Chemistry II: Introduction to Molecular Spectroscopy

Prof. Mangala Sunder
Department of Chemistry and Biochemistry
Indian Institute of Technology, Madras

Lecture - 19
Microwave Spectra of Polyatomic Molecules

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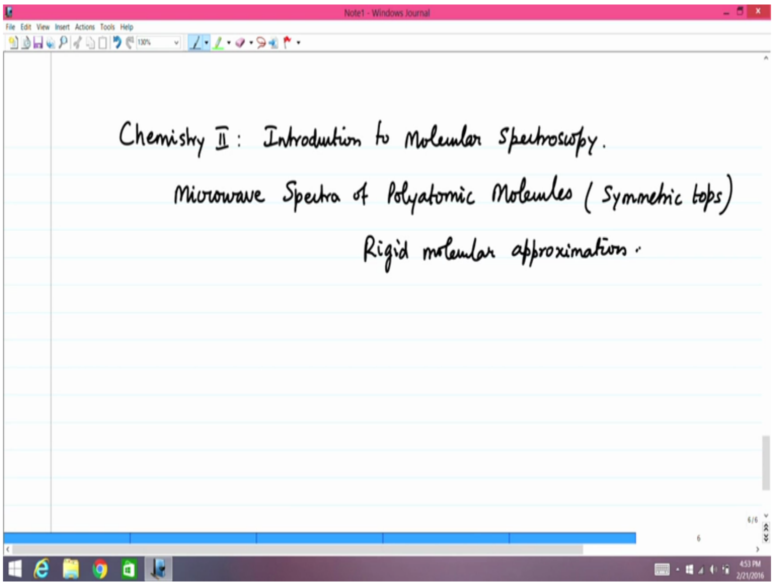

Chemistry II : Introduction to Molecular Spectroscopy.

Microwave Spectra of Polyatomic Molecules (Symmetric tops)

Rigid molecular approximation.

Welcome back to the lectures on Chemistry and Introduction to Molecular Spectroscopy. In this short lecture, we shall examine the microwave spectra of polyatomic molecules, again subject to the rigid molecular approximation. Spectra of symmetric top molecules are the first region in which we start getting more and more details from microwave spectra regarding the structures and so on, but you be surprised to see some patterns of for symmetric top being very similar or identical to the pattern of the spectra of diatomic molecules.

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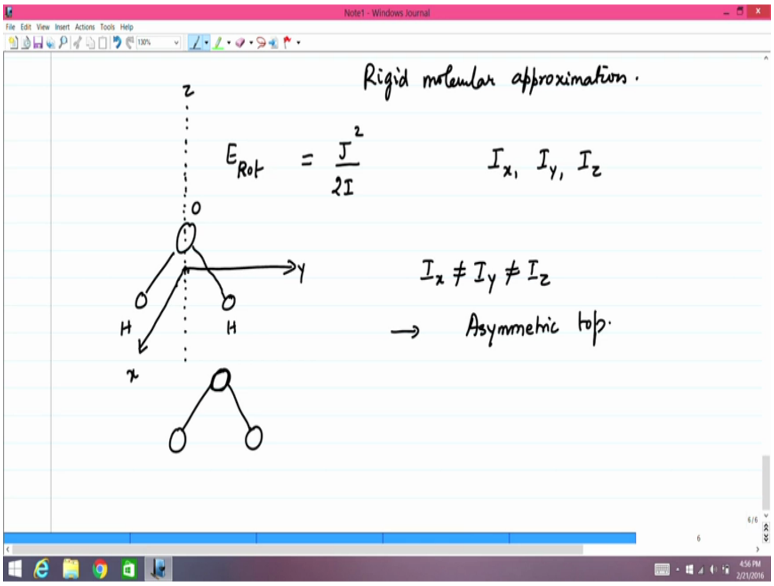

Rigid molecular approximation.

$E_{Rot} = \frac{J^2}{2I}$

I_x, I_y, I_z

$I_x \neq I_y \neq I_z$

→ Asymmetric top.

Now, please recall that we always take the rotational kinetic energy, and the rotational kinetic energy when the moments of inertia are all identical is given by the angular momentum squared divided by the moment of inertia. However, if a molecule is such that its moment of inertia above three mutually orthogonal axis are not the same then we have to worry about those axis systems, and write to the moment of inertia as I x, I y and I z.

Let see some examples in the case of water molecule. We first diatomic molecule with the two hydrogen atoms, and the oxygen atom here; the center of mass is somewhere here it is on the axis which bisects the two hydrogen that is the hydrogen O hydrogen bond, therefore this is half of the bond angle. And if this is a center of mass this axis which is also the molecular symmetry axis is usually called z-axis. Then what you have is y-axis, which is perpendicular to that; and in x-axis which is actually perpendicular to the plane of the screen that you have, so which we normally write as like that. So, if these are the three axis x, y and z; and if the moments of inertia are calculated about these three different axis you would see that the, I x is not the same as I y and is also different from I z. Such molecules in which all the three moments of inertia these are principle moments of inertia we have chosen the axis system such that we worry only about these three moments, and these principle moments of inertia which are different lead to characterizing these molecule as an asymmetric top.

