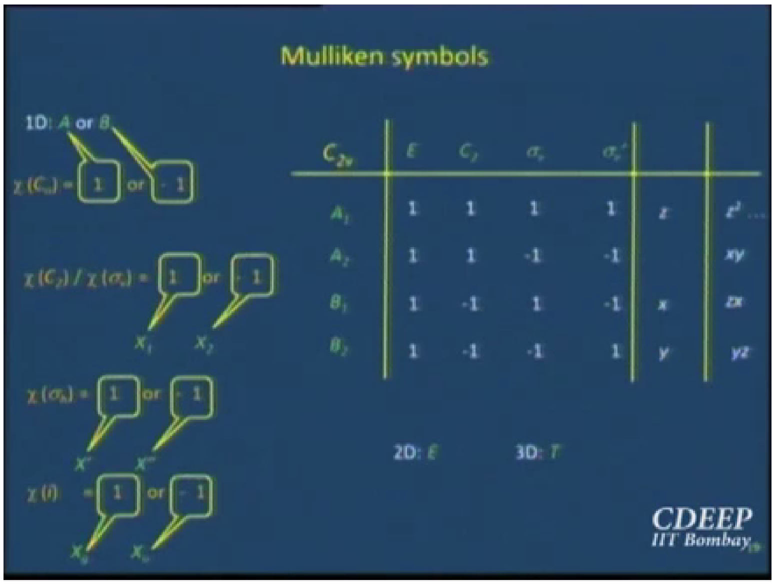
Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

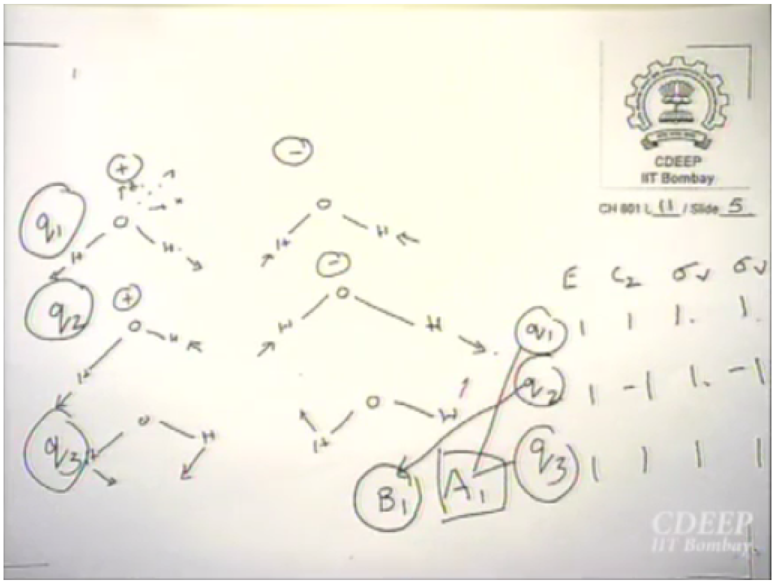
Lecture – 30
Character Tables: C2v and C3v

(Refer Slide Time: 00:23)



Okay, after this, we will go and discuss another character table but before that let us do something, I am kind of bored of these bases, you are only talking about xyz is boring, let us use some other kind of base, you are talking about C2v, right.

(Refer Slide Time: 00:43)



What is the most well-known C2v molecule, water, that is also boring answer, water, now, what I like to talk about with in what might seem to be a certain jam from what we are talking about now is; now on modes of vibration of water. Do you know, what are normal modes of vibration, what are abnormal modes of vibration? If there is normal mode, there is too some abnormal mode also, so why are these; are these the only same modes of vibration and the others have mad modes or what.

As before, you get into all that let me draw something that everybody knows, let me draw the 3 normal modes of vibration of water. Okay, what is the first one, symmetry state, what is the meaning of symmetry states; the 2 bonds lengths become long at the same time and then we are not spot at the same time, so this is + phase, this is – phase, okay. So this is + phase, what will be the – phase?

