Introductory Quantum Mechanics and Spectroscopy
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Lecture – 10
Microwave Spectroscopy of Diatomic Molecules

Welcome back to the lectures on chemistry. In today's lecture, we will look at one of the most important branches of molecular spectroscopy namely known as the microwave spectroscopy or rotational spectroscopy.

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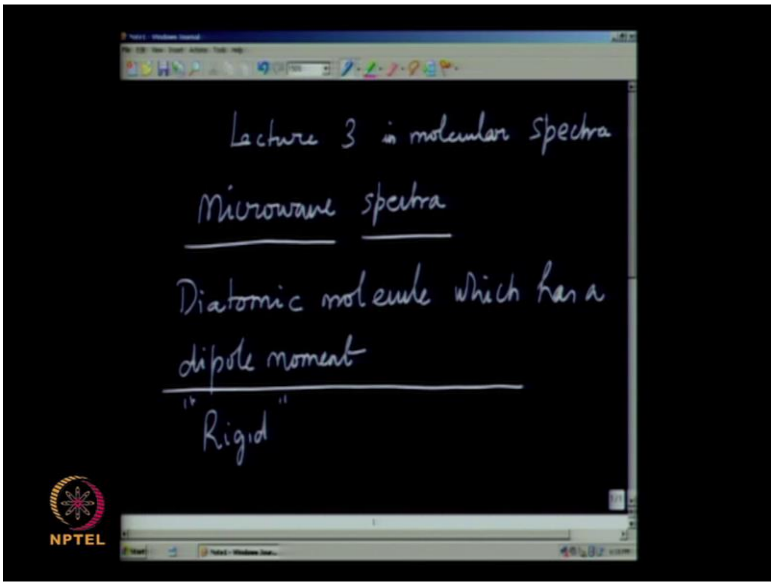

Lecture 3 in molecular Spectra

Microwave spectra

Diatomic molecule which has a dipole moment

"Rigid"

In molecular spectroscopy, spectra; and in today and possibly the next lecture we will examine microwave spectra. Some of the reasons for why we have to study microwave spectra, let me give you in detail. If you want to know to the geometry of the molecule or the equilibrium structure of the molecule and if the molecule possesses a dipole moment; then in the gas waves, micro wave spectra give you the most accurate geometry later that you can obtain. Rotation, which is in the phenomena that is associated with the microwave spectra, is one of the most fascinating phenomena in quantum mechanics. Angular momentum associated with that, the rotations of molecules, the rotations of molecular species or molecular complexes – all of them give rise to very rich spectra in the microwave region, whose analysis tells you more about the electric charge distribution that is presented in the molecule; and therefore also gives you a feel for how the atoms are bonded to each other and so on. So, the precise geometry and the shape of the molecules is something that we always worry about from the gas wave spectra of many of the compounds. But, what is important is of course for the rotational spectrum or microwave spectrum to be obtained, the molecule must have a permanent dipole moment or a charge asymmetric – the plus and minus charge centers must be separate from each other.

So, let us look at the microwave spectrum for a typical diatomic molecule, which has a dipole moment. Let us assume that, the diatomic molecule is a rigid molecule. This is an important assumption, because no molecule is rigid even at 0 kelvin. In harmonic oscillator model, you have studied that, molecules have zero-point kinetic energy – zero-point energy. And therefore, molecules vibrate even at 0 kelvin. Therefore, the assumption of a rigid molecule is something that we will do for convenience. And if necessary, this can be relaxed depending on the molecular energies. The rigid diatomic molecule essentially means the following that, the molecular geometries do not change. If the molecular geometries do not change, then it is easy to calculate the moments of inertia; it is easy to calculate using the bond angles and or a attentive model of bond angles and bond lengths; calculate the moment of inertia; calculate the spectral parameters; verify them with the experiments and then go back and redo it again.

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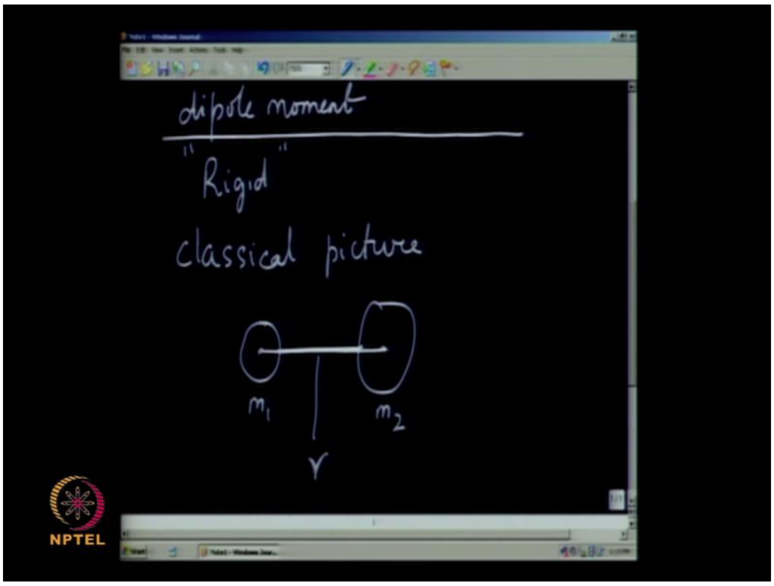

Let us do a simple example of a rigid diatomic molecule and let us assume a classical picture to begin with. Supposing we write a diatomic molecule as two different masses: m 1 and m 2 connected by a bond length, which is connected to their centers of masses and the distances r.

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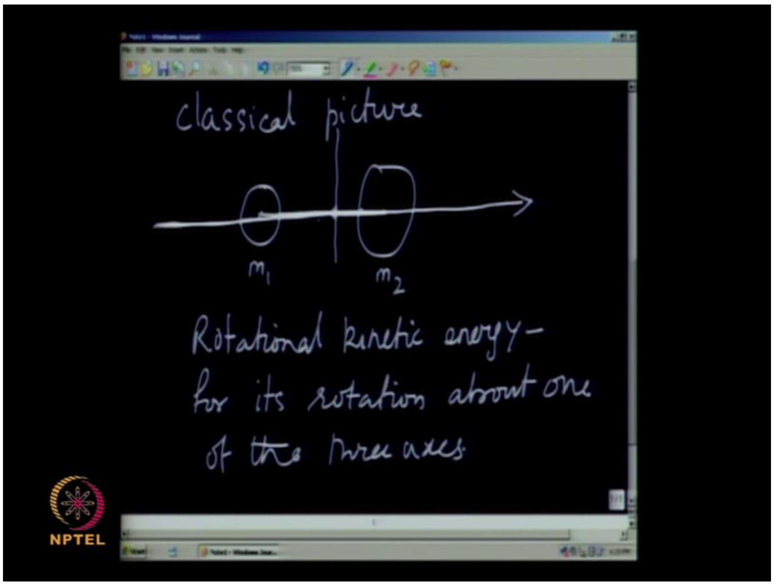

classical picture

Rotational kinetic energy – for its rotation about one of the three axes

Then, the rotational kinetic energy of this molecule about the axes of rotation; there are three axes of rotation; there is an axis, which passes through the bond – coaxial to the bond; then there is a bond axis, which passes through the central mass; perpendicular to that – let me remove this r for the time being; and then there is an axis, which is perpendicular to both these bond axes; and the bond here basically perpendicular to the plane of the screen that you are watching. So, there are three axes.

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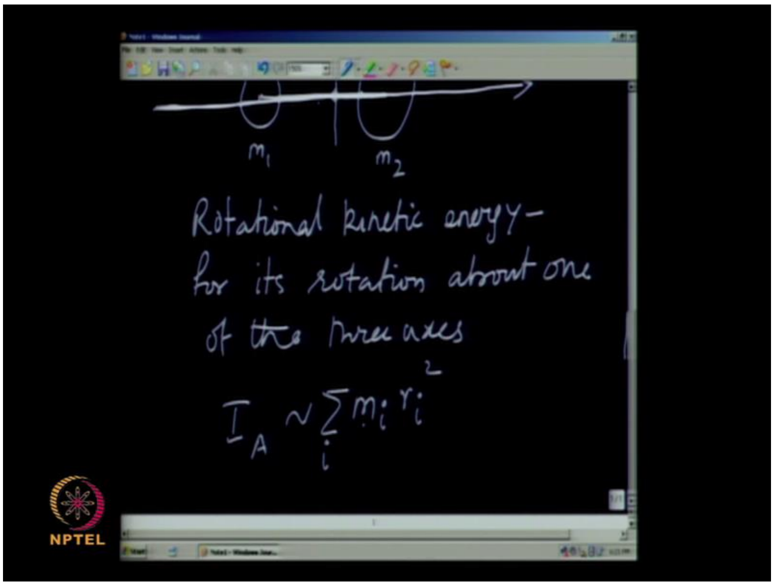

Rotational kinetic energy – for its rotation about one of the three axes

$$I_A \sim \sum_i m_i r_i^2$$

Now, when we calculate moments of inertia for this molecule in order to calculate to the rotational kinetic energy for the system for its rotation about one of the axes – one of the three axes; what do we do? Classically, we calculate the distance of the atoms – the perpendicular distance of the atoms from the axis multiplied by their masses; then we do what is called the mi ri square. I classically about any axis A is essentially sum over all the masses multiplied by their perpendicular distances from the axes and summed over all the atoms. Here there are two atoms. And therefore, what you will have is the distances from the axes m 1 r 1 square plus m 2 r 2 square.

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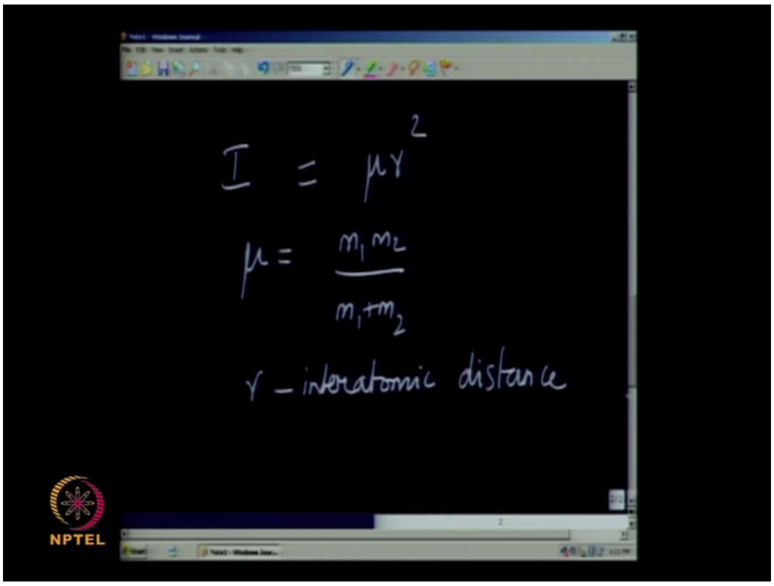

$$I = \mu r^2$$

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

r – interatomic distance

A simple two-body kinematics tells you that, the moment of inertia can also be expressed by this formula mu r square; where mu is given as the reduced mass m 1 m 2 by m 1 plus m 2 and r is the interatomic distance. Now, the question is – about what axis? I mentioned that, there are three axes associated with the simple linear molecule – a diatomic molecule. There are three mutually perpendicular axes. And if we assume the atoms to be point masses; then the perpendicular distance of the atoms m 1 and m 2 about the bond axis is 0. Therefore, there is no moment of inertia associated with rotation about to this axis. There is no kinetic energy; there is no rotational kinetic energy associated with that axis.

Now, what about the rotational kinetic energy associated with this axis or with the axis perpendicular to this line as well as the bond axis? The perpendicular distances are the same for both of them; and the masses being m 1 and m 2, this formula tells you for both those axes, the moments of inertia i is given by the simple formula mu r square. It is a classical; it is a very elementary classical mechanical formula; you can derive that. And in fact, that should be one of the exercises for you to derive this. The mu being a reduced mass and r being the interatomic distance, leads you to this formula that, the moment of inertia I is that.

