Chemistry II: Introduction to Molecular Spectroscopy
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Lecture - 21
Video Tutorial 2 – Part II

Welcome back to the video for solving problems in elementary spectroscopy. This continues from what I just did for four problems in the video tutorial 2. And we shall start with next problem namely problem 5.

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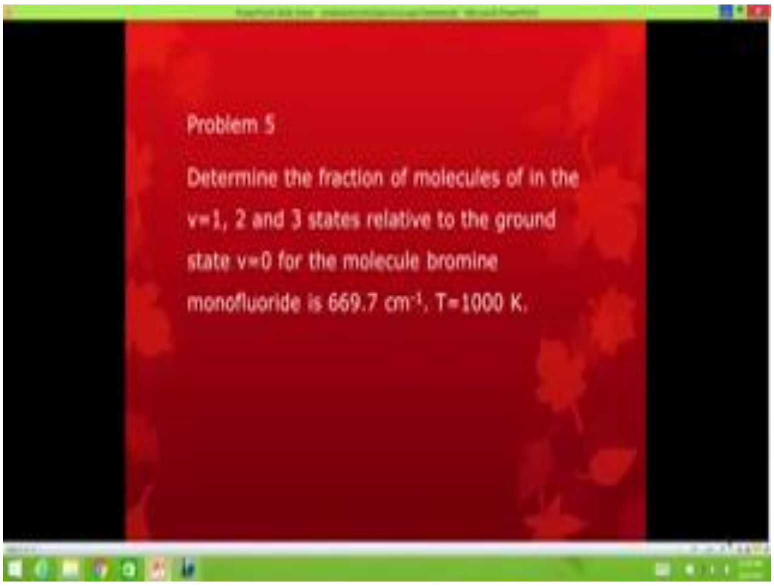

Problem 5

Determine the fraction of molecules of in the v=1, 2 and 3 states relative to the ground state v=0 for the molecule bromine monofluoride is 669.7 cm^{-1}. T=1000 K.

In which we are asked to do the following: determine the fraction of molecules in the v is equal to 1, 2, and 3 state relative to the ground state v is equal to 0 for the molecule bromine, monoflouride being, I think the last some type of graphical things here. The frequency of the transition is 669.7 centimeter inverse. So, what the problem say is at T is equal to 1000 Kelvin.

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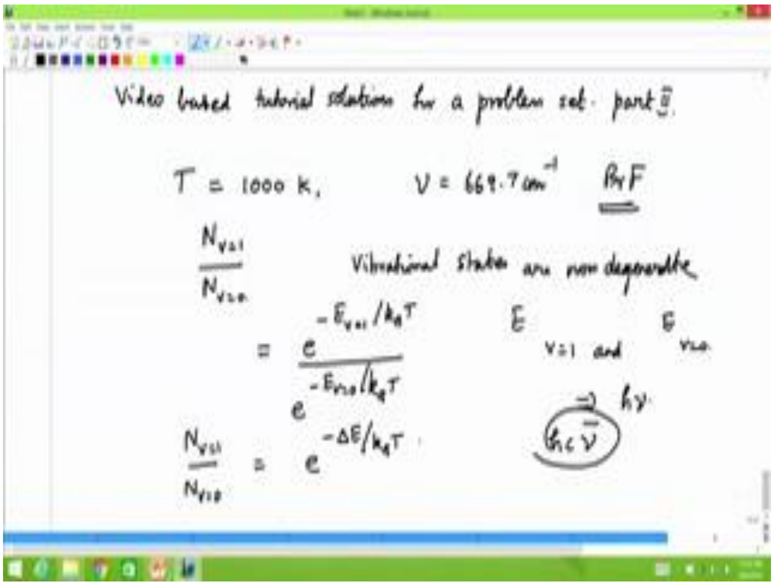

Video based tutorial solution for a problem set. part II.

$T = 1000\ \mathrm{K}$, $\quad \nu = 669.7\ \mathrm{cm}^{-1}$ $\quad$ BrF

Vibrational states are non degenerate

$$\frac{N_{v=1}}{N_{v=0}} = \frac{e^{-E_{v=1}/k_BT}}{e^{-E_{v=0}/k_BT}}$$

$E_{v=1}$ and $E_{v=0}$ $\rightarrow h\nu$

$\boxed{hc\bar{\nu}}$

$$\frac{N_{v=1}}{N_{v=0}} = e^{-\Delta E/k_BT}$$

At T is equal to 1000 Kelvin and when nu is given by 669.7 centimeter inverse for the molecule bromine monoflouride. You are asked to calculate the number of molecules in the v is equal to 1 relative to the number of molecules in the v is equal to 0 state. This is very elementary problem in the sense it looks at the Boltzmann population at equilibrium, and since vibrational states for this single degree of freedom or non degenerate; vibrational states are non degenerate.

The ratio is given by the simple exponential factor namely exponential minus E v is equal to 1 by K B T divided by exponential minus E v is equal to 0 by K B T. And you know the difference between v is equal to 1 and v is equal to 0, the energy. The answer is h nu, and nu is given as 669 therefore hc nu bar. Therefore, the e to the minus delta E by K B T for this ration N is equal to v is equal to 1 to N at v is equal to 0, this delta E is given by hc nu bar. And the nu bar is given as 669.7 centimeter inverse.

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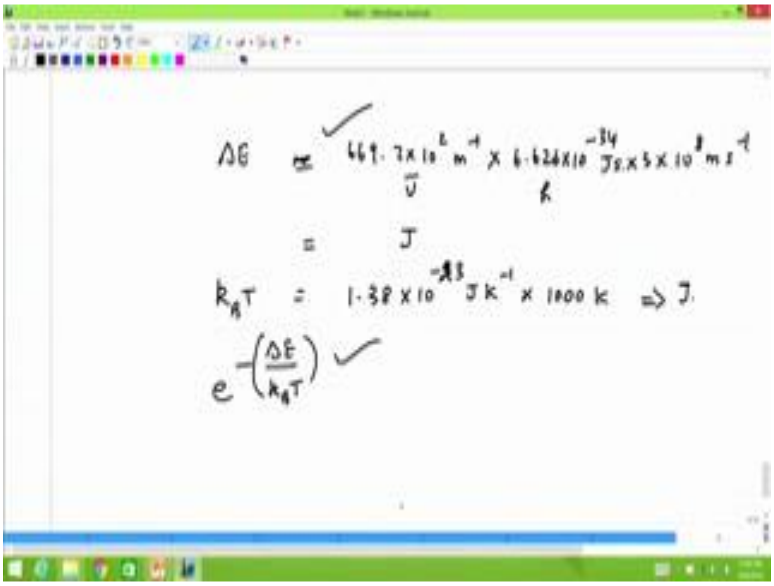

$$\Delta E = \underset{\bar{\nu}}{669.7 \times 10^{2}\, m^{-1}} \times \underset{h}{6.626 \times 10^{-34}\, Js} \times 3 \times 10^{8}\, m\, s^{-1} \checkmark$$

$$= J$$

$$k_B T = 1.38 \times 10^{-23}\, J K^{-1} \times 1000\, K \Rightarrow J.$$

$$e^{-\left(\frac{\Delta E}{k_B T}\right)} \checkmark$$

Therefore what you have to do is to ensure that we use the right units namely it is given as 669.7 into 10 to the 2 meter inverse times 6.626 into 10 raise to minus 34. This is h this is nu bar times 3 into 10 to the 8 meters per second. And this is joules and the meter inverse and so what you see is the delta E is given as joule second times r. Therefore, the answer is given in terms of joules. So, this can be calculated and K B T is 1.38 times 10 to the minus 23 joules per Kelvin and it is calculated at 1000 Kelvin, so that is given as joules.

Therefore, delta E by K B T is a numerical exercise. For you have to do that and take the exponential of minus that in order to calculate the ratios of N between the two different levels. And the only thing that you have to do for 2 and 3 is that for 2 the energy difference between e 0 and e 2 is 2 h nu and for three it is 3 h nu. Therefore, you will see that there are relative populations in the first second and third excited state drastically come down to very, very small values.

That is the purpose of this exercise to show that in vibrational spectroscopy the number of molecules in the higher energy levels is much less than the number of molecules in the ground state. And this number is less if the frequency is even more. That was the idea for this problem therefore you can calculate that.