Both are getting short, okay, now, what is the next one? One bond gets elongated and at that time, the other bond gets shortened, okay, something like this, the 2 bonds move at 180 degree phase difference with each other, okay. So, if this is + phase of that, what will be the – phase, how can I draw it? Opposite kind of reflection, what is the third one, what is the third mode? Bending, right like flying actually, this is a + phase, what is a – phase, right, +, -.

Now, what are the symmetry operations? So, maybe I will call this q1, I will call this q2, I will call this q3. So, now see E C2 sigma v, sigma v dashed, let us see if I can find out if q1, q2, q3 belong to some symmetry species or not, symmetric states, right, let me write down the most difficult column. Now, what you do; the first column would better be want, okay, so now we are left with only 6 or 9 that is great.

If I perform a C2 operation, what happens to q1, that is remain the same or does it become negative, please understand what is +, what is -, the whole thing is +, the whole thing is -, okay. So, if you turn by C2, it is true that the 2 hydrogen atoms change places but now, look at the arrows, now actually you are looking at the arrows nothing else, the arrows were going out still keeping going out, right, so that character is 1.

What about sigma v, where is sigma v? Yes, okay, this is z, this is x, and so y has to be on the other side perpendicular to the plane of the paper, all right. Sigma v is zx, sigma v dash is yz, okay, now tell me what is the character of sigma v for q1, are you all convinced this is 1, what, what about sigma v dash, sigma v dah is like this perpendicular, + 1 or -1, now once we understand this, the rest would be came cakewalk.

See, outgoing arrow, outgoing arrow, right, if I do this reflection, these 2 arrows interchanged places, outgoing still remains outgoing, show me, this is the arrow, right, this is the mirror, this is where it is, is not it? Right, are you all convinced, this is what we need to understand, once we understand this, its life is simple, do you all agree, it is easy but is just that initial visualisation might be a little difficult.

This is the arrow and this is my plane, when I reflect, this is the arrow, same direction, it does not become the opposite direction, all right. So, will you allow me to write 1, so see we call it symmetric state, is not it, perhaps you know this already, symmetric state is symmetry with respect to everything, with respect to all the symmetry operations that are there in C2v point groups.

Symmetric states mean symmetry with respect to everything, all right and the symmetry states; first one is 1, fine, C2, what happens when I apply C2? Does not + phase, become – phase, if I apply C2, that means it is anti-symmetry, I have forgot your name again, **"Professor – student conversation starts"** what is your name, yeah and you, Anup; Anup, you understood, come on (()) (08:03) I can see, Anup, have you understood, sure, + goes to -, - goes to +, understood, okay, very good. **"Professor – student conversation ends."**

So, we will let me write -1 here, yes, what about sigma v, sigma v is the molecular plane with respect to molecular plane, is there any change, no because it is on the plane, right, so character is what, -1, +1, what about sigma v dash? That now you understand -1, as your -1, +2, not +2, okay, what about q3, bend, if you apply C2, then what happens, this is +, this is -, do not forgot. So, if I apply C2 then what happens?

Same 1, if I apply sigma v, same, unless it is out of plane bending or something and here out of plane bending is not even possible, it has to be symmetry. What about sigma v dash? 1, -1, 1 okay, so q1 and q3 they both belong to A1, is not it, A1 symmetry species, totally symmetric and they do not even need to see the character table for A1 because A1 means character with respect to C2, the principal axis is 1, character with respect to sigma v is also 1 that is all I need, okay.

And what about q2, what is q2? V1, why v, because character or the principal axis are symmetry is – 1, therefore v and y1 because character with respect to sigma v is +1, so you see if you are defined your x and y axis differently, the name would have changed, okay. So, you have to be very clear about how we define our axis, all right, so this is what B1, fine, this is something that is very common question people like to ask.

Before I go back, I am talk about the C3v point group; I want to ask once again, what is the meaning of normal mode? Yes, yes, the normal not as in opposite of mad right, normal not as in opposite of abnormal, normal as in orthonormal, we are talking out orthonormal vectors all the time, so now these normal modes means that these are ways of mode way, right, how, how it does?

