Chemical Applications of Symmetry and Group Theory
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Lecture – 35

Hello, welcome back. So, where we were looking at the selection rules of fundamental transitions, so we will start from there today again.

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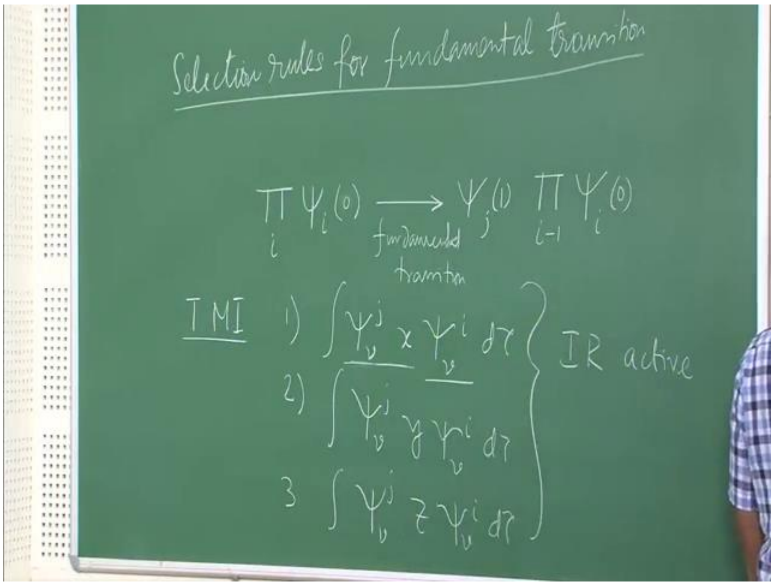

Selection rules for fundamental transition

$$\prod_i \psi_i(0) \xrightarrow[\text{transition}]{\text{fundamental}} \psi_j(1) \prod_{i-1} \psi_i(0)$$

<u>TMI</u>

$$\left.\begin{array}{l} 1)\ \int \underline{\psi_v^j}\, x\, \underline{\psi_v^i}\, d\tau \\ 2)\ \int \psi_v^j\, y\, \psi_v^i\, d\tau \\ 3\ \int \psi_v^j\, z\, \psi_v^i\, d\tau \end{array}\right\} \text{IR active}$$

So, for fundamental transition we explained in the last class, what is a fundamental transition? Will again recap that, if I have n number of normal modes for a given particular molecule and the out of initially the ground state means that all of the normal modes will be staying at Vibrational level 0, so which is return as, the product of all the wave functions. Now if I say this is my Vibrational quantum number, then if n equals to 0, then if all of them all of wave functions are at 0 Vibrational level, then this is my molecular ground state and if one of the normal modes is excited to the level 1, then I have suppose this is the jth normal mode. So, kth normal mode is was stain or residing at Vibrational level 1 and rest of the normal modes which is I that number will be now i minus 1. We still stay in the level 0. So, this transition is a fundamental transition.

So, we want to study fundamental transition because that is the most intense one compared to any other possible transition that we mentioned like an overtone or combination banks, combination transition. Now we got ultimately the rules in terms of the transition moment integral. So, when we were looking at the infrared spectroscopy transition, we got the transition moment integral as 1 as integration psi v j; we use this particular terminology instead of using this terminology; we use this one v is vibration and j is the particular normal mode jth normal mode, which is being excited. And you have either x or y or z.

So, this was 1 and second was a singular integral with y as operator, and third one was integration for z and we say that since this psi v i is my ground state, and we already said in the last class, in normal mode in the ground state, will always form the basis for totally symmetry irreducible representations. So, this one I do not have to care about. So, I have to only care about this part.

So the normal mode that is being excited at the operator, if know the irreducible representation for which this x forms the basis of, then all I need to know what is the irreducible representation for which this normal mode, that is being excited from the bases off and as per the rule of transition moment integral whether that will be 0 or non 0, will depend on whether this overall integral is forms the basis of totally is symmetric irreducible representation or contain the total symmetric irreducible representations.

So, when we represent this particular product by direct product of the respective irreducible representations. So, that will mean that I need to know the particular irreducible representations of this normal mode. So, the moment this and this belong to the same irreducible representations, I have a non 0 value for this integral. So, this 3 all together will give me that selection rule for a fundamental transition in infrared spectroscopy. So, a normal mode will be inferred active; if this belongs to the irreducible representations for which either 1 or more of the Cartesian coordinates that is x, y, z said from the bases of this is for IR activity.