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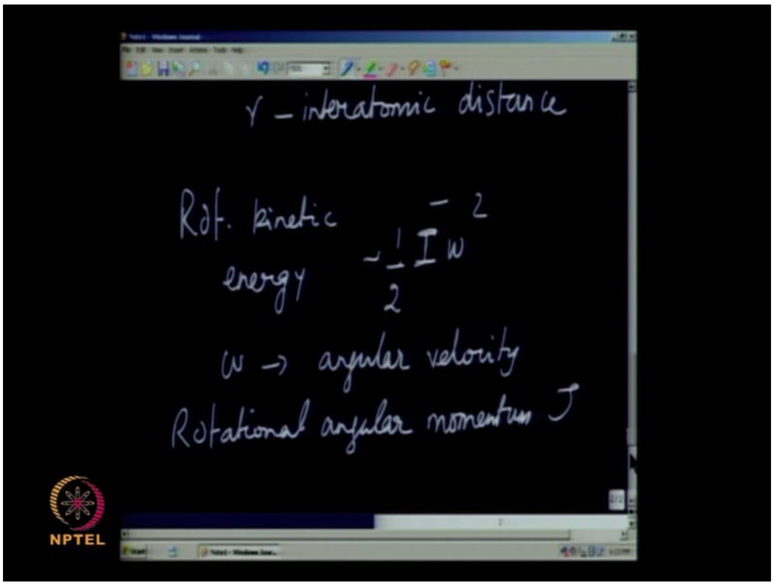

r – interatomic distance

Rot. kinetic energy $\sim \frac{1}{2} I \bar{\omega}^{2}$

$\omega \rightarrow$ angular velocity

Rotational angular momentum J

Given this as the moment of inertia, the rotational kinetic energy classically is given for such bodies as the rotational velocity times – rotational – the angular velocity times the moment of inertia multiplied by half I omega square, or where omega is the angular velocity, which is nothing but the speed of rotation about the given axis.

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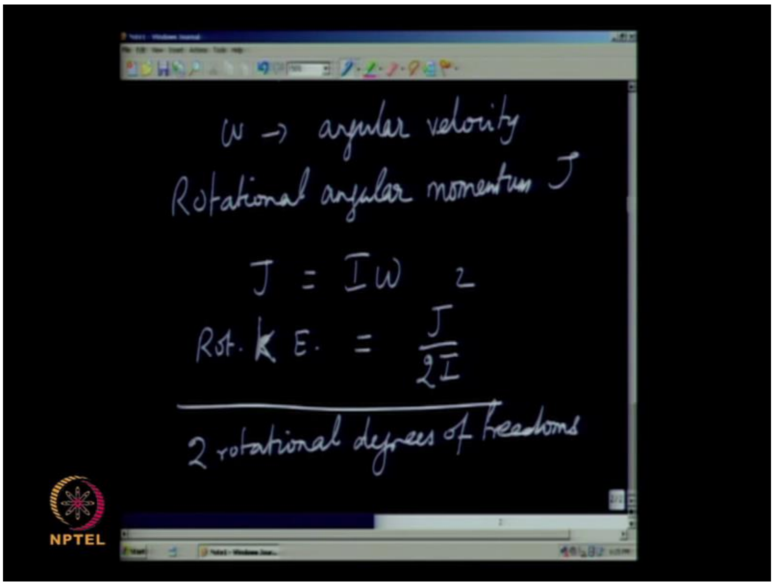

$\omega \rightarrow$ angular velocity

Rotational angular momentum J

$J = I\omega$ 2

Rot. K E. $= \frac{J}{2I}$

2 rotational degrees of freedoms

In terms of rotational angular momentum J, which you know; again from classical mechanics, J is given by I omega. You know that, the rotational kinetic energy is given by J square over 2I. This is the classical formula. And the rotational kinetic energy is the same about both the axes. And under the point mass approximation, remember that, the moment of inertia is 0. Therefore, there are only two degrees of freedom associated – two rotational degree of freedom associated with a linear molecule under the point-mass approximation. If the masses are not point masses, but the atoms have the mass distribution – a size and charge and all those things, you might find out that, the moment of inertia is so small that, you still need not have to be concerned with the rotational degree of freedom about the axes. It is almost a free rotation with no energy associated with it. Therefore, there are only…

For a linear molecule, there are only two rotational degrees of freedom. And for a rigid molecule, both these degrees of freedom have the same moment of inertia. And therefore, there is only one moment of inertia associated with the rotational motion of a linear molecule. Now, this is classical mechanical formula the spectroscopy is studied by looking at the molecular energy levels, which are obtained by solving the molecular Schrodinger equation. And the Schrodinger equation as you know from the previous models and the lectures, we write down the classical kinetic energy and the potential energy; we write down the classical Hamiltonian and then we transform that into the quantum mechanical formula.

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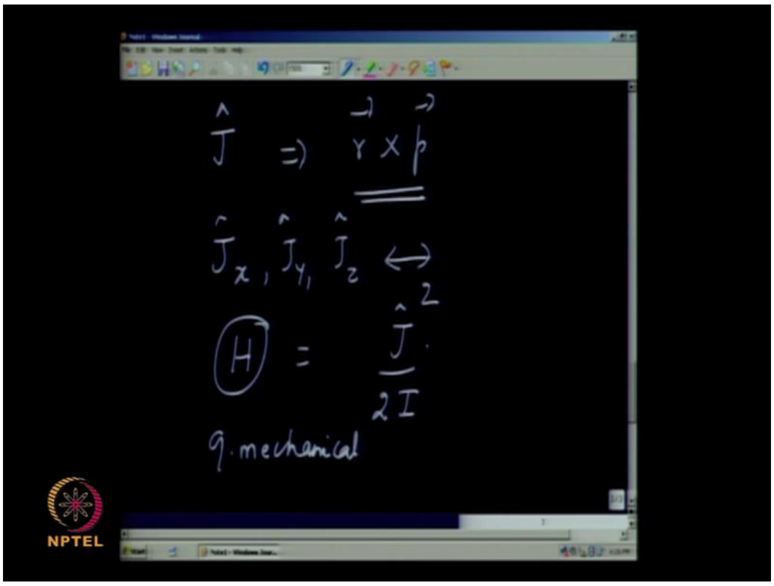

$$\hat{J} \Rightarrow \underline{\underline{\vec{r} \times \vec{p}}}$$

$$\hat{J}_x, \hat{J}_y, \hat{J}_z \leftrightarrow$$

$$\boxed{H} = \frac{\hat{J}^2}{2I}$$

q. mechanical

And when we do that, the angular momentum J in classical mechanics, which is given by r cross p formula becomes the corresponding the quantum mechanical operators; for J become the J x, J y and J z component just like you had in the case of momenta. And these can be written down and you can go through a whole lot of algebra to write down the Hamiltonian for system again as the operator J square by 2I with the difference that, this is quantum mechanical; and the angular momentum J is now a quantum mechanical quantity. And therefore, it has very special properties, which are not the same as the classical angular momentum.

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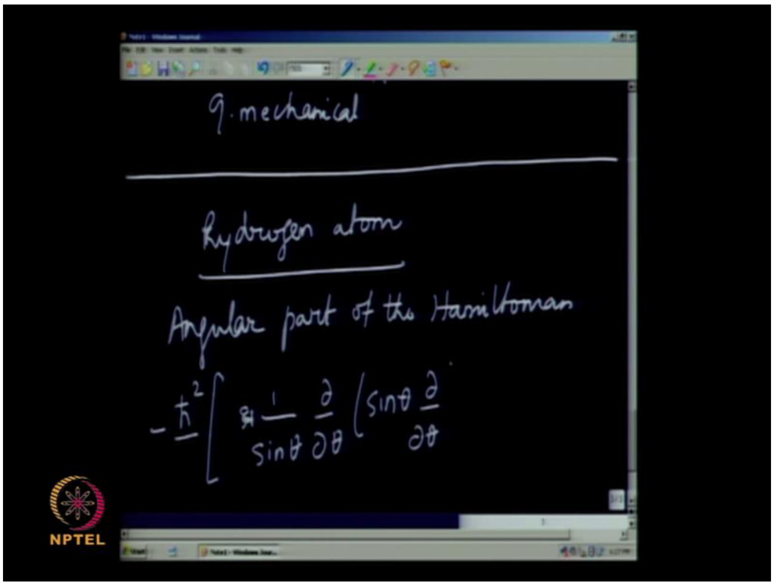

q. mechanical

Hydrogen atom

Angular part of the Hamiltonian

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right.\right.$$

Just let me take you aside to the rotational to the problem of the hydrogen atom, which was done several lectures ago. In hydrogen atom, when we solved the Hamiltonian, we expressed the hydrogen atom Hamiltonian in terms of spherical polar coordinates. And you might recall that, the angular part of the hydrogen atom Hamiltonian.

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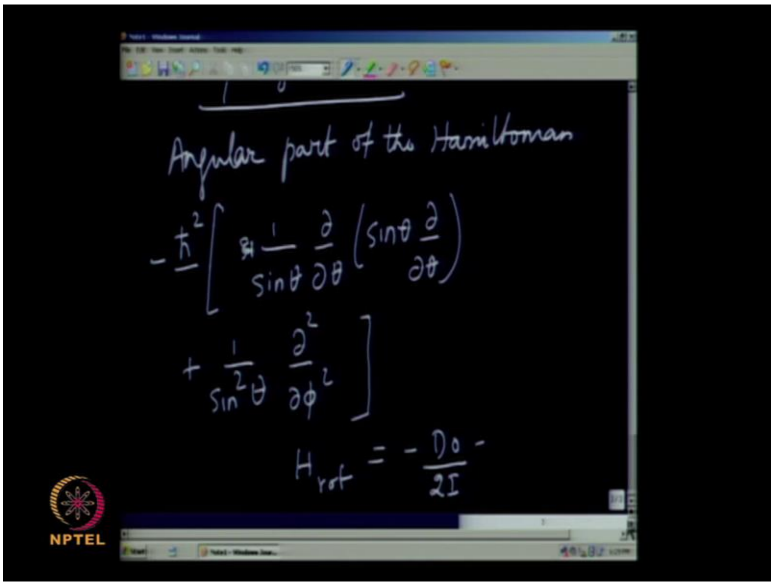

Angular part of the Hamiltonian

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$H_{rot} = -\frac{D_0}{2I} -$$

If you recall, remember that, that was nothing but minus h bar square 1 by sin theta dou by dou theta sin theta dou by dou theta plus 1 by sin square theta duo square by duo phi square. This was the angular part that you recall from the hydrogen atom solution. Now, the properties of the angular momentum operators J x, J y and J z – the components of the angular momentum operator in an xyz co-ordinate system, that is, associated with the central mass of the molecule. If it is expressed in spherical polar coordinates, you get exactly the same form as you have in the case of hydrogen atom angular parts. Therefore, the Hamiltonian for the rotational motion becomes exactly ditto of what you have here with the one difference that, there is a 2I in the denominator, which corresponds to the J square by 2I part of it. The J square – the angular momentum part is given by this formula.

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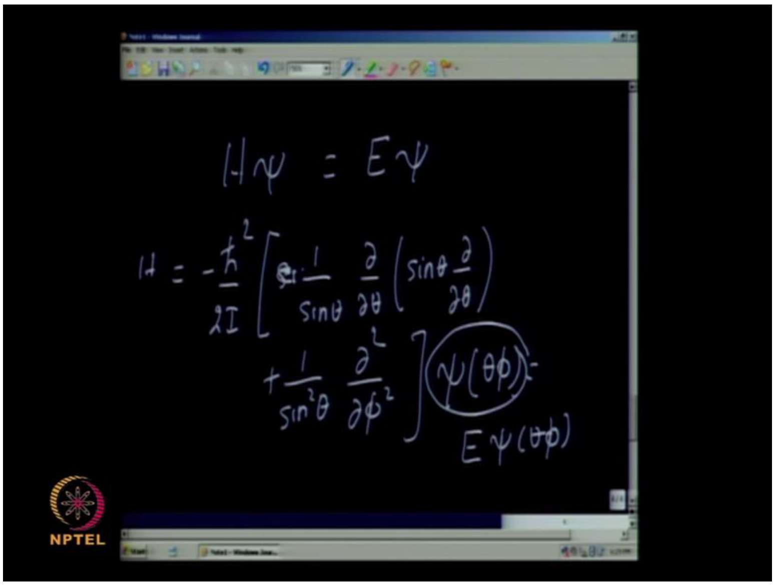

$$H\psi = E\psi$$

$$H = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\theta\phi) = E\psi(\theta\phi)$$

Therefore, what is obvious immediately is that, if we have the Schrodinger equation written as H psi is equal to E psi. And if the H is written as minus h bar square by 2I times the formula that you have 1 by sin theta duo by duo theta sin theta duo by duo theta plus 1 by sin square theta duo square by duo phi square psi, which is the function of theta and phi is equal to E times psi theta and phi. Then the solution psi theta phi – you know exactly what it should be. And this is nothing other than the spherical harmonics that you derived earlier.