So, these are the modes of motion, which do not have contributions in each other, so vibration is like a molecular dance, right, the molecules are dancing different way, so now whoever has learn dancing here, if you remember in your initial classes, what was taught? 1, 2, 3, 4, right, all initial dance lessons are 1,2,3,4, what to do with your legs, what to do with your feet, right, so once we are okay with that then what to do with your hand, arms.

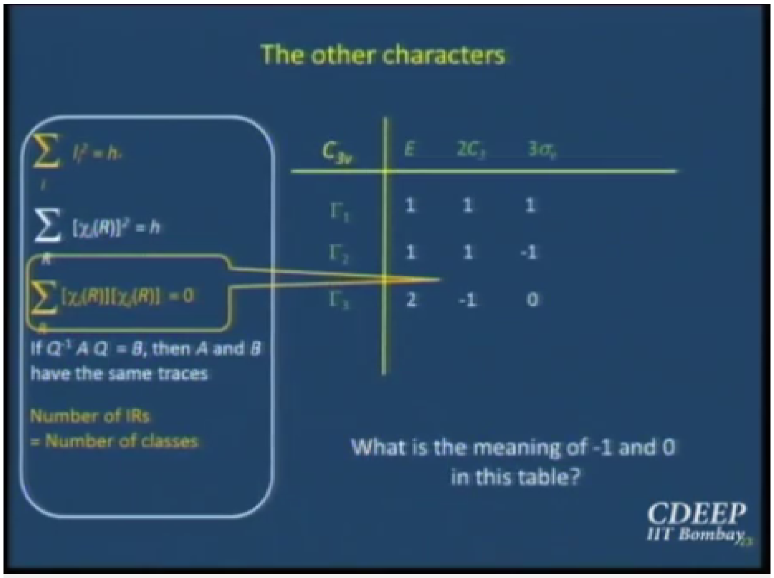
Once you learn that you are taught how to move your feet a little differently, and then may be how to move your head differently and then, when the actual dance is performed, the dance is really a linear some of all these normal modes, I know it is like a killing, I hear that one has for dance that it is what it is, even if a human dance is nothing what a superposition of normal modes.

So, please understand this, molecular vibration is a complex motion and at any given time, what have does not have to perform a symmetric stretch, pure symmetric stretch or a pure bend or a pure anti symmetry stretch. What it does is a complicated motion as long as there is no displacement in the centre of gravity, it is a pure vibration motion, right, see if we leave that out and look at even a pure vibration motion, what you have is really a linear sum of q1, q2 and q3.

The molecule dances but what is uses is these basic ways in which it moves the atoms, this is the meaning of normal modes in a very simple layman's terms, okay, normal mode is not sum, it is not just the equations, this is the actual meaning of normal mode, so that out of plane blocking that you are saying that will take place, if it is not water but if it is a CH2 group bound to a molecule, a bigger back bone of a molecule.

Then, you do see out of 10 motion there also, there is no problem, but if it is water, then it becomes rotation, right. Now, let us come back to the; this is what we have studied so far, mulliken symbols, now, I think we can do it a homework is please practice mulliken symbols from character tables, I am well within my rights to ask you to give the mulliken names to some symmetry species that I choose, which remains me before you go to the last part of the discussion.

(Refer Slide Time: 14:28)



So, we have worked out C2v, if you have worked out C2v, it is very simple for you to work out C3v also, let us do that and the reason why I want to do this is that C3v gives us an example of a 2 dimensional irreducible representation, 2D IR + spectroscopy really means 2 dimensional infrared spectroscopy, we are not talking about that we are talking about 2 dimensional irreducible representation, fine, C3v, how do you proceed, where is the first question we ask?

The last question we have on the slide is the first question we ask, how many classes, how many IR's, how many classes? E, then c3, 2 kinds of c3 and 3 sigma v's; 3 classes, right, so this one class that means, that there are at least 3 classes, good. So, 3 irreducible representations right, gamma1, gamma 2, gamma3, all right, question, all right, fine, what do you ask next? What are the dimensionalities that is the next question, right?

