Quantum Mechanics and Molecular Spectroscopy
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Lecture – 35
Rotations of Polyatomic Molecules (Part 2)

Hello. Welcome to the lecture number 35 of the course Quantum Mechanics and Molecular Spectroscopy. In the last class, we talked about the rotations of the polyatomic molecules and discussed the spherical rotors. In this lecture we will talk about symmetric rotor and asymmetric rotor.

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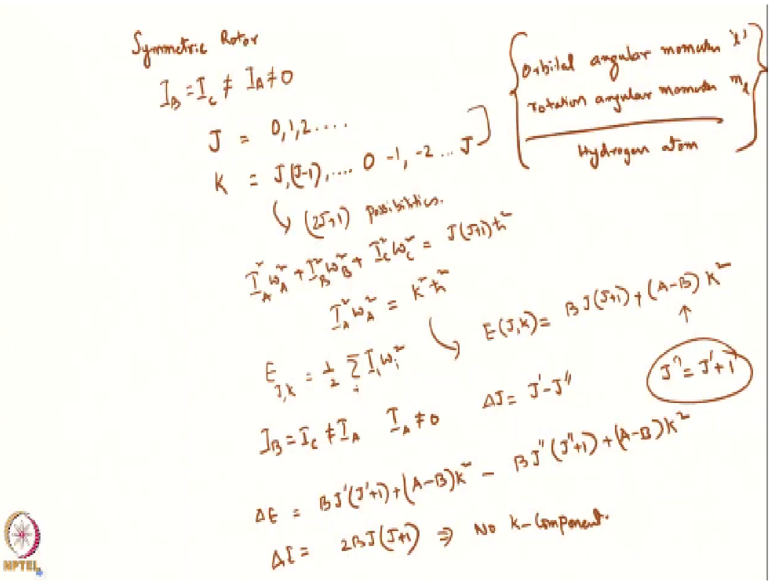

Symmetric Rotor

$I_B = I_C \neq I_A \neq 0$

$J = 0, 1, 2 \ldots$

$K = J, (J-1), \ldots 0, -1, -2 \ldots J$

↳ $(2J+1)$ possibilities.

Orbital angular momentum l

Rotation angular momentum m_l

Hydrogen atom

$I_A^2\omega_A^2 + I_B^2\omega_B^2 + I_C^2\omega_C^2 = J(J+1)\hbar^2$

$I_A^2\omega_A^2 = K^2\hbar^2$

$E_{J,K} = \frac{1}{2}\sum_i I_i\omega_i^2$

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

$I_B = I_C \neq I_A \quad I_A \neq 0$

$\Delta J = J' - J''$

$\boxed{J'' = J'+1}$

$\Delta E = BJ'(J'+1) + (A-B)K^2 - BJ''(J'+1) + (A-B)K^2$

$\Delta E = 2BJ(J+1) \Rightarrow$ No K-component.

Now in the case of symmetric rotor two of the rotational constants let us call it as I B and I C they are equal and this is not equal to I A. Further, we will also consider I A not equal to 0. If I A is equal to 0 then it will of course it will become a linear molecule. Now in this case there are major, two major axis of rotation. Okay, I A and I B of course since they are equal you will not be able to distinguish, but since I B and I C are equal you will not be able to distinguish rotations around I B and I C or axis B and C, but I A will be different.

So, in such case you will have total angular momentum J which will be around the axis B and C so that will have the values 1, 2 etcetera and to represent the rotation along A axis you will have additional quantum number K which will take the values of J, J – 1 etcetera, etcetera 0, -1, -2 etcetera up to J. Now this is something that is already familiar to you. What is that?

This is like your orbital angular momentum l and the rotational angular momentum m 1in the case of hydrogen atom. It turns out that the energy for this will be of course you can see that you know K will have 2 J + 1 possibilities. In such scenario your I square A / omega A square + I square B omega B square + I square C omega C square will be equal to J into J + 1 h bar square and in addition this is the total angular momentum.

Apart from that you have I A square omega A square will be equal to K square h bar square and so your energy total energy will be E J K is equal to 1 / 2 sum over i I omega square and from this what you will get is the following. So your energy of J K will be equal to B into J, J + 1 - sorry + A – B into K square. So when you have such an equation you will see it will depend on the absolute value of K and + K or – K will now so similar to the m l values.

So the ml value does not even polyelectron atoms m l value does not change the energy only the l value changes the energy. Similarly, in this case the value of K will not change the energy. So now if you had I B equals to I C and not equal to I A and I A is not equal to 0 then you have delta J transitions, delta J is equal to J – J prime. So, going from or J prime – J double prime going from one value of J to other value of J.

Now, if you now subtract this delta E will be equal to B J prime J prime + 1 + A – B K square – B J double prime J double prime + 1 + A – B K square. So if you take this, this will be nothing but 2 B J into J + 1 where J prime is equal to J – 1 that is because you know this is a selection rule for J. Okay, J double prime is equal to J + 1. Now we will see delta E does not have any K component.

Within the rigid rotor approximation you will see that the symmetric rotor for symmetric rotors the K has no contribution to the rotational spectrum.