So, the particular normal modes which we lead 2 non 0 value, we will say they are inactive normal modes.

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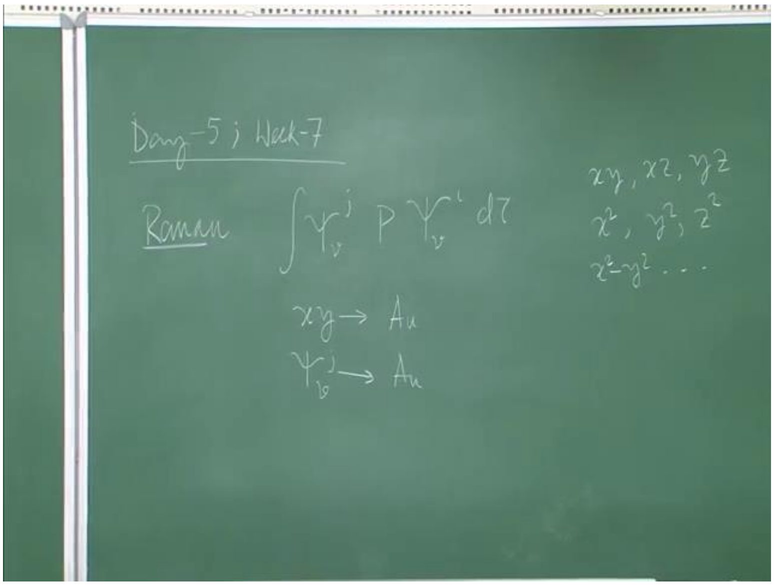

On the other side for Raman spectroscopy, we got an integral which is psi v j P, per P is that polarizability things are component. So, just like here, we can look at the symmetry properties of the polarizability component, which are like this binary products xy or xz or yz or the square like x square or y square z square or any of the combinations like x square minus y square and so on. So, this kind of functions we form the polarizability tensor they represent the polarizeability tensor component.

So, I need to know the symmetry of those xy or yz x square or y square so on and the normal mode that is being excited, that should form the basis of the same irreducible representation, for which the particular polarizability component from the basis of. So, suppose I have a component xy, suppose which forms the basis for say Au, then my selection rules says that this transition will be allowed only when psi v j also from the basis for Au because the direct product of 2 Au’s will give me the totally symmetric irreducible representation and then my integral will survived. So, here what is the selection rule for Raman spectroscopy, sectional for fundamental transition that will be Raman active? That is particular normal mode of vibration will be Raman active, when the normal mode belongs to the same irreducible representation to which this binary combinations that is xy, xz etcetera which form the basis form.

So, after getting this thing, we are in a position to talk about which particular normal modes that we deduced say for CO32 minus or n 2f 2. So, which one of them will be IR active, which one of them will be infrared active.

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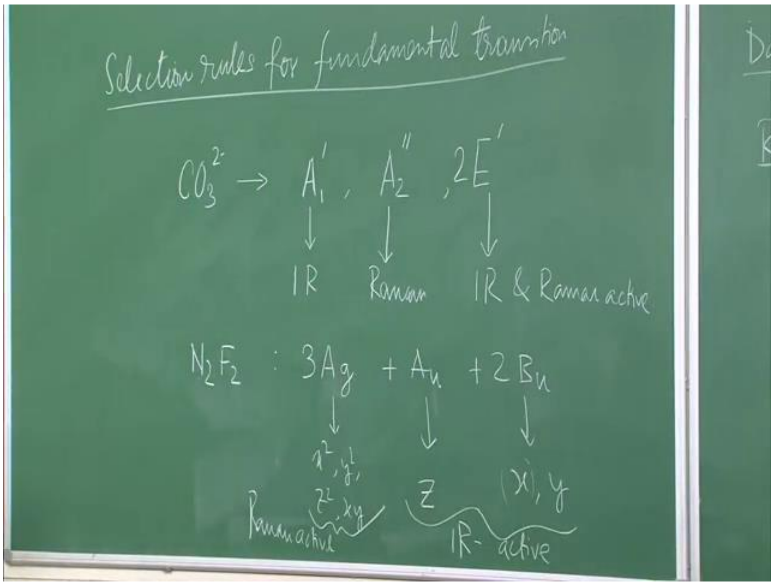

