Molecular Spectroscopy: A Physical Chemist's perspective

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Lecture No. – 43

A Shortcut to Symmetry of Normal Modes

Knowledge is supreme.

Looking at how the xyz coordinates of each atom has formed in response to every symmetry operation we have been able to come up with a reducible representation and if you remember this is what the representation is. this is what we call gamma 3n 12 0 -4 2 -2. We learned our learned our shortcut to how to arrive at this reducible representation without having to explicitly look at the transformation of each of those Xi, Yi, Zi coordinates one by one.

If you remember in the last class we took maybe 20 minutes to understand c3 what happens to c3. What is the character of c3. And then in 15 minutes we would work out all the characters. Today we are going to learn a trick that will let us arrive at this gamma 3n without even having to do all that. And of course once you know that trick it's a blackbox. But the issue is that we should know how we arrive at the blackbox. That's what we are trying to do right now.

Let us think a little bit how we arrived at gamma 3n. What did we work with? We worked with the xy and z coordinates and we said that any atom that moves from its position is not going to contribute to the overall character. So essentially we have worked with the atoms that have not moved from their own position. Let us say the number of such atom that remain unchanged by a particular symmetry operation is n. Let us work out what n is for every symmetry operation. How many atoms are there in the molecule? We are still working with bf3 or carbonate. Four atom bf3 so there are four atoms. How many of these remain unchanged upon operating e? E is the identity operation. How many atoms remain in their own place if I apply e? The answer is all. All four. So n is four for e. How many atoms do not move from their position upon applying c3 plus or c3 minus? One. Only the central atom. What is n? One.

How many atoms remain in their place upon applying c2? Two. The way we drew c2 was through the central atom and one of the other pendant atoms. N is two. What is n for sigma h? Does any atom move from its position? Four. What about s3? I have got two answers. Four and one. Which one is correct? Or is there any other answer? One? Sure. Only the central atom remains in its place. All other atoms change place like c3.

What about sigma v? Two. The two atoms that are in the plane like c2. So this is n. Now what I have to do to arrive at this characters of gamma 3n is that I have to multiply each n by the character of the representation that we get by using xyz as basis. Is that right? After all if you remember it doesn't matter whether it is X1, Y1, Z1 or X2, Y2, Z2, X3, Y3, Z3, X4, Y4, Z4 they transform in the same way the blocks are all the same. It is just that the atoms that move from their positions for them the non-zero blocks go off diaganoal. That's why they don't contribute. Do we agree that blocks are all the same? Remember c3. Aren't the blocks all the same? Minus half root 3 by 2 root 3 by 2 minus half, one everything else is zero. This is what you get for each of the blocks because after all xyz transforms in the same way no matter which atom it is associated with depending on whether the atom moves from its own position or not you get that block along the diagonal or off-diagonal. Are we clear about that?

So how did we get a character of zero for c3? How did we get a character of zero for c3? We multiplied the character of this block by one. Number of atoms that did not move from its position was one. We multiplied that by the character of this. How did we get c2? Once again same blocks only the diagonal blocks matter. Two atoms don't move from their position so character multiplied by that atom.

So that is basically what we have to do for everything. And we have worked out already. Now to do it we need to know how xyz transform with upon operation of each of these operations that are there, upon using each of these operations. So tell me how will I get the character of whati call gamma xyz? Gamma xyz is the reducible representation for which x, y and z form the basis. How do I get gamma xyz? Remember what we did for water. For water we used xyz as basis and then we got these metrics for this basis and then we could nicely block factorize them. That gave us the three reducible representation. So for water c2v it turned out that gamma xyz is equal to A1 plus has anybody remember what it would be for x, what it would be for y? We can work out quickly actually. Will it be A? Will it be B? If I take x or if I take y will the character of c2 be plus one or minus one?

Water is very easy. We can work it out anytime. Xyz. The z is the c2 axis. Will the character of x or y be plus one or minus one? Minus one, so will it be A or B. B. So A1 plus B1 plus B2. Which one will be B1, which one will be B2? How do I decide one or two character of Zx sigma v if you remember. So which one will have a character of one for sigma v Zx, x or y? X is on the plane. So character should be one. Y is perpendicular to the plane. Character should be minus one. So A1 is for x over z. B1 is for x. B2 is for y. So gamma xyz can be written as a sum of irreducible representations where A and B belong. For this D3h what is gamma xyz? Sum of which – so now we are doing the reverse process. Here I had given you the xyz and then we broke it down into considerate irreducible representations. Now I have shown you the character table. You already know where x belongs to or y belongs or z belongs. So what is gamma xyz? How do I get it? Just by adding them. Where x belong, where does y belong, where does z belong? X and y jointly form the basis for E dash. E dash is a two dimensional representation and z is in A2 double dash. It's not just A2.