And other example of asymmetric top; in fact, most molecules is asymmetric top. Other example is again ozone in which you have all the three oxygen atoms, of which the one oxygen atom is connected to the other two in a different way. This is also I mean its identical in symmetry to the water molecule and you have sulfur dioxide as an example, if you think about this nitrogen dioxide nitric there are many, many examples of molecules which are asymmetric tops.

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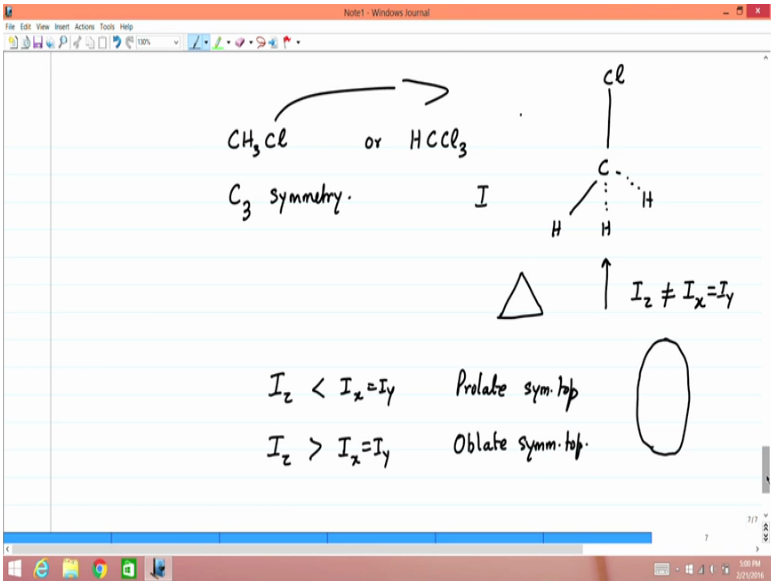

CH_3Cl or $HCCl_3$

C_3 symmetry.

I

$I_z \neq I_x = I_y$

$I_z < I_x = I_y$ Prolate sym. top

$I_z > I_x = I_y$ Oblate symm. top.

Now, it is possible that in molecules two of the moments of inertia may be equal to one another, but different from the third. And that happens in molecules such as methyl chloride or chloroforms for example, any molecules which has a C 3 symmetry, C 3 meaning a threefold axis about which the molecule has symmetry any such molecule will have two of the moments of inertia in this case of course, the C lets take CH 3 Cl. So, we have C-Cl bond axis and then we have the three hydrogen atoms which form an equilateral triangle plane. I mean if you connect that in the plane of the three atoms will be an equilateral triangle and such molecules have the moment of inertia about the z-axis I z is different from the moment of inertia about the x axis which is equal to the moment of inertia about the y axis.

And there are two categories here that the different moment of inertia from the other two which are equal may be less than the other two or greater than the other two. If it is less than the other two, we call that as a prolate symmetric top. If I z is less than I x which is equal to I y it is called prolate symmetric top. Typically, such symmetric tops are written or depicted using an ellipsoid of this form. The other in which the different moment of inertia is actually greater than the two equal moments of inertia, this is called oblate symmetric term.

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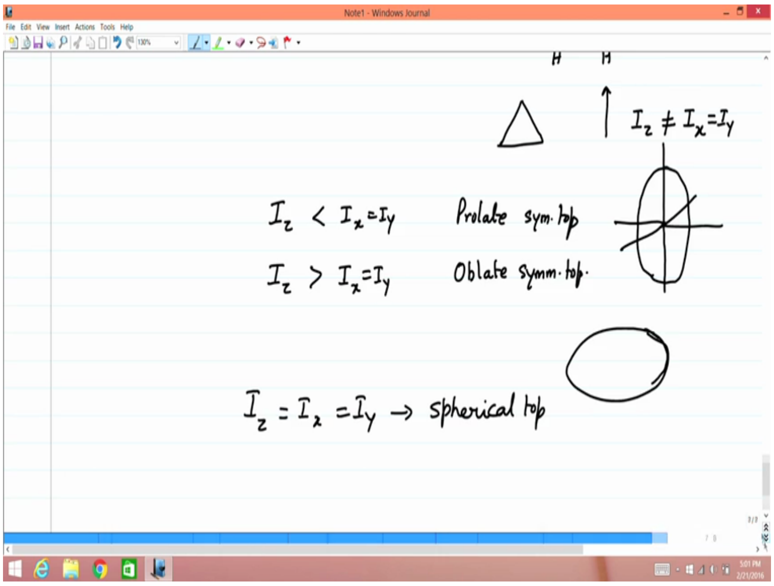

$I_z \neq I_x = I_y$

$I_z < I_x = I_y$ Prolate sym. top

$I_z > I_x = I_y$ Oblate symm. top.

$I_z = I_x = I_y \rightarrow$ spherical top

The oblate symmetric term is usually written or depicted like an ellipsoid of this curve, this is of course an ellipse into dimension, but the whole thing is an ellipsoid. The three moments of inertia actually become the three axes system for drawing the ellipsoid, and the axes are the one of the axes and the other two axes are like that perpendicular. If all the three moments of inertia are equal such a molecule is called as spherical top.

