Chemical Applications of Symmetry and Group Theory
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Lecture – 30

Hello everyone. Today is the day 5 of the 6th week of this lecture series. let us quickly recap whatever we learnt in last class. So, we took an example of Naphthalene to illustrate all the knowledge about SALC formation using the projection operator and ultimately utilizing those SALCs to form the energy state of the molecule. So, essentially the molecular orbital of Naphthalene molecule, so what we did let us go through that quickly before we move on to our next lesson.

So, first we figured out point group of the naphthalene which is D 2h and then we took the 10 P Pi orbital sitting on 10 carbon atoms. So, using those 10 P Pi orbital we formed an irreducible representation which is gamma.

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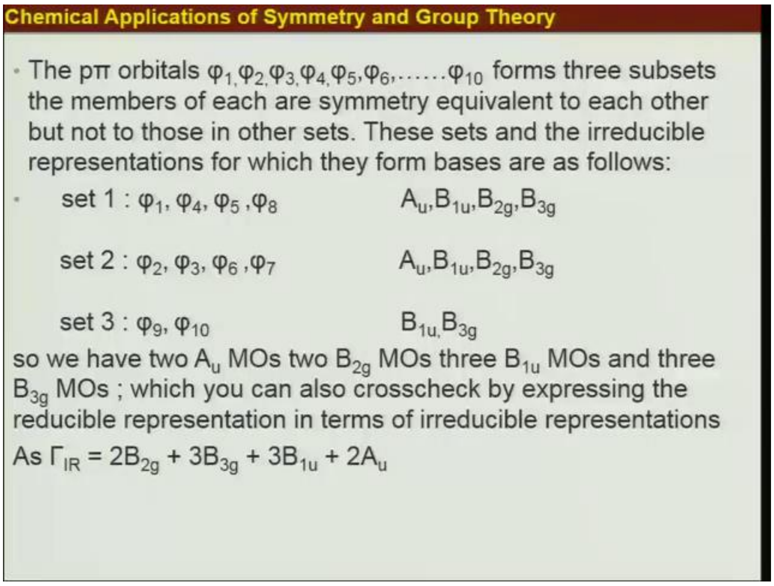

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- The pπ orbitals $\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6, \ldots\ldots \varphi_{10}$ forms three subsets the members of each are symmetry equivalent to each other but not to those in other sets. These sets and the irreducible representations for which they form bases are as follows:
- set 1 : $\varphi_1, \varphi_4, \varphi_5, \varphi_8$ $A_u, B_{1u}, B_{2g}, B_{3g}$

  set 2 : $\varphi_2, \varphi_3, \varphi_6, \varphi_7$ $A_u, B_{1u}, B_{2g}, B_{3g}$

  set 3 : φ_9, φ_{10} B_{1u}, B_{3g}

so we have two A_u MOs two B_{2g} MOs three B_{1u} MOs and three B_{3g} MOs ; which you can also crosscheck by expressing the reducible representation in terms of irreducible representations

As $\Gamma_{IR} = 2B_{2g} + 3B_{3g} + 3B_{1u} + 2A_u$

So, we also said that we can actually you know separate this P Pi orbital into 3 different sets because this you know different carbon atoms forms different sets of equivalent carbon atoms.

So, we therefore made set 1, set 2, set 3 comprising 4 and 2 P Pi orbital and individually we form the representations of using the you know basic set 1, 2 and 3 and ultimately we reduce them and we got the irreducible representation to which this we found the irreducible representation, that occurred in the irreducible representations that is found out of set 1, 2 and 3 and we also you know said that either way, that is you know form the separate 3 representation and then ultimately reduce it to the irreducible representation or you know take all the you know P Pi orbital forms at you know representation which is 10 dimensional and then reduce it. The result will be ultimately same.

