Quantum Mechanics and Molecular Spectroscopy
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Lecture No -29
Rotational Spectrum

Hello, welcome to the lecture number 29 of the course Quantum Mechanics and molecular spectroscopy. The last class we are looking at the rotational transitions. One of the features of the rotational transitions is the spacing between the rotational lines.

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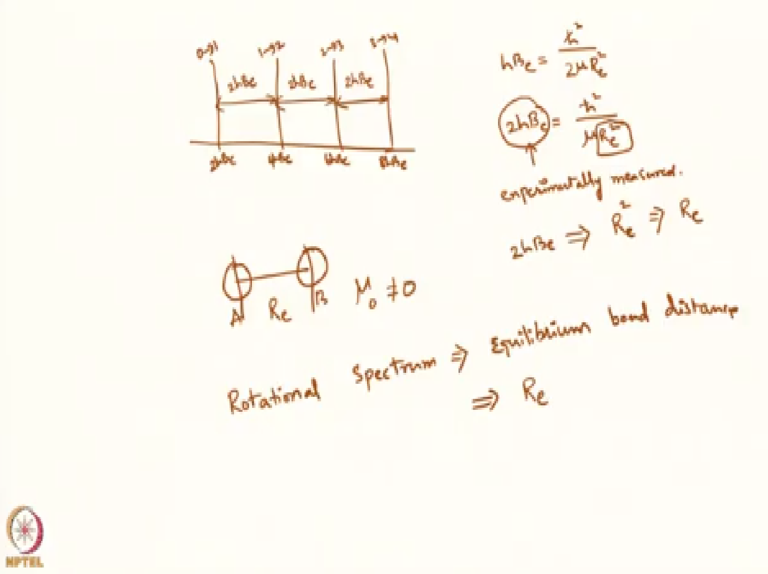

So I showed you that the rotational lines are evenly spaced by 2h B e, 2h B e, 2h B e; so this is from so let us call it as 2h B e, 4h B e, 6h B e, 8h B e. This is from 0 to 1, this is from 1 to 2, this is from 2 to 3 and this is from 3 to 4, this is the values of J. J is equal to 0 to J is equal to 1, J is equal to 1 to J is equal to etcetera. We know that h B e is nothing but h bar square by 2mu R e square. When I multiply 2 h B e this will come out to be h bar square by mu R e square.

So if 2h B e, you can be experimentally measured. Then based on this one can estimate R e square. So 2h B e will give us R e square in term we can get R e. What was R e? R e is nothing but if we had a molecule A B, R e was the equilibrium distance. So by measuring the rotational spectrum one can measure the equilibrium bond distance of molecule A B. So rotational spectrum tries to equilibrium bond distance.

Which is nothing but your R e. So rotational spectrum or rotational spectroscopy is the only spectroscopic method by which one can estimate the bond distances. That is geometrical parameters. No other spectroscopic technique can measure bond distances as the rotation spectrum can do. So that is the power of the rotational spectroscopic. However, one can all one must always remember that this is only possible if mu0 is not equal to 0.

That means you can only measure the bond distance of hetero diatomic molecules or molecules that have permanent dipole moment.

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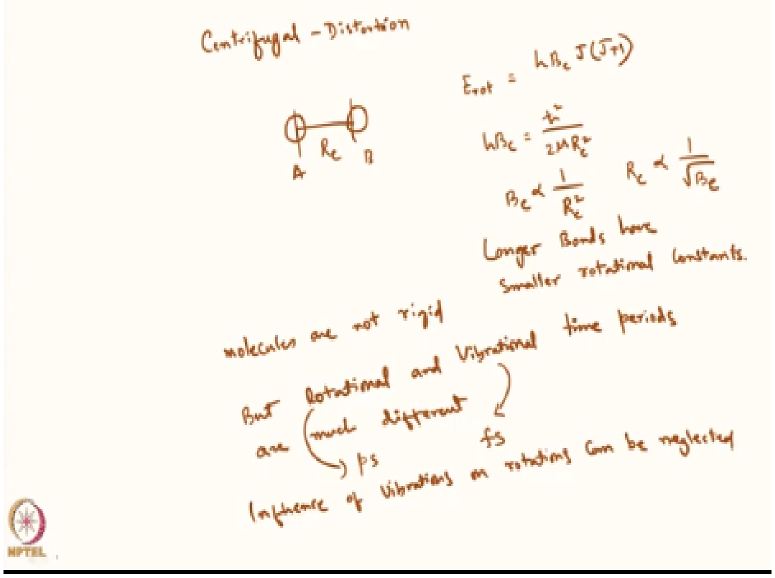