LI square = H, so the question; before the next question is what is h, 6 or 3, because h is a number of symmetry operations, please do not forgot, E; number 1 E, C3 is number 2 and number 3, C3 +, C3-, do not forget, there are 3 planes of symmetry sigma v, so 1 + 2 + 3 = 6, h = 6, so now see li square = 6, l1 square + l2 square + l3 square = 6, so what is l1, what is l2, what is l3? 112, 121, whatever so you have; you can write it in many options, in many ways.

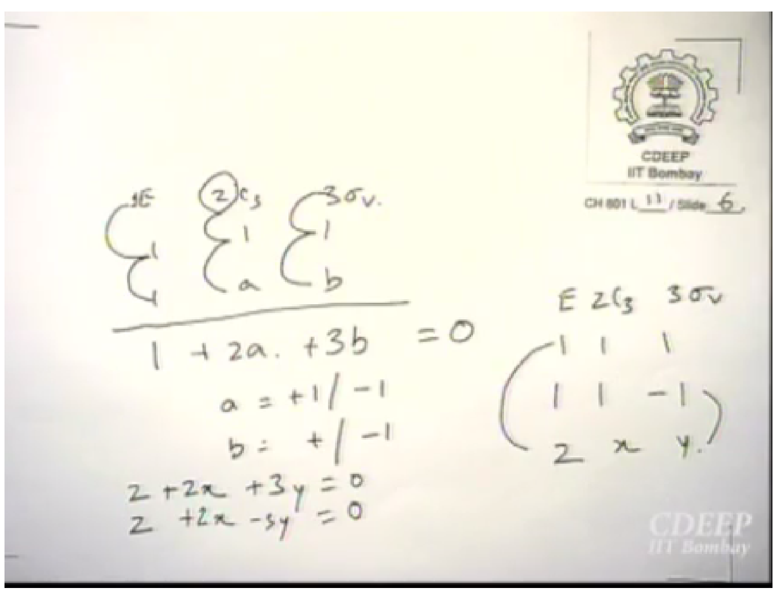
So, since you can write it in many ways instead of creating a tower of devil, it makes sense to decide in which order we will write, we will write the first; I mean 1 dimensional representation is first followed by 2 dimensional representation followed by 3 dimensional representations and so on and so forth if they arise, okay. So, l1 is1, l2 is 1, l3 is 2 that is how we will write, convention, nothing else, all right.

So, now first column, first row is very easy, right, first column is 1 1 to this time and do not forget lc is 2, is not it? And what we said is that the character of E = dimensionality, right, in case there is a problem just think what is the matrix here, what is the matrix for E in a 2 dimensional representation, 1001, so what is the character? 1 + 12, right, so are you all okay with the fact this character here is 2, fine, first row is always 11.

So, now see our job is simpler, we just have to write 4 elements now, how do I do it? How do you do it? By this, so what I do is; you write a, b, c, d once again, right and then you work it out, can you work this out, actually to start with work only with gamma 2, work only with gamma 2, oh no, maybe not, work with both, write down the equations, what do you get? So, even here, we can have either +1 or -1, right, so what it should be, how many +1's, how many -1's should it be?

Because this has to hold sum over R chi iR chi jR = 0, now take this as I, gamma 1 is gamma I, gamma 2 is gamma j, let us say this is s a, this is b, what is equation you have? 1 + 2 * 1 * a + 3 * 1 * b = 0, is not it, right.

(Refer Slide Time: 19:53)



So, what do we need to do, coefficient of this, I will write 1 explicitly, multiplied by this character, multiplied by this character that gives me 1, then coefficient of C3, why we are take the coefficient because actually, what are we working with, if you are not working with symmetry elements, symmetry operations, you have C3 and you have C3 square, okay that only reason we write 2C3 is that as we know already these symmetry operations in the same class has the same character.

