Symmetry and Group Theory
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Lecture – 42
IR and Raman Activity: Examples

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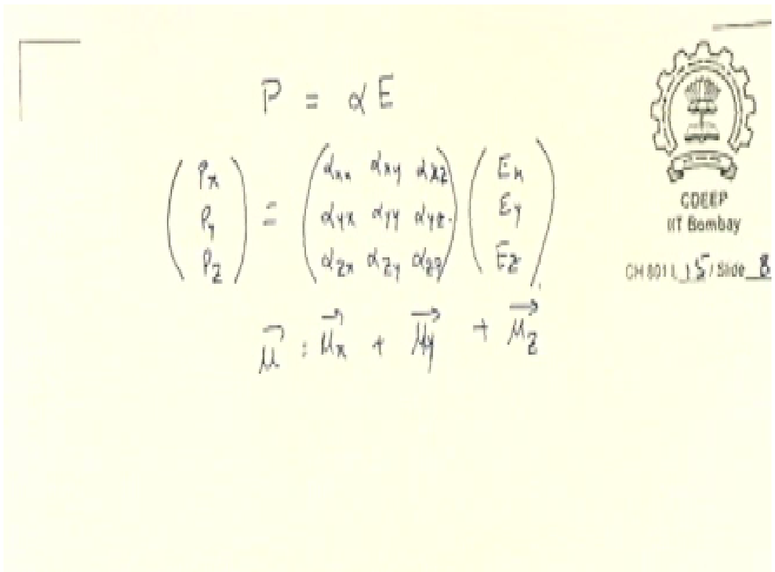

So, in gamma spectroscopy what we said is what is important is polarizability, how polarizable your molecule is? what is the meaning of polarizability? Before you start telling me some story I will write this is the definition of polarizability what is E? **"Professor - student conversation starts"** Electric field fine and what is P? no P is induced polarization okay induced polarization okay alpha is polarizability "**Professor - student conversation ends."**

So, everybody knows how to write it in this format but there is more to it. The thing is polarizability is a very tricky customer. Let us say polarizing the electro cloud and you apply an electric field in this direction, you will think the cloud will get distorted in that direction but then you are talking about a finite cloud right. It is an answer so what will happen is that even though you apply the field in this direction you are going to see distortions in this direction.

And these directions also think of a balloon. Okay take a balloon and press it stretching a balloon is little difficult that is why I said press it. But that should not come in the way of your imagination press the balloon what happens. Does it only get distorted along this direction it gets you distorted on this direction or this direction also that is exactly what happens here as well. So, that is why it is not necessary you cannot just restrict it to one direction you cannot expect that a field in x direction is going to cause polarization in x direction only.

Field in x direction is going to cause in xy and z direction. So, you have to write it in this kind of metric form Px Py Pz=alpha will come as matrix here Ex Ey Ez right what you write here is alpha xx alpha xy alpha xz. What is the meaning of alpha xx it is a proportionately constant right for or you can say polarizability for field applied or polarizability along x direction for a field applied in x direction.

Alpha xy is the polarizability along x direction for a field applied in y direction alpha xz is polarizability in x direction for field applied in z direction. Again fill in the remaining ones for alpha yy alpha yz alpha zx alpha zy alpha zz and the other thing is alpha yz=alpha zy. We are not going to prove it but then you can take it axiomatically. Alpha yz= alpha zy and alpha xy=alpha yx. Is there anything else? alpha zx= to alpha xz.

Okay now like you mu=mux+muy my hand writing taking over +muz. You took the components of the dipole moment along xyz vectors. Here you see the components of polarizability come along planes. Is not it xx xy when you write something like that two coordinates are specified where there is a plane so components of polarizability are along planes. So, you can think like this polarizability and you can think polarizability as a three dimensional object.

If you read binomials spectroscopic books for example they talk about polarizability ellipsoids right and so think of maybe a watermelon okay watermelon is an good model for polarizability ellipsoids. When you cut a watermelon what kind of section do you get? Watermelon knife cut, cut like this cut like this cut like this and whatever what is a section what does the section look like.

Unless you are very bad at cutting watermelons you get a plane and see that plane as a section. So parabola, hyperbola not interested in that. All I wanted was that we get up a plane or section is not it that all that I want it. So, this is a meaning of these components along planes. Unless for some reason you cut like this then that is a different issue okay so planes are important here. So, now if you want to know Raman activity what is important? x y z are not important anymore.

