Symmetry and Group Theory
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Lecture – 38
Contribution of internal motion to normal modes

What was the answer?

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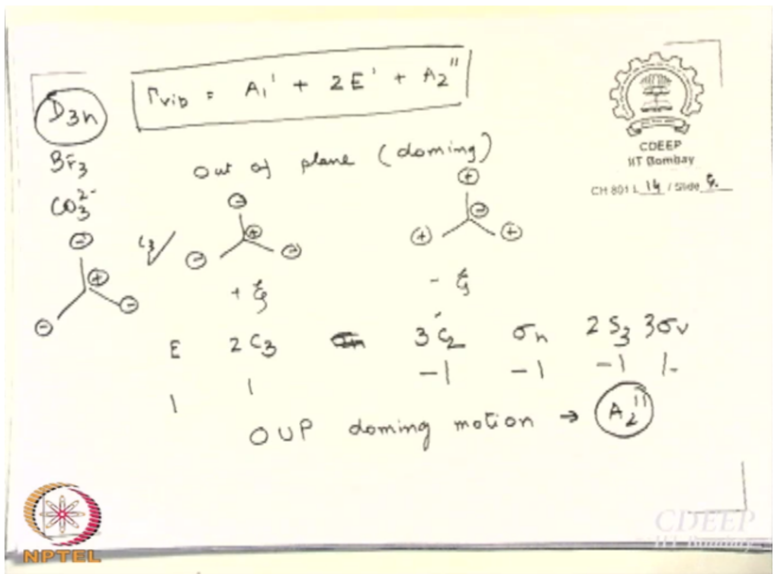

You are saying gamma vib = A1 dash + 2 E dash or double dash? I think E dash just because there is a 2 outside does not mean it will become 2E double dash. 2 E dash + A2 double dash. Hope you got this for what? For D3h not only for D3h for something like BF3, CO3 what is CO32 - so on and so forth. So thing you can get using the formula I wrote let us see we will take some other molecule also, but let us proceed further.

Now I do not want to stop here, but what I want to do now is now I want to proceed a little further will not be able to go to the end of this vibrational spectroscopy unfortunately then I cannot teach anything else, but let us see if it is possible for us to try to ascribe the actual molecular motion to some of the symmetric species. Yes, if we can go at least 1 step forward. What I am saying is that what are you know what the normal modes look like.

And I started this exercise by saying is it possible for us to develop a method by which we will be able to tell what the normal modes of BF3 look like that is what we are trying to do is not it? So let us see if you can go 1 step ahead in that direction at least. What are the internal motions of the molecule that are involved in vibration for BF3 for example? Your bonds and your bonded angles so what are the different motions that you have stretch, stretch, the bonds can stretch.

So this is +, this is - and then there can be 2 kinds of bends. One is in plane and the other as we discussed bending motion. So which is which? Which, which is which that is what we want to find out? Let us see if we can do that? So what we do is we first separate the outer frame motion and the in plane motion what happened? Out of frame motion and in plane motion let me draw the outer frame motion first because it is one of a kind, is not it?

So it is likely to belong to some 1 dimensional symmetry species. It is difficult for it to mix with anything else. So let us see. So out of frame motion. How did you write? So I can say this is + and all these are - What does that mean? There is relocalization of charge from the B atom to the fluorine atoms. So the fluorine atoms become all negatively charged and B becomes positively charged. You are talking about vibration here no question of charge + means this atom is coming and trying to hit you and - means these atoms are scared of you and they are running away from you.

Right now they are in the plane. This atom gets curious and comes towards you. It wants to see what exactly are made up of and these 3 atoms have had enough and they are running away. That is a meaning of + and – here, is not it? + means out of plane motion towards me - means out of plane motion away from me without vibration got it everybody got it. Forgot the name Sumit got it sure. So I call this as the + phase and I will call it say + xi what will - xi be what will the - phase be.

Just replace the – by the +s and other. So this becomes - these 3 become +. Now the fluorine atoms are inquisitive and they are coming towards you and the boron atom has added up and running away. So this is +, this is -. Now can we apply the symmetry operation and see what the characters will be let us see. What are symmetry operations E then 2C3 just C3 is enough then sigma h then 3 C2 comes earlier, is not it? Sigma h then 2S3 then sigma v how many 3.

What will be the character of E of course 1. If I apply C3 then what happens? What should the character be + or - don't forget this is + the whole thing is +. This whole thing is -. So if I apply C3 what happens? The - remain - wherever you have - sign now you have - sign even after applying C3 wherever you have + sign now you have + sign after applying C3. So you agree with me that is + xi, + xi remains + xi and - xi remains - xi agreed?