Centrifugal - Distortion

$E_{rot} = hB_e J(J+1)$

$hB_e = \frac{\hbar^2}{2\mu R_e^2}$

$B_e \propto \frac{1}{R_e^2}$ $R_e \propto \frac{1}{\sqrt{B_e}}$

Longer Bonds have Smaller rotational constants.

molecules are not rigid

But Rotational and Vibrational time periods are much different

ps fs

Influence of Vibrations on rotations can be neglected

Now one of the problems of rotational spectroscopy is something called centrifugal distortion. Now, what is centrifugal distortion? Now, let us suppose if you have a molecule A, B with the distance R e and it is rotational energy E rot is given by h B e into J into J + 1 and we see that as E rotation is h B e J into J +1. It turns out that as the B e decreases and you see B e is equal to h B e is equal to h bar square by 2 mu R e square.

So B e is inversely proportional to 1 over R e square or that is what it is or R e is inversely proportional to 1 over square root of B e. That means as the equilibrium bond length increases the rotational constant goes down, so longer bonds have smaller rotational constants. So this is something that you must remember as if I take A B the same molecule and keep increasing its bond length in the rotational constant keeps going down.

Now fortunately or unfortunately molecules are not rigid rotors, that means that molecules are not rigid. That means you cannot hold molecule A B such that the position of A and B are at the are logged up. They are going to move, so one of the things of course they vibrate but the rotational motion and vibrational motion have different time periods. So we will not able to we will not consider this, what does it mean?

Vibrational time period is far smaller than the rotational time period? So since there is a mix match in time periods the effect of vibrations on rotation is minimal and one can ignore that. So, molecules are not rigid but rotational and vibrational time periods are much different, how different? For example the rotational time periods are picoseconds and vibrational time periods are femtoseconds.

So there are three orders of mine cube different. Therefore the coupling between the rotational or influence of vibrations on rotations can be neglected. This is a very general statement, there will be cases when you cannot neglect it but that is kind of advanced level spectroscopy but a at a level that this course is intended one can always assume that the rotational motion and the vibration motion are independent of each other.

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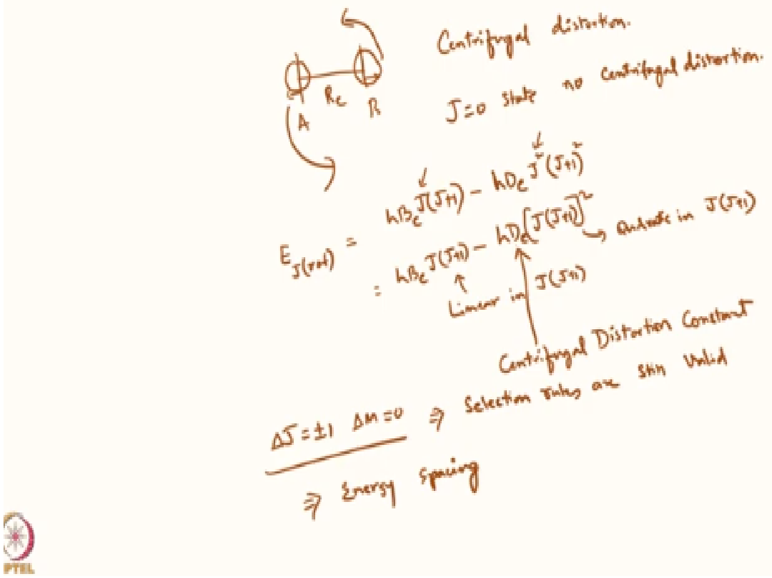

Centrifugal distortion.

J = 0 state no Centrifugal distortion.

$$E_{J(rot)} = hB_eJ(J+1) - hD_eJ^2(J+1)^2$$

$$= hB_eJ(J+1) - hD_e[J(J+1)]^2 \rightarrow \text{Quadratic in } J(J+1)$$

Linear in J(J+1)

Centrifugal Distortion Constant

$\Delta J = \pm 1$ $\Delta M = 0$ ⇒ Selection rules are still valid

⇒ Energy spacing

Now if that is the case a vibration is not influence the rotation what else can there? Now think of it like this if you have an object A B or a molecule A B such that this is R e and you want to rotate it. So you rotate then what happens is something called centrifugal force which kind of throws away A and B away from each other. So what happens is that A and B start moving away from each other and this is called centrifugal distortion.