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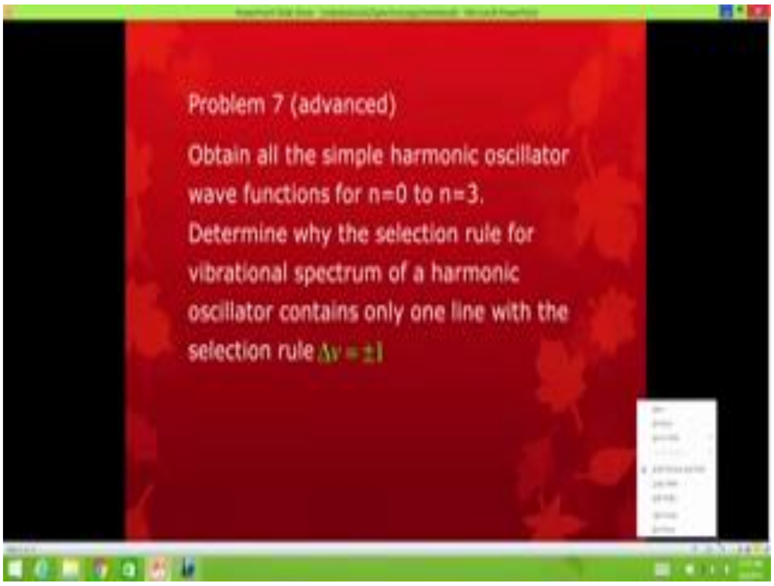

Problem 7 (advanced)

Obtain all the simple harmonic oscillator wave functions for n=0 to n=3. Determine why the selection rule for vibrational spectrum of a harmonic oscillator contains only one line with the selection rule $\Delta v = \pm 1$

Then next problem is formal process, it is basically asking you to write all the simple harmonic oscillator wave functions for N equal to 0 to N equal to 3. Is a text book exercise, and most important for this is determine why the selection rule for vibrational spectrum of a harmonic oscillator contains only one line with the selection rule delta v is equal to plus minus 1.That is important.

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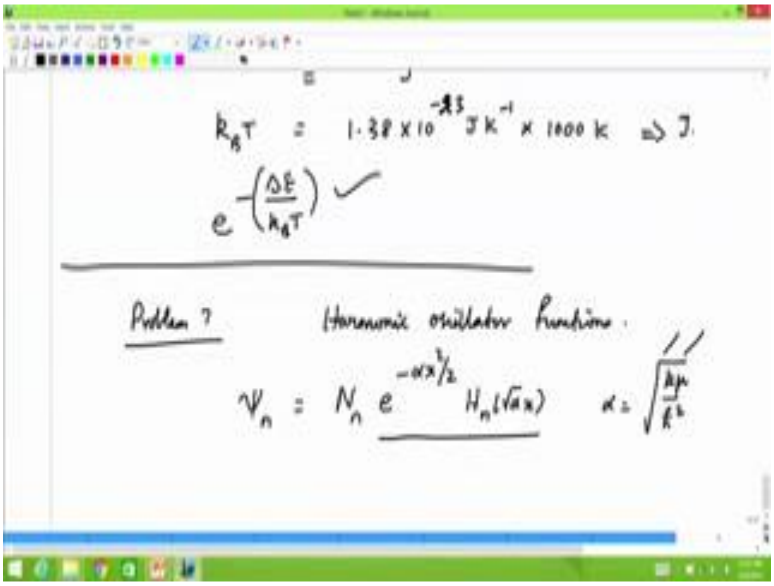

$k_B T = 1.38 \times 10^{-23}\, J K^{-1} \times 1000\, K \Rightarrow J.$

$e^{-\left(\frac{\Delta E}{k_B T}\right)}$ ✓

Problem 7 Harmonic oscillator functions.

$\psi_n = N_n \underline{e^{-\alpha x^2/2} H_n(\sqrt{\alpha} x)} \quad \alpha = \sqrt{\frac{k\mu}{\hbar^2}}$

Problem 7: and you are asked to write the harmonic oscillator functions. So, text book exercise please remember that the psi n is a normalization constant which is a function of N and then it is e to the minus alpha x square by 2 times H n of root alpha x.

Therefore, what is alpha, alpha is equal to square root of k mu by h bar square. So, k is the force constant mu is the reduced mass and those are the only two parameters of this problem. Therefore, this is the vibrational wave function.

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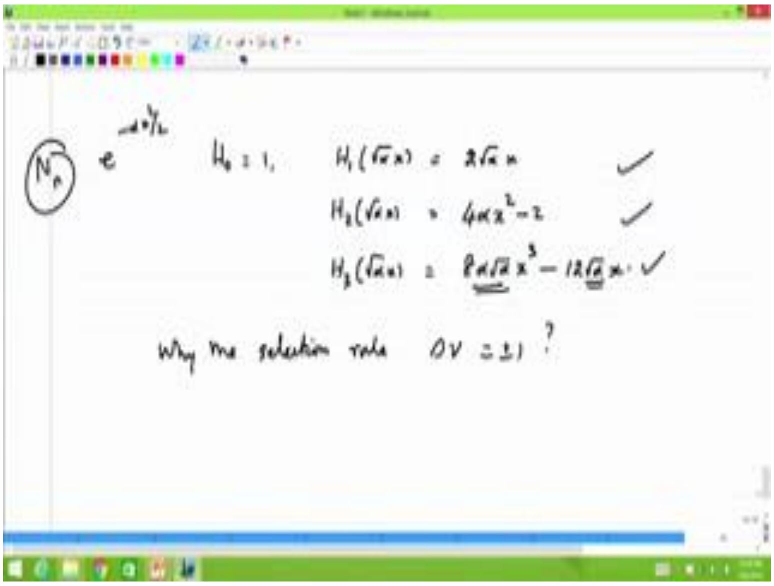

$\boxed{N_n}\ e^{-\alpha x^2/2}$ $\quad H_0 = 1,$ $\quad H_1(\sqrt{\alpha}x) = 2\sqrt{\alpha}x$ ✓

$H_2(\sqrt{\alpha}x) = 4\alpha x^2 - 2$ ✓

$H_3(\sqrt{\alpha}x) = \underline{8\alpha\sqrt{\alpha}}x^3 - 12\underline{\sqrt{\alpha}}x.$ ✓

Why the selection rule $\Delta v = \pm 1$?

And H 0 is 1, H 2 of root alpha x is 2 root alpha x, H 2 of root alpha x is 4 alpha x square minus 2, and the third H 3 root alpha x is 8 alpha root alpha x cube minus 12 root alpha x. Please remember this makes the whole expression dimensionless, because the alpha has a dimension of 1 by length. And therefore, you see that the harmonic oscillator x is the length parameter it is distance from the equilibrium for vibration, and therefore this all quantity polynomials are dimensionless.

So, these are the corresponding forms and each one of them you have to multiply by to the minus alpha x square by 2 and also put down the general formula for N n. These are available in text books. But the second part of the problem is important namely why the selection rule delta nu is equal to plus minus 1.

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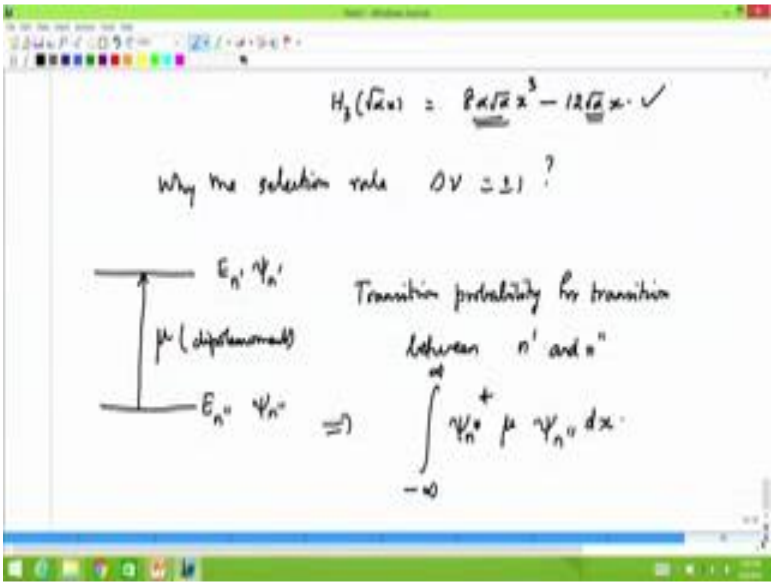

$H_3(\sqrt{\alpha}x) = 8\alpha\sqrt{\alpha}x^3 - 12\sqrt{\alpha}x$ ✓

Why the selection rule $\Delta v = \pm 1$?

Transition probability for transition between n' and n''

$$\Rightarrow \int_{-\infty}^{\infty} \psi_{n'}^{*} \mu \psi_{n''} dx$$

This is a mathematical statement that the selection rule for transition between E n with the wave functions psi n and e, let us write n double prime n prime psi n prime n double prime. The selection rule for vibrational transition is due to the dipole moment matrix element which connects these two states. In fact, the transition probability, this is the statement you have to take it from me. Transition probability for transition between n prime and n double prime is given by the absolute square of the integral from minus infinity to plus infinity psi n prime star mu which let me not write here, mu is he dipole moment here dipole moment not the reduced mass, Mu dipole moment psi n double prime dx.