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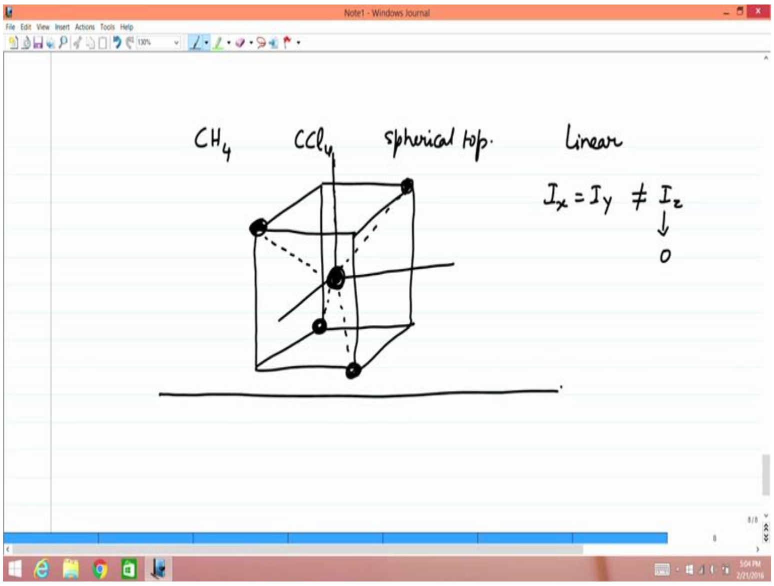

Now, methane for example, or the carbon tetra chloride, these are examples of spherical tops that is it is easy to see that if you draw a cube approximately and envision the tetrahedral symmetry using the cube the tetrahedral symmetry essentially means that the cube has opposite corners of the face occupied by the four atoms. So, here are the hydrogen atoms, if you want this as the carbon, then the face diagonal to that is this. So, if you draw the bond like that and the bond here; and the other two face diagonals are these. So, these are the face diagonals in this face. These are the face diagonals in this face. And you can see that they come out.

And if you connect all four of them you see that the tetrahedron is actually half the symmetry of a cube or an octahedron. And in this structure, it does not matter to you whether you are looking from the top face or whether you are looking from the side face, or this side etcetera, because the molecule is identical whichever way you look at it. And therefore, if you draw the three mutually perpendicular axis as the axis for the principle moments of inertia it is seen that atom at the same distance away from each of these axis and so it is immediately clear that the three moments of inertia should be the same. And likewise, for an octahedron molecule, perfectly octahedral molecule also has all the three moments of inertia identical if all the six atoms are the same.

So, these are three different cases that you can think about and the linear molecule is a special type where two moments of inertia are equal and unequal to the third, but unfortunately the third is 0. It is a point mark approximation therefore, it is not a spherical top a is not a symmetric top. The symmetric top has both the moments of inertia non zero reasonably big enough for them to be observed in one way or the other. But in the case of a linear molecule, it does not have there is only one moment of inertia two of the two components are equal, but the third is 0. So, there is a difference in the fundamental classification of the molecular moments, moments of inertia.

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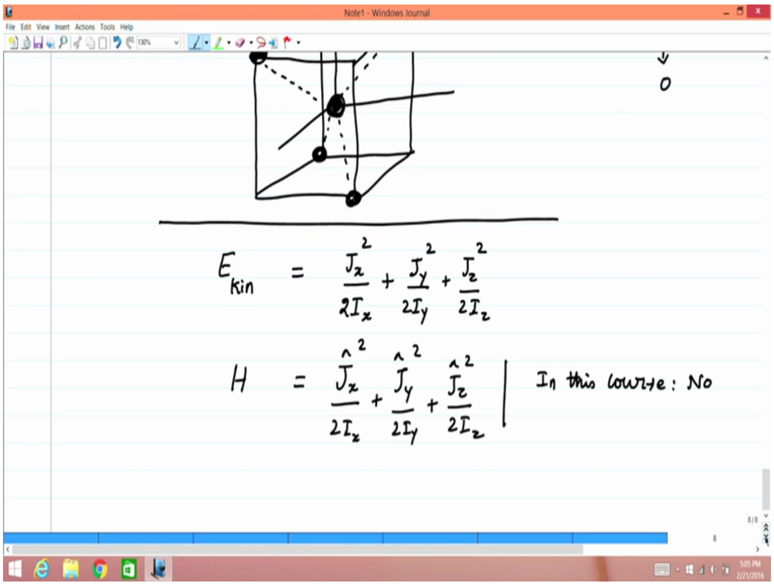

$$E_{kin} = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}$$

$$H = \frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} + \frac{\hat{J}_z^2}{2I_z}$$

In this course: No

Now, what happens is the rotational kinetic energy. When there are three different moment of inertia; is given by the angular momentum components in those directions divided by the moments of inertia about that axis J y square by 2 I y plus J z square by 2 I z. We shall not study the general Hamiltonian and energy levels of the asymmetric top, if you write this as the operators, then its 2 I x plus J y square the operator for that 2 I y and the J z square by 2 I z, we shall not do that in this course. Now it requires slightly more detailed analysis.