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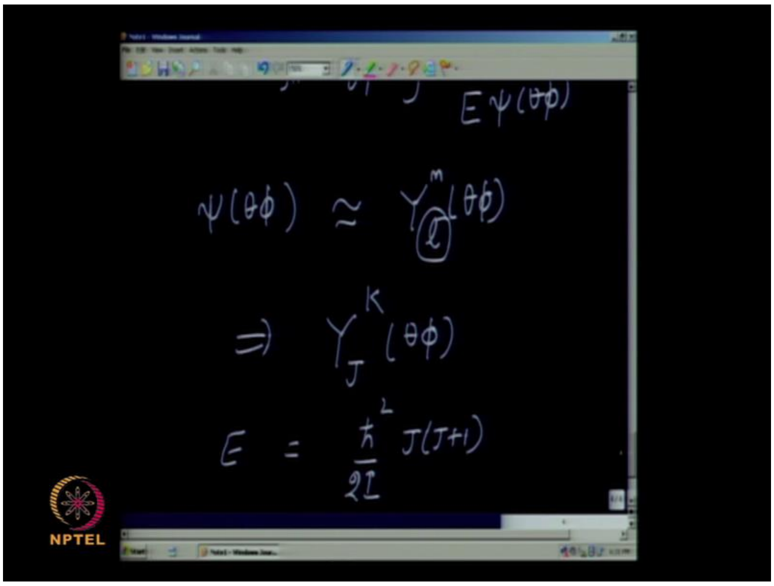

$$E\psi(\theta\phi)$$

$$\psi(\theta\phi) \approx Y_{\boxed{l}}^{m}(\theta\phi)$$

$$\Rightarrow Y_{J}^{K}(\theta\phi)$$

$$E = \frac{\hbar^2}{2I} J(J+1)$$

Psi theta phi is the spherical harmonics Y. I use the symbol l m theta phi earlier for denoting the orbital angular momentum; but here now the quantum number is the rotational angular momentum quantum number. And this is now replaced by Y J K theta phi; where K has the same role as the m; and J has the quantum number associated with the rotational motion of the molecule. This also tells you immediately what should be the value of the energy. And the energy is you remember that, there is h bar square by 2I, which is their on the left-hand side here – h psi equal to E psi gives you… Earlier it gave you l into l plus 1. Now, you will get J into J plus 1, which is the quantum number associated with the rotational motion. And therefore, what you have is h bar square by 2I times J into J plus 1, is the rotational kinetic energy associated with the diatomic molecule.

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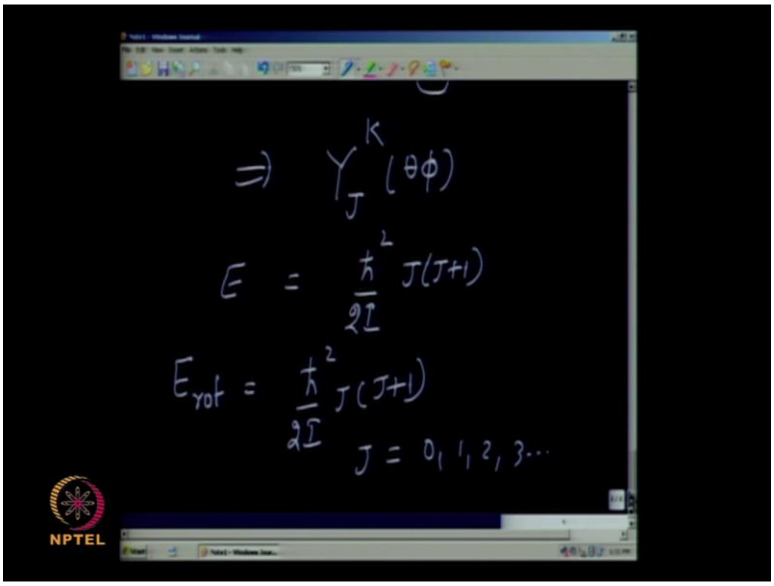

$$\Rightarrow Y_J^K(\theta\phi)$$

$$E = \frac{\hbar^2}{2I} J(J+1)$$

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1)$$

$J = 0, 1, 2, 3\ldots$

E rotational – there is no potential energy here; we are only worried about the rigid atom – rigid body motion. The rotational kinetic energy is the total energy of the rotating diatomic molecule. Therefore, E rotation is now given by h bar square by 2I into J into J plus 1. This is the simple rigid diatomic model with the values of J being 0, 1, 2, 3, etcetera all the way up.

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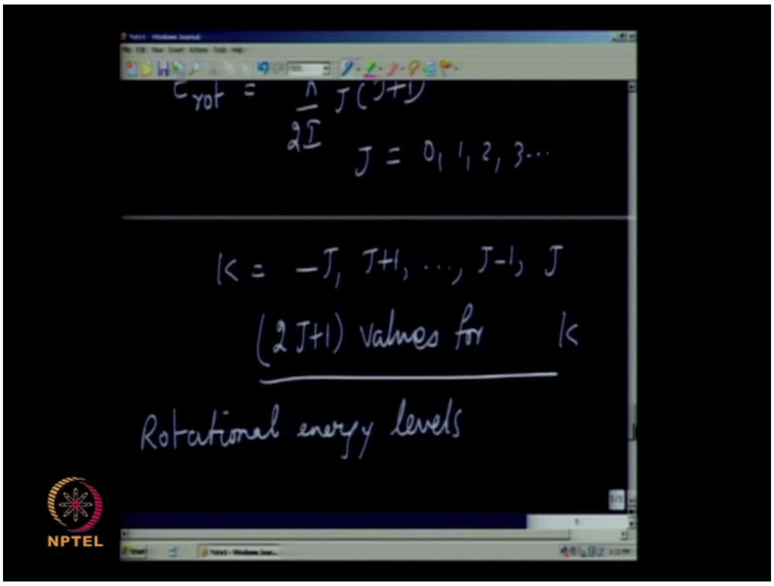

$$E_{rot} = \frac{\hbar}{2I} J(J+1)$$

$J = 0, 1, 2, 3\ldots$

$K = -J, J+1, \ldots, J-1, J$

$(2J+1)$ values for K

Rotational energy levels

And the value of K if you remember is the same as the value of m earlier. K goes from minus J, minus J plus 1 to J minus 1 up to J.

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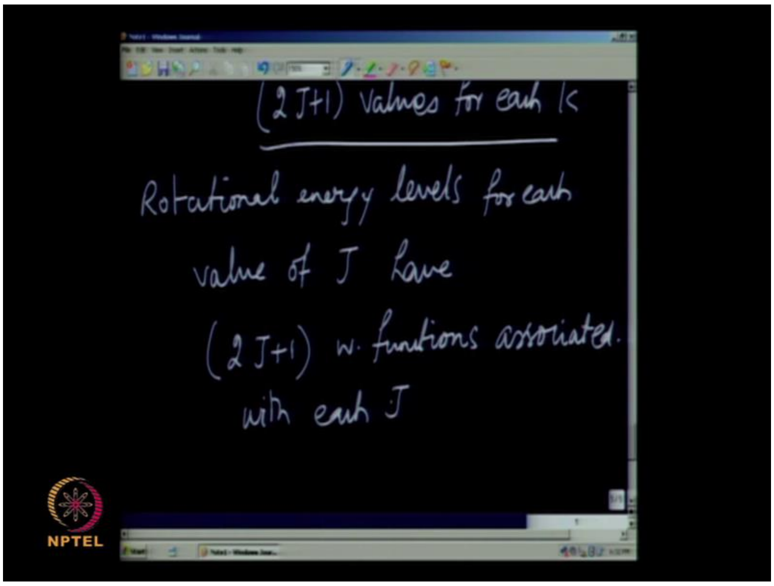

(2 J+1) values for each K

Rotational energy levels for each
value of J have
(2 J+1) w. functions associated.
with each J

So, there are 2 J plus 1 values for K, which means that the rotational energy levels associated with the diatomic molecule for each value of J have 2 J plus 1 wave functions associated with them – associated with the each J.

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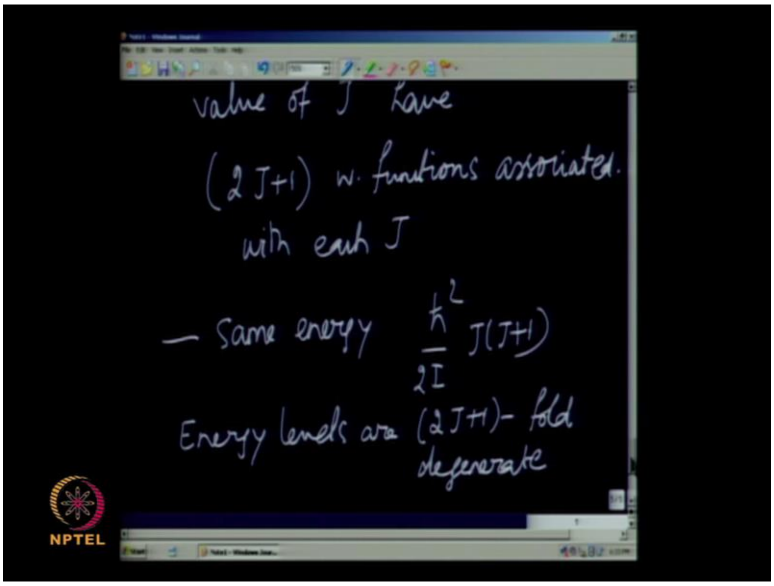

value of J have
(2 J+1) w. functions associated.
with each J

– Same energy $\frac{\hbar^2}{2I} J(J+1)$

Energy levels are (2 J+1)- fold
degenerate

The all of them have the same energy given by this formula h bar square by 2I J into J plus 1. Therefore, the energy levels are degenerate or 2J plus 1 – fold degenerate.

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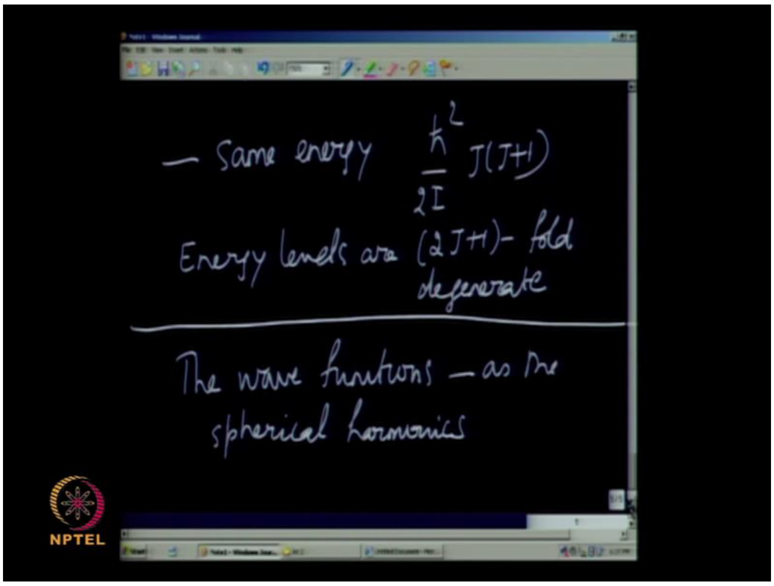

— Same energy $\frac{\hbar^2}{2I} J(J+1)$

Energy levels are $(2J+1)$- fold degenerate

The wave functions — as the spherical harmonics

The wave functions associated with each of these energy levels have the same form as the spherical harmonics.