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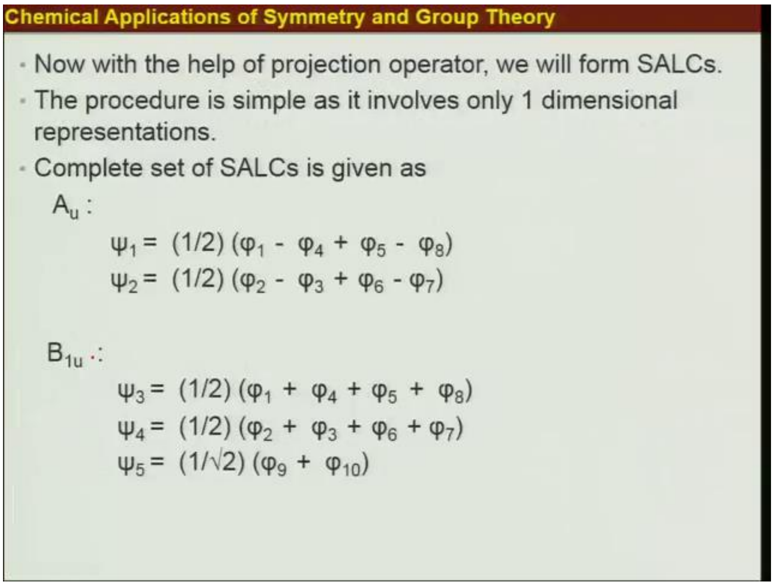

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- Now with the help of projection operator, we will form SALCs.
- The procedure is simple as it involves only 1 dimensional representations.
- Complete set of SALCs is given as

A_u :

$\psi_1 = (1/2)(\varphi_1 - \varphi_4 + \varphi_5 - \varphi_8)$

$\psi_2 = (1/2)(\varphi_2 - \varphi_3 + \varphi_6 - \varphi_7)$

B_{1u} :

$\psi_3 = (1/2)(\varphi_1 + \varphi_4 + \varphi_5 + \varphi_8)$

$\psi_4 = (1/2)(\varphi_2 + \varphi_3 + \varphi_6 + \varphi_7)$

$\psi_5 = (1/\sqrt{2})(\varphi_9 + \varphi_{10})$

So, after you do that you use the projection operator for each individual IRs that are you know obtained and you find the SALCs. So, we saw that there are certain number of irreducible representation occurring; for example, like you know A u irreducible representations occurs 2 times B 1u occurs 3 times B 3g occurs 3 times while B 2g occurs 2 times.

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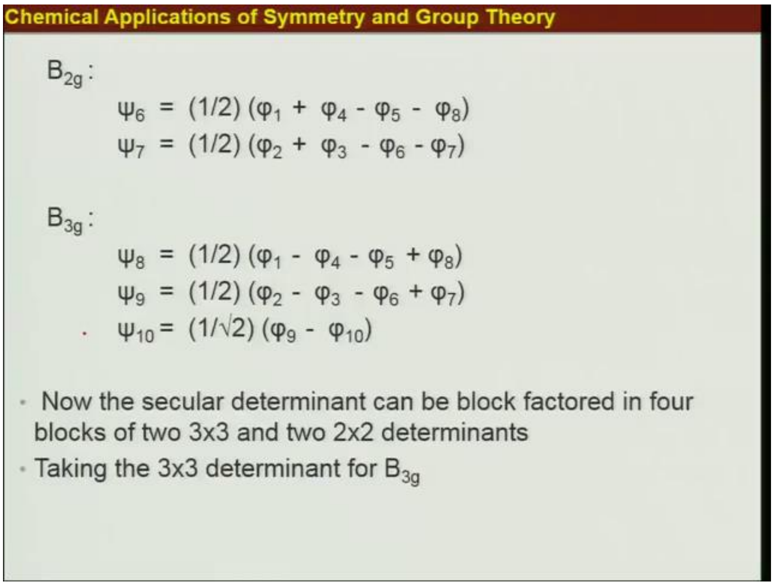

