Chemical Applications of Symmetry and Group Theory
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Lecture – 31

Hello all, and welcome to the first day of the 7th week of the lecture series. Last week we started looking at the molecular vibration and his symmetry properties. So, just quickly recap of whatever we discussed in the last class. We mentioned that there are different degrees of freedom available for given molecule. So, out of this three different degrees of freedom that we know about one is translation one is (Refer Time: 00:53) another is vibration.

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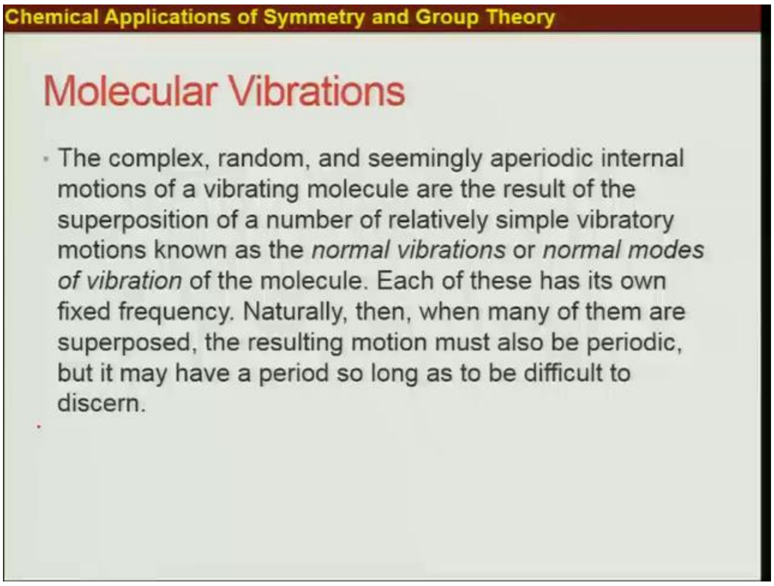

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Molecular Vibrations

- The complex, random, and seemingly aperiodic internal motions of a vibrating molecule are the result of the superposition of a number of relatively simple vibratory motions known as the *normal vibrations* or *normal modes of vibration* of the molecule. Each of these has its own fixed frequency. Naturally, then, when many of them are superposed, the resulting motion must also be periodic, but it may have a period so long as to be difficult to discern.

And this period of the lecture this week or will part of the next week also we will be dealing with this molecular vibration and their symmetry properties.

So, we mention that molecule can vibrate its bond can strange its angles can bend and it can go in a plane or out of a plane. So, different bonds will make different kinds of would mean different angles will make different movement. So, apparently it may look like that it is a random motion, but if one takes a choose look at this motion then one all will find that in this randomness there is actually a symmetry involve, there is a regularity there. And this seemingly periodic or random internal motions of vibrating molecule that are the result of superposition of number of relatively simple vibratory motions which are known as the normal mode of vibration. Now each of these normal mode of vibrations they have their fixed frequencies. And we need to know for a given molecule; what are the normal modes of vibrations; and what are their symmetries so that we can develop something further in understanding this molecular vibration emotion and the energic transactions form the one vibration state to another vibrational state how it is governed by the symmetry rules.

So, we started talking about the properties of these normal modes of vibration, and in that case that we said is that each of the fluid we actually defined the normal mode of vibrations for a particular molecular iron and which is carbonate iron.