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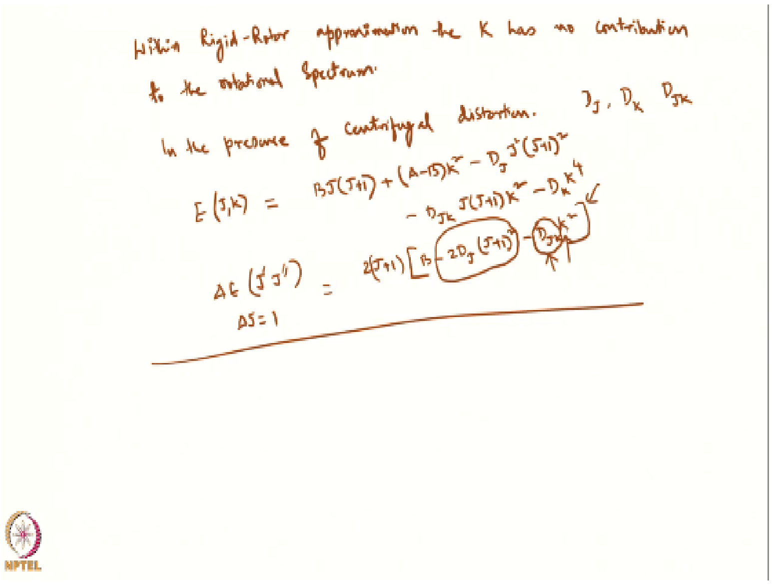

Within Rigid-Rotor approximation the K has no contribution to the rotational Spectrum.

In the presence of centrifugal distortion. D_J, D_K D_{JK}

$$E(J,K) = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

$$\underset{\Delta J = 1}{\Delta E(J'J'')} = 2(J+1)\left[B - \boxed{2D_J(J+1)^2} - D_{JK}K^2\right]$$

But that is not always true because that is under rigid rotor approximation. However, if it is not rigid so if there is in the presence of centrifugal distortion, if you have centrifugal distortion and let us call the centrifugal distortion as D J, D K and of course you know there is always a mixing term that is D J K. Now in that case your energy is given by of J and K is given by B J into J + 1 + A – B K square – D J J square + J + 1 whole square – D J K into J into J + 1 K square – D K into K to the power of 4.

Now if you take delta E between J and J prime, J prime and J double prime with delta J is equal to 1 then what you will get is that 2 J + 1 into B – 2 D J into J + 1 square – D J K into K square. Now you will start and see that this will depend on value of K and this centrifugal distortion cost and D, J, K.

So only when you have the centrifugal distortion or when the molecule is no longer rigid rotor then you will start seeing the effects of the K, the rotational constant K. So what will happen then the values will move up and down. Okay depending on the value of D, J, K. We generally know that when you have centrifugal distortion because of this the lines come closer.

And now you have one more quantity so lines becomes even more closer because the value of K and that goes as a value of K square so which means as the K keeps increasing the rotational levels are more and more closely spaced.

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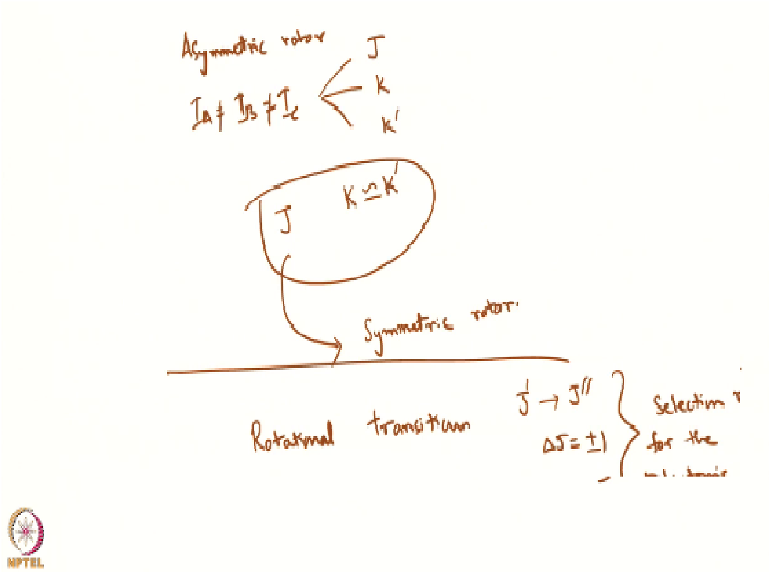

Now in the case of the asymmetric rotor then you will see that I A is not equal to I B is not equal to I C. So in principle one could have three rotational constants, so one will have J and one will have K and one will have K prime. So the analysis of spectrum becomes even more difficult. So one way to look at is that when you have J and what you do is that you think that K is approximately equal to K prime.

When K is approximately equals to; so any of the two rotational constants are close to each other than the third one sorry this has to be not equal. So when any two of them are very close to each other then what you can think of is the same treatment under this approximation one can do the same treatment as a symmetric rotor it is a possibility, but this cannot be guaranteed than it becomes even more complicated.

But one can think of then your energy value will depend on you know A – B and B – C and C – so this will be much more complicated. However, one can do an approximation when K is almost equal to K prime that means two of the rotational constants are very close to each other than third one is much larger than one can do treatment which is very similar to the symmetric rotors.

But having all this one of the things that you must remember it is the rotation transitions are generally divided by J to J prime or J prime to J double prime with delta J is equal to + – 1 and delta K is equal to 0. So this is the selection rule for the polyatomic molecules. We will stop here and continue in the next lecture. Thank you.