Very simple. So character is 1. **"Professor - student conversation starts"** If there is a question please ask? That is what we are saying. We apply C3 what happens. Apply C3 here. This is what you get. It is true that the atoms change phase, but the motion as a whole that does not change phase, is not it? So this is +, this is - so in + phase if you apply C3 what happens, this change place fine, but + remains + See the thing is we are facing opposite directions so what is + for you is - for me.

Whatever it is let us say this is + I understood what you are saying. Let us say this is - alright. We apply C3 this is what you get (()) (08:05) now so - remains - this is - this is also -. - does not become + by C3 does it. So what about C2? What happens when you apply C2? Let us see. Now these are situations where I wish I had 1 more hand. Where will the C2 be? Do not forget what we have said in the last class.

We have turn over simple harmonic motion which means very small displacement, otherwise if it is really as big as displacement as I have shown here then what would happen? It would not remain a D3h loop anymore it would have become C3v. So the only reason why we can carry out this discussion is that we are talking about simple harmonic oscillation which means very small maximum displacement. So where is C2 then, this is C2 agreed.

If you turn the C2 what happens - becomes +, + becomes -. This is + this is C2 apply C2 it becomes - and other hand would have really helped. Got it everybody. Convinced? **"Professor - student conversation ends"** So I will write + 1 - 1 after saying all this you might write + 1 then what is the point of discussing so much. Sigma h - 1. S3 - 1 the sigma temperature is involved. Sigma v is + 1, is not it? Now let us compare with the character table.

Remember 1, 1, - 1, - 1, - 1, 1. Do I need to compare with the character table? **"Professor - student conversation starts"** Looking at this A1 dash, A2 double dash the only options are there right. A1 dash and A2 double dash means totally symmetry and A2 double dash what is the meaning of double dash. Double dash means it is antisymmetric with respect to sigma h this is definitely antisymmetric with respect to sigma h.

So even without character table looking at character table I can say that this A2 double dash mode has to be the domain mode, is not it? Understood? **"Professor - student conversation ends"** so I do not even have to look at the character table in this case just because it is double dash I can say that it has to be the out of plane motion.

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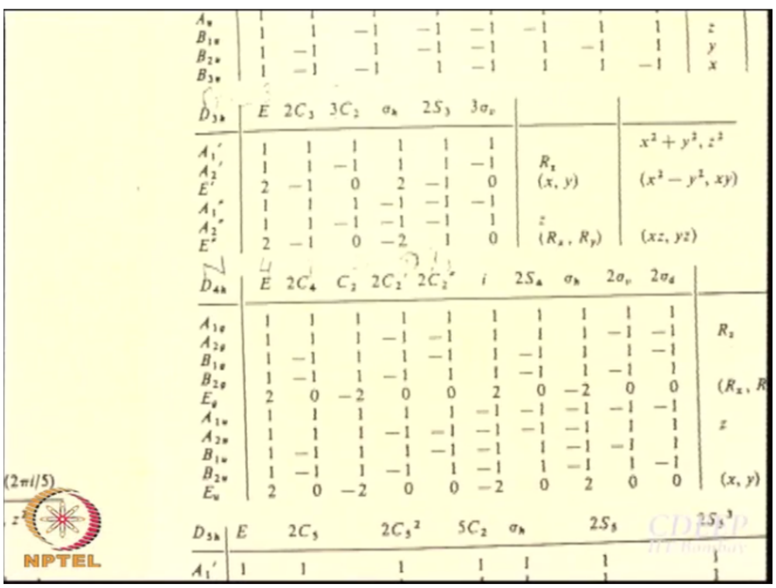

A_u	[illegible]								
B_{1u}	1	1	−1	−1	−1	−1	1	1	z
B_{2u}	1	−1	1	−1	−1	1	−1	1	y
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1	
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1	
E_g	2	0	−2	0	0	2	0	−2	0	0	$(R_x, R$
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1	
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1	
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$
A_1'	1	1	1	1	1	1	1

A2 double dash is 1, 1, - 1, - 1, - 1, -1. So perfect match that where it is. So you have identified so far is that this domain motion of that we could draw easily without much hassle we identified that the domain motion is the titration you will get impatient at the end point and then it is gone. So what we are saying is that the out of plane domain motion. **"Professor - student conversation starts"** What is the other famous what does the OUP stand for.