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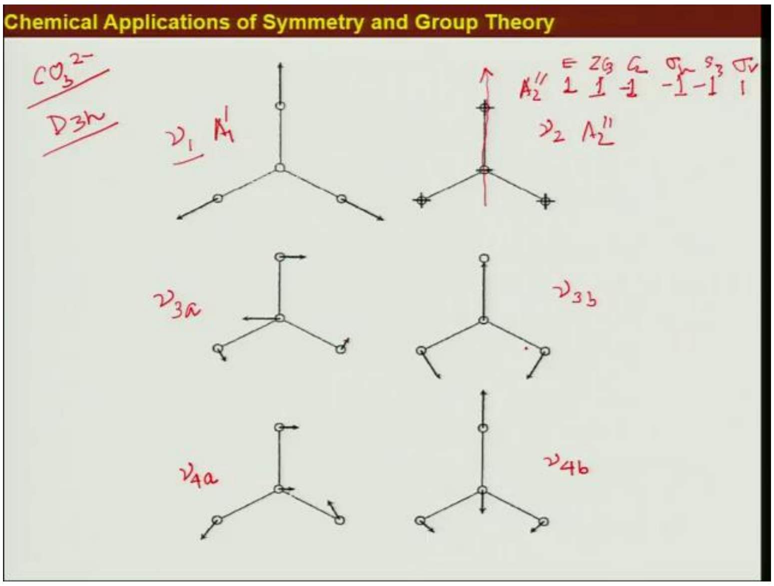
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So, you looked at and this carbon c o 3 2 minus and we depicted all the possible normal modes. So, first we did used what is the number of normal mode of vibration that is possible for this. So, we also looked at the way to find out the number of normal modes for a given molecule and we found that a two molecule is non-linear then 10 minus 6 is the number of normal modes by n is the number of atom in that molecule and for a for a linear molecule the number will be 3 and minus 5. So, using that formula we could say that for carbonate iron if you are taking as a planar molecule. The number of normal modes are 6 and we do all 6 normal modes of vibration and we mention that this normal mode are depicted by arrows, which tells us about the particular duration and a little magnitude of the motion of the atom involved in a particular direction or in a change of angle because of this motion both in plane and out plane.

So, we said that this 6 motions that are possible that is 3 6 normal modes of vibration we given them this discrete frequencies say that is a property of normal mode that each and individual normal modes will have a distinct frequency. So, we mentioned this one as nu 1 this is nu 2 and this is nu 3 a and this is as nu 3 b. While this is nu 4 a and this is nu 4 b now it will be clear in the movement why we are calling this as 3 or 3 v not like 3 4 5 6 there is a reason and that is also given by the symmetric properties of this motions.

Now, there are two distinct properties of this type of motion that is normal mode of vibration, that is here this vectors that we are represent using to represent their motion of a particular atom or a particular bond in a particular direction. They can be expressed as a linear combination of the basis vector that will use and second that each one of this normal modes. So, nu1 nu2 nu3 and nu 3 b and. So, on all of them each one of them will transform as one as the universal representation to which this particular molecule belong to. So, here this particular structure if we look at we easily can say that this molecule as a point know for D 3h. If remember you have basic perform this course. So, it has as a c 3 axis and it as three perpendicular C2 primes and it as sigma h this is spay because, I will consider a planar molecules. So, it as a point group of D 3h. So, what you say there is that each of these normal modes will belong to the higher of this particular point of D 3h.

Now, we have to first ask that how to assign the symmetries of these normal modes. So, what we need to do for that. So, we need to look at the effect of all the symmetry operations of D 3h point 2 on these particular normal modes. So, will look at this 1 2 and 3 a 3 b 4 a and 4 b. So, if we look at say first this structures for which the frequencies nu1 will see that whatever be the symmetry operation. So, what are the symmetry operations for D 3h? So, for that if you want a quick answer for that you what you have to do you have to look at the character table right, you will know by now that if you look at. So, this is our form of character table you can get it anywhere. So, you look at the character table for say any the particular point group.