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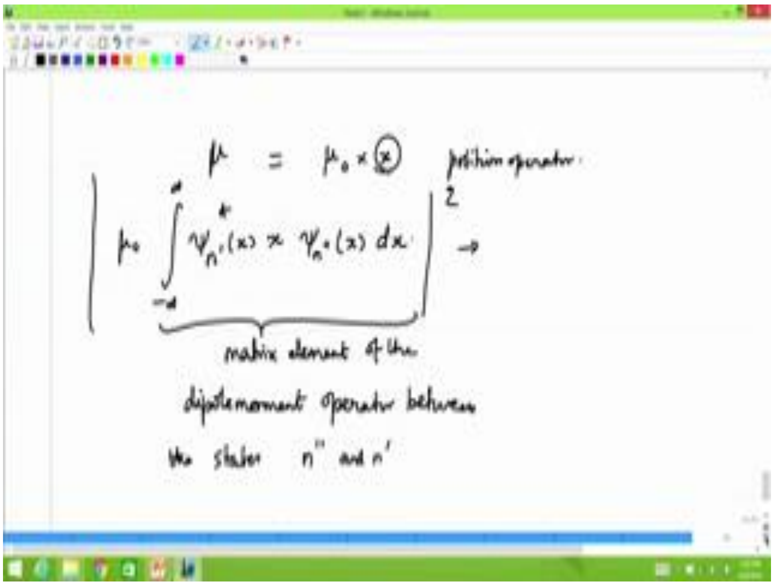

$$\mu = \mu_0 \times \textcircled{x} \quad \text{position operator}$$

$$\left| \underbrace{\mu_0 \int_{-\infty}^{\infty} \psi_{n'}^*(x)\, x\, \psi_{n''}(x)\, dx}_{\text{matrix element of the dipole moment operator between the states } n'' \text{ and } n'} \right|^2 \rightarrow$$

Therefore mu is essentially mu naught times x. And this x keeps changing therefore during vibration the dipole is created and changed destroyed and so are increased and decreased. Therefore, this x is the position operator and the mu naught is the constant for the permanent dipole moment position operator. Therefore, the dipole keeps changing from mu naught to mu naught times x during the process of vibration. And the integral that you needed to calculate is psi n prime of x from minus infinity to plus infinity star mu naught times x and then you have psi n double prime x dx.

This is what is calling the transition probability amplitude and the absolute square of this is the transition probability per unit time whatever units that you wanted to use. But the absolute square is the one which is connected with the actual process of transition between vibrational levels. Therefore, it is important for this bit what is called the matrix elements of the dipole moment operator, between the two states x n prime and n prime, n double prime and n prime.

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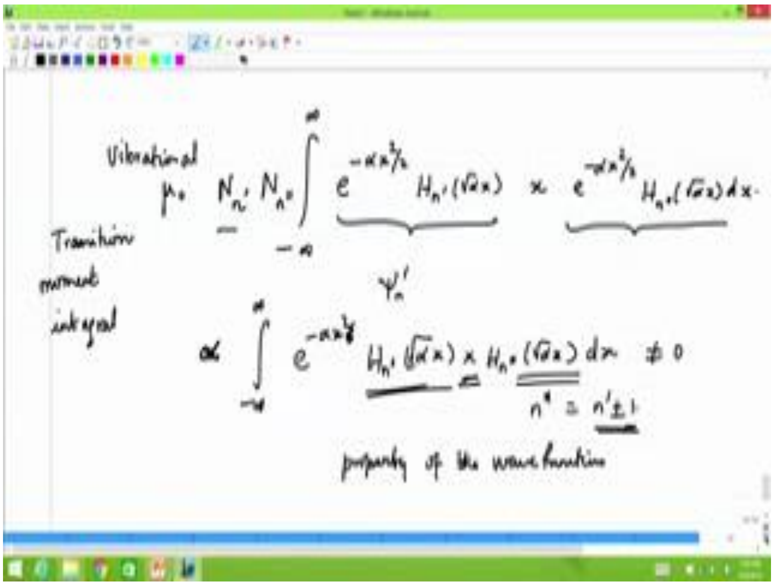

Vibrational

$$\mu_0 \; N_{n'} N_{n''} \int_{-\infty}^{\infty} \underbrace{e^{-\alpha x^2/2} H_{n'}(\sqrt{\alpha}x)}_{\psi_n'} \; x \; \underbrace{e^{-\alpha x^2/2} H_{n''}(\sqrt{\alpha}x)\,dx}$$

Transition moment integral

$$\propto \int_{-\infty}^{\infty} e^{-\alpha x^2} H_{n'}(\sqrt{\alpha}x) \times H_{n''}(\sqrt{\alpha}x)\,dx \neq 0$$

$$n'' = n' \pm 1$$

property of the wave function

So, the calculation essentially boils down therefore to writing down in the case of vibrational spectroscopy the psi n are given by the exponential minus alpha x square. So, let us write that minus infinity to plus infinity. The normalization constant associated with psi n prime which is en n prime and to the function is e to the minus alpha x square by 2 times h n prime root alpha x. This is psi including this, this is psi n prime. And then you have x times the mu not and then you have e to the minus alpha x square by 2 h n double prime root alpha x dx. So, it turns out to be from minus infinity to plus infinity proportional to let me drop the constants out, there is also n double prime for the wave function associated with this state that is the normalization concept for that state. So, this is the integral that needs to be calculated it is called the transition moment integral.

Now, without any further explanation I will just make the statement that this integral will be non zero only if when you write that like that the alpha x square by 2 the alpha x square by 2 ads up. And then this integral will be non zero only if n prime and n double prime differ by plus or minus 1, because it involves x. If it involves x square then the dipole moment is now being considered as the square of the amplitude for vibration that I mean those kind of things do happen when you talk about the unharmonic states of the molecule and so on. The dipole moment in the lowest level of approximation is simply proportional to the length. And therefore, what you see is the length x itself and this is harmonic oscillator model. And therefore, the harmonic oscillator model this integral is non zero only if n double prime is n prime plus or minus 1 because of the nature of the hermite polynomial.

Please understand the hermite polynomials are odd and even and so what you see here as that the integral becomes even only when n prime and n double prime and x these three products give you an even function. But, that argument should be very carefully stated because this does not mean N and n prime can differ by three, no does not work this integral is still 0. It cannot differ by other than 1.

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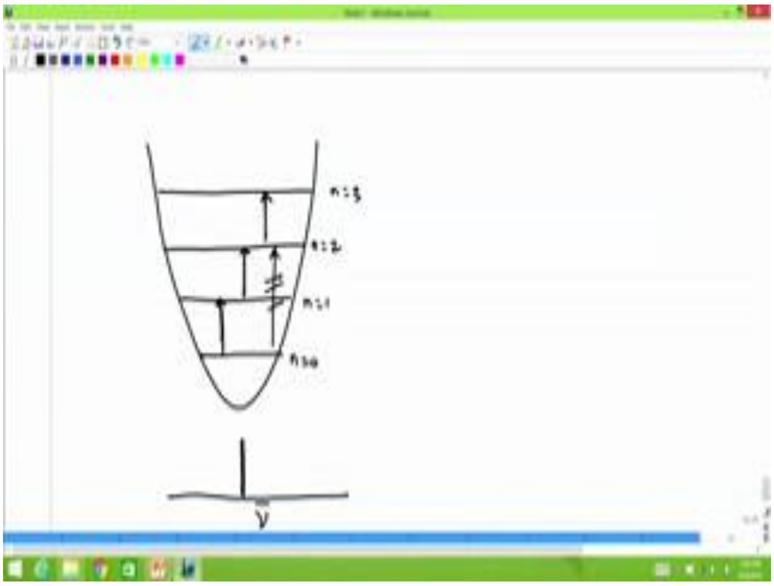

And therefore it is a property of the wave functions which results with the transition moments being connected only in the vibrational energy levels, if I have to write the potential energy and then simply write the vibrational energies as something like that N equal to 0 N equal to 1 N equal to 2 and so on, N equal to 3. The only transitions that possible that can be measured experimentally are this, because of the nature of the wave functions.

Therefore, the transition moment integral needed to be introduced in order for you to understand this problem. This will not happen. So, vibrationally there is only one line for a harmonic oscillator corresponding to this frequency, they are all the same. Therefore, there is only one line nu bar that is the important point. Next problem, I miss problem 6. So, let us go back to problem 6.

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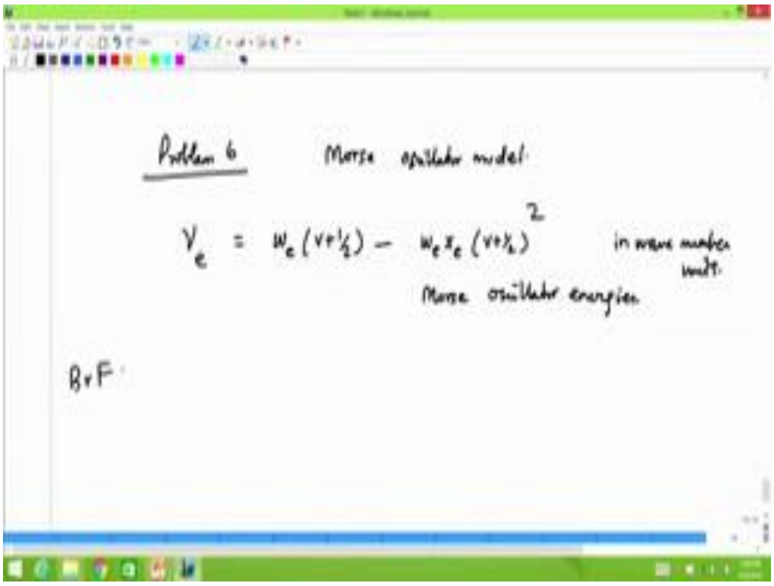

Problem 6 Morse oscillator model

$$\nu_e = \omega_e (v+\tfrac{1}{2}) - \omega_e x_e (v+\tfrac{1}{2})^2$$ in wave number unit.