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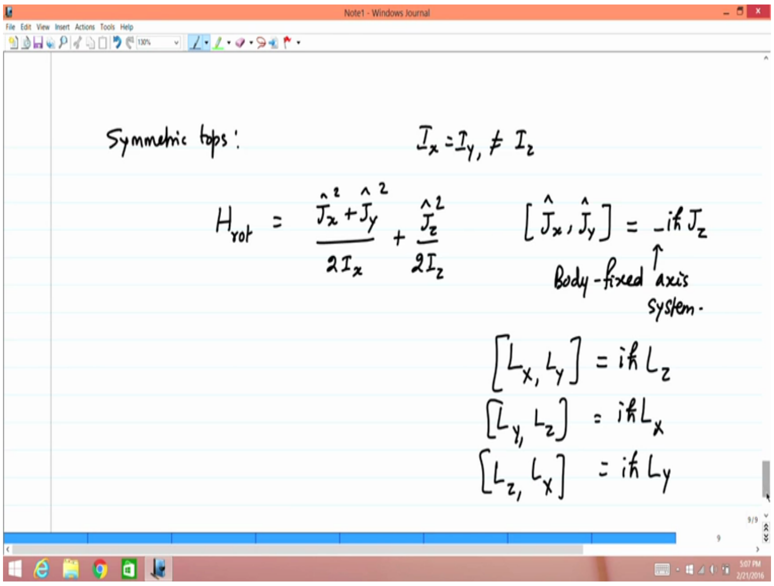

Symmetric tops: $I_x = I_y, \neq I_z$

$$H_{rot} = \frac{\hat{J}_x^2 + \hat{J}_y^2}{2I_x} + \frac{\hat{J}_z^2}{2I_z}$$

$$[\hat{J}_x, \hat{J}_y] = \underset{\uparrow}{-}i\hbar J_z$$

Body-fixed axis system.

$$[L_x, L_y] = i\hbar L_z$$
$$[L_y, L_z] = i\hbar L_x$$
$$[L_z, L_x] = i\hbar L_y$$

So, what we will look at the case look at is the case of symmetric tops. For the symmetric top, let us consider the particular case that I x is equal to I y, and I z is different from both of them. Therefore, you have the Hamiltonian rotational which is only the kinetic energy component of the rotational motion is J x square plus J y square divided by 2 I x because x and y are the same and then you have J z square divided by 2 I z. This is the symmetric top Hamiltonian that the operators and one must know that the angular momentum operators J x and J y do not commute in the sense of in quantum mechanics.

And in these have a particular commutation relation minus i h bar J z, I use the minus sign because these axis the x and y and z are fixed in the molecule, and they are actually rotating and moving with the molecules right there. They are fixed on the center mass of the molecule, but they are rotating with the molecule. So, these are called body fixed axis system, and this is different from what you studied in the case of a hydrogen atom where you would have studied that the angular momentum L x and L y be the components of the angular momentum do not commute, but give you something like that. And then correspondingly L y, L z give you i h bar L x and L z, L x give you the commutates gives you i h bar L y and so on.

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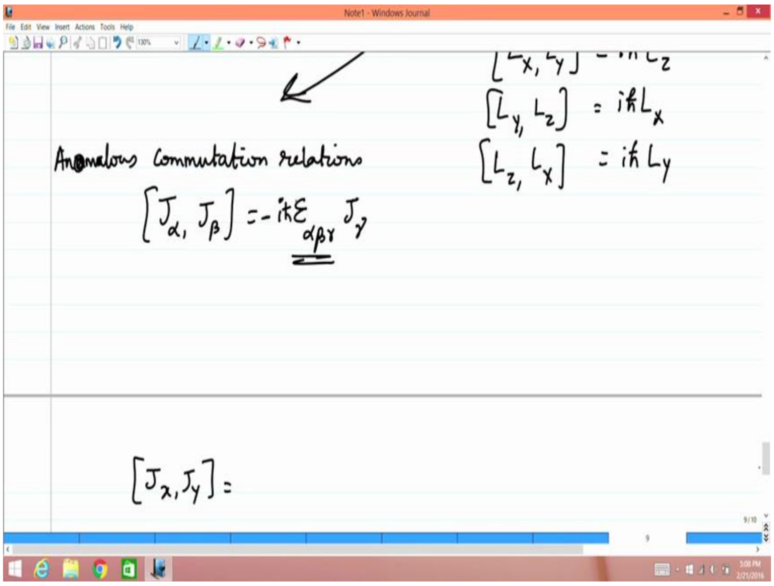

$[L_x, L_y] = i\hbar L_z$

$[L_y, L_z] = i\hbar L_x$

$[L_z, L_x] = i\hbar L_y$

Anomalous commutation relations

$$[J_\alpha, J_\beta] = -i\hbar\underline{\underline{\varepsilon_{\alpha\beta\gamma}}} J_\gamma$$

$[J_x, J_y] =$

Whereas, for molecular spectroscopy the components that we have here are such that they have the minus sign they are called anomalous commutation relations. And what they have is J alpha, J beta is i using some specific notation called a third rank tensor notation epsilon alpha beta gamma it is called j gamma. If you do not know about this, do not worry all it means is that J x plus comma J y the commutator is sorry that one should be minus i h bar and this is J x comma J y minus i h bar J z these are operators.