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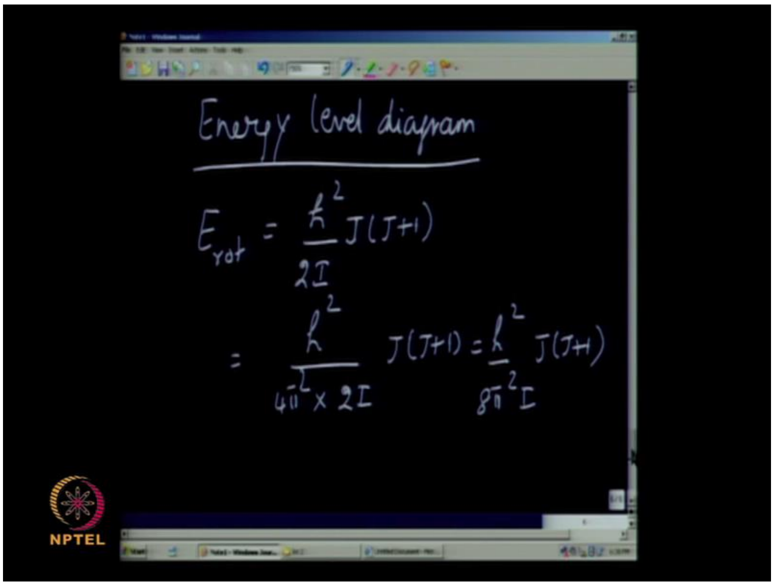

Energy level diagram

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1)$$

$$= \frac{h^2}{4\pi^2 \times 2I} J(J+1) = \frac{h^2}{8\pi^2 I} J(J+1)$$

Now, let us look at the energy level diagram for the microwave spectrum. Before I do this, let me introduce the convention that, spectroscopy use when we write the rotational kinetic energy – rotational energy – quantum mechanical rotational energy associated with the system as h bar square by 2I into J into J plus 1. Let us right this out explicitly; it is h square by 4 pi square into 2I J into J plus 1, which is h square by 8 pi square I into J plus 1.

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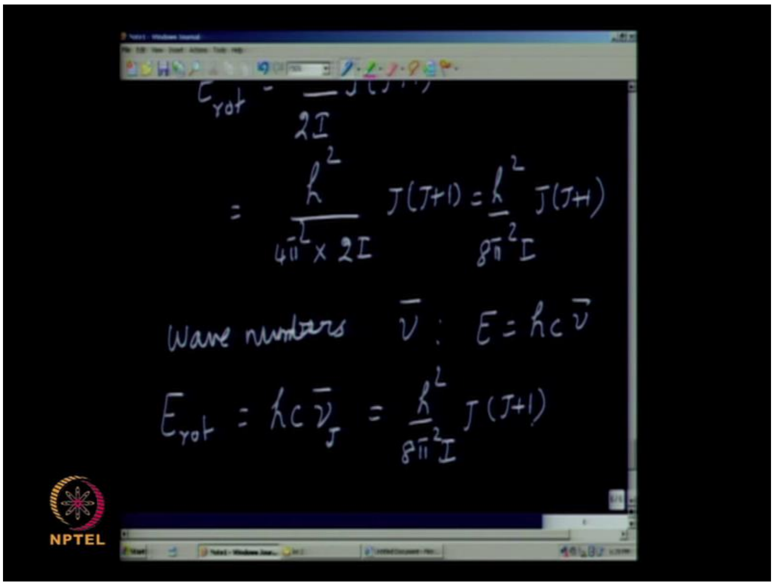

$$E_{rot} = \frac{}{2I} J(J+1)$$

$$= \frac{h^2}{4\pi^2 \times 2I} J(J+1) = \frac{h^2}{8\pi^2 I} J(J+1)$$

Wave numbers $\bar{\nu}$: $E = hc\bar{\nu}$

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

Now, remember that there is another way of writing the energy in terms of wave numbers – wave numbers nu bar such that E is given by this formula h c nu bar. Therefore, if we write the E – rotational energy as h c nu bar corresponding to the quantum number J; h is a constant; c is a constant; h is Planck’s constant; c is a speed of light. Therefore, there is no association. The nu bar is associated with the quantum number J; and that is given by h square by 8 pi square I J in to J plus 1.

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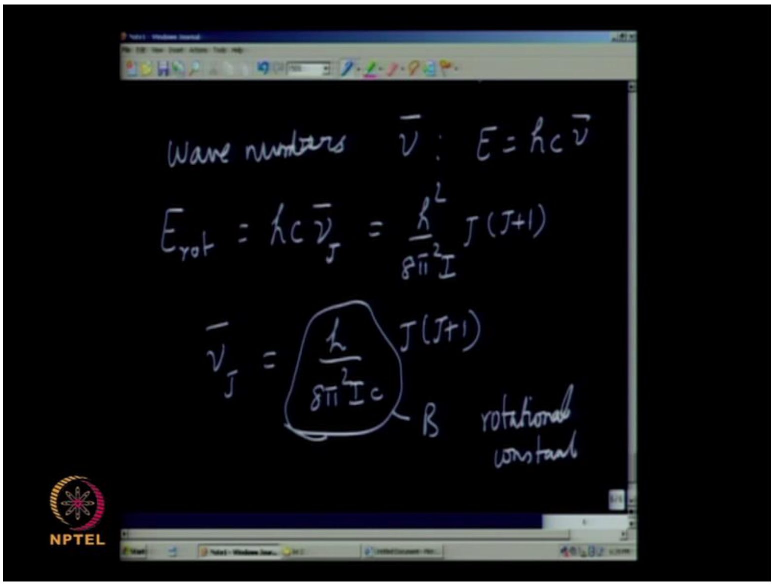

Wave numbers $\bar{\nu}$: $E = hc\bar{\nu}$

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

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

B rotational constant

And therefore, if we write the wave numbers nu J – nu bar J as h by 8 pi square I c J into J plus 1. Spectroscopists have a notation for this constant. And you see this is a molecular constant; h is a Planck's constant; the c is the speed of the light; and I is of course the moment of inertia associated with the molecule. So, this is a constant associated with each molecule and this is given the symbol B. And it is called the rotational constant for entire atomic molecule.

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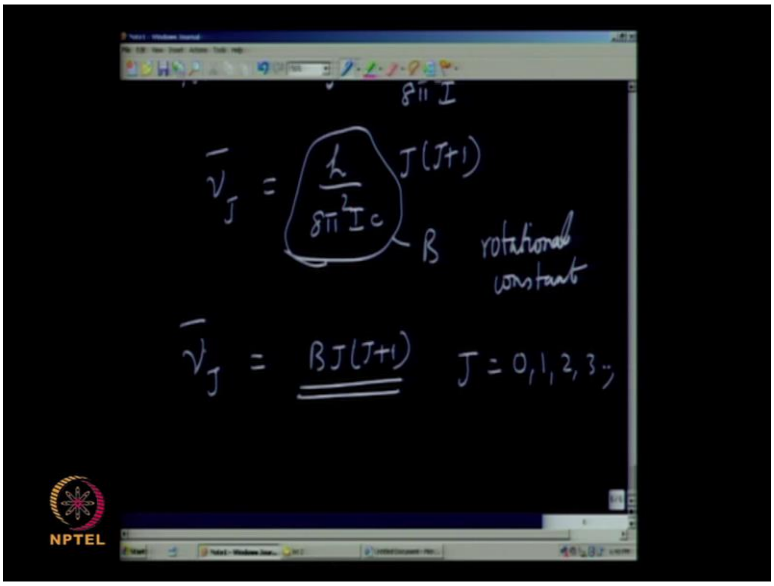

$8\pi I$

$$\bar{\nu}_J = \underbrace{\boxed{\frac{h}{8\pi^2 I c}}}_{B} J(J+1)$$

B rotational constant

$$\underline{\underline{\bar{\nu}_J = BJ(J+1)}} \quad J = 0, 1, 2, 3 \ldots$$

Therefore, the value nu bar J is B J into J plus 1, is what everybody uses. Now, what is the dimension of B? It is clear from the way it is written – h by 8 pi square I c. And the fact that, J takes only J is equal to 0, 1, 2, 3 as quantum numbers. It is very clear that, J does not have any dimension. And therefore, the dimension of B has to be the same as the dimension of the nu bar j, which is a wave number unit. And the wave number unit is 1 by length; that is a number of waves in a given unit length if you remember the definition of wave numbers. Therefore, this is per unit length or per centimeter in or centimeter inverse.

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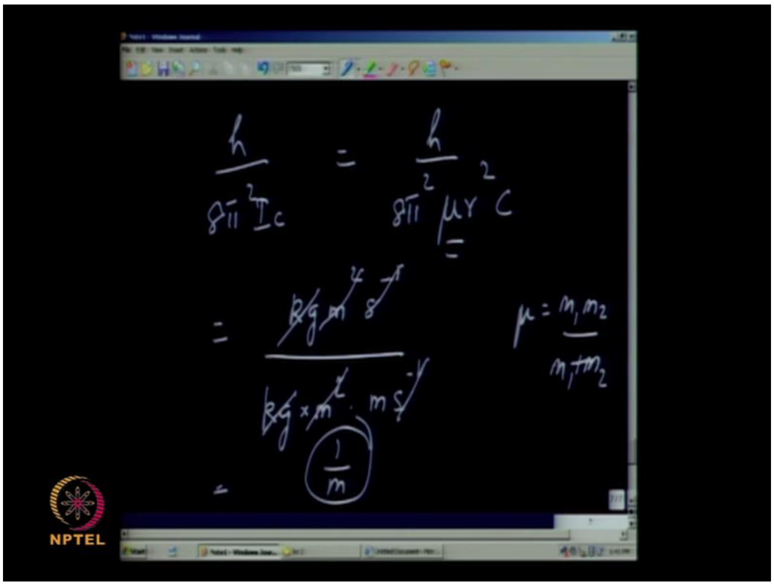

$$\frac{h}{8\pi^2 \underline{I} c} = \frac{h}{8\pi^2 \underline{\underline{\mu}} r^2 c}$$

$$= \frac{\cancel{kg}\,\cancel{m^2}\,\cancel{s^{-1}}}{\cancel{kg} \times \cancel{m^2} \cdot m\,\cancel{s^{-1}}}$$

$$= \boxed{\frac{1}{m}}$$

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

And let us see if B has the same dimension – h by 8 pi square I c is nothing other than h by 8 pi square mu r square c recalling the definition of I. And h has the units joule second, which is kilogram meter square per second divided by mu in kilograms; it is a reduced mass. Remember mu is m 1, m 2 by m 1 m 2. And therefore, it has the dimension of the mass – kilogram – r square is meter square and c – speed of light is nothing but meter per second. Therefore, canceling out the appropriate quantities, what you end up is 1 by meter. Thus, B has the dimension of the wave number given that, J is the quantum number. Therefore, dimensionally, we are saying the right things; it is correct. And the quantity B is a characteristic of every diatomic molecule. How it is? It is dependent on two parameters corresponding to the molecule: one is the reduced mass of the molecule and the other is the inter-atomic distance between the two atoms in the molecule. Therefore, on both counts, it depends on given diatomic molecule. Therefore, B is very specific to the given molecule. It is a property of the molecule under the rigid rotor assumption.

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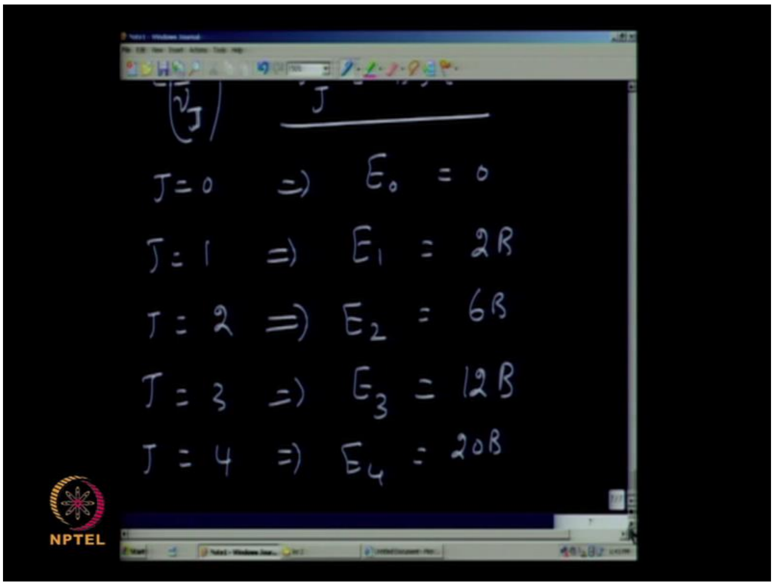

$(\bar{\nu}_J)$ J

$J = 0 \Rightarrow E_0 = 0$

$J = 1 \Rightarrow E_1 = 2B$

$J = 2 \Rightarrow E_2 = 6B$

$J = 3 \Rightarrow E_3 = 12B$

$J = 4 \Rightarrow E_4 = 20B$

Now, let us look at the energy levels – E as a function of nu J bar. That is what we want to write. Since the formula for nu J bar is B J into J plus 1, let us write a few values J equal to 0 corresponds to E 0, which is 0. J equal to 1 corresponds to E 1, which is 2B J into J plus 1. J is equal to 2 corresponds to E to the second energy level, which is 2 into 3; it is 6B. And J equal to 3 for example, E 3 is 12B and so on. Let me write just the last one more quantity J equal to 4 and write E 4 – also has 20B. Therefore, what you see is the energy levels increasing as a function of J square – J into J plus 1 for very large values of J functions like J square. Therefore, you see that, the energy levels increase and the differences between the energy levels, which is what you see as a spectroscopic transition; now, will be determined by the differences that you have between these levels.

