Symmetry and Group Theory
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Lecture – 39
Normal mode analysis: some examples

I want you to work them out. Let us see.

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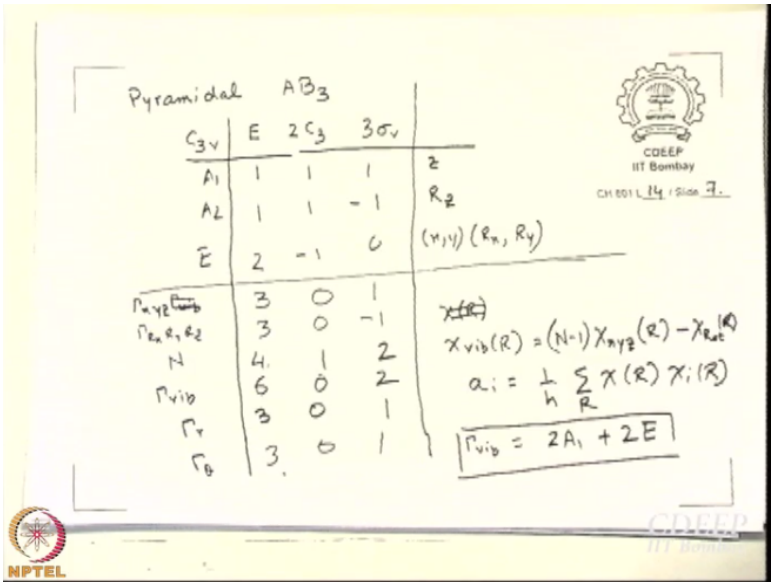

All of these are worked out examples of quadrant. So you can refer to the book anytime and you can do it. Molecular vibration chapter 10. So let us see, let us say pyramidal AB3. Any example you know? C3v very good. Now what we need to do? I need to work out the symmetries are normal modes. Let us see. C3v. What are the operations E how many C3 then 3 sigma v.? Now to start with what I will do is I will write the character table for you.

This small character table I can write. Can you write? First word list. 1, - 1, 1 and column 1, 1, 2 very good. Now ferritin what do I have. We have worked this out did we? 1, - 1, and 2, - 1, 0 and you know very well that this - 1 is not equivalent to this - 1. This - 1 means the change in sign, this - 1 is - 1/2 + - 1/2 we are mixing. Where does x belong? Where does y belong? Where does z belong? However, first name them? A1, A2, E.

Then when z is here what about x and y? X and y jointly form a basis for E and I will also tell you that Rx and Ry also jointly form a basis for E and Rz actually forms a basis for A2. What we are trying to do now is that we are trying to use the tabular method of what we have this problem. This is discussed in Carter's book. It is a little neater method than doing it line by line. In physical chemistry if you learn to construct nice tables and that helps you in many places.

For example, trying to work out how many people will move from which hostel so that everybody in the 4th year get single room tables help a lot. Now the thing is where these table help us and we our actual tables made of food that do not help us because they do not come in time. Both are there. What will I do. I want to construct your gamma vib. How will I construct gamma vib. Remember that formula for chi (R)?

What is it? Chi (R) for gamma vib how I did chi vib (R) = (N - 1) chi xyz (R) then - chi rot (R) so I will just write chi ro(R) because I am running out of paper. So instead of trying to write gamma vib first what we can do is we can do it in steps. What is your gamma xyz write that? Gamma xyz, what will it be? Tell me quickly? 4? 3, 0, 1 (FL) (05:26 - 05:30) Gamma xyz, next I will write gamma Rx, Ry, Rz what is that? 3, 0, - 1. I am adding E with A2, is not it?

No what do I want now? I will write N also just to be a little more methodical. N for this. Do not forget how many atoms are there? How many atoms are there? 4. How many atoms change place under identity operation? 0, 4. Number of atoms that do not change places 4. How many atoms do not change places upon operation of C3? 1 very good. What about sigma v? 2. Sure not 3? 2 atoms and a ghost atom if it is ammonia for example that lone pair is called a ghost atom, but we do not consider ghosts.

So this is what sigma v 2. 4, 1, 2. Now it has become a little simple, is not it? Now what I want is I want gamma vib. Can you do it quickly? N - 1 * chi xyz (R) - chi rot (R) 3 * 3 = 9. 9 - 4 = 5, - 3. 9 - 3 is 6, it is not 9 - 4 fine, fine 6. How many normal modes should it be? 6 How many normal modes should I have here? 3N - 6 what is N here, N in the sense what is the number atoms? 4. So 3 * 4 - 6 is 6. It is the same as BF3. Same as D3h.

It is just that there is a planar molecule this is a non planar molecule but they are not linear molecules. It is linear molecular then only it will be 3A - 5 so 6. So this is correct then is not it? Dimensionality. I am only 2 more to work out. So 1 - 1 is 0 anyway. 0 * 0 is 0 definitely. 0 * 0 - 0 is 5. Then 0. Then 2 - 1 is 1. 1 * 1 = 1. 1 - - 1 = 2 or 0? 0.. 6, 0, 2. Can you now break it down using ai = 1/h sum over R chi (R) chi i (R). So what is h. 3? Let us see 1, N - 1 = 1 * 1. 1 * 1 = 1.