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B_{2g} :

$$\psi_6 = (1/2)(\varphi_1 + \varphi_4 - \varphi_5 - \varphi_8)$$

$$\psi_7 = (1/2)(\varphi_2 + \varphi_3 - \varphi_6 - \varphi_7)$$

B_{3g} :

$$\psi_8 = (1/2)(\varphi_1 - \varphi_4 - \varphi_5 + \varphi_8)$$

$$\psi_9 = (1/2)(\varphi_2 - \varphi_3 - \varphi_6 + \varphi_7)$$

$$\psi_{10} = (1/\sqrt{2})(\varphi_9 - \varphi_{10})$$

- Now the secular determinant can be block factored in four blocks of two 3x3 and two 2x2 determinants
- Taking the 3x3 determinant for B_{3g}

So; that means, that I will have total 10 molecular orbital which are you know I mean given by the SALCs that we have formed and these 10 SALCs will have their own energies.

So, in the next step we are supposed to find out these energies. So, how did we do that? We form the secular equations in terms of the secular determines and here in this case you know because we form this you know individual SALCs and from there we found that essentially 4 individual irreducible representations are there and correspondingly we had like 2 or 3 number of SALCs which transform according to the particular irreducible representation that we ultimately found.

So, we get this secular determinant to be you know block factored determinant and we took out each block and then formed 4 individual secular equations, in terms of 4 individual you know this blocks and solving that utilizing Huckels approximation which says, that you know interaction energy between 2 orbitals are 0 until or less these 2 orbital are adjacent to each other and that you know energy of the interaction is expressed in terms of Beta and Beta is the unit of energy here and the interaction with itself that is Pi I H Pi I this quantity is written as alpha and alpha is taken to be the 0 of energy according to Huckel approximation and the interaction the overlap integral, that is you know Phi on Phi 2 integration over all the space is taken to be 0 under Huckel approximation, so utilizing that we could find out all the energies of the 10 different SALCs that we can have.

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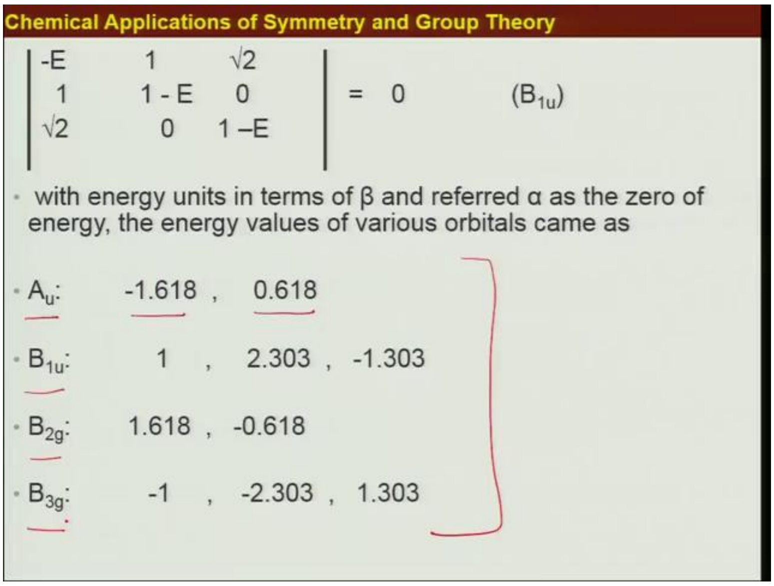

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$$\begin{vmatrix} -E & 1 & \sqrt{2} \\ 1 & 1-E & 0 \\ \sqrt{2} & 0 & 1-E \end{vmatrix} = 0 \qquad (B_{1u})$$

- with energy units in terms of β and referred α as the zero of energy, the energy values of various orbitals came as
- A_u: -1.618 , 0.618
- B_{1u}: 1 , 2.303 , -1.303
- B_{2g}: 1.618 , -0.618
- B_{3g}: -1 , -2.303 , 1.303

So, ultimately we found the energies of the possible MOs to be like this. So, 2 SALCs which you know has the same symmetry Au has 2 different energies all right. Similarly for B 1u and B 2g and B 3g we found you know number of energy levels. Now our job was to adding these energy levels. So, Beta is negative.