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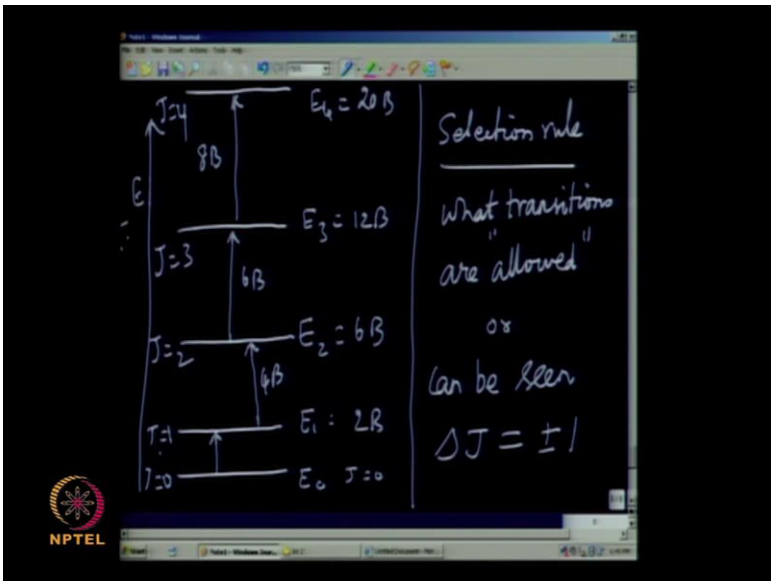

Selection rule

What transitions "are allowed"

or

can be seen

$\Delta J = \pm 1$

So, let us draw the energy level diagram now. E 0 is 0. This is J equal to 0. E 1 – if I draw this, it is 2B. E 2 is 6B. Therefore, on a scale of the appropriate energy, this is the increasing energy scale E. This is the value. E 2 is 6B. The difference between E naught and E 1 is 2B. The difference between E 1 and E 2 is 4B. And write the next one – it is 8… E 3 is 12B. And the difference between these two is 6B. And of course, E 4 goes out of this screen here is 20B somewhere. Let me write at the top. And the difference here is now A to B. So, successive energy levels corresponding to the value J equal to 0, J equal to 1, J equal to 2, J is equal to 3 and J is equal to 4 – as you see it, the successive energy levels differ by 2B, 4B, 6B and 8B. There is a selection rule in quantum mechanics for spectroscopic transitions that can take place in a rigid diatomic molecule.

The selection rule is that, what transitions are allowed or can be seen for a rigid diatomic molecule. The transitions that are allowed correspond only to this value delta J is equal to plus or minus 1; which means that, if the molecule is in a state J equal to 1; it can undergo a transition if a microwave radiation is ((Refer Time: 27:38)) molecule; it can undergo a transition to the next level – J equal to 2 by the process of absorption; or, it can undergo a transition from J equal to 1 to J equal to 0 by the process of emission, which is either spontaneous emission or stimulated emission – either one of these processes. But, it cannot jump from J equal to 1 to J equal to 3 under this assumption or within this model of setting up the rigid Hamiltonian as a classical Hamiltonian converting it into the quantum and following through this rigid approximation. This model does not permit a transition from a J to a J plus 2 or a J minus 2 or a J to a J plus 3 or J minus 3. Delta J has to be plus minus 1.

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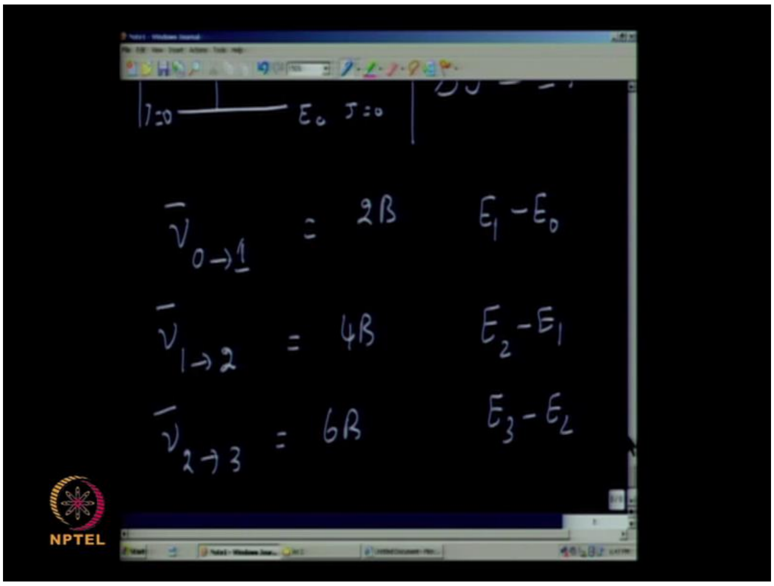

$J=0$ —— E_0 $J=0$

$\bar{\nu}_{0\to 1} = 2B \qquad E_1 - E_0$

$\bar{\nu}_{1\to 2} = 4B \qquad E_2 - E_1$

$\bar{\nu}_{2\to 3} = 6B \qquad E_3 - E_2$

Now, with that, you see that, the first nu 0 to 1 – nu bar corresponds to 2B, because that is nothing but the energy difference between E 1 and E 0. The new bar between 1 and 2 – transition from energy level 1 to 2 is 4B, which is the energy difference between E 2 and E 1. And the nu bar 2 to 3 is 6B – the energy differences between E 3 and E 2.

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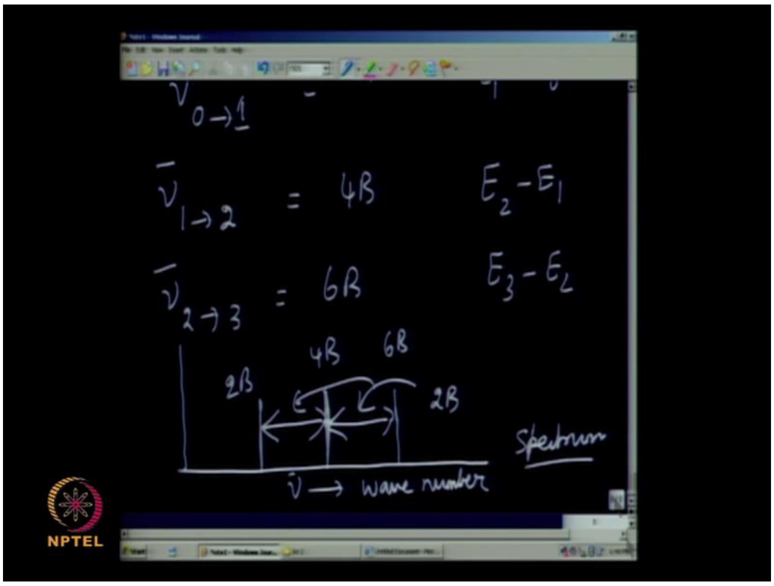

$\bar{\nu}_{0\to 1}$

$\bar{\nu}_{1\to 2} = 4B \qquad E_2 - E_1$

$\bar{\nu}_{2\to 3} = 6B \qquad E_3 - E_2$

And what you see is nothing but if you were to obtain the spectrum of this molecule, you will see if we plot this as the wave number unit and we plot the absorption or the absorbance along the y axis, what you will see is a transition corresponding to the frequency 2B, which is a transition from the ground state – rotational state to the J equal to 1 state. You will see one other transition. If there are enough molecules in the J equal to 1 state, you will see a transition from 1 to t – 2. If we plot the absorbance, we will see a transition corresponding to 4B. And if the molecule is in the J equal to 2 state, the absorption spectrum from J equal to 2 to J equal to 3 will give you a line corresponding to 6B. So, what you see is a series of equidistant lines – spectral lines. Remember that, the energy levels are not equidistant. The energy levels separate or separate from each other by different orders – different values – 0 to 2B to 6B, 6 to 12. The energy levels are not equidistant. But, the spectrum that you obtain, which are due to the transition between these energy levels, the spectrum is equidistant. Therefore, any two lines – adjacent lines – the gap between them gives you a value of 2B.

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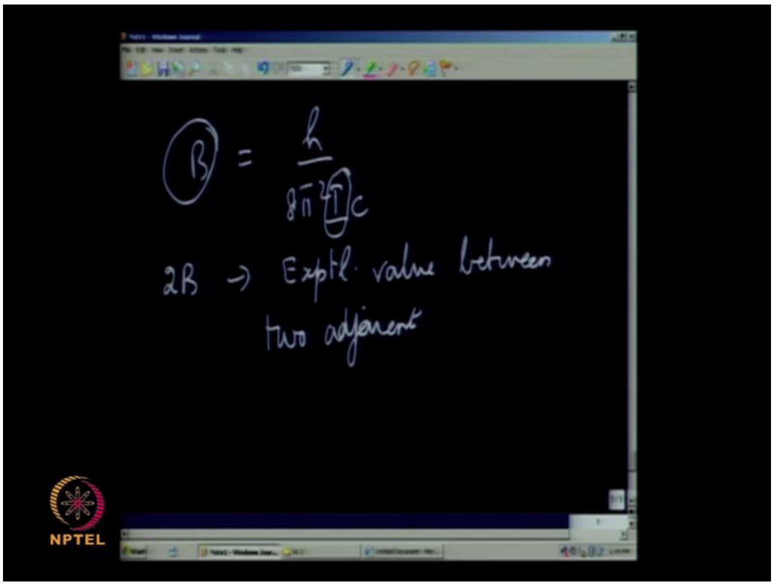

$$\boxed{B} = \frac{h}{8\pi^2 \boxed{I} c}$$

2B → Exptl. value between two adjacent

If you recall that, B is nothing other than h by 8 pi square I c. And if you know from the experimental spectrum, the gap between two successive lines as 2B as the experimental value between two adjacent lines; then a measurement of this from the experimental spectrum, immediately tells you how to get the values for I by simple multiplication. And given that, you know what molecule you are taking the spectrum on – whether it is hydrogen chloride or carbon monoxide for example, molecules which are permanent dipole moment, which are the only ones that you can see using microwave spectra. You see that, the reduced mass is something that you know immediately. And therefore, knowing I from the experimental spectrum, allows you to calculate the interatomic distance in that molecule. The more accurately you know the value of B; the more accurately you can calculate the value of the interatomic distance and so on.

Today, after 50-60 years of research in Microwave spectroscopy, one can get the bond distances in experimental diatomic spectra up to about the third or the fourth decimal in angstroms, which is a very, very high level of accuracy. Therefore, experimental microwave spectroscopy is the most important means for determining the interatomic distances in a diatomic molecule experimentally. And confirming the value through various theories, you can predict the value of the interatomic distance and verify with the experiments.