Then - - 1. First tell me what is h? 6 sure = what + what + what? 2A1 + 2E. Once again this is the step where we can check whether we have gone wrong somewhere. 2A1 + 2E so what is the dimensionality total? 6. And we are talking about 6 dimensional basis anyway. So seems to be right. At least consistent. Fine now what we need to do? We need to assign the internal motions. What are the internal motions here once again? The bond lengths and the bond angles?

What is the difference between then and now? There is no restriction on the thetas. Is not it? They can actually expand at the same time. All can expand at the same time. So A1 is possible. So can you do this now? Gamma R and gamma theta. See this is a nice way of doing it is not it? In 1 table you can do it step by step and it is very easy to find out if you are going wrong or not. So try to do it this way. Gamma R now you know what the Rs are? Pyramidal Nh3.

What is the character for E? What is the character for C3? C3? What about sigma v? 1, 1 sigma v is 1. This has to go through 1. 3, 0, 1. Now look at these 2. You do not even have to use the thetas. Because gamma vib is 6, 0, 2 and gamma r is 3, 0, 1. 6, 0, 2 - 3, 0, 1 is 3, 0, 1. Is not it? Gamma vib has to be gamma + gamma theta if there is no redundant coordinate. Either redundant coordinate then there is an issue.

And then 6, 0, 2 is very nice and this is coming out 2, 3, 0, 1. So but just to satisfy yourself let us work out the representation using the thetas. Expansion is +, contraction is -. +, -. What will be the character for E, it will be 3. If you apply C3 then what will happen? The 3 angles will all move, theta 1 goes to theta 2, theta 2 goes to theta 3, theta 3 goes to theta 1. All are rolling stones and according to Shanthanu they will gather no more. So character for them is 0. What about sigma v?

One of the angle remains where it was, is not it? So once again the character is 1. 3, 0, 1, 3, 0, 1 you can break it down they will turn out to be A1 + E. No what does this mean? That means the A1 modes how many A1 modes are there? 2A1 modes. They involve stretch as well as bend is not it? There should be 2A1 modes of vibration you have said and then these are turning out to be A1 + E. Each is turning out to be A1 + E.

So the A1 modes are going to have stretch as well as bend. So what will the A1 modes look like? So what I am saying is that now can you think of symmetric vibration involving stretch as well as a bend? A1 means totally symmetric. No matter what will you do it is not going to change sign. So think of a vibration that involves stretch as well as bend and this totally symmetry. No what I am saying is that they have to expand also. Your umbrella does not expand.

The spokes of the umbrella remain the same only this is a folding umbrella. So 1 can be it is when the bond stretch the angles also increase that could be 1. You can say that. When the bond stretch, the angles also increase that could be 1 normal mode. You understand what I am saying not only is it going out the umbrella is opening, but the umbrella is becoming bigger also. It is an umbrella already, but it is opening out and at the same time it is becoming bigger let us say that is 1. Let us see if it fits? What will be - phase. Let me see if I can draw it?

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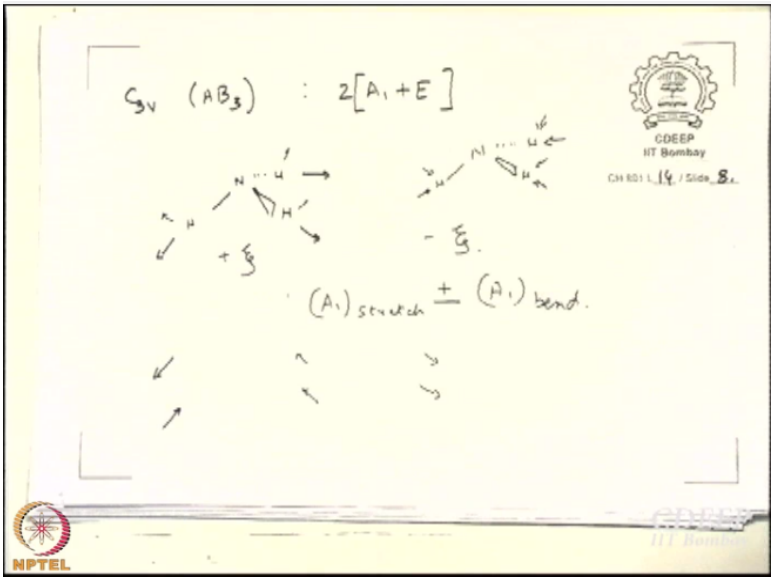

So we are talking about C3v (AB3) kind of molecule. We have already seen that you have A1 + E. I will write like this and all the modes involve stretch as well bend. What I am saying is let us think like this. Here nitrogen, hydrogen, hydrogen, hydrogen going out and while it is going out the angles also increase at the same time. I just erase that I cannot write. **Professor - student conversation starts"** At some point of time it will become planar right? If it not simple harmonic.