Morse oscillator energies

B r F

Problem 6 is on a Morse oscillator model. Please remember the Morse oscillator model the energies are given as h omega e h bar omega e v plus half minus. Here I am using omega e in terms of wave numbers therefore let me write to this as h omega e, and then minus h omega e x e v plus half whole square. This is the expression for the Morse oscillator energies. If you are writing this in terms of centimeter inverse let us do one more thing, let us get rid of this and let us write this as sum nu e as omega e x e minus omega e time’s e plus half minus omega e x e time’s v plus half whole square. Therefore, all are in wave number units.

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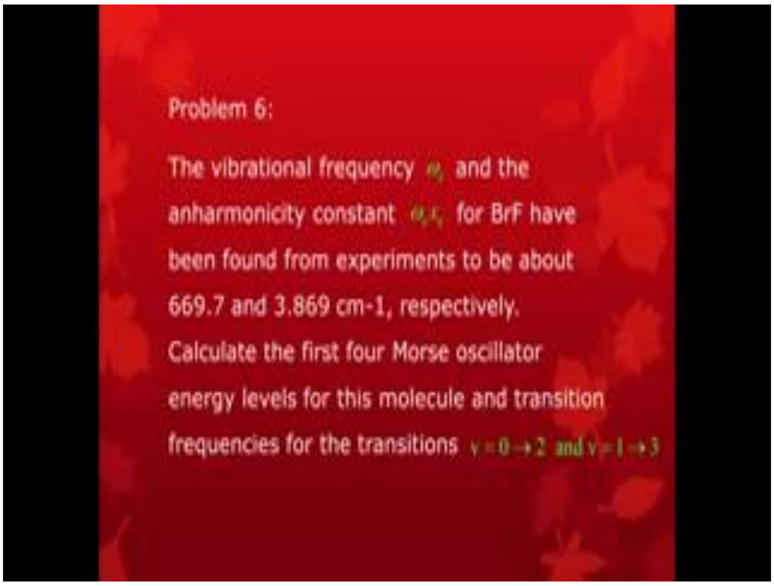

Problem 6:

The vibrational frequency ω_e and the anharmonicity constant $\omega_e x_e$ for BrF have been found from experiments to be about 669.7 and 3.869 cm-1, respectively. Calculate the first four Morse oscillator energy levels for this molecule and transition frequencies for the transitions $v = 0 \rightarrow 2$ and $v = 1 \rightarrow 3$

Now, the problem that is given to you is B r F. Let me now read the problem. The problem given to you is that the vibrational frequency omega e and unharmonocity constant omega e x e have been given from have informed from experiments to be about centimeter inverse to be 669.7 and 3.869 centimeter inverse. And you are asked to calculate the first four morse oscillator energy levels for those molecule and also the transition frequencies for the transitions v is equal to 0 to 2 and v is equal to 1 to 3. So, let us look at that.

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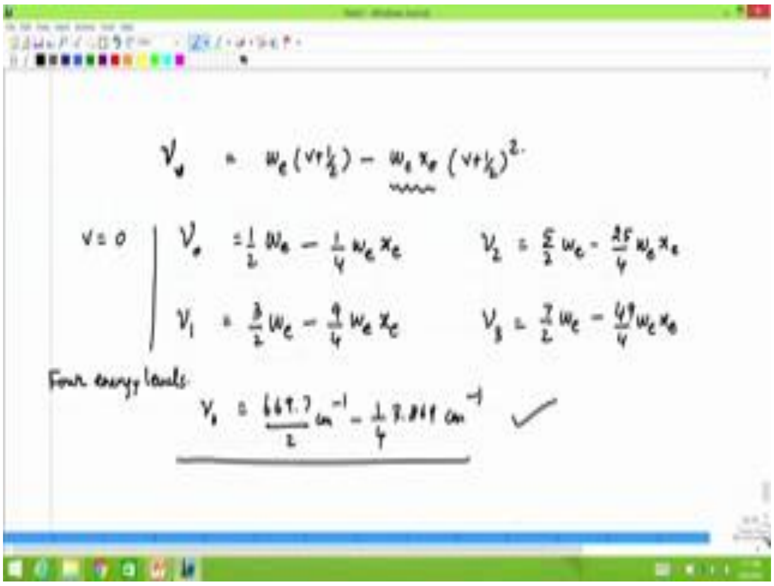

$$\nu_v = w_e(v+\tfrac{1}{2}) - \underset{\sim\sim\sim}{w_e x_e}(v+\tfrac{1}{2})^2$$

$v = 0$

$$\nu_0 = \tfrac{1}{2}w_e - \tfrac{1}{4}w_e x_e \qquad \nu_2 = \tfrac{5}{2}w_e - \tfrac{25}{4}w_e x_e$$

$$\nu_1 = \tfrac{3}{2}w_e - \tfrac{9}{4}w_e x_e \qquad \nu_3 = \tfrac{7}{2}w_e - \tfrac{49}{4}w_e x_e$$

Four energy levels

$$\underline{\nu_0 = \frac{669.7}{2}\,\text{cm}^{-1} - \frac{1}{4}\,3.869\,\text{cm}^{-1}} \quad ✓$$

So, the nu corresponding to the vibrational quantum number v is omega e times v plus half minus omega e x e, this is the unharmonocity v plus half whole square. So, when v is equal to 0 nu 0 is half omega e minus 1 by 4 omega e x e. nu 1 is 3 by 2 omega e minus this is 3 by 2 square, therefore 9 by 4 omega e x e. And likewise you are asked to do that for four levels is not it. So, nu 2 is 5 by 2 omega e minus 25 by 4 omega e x e.

And the last one omega 3 is 7 by 2 omega e minus 49 by 4 omega e x e. Because the second term is the square v plus half square so everything is a square here. So, these are the expressions for the four energy levels of the Morse oscillator. Now you are given omega e and omega e x e. So, this is given as 669, so if you write nu 0 it is 669.7 by 2 centimeter inverse and the other is 1 by 4 minus 1 by 4 times 3.869 centimeter inverse. So, you know that therefore in a similar way you can calculate nu 1, nu 2, and nu 3.

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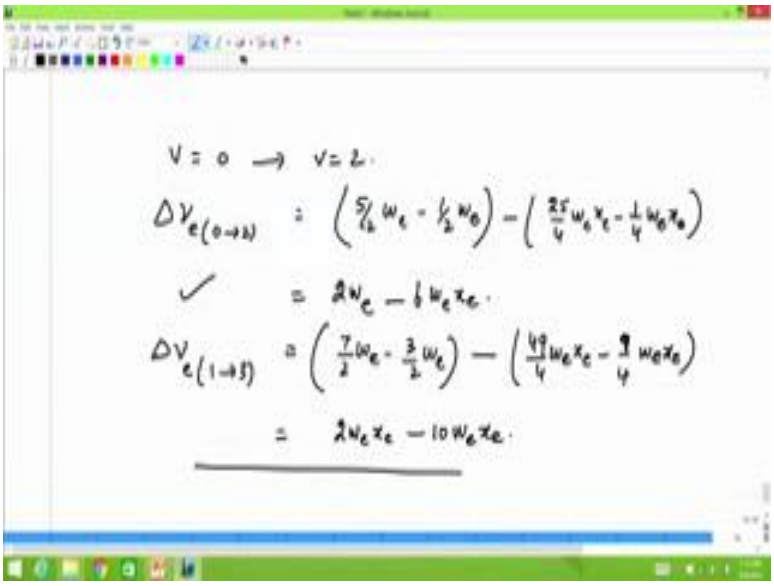

$v = 0 \longrightarrow v = 2$

$$\Delta\nu_{e(0\to 2)} = \left(\frac{5}{2}\omega_e - \frac{1}{2}\omega_e\right) - \left(\frac{25}{4}\omega_e x_e - \frac{1}{4}\omega_e x_e\right)$$

$$✓ \quad = 2\omega_e - 6\omega_e x_e$$

$$\Delta\nu_{e(1\to 3)} = \left(\frac{7}{2}\omega_e - \frac{3}{2}\omega_e\right) - \left(\frac{49}{4}\omega_e x_e - \frac{9}{4}\omega_e x_e\right)$$

$$= 2\omega_e x_e - 10\omega_e x_e$$

Now, what is important is the next step which is v is equal to 0 to v is equal to 2, so what is delta nu e 0 to 2. If you look at that its 5 by 2 omega e minus 1 by 2 omega e that is the first term minus 1 by 2 this is between 2 and 0. And the next one is minus 25 by 4 omega e x e minus 25 by 4 omega e x e minus 1 by 4 omega e x e. And so what you have is 2 omega e minus 6 omega e x e.

So, this is the second frequency. And likewise delta nu e from 1 to 3 is 7 by 2 omega e minus 1 to 3 is 1 is 3 by 2 omega e minus 7 by 2 corresponds to 49 by 4 omega e x e minus omega 1 corresponds to 9 by 4th 3 by 2 whole square, therefore 9 by 4 omega e x e. So, what you have is, 2 this is also 2 omega e x e minus 40 by 4, so it is 10 omega e x e. What do we gain from this process of calculating, that is important is not just the problem.

