Quantum Mechanics and Molecular Spectroscopy
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Lecture – 34
Rotations of Polyatomic Molecules (Part 1)

Welcome to lecture number 34 of the course Quantum Mechanics and Molecular Spectroscopy. Previously, we have been looking at the selection rules for rotational vibrational and electronic transitions of diatomic molecules. In this lecture, I am going to talk about rotations of a polyatomic molecule and the consequent selection rules.

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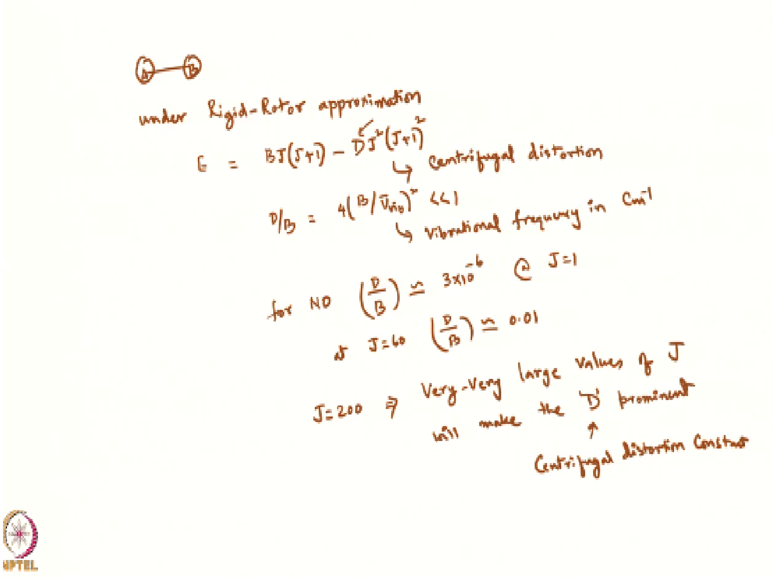

under Rigid-Rotor approximation

$G = BJ(J+1) - DJ^2(J+1)^2$

↳ Centrifugal distortion

$D/B = 4(B/\bar{\nu}_{vib})^2 \ll 1$

↳ vibrational frequency in cm^{-1}

for NO $\left(\frac{D}{B}\right) \simeq 3\times10^{-6}$ @ $J=1$

at $J=60$ $\left(\frac{D}{B}\right) \simeq 0.01$

$J=200 \Rightarrow$ Very-Very large values of J will make the 'D' prominent

↑ Centrifugal distortion Constant

If you look at the rotations of a diatomic molecule let us consider diatomic molecule A and B and under rigid rotor approximation we have the energy is given by B into J into J + 1 and if this has centrifugal distortion then this will be given by D into J square + into J + 1 square. We talked about the centrifugal distortion because when a rotating body what happens is that the length increases because of the centrifugal force.

So that is (()) (01:59). For most of the molecules D / B is equal to 4 times B divided by vibration whole square and this is much less than 1. V vibrational is the vibrational frequency in centimeter inverse. For diatomic molecule such as NO okay D / B is approximately equal to 3 into 10 power – 6 at J equals to 1, but if I go at J is equal to 60 D / B will be approximately equal to 0.01.

That means even for very large values of J one can ignore D / B or the D / B value is very small that means the value of this D is going to be really very, very small. Only when you goes to very large means let us say if J is equal to 200 then the centrifugal distortion constant will start making effect. So one has to go to very, very large values of J will make the D that is your centrifugal distortion constant.

We will make D prominent otherwise in general one can ignore. Now this is about the diatomic molecules. What about molecules that are larger than diatomic, triatomics, polyatomics because in chemistry most of the time you are encountering with the molecules that are much larger in shape. Now if you take a polyatomic molecule before we get to the selection rules for polyatomic molecules.

And how the rotation spectra of the polyatomic molecules is interpreted let us look at how polyatomic molecules will generally behave.