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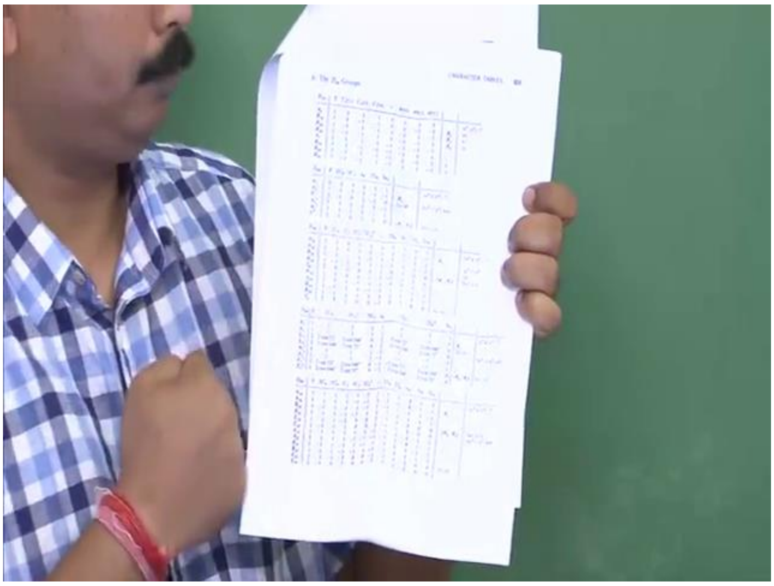

Let us look at the point group of D 3h right and. So, here we go. So, if you look at the point group of D 3h he will find all the symmetry operations there and the corresponding illusive representations the terminologies you will also get the linear or non-linear functions which also transform as the illusive representation of this particular point group. So, if I look at this and we can easily figure out what are the symmetric operations that is has.

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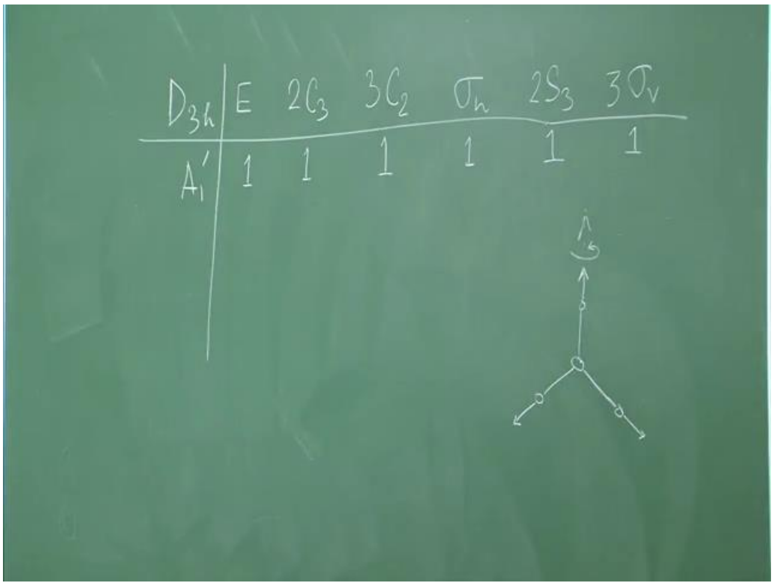

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1

So, I will just quickly mention. So, it as identity it as C3, C3 square, it has 3C2 primes, it has sigma h, it has S3 and S3 5 and it as 3 sigma vs right, all right.

Now what you have to do you have to deal with the transformation of how this vectors that are that are representing the motion of this atom within the normal mode of vibration, how they behave right. So, if you apply identity on this particular structure what you will get everything will remain unchanged. So, if you take this structure as a whole. So, if I can just redraw the same structure here what I have, three equal arrows which are along the three bonds in the same direction of this see your bonds right. Now, if you apply identity it will give back that the same structure. Now if you apply C3 on this motion.

So, if you rotate C3 and if you are not numbering them actually just looking at their overall this position of these arrows, then C3 also will give you the exact indistinguishable structure. So, that will also give you a same structure back. So, if this gives me 1 and this gives me 1 and next you look at the C2. So, C2 also because after rotating above say I am considering this as my C2 axis. So, if I do C2 around this 1. So, this will rotate and since this are not numbers. So, I have an indistinguishable structure. Ultimately after applying C2 you will get just an indistinguishable structure. So, over all it will give me a character 1 and while am writing this characters I am recreating that here, I am not taking this 3 has separate 3 basis vectors, but as a whole this is my structure and this is as if acting as 1 basis function right.