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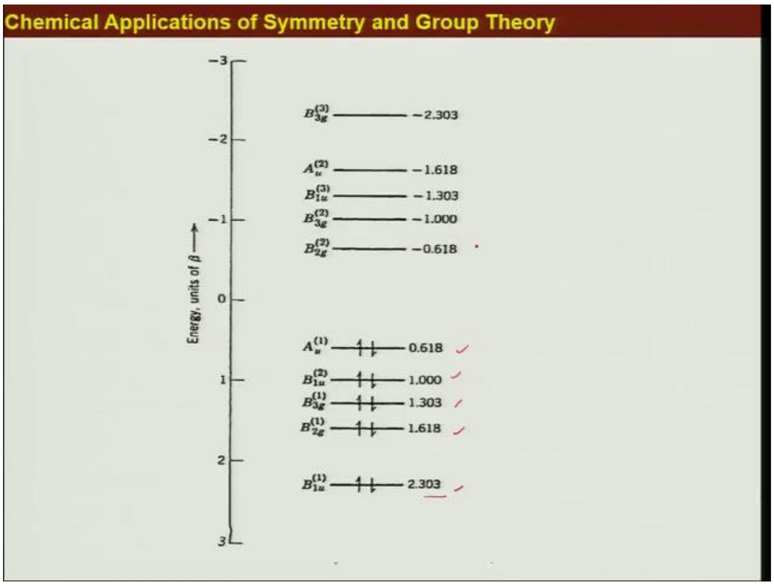

Therefore, the ordering of energies is done in such a way that is shown on your screen. So, these are expressed in terms of Beta and Beta itself is negative. So overall this energy here is negative and zero as it mentioned corresponds to the energies of the atomic orbital which are not interacting; that means, before the formation of the molecular bonds whatever the energies, the atoms have they are taken to be the 0th of energy and whenever there is an interaction, favourable interaction we have you know lowering of energy which is given here, so these are expressed in terms of Beta. So, Beta is negative. So, overall these energies are all negative.

Why this terms here that is minus 0.618 that is also expressed in terms of Beta which is negative. So, overall this is a positive energy correct. So, these are higher energy. In the next step we are supposed to fill out these energy levels with the electrons. So, there we utilize the Hund's rule and the exclusion principle.

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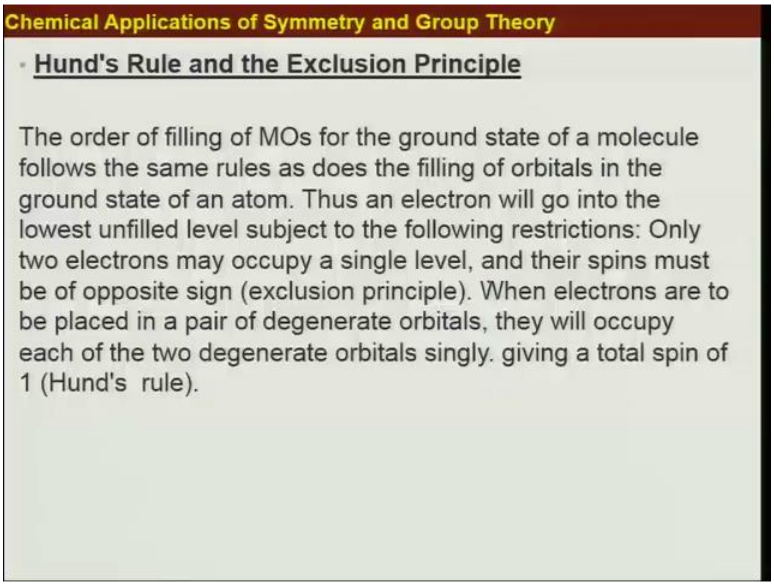

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- **Hund's Rule and the Exclusion Principle**

The order of filling of MOs for the ground state of a molecule follows the same rules as does the filling of orbitals in the ground state of an atom. Thus an electron will go into the lowest unfilled level subject to the following restrictions: Only two electrons may occupy a single level, and their spins must be of opposite sign (exclusion principle). When electrons are to be placed in a pair of degenerate orbitals, they will occupy each of the two degenerate orbitals singly. giving a total spin of 1 (Hund's rule).