Selection rules for fundamental transition

$CO_3^{2-} \rightarrow A_1', \; A_2'', \; 2E'$

$A_1' \downarrow$ IR; $A_2'' \downarrow$ Raman; $2E' \downarrow$ IR & Raman active

$N_2F_2 : 3A_g + A_u + 2B_u$

$3A_g \downarrow x^2, y^2, z^2, xy$ Raman active

$A_u \downarrow z$; $2B_u \downarrow (x), y$ IR - active

So, say for Co32 minus we got normal modes which are genuine with represent genuine vibration; they were A1 prime, A2 prime; I think A2 prime. A2 double prime and 2E primes. Now if you consult the character table, you will see that among these this A1 prime that has this Cartesian coordinate component as its basis. So, this 1R will be infrared active; while this one has this binary function as its basis. So, this one will be Raman active, and this E prime it has both the Cartesian coordinate component coordinate at basis, as well as the combination of Cartesian in binary combination of this Cartesian coordinate. So, this will be IR active as well as Raman active. So, we also had this N2 F2 molecule for which we had these Vibrational modes like 3 Ag plus Au plus 2Bu.

Now if I look at the character table of C28. So, what I see, that Ag has this only the binary functions like x square or y square z square, xy. So, this binary function tells me that Ag will be a Raman active mode. While this Au it has z as its basis and Bu has x, y as its basis. So x, y and z get that transformed as either Au or Bu. So, this Au and Bu the most which transform as Au and Bu will be infrared active.

So, this 2 will be infrared active normal mode, why this 3 Ag will constitute Raman active normal mode, now one thing you notice here in this particular molecule, CO32 minus I have one more which is IR active, but Raman inactive, another mode I have Raman active, but IR in active, and we have certain modes which are both IR active as well as Raman active. So, when you look at N2 F2, I see that none of the modes are Raman as well as IR active. So, those modes which are IR active are not Raman active and vice versa. So, there is a difference between this 2, we will talk about this one will take another example, another particular molecule for example, like ammonia and look at the practical example, and see what happens there. Then we will come to some conclusion about this are the reason behind this kind of observation.

So, now after we could separate out the Raman active our infrared active modes using this symmetry, now we will go back to the original problem of this N2 F2 molecule and its normal modes. So, we got these 6 normal modes and there is symmetry, now we do not have any idea what are this normal mode? So, how do they look like? So, how do we do that? So here at this point we will take help from so called internal coordinates. So, what are internal coordinates? We mentioned it earlier; let me tell you again. So, this internal coordinate will be either the bond distance or a bond angle.

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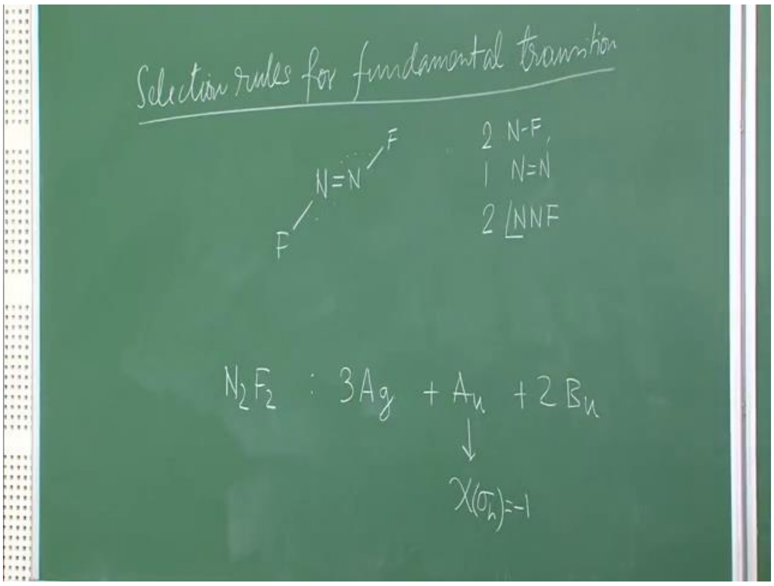

So in case of N2 F2, I have this is the structure. So, how many bond distances I can take, I can have NF to NF bond distance and one NN bond distance. So I have 2NF, I have 1

NN then I have this angle as well as this angle, both of them are same. So, I have NNF angle.

So, there is no hard and fast rule that which one I will use as my coordinate and which one I will use1st, which one I use later. So, it depends on what you want to do? Now since we are dealing with the vibration, which means either the bond distance will alter or the bond angle temperature doing altar in plain or out of plain.