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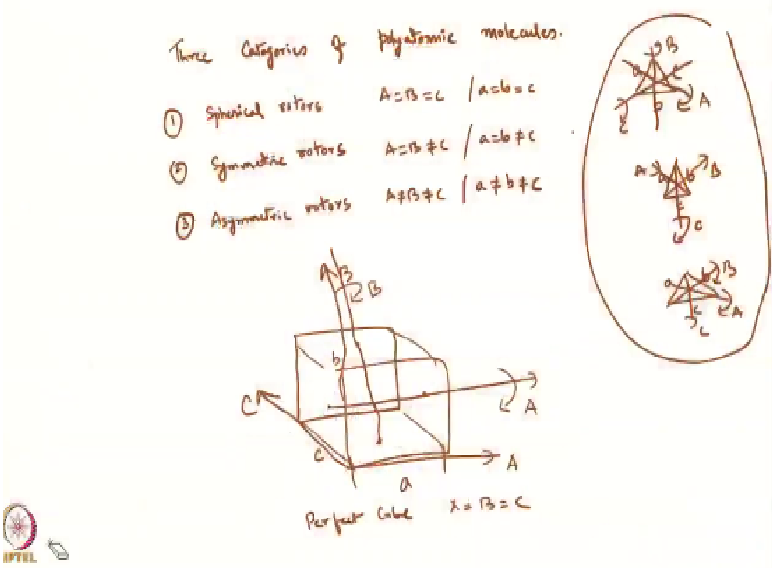

Three Categories of polyatomic molecules.

① Spherical rotors $A = B = C$ / $a = b = c$

② Symmetric rotors $A = B \neq C$ / $a = b \neq c$

③ Asymmetric rotors $A \neq B \neq C$ / $a \neq b \neq c$

If you have a molecule in which if you have let suppose so in general the polyatomic molecules are divided into three possibilities. There are three categories of polyatomics one is called spherical rotors second is called symmetric rotors and third one is called spherical symmetric and asymmetric rotor. Now one of the analogy that I can give between spherical rotors, symmetric rotor and asymmetric rotors is like triangles.

One of things that I can tell about these rotors in terms of a triangle think of it in terms of a triangle. There are three sides A, B, C and correspondingly one could have three different ways one can. So there is one rotation axis around this I will call it as axis A and there is another rotation one can rotate along B and other one is along C. Now for an equilateral triangle you will see that A, B, C will be same.

So spherical rotor is analogically is like a equilateral triangle. Now the other thing is isosceles triangle where a and b are same and c is different one could have like this or one could have it like this. So you will see that the C axis and one you can see that A and B are equal in such case one can write A equals to B equals to C which is a consequence of A is equal to B is equal to C.

In the symmetric rotor is more like A is equal to B not equal to C which is also a consequence of A is equal to B not equal to C. Similarly, if you have a scalene triangle then of course all three sides are different so A, B, C in that case the rotation along A, the rotation along B, and the rotation along C are different. So A is not equal to B, not equal to C. This is a consequence of A not equal to B not equal to C.

So what is that I am trying to tell you here is that if A, B, C are the length of the sides of the triangle then depending on how they are placed with respect to each other you can form either a equilateral triangle or an isosceles triangle or a scalene triangle. Similarly, if you have a spherical rotor depending on the rotational constants A, B and C then they can be categorized into three of them that is the spherical rotors, symmetric rotors and asymmetric rotors.

Now how do I call this. For example, you should take an object a cube this is just an example, but of course when you have molecules they are three dimensional objects. So, if you just think of a cube then one one axis is this axis, second axis is this axis and third axis is this axis and the lengths are let us call it as a and I will call this as A axis, this is b this is B axis, this is length is c and this is C axis.

Now simply A axis does not mean it is like this, but it is going to be rotation along this axis is A. Similarly we will see that if I want to rotate along this axis that is my B axis and the C axis will be perpendicular to A and B. Now conventionally you can have three axis, but if it is perfect cube for a perfect cube you will see that A must be equal to B must be equal to C. So, whenever you have such a possibility now you can think of a cube as a all the eight corners being on a surface of a sphere.

Similarly one can think of the a molecule that is tetrahedral in shape like methane, methane also is a cubic molecule because the carbon atom will be at the center of the cube and the hydrogens will be at the four opposite vertices four opposite vertices. So then you will have a methane that is a tetrahedral. So anything that is more of cubic in nature or any cube can be fitted on a surface of a sphere. So if molecules have that kind of shape they are called spherical rotors.