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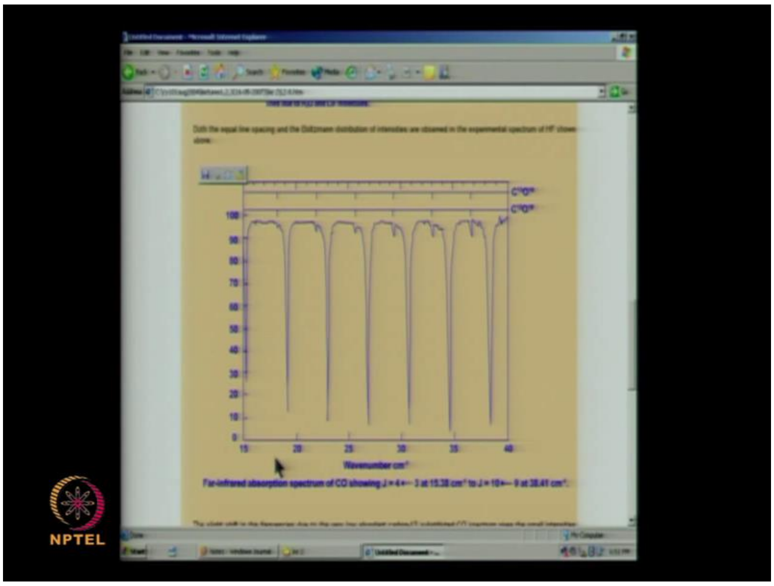

Let us see a few diatomic molecular spectra before we move on to the next topic in this subject. I will show you two spectra here. The spectrum that you see in this picture is the spectrum of carbon monoxide. And let me read the lines of the text here. It is the x-axis is the wave number axis, which corresponds to centimeter inverse – 10 centimeters, 20 centimeters, etcetera inverses. And then the y-axis corresponds here to the absorption – the extent of absorption. And you see a beautiful equidistant spectrum as you see between the nearby fix. And the scale here tells you that, this is an overlapping spectrum of two molecules – molecule carbon monoxide with the carbon isotope – the naturally abundant isotope C 12 and O 16. That is a lower line corresponding to these ticks that you see here – the large ones – C 12 O 16. And then you have the C 13 O 16 – its natural abundance of C 13 is very low. And you should know immediately why the isotopic masses will give rise to different spectrum.

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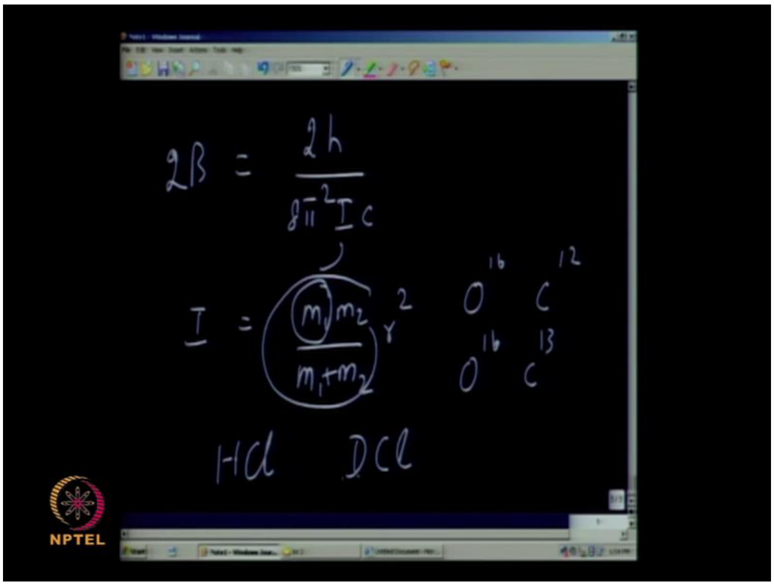

$$2B = \frac{2h}{8\pi^2 I c}$$

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

But, for both cases, what you see is between the different lines that you have here – 1, 2, 3, 4, 5 or between the lines here – 1, 2, 3, 4, 5, they are equidistant that, the two different isotopes of carbon give to different spectra should be obvious from this formula, which is given by that, the 2B is nothing but 2 h by 8 I square I c. And I is m 1, m 2 by m 1 plus m 2. Therefore, if the mass of one of the atoms is oxygen 16 and the other atom is carbon 12; you get one value for this times r square; you get one value for the reduced mass; and if the molecules – oxygen 16 and carbon 13; then you get another value for the reduced mass. And therefore, you see that, you get two different spacings – rotational spacings for the same molecule dependent on the isotopic masses of the compound.

Now, where do you think that, this difference will be maximum? The difference will be maximum; you recall the reduced mass will differ by a maximum value if for example, one of the masses double. You take the hydrogen spectrum – take HCl. And if you compare the hydrogen chloride spectrum with deuterium chloride DCl; you see that, the reduced masses will differ by a large amount. And therefore, any replacement of a hydrogen by a deuterium or a tritium will give you a very large shift in the microwave spectrum of the compound. Therefore, isotopic masses do play a role – a significant role in the microwave spectra of many of these compounds. So, the energy level is one part of the story.

As you recall from the first lecture, in a spectrum, we are interested in at least 2 or 3 different things. And as far as this course is concerned, we are interested in 2 of the 3 things namely, the line positions and the line intensities. The line widths are very complicated. So, we will try and avoid a description on line widths, which is usually a subject for the advanced course in molecular spectroscopy. Let us look at to the… We have looked at the line positions for a diatomic molecule as basically happening in a spectrum plotted with respect to the frequency or a wave number that, it will happen at 2B, 4B, 6B, 8B etcetera. So, there is the discretization of energy of the molecule due to the fact that we saw the Schrodinger equation; and which gives rise to quantum numbers. Here both the degrees – the rotation degrees of freedom have the same moments of inertia. And therefore, we have only one free running parameter namely, the moment of inertia. And we get a quantum number dependence J into J plus 1 as the energy level. So, in a sense, the line positions are now very clearly understood as far as the rigid microwave spectrum of a molecule is concerned. But, what about the intensities?

Let me show the spectrum of the same molecule carbon monoxide for both the cases: the C 12 O 16 and C 13 O 16. What you see here if you recall that, now, we understand why lines occur in this place, in this place, in this place, this place, etcetera. This is due to the B J into J plus 1 energy level structure. But, if you look at the intensity of this line verses the intensity of this line verses the intensity of this line, you see the intensities are clearly different as you go from one rotation to another rotational transition and so on.

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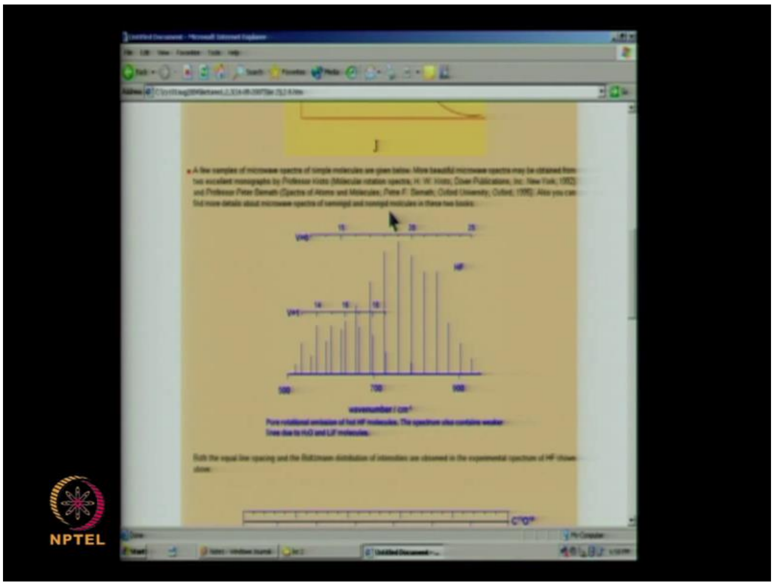

Now, we look at the other spectrum. Here is the rotational spectrum of the hydrogen fluoride – hot hydrogen fluoride gas phase molecule. And what you see here is two series of lines: the lines due to water molecule and the lines due to the lithium fluoride molecule. So, let us only concern ourselves with the lines corresponding to the hydrogen fluoride molecule, which you can see on this side. You see that, the lines – the spectral lines; there is something called a central line; this is pure rotational transition as the function of various quantum numbers. You see that, if you think about these lines – this one, this one – these are the rotational lines corresponding to the rotational lines of spectrum of hydrogen fluoride. So, what you see is a sort of an envelope pattern that, the rotational intensities seem to increase as you go further in wave numbers from smaller wave number here to larger wave numbers here; you see that, the rotational patterns seems to be like an envelope falling.

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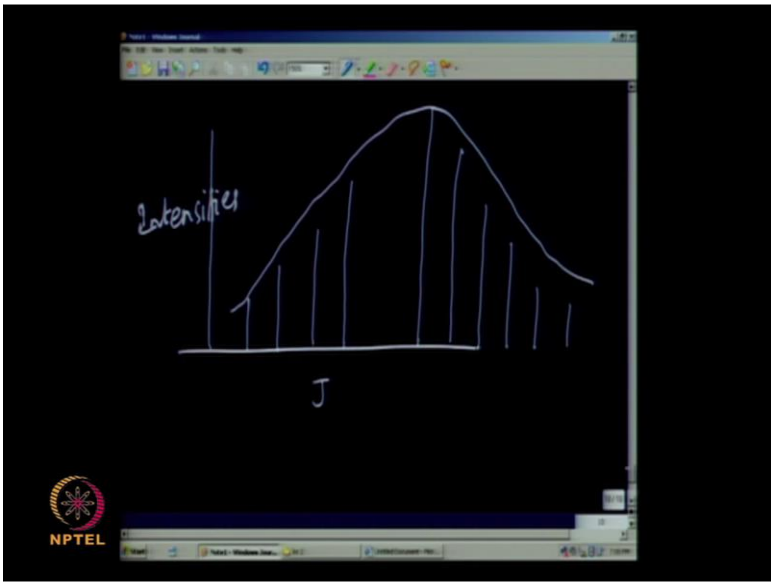

Typically, we can draw this rotational pattern for a diatomic molecule as a function of various values of J. The intensities if we have to plot, what you will see is – for J equal to 0, J equal to 1, J equal to 2 – equidistant lines and so on. And eventually, after a certain value of J, the lines will start thinning down again; the area will be small and you see a spectrum. And therefore, what you see is some sort of a shape like that as far as the intensities are concerned.

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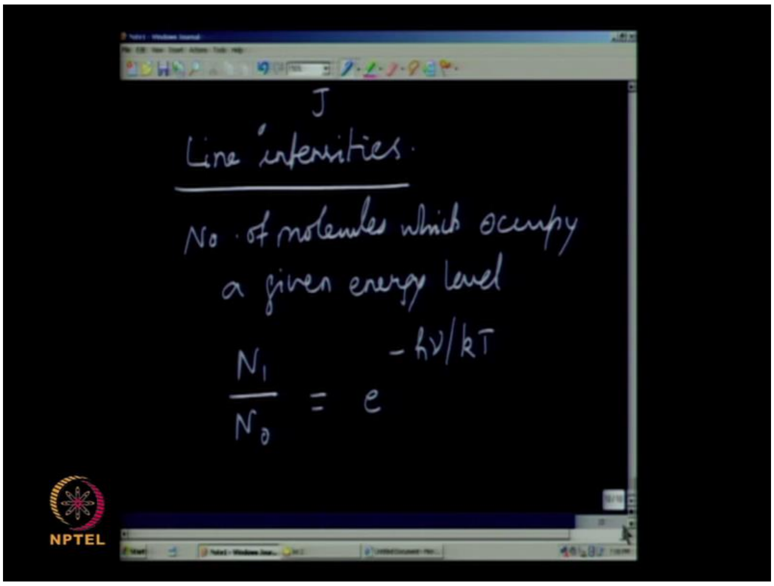

J

Line intensities.

No. of molecules which occupy a given energy level

$$\frac{N_1}{N_0} = e^{-h\nu/kT}$$

And there is a simple explanation in the case of rotational spectra while the line intensities vary as they are. So, if we think about the line intensities, recall from last lecture, the number of molecules, which populate a given energy level or which occupy – let me not use the word populate, but which occupy a given energy level; for a two-level system, you recall that we use the formula N 1 by N naught as E to the minus h nu by k T.