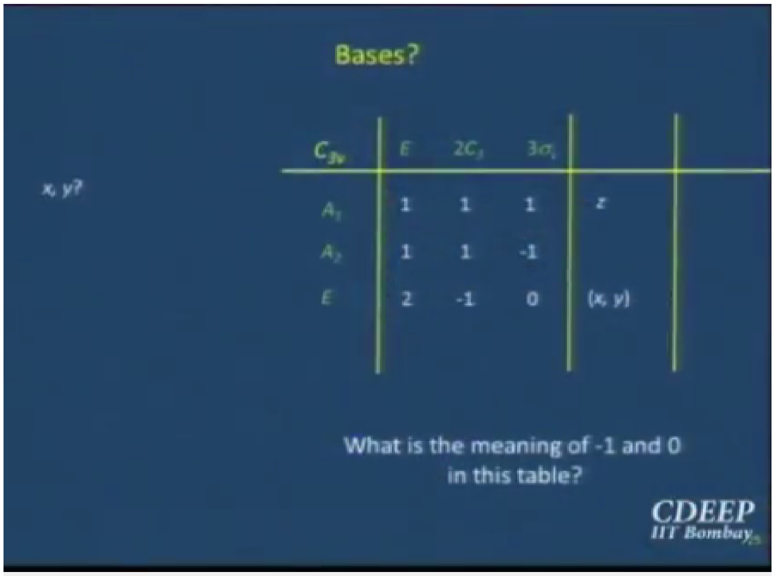
We are saving, space, time, and forest, using less paper, right, so that is why, so that does not mean that we are going to keep 1and you are not going to keep the other one, you must keep 2, so what you have to do is; you have to multiply 2/ 1/ a, so what you have is +2a, similarly here you have 3 * 1 * b, so that is +3b = 0, a = either +1 or -1, b = either +1 or -1, now tell me what is a, what is b naturally, right.

So, 11 – 1, so here is 11-1, I just write it once again 11111-1, E C3, sorry 3 sigma v, now here I have 2 already now, this is x, this is y, how do I get x and y, I will need 2 equations; first multiplied these 2, then multiply these 2, as easiest we are going about it, so it is 2 + 2x + 3y * gamma 1 and gamma 3 and if you multiply gamma 2 with gamma 3, what do you get? 2, then +2x, then, louder, -3y and both are = 0, are you all okay with this.

Some of us are done this already in c442 or in other courses as well but for those who have not done it earlier, are you all okay with this so far, simple. So, now see, look at the 2 equations, you have 2 + 2x and to that whether you add 3y or whether you subtract 3y, it does not make a difference, it is still 0, what it does that mean? That means y =0, so put y =0, now 2 + 2x = 0, x = -1, 111, 11-1, 2-10, okay.

Now, the question is we know what -1is already for 1 dimensional representation, right, it means anti symmetry changing sign, what does this -1 mean? And then what does this 0 mean, annulation; no, if you do the annulation, we would not (()) (23:34) in the character table, so we will see what it means, give me a sec.

(Refer Slide Time: 23:42)



But before that let us write the mullikens symbols, I have written the first one, the A1, what will the second on be; will it be a A2 or will it be B1? Why A2? Because character of the principle axis is 1, so A character sigma v is -1, so 2, A2, then is E. Now, the thing is this, you could have written E1 or E2 rather, E2 but we do not have to be because this is only one E.

So, in mullikens symbol, please remember that we only use superscript, subscript etc. when it is absolutely required, when it is not required, we do not use them always, so do not get confused if you see that this prime or double prime are missing even though, you have sigma h that is there in many cases but the reason why they are not used is it is not required, okay, if you have 2 archipreneurs in the class, you have to say, you have to; you need another quantum number right.

So, may be use a (()) (25:01) or something but you have only one, then you do not need it, so that is what is used, all right. Now, let us work out the bases, almost done, where does that belong? Here also z belongs to the first one; A1, totally symmetric representation. Please do not forgot it is called the totally symmetry representation, the totally symmetry representation can have different molecular names though.

Here it is A1, some where it might be A1 double dash, sorry A1 dashed, A1 prime, if you have horizontal plane or symmetry, it can be A1g, if you have a centre of inversion, it can be A1 prime g depending on what are their symmetry elements you had, okay. Now, what about x and y, what do they belong? Where would x and y belong, you are taking C3 along the z axis, what happens to x and y?