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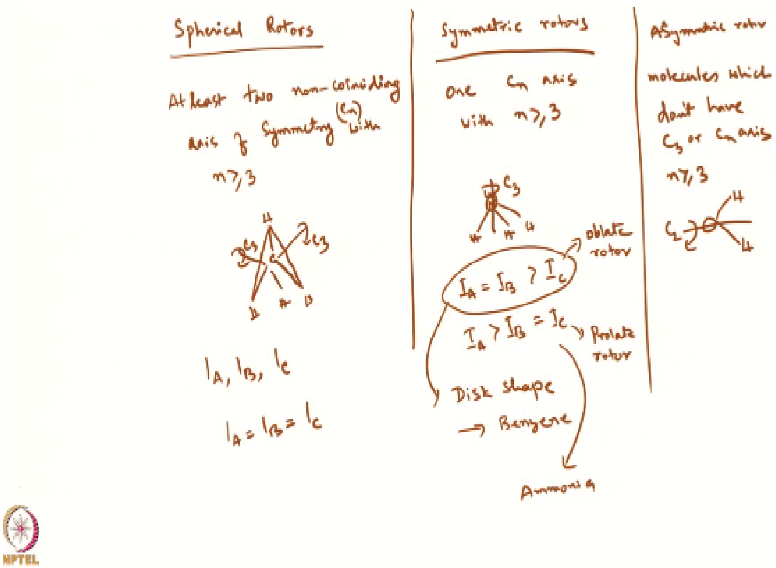

Spherical Rotors

At least two non-coinciding axis of symmetry (C_n) with $n \geq 3$

I_A, I_B, I_C

$I_A = I_B = I_C$

Symmetric rotors

One C_n axis with $n \geq 3$

$I_A = I_B > I_C$ → oblate rotor

$I_A > I_B = I_C$ → Prolate rotor

Disk shape → Benzene

Ammonia

Asymmetric rotor

molecules which don't have C_3 or C_n axis $n \geq 3$

For spherical rotors in general for spherical rotors there should be at least two non-coinciding at least two non coinciding axis of symmetry with n greater than or equal to 3 that means that will be at least two non-coinciding axis that are C 3 or more. Coinciding axis of symmetry C n okay of course S n will also do because S n has an element of C n in it in proper axis of symmetry.

Now for symmetric rotors one C n axis with n greater than or equal to 3 otherwise for a symmetric rotor of course if you do not have any C 3 axis molecules which do not have C 3 axis C 3 or C n axis with n greater than or equal to 3. Simplest thing that I can think of is for example if you have to take ammonia and we know there is a C 3 axis, but if you take water there are only C 2 axis.

The maximum axis is C 3 for ammonia while that is C 2 for water molecule so for water it becomes an asymmetric rotor and ammonia becomes a symmetric rotor and you can think of many other situation for example if you have methane that is or you can think of you know this has one if you think of this has a plane and this is another plane each plane will have one C 3 axis.

So there will be one C 3 axis here and this is another C 3 axis. Since there are two C 3 axis which do not coincide with respect to each other then methane becomes a say spherical rotor. So that is how you classify. One can take a look at the text books and will be list out how various molecules will be classified as spherical rotors, symmetric rotors and asymmetric rotors.

Now if you take a spherical rotor it has three axis A, B, C and there is a moment of inertia along each of them. So then you will have I A, I B, and I C and since it is a spherical distribution you will see that I A must be equal to I B must be equal to I C that means the moments of inertia are basically distributed similarly along all the three axis, but when you come to symmetric rotors there were two possibilities I A equals to I B which is greater than I C or other possibilities I A is greater than I B equals to I C.

In this case two of the moments of inertia are equal and third one could either be smaller than the other two or larger than other two. If such is the case it is called oblate rotor and this is called prolate rotor. Now one can think of oblate and prolate (()) (16:58). Oblate and prolate are various shapes that you can think of in a symmetric rotor. For example benzene if something is like a disc then it is an oblate rotor. So this has a disc shape.