So, what does that say? That you know in case of the order of filling of molecular orbitals for the ground state of the molecule, it follows the same rule as does the filling of atomic orbitals in the ground state of an atom.

So, an electron will go into the lowest and filled level subject to the certain restriction. What are those restrictions? The only 2 electrons may occupy a single level and their spins must be opposite. That is the exclusion principle right Pauls exclusion principle. When electron are to be placed in a pair of degenerate orbitals, suppose you have 2 orbitals having same energy we call them as degenerate orbitals. So, if you have to fill them. So, you have to fill both of them having the same spin. So, that overall the total spin becomes 1. So, which is the Hund's rule right. So, using this exclusion principle and Hund's rule we fill out this energy level.

Now, after getting this overall molecular orbital picture and their energies next we will talk about the you know this interaction between different energy levels, meaning the you know transition from one electronic level to another electronic level and the corresponding selection rules. So, we will stop the discussing right here about this you know molecular orbitals and the corresponding electronic levels and the transitions involves between the electronic levels.

We will come back to this after a while. So, in the meantime what we will try to look at, is to look at certain internal motions of the molecule the bonds and specifically we will deal with the molecular vibrations, the normal modes and we will try to see; how symmetry properties of the molecule can be applied to molecular vibration to you know find out exact normal modes, their symmetries and their you know many Vibrational transitions or (Refer Time: 09:39) transitions and their probabilities and the corresponding selection of rules.

So, this is what we are going to you know study for another 5 or 6 lectures. So, to start with, if I take any given molecule they will have 3 different ways to store the internal energy. So, one is translation, you know rotation, vibration. So, if I have a molecule having certain you know atoms and then certain bonds there. So, these bonds can move in any particular direction or by changing an angle with respect to another bond; in such a way that there this motion will not displays the molecule in a particular direction; that means, it will not lead to any translational motion. That is there will be no movement of the centre of mass of the molecule and also this type of motion that I am talking about that you know may not change the net angular momentum of this molecule meaning that there will be no rotation and such motions of the you know bonds in a molecule is known as the vibration.

So, if I take you know any particular molecule and consider the internal motions of this bonds or atoms we can see that you know there are bonds are moving in different directions or you know changing the angles like for examples if I take just water molecule. So, I can see there is you know edge bonds can move in different way or you know it can changes angles. Apparently it may seem that all this motions are very much random, but if it takes a close look at that observe it you will see that nothing is random, but they are well you know this motion is very much regular. The moment I say that motion is regular; that means, that there must be some symmetry into it right because in the very first class, if you remember we said like what are the meaning of this word symmetry one of the thing is there must be some regularity in whatever the phenomena or you know process or in structure.

So, sometime it may be that you know that is you know regularity in this motion can be bit time taking. So, that you know apparently it may seem like that there is no regularity, but actually there it is and you know how do we classify this you know particular vibration? Because there may be several bonds are moving you know executing vibration and all of these can be superimposed is actually superimposed and then we get an overall you know internal motion of this bonds in a molecule and these are actually quantized by the so called normal modes.

So, many of us are familiar with terms like you know for a given molecule that. there is a stretching or there is a bending there is you know symmetry stretching or asymmetric stretching or you know in plane bending out of plane bending. So, these are actually the individual normal mode and we will be dealing with this normal mode to find out about the molecular vibrations and their associated properties of these molecular vibrations. Now first and for most thing is that how do we find out; what is the number of normal mode in a given molecule and probably many of you all ready know that because many times you get a simple formula and then you just use that formula and get the number of normal mode that is possible, but many occasion you do that without actually knowing the reason behind this formula.

So, if you take any given molecule; say for example, I will take a very simple example say I have ammonia.