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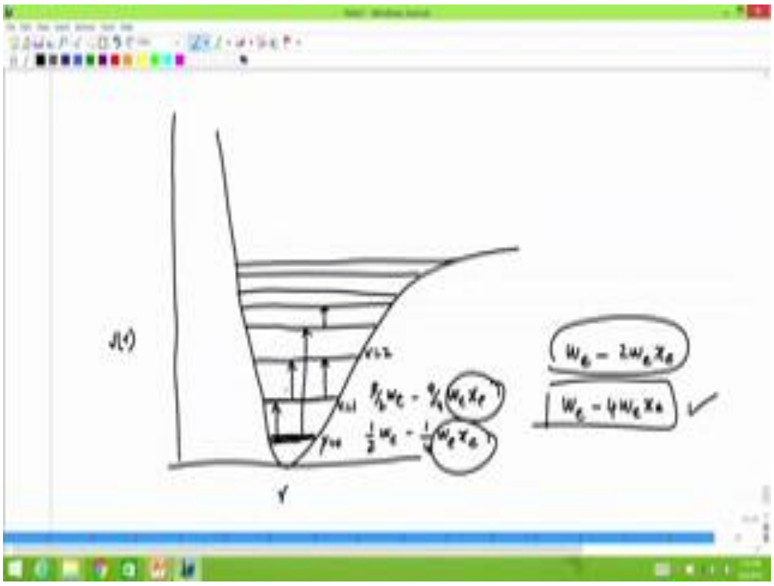

What is important from this problem is that if you look at it him Morse oscillator model which has a potential energy r v of r if you remember has something of this kind we saw in another problem. If you look at it the lowest energy level is half omega e minus 1 by 4 omega e x e. The next energy level if you look at it s 3 by 2 omega e minus 9 by 4 omega e x e. The difference between the two is 2 omega e x e the unharmonocity term is 2 omega e x e.

But, if you go to the next level the levels are closing in that is a purpose of doing this exercise. The levels are closing in that is successive energy differences are smaller because you remember this omega e x e term is negative to any omega e term, because you see any nearby energy level say v is equal to 0, v is equal to 1. If you look at the transition between 2 nearby levels you see this is 0 to 1 is omega e minus 2 omega e x e. But from 1 to 2 if you look at that v is equal to 2 it is again omega e, but 1 corresponds to 9 by 4 and 2 corresponds to 25 by 4 that is 5 by 2 whole square. Therefore, the difference between the two is 4 omega e x e.

So, the second energy level difference v is equal to 1 to 2 is smaller than the first energy level difference, therefore the morse oscillator energy levels actually (Refer Time: 24:20) they converge and so what you see is that there are many lines that you can see in the vibration spectrum, because not every one of them is not equal to any every other thing they are different. And also in Morse oscillator this possible for you to have multiple transitions v is equal to 0 to 2 v is equal to 1 to 3 and so on. Therefore, you see Morse oscillator gives you a real model of what is called the vibrational spectrum. A spectrum not one line, that is the purpose for doing this exercise.

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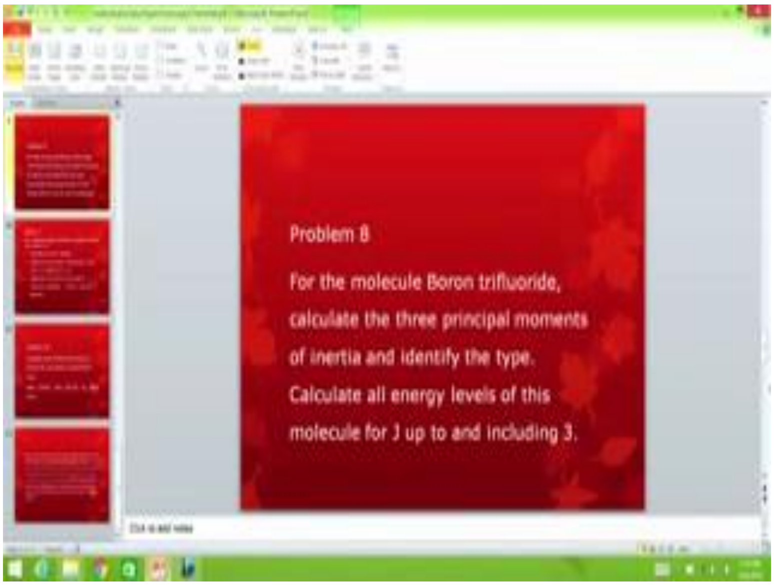

Problem 8

For the molecule Boron trifluoride, calculate the three principal moments of inertia and identify the type. Calculate all energy levels of this molecule for J up to and including 3.

Let us go to problem 8 now. Problem 8; talks about molecule boron trifluoride, and it asks you to calculate the three principle moments of inertia and identify the time. And it also calculates ask us to calculate all the energy levels of this molecule for the rotational quantum number j up to and including 3.

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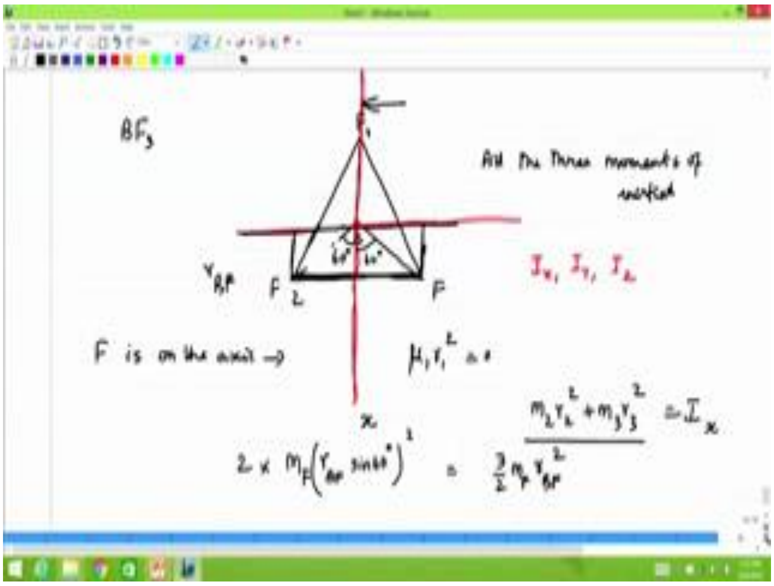

First of all this is a symmetric top B F 3. So, is actually a equilateral triangle that you can draw b, the three florents and these are the bond distances between the three fluorines they are identical, this is what you have. Now, you are asked to calculate all the three moments of inertia is a very simple exercise.

So, what are these axes? So, we can choose one axis; let me use a different color. Let me choose one axis as the axis that passes through one of the bonds. The center of mass is right way the boron is because of the symmetry of the system, and therefore the second axis which is perpendicular to that is that axis again passing through the boron. And the third axis is perpendicular to the plane of this screen that is perfect that is a third axis. So, you have what is call I x I y and I z axis. Now is easy to see that with respect to these two axes this axis as well as this axis, the moment of inertia that you calculate let us do that.

The B F bond distance is given, please remember these angles are 120 degrees therefore, you can see that for if we calculated for this axis we call it as the x y and z will be up the other (Refer Time: 27:33) so let us call this as a x axis. One fluorine is on the axis and therefore it does not contribute to the moment of inertia, mu I, mu 1, r 1 square call it as 1 that is 0 r is 0. The other two fluorine atoms, if you think about that these are 60 degrees and this is the fluorine boron bond distance. So, if you write this as r B F this distance as r B F. Then this perpendicular distance of the fluorine atom from the bond axis is r B F time’s sin 60. So, you get the r I the r 1 r 2, this is 2, this is 3. So, m 2 r 2 square plus m 3 r 3 square we want to calculate this for the moment of inertia I along the x axis because m 1 r 1 square is 0.

The mass of the fluorine atom being m of f. We have r 2 which is the perpendicular distances given as the r B F sin 60 degree whole square and into 2, because this atom is also exactly at the same distance from the axis therefore this is what you have sin 60 is root 3 by 2. Therefore, you have m f 3 by 4th 3 by 2 so it is 3 by 2 m f or B F square; that is the first one.

Now, what about this axis? Let us look at this axis. If you look at this axis all the three atoms are away from this axis. The distance of, let me now remove some of these things make it easier. The distance is this, the distance of this atom is this they are both identical and the it is easy to see that this distance is and also this one.