So, let us start with this, now before even starting with this internal coordinate, what we will do? We will have a look at the character table once again. So, if I look at the character table here for sit wait, what we have? If we have 3 different types of irreducible representation I know according to which the normal modes get transformed. So, out of this 3 Ag, Au and Bu, I have this Au particularly this 1, this has character of minus 1. So, sigma h equals to minus 1, why for Ag and Bu, the character for sigma h is plus 1.

So, what does that mean? That in this Au mode, the bond displacements or when a bond angle change such that, the structure is not symmetric with respect to the sigma is plane, so whether it is antisymmetric - what does that mean, that there is some part of the structure, the above plane or below the plane. So that means, the particular normal mode which transforms according to Au has some motion; which goes out of this plane, now we started with a planar molecule and now I have a situation, where I see that, sigma 8 produces minus 1 as the character; that means, that this bonds; when one of this one is upward, one is downward meaning that, this motion of this bonds, they are not in plane rather they are out of plane.

So, they are doing some kind of out of plane motion. So, I can safely to start with, I can describe this one as out of plane bend; why bending? Because this bond stretching if it goes on in the same direction, it will still remain planner, but in this particular case of Au type of irreducible representations, I can clearly see that will be out of the plane. So therefore, the angle says if I say this, this angle here, which was in the plane, so after this movement of this F out of the plane, that is a creation of an angle here.

So, without worrying about anything, I can see that, this is a bending motion because from planarity I have, Au I say this is out of plane bending.

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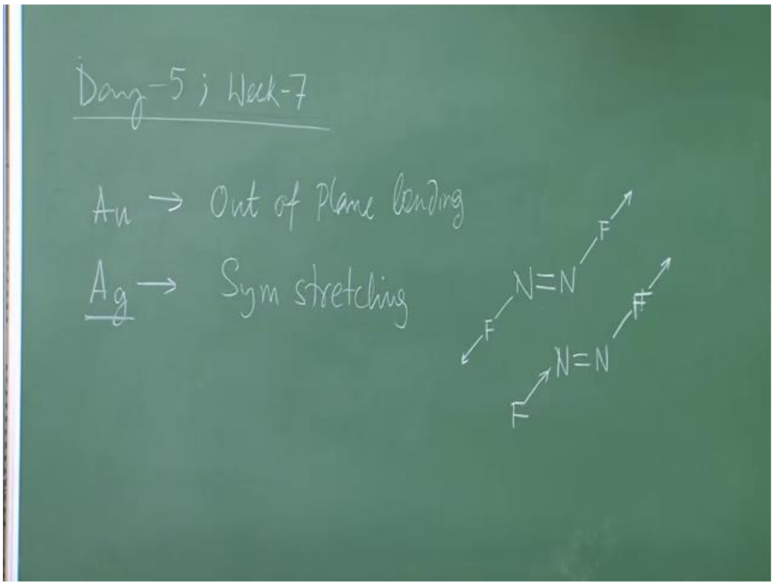

Day-5 ; Week-7

A_u → Out of Plane bending

A_g → Sym stretching

So, it is like this one is plus and this one is minus. So, in that way or it can be in this direction.

Now, we are left with 5 other, so Ag 3 Ag and 2Bu and if we use this as my internal coordinate, then I find because I am using 5 internal coordinates, and I am going to find out about the properties of the normal modes of 5,6 normal mode belonging to 3 Ag and 2Bu IR. So, let us do that now here we use this to enough bonds together, so, let us look at the representation.

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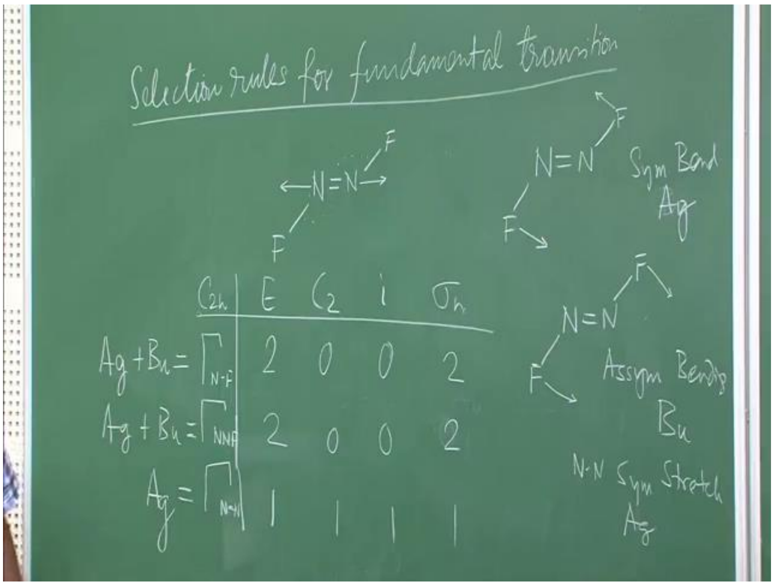