What is the famous? Oxford university press. That definitely has A2 double dash symmetry. So 1 is assigned already. What are we left with? A1 dash and 2E dash. So 3 normal modes, is not it? Is it a yes or is it a no? A1 dash + 2 E dash that is 3 normal modes or what? 5 normal modes so that is a no. It should be no. 5 normal mode. So forget that each E dash it is 2 normal modes. 2 dimensional with limitation. **"Professor - student conversation ends"** So 1 is assigned.

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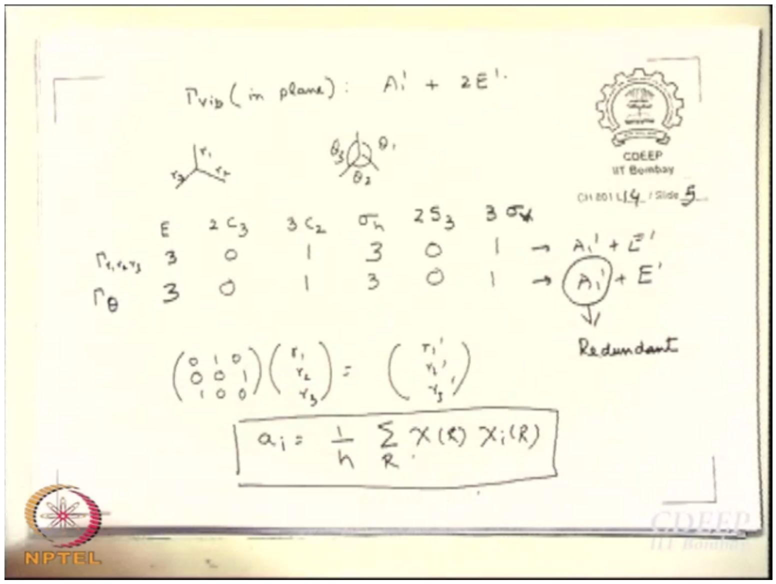

So what I can write further is gamma vib in plane has to be A1 dash + 2 E dash. There is only kind of out of frame motion is already accounted for. So none of these is antisymmetric with respect to sigma h. So these whatever normal modes you have belonging to these symmetry species all these normal modes must be symmetric with respect to sigma h. If they are symmetric with respect to sigma h, then they cannot be out of plane, is not it?

If they are out of plane automatically if you apply this frame, then it has to change sign. So the remaining 5 normal modes have to be in planes. So there is a second information that we have got. What we have left now. A1 dash + 2 E dash. What will be the character of sigma h for these? E dash I understand it is little problematic, but A1 dash is totally symmetric. So character of sigma it has to be + 1 even for E dash the thing is that dash should give you the hint.

Since it is dashed that means now what you do it is symmetric with respect to sigma h which is antisymmetric or if it was not symmetric with respect to sigma is then it would have been E double dash. So what I am saying is that anything that goes out of plane that has to be anti-symmetry with respect to sigma h so we conclude that A1 dash + 2E dash all these normal modes of vibration have to be in plane motion.

One of the different in plane motions you can have stretch and bend. So what I will do now is I should construct reducible representations using the bond lengths and the bond angles. What is the meaning off stretch change in bond length? What is the meaning of bend, change in bond angle? So this is what I will do. Let me call this what do I want to call this. I will call this R1, R2, R3 and I will call this, this theta 1, theta 2, theta 3.

Of course nothing takes place when R1 = R2 = R3 and theta 1= theta 2 = theta 3 these are the mean positions. Now once again let me write down this E, 2C3 then 3C2. how many sigma h? 1. **"Professor - student conversation starts"** Can I have more than 1 sigma h in some molecule? (()) (16:13) Platonics solids, octahedral, octahedran principal axis, sigma h, but there are 3 principal axis. So there can be more than 1 sigma h also, for platonic solids only. Sigma h then 2 S3, then 3 sigma h, then 3 sigma v.

I just congratulate myself thinking that I will be able to write a line without missing up you should never congratulate yourself it is where it is. **"Professor - student conversation ends"** Now what I want now is I want to write gamma R1, R2, R3. So E what will be the character of E. There are 3, R1, R2, R3. Now they are separate stretching. So this can stretch and this cannot stretch. So it is a 3 dimensional basis.

When I have R1, R2, R3? Is not it? a 3 dimensional basis? right or wrong? Earlier what I was saying is that they all moving together the domain motion all the 3 bonds were moving together like this. This correlated motion that is why what is considered to be 1, is not it? Right or wrong? Out of plane motion you cannot have an out of plane motion like this why, why not. Centre of gravity will move, is not it?