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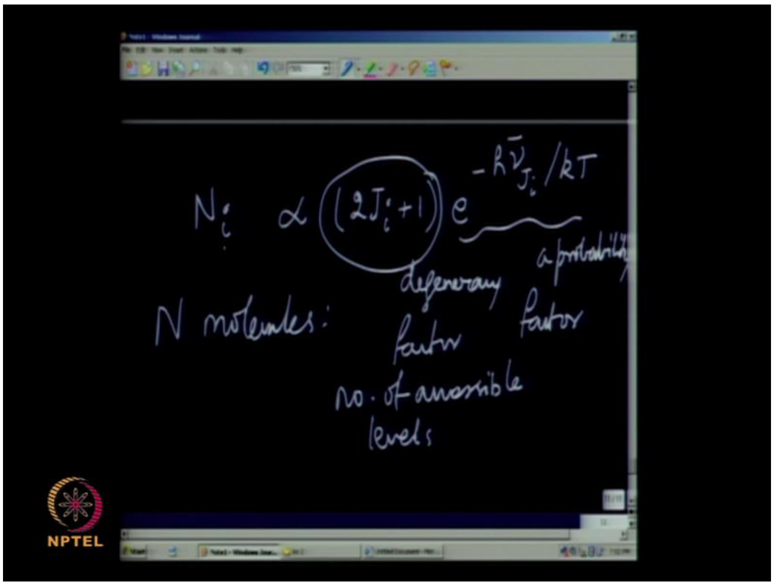

$$N_i \propto \boxed{(2J_i+1)}\, \underbrace{e^{-h\bar{\nu}_{J_i}/kT}}$$

degeneracy factor

no. of accessible levels

a probability factor

N molecules:

There is a general principle by which we can describe the thermal distribution of molecules over various energy levels that you see here. Here it is a two-level energy system – two energy level system. And if you have multiple energy levels like the rotational case, the number of molecules N i in a given energy level i is approximately proportional to the degeneracy associated with that level 2 J i plus 1 times e to the minus h nu J i by k T. If there is a total of N molecules in the system and if there are various energy levels that the molecules can access; then what you see is the relative populations of molecules in each of these levels I corresponding to the quantum number J i is given by the product of a degeneracy factor, which is number of accessible levels for each value of J multiplied by a probability factor, which is a probability factor, which tells you what is the likelihood that, the energy level will be occupied. Now, the total number N is nothing but the sum over all the N i's.

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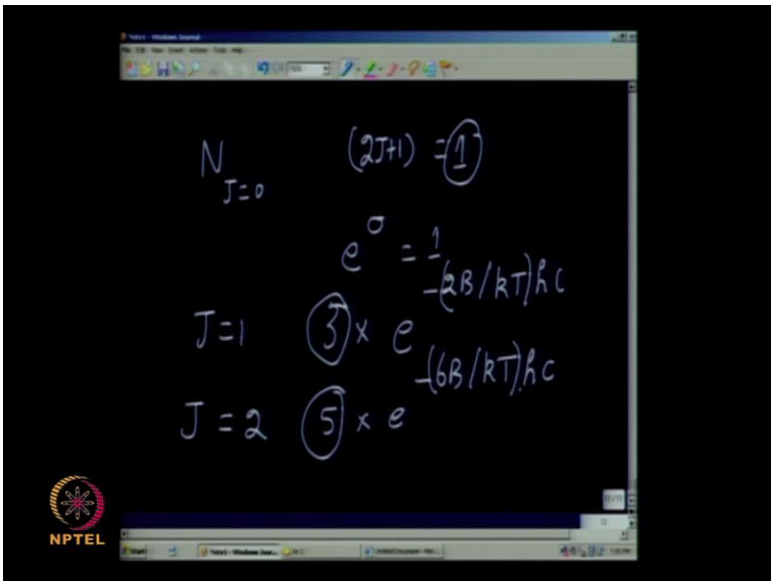

$N_{J=0}$ $(2J+1) = ①$

$e^{0} = 1$

$J=1$ ③ $\times\ e^{-(2B/kT)hc}$

$J=2$ ⑤ $\times\ e^{-(6B/kT)hc}$

If you write the total as nothing but the sum over N i; what you see is clearly that, N i is a fraction less than 1 for each value of i, each value of the energy levels; and the fraction are multiplied by the number of such degenerate energy levels available for the system multiplied by a probability factor. This probability factor is not very different from the Maxwell-Boltzmann distribution factor that you are associating with thermal equilibrium. It is a same thing. Therefore, under thermal equilibrium in a gas phase, the molecules occupy energy levels according to this formula. And it is immediately seen that, when you write it for J equal to 0, the degeneracy factor – 2 J plus 1 is 1; and the energy is e to the minus h nu – is the energy level associated with J equal to 0 is 0. Therefore, it is e to the 0. So, it is 1. So, J equal to 0 is simply 1 in a total of many such energy levels. If you look at J equal to 1, it is this 3 – 2 J plus 1 is 3. And the probability factor is e to the minus h nu is minus 2B by kT. And for J equal to 2, it is five times e to the minus 6B by k t. The h nu corresponds to the value of the energy.

If you remember, N i corresponds to h nu J, which is the energy level associated with nu J – with the quantum number J. Therefore, what you have is the energy. The energy is 2B in wave numbers. k T is to be technically right. I should write in a addition to this, this whole thing should be multiplied by h c. This whole thing should multiplied, because k T has the dimensions of energy. And therefore, B into h c is the energy associated with the system. So, what you have is 6B h c divided by k T dimensionally. So… But, what is important to see is that, as the J value increases, the degeneracy factor keeps on increasing, but the exponential factor that you see has this strange property that, exponential minus 2B by k T minus 6B by k T times h c and so on. So, the exponential factor seems to decrease.

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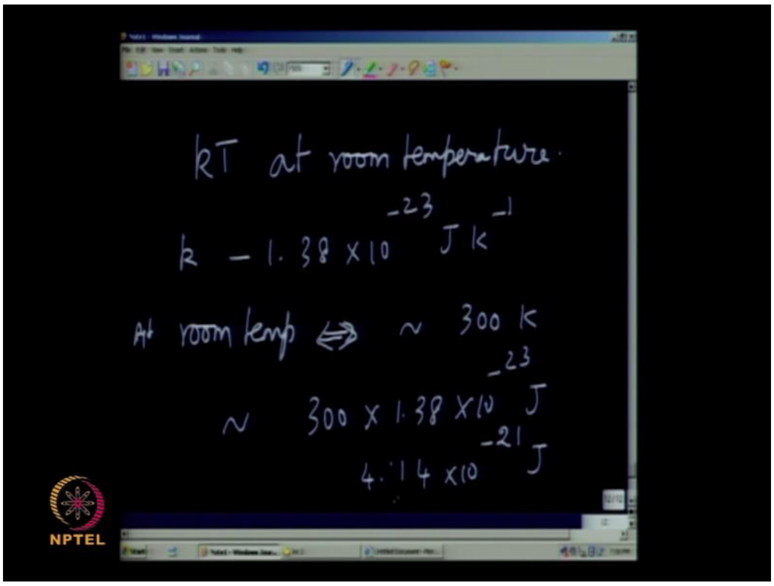

kT at room temperature.

$k - 1.38 \times 10^{-23}\ J\ K^{-1}$

At room temp $\Leftrightarrow \sim 300\ K$

$\sim 300 \times 1.38 \times 10^{-23}\ J$

$4.14 \times 10^{-21}\ J$

But the think about at room temperature, what is the value of k T; k T at room temperature. The Boltzmann constant k has the value 1.38; approximately, I am writing down as 10 raise to minus 23 joules per kelvin. And at room temperature… Let us not worry about India, the room temperature generally in the text book that you see is about 300 kelvin. And the assuming that, we are looking at the average temperatures of 300 kelvin, k T is of the order 300 into 1.38 into 10 raise to minus 23 joules. Now, there is a kelvin is taken care of here. That is the total energy. So, what you have is 4 3 1; and then what you have is 4.14 times 10 raised minus 21 joules approximately.

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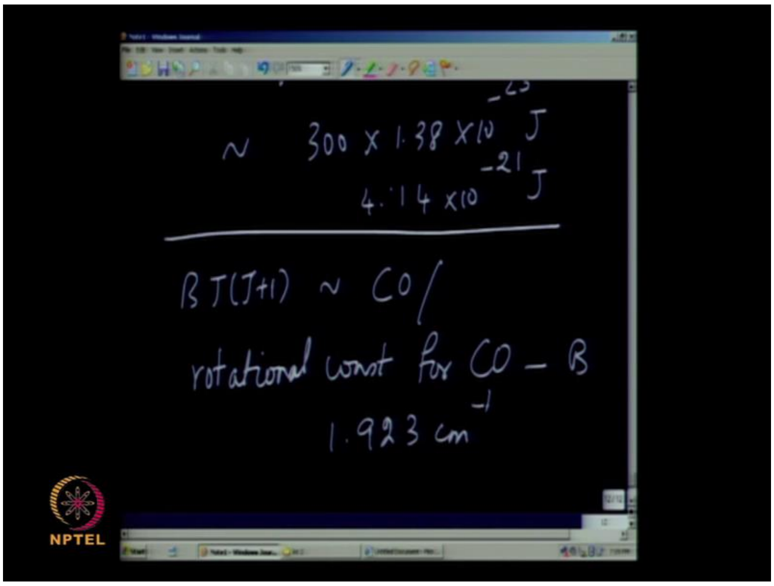

$\sim 300 \times 1.38 \times 10^{-23}$ J

4.14×10^{-21} J

$BJ(J+1) \sim$ CO/

rotational const for CO – B

$1.923\ \text{cm}^{-1}$

Now, compare this with the B J. Let us calculate the values of B J into J plus 1 for something like a simple molecular state carbon monoxide or h… Let me see what data I have with me here. The rotational constant for carbon monoxide B, the value of B is given as 1.923 centimeter inverse. So, given this as the B value, h c B is something that you can calculate; h is Planck’s constant; c is the speed of light.

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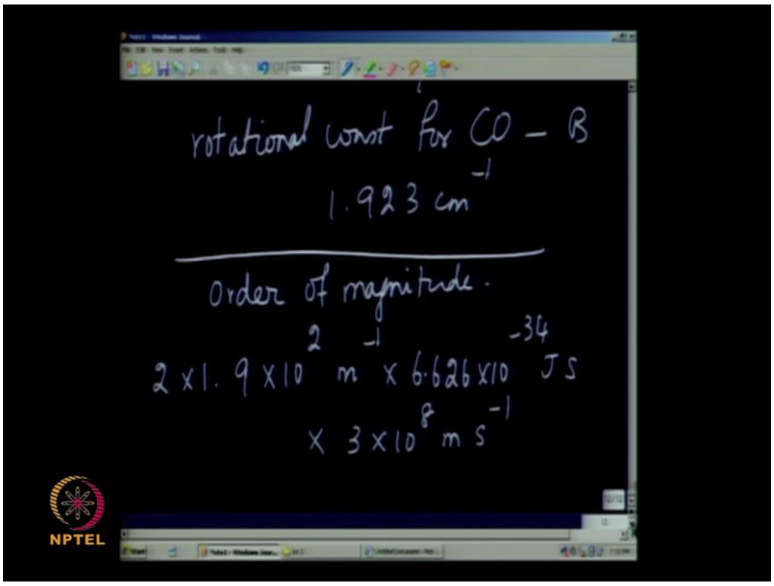

rotational const for CO – B

$1.923\ \text{cm}^{-1}$

Order of magnitude.

$2 \times 1.9 \times 10^{2}\ \text{m}^{-1} \times 6.626 \times 10^{-34}\ \text{J s}$

$\times\ 3 \times 10^{8}\ \text{m s}^{-1}$

So, a quick order of magnitude estimate; let us just do a quick order of magnitude calculation; let us not do the actual numbers. Order of magnitude is 1.9 into 10 raised 2 meter inverse; we are using SI units. This is the B value. And the energy is let us say 2B; for the first J equal to 1, it is 2B. So, this is 2B. And the h is 6.626 into 10 raised to minus

34 joules second. And c – the speed of light; let us simply write 3 into 10 raised to 8 meters per second. So, the approximate energy that you have for h c B to h c B; this corresponds to E 1.