What is important are the quadratic quantities involving x and y and z. Alright once again let us do our zooming in zooming out trick but before that let us go back to the previous slide.

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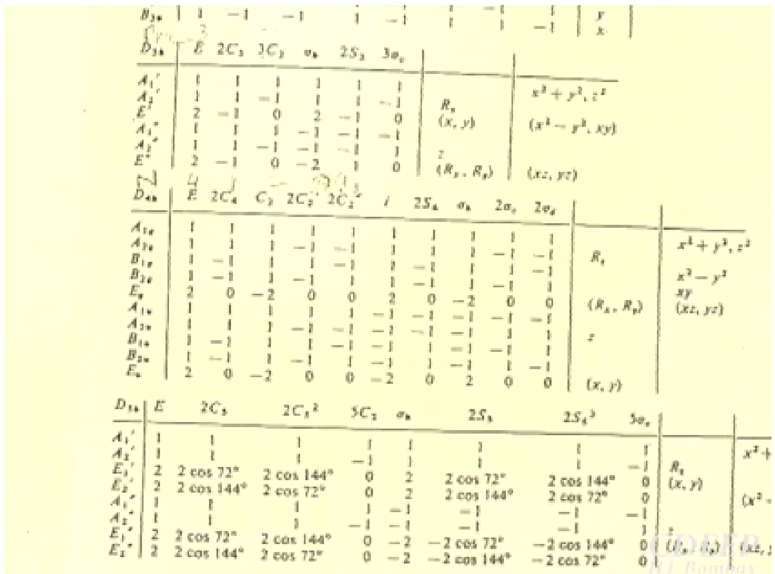

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

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		x^2+y^2, z^2
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		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
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	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		x^2+
A_2'	1	1	1	−1	1	1	1	−1	R_z	
E_1'	2	2 cos 72°	2 cos 144°	0	2	2 cos 72°	2 cos 144°	0	(x, y)	
E_2'	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	2 cos 72°	0		$(x^2-$
A_1''	1	1	1	1	−1	−1	−1	−1		
A_2''	1	1	1	−1	−1	−1	−1	1	z	
E_1''	2	2 cos 72°	2 cos 144°	0	−2	−2 cos 72°	−2 cos 144°	0	(R_x, R_y)	$(xz,$
E_2''	2	2 cos 144°	2 cos 72°	0	−2	−2 cos 144°	−2 cos 72°	0		

We want to see whether A1dash is Raman active or not and while we are adding also want to see whether these is Raman active or not. You can see A1dash does it have some quadratic power z square x square and all that. You cannot see there is something in second column that is good enough second column is quadratic power. Now do you see something is there right and it is going to be Raman active what the wrong page B38 A1 dash upper one and not the lower one.

What does it have does it not have x square + y square + z square and it is going to be Raman active. Because it is in the same symmetry species as some component of polarizability. It is not IR active because it does not share a symmetry species with x or y or z. But it does share a symmetry species with some component of polarizability and that is why it has to be Raman active.

What are the other normal modes of vibration that we already talked about E dash*double dash they are IR active. Are they also Raman active let us see E dash something is there. What about A2 double dash no right. So now let me complete the story.

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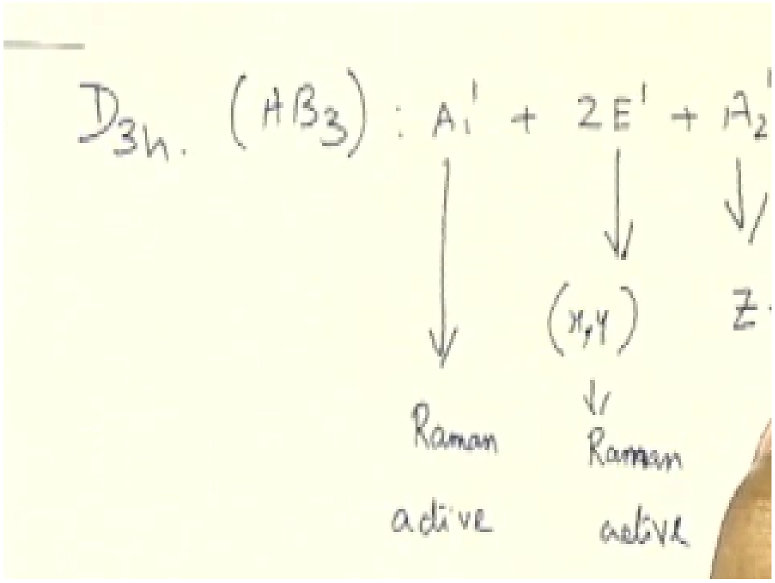