So, similarly sigma which also will give you 1 because there will be no change s three is also going to be mean 1. So, will sigma v. So, looking at this character we can find out that this is a totally symmetric illusive representation. So, what is there totally illusable representations in D 3h say, that it we gives a term A1 prime all right. So, in the same way if you look at the structure nu2, so if you look at the structure nu2 what you see that 3 oxygen atoms are out of the plane that is above the plane while the carbon atoms in central carbon that is bellow the plane that is given by the plus and minus sign. So, plus means it is about the plane and minus is below the plane. So, what happens here if you apply identity? So, identity will give you say if I write down for this particular structure say here, so, identity will give me a character of 1 while say C3 that will also give me 1, because after rotation by 2 phi by 3 I will getting indistinguishable structure. So, if I go for C3 that is also going to give me 1.

Now, for let us these C2 prime C2 prime is also going to give me the same thing. So, C2 will give me character of 1 and then we have sigma h. So, sigma h is going to inward the science right. So, whichever was above the plane they will now go below the plane and whatever was the below the plane now will come up. So, that will inward the structure, so it is going to give me minus 1 right and then we have S3. So, S3 is what it is the effect of C3 which does not do anything, but then there is a perpendicular sigma plane. So, that is going to reward invert everything. So, then again S3 is going to give me minus 1 and then we are left with sigma v. So, sigma v is not going to change anything right. So, sigma v will give me plus 1. Now, if I compare this particular illusive representation because here, the representation I given me only 1 as the matrix element only 1 matrix elements is there, so it is the 1 dimensional representation. And therefore I can just quickly check in I correct it in and find out which illusive representation this 1 is.

So, only the character of sigma h and S3 they are negative right. So, if I compare that then I have to. So, for D 3h if I have this C2 actually if look at, if I take this as C2. So, what is happening this 2 are going bellow the plane and so is base 1. So, every atom and their position know that position is getting inverted for C2 as well all right. So, the C2 primes so therefore, what we have is C2 is also giving me a minus 1. So, that was a mistake. So, if I correct everything. So, now, I have C2 sigma h and S3 as negative 1. So, now, let us compare. So, that gives me A2 double prime. So, this belongs A2 double prime right. So, now, what you can see that both of this normal mode, but we consider when we operate this symmetry operator we are finding that they transform according to 1 particular illusive representation. The first 1 we found it to be A1 prime and this 1 now we are finding to be A2 prime. So, in this way we can keep going on. So, here like this nu3 and the structure correspond to nu3 b, they actually form the basis for the illusive representation E prime together. So, that can be shown and we will show that will quick shortly.

So, what we can think of is the following. So, when you apply the symmetry operation say for example, C3 on this 1 of the structures nu 3a. So, what it will do it will transform to a nu configuration which will be nu 3a prime say for example. So, what will be the form of nu 3a prime? So, what you are saying is this nu 3a prime will be a linear will be a linear combination of nu 3a and nu 3b and similarly nu 3b when you operate say any symmetry operation that will also be a linear combination of nu 3a and nu 3b. So, let us show how it is going to work. So, here see an example how that C3 aspects this structure with nu 3a.