So for D3h gamma xyz is E dash plus A2 double dash. Are we clear about this? If there is a question please ask. Did you understand what I did? Can I go ahead? Okay.

so if this is the case gamma xyz is E dash plus A2 double dash then I should be able to find the characters of gamma xyz by adding the corresponding characters of E dash and A2 double dash. Is that right? Can you tell me what the characters will be? What is the character for E I can tell you that, it's going to be three. What is the character for gamma xyz for c3? Yes. What is the character for E dash? Minus one. What is it for A2 double dash? Last one, what is the sum? Zero. Understand we are just adding characters. So what will be the character for c2 dash? Yeah. C2 dash. Zero plus zero minus one is that minus one? What will the next character be? What is the character for sigma h? Yes? Two minus one equal to one. What is the character for s3? Yeah. Minus two. This is just addition. So what is the character for sigma v? [Indiscernible] [00:11:40] one. So this is gamma xyz.

How should I be able to get gamma 3n now? If I multiply n by gamma xyz should that not give me gamma 3n? Let us see if it does. It does. I mean it should work it out. 3 4s are 12. 0 into 1 is 0. -1 into 2 is -2. 1 into 4 is 4. -2 into 1 is -2. 1 into 2 is 2.

So what we have established is n multiplied by gamma xyz gives me 3n, gamma 3n. So to work out gamma 3n, gamma 3n is the reducible representation for which the 3n coordinates of motion

[Indiscernible] [00:12:37] the basis can be worked out by simply looking at the character table working out the reducing representation for which xyz are the basis and multiplying it by the number of atoms that do not move from their position as a result of a symmetry operation. So now that's a shortcut.

But it's not the complete shortcut. We are only half way through the shortcut. So what we have established is this gamma 3n it's really n into gamma xyz. Now what am I trying to do? Am I really interested in the 3n coordinates? We are trying to arrive at the symmetry of normal coordinates of vibration. All these are normal coordinates but we are only interested in normal coordinates of vibration. This is a symmetry of all the 3n coordinates. I am looking for symmetry of 3n minus 6 coordinates. How do I do that minus 6 from here?

What are the six coordinates that I have to deduct from here? Xyz for translation motion movement of the center of mass and rx, ry, rz. So this is your gamma xyz. You have worked out already. What is gamma rot. Gamma rot means the reducible representation using Rx, Ry, Rz as the basis. Can you work that out for me? Rx, Ry when do they belong? E double dash and A2 dash. So if I add E double dash with A2 dash then I should get gamma rot. Can you work that out for me? Let's work out gamma rot by adding the irreducible representations for which Rx, Ry, Rz are the basis. [Indiscernible] [00:14:44] what are the characters for gamma rot? Three, three zero minus 1, minus 1, three zero minus one, minus one hold on. Rx, Ry, Rz so here I made a mistake.

Three zero minus one then minus one two minus one. Three zero minus one minus one two plus one. Then we can work out gamma vib from there. How do I work our gamma vib? Yes [Indiscernible] [00:15:29]. So gamma vib is equal to n multiplied by gamma xyz minus gamma xyz minus gamma rot . In fact when you want to use this formula as a blackbox it makes sense to do it directly and write n minus one multiplied by gamma xyz minus gamma rot. What will it be? What is gamma vib tell me. Yeah. N into gamma xyz is given, gamma xyz is also given. So 12 minus 6 should be first of all 6 – actually I didn't work it out. That is why I have such [Indiscernible] [00:16:26] here numbers. So I have 6. Then what is it – what do I have next? What is this character second one? Zero. Third one? So that is wrong because that is gamma rot copied. So don't think what you see on the projection is right. I didn't finish making the transparency today. It is zero. Then what do you have? Four minus one is three. Minus minus one is again four. Is that right, is that four? See I am not very good at [Indiscernible] [00:17:12] arthimetic. So you need to tell me when I go wrong. Then minus two isn't it? And the last one. Two minus one is one. One minus minus one is this the answer we all get, gamma vib is 6 0 0 4 – 2 2 is that right? What is the next step? Did we derive A small working formula in the last class which tells you how to break down reducible representation into its consequent irreducible representations? What was that? So we said that we write a reducible representation as sum over I Ai gamma I and the way we find Ai is or Aj way we find Aj is what was it? One by h sum over r chi jr, x not x chi chi of r where chi of r is the character of symmetry operation r in the reducible representation. Chi j of r is a character of r in the jth irreducible representation. This is our working formula.