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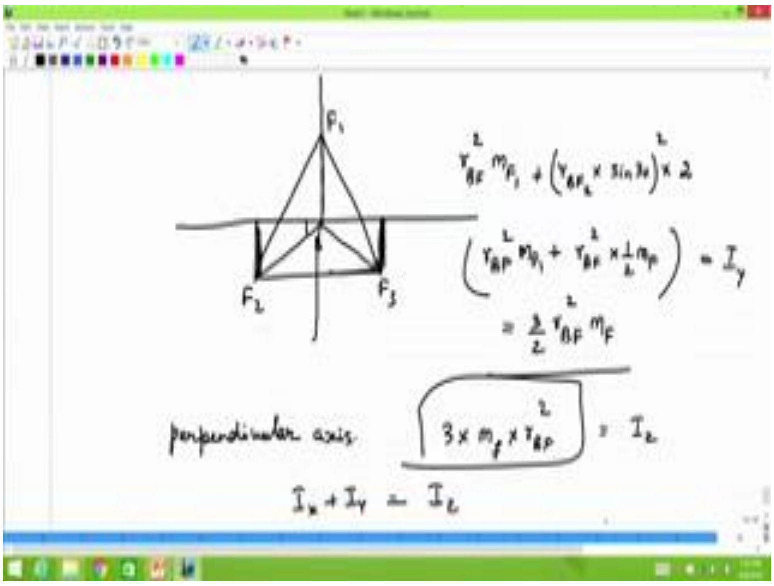

$r_{BF}^2 m_{F_1} + (r_{BF_2} \times \sin 30)^2 \times 2$

$\left(r_{BF}^2 m_{F_1} + r_{BF}^2 \times \frac{1}{2} m_F\right) = I_y$

$= \frac{3}{2} r_{BF}^2 m_F$

$\boxed{3 \times m_f \times r_{BF}^2} = I_z$

$I_x + I_y = I_z$

So, let me redraw the boron trifluoride. This is the bond, so the axis that we have is this. So we wanted to calculate this distance and we wanted to calculate this distance, they are both the same. And then you have this is simply r B F whole square it contributes m f 1, this is f 1, this is f 2, this is f 3, this is boron. Therefore, this you can see immediately as this is again 30 degrees so this distance will turn out to be r B F 2 times sin 30 whole square times 2 of them because f 2 and f 3 so that would be the answer. So, this gives us as r B F square m f 1 plus all the r B F are the same, therefore this is sin 30 is 1 by 2 so its 1 by 4 times 2 it gives you r B F square times 1 by 2 mf. So, this is the total moment of inertia I, and this is also 3 by 2 r B F square mf. So, this is identical to the moment of inertia about this axis; that is also 3 by 2.

Now, what about the perpendicular axis? To talk about the perpendicular axis it is something which is like that. Therefore, you see all the three atoms are away from this axis by exactly their bond distances. Therefore, the perpendicular distance from this axis is actually the B F bond distance. So, you have 3 times mf times the r B F square so this is what you get this is for I z. Now is interesting that I x plus I y is equal to I z, because you have 3 by 2 here you have 3 by 2 for the previous case and this is 3. This is a planarity in fact this is a planarity condition for the moment of inertia, the personal reason for including this as an example.

Therefore, you see you have to sit down and try to calculate the moments of inertia from simple geometries and you must know he actual structure the equilibrium structure of the molecule the bond is (Refer Time: 33:23) the bond angles and then go back and calculate the rotational constants using that and see in experiments whether that is the rotational constants you get and so on that is a reason for this particular problem.

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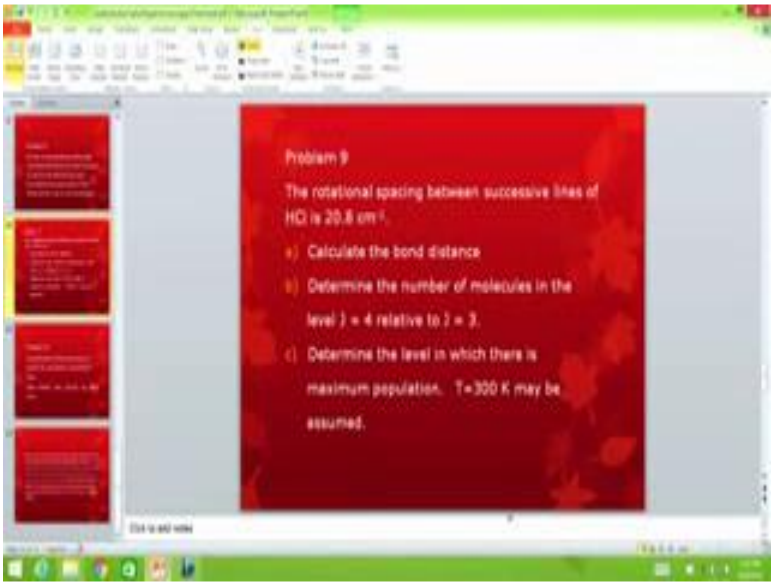

Problem 9

The rotational spacing between successive lines of HCl is 20.8 cm⁻¹.

a) Calculate the bond distance

b) Determine the number of molecules in the level J = 4 relative to J = 3.

c) Determine the level in which there is maximum population. T=300 K may be assumed.

The next problem talks about rotational spacing between successive lines of HCL as 20.8 centimeter inverse and it is asking you to calculate the bond distance. It is also asking you to determine the number of molecules in the level j is equal to 4 relative to j is equal to 3. And then one more thing namely determines the level in which there is maximum population that is T is equal to 300 k may be assumed.

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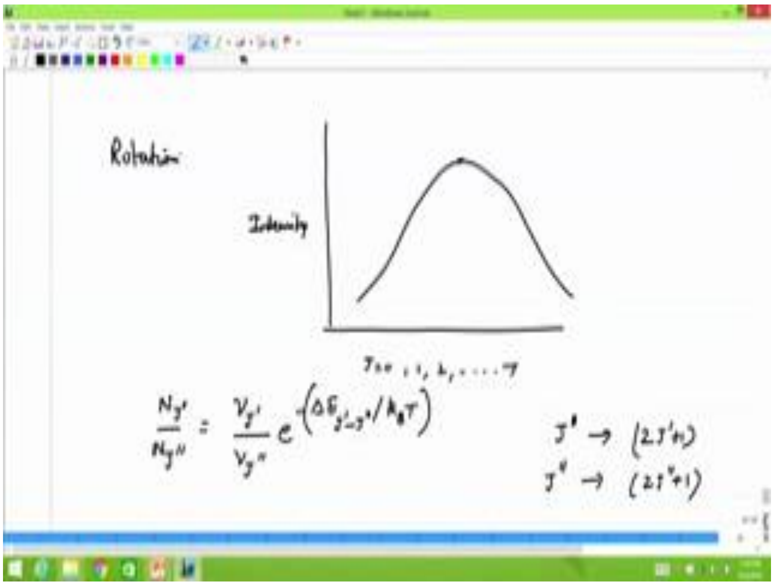

Rotation

$$\frac{N_{J'}}{N_{J''}} = \frac{\nu_{J'}}{\nu_{J''}} e^{-\left(\Delta E_{J'-J''}/k_B T\right)}$$

$J' \rightarrow (2J'+1)$

$J'' \rightarrow (2J''+1)$

It is important to remember that in the case of rotations, the line intensities actually increase as you go from j is equal to 0, 1, 2, 3, etcetera and if you talk about the intensity here the rotational line intensity is increases something like that, and there is a maximum. And this we remember is due to the fact that N J divided by N J let us write it as prime for the upper level double prime for the lower level, this is given as the nu j prime the degeneracy of j prime and the degeneracy of nu j double prime therefore the ratio times exponential minus delta E from J prime to J double prime divided by K B T.

So, the difference between vibrational population and the rotational population in this case is that here is a degeneracy factor associated with nu j prime and j double prime. And in the absence of any external field the j prime level has a degeneracy j prime level has a degeneracy of 2 j prime plus 1. And likewise the j double prime level has a degeneracy of 2 j double prime plus 1. Therefore, these problems ask you to calculate.

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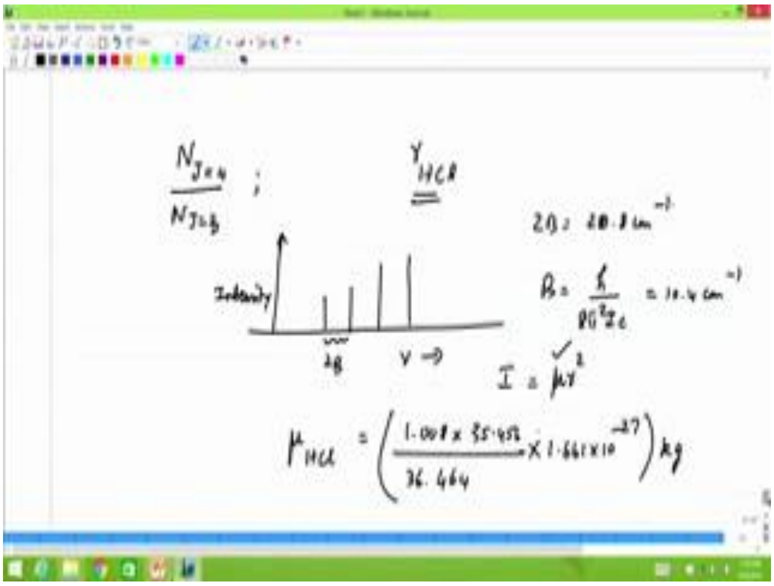

$\frac{N_{J=4}}{N_{J=3}}$; r_{HCl}

$2B = 20.8\ cm^{-1}$

$B = \frac{h}{8\pi^2 I c} = 10.4\ cm^{-1}$

$I = \mu r^2$

$\mu_{HCl} = \left(\frac{1.008 \times 35.453}{36.464} \times 1.661 \times 10^{-27}\right) kg$

The energy level N J is equal to 4 divided by N J is equal to 3. This is a second subdivision, the first division is the bond distance itself for r HCL, and this is easy. Please remember the successive rotational lines when you write the intensities the successive rotational lines are all differ by 2 b. This is intensity this is the wave number they all differ by 2 b, and therefore 2 b is equal to 20.8 centimeter inverse.