And is this Raman active or not? It is Raman active. I will write active only once and hence forth I will write only Raman Raman was a very active scientist anyway you should read Ramans biography. A lot of things Raman worked as an accountant in AG Bengal that is accountant general in Bengal so before going to office and after coming from office he discovered an Indian association for the division of science very thankful for that.

Because eventually id also did my PHD from there so he discovered that institute first defunct institute at that point of time. He would go and do his research just out of curiosity. And nothing else and then from there he would go to his office come back directly from office to their work till late night and go back home, of course needless to say Mrs. Raman was very understanding lady. Otherwise it would have been impossible this is Raman activity.

What about E dash is E dash Raman activity or not? this one is IR active as well as Raman active. Moreover, the IR section is going to be xy polarization. So, now see you can very easily identify which vibration we are talking about. Nobody does that in regular usage of IR but this is really the power of IR spectroscopy that we are learning today. And what about A2 double dash it is z polarized IR active but Raman inactive.

Now if you record the IR spectra at different polarizations. And if you record Raman spectra compare them you can actually identify which transaction is due to which normal mode. So, whatever we are saying now can be verified directly by experiment. Right fine let us take one more example which our example did we take yesterday ammonia but since we are nearing 6.30pm I am not going to take an example of ammonia.

And I am going to take another example that you are supposed to have worked out last evening okay yes.

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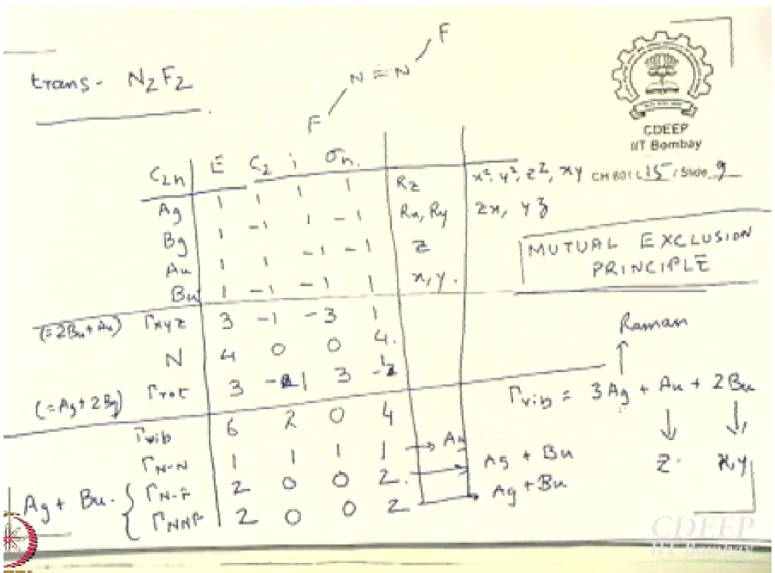

And of course there is a reason why I want to take N2 tell me which point is this C2H OR D2H C2H sure where is C2. This is C2 we cannot even see okay this is C2 right horizontal line of symmetry is very easy to see and what else is there. I is there right. Centre of inversion and that is exactly why I want to discuss this and not some other example something nice will come out and what are the symmetry operation can be possible E of course what else E, C2, I sigma H.

Okay and since we are doing it lets go all the way for the benefits of esteemed members of this class who were not present yesterday. We will work this out even though some of you might have worked it out last night, we will work it out now. I will write the character table for you first line I think everybody can write 1 1 1 1and even first column everybody can write 1 1 1 1. Are you convinced? It is 1 1 1 1. L1 square sum over I LI square= 4.