Using this working formula can you work out the values of A for these symmetry operations that are there, sorry these symmetry species that are there in this gamma wave which is irreducible representation. Can we do that? Is the problem defined? Have you understood the problem? No. Are you okay with this? So I am asking you to find Aj for A1 dash, A2 dash, E dash, A1 double dash etc, for this gamma vib which is irreducible representation. So gamma vib is the representation. What is the [Indiscernible] [00:19:40]? six because character for E is six. Look at the character table. Is there any six dimensional representation? No. that means this is a reducible representation. So I should be able to write it as a sum of irreducible representations. So I want you to find out the coefficient of each of the irreducible representation that is there. So your job is essentially to multiply six by one plus zero by one plus zero multiplied by one, four multiplied by 1 minus two multiplied by one plus two multiplied by one divided [Indiscernible] [00:20:22] by 12 how much time does that take? I have the answer for the first coefficient. This is very easy. What is the answer for the first one? For A1 dash what is the coefficient? One. Is that right? One. For A1 dash there is the coefficient is one that means there is one totally symmetry vibration and in fact when we do showed you the normal modes without deriving we have shown you the symmetric stage right. That is the totally symmetric vibration.

Alright. What is the coefficient for A2 dash? It won't be half. Anything other than half? See this always – that's the – that is a check the coefficient will never be anything other than a positive whole number for the integer. Half cannot be. You cannot have half of vibration. Okay. Let us work it out. One multiplied by six is six. Plus zero plus zero plus four multiplied by one is ten. Is that right? Plus minus two multiplied by one multiplied by two that is where we always go wrong. Do not forget you are summing over all r. And there are 12 symmetry operations. The way you get 12 symmetry operations is by counting s3 twice. So the reason why you got half is because you forgot the coefficient of s3 and sigma v for that matter.

Are we getting zero? Are we getting zero or are we getting one? Zero? So coefficient of A2 dash comes out to be zero. There is no A2 dash vibration. What about E dash? E dash is even more interesting because E dash is two dimensional. What is the coefficient of E dash? Two? So let's see what we have so far. We have gamma vib is equal to A1 dash plus you are saying 2E dash. Can you tell me how many normal modes are accounted for so far in what I have written? How many normal modes have I accounted for? One A1 dash and two E dash so how many is that? So this is the second point where we often go wrong. It is not one plus two three but one plus two into two five. Don't forget E dash is a two dimensional irreducible representation. So each E dash contains two vibrations that transform together.

Look at the character table. What does E dash contain. xy. What does that mean? That means x and y are not separable. They transform together but x is one coordinate. Y is one coordinate. So it has two coordinate. Similarly whatever normal modes of vibration you have there are two in each E dash. We have accounted for not three but five. What I am trying to say is this, do not first thing is what we have said already do not forget to multiply by the coefficient because we are talking about symmetry operation not symmetry elements. Second thing very important to understand is do not forget that when you have a more than one dimensional representation their dimensionality gives you the number of element in the base basis.

So when you have E dash that's a two dimensional representation. Each E dash stands for two coordinate. That is what you see in the character table. See xy together. That's two coordinate, isn't it. Xy together is not one coordinate. X is one coordinate, y is one coordinate. Similarly x square minus y square is one. Xy is another. Together they transform that's why it is a two dimensional representation. So each E dash actually contains two coordinate of vibration. So one A1 dash, and two into two four. Four E dash vibrations. Have you understood now? So we have only one left to do. If you account for one more we are done.

Alright. What is the coefficient of A1 dash, A1 double dash sorry? That is a job of whom? Zero. No A1 double dash vibration. What about A2 double dash? A2 double dash. One sure? So if this is correct then of course the last question is only a formality. What is the coefficient of E double dash? Zero. You have accounted for all the normal modes already. There are six normal modes we have accounted for them. So what we say is there is one totally symmetric representation. One A2 double dash vibration. And there are four vibrations that belong to E dash. So this is where we have got so far. Next thing we want to know is can we now say a little bit about what kind of molecular vibration, which bond states which bend has what kind of symmetry. That is what we will take in the next part of the discussion.