One starts getting centrifugal distorts and you will see the faster you rotate the more will be centrifugal distortion. Of course, you will realize that for J = 0 state is essentially no reservation energy 0 that means for J is equal to 0, so there will be no centrifugal distortion. So as the J state keep increasing the centrifugal distortion becomes more and more effective. Now what is that it is doing? It is increasing the bond length.

So here A B is no longer R e, but something else slightly more than R e and we know as the distance increases the rotational constant goes down. So effectively when the rotation constant goes down the delta E goes down, so therefore E J rotation will now be equal to h B e J into J + 1 - h, D e J square into J + 1 square. So essentially what you are doing is you are writing a series, this is the first term that is J into J + 1 that say linear in of course, this is linear in J and this is quadratic in J.

So you are trying to add up more terms. So essentially what you have done is nothing but J h Be

J into J + 1 this h D e J into J + 1 whole square so this is for J into J + 1, this is a linear in J into J + 1 and this is quadratic in J into J + 1. So this is just the first correction then you can have the third order correction etcetera. But it turns out that the second order term or this D e itself is so small do not have to worry about the terms later on.

Now this is what you get and you can see that this is a subtraction that means as you keep increasing the D e by the way D e is called centrifugal Distortion constant. Now as you keep increasing D e or as you keep increasing J value the D e becomes more and more effective. So now let us look at and all having done this the way nature of the wave function has not really changed you are still using spherical harmonics.

So delta J is equal to +- 1 and delta M is equal to 0 these selection rules are still valid. However what you are changing is the energy spacing. So what you are doing is you are changing the energy spacing.

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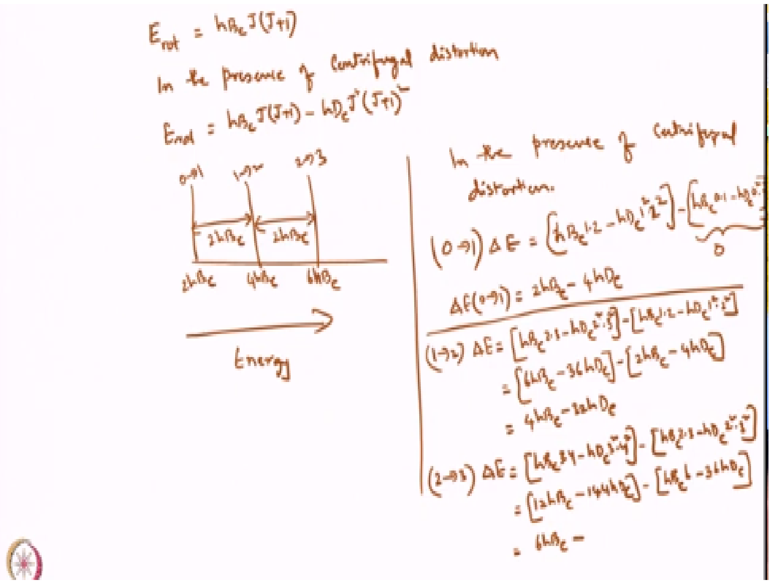

$E_{rot} = hB_e J(J+1)$

In the presence of centrifugal distortion

$E_{rot} = hB_e J(J+1) - hD_e J^2(J+1)^2$

In the presence of centrifugal distortion.

$(0\to1)\ \Delta E = \left[hB_e 1\cdot2 - hD_e 1^2 2^2\right] - \underbrace{\left[hB_e 0\cdot1 - hD_e 0^2\right.}_{0}$

$\Delta E(0\to1) = 2hB_e - 4hD_e$

$(1\to2)\ \Delta E = \left[hB_e 2\cdot3 - hD_e 2^2 3^2\right] - \left[hB_e 1\cdot2 - hD_e 1^2 2^2\right]$

$= \left[6hB_e - 36hD_e\right] - \left[2hB_e - 4hD_e\right]$

$= 4hB_e - 32hD_e$

$(2\to3)\ \Delta E = \left[hB_e 3\cdot4 - hD_e 3^2 4^2\right] - \left[hB_e 2\cdot3 - hD_e 2^2 3^2\right]$

$= \left[12hB_e - 144hD_e\right] - \left[hB_e 6 - 36hD_e\right]$

$= 6hB_e -$

Now when you did not have the rotation energy E rod is given by h B e J into J + 1. If you have centrifugal distortion in the presence of, centrifugal distortion so your E rotation will now be given by h B e J into J + 1- h D e J square into J + 1 whole square. So in general if you look at the transitions of the rotations the one can think of 0 to 1, 1 to 2, 2 to 3, this will be 2h B e, this will be 4h B e, this will be 6h B e and separation will be 2h B e.