Right so now I will put in the others 1- 1 1 -1 and then 1 1 -1 -1 and 1 -1 -1 1. Almost like your water is it not like that and we are going to do it in a tabular fashion like what we did yesterday. This is Rz x square y square z square xy Rx and Ry belong here zx and yz belong here the z belongs here x and y belong here. You need to tell me what are the molecule names I do not have to write 1 here because G is enough.

And whatever is symmetric with respect to inversion you give it great respect and you can call it G and whatever is anti-symmetric you can point your finger and say it as U gerade or no gerade okay this is the character table for you. Before we go any further let us talk about Rx Ry and Rz. I promised to do this yesterday Rz Rx and Ry, how do I talk about Rx Ry and Rz the principle axis is always taken as z axis right.

So, xyz this is z axis and this is x axis right so Rx means what this kind of rotation and rotation with respect to the x axis you can draw it like a little curve pointing this way. This is + Rx and what is – Rx this now let us see if we can work out for the characters of Rx. Of course it is given in front of you and that is not an issue what is the character of E for Rx is 1 of course. If I apply C2 what do, I have to do I have to go this way right.

This is C2 axis and this is how I was rotating my arm okay now I am performing C2 without changing the rotation of my arm. Keep watch on me and this is how it is see what do I have the original co-ordinate this is what the motion is like and in the transform coordinate this is what the motion is like this right. This and this and minus of each other when I come towards you I come down and here when I come towards you I come up the negative alright.

What is the character of Rx then - -1 what about I? what about I not I? if you inward what will happen will it change or will it even the same. Let us say I am coming down like this I will invert and come here. The direction will not change still it will be like this. Draw the small errors and see you will get it what about sigma x where is sigma x here right and coming down from here what will be the reflection going up that is -1.

That is how you can work out the characters of Rx Ry Rz also. Okay not difficult and of course I mean in a public place if you start doing all the scenes with your arms then people will think that either you are crazy or professor or both. So, you should learn to draw small curved errors and do it from there not difficult. Let us come back to an actual problem what do I need to do first of all I should write gamma xyz.

Check with that gamma xyz, gamma xyz is just the reducible representation which contains x as well as y as well as z. How will I get it 2 Bu + Au right in fact I will write it here also 2Bu + Au. Okay understand what I am saying because x is 1 y is also 1 **"Professor - student conversation starts"** very good to which symmetry species is x and y belong that is already a two dimensional representation isnt it.

That is way it is a very good question this is a doubt should come to your mind if you are alert. Got what I am saying if x y jointly makes up the species for a two dimensional representation then you do not have to add it is only two dimensional. "**Professor - student conversation ends"** But here x and y both belong to some 1 dimensional species so that why you have to add 2B u + Au now what will help me 3 -1 -3 1e everybody agrees.

Now how many remains unchanged and how many atoms are there? 4. what is the number of atoms that remains unchanged under each operation E4, C2 0. I 0 very easy and what is the next step what do I do N – 1 1 gamma xyz. Right may be you can just make it gamma rot what is gamma rot Ag +2Bg. I hope you are not too busy to miss why it is 2Bg. You know why it is 2Bg tell me what it is then 3 and I will give some pause for 3 -2 -2.

I tend to think 1+1=2 **"Professor - student conversation starts"** 3-1 3 -1 very good, then what I do after that now I work out gamma vibration "**Professor - student conversation ends"**. Sure this is exactly what we did yesterday are you following what we are doing what is gamma vibration and how will I find the characters n – 1* by the character of gamma xyz - the character of gamma rot.

So, 3*3 is 9 - 3 is 6 quick check how many normal modes of vibration should we have 6 right okay so far at least we are fine. Then N -1 -1 is -1 * -1=+1 and +1 - -1=2 here what is it -1 *-3 is +3 -3= 0 then N -1 here is 3 and 3 multiplied by psi of xyz is 3 right + 1= 4. Have you all on the same page can you understand? Shumangali this is okay can you follow everybody okay sure and Avinashes? Okay now what do I do I break it down to constituent reducible representations by using that important relationship.

So, I get gamma field equal to what gamma field equal to what it will be 3Ag 3Ag + Au + 2Bu. 3 + 1+4+2= 6. Do you all know how I am getting this 3Ag + this thing are you all okay. Now what do I do next I want to assign the internal motion way but even before that we can do it we can see which one is in IR and which one has IR in it. For that we have done the character table What is 3Ag 3Au Bu you are entitled to be forgetful when you are a professor right.