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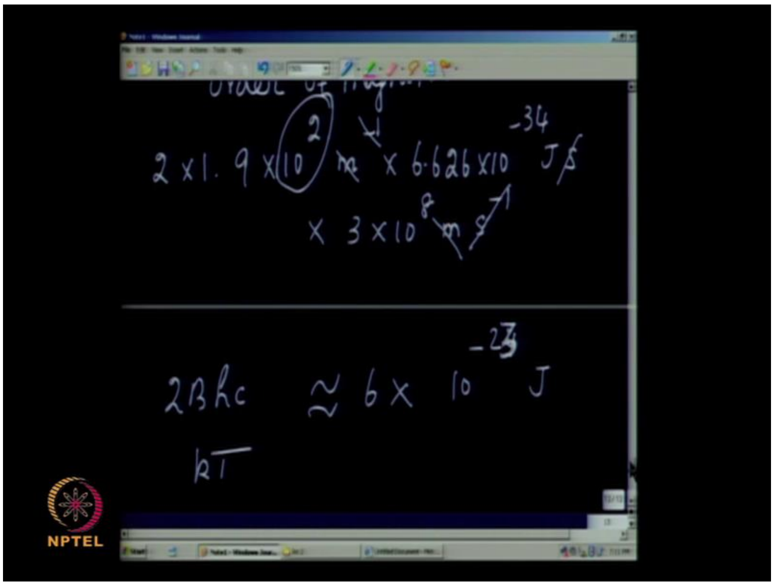

$$2 \times 1.9 \times \boxed{10^{2}}\, \cancel{m}^{-1} \times 6.626 \times 10^{-34}\, J\, \cancel{s} \times 3 \times 10^{8}\, \cancel{m}\, \cancel{s}^{-1}$$

$$2Bhc \approx 6 \times 10^{-23}\, J$$

$$\overline{kT}$$

The approximate value; let us first collect to the orders in terms of the powers of 10. What you have is minus 34 plus 8, which is minus 26 and 2 minus 24. So, you have 10 raised to minus 24. The energy is joule, because the joule second – second inverse and the meter and the meter inverse cancel out. So, the dimension is that of the energy. And you have roughly 3.8 here into another 3 into another 6.6. So, you are looking at about 18, about 20 into 3 – approximately 60. So, let me write to this in a gross approximation as 6 into 10 raised to minus 23 joules.

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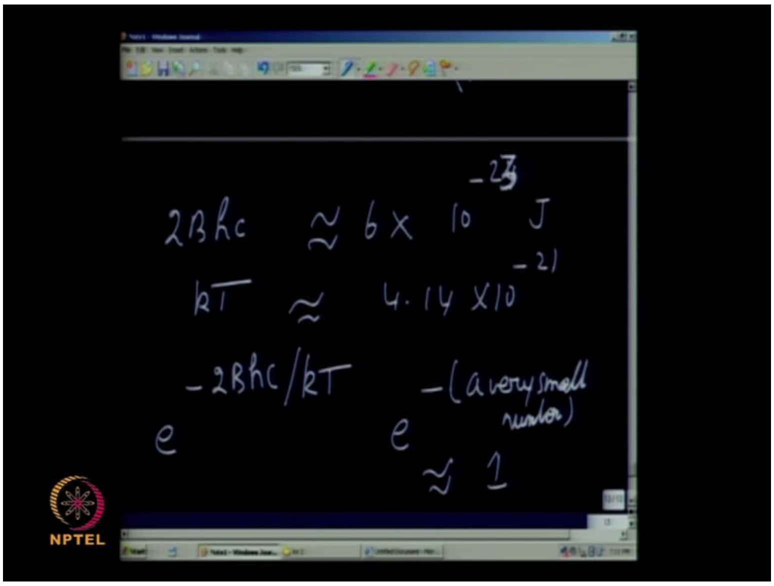

$$2Bhc \approx 6 \times 10^{-23}\ J$$

$$kT \approx 4.14 \times 10^{-21}$$

$$e^{-2Bhc/kT} \quad e^{-(\text{a very small number})} \approx 1$$

Given this as the 2B h c and given k T earlier as approximately 4.14 into 10 raised to minus 21, k T is 4.14 into 10 raised to minus 21. So, you see that, the value e to the minus 2 B h c by k T is e to the minus – a very small number. And this is almost equal to 1 – almost equal to 1; it is not exactly 1, but the difference between 1 and this is very very small.

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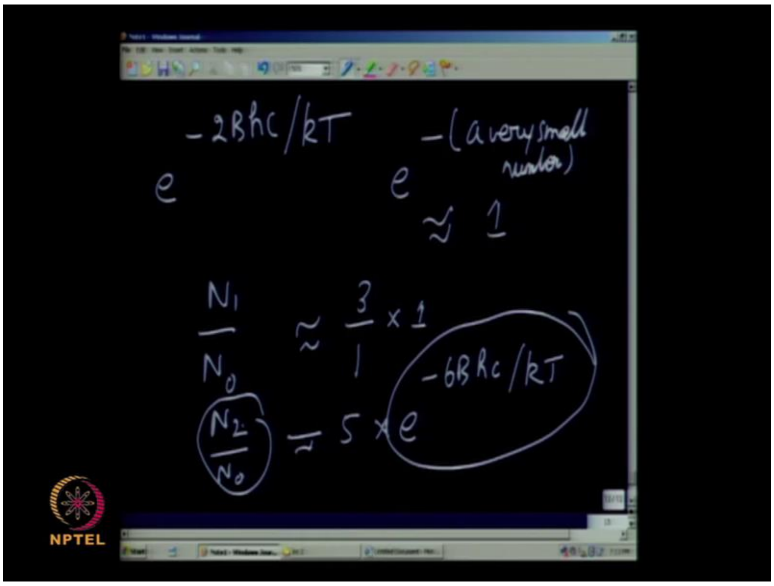

$$e^{-2Bhc/kT} \quad e^{-(\text{a very small number})} \approx 1$$

$$\frac{N_1}{N_0} \approx \frac{3}{1} \times 1$$

$$\frac{N_2}{N_0} \approx 5 \times e^{-6Bhc/kT}$$

And therefore, what you see is that, when you write the number N 1 by N 0 is the degeneracy factor is 3 here; the degeneracy factor is 1. And this factor is approximately 1, because the different between the 2B and the 6B here is very small. Likewise, when you do by N 2 by N naught, it is now of the order of 5; and of course, there is an exponential. If you want to calculate exactly, it is N 2 by N naught is 5 into the differences between E 2 and E 0; E 2 is 6B. So, what you have is minus 6B h c by k T, which is still a small number. And therefore, N 2 by N naught is greater than N naught; and N 1 by N naught is greater than N naught. Therefore, the intensities of these lines for the first energy state and the next energy state etcetera keep on increasing up to a certain value of J when this becomes an important number and it starts reducing the ratios. And this is exactly what you see as the pattern in what we have here that, 2J plus 1 times the exponential of minus e J by k t keeps increasing the ratios – keeps increasing because of the 2J plus 1 up to a certain value of J. And beyond that, the exponential factor is important. Therefore, you see that the intensities come down. This is purely the case of a diatomic molecule. So, let me summarize the part of microwave spectroscopy that we have today.

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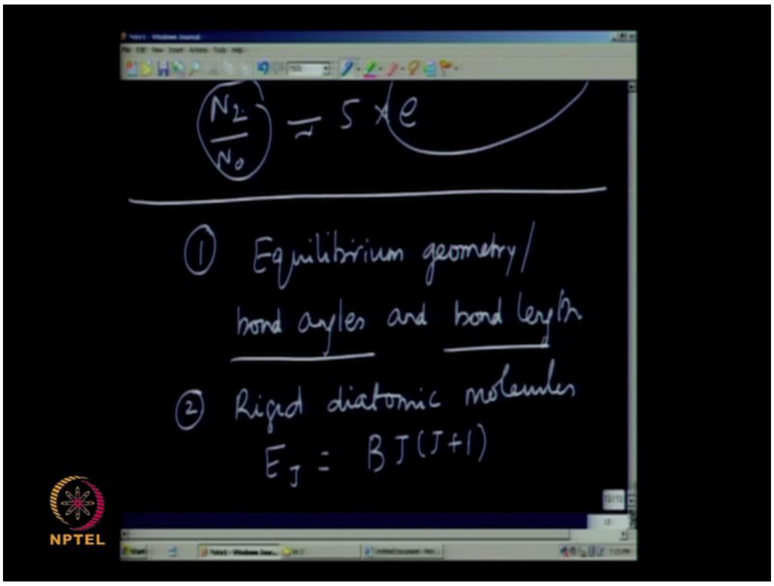

$\frac{N_2}{N_0} \simeq 5 \times e$

① Equilibrium geometry/ bond angles and bond length

② Rigid diatomic molecules
$E_J = BJ(J+1)$

What is important is of course, determines equilibrium geometry. And therefore, it is a very important tool; you can get bond angles and bond lengths. We have not worried about bond angles, because we were worried only about the linear molecule today – the bond length to very high order in the gas phase. For a rigid diatomic molecule, the model is extremely simple and it gives you energy levels, which are a function of the E J is nothing but B J into J plus 1; where B is the rotational constant associated with the diatomic molecule.

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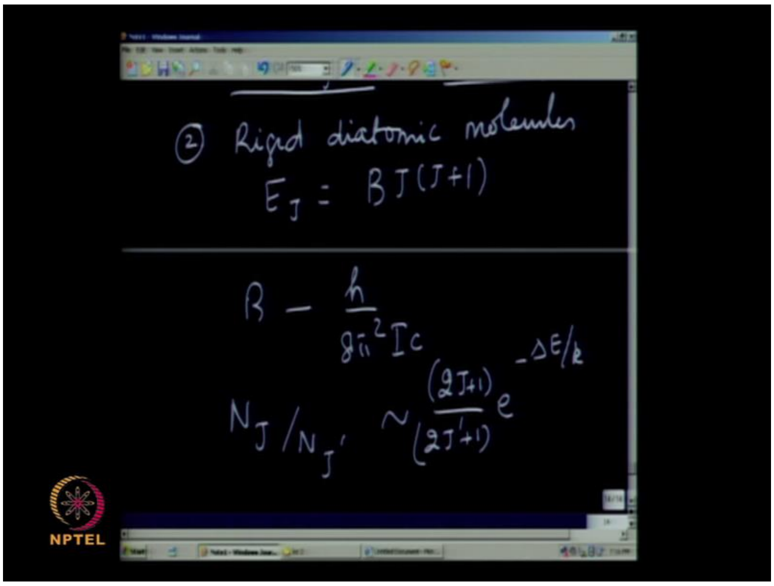

② Rigid diatomic molecules

$E_J = BJ(J+1)$

$B - \frac{h}{8\pi^2 Ic}$

$N_J / N_{J'} \sim \frac{(2J+1)}{(2J'+1)} e^{-\Delta E/k}$

B is h by 8 pi square I c; I is the moment of inertia. And therefore, given the reduced mass of the molecule, the interatomic distance can be calculated.

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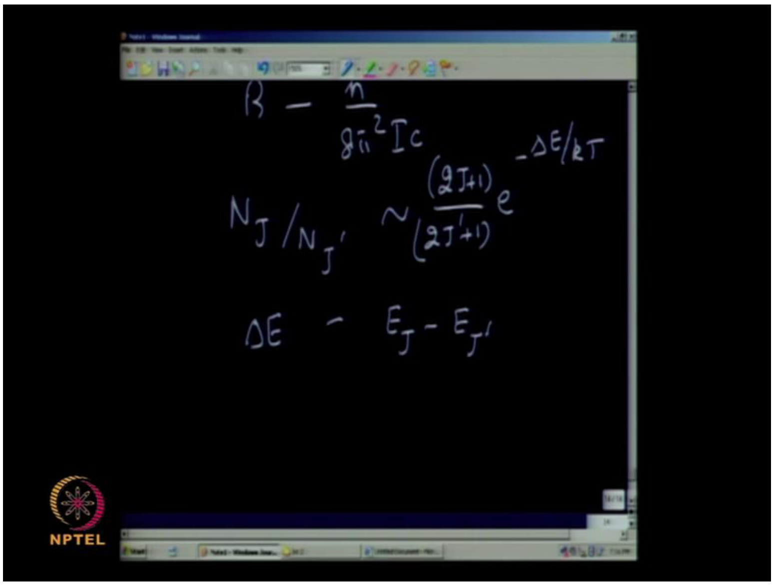

$B - \frac{h}{8\pi^2 Ic}$

$N_J / N_{J'} \sim \frac{(2J+1)}{(2J'+1)} e^{-\Delta E/kT}$

$\Delta E - E_J - E_{J'}$

And also, the ratios N J verses N J prime in the form of a Boltzmann distribution gives you 2J plus 1 divided by 2J prime plus 1 e to the minus delta E by k T; where delta E is the energy difference E J minus E J prime. Given this distribution, what you see as the Boltzmann distribution is what you get in the experimental spectrum of these molecules.