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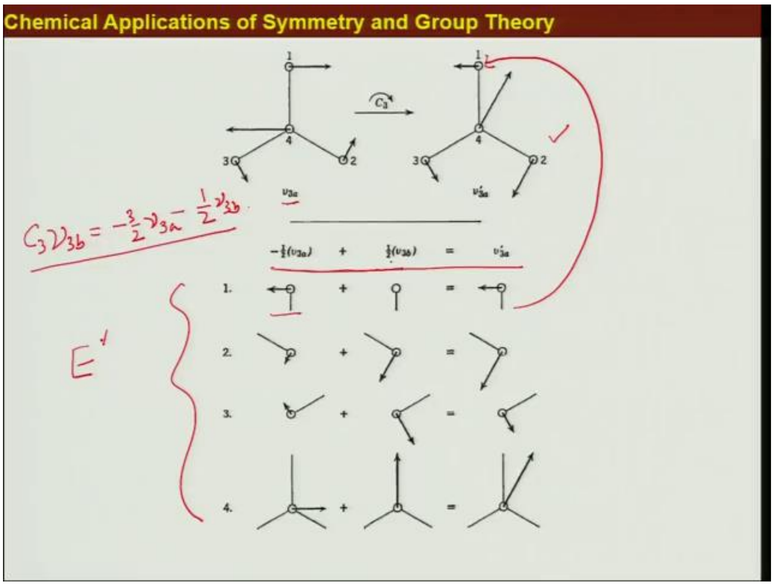
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So, this is 1. After operating C3 what will happen? So, this arrow here, on this atom 1 so here when we are doing this operations, so we are only dealing with this vectors all right. So, this guy will now go over here right. So, accordingly it is orientation will also change now you see this 1 which was on atom a is now coming over here with this orientation and this guy on the carbon atom this big arrow will now go to a particular 180 degree duration. So, it will come over here and let us have a look at this is the nu position of this arrow. In this way you can find out what will be the final structure, now this final structure which we are calling as nu prime 3a how we can express this in terms of nu 3a and nu 3b.

So, if I say that this nu structure that is 3a prime is expressing this passion and if you can show that and prove that then you are proved our point. So, you take a particular mode of normal mode of vibration. So, you take part of it, so here like you look at the structures nu 3a and nu 3b. So, you see here right. So, this 1 if you operate and you will get an ultimate structure that we have just shown, now if you take some portion of this 1 and some portion of this 1 and can generate that results in nu prime 3a then our job is done and that is what shown here. So, if we say that minus half of nu 3a plus half of nu3 b is equals to nu 3a prime.

So, this is a linear combination of this know this is some sort of combination. So, what is minus half of nu 3a that is this 1? So, if you take the original structure the arrow and if apply this minus half on that. So, you will get this structure similarly plus half of this nu 3b will give this. So, you will see that this length as been reduce to half of this original length and here, the length as been reduce to half of its original length as well as the direction as been reversed because the minus sign and now if you add this 2 you get this 1 which is if you compare here you see this 1.

So, you could if express this new structure as a combination of this nu 3a and nu 3b similarly for any other particular motion on the any particular atom say 1 2 3 or 4 you can express them in this particular passion. So, this is true for this whole normal mode right. So, all this things are like breaks up those a individual arrows that are situated on each and every atom and you take this particular combination rule and you see that ultimately you can generate this structure starting from nu3. Similarly you can show that for nu 3b and there will be another type of combination where here this nu 3a prime is a combination where is minus of nu 3a plus the plus of nu 3b and for say for nu 3b, if I operate C3 on that, so that I can write as minus 3 by 2 nu 3a minus half nu 3b.

So, in this combination I can express the new form of nu 3b after operating C3 all right. So, in this way if I can show for the nu4a and nu4b also now what does it mean that nu3 and nu 3b upon the symmetry operations on them. They cannot transform in as 1 of the illusive representation of d3h point group alone, but together that is nu 3a and nu 3b together they can form the basis for a particular representation and that must be a 2 dimensional representation because we are taking 2 basis functions as if right. So, nu 3a and nu 3b together they will form 2 dimensional illusive representation and if find out all the operations the effect of this all the operations on of nu 3a and nu 3b you will see that it belongs to it forms a basis of E prime representation of the d3h point group. And the ultimately you can see that all the normal modes they form the basis for illusive representation to which for the point group to views the molecule belongs to, all right.

