harmonicity can be modeled by many different processes we will see one important vibrational and harmonic model called the Morse oscillator in the next part of this lecture

Until then, Thank you very much.