Selection rules for fundamental transition

C_{2h}	E	C_2	i	σ_h
$A_g + B_u = \Gamma_{N-F}$	2	0	0	2
$A_g + B_u = \Gamma_{NNF}$	2	0	0	2
$A_g = \Gamma_{N-N}$	1	1	1	1

Sym Bend A_g

Assym Bending B_u

N-N Sym Stretch A_g

So, I have this, and then I can have 3 different presentation based on NF, NN our let us say NNF which is an angle and then we have the representation based on N double bond N distance.

So, E will not do anything. So, where 2 bases set its basis functions, will give me a character of 2. So, if I do C2, hear this EF together, they are getting interchange. So, I get nothing here. Same is true for i and sigma n I get 2. Now if I look at the angle it has the same fact took it is that the 2 angles that I am getting. So now, when I have this NN bond distance, then identity of course, it gives 1 and C2 and I sigma 8, all of them will contribute 1 to the diagonal. So, I get this is ready presentation.

So, this one I do not have to do anything, I immediately see this is all symmetric with respect to all the symmetric operations, there for the representation that I am having, this belongs to totally symmetric irreducible representations. So, this was very easy. Now I have to reduce this 2 and what about I get for gamma NF will be same as gamma NNF, because this one is 2 they are identical and if you reduce this one, then what you will see that this one is equal to Ag plus Bu and obviously, this one will also be Ag plus Bu.

So, I got back my original result that, we got earlier using that 3 in Cartesian coordinate system, that is good that says that I have chosen the right internal coordinates, why did I do all these things? I have already got this one. so what was the need for getting this one? This is because I need to have some idea about that particular motion of the normal mode. So now, I get this Ag and Bu based on this NF bond; that means the normal mode which transforms as Ag and Bu, they we have some motion of this bond distance, NF bond distance. Now if you look at the characters of Ag and Bu let us have a look at the respective characters.

So, Ag is totally symmetric correct. So, then I can safely say that, Ag is my symmetric stretching mode; why? Because it is concerned with the NF bond distance, so NF bond will increase in both the direction in equal manner; both of them will contact the same manner and then only it will belong to Ag representation. So, this particular mode is obviously, the symmetric stretching mode. So this is symmetry stretching and if of course, belongs to Ag. While if I look at the beauty presentation, then I see that with respect to i expect to see to this is a symmetric.

So, what does that mean, here since this is best on NF bond distance, again it has to do something with the change in the bond distance, and it says that if I operate C2, C2 what it will do? It will take this guy over here and this guy will here. So, this NF bonds they will get interchange, and that will give me minus 1 as character for the overall molecules factor. That means that change in the bond distance due to the normal mode of vibration, which transforms as this Bu will change to NF bonds in different ways, meaning it will be something like this.

So, one will increase; while other one will decrease. So, it is like I have N2 so like this. So, this is my NN bond and this is F2, my bond is increasing; while this is shrinking, and then when this one is shrinking and this one is increasing. So, this is A symmetric stretching. So, this Bu gives me and asymmetry stretching which is soon shown here. So, that was obtained from the representation that we got using Nth bond distance.

Now if I look at the representation that I got out of NNF. So, NNF is an angle, so whatever the normal modes that I am talking about have to do something with the change of these angles. So Ag is a total symmetric IR. So, normal mode which transforms according to this Ag; must change this bond angles in a free symmetric way, that means if this bond goes here, making this angle shorter and this will also go in this direction making this one similarly shorter. So, this will be a symmetry bending mode. So, if I can write here, in what it will happen? So, both of them will move in opposite direction by equal amount. So, that this angle is changed by the same amount.

So, this is symmetric bending and this will be corresponding to Ag, I am talking about this particular Ag. Now what will Bu? The Bu will also be a bending mode because it deals with this angle and in this case if I look at the character table of the Bu, like before it has a it is a symmetry with respect to C2 or i. So, there it should be an asymmetric kind of movement. So, therefore, it will be a symmetric bending. So, if I have F here, F here, then if this angle becomes shorter, then this will become larger. So, if this goes in this direction, this also goes in this direction or vice versa. So, this is asymmetric in bending motion and has symmetry of Bu.