Symmetrical is small motion, but can you have just 1 thing moving like this, that will not be a pure vibration. For pure vibration all 3 have to move because what is happening is see remember

I had drawn 4 signs when these were + this was - that means all the atoms were moving. These 3 atoms were moving towards you and the central atom was moving away from you or the other way round. So thereby keeping the centre of gravity in its place.

If centre of gravity moves what kind of motion is it translation. Of course this is not pure translation also. So this is a mixture of translation and vibration. So centre of gravity has to be kept in the same place if you are to talk about a pure normal mode of vibration. Do not forget that. That is why this was 1 motion the whole thing is 1 motion. Now what we are saying is this can stretch and then the whole thing can go down no issue.

This atom moves out and then these 3 atoms move down. So this central gravity will not move then, but effectively what will happen is only this bond length will change these 2 bond lengths will not change that is possible. This atom moves out and the central atoms moves in so that can happen for each of these atoms each of these bonds. So R1, R2, R3 these are 3 separate bond lengths and they form a 3 dimensional basis understood.

So I want to draw right matrixes like this. R1, R2, R3 gives me r1 dash, r2 dash, r3 dash. **"Professor - student conversation starts"** So then what will be the character of E as a Freudian slip. What will be character of C3? What happens when you apply C3? r1 becomes r2, r2 becomes r3, r3 becomes r1. What is r1 dash. r1 dash is r2, is not it? So what will be the matrix. 0, 1, 0. What is r2 dash r3 so 0, 0, 1. What is r3 dash r1 so 1, 0, 0. What is the character?

Why is the character 0? Because once again the rolling stone gathers no mass. Rolling stone gather no mass. Earlier remember the atoms that moved did not contribute to the character. Here also the bonds that move do not contribute to the character because they go off diagonal. Understood. I do not need to draw the matrix anymore after this. Just remember what we learned earlier.

We learned that if something moves from its place then it does not contribute to the character because it goes off diagonal in the transformation matrix understood clear, crystal then tell me what is the character of C3, what about C2. If you apply C2 along r1 for example, then r2 and r3 change places r1 remains where it is so r1 does not move. So something that does not move has some character here also something that does not move has character contributes to the character.

So what is the character then? 1. Sigma h 3 do you agree 3. r1 remains r2 remains r2, r3 remains r3. 3. S3? See for S3 first of all you have to apply C3. The moment you apply C3 r1 goes to r2, r2 goes to r3, r3 goes to r1 and then when you reflect by sigma h there is no further change. So once again they go off diagonal. So a character of S3 is the same is character of C3 here. So 0 and what about sigma v 1, once again without much I do.

So see your representation is also nicely symmetry. It is not symmetry it is repetitive. That is a kind of crystal symmetry. 3, 0, 1, 3, 0, 1. This is gamma theta. If the theta is now if you do the same operation what will be the character of v that even I know, even I know that it is going to 3, right 3 or not 3. 3. Theta 1, theta 2, theta 3 once again theta mention as representation. What about C3 where you have + C3 0 do you agree theta 1 goes to theta 2, theta 2 goes to theta 3, theta 3 goes to theta 1. So 0. C2? What about C2 it is 1.

"Professor - student conversation starts" You see if you apply C2 along this theta 1, theta 3 interchange. Theta 2 remains theta 2. It is just the angle it does not matter whether it is between r1 and r2 or whether it is between r2 and r1. It is same nature love symmetry you cannot do anything. You cannot do anything. 3, 0, 1 again. **"Professor - student conversation ends"** This is as exciting as playing housie what about sigma h 3. S3 0. 3 sigma v again 1.

So once again we apply sigma v theta 1, theta 3 will interchange theta 2 will not. It is not a black and white camera if I cannot differentiate between black and red anyway it is 1. 3, 0, 1, 3, 0, 1. So now what is the next step I have to break this down break these reducible representations down into consequent irreducible representations how will I do it. aj or what do I say ai? ai = 1/h sum over R chi(R) chi i(R) very good.

You can do it, but even before you do it do you anticipate a problem. I anticipate the problem. What is the problem? See what is this character of E. What is the character of E? if you do not remember character of E = the dimensionality. This also dimensionality. So when you break this down you should get either 3 1-dimensional representations or 1 1-dimensional representation + 1 2-dimensional representation. Same here. So total dimensionality here is 6.