So for example benzene and this is ammonia more of a ball shaped or egg shaped. So in the symmetric rotors we have two possibilities one is the prolate rotor and other is an oblate rotor while there is only one in the case of the spherical rotor, but in the asymmetric rotors it can either by towards this asymmetric rotors could either tend to a prolate (()) (17:55) prolate rotors or an oblate rotor.

For example, substituted benzenes with no elements of symmetry will be more like an oblate rotor, but what are will be more like a prolate rotor so it will depend on the shape.

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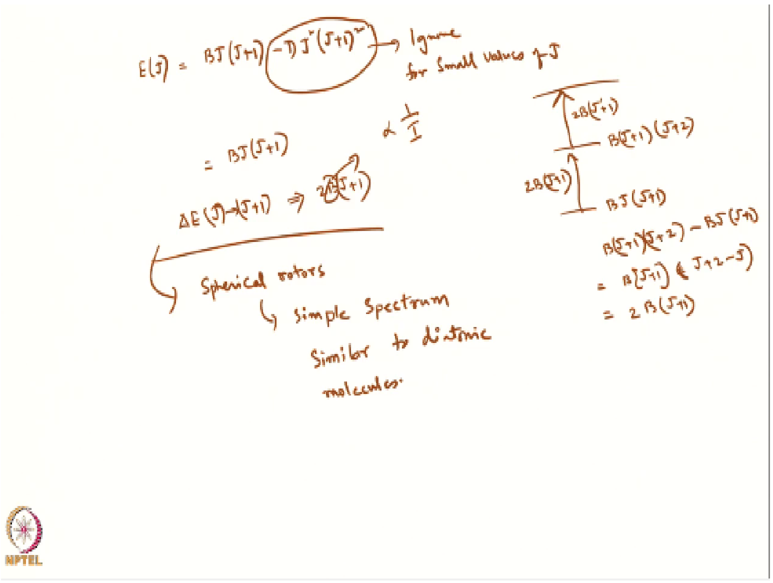

$E(J) = BJ(J+1) \boxed{-DJ^2(J+1)^2} \rightarrow$ Ignore for small values of J

$= BJ(J+1)$ $\qquad \propto \frac{1}{I}$

$\Delta E(J)\rightarrow(J+1) \Rightarrow 2B(J+1)$

Spherical rotors

↳ simple spectrum similar to diatomic molecules.

$B(J+1)(J+2) - BJ(J+1)$

$= B(J+1)(J+2-J)$

$= 2B(J+1)$

The energy which is function of J so that will be equal to B J into J + 1 okay and if you have centrifugal distortion constant that will be D into J square into J + 1 square and we found that of course one can ignore this let us not think of rotor ignore for small j's, so what you get is B J into J + 1 and when you look at the transitions delta E J to J + 1. This will go from now what will it go from so this value will be B J into J + 1 into B J + 1 into J + 2.

Now if I look at the transitions then what will happen so B J + 1 J + 2 – B J into J + 1. So this will be equal to when I calculate this will be equal to B into J + 1 if I take common and this will be nothing, but J into J + 2 – J so that will be equal to 2 B J + 1. So this transition will be equal to 2 B J + 1. So delta E will be equal to 2 B J + 1 okay. Now it turns out that each transition of course the next one will be also 2 B J prime + 1 whatever that value of J will be.

So it will keep increment by one value all the time. Now it so turns out that this is also true for spherical rotors why because one cannot distinguish between the three axis of symmetry that is A, B and C are I A the three moments of inertia are exactly the same because the value of B is inversely proportional to 1 over I okay is inversely proportional to moments of inertia. So what happens is that since all of them are same so will not be able to distinguish between each direction that is A, B, C.

Even though it is a three dimensional molecules you will not be able to separate out the A, B, and C dimensions. Therefore, the spectrum will look like a spectra of a diatomic molecule. So, spherical rotators will have a very simple spectrum similar to diatomic molecule.

However, in the case of symmetric and asymmetric rotors the spectrum will get complicated which we will discuss in the next lecture. Thank you.