Remember that matrix that we have worked out, rotation by theta or rotation by 180 degrees, we have worked out that also, what was that? -1/2 then, root 3/2, then -root 3/2 -1/2 again, right that was the matrix and what we have said that at that time is that as the action of C3 along the z direction, we are essentially mixing x with y that is where it is the 2 dimensional representation, x and y are getting mixed, x does not remain pure x, y does not remain pure y, they mix.

And when they mix, that is when your half diagonal elements become non zero and that is when you have more than 1 dimensional symmetry species, irreducible representations, it is just not possible to simplify any further, there is no way in which you can apply one of the symmetry operations and leave x as a function of x only, it has to mix with y, all right, so that is why so you can work it out and you will see that x and y belong to E.

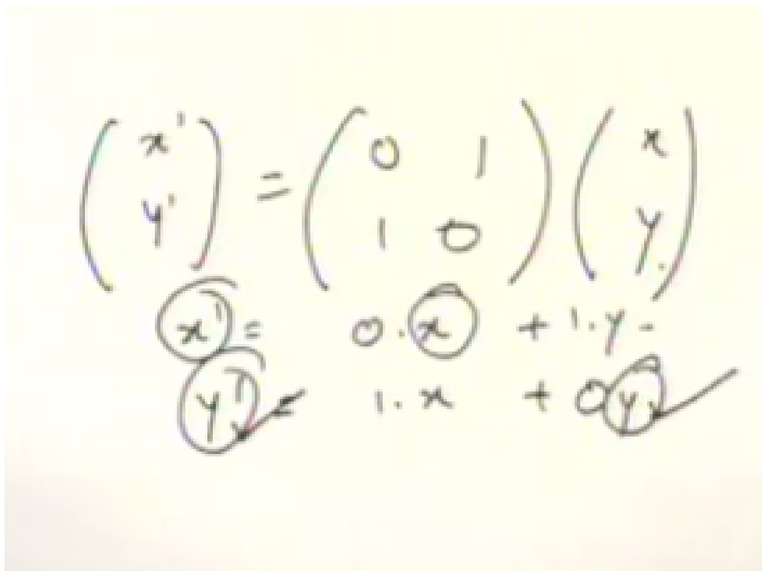
And since they belong to E jointly not by themselves what we do is; we put them in brackets and put a comma between them that is a notation we used for more than one dimensional symmetry species, right. Now, let us come back to that question, want is the meaning of -1, what is the meaning of 0, -1 as somebody was saying correctly is because you are turning by C3, remember the matrix, -1/2 forget about half diagonal elements.

The next diagonal element is -1/2, how did we get that? X dashed = -1/2 x, right, so on so forth, so you are adding -1/2 with -1/2 and there by getting this -1, so it is important to understand that this -1 is not equivalent to that -1, in a 1 dimensional representation, -1 means reversal of sign, in 2 dimension or 3 dimension, or whatever dimension rather than 1, it is reversible representation, -1 does not mean a simple reversal of sign.

It is merely the sum of the coefficients of the different bases that are there, so even though this is -1 that is -1, they do not have the same implication. Similarly, what about this; what about this 0, we have worked out these matrices also, right sigma v remember, what was the matrix, as I said correctly, 0110 is a matrix, so 0110 means what; in the transformed coordinates, the original coordinates do not have any contribution in themselves.

So, x does not have any contribution in x dash, y does not have any contribution in y dash that is the meaning, okay. Do you remember the matrix 0110? Yes, or no, I can open it up, although good things, all representations are here, right, so the matrix we had when we applied sigma v to xy, once 0110 that means what you write xy may be we will write it here.

(Refer Slide Time: 30:04)



This was the transformation matrix that we have worked out, right, so what does that mean? X dashed = 0 * x + 1 * y, y dashed = 1 * x + 0 * y that means, see x does not have any contribution in transformed x, y sorry, circle the wrong y, y does not have any contribution in the transformed y that is the meaning of this x, okay, it is not complete annulation, it is annulation in this sense that a coordinate does not contribute to the transformed coordinate to the transformed form of itself, right.