Chemical Applications of Symmetry and Group Theory

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Lecture – 33

Hello and welcome. Today is the third day of the 7th week of the series. We have been discussing about the molecular vibration and its symmetries. We looked at one example of C O 3 to minus which had D 3h symmetry. What we did? We used all the Cartesian coordinates seeking on each atom and using those coordinates, we found a representation and reducing those representations. We could ultimately find out, what are the irreducible representation that any kind of molecular motion can have and from there with help of the character table we eliminated the (Refer Time: 01:07) that are represent translation and rotational motion. Thereby we got the irreducible representations that can be assigned to the genuine vibrational modes.

Till that point, we did and we all say that if we do not have any idea about the particular normal mode then using something called internal coordinates as my basis function 1 can actually find out that what are the different motions that, this particular molecule can execute in terms of vibrational motion. Today we will take another example here and we will find out not only the irreducible representations that it is vibrational motions can transform as, but also we will try to use the internal coordinates to find out about the normal modes themselves. We would like to find out the exact directional motion this, which the atoms of this molecule will execute about it about its equilibrium opposition.

And also we will try to find out that out of these vibrational modes which term some as certain irreducible representations which one of them is infrared active, which one of them is roman active because these 2 are these 2 gives information about the vibrational transitions in a molecule. Let us get started with 1 particular molecule. The 1 that will first consider is N 2 f 2.

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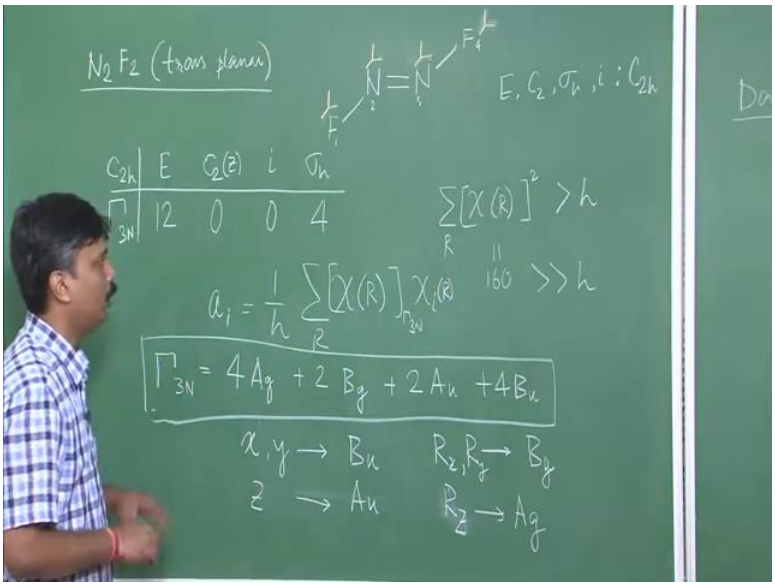

And one particular form that is Tran's planer consideration will be considered today. As usual, see this particular example will take you through many various cases that you have learnt. So far, each every example that we discus here will give a recap of whatever we have learned and every time something added to it. So that you get an overall idea, what we can do with the symmetry and group theory. First things, first we have to know the structure, this is the Trans planer. Usual they have their lone pairs of electrons, which will not consider here even if you want to take it. You can take it as per your wish. If you take it in this way, this is fine, but we will ignore the presence of the lone pairs of electrons here.

First we have to find out what is the point group of this particular molecule. This has C 2 which is toward you. Along Z access if I ensure and then this is the sigma H plane. I have A I have C 2, I have sigma H and also I have an inversion center right because if I start from here it will go here and it will be coming to the place of 1 and this 2 and 3. They will also interchange the position. I have also I and never less I have E. So, my point group is C 2h, Alright, fine. We have found the point view of C 2h, next what we suppose to do? Next we have to find out the representation for this particular point group and we have to choose up basis sets for doing that. In this cases when we want to deal with the molecular motion we choose generally the (Refer Time: 05:44) coordinate system on each and every atom. We will consider the X Y Z coordinates on each 1 of these atoms.