Where this is your energy, now if you have centrifugal distortion, so in the sense of centrifugal distortion what will have here 0 to 1 delta E will be equal to h B e 1 into 2 - h D e 1 square into 2 square - h B e 0 1 - h D e 0 square into 1 square. So this term essentially is going to be 0 so your delta E 0 to 1 will be equal to 2h B e - 4 h D e. Now for 1 to 2 delta E will be equal to h B e 2 into 3 – h D e 2 square into 3 square – h B e 1 into 2 – h D e 1 square into 2 square.

So this will be nothing but 6 h B e - 2 square is 4, 3 square is 9, 4 into 9 is 36 h D e -2 h B e - 4 h D e. So this will turn out to be 4h B e - 32 h D e. Similarly when you have 2 to 3 transition delta E that will be equal to h B e 3 into 4 - h D e 3 square into 4 square - h B e 2 into 3 - h D e 2 square into 3 square, so this will be equal to 12 h B e - 3 square is 9, 4 square is 16, so 144 h D e - h B e 6 – 36h D e. So this will be 12- 6h B e - 144 – 36 that is equal to 108. So this will be 108h D e.

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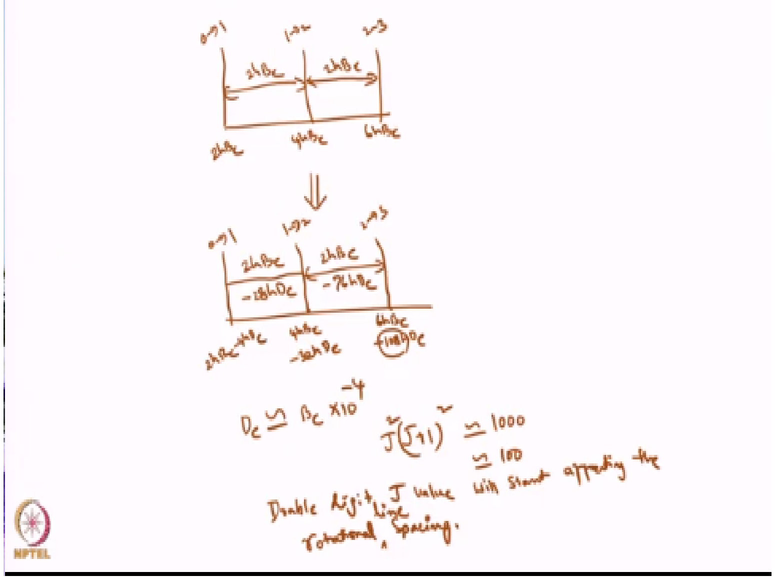

Now if we start plotting the spectrum earlier what we had 0 to 1, 1 to 2, 2 to 3 so this is 2h B e, 4h B e, 6h B e. Now it will transform to 2h B e 0 to 1 – 4h D e, second one will be 1 to 2, that will be 4h B e -32h D e, the third one will be 2 to 3, this will be 6h B e - 108h D e. So now the lines are becoming narrower. So this was just 2h B e separation was 2h B e. Now in this case, this will be 2h B e - 4 -32 is 28h D e and this will be 2h B e - 108 – 32, so 76 - 76h D e.

So the lines are getting closer. So if you keep moving to the higher values of J the lines will get closer and closer. Generally the B e and D e, B e is about 10 power 4 times larger than D e. So D e is approximately equal to B e into 10 power – 4 so 10,000 more. So that means when you start multiplying this number at least to a value of that order of B e it will start getting affected. That means J into J + 1 square should be of the order of 10,000.

Or at least of the order let us say even 10% of it should be of the order of 100. Only then it will start affecting the rotation line spacing. That means we have to go to very high values of J, what is the high values of J? The values of J that are at least in double digits. So double digit J values will start affecting the rotation spacing or rotational line spacing. So for large values of J the lines become closer and closer and that is the indication of say the presence of centrifugal distortion. Will stop it here and continue the next class. Thank you.