See planar will dome there is no issue, but a molecule there is already like this if it has to become planar then it has to be a very, very major displacement is not it? It has to be a very major displacement Which is not going to happen. Can you think of linear combination that is what I am saying? Linear combinations of stretch and bend which will also be of A1 symmetry. One thing I can say is they expand together and also the angles increase together this is + this way a good way of trying it.

Let us say this is + xi what will be - xi? The direction of the arrows will reverse. In linear motion, one will be A1 + A1 bend and one will be A1- A1 bend. That is what we are arriving at. This is + xi that is - xi. This is A1 that is what I am asking. This has to be A1 is not it? because the way of drawn the arrows there are 2 sets of errors, 1 along the bonds and other perpendicular to the bonds. **Professor - student conversation ends"** Let us say. What will be the character of E? Of course 3. I am taking this combination of error as 1 alright.

Now what will be C3 what will be the character of C3? Now what we are doing is we are taking this whole thing as 1 like domain motion. All these 1, 2, 3, 4, 5, 6 are rows they form 1 kind of motion that is what I am saying. This is +1, that is - 1. If you apply C3 to this the arrows going up still keep going up is not it? Consider the whole thing to be 1. When array is going up keep going up they do not come down. Arrays going out keep going out they do not come back.

So even when you apply C3 character is 1. If you apply sigma v then what happens same thing happens because this will remain unchanged this 2 interchange fine, but the whole thing is considered to be 1 motion. So this A1. xi never becomes - xi. So next what you could do simply

reverse the direction of these arrows. I said correctly what we have is we have say A1 stretch and we have A1 bend the possible linear combinations are + and -. Understood what I am saying?

What we are saying is that you have to have 2 A1 normal modes. That is what we have shown. Now it is impossible to distinguish between stretch and bend here. Since the symmetries are the same what must be happening is a linear combination. So since this all arrow is going together is A1 and all arrows going up together is another A1 first is from the bond length and the second is from the bond angles. When you just add then you get A1 symmetry.

When you subtract 1 from the other then also you get A1 symmetry that means while stretching just think of stretching. While stretching in 1 case, the bond angle increase, in the other case while stretching bond angles decrease. These are the 2 normal modes of vibration of say NH3 which have A1 symmetry. What have you got?

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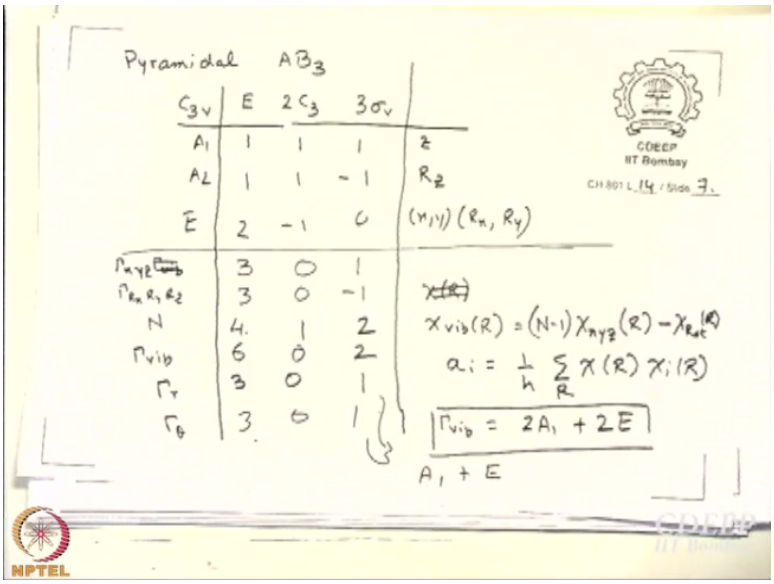

This is what we have got and what I am saying is that when I breakdown the reducible representation which I constructed using only the stretch I get A1 + E when I break down the reducible representation that I got from only the bends then also I got A1 + E. Now what I am trying to say is E is always more complicated because there is mixing of too many things I do not want to do that now. What I am saying is can we identify what are the A1 stretch actually.

What is the A1 vibration actually not stretch? For stretch it becomes confusing. What are the A1 vibrations? What are the V1 vibrational normal modes? So what I am saying is these are 2 completely different kinds of vibration since they have the same symmetry they have to mix. They have to mix you cannot have a pure stretch and a pure bend like that it has to be a linear combination like this.

So one of them will be angles opening up while the stretching is taking place the other will be angles closing down when the stretching is taking place. See these 2 are not related by + or – is not it? They are different. Let us take it like this when let us first talk about this when stretching takes place. What we are saying is in 1 case the angles are increasing in the other case the angles are decreasing.

The other would be when it is in the opposite phase then again angles can be opening up or angles can be closing down. So, it is just the negative phases nothing else. So see for BF3 or for any state list we had been exactly able to tell what are the 2 normal modes? Stretching and bending had to be together. What is the difference from say BF3 for BF3? we had said that there has to be a pure stretch. A pure stretch without any bending motion at all. Here what we are saying is that you cannot have a pure stretch.

A stretch has to be accompanied by a bend at least for the total symmetric one. E ones are more complicated will not get that.