Total I have 4 into 3 equals to 12 cut then coordinate as my basis function now whenever we talk about the molecular motions. We talk about the degrees of freedoms in whatever direction I can have the motion right, be it translation rotation or vibration. Now if I talk specifically about vibration, vibration is nothing, but the moment of any particular atom with in a molecule in a particular direction by a particular amount. This vectorial motion can be a result of 3 unit vectors in that direction in on that atom. I can take this orthogonal Cartesian coordinate system X Y and Z coordinates through find that particular motion of atom right. It can be a stretching vibration; it can be bending of an angle it can be out of plane or in plane motions.

All this things say like translation I can express all this motions by combining this X Y Z, Cartesian coordinate system on each and every atom rather I said each and every nuclei. That is why we used this (Refer Time: 07:40) Cartesian coordinate system as my basis set, whenever I deal with this kind of problem particularly involving molecular vibration. I have to form a representation for this particular molecule using (Refer Time: 07:58) Cartesian coordinate. I have E I have C 2 I will specify this as C 2 Z then I have inversion symmetry and then I have sigma H, alright. I have to find out what are the characters of my representation. So identity operation, we not change any of the atomic positions. So there by all this is functions also we contribute to the diagonal because all the basis functions we also remain identical.

Therefore, total 12 basis functions will contribute 12 to the overall diagonal and thereby to the character. No, what will be the fate of C 2 Z C 2 Z will, which is right here, right toward you. So that will shift all the atoms. So shifting all the atoms from its place means the basis functions also will change their place, thereby we will not be able to contribute anything to the diagonal and then ultimately you get a character 0 now if about the C 2 then I does the pretty same thing. It will inter change all atoms like 1 and 4 will be interchange their place, 2 and 3 will interchange their places. Therefore, the overall contribution coming from any un-shifted atom in this molecule by the operation is 0. To character this 0 and sigma H, what it will do? Sigma H will not disturb any of atom in the molecule, therefore, all the basis functions will contribute to the diagonal now by what and which amount. This sigma H playing is nothing but X Y plain. So X and Y coordinates will contribute 1 1 each. Overall I have total 4 Z and 4 Y. So, total

contribution coming to the diagonal is plus 8 while Z will be reflected to the minus Z. So, 4 Z coordinates will give me minus 4 contributions.

Over all contribution toward the diagonal of the representation for sigma H is 8 minus 4 equals to 4. This is what I get as my representation and we have got this representation based on (Refer Time: 10:40) Cartesian coordinate. So, I will name it as gamma 3 N. In the next step what I have to do? I have to see whether it is reducible or irreducible. How do I know if it is reducible? If my sum over square of this characters sum over all the symmetry operations is greater than the order of group now, what is this amount for our presentations? It is 12 square plus 4 square total is 160. This is 160 which is very greater than the order of the group which is equals to 4.

Therefore this is a reducible representation. In the next step I have to reduce it, how do I reduce? I know that if I want to find out if ire irreducible representation of this particular point group point exist in the representation that I have just formed then the number of such occurrence given as A I is equals to this is for I gamma 3 N multiplied by the character of the same operation belonging to the ire irreducible representation remembered that we have ignored the complex conduit here and because the character table that we have considering right now it does not contain any complex quantity, but remember that it is there in general.

If I use this formula then I can find out what will be the numbers of time any particular irreducible presentation will occur in this reducible presentation. So, what I can write here is that this gamma 3 N is equals to. We will now solve this explicitly rather what we will do? We just review the final result. If I write this it will be 4 Ag plus 2 B subscript g plus twice Au and Bu will occur 4 times. So, if I just check if this one is correct or not then all the dimensions will match up to the dimension of this particularly representation.