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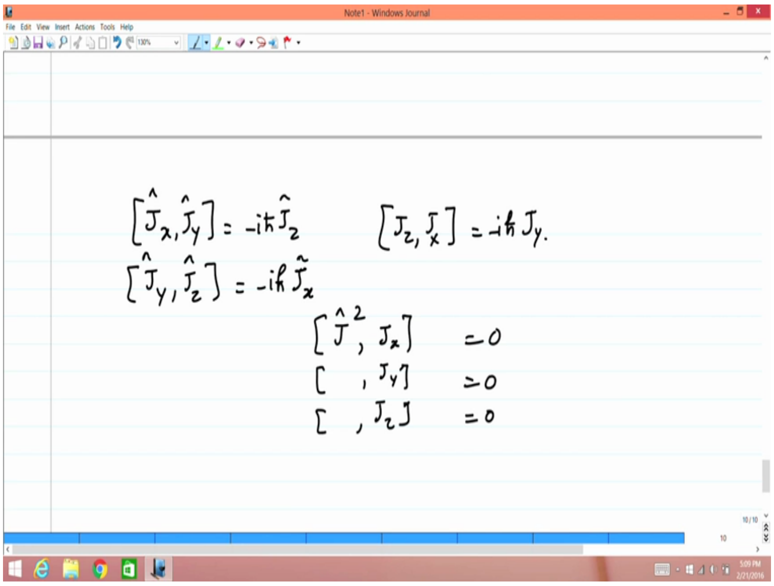

$[\hat{J}_x, \hat{J}_y] = -i\hbar \hat{J}_z$ $\quad [J_z, J_x] = -i\hbar J_y.$

$[\hat{J}_y, \hat{J}_z] = -i\hbar \hat{J}_x$

$[\hat{J}^2, J_x] = 0$

$[\ \ , J_y] = 0$

$[\ \ , J_z] = 0$

And J y, J z are operators with the minus i h bar J x. And the third one J z, J x is minus i h bar J y, all of them commute with the square of the angular momentum operator whether write J x or J y or J z all of them that commutator is 0. Therefore, what it means is that in quantum mechanics, it is possible in our description of the molecular rotations, it is possible for us to find Eigen values for operators, which commute with each other, and here the operators that commute are square of the angular momentum and one component of the angular momentum. And usually if this component is chosen as the z component or the component in the molecular symmetry axis which is the highest symmetry axis for any molecule.

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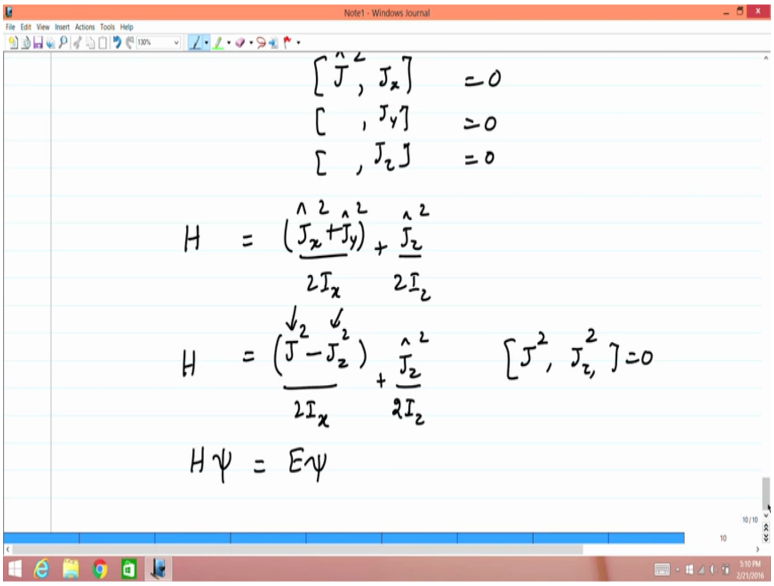

$$[\hat{J}^2, J_x] = 0$$
$$[\ \ , J_y] = 0$$
$$[\ \ , J_z] = 0$$

$$H = \frac{(\hat{J}_x^2 + \hat{J}_y^2)}{2I_x} + \frac{\hat{J}_z^2}{2I_z}$$

$$H = \frac{(\overset{\downarrow}{J^2} - \overset{\downarrow}{J_z^2})}{2I_x} + \frac{\hat{J}_z^2}{2I_z} \qquad [J^2, J_z^2] = 0$$

$$H\psi = E\psi$$

Given that therefore, when you write the Hamiltonian for this system the symmetric top particular when you write this as J x square plus J y square by 2 I x and J z square by 2 I z, you replace this combination by the total angular momentum square minus the z square component and you write 2 I x plus J z square by 2 I z. This is the Hamiltonian, which contains the operators J square and J z square. And they of course, commute to each other, therefore it is possible for us to actually find the solutions to the angular momentum problem by solving the Schrodinger equation H psi is equal to E psi, but there are two operators J and square on J z