So, we are left with this last normal mode having Ag symmetry and this was born out of this in N bond distance is totally symmetric. So, this in NN bond distance either increasing or decreasing its purely symmetric you can say. So, if you talk about this one.

So, they will go apart and they will come closer, so in a very symmetric way. So, overall that will be a completely symmetric with respect to all this symmetric operations. So, this one will be there NN symmetric stretch. So, that will be the symmetric stretch.

So see now, if you look at all the symmetry in all the normal modes and when you look at this presentation of this normal mode, it is absolutely clear. So, to start with we did not have any idea like what are those normal modes? How will they look like? Because if I will give you the molecule structure and ask you to drop down almost structure you may not be able to draw exactly what we operated just now, but if you go in this way you exactly no I have use this as my (Refer Time: 32:38) so what about changes is happening, is happening on this particular bond, or on this particular angle; for this particular bond.

So, looking at the symmetry of that particular presentation that we got using those basis functions, I can unequivocally comment on these particular normal modes. So, this is how we get the character of the normal modes and knowing get symmetric properties.

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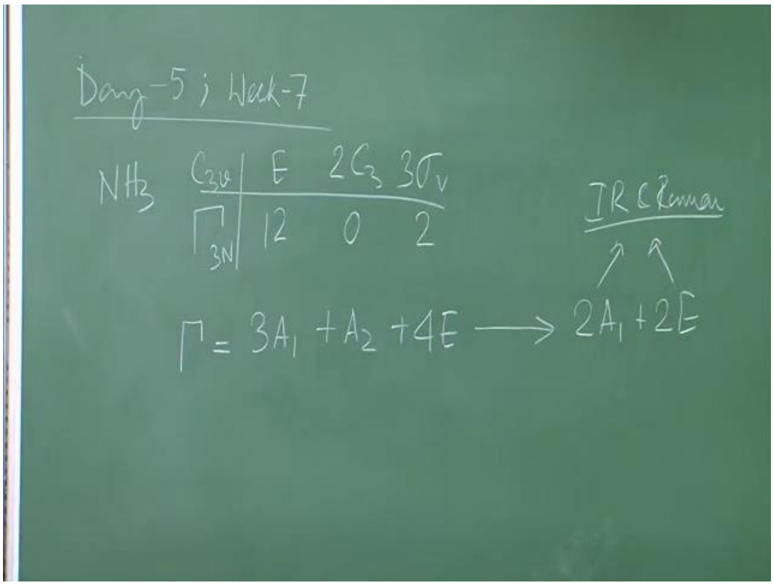

Day-5 ; Week-7

NH_3

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{3N}	12	0	2

IR & Raman

$$\Gamma = 3A_1 + A_2 + 4E \longrightarrow 2A_1 + 2E$$

Now before we stop today, will mention one more thing suppose I take another molecule, say ammonia and tick all 3 and coordinates and for the representation. So, for ammonia belongs into to C3v point group, I have E, C3 and sigma v. So, if I form gamma 3n.We have 12 for E, C3 is nothing and sigma v will 2. So, you can verify yourself this one and once you reduce it, you will get the total number, all the irreducible representations containing this representation, which will 3A1 plus A2 last 4E and out of these representations what you will get is for normal vibration you get to 2A1 2E. Now if you try to find out which one of these normal modes will be infrared active and Raman active, you will see both of this will be IR as well as Raman active.

Now, let us compare the 3 compounds that we looked at, one belonging into d 38 symmetry another belonging to C28 symmetry and this 3rd one that we just looked at is it C3v symmetry. Now d3h had a thing like certain normal modes will be infrared active only certain normal modes will be Raman active only, and sudden normal mode will be both Raman as well as infrared active.

In case of C3V I have all the normal modes are simultaneously Raman active, as well as infrared active. In case of that molecule N2 F2 which belongs to C2H point group and these sent to symmetry. I get those particular normal modes which are Raman active are not infrared active and vice versa, meaning that for that particular molecule and a particular point group the Raman active modes and infrared active modes are mutually exclusive.

This is a special character of molecules which are central symmetric in nature. So, we will stop here today and we will elaborate this issue in the next class.

Thank you very much for your attention.