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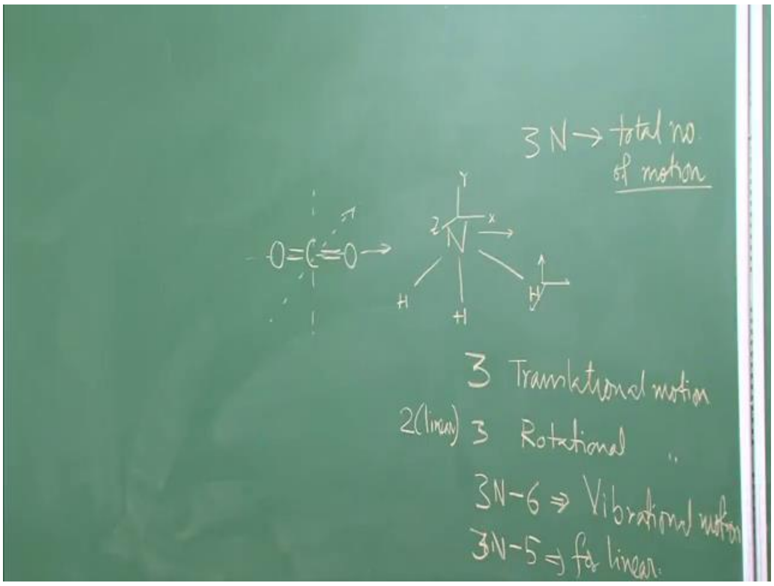

So, each of this bond can execute certain motion such that this does not lead to any translation or notation. Now what I can think of that for each and every atom will have their coordinates correct. So, x y and z this is true for each and every atom on the molecule. Now each coordinate is independent of the other coordinates.

Therefore, this N can move in the x direction by certain amount without worrying about what is going to happen in y and z direction and H also can do the same thing and it can do it in any direction. It can do it in the z direction or y direction or in x direction which are all independent. Now suppose a situation when all the atoms starts moving in x direction by definite amount right. So, what happens in that case? You are moving the centre of mass in x direction by that definite amount meaning the whole molecule is translating in x direction by a definite amount.

So, I can do the same thing in y direction as well as in z direction. So, each of this directional motion will give me one translational degree of freedom. So, in x and y and z direction I get translational motion right. So, this 3 directional, 3 individually you know individual direction of motion will give you total 3 translational degrees of freedom. Now if I think about motion of this you know atoms in a angular path about either x or y or z axis. Now if all the atoms start you know executing this angular motion about one particular axis say x axis then that will amount to the rotation of a whole molecule by a definite amount right.

So, it can be about x axis separately it can be about y axis and z axis. So, this 3 different you know angular motion about 3 different axis at 3 rotations. So, I have 3 rotational degrees of freedoms. Now overall how many I have? So, I say that the each and every atom can execute certain motion in either x or y or z direction or all together it can do and all 3 motions will be independent of each other. Therefore, if I have N number of atoms, total number of motion, directional motions that can be executed by this whole molecule will be 3 N right 3 N is a total number of motions possible. That is total number of degrees of freedom that it can execute.

So, therefore, I have 3 translational and 3 rotational. So, the rest should be the vibration. So, I have total 3 N minus 6 number of degrees of freedom left for the molecule to execute Vibrational motion. So, that is how we get this number 3 N minus 6. Now this is in general for any molecule, but when we consider a linear molecule. For example, suppose I have a case of carbon dioxide, this is a linear molecule. So, here each and every molecule can execute translational in x or y in z direction. So, the molecule can have 3 translational motions like this. When I talk about the rotation then it can have you know about this axis. It can have a perpendicular axis to this, but there is no meaning of having a rotation about this axis because all the nuclei are contained by this axis. So, I have essentially 2 rotational motions. So, instead of 3 here I have 2 for linear molecule.

Therefore, for linear molecule we have 3 N minus 5 for linear all right. So, let us take some you know definite example. So, this suppose I have a non linear molecule and I have 3 N minus 6 number of you know Vibrational degrees of freedom. So, each of these Vibrational degrees of freedom is expressed by the normal vibration or you know normal modes. So, we will take an example of a planar molecule that is carbonate ion.