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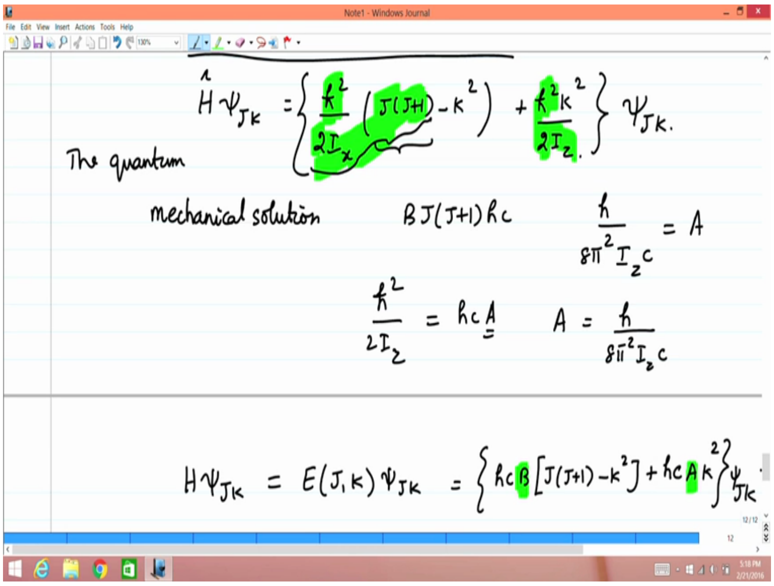

$$\hat{H}\psi_{JK} = \left\{ \frac{\hbar^2}{2I_x}\left(J(J+1) - K^2\right) + \frac{\hbar^2 K^2}{2I_z} \right\} \psi_{JK}.$$

The quantum mechanical solution

$$BJ(J+1)hc \qquad \frac{h}{8\pi^2 I_z c} = A$$

$$\frac{\hbar^2}{2I_z} = hcA \qquad A = \frac{h}{8\pi^2 I_z c}$$

$$H\psi_{JK} = E(J,K)\psi_{JK} = \left\{ hcB\left[J(J+1) - K^2\right] + hcAK^2 \right\}\psi_{JK}$$

And both of these are found to satisfy the property that J z acting on the molecular function gives you a quantum number k h bar psi and J square on the quantum number on the wave function gives you h bar square J into J plus 1 psi. Therefore, you see that the wave function is simultaneously the Eigen functions of these two operators. We write this by writing the values Eigen values here J and K, J and K, and J and K to denote that the difference such the different Eigen functions you have namely K going from minus J, minus J plus 1 to plus J. So, there are 2 J plus 1 Eigen functions. This was also mentioned in the last lecture when I talked about the bracket notation J K, these are psi J K or this. So, there are 2 J plus 1 Eigen function and this is important because this differentiates the spectroscopy in principle of a symmetric top from that of a linear diatomic molecule.

Now, these are the input for us to calculate the Hamiltonian the on psi J, K and Hamiltonian is of course, h bar square by 2. What we have here is h bar square by 2 I x and the operator J square gives you J into J plus 1, and the operator here the J z square gives you h bar square K square. And the other term in the Hamiltonian which is J z square by 2 I z gives you simply h bar square K square by 2 I z. All of this being the Eigen value multiplying the Eigen function psi J K this is the quantum mechanical solution.

So, the notation that spectroscopy use or keep in mind remember B J into J plus 1 times h c as the energy of a diatomic molecule and now the energy for a poly atomic molecule which is a symmetric top has that and some additional terms. Let us call the quantity h by 8 pi square I Z c, which comes from this term h bar square by 2 I z, if you call this h c times A, again a wave number then A will be h by 8 pi square I z c. And so this is A, this will be B, therefore the energy level if you look at it. When you write h psi J K as the energy, which is now dependent on the two quantum numbers E J K psi J K. And if this E s therefore, given in terms of h c B J into J plus 1 minus k square plus this term and then you have the other term which is given as plus h c A k square on psi J K. So, all I have done is to associate the rotational constant with the this term as the old B constant this one with the h c and the rotational constant with the principle moment of inertia along these bond the symmetric axis as the A constant.

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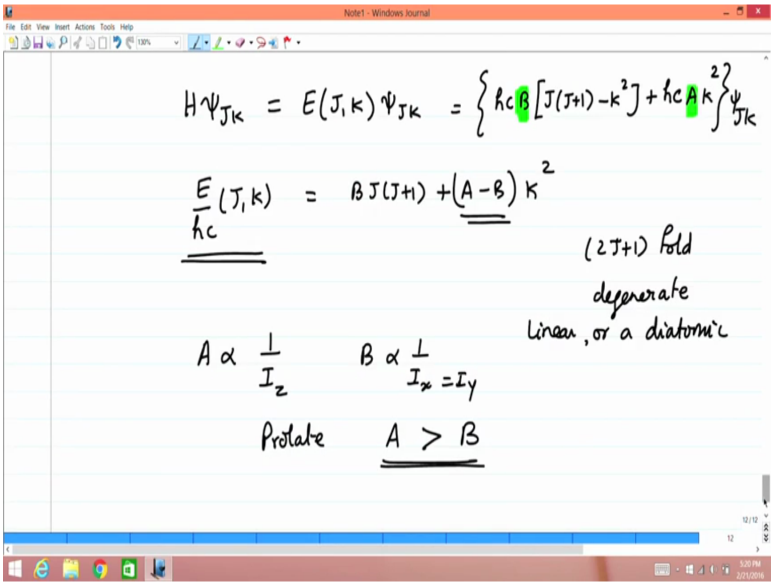

$$H\psi_{JK} = E(J,K)\psi_{JK} = \left\{hcB\left[J(J+1)-K^2\right]+hcAK^2\right\}\psi_{JK}$$

$$\underline{\underline{\frac{E}{hc}(J,K)}} = BJ(J+1)+\underline{\underline{(A-B)}}K^2$$