Character table is already there so tell me which one is IR active Au is IR active and it is z polarized. What about Bu? IR active and xy polarized is Ag IR active Ag is not IR active right Is Ag Raman active so this is Raman active. So now let us complete our search is Au Raman active or Bu is Raman active this is the manifestation of a general principle called mutual exclusion principle.

What is the meaning of mutual exclusion? it is somewhat like saying if you are absent for the class then you are not present in the class. Being absent and being present mutually exclusive okay whatever is IR active is not Raman active whatever it is Raman active is not IR active. When does mutual exclusion principle hold, it holds when you are in center of symmetry and why see the point is this x and y and z.

Wont you agree with me and when I say that x and y and z all have to be anti-symmetric with respect to center of inversion anti-symmetric with respect to inversion right. Because your plus+ on the top you have - at the bottom. You do whatever you want except for E well no not for whatever you want. If you invert this is what happens it becomes - + -, no matter whether it is x or y or z it has to be u symmetric.

Okay that is what is involved in the transitional moment integral for IR activity what is involved in Raman activity the quadratic terms x square y square xy and so on so forth. So, now you have something like U cross U right U cross U is G it is like -1*-1=+1 that kind of thing. That is why we have nice situation where you have mutual exclusion. If you have point of inversion, then the modes that are IR active are necessarily Raman inactive.

Modes that are Raman active are necessarily IR inactive and this is a very good way of experimentally determining whether the molecule has a symmetry of and has inversion symmetry or not. Alright mutual exclusion principle so to complete our discussion here what we should do is we should talk about the internal motion what are the parameters that I can use I can use gamma NN.

And that is going to be very unique right and that is a one dimensional representation and what will be the characters all 1. Is that right I am right I have only come out of the bottle neck there is no+ no -. So, it is totally symmetry okay and that is definitely going to contribute to this Ag vibration an instance. What else is there NF gamma NF what is the dimensionality of the basis **"Professor - student conversation starts"** mam problem.

Before that you understood up to here. "**Professor - student conversation ends."** Now I want describe the symmetry I already know what is the symmetry of vibration. Now I want to see out of this vibrations that are there 3Ag vibration and 1Au vibration and 2 Bu vibrations which vibrations involves NN stretch and which vibrations involves NF stretch which vibration involves bend.

Okay alright so NN stretch you have to use NN bond as the basis when you use NN bond as basis then it is totally symmetric. Okay now NF, how many NF bonds are there this is one and that is one what is the dimensionality of basis 2. And what will be the character of E what would happen if you apply to C2 the 2 bonds interchange so 0 right.

I will not bore you by repeating that thing again then what about I0 and what about sigma H 2 what else can I use the angle gamma NNF NNF is the angle right. So what will be gamma NNF, how many anglers are there 2 so what will be the dimensionality 2 this will be 2. So, quick check how many Raman nodes have you already accounted for 1 2 3 and 2 5. How many are left 1 what would that normal mode be is this a molecule? can this be a normal mode of vibration.

This one coming towards you and this one coming towards me it is not a normal mode of vibration it is a normal mode of rotation. Isnt it that is rotation but this is a normal mode of vibration both coming towards you out of the plane and both coming towards me that is minus face right that is out of plane. Let us finish with this story N and F what will be the character for C2 0, what will be the character for I 0.

What will be the character for sigma H so when you break this down what do you get? Do you get Ag +Bu so 1Ag + Bu for NF and 1Ag + Bu for NNF have you accounted for everything? What have you not accounted for yet Au have you accounted for the 3Ags. Yes, this gamma NN is Ag this is Ag and this one you said as Ag + Bu this one is also Ag + Bu what is left Au? Au is left okay.

Can you see that out of plane motion is Au look at the character sigma H out of plain where is sigma H. The plane of the molecule is sigma H is it right I am saying this is + and this is a minus + minus so this is + if you perform sigma H now what you get do you not get this + - + sigma H and I dont have I wish in had long nose now and this would have been the plane then right this is minus that I will converse it as Au at least the character of sigma H is -1.

So, that is your Au so what we have done is transit to F2 and t we have done a complete analysis now you should be able to handle the rest okay.