All of them are 1dimensional representation and I have total 12 as my dimension which is same as this. My reduction of this representation is correct now; next step what we have to do? We have to find out which of these irreducible representation will give me the genuine vibrational normal modes or in other words which one of these all 12 know possible modes of degree of freedom, how many will be the vibrational normal mode that answer we know that will be 6. I have to find out. So, which 6 ideas actually form the set of genuine vibrations? In order to do that, what I have to do? I have to eliminate

all the other contributions those are coming from translation and rotational motion. So, translation, it transforms as translational motion. So, that transforms as 1 of this transform translation motion transforms as either X or Y or Cartesian coordinates and rotational motion take transform as R X or R Y or R Z, fine. So, what I can do? I can take this X Y Z or R X or R Y or R Z. Individually as my basis function form a representation and then find out the which particular irreducible representation that is.

And assigned it to a particular translational mode or rotational mode on the other hand easily, what I can do without taking their trouble of for mining the representation. We can just take the help of the character table of this particular point group C 2h. So, we will now check with the character table and concentrate on the area 3. Area 3 will give me that functions which transform as one of these ideas correct. If I look at the area 3, what I get. So, I gave that X and Y transform together now both X and y, they transform as the Bu representation for C 2h and Z transforms as Au representation. X transforms as Bu Y, also transforms as Bu.

You can immediately figure out that X Y do not transform as Bu together, but individually because this is on 1 dimensional representation right. So, one function can which is select, it is like X is not like X Y or X Z. So, X alone can give you only 1 dimensional representation. So, X also transform as Bu Y also transform as Bu and Z transforms as Au while R X transform as Bg irreducible representation R Y also transforms as Bg. So, R X as well as R Y both transforms as Bg representation and Ag transform as Z also I can write R Z transform as Ag irreducible representation.

These are the information that I require, correct and we have taken them from the character table. So, this is my over all irreducible representation and then I have to get rid of the translational rotational contribution.

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For translational contribution, translational contribution comes from this X Y and Z. Both X and Y transforms as Bu and Z transforms as Au. I have ultimately contribution coming from X Y and Z as 2 Bu - Au right away 2 because both X and Y transform as Bu. Each contribution I have to take care of and then I get this 2 and rotational I have 2 Bg similarly plus Ag.

I have to remove these contributions from this total list. If I do that, Bu and Bg occur twice in that list. Bg is gone and Bu becomes 2 rights. The genuine vibration refers to A occurs 1 time less from 4 I remove one. So, I have 3 Ag I have 2 Bg here. So, Bg does not occur in the final vibrational modes and then I have 2 Au. I have 1 Au here. I remove one contribution. So, I have 1 Au and then I have 2 Bu here. So, if I subtract 2 from this 4 B, I am left with 2 Bu, correct. Let us cross check I have got 3 Ag and 1 Au 1 Au and 2 Bu, right. Total numbers of irreducible representation that form to which the normal modes of vibration form the basis of is this we have got the irreducible representations that is that we wanted now what we need to do we need to assign particular normal mode to their symmetries.

So, right now do not know what the particular normal modes that exist here right are. So, I have to do that and second I think that these Vibrational motions how can I talk about this Vibrational, how can I find out about this vibrational motion experimentally. So, I can find that out by using spectroscopy. So, what are the vibrational spectroscopic

techniques that will give me the transition energies or any particular Vibrational mode? So, 1 is in infrared spectroscopy and another is roman spectroscopy. So, I have infrared spectroscopy and roman spectroscopy as my tool to find out about the vibrational transition frequencies for any given particular normal mode.

Now, I have got number of vibrational mode total 6 vibrational modes. So, each 1 of them will make some kind of transitions now, how will I know that which particular mode will be infrared active infrared spectroscopy active and which one will be roman active or in other word what I can say is that particular vibrational mode can be seen using infrared spectroscopy and some particular vibrational modes can be seen by roman spectroscopy. It is possible that I can see 1 or more normal modes transition involving 1 or more normal modes using both I R or roman spectroscopy or it can be either of them.

So, we need to know about such selection rule, then only we can comment on that out of this 6 Vibrational modes which one will be the roman active, which one would be infrared active and also we should be able to tell that if some mode is I R active or some mode is roman active then what particular co-realization this transition will follow. With those things we will come back in the following.

Thank you for your attention, and see you tomorrow.