(2J+1) fold degenerate

Linear, or a diatomic

$$A \propto \frac{1}{I_z} \qquad B \propto \frac{1}{I_x = I_y}$$

Prolate $\underline{\underline{A > B}}$

So, now we have two constants for the symmetric top, because there are two moments of inertia. So, if you write the energy divided by h c J K then this is B J into J plus 1 plus A minus B times K square. Therefore, you see that the energy levels are no longer 2 J plus 1 fold degenerate as they were in the case of a linear diatomic molecule. The energy levels for a diatomic molecule where the same for all values of K for any given J, and we use this in the last lecture in determining the intensities by saying its each energy corresponding to a given J is 2 J plus 1 fold degenerate.

Now, in the case of symmetric top, we see that that is no longer there, the symmetry is now reduced. And what you have is the energy level is now a function of the square of K, and it is of course, a B J into J plus 1 with the additional term. Also look at the magnitude of A and B. If you look at it A is proportional to 1 by I z the principle moment of inertia a along the symmetry axis and B is proportional to 1 by ix and this I x and I y are equal, I z is different. Therefore you see if I z is smaller than I x and I y. we said it was a prolate symmetric top. Therefore, for a prolate symmetric top, A is therefore, greater than B because the moment of inertia is smaller than the equal moment of inertia; the unequal one is smaller than the other two moments of inertia which are equal. Therefore, the rotational constant will have the inverse relation the rotational constant A which corresponds to the inverse moment of inertia along the symmetry axis is actually greater than that of the other moments of inertia namely the rotational constant B. So, this is important.

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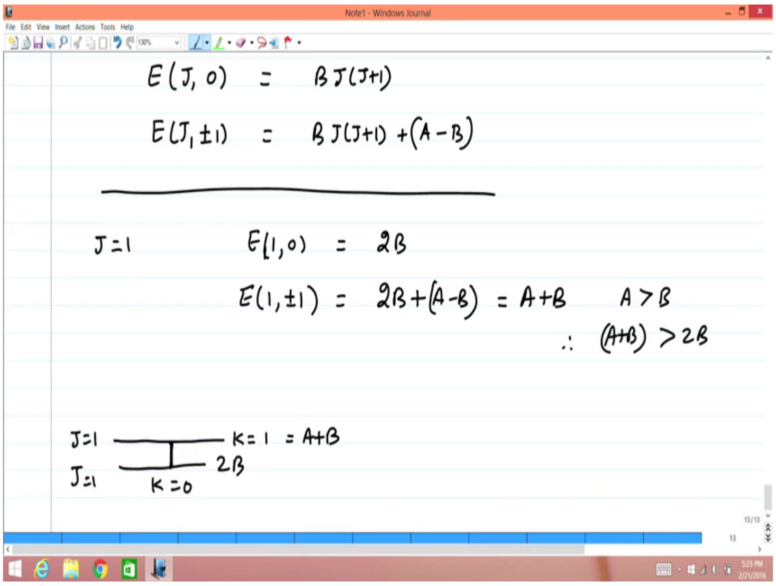

$$E(J, 0) = BJ(J+1)$$

$$E(J, \pm 1) = BJ(J+1) + (A-B)$$

$J=1$

$$E(1, 0) = 2B$$

$$E(1, \pm 1) = 2B + (A-B) = A+B \qquad A > B$$

$$\therefore (A+B) > 2B$$

Now, since for any given J, we have K going from minus J to plus J, we can write this as 0, plus minus 1, plus minus 2 to plus minus J K. Therefore, we can write the e j with k is equal to 0 as one energy and that will be simply B J into J plus 1, because the other term if you look at it B J into J plus 1plus A minus B times K square. So, let us keep that in a corner somewhere E J, K is B J into J plus 1 minus sorry plus A minus B K square let us keep that this is what we are using to write down for expression for different energy levels. And when K is 0 you get only that. And when K is plus or minus 1 you get B J into J plus 1 plus A minus B and so on.

So, let us right now the energy levels for j is equal to 1 to start with .This is nontrivial case. Therefore, E 1, 0 is 2 B; E 1 plus minus 1 is A 2 B plus A minus B, 2 B plus A minus B, K square is 1, therefore that is A plus B. And please remember A is greater than B, therefore A plus B is greater than 2 B. So, if you write the energy level expression, the J is equal to 1, K is equal to 0, which corresponds to 2 B will be slightly lower than the energy level for J is equal to 1 and k is equal to 1, this will be A plus B. The difference here is of course, A minus B, which is positive. Therefore for a prolate symmetric top the energy levels actually increase for a given J from K is equal to 0 to K is equal to plus minus 1 to plus minus 2 plus minus 3 and so on.