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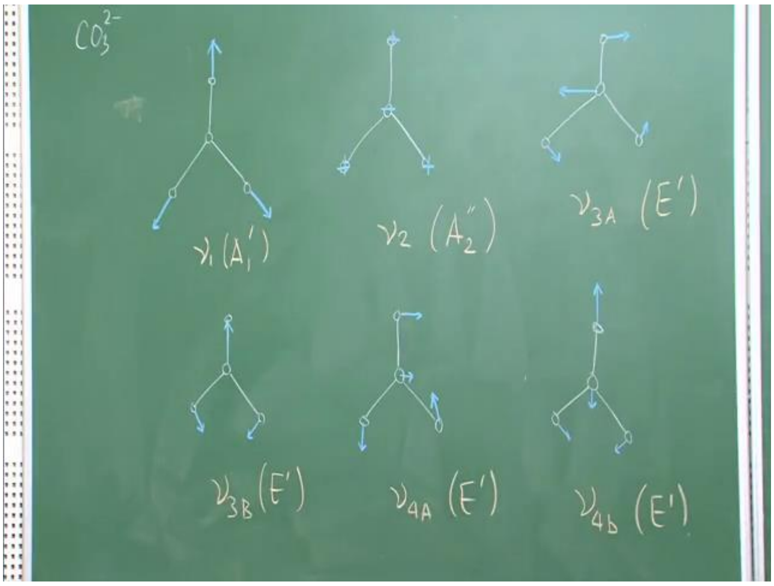

So, we will be talking about CO 3 2 minus. So, if I represent this you know carbon and oxygen by this sample thing, I can take this to determine carbonate ion. So, the central part is the carbon and then 3 oxygen’s are there.

So, I will have total how many? There are 4 atoms. So, 4 into 3 12 minus 6, so I will have 6 number of degrees of freedom; so let us see how this normal mode actually look like. So, I will first have 6 structures of carbonate ion and then we will look at their normal modes. So, take that all the bonds are actually identical. So, I have got total 6 number of structure to show 6 conditional normal modes. So, say first mode is, I will use the different colour to identify this. So, is this colour visible? So, this arrows, so 1, 2, 3 arrows they say signify their direction of the movement of the atom right. So, also the length that we you know provided to this arrows they signifying the amount of the movement. Though, it is quite a bit of exaggerated. Now let us draw all the other modes then it will be lot more clear.

So, these are given as sign. So, plus and minus, I will explain what the sign means and. So, we need to understand the exact meanings of these arrows, their links, you know from where they are originating and all these things in order to understand these motions properly and then the last one and we will also give this motion because these are some vibrations. So, they will have their associated frequencies. So, we will have nu 1 and we will call write it here, this is nu 1, this is nu 2, this is nu 3 and we will call this nu 3 A.

There is a reason for doing that. We will talk about that and this is as nu 3 B and then we have nu 4 A and nu 4 B all right. So, now, here we have mostly this motion showed by arrow and in one case it is shown by the plus and minus sign. So, now, you can see that in many of this normal mode picture, the arrows are having different lengths.

So, what does that mean? Suppose here you have longer arrow compared to the arrow which is sitting on the centre carbon. This meaning that this atom over here this oxygen is moving in this direction without worrying about what happening to the rest of the molecules. While this carbon is also moving in this direction, but the amount of movement in that particular direction by this atom and this atom are not equal and the length you know the length, the ratio of this length is actually the ratio of the amount of movement that two individual atoms are making in a particular direction.

Now, as I said this lengths are quite exaggeration because this atoms do not really move this much which are comparable to the bond length. So this is just to make things be prominent to you and here this plus and minus sign this means that you know this particular atom is coming up above the plane of the board, while this oxygen is coming above the board and this carbon atom is having the minus sign means that it is moving down the board. So, this is an out of plane motion, while all these things, all these other structures that nu barring nu 2 all the others motions are in plane. That is this molecule is a planar and all the motions of this atoms are within the plane.