And you know b is given by the formula h by 8 pi square I c. And therefore, h by 8 pi square ic is 10.4 centimeter inverse. And since I is equal to mu r square and in the case of HCL mu of HCL is 1.008 into 35.456 divided by 35.464 times 1.6661 into 10 raise to minus 27 kilograms.

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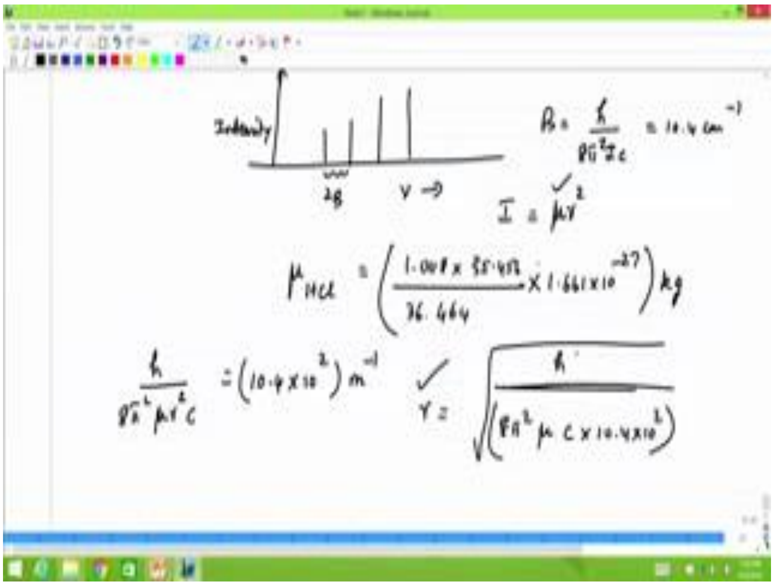

$$B = \frac{h}{8\pi^2 Ic} = 10.4\ \text{cm}^{-1}$$

$$I = \mu r^2$$

$$\mu_{HCl} = \left(\frac{1.008 \times 35.453}{36.464} \times 1.661 \times 10^{-27}\right) kg$$

$$\frac{h}{8\pi^2 \mu r^2 c} = (10.4 \times 10^2)\ m^{-1}$$

$$r = \sqrt{\frac{h}{(8\pi^2 \mu c \times 10.4 \times 10^2)}}$$

Therefore mu is known, r square is what you are asked to calculate. So, you write h by 8 pi square mu r square c is equal to 10.4 into 10 raise to 2 meter inverse. Make sure that you use the same SI units, because we are using kilogram and r is in meters. Therefore you see immediately r is given as square root of h by 8 pi square mu c times 10.4 into 10 raise to 2. And h is known, mu is known, and c is known, therefore you can calculate r. Therefore this is a very straight forward substitution formula.

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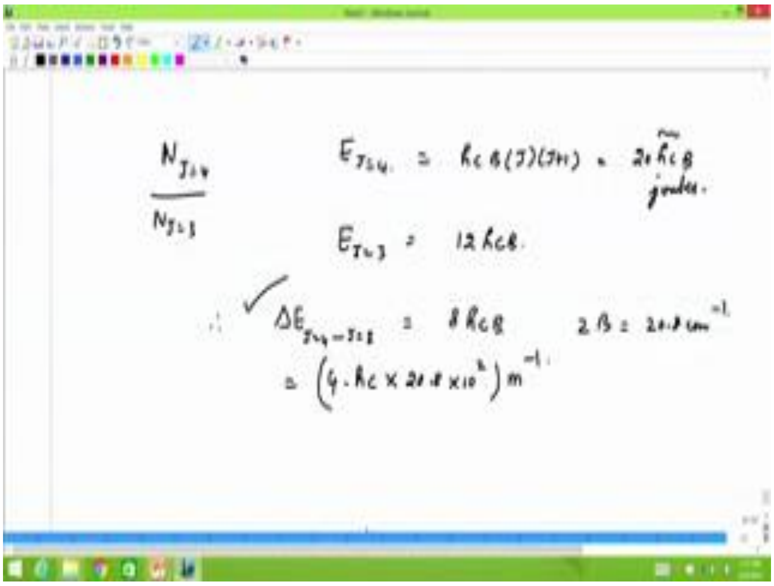

$$\frac{N_{J=4}}{N_{J=3}}$$

$$E_{J=4} = hcB(J)(J+1) = 20\,hc\tilde{B} \text{ joules.}$$

$$E_{J=3} = 12\,hcB.$$

$$\therefore \checkmark\ \Delta E_{J=4-J=3} = 8\,hcB \qquad 2B = 20.8\ \text{cm}^{-1}$$

$$= \left(4 \cdot hc \times 20.8 \times 10^{2}\right) \text{m}^{-1}.$$

Now, the second is of course N J is equal to 4 divided by N J is equal to 3. Please remember e j is equal to 4 if you recall for the microwave spectrum of rigid diatomic molecules it is hc B j into j plus 1. Therefore, for j is equal to 4 it is 20 hc B in terms of joules; that is why the h and c are here. For e j is equal to 3 it will be 3 into 4, so it will be 12 hc B.

Therefore, the delta E between j is equal to 4 to j is equal to 3 is 8 hc B. And you are given 2 b as 20.8 centimeter inverse. Therefore, 8 the delta E is given as 8 into hc into this is 2 b therefore I would say 4 hc times 20.8 into 10 raise to 2 meter inverse.

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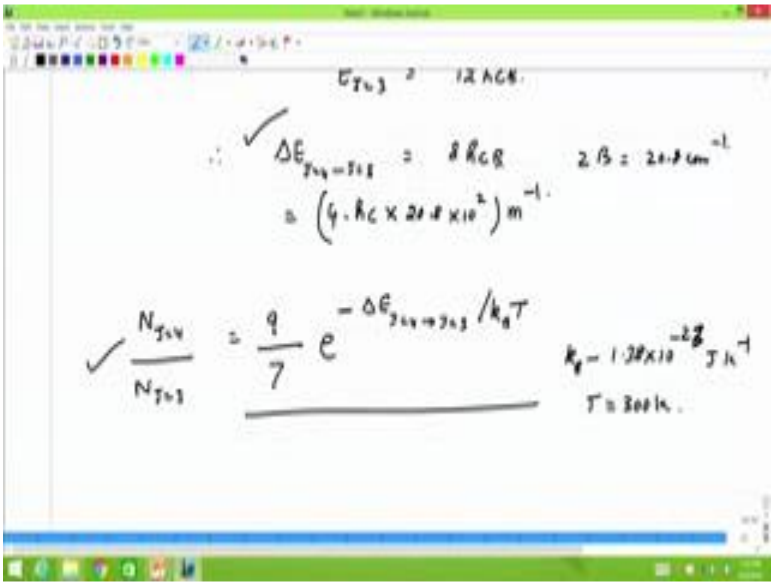

$E_{J=3} = 12\,hcB$

$\therefore \Delta E_{J=4 \to J=3} = 8\,hcB \qquad 2B = 20.8\ \text{cm}^{-1}$

$= (4 \cdot hc \times 20.8 \times 10^{2})\ \text{m}^{-1}$

$$\frac{N_{J=4}}{N_{J=3}} = \frac{9}{7} e^{-\Delta E_{J=4 \to J=3}/k_B T}$$

$k_B = 1.38 \times 10^{-23}\ \text{J K}^{-1}$

$T = 300\ \text{K}$

So delta E is known, and N J is equal to 3 to 4 to 3 is N J is equal to 4 divided by N J is equal to 3 is 9 to j plus 1 j is equal to 4 2 j plus 1 7, and then you have e to the minus delta E j is equal to 4 to j is equal to 3 divided by K B T, where kb is 1.38 into 10 raise to minus 23 joule per Kelvin and T is 300 Kelvin. Therefore, you can calculate this number by doing the numerical work.

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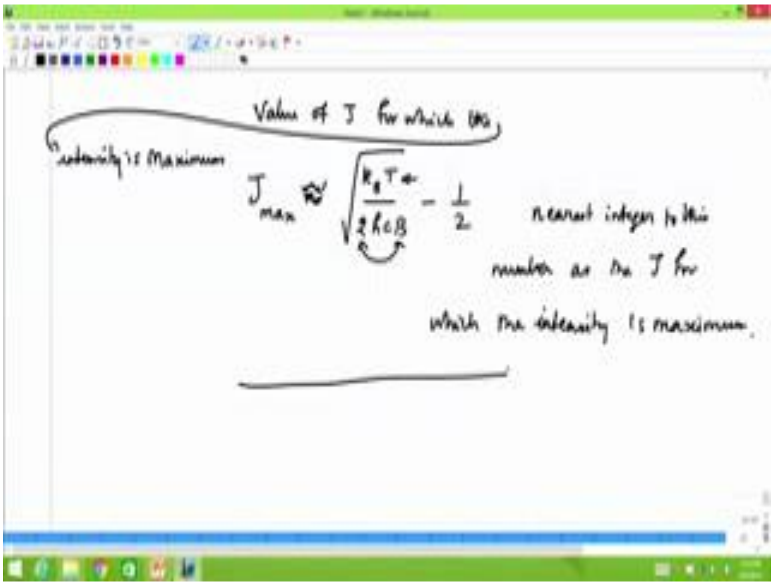

Value of J for which the intensity is maximum

$$J_{max} \approx \sqrt{\frac{k_B T}{2hcB}} - \frac{1}{2}$$

nearest integer to this number as the J for which the intensity is maximum.