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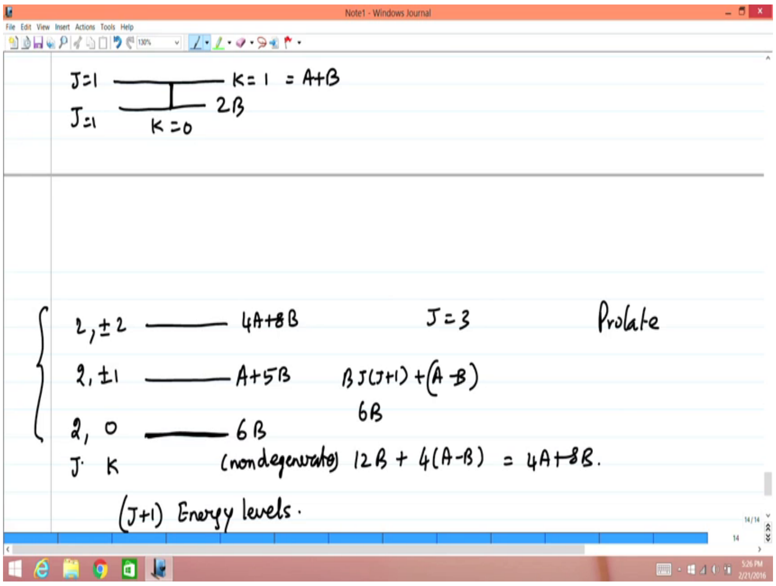

Therefore, if you write this again now for J is equal to 2, and J is equal to 3, we will write this for 2 or simple examples, this will be 6 B, when 2, 0; 2 is the quantum number for J, and 0 is the quantum number for K. So, this will be 6 B and 2 plus minus 1 will be remember B J into J plus 1 plus A minus B, this is 6 B plus A minus B. So, what you have is A plus 5 B, and for J is equal to 2, you have 12. And this is of course, K square therefore, that is 4 A. So, what you will get is 12 B plus 4 times A minus B, which will give you 4 A plus 8 B. So, for a symmetric top, for any given J, there are J plus 1 energy levels.

The plus 1 is due to the fact that the K is equal to 0 say it is non degenerate; and for all the other states, J is equal to 2 this is K is equal to plus minus 2 that is the maximum. And for J is equal to 3 of course, there be four energy levels corresponding to 3, 0, 3 plus minus 1 3 plus minus 2 and 3 plus minus 3 and so on. This is for prolate symmetric top. For the oblate symmetric top, the energy level expression is still the same, it is E J, K which is B J into J plus 1 plus A minus B K square. But for oblate symmetric top, A is less than B, and therefore what you see is this term is a negative contribution to the J, K is equal to 0 state, therefore E J 0 will be the highest among all the energy levels E j 0 E J, K, where K goes from plus minus 1 plus minus 2 to plus minus J among all the energy levels highest 1 will be the 1 with K is equal to 0 because the other term is negative for any value of K. Therefore, the energy levels decrease. Precisely what you see here as in increasing progression of energy levels you will see the reverse with the highest level being the 2, 0 and the next one being 2 plus minus 1 and the next lower one being to 0 and so on. So, the relations are inversed this is about the symmetric top energy levels.

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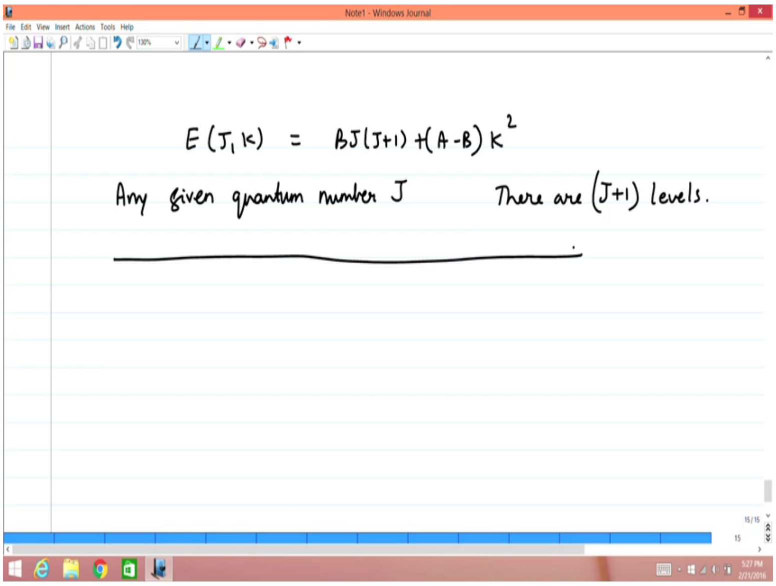

$E(J, K) = BJ(J+1) + (A-B)K^2$

Any given quantum number J There are $(J+1)$ levels.

So, in summary, what we have to remember is that E J, K is equal to B J into J plus 1 plus A minus B times K square. And for any given quantum number K, quantum number J, for any given quantum number J, there are 2 J plus 1, there are sorry J plus 1 level, J plus 1 level. So, we shall stop here, and take a look at the some of the examples of the symmetric top molecules and study the energy level and the transitions in the next half of the lecture.

Until then thank you very much.