So, now here we started with showing the normal modes of a particular group and then we showed that they have their symmetric property that is they belong to they form the basis for the illusive presentations. Now how do I if I do not have this normal modes present in my in front of me can we (Refer Time: 24:08) find the normal modes and its symmetry properties. So, we can show that by using the same particular molecule. So, how do we do that? So, first of all we need set of basis functions right.

So, we can do that in 2 ways because we are dealing with the molecular the internal motion of the atoms and bonds in a molecule while you talked about vibration. Then we can actually take the all 3 Cartesian coordinates sitting on each atoms of the molecule. Because we stated at the beginning that all those arrows right all this motions of this individual atoms when they execute 1 mode of particular vibration. This each arrow can be expressed as a resultant of 3 basis of the resultant of the basis vectors that we choose. So, if we take X Y and Z coordinates or each atom. So, this arrow which defines of the part of this normal mode that can be expressed as some sort of combination of this X Y Z. So, what I mean is following.

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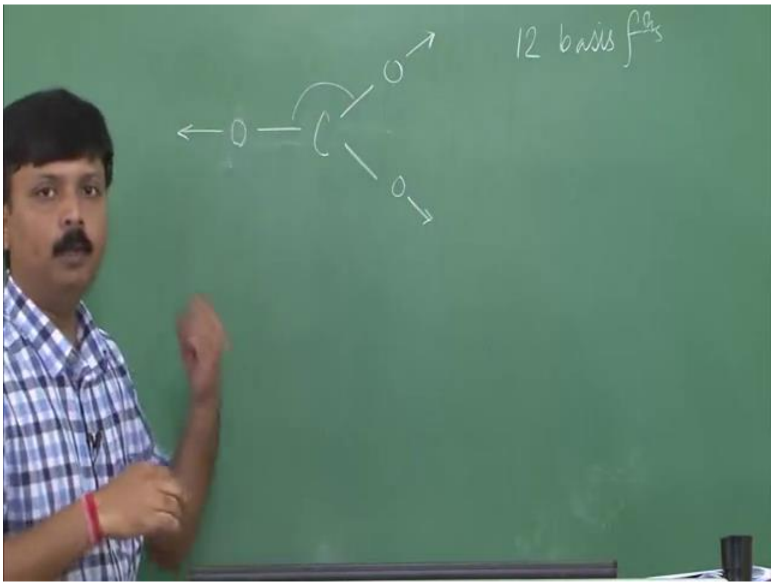

So, if I have say let us just say tell it like this. So, I have right. So, now, in 1 of the motion that I showed like this, what you say is I can take this X Y Z and take this atom to be sitting at the origin all right. So, then if I take the coordinate accordingly, then this particular arrow I can express as some sort of combination of this basis vectors. So, I can take the Cartesian coordinate of all the atoms.

So, when in each case what I will do I will take the atoms to be sitting on the origin and I will consider there X Y and Z coordinate system to be acting my basis. So, therefore, what I can do for this 1 I will have total 4 atoms. So, 4 into 3 total 12 basis functions right in my set. And we can do whatever we want to do that the other option is that we can take the internal motion of this molecules as such what do I mean. So, here what I do is like I have these arrows defining my internal motions right. So, suppose I take this carbon oxygen bond.

So, by this arrow what I say that this oxygen is moving away from carbon. In other word, this C O bond is getting scared right or while it is coming back then it is reducing the bond. So I can also take the angle between these 2 C O bonds. So, I can take this angle as one of my basis function. I can also take a dihedral angle meaning that I have a sigma plane here and I have this angle here or I have this plane here and then I have this bond here.

So, the angle between that I can take all this internal coordinates to be my basis function and we will show in the following class that in either of the cases I can get the required information. And in certain cases without knowing or with this simple use of symmetry I can really talk about what are the particular normal modes that this molecule have. In other words, I can draw exact the normal modes of these molecules of any given molecule. So, that is what we will start with in the following class till then.

Thank you very much for your attention.