So, these are in plane Vibrational motion, while this is out of plane all right. Now one thing you should notice that you know many cases we have you know misconception about how to draw this normal mode. So, here if you look at carefully the arrows starts from an atom and goes to particular direction. So, this particular thing means that this atom is moving. In many cases you know you will find that people write the motion in a way like they write like this or this. This is completely a wrong way of representation. So, when you want to present the normal mode, you exactly have to do it in this way that is start on that particular atom and then put the arrow in the direction into which it is executing the motion all right and you have to take care of the relative length of the arrows you know within a particular normal mode right correct for example, if you look at this one or this one this is very clear or this one right.

So, that will tell you that by which amount one particular atom is moving in a particular direction, relative to other atom within the molecule. So, now here looking at this I can have two important properties of these normal modes.

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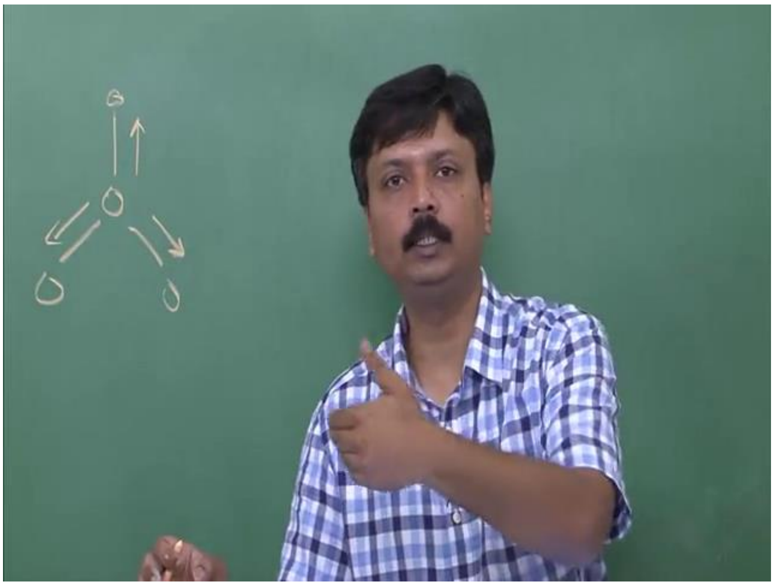

So, these are the normal modes, these are possible. Now right now I am just drawing this on the board, but you know how can I get this one? Suppose I draw some arbitrary you know motions with arbitrary arrow direction, will I able to tell that this is the right normal mode or not? So, that must have certain rules and this you know rules are governed by the symmetry and group theory and you know in the following lessons we will learn how to actually use group theory to find out exact normal modes. Now before ending today's lecture I will mention two important properties of these normal modes. One is that you know each of the vectors. So, all these arrows that we are you know using I said that they have a definite you know length and they have of course, the direction. So, they are the vectors of motion.

So, each of this vectors representing this instantaneous movement of this atoms and they you know giving the displacement, they may be regarded as the resultant of three basis vectors. So, we can consider each of this atom having their own Cartesian coordinate x 1, y 1 and z 1 and then we can think of this movement in a particular direction by a particular amount to be the resultant of these three basis vectors right and second thing is that which is extremely important to us that each of this normal mode they form a basis for an irreducible representation of the molecular point group. They may form the basis by themselves or they may actually belong to one of this IRs of the molecules. So, therefore, the structure that I drew they will be assigned to particular irreducible representation.

So, just for your information if I put so, this one will form a representation of A 1, this 1 will form the representation of A 2 while the nu 3 A will form the representation E prime 3 B will form the representation of again E prime, while nu 4 will also form the representation for E prime. So, we will do the normal mode (Refer Time: 32:08) 4 B. So, these are the two main points about the normal modes, that is their motions can be expressed by the resultant of three basis vector and second, each of this normal mode can you know form the basis you not only can, but they form the basis for the irreducible representation of the molecular point group.

So, we will utilize these ideas and then we built on our knowledge about this molecular vibration, their relation with the symmetry and ultimately having the applications. So, we will commit those things in the following week and till then have a good day.

Thank you very much for your attention.