What is the total dimensionality here? 5. So out of the blue you got an extra dimensionality. This is what is called a redundant coordinate. We will come back to that. First can you please take it down. You need to see the character table should I project the character table? First take this. This you can remember right. 3, 0, 1, 3, 0, 1 very easy. 3, 0, 1, 3, 0, 1 break it down quickly what is it. A1 prime + E prime very good. If I were you I would have perhaps guessed, it.

It cannot be anything other than sums of A1 prime and E prime anyway right. So see now the problem is this gives you A1 prime + E prime. This also gives you A1 prime + E prime. So we have got extra coordinate. We do not have 2 A1 primes. E prime is fine, but we have an extra A1 prime where has this extra spurious redundant A1 prime come from. What is saying is that the 3 are 3 bond lengths are completely independent of each other.

They can the length of 1 is not dependent on the other very good, but the thing is since this is in plane either out of plane it could have been fine. Since we are working inside the plane this theta 1, theta 2 and theta 3 are not independent of each other. Only theta 1 and theta 2 should be independent theta 3 should be dependent because theta 3 = 360 degrees - theta 1 + theta 2 in brackets. So that is where the spurious coordinate has come from.

So I am trying to say is that this A1 dash that we get from gamma theta this is A redundant coordinate and you can identify the redundant coordinate pretty easily because what does A1 dash mean. A1 dash is the totally symmetric representation. Now is it possible that all these angles will increase. So what is + what is - in this case. Increase is +, decrease is -. So if this A1 dash is really to be there then what we are saying is that all the bond angles should be able to expand at the same time that is not possible.

If 2 bond angles expand the third dash has to contract. So A1 dash is just not possible. So what is good for us to do is work with theta 1 and theta 2 only that will be a 2 dimensional representation work it out we will see you will get E dash. So what we have learnt so far. We have learned that

A2 double dash is the out of plane motion. We have learned that this A1 dash is A symmetric stretch. So at least 2 of these normal modes can be identified on ambiguously.

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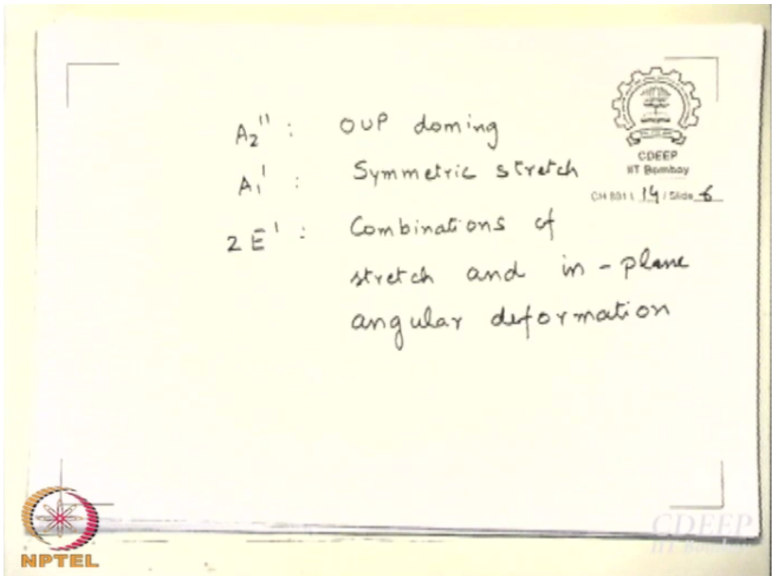

"Professor - student conversation starts" If we are working with only theta 1 and theta 2, we can take C3 and Sigma v. That is the problem why we actually work with theta 1, theta 2, theta 3 that is actually a problem so in any case it should become E dash, is not it? because we are working only with character. You can get either 1 or 0. Then we have got a problem. So that is why we work with theta1, theta 2, and theta 3 and eliminate the redundant coordinate this way. **"Professor - student conversation ends"**

Fine so what have we learnt? We learn that A2 double dash is unambiguously the out of plane domain motion. We have learned that the A1 dash mode is unambiguously the symmetric stretch. What is left? The 2E dash modes. These have to be combinations of stretch and in plane angular deformation. We have been able to go some distance further, is not it? Now if we can actually go all the way.

And we can say that this is exactly this kind of mode for that we need to convert this whole problem into what are called symmetric coordinate and we need to discuss internal f and g matrices. The problem is if I want to do that that will take us to the end of the course. So we do not want to do that we want to do one more thing about vibrations and that is IR and Raman activity.