Now the last section of this problem is to ask you, what is the value of j for which the intensity is maximum? That is what is you are asked to do. And I think you must remember this formula that the nu the j max, this was discussed in the in the lectures j max is approximately the nearest integer to K B T by 2 hc B minus one half. You have already been given b, you know T, you know hc; therefore whatever is the integer nearest to this number, this will not be an integer because the square root factor will not give you round integer value or half integer value for you to substitute therefore take the nearest integer to this number as the j for which the intensity is maximum; that is that.

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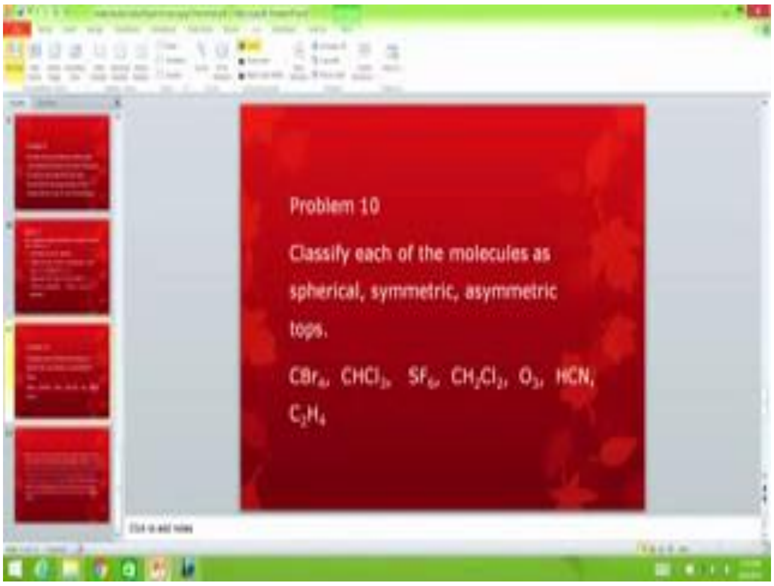

Problem 10

Classify each of the molecules as spherical, symmetric, asymmetric tops.

CBr_4, $CHCl_3$, SF_6, CH_2Cl_2, O_3, HCN, C_2H_4

So, we will come to the last problem. This is purely a classification of the molecules as spherical symmetric or asymmetric tops which is important for understanding the molecular spectroscopy, and therefore we need to make sure that the geometry of the molecules are visualized and that you see that the moments of inertia about the three different axis whether they are the same or whether two of them are the same and different from the third or if all the three of them are different, you have to have a mental picture.

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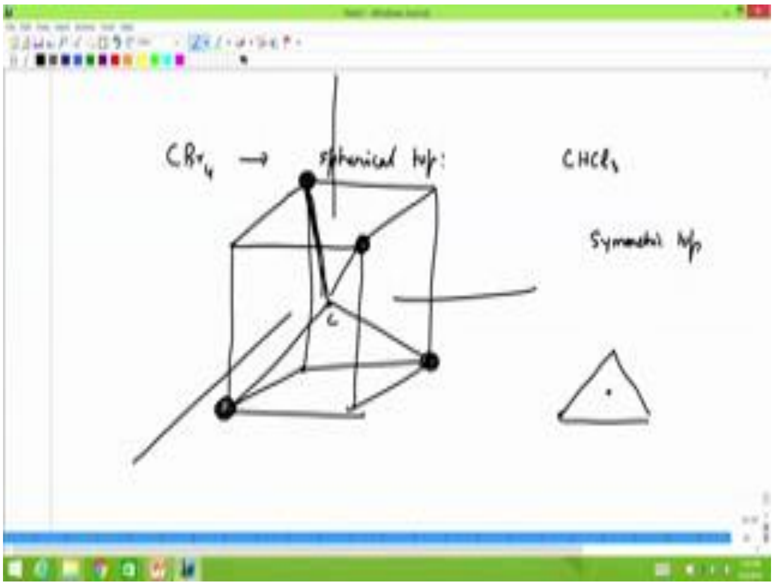

And it is very clear from some of these. For example the tetrahedron, now CB r 4 you should be immediately obvious that this is the spherical top, the reason is tetrahedron is the half the symmetry of the cube. So, you know that if you place this molecule in the cube, and then you start worrying about what those moments of inertia are. You will immediately see that the moments of inertia are identical about any 3 axis, because this is 1 B r this is another B r and the third B r is going to be here and the fourth B r is going to be here and the carbon is right on the middle c. Therefore, you see that this is a tetrahedral molecule inside the cube, if you want to do that it has half the symmetry of the cubes.

Therefore, you see that with respect to the structure whether the axis as this or whether the axis is this or whether the axis is perpendicular to this phase, the moments of inertia is same because the molecules are ideally displaced from these axes by the same distance. Therefore, something should be immediately seen as based on the geometrical conservations that it is a spherical top in this case. Now CHcl 3 again you should see that this is actually a symmetric top. The reason is the three chlorines actually form the base of an equilateral triangle, and then the carbon is the hydrogen bond is above.

Tetrahedral molecule, if you put the three molecules as the base of a of an equilateral triangle then it does not matter whether the axis is this whether the axis is that, all the three atoms are away from those two axis by the same distance and so is the hydrogen because it is in the plane. Therefore, two of the moment of inertia right away equal. And the third moment of inertia which is the moment of inertia along the CH bond the symmetry axis of the molecule is different. So, this is the symmetric top.

S of 6 octahedron when I talked about cube and symmetry of the tetrahedron is half of this symmetric of the cube, octahedron has the same geometry of as that of the cube, because those are the six mid points of the faces therefore, it does not matter whether you draw the axis about any two of these atoms the moments of inertia for all these three axis will be identical, so s of 6 will be a spherical top. CH 2 cl 2, we notice that it is an asymmetric top because it has only the symmetry of a twofold axis. Molecules which have only two fold symmetry as a rule you can also try and remember will have to be asymmetric top, molecules need a minimum of a threefold axis in order for them to be asymmetric top.

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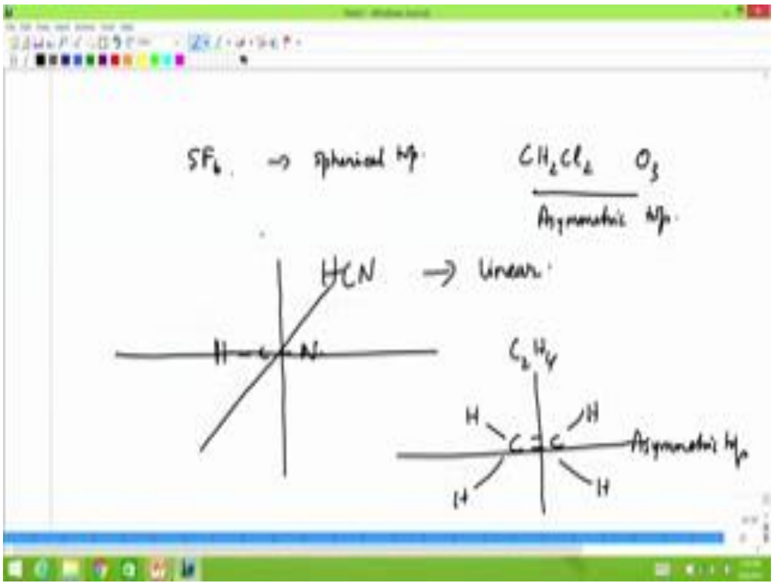

O zone has only a twofold axis symmetry, the bond ax the bisecting the bond of the oxygen, oxygen, oxygen and therefore that you can see right away that o zone is these two are asymmetric tops. HCN, no problem it is a linear molecule. Therefore two of its moment of inertia are the same about the both axis are perpendicular to the HCN bond. It is a linear molecule, therefore there is carbon hydrogen so I would say that the center mass is here and the other axis is that, but about this axis the moment of inertia is 0. Therefore, it is a linear molecule.

And last c 2 h 4 also has only two fold axis symmetry. So, despite the fact that it looks to be very symmetric, this is an asymmetric top. Because the axis here and the axis here the atoms are at different distances compared to those and the third axis is of course perpendicular to the plane of this molecule, therefore it is an asymmetric top.

So, the purpose of this video tutorial is to tell you a little bit about how to look at problems from the point of view of not just solving them, but in terms of relevance of these problems in understanding the concepts and so on. And therefore, I suggest that you solve many such problems by yourself. If you have questions please feel free to write that in the forum. I wish you all the best.

Thank you.