Molecular Spectroscopy: A Physical Chemist's perspective

Prof. Anindya Datta
Department of Chemistry, IIT Bombay

Lecture No. – 45

IR and Raman Activity–I

Knowledge is supreme.

What we have learned so far is using D3h molecule BF3 of carbonate D3h molecule with four atoms we have learned how we can figure out the symmetries of the normal modes without knowing what they actually look like because as we understood we will not be able to say what the normal molecules look like just by looking at a molecule if the molecule is any bigger than carbon dioxide or water but even without that we have been able to figure out their symmetries.

And then what we have been able to do is to some extend we have been able to assign specific internal motion bond stretch and bend to these normal modes of different symmetry. If you remember for BF3 or carbonate whatever you like, which is D3h and four atoms what are the symmetries of vibrations we have got? One was a1 dash. How many a1 dash? One or two? One. What is that a1 dash? We assign that two symmetric stretch. And we can even draw it. It's something like this. Since it's symmetric stretch is not very difficult to draw it. There is no component of bond bend here at all. What was the other one dimensional representation we got? a2 double dash. And remember why am I using small letters here we said that we are going to use small letters for wave functions and normal modes in this case. We are going to use capital letters for states. When we talk about states next week electronic states or maybe on Thursday you will see that we are going to use capital letters as well.

But a2 double dash what kind of motion was that? Doming motion. The way we drew doming motion was plus and these are minus or the other way round. The central atom coming towards you or going away from you and the terminal atoms the pendant atoms making sure that the center of mass doesn't move. What else did we get?

We got two what was that e dash or e double dash? Two e dash vibrations. And what are they made up of? In plane bend plus stretch. In plane. In plane. That is very important to remember. In plane. And when you talk about doming motion do the bond links change? Do the bond links change in doming motion? Actually they don't. There is no component of stretch there. If you remember using the bond stretch stretches as the basis element we got a1 dash plus e dash. So only these two symmetries you are going to see contribution from stretch.

When we took doming motion we got a2 double dash. So doming motion is a pure change in angle kind of thing. It is such that it is not in plane, coming forward, going back but there is no change in bond angle. Please let us have this very clear. And the other thing we got was using the three angles theta1, theta2, theta3 as we wrote them in plane. We also got a1 dash plus e dash but then we realized that a1 dash cannot be a correct solution because if a1 dash is a correct solution then all the three angles have to increase at the same time. It is not possible to do that because theta1 plus theta2 plus theta3 is 360 degrees. If theta1 and theta2 increase theta3 has no other option but to decrease. That is how we eliminated what we called a redundant coordinate that was a1 dash from bending and we had only e dash. But then in e dash it is not possible for us to say that we have one e dash, well one pair of e dash, that is only stretch and one pair of e dash that is only bend. We cannot say that. It's a mixture.

How do you find the coefficient of mixing? That is something that is beyond the scope of this course unfortunately. That is done using Wilson FG matrix method and once you do that you can actually draw diagrams like this. You might remember we had shown you the pictures of the normal modes. Now you see this is a symmetric stretch a1 dash. This here is the doming motion. A2 double dash. Now if you look at these four these two form e dash one set of e dash. These two together form another set of e dash. And now if you look at the arrows say this one it looks fairly complicated. What does this mean? This is moving in that is moving out. This is moving to this side. That is moving to that side. So first of all all bond angles are changing besides the lengths of the arrows are not all the same.

So there will be distortion in bond length as well. This is kind of not very difficult to see in fact this is perhaps best normal mode to look at because this one is a bend. This is a bend. These two arrow indicate a bend and this thing is going up which says that the bond links are also changing. So here you see I think this is where you see best how it is a mixture of in plane bend and stretch. But how exactly you come up with this figures that is something that we will not go to. We will stop at where we have reached so far.

But from there we will embark upon another discussion and that discussion is which of these normal modes are IR active, which of these normal modes are Raman active. Of course as we know in order to say whether a transition is IR active or Raman active or whether a transition takes place or not the condition that we have established in this course is that transition moment integral must be non zero. Suppose transition moment integral is not zero. Can is it still possible that the transition doesn't take place? Transition moment integral is non-zero. But transition doesn't take place. Is that possible. Yes. Example. So take the rotational levels j equal to 0, j equal to 1 for dyhyrogen molecule. Well transition moment integral is zero there. That's not a good example. But well what I am trying to say is even in transition moment integral is non-zero there might be some other factors that can mesh things up but for now what we are doing is at least is a transition moment integral non-zero that's what we are trying to say. The question was you have a particle in a box which transition are allowed say that using symmetry. And this is something I think we have discussed in class, even and odd symmetry.

What was the argument we had used there? We had said that if this transition moment integral is something like this I will write psi two and psi one this time, this is to be non-zero if and only if this triple product psi two mu, I have written psi two twice. Psi two psi one that remains invariant with respect to a symmetry operation. Remember at that time we had only talked about parity and then we talked a little bit about inversion. Now that we know that a symmetric species means how – what is the response to every symmetry operation that is there in the point group, now we can expand a little bit. What will be our update definition, what will be our update condition for a transition moment integral to be non-zero.

Yes. Transition moment integral is non-zero when this is called a triple product, product of three functions. This triple product what kind of symmetry should it have? It should be invariant with respect to each and every symmetry operation. Invariant means symmetric. So which symmetry species is symmetric with respect to each and every symmetry operation? Yes. Identity element. E. No capital E is only one operation. I am saying we have – well totally symmetric representation is the answer. So they are saying a1, a1 is true for things like water but then it is called different things in different point groups, isn't it? So instead of saying a1, it is better to say the totally symmetric representation because if there is a point of inversion you will call it a1g. If there is a sigma h very often you call it a1g dash. So instead of saying a1 better say that this triple product must belong to the totally symmetric irreducible representation. This is the condition for the dipole moment – for the transition moment integral to be non-zero. So this is the condition.

This is what we are going to focus on for the rest of this discussion and not only this when we talk about electronic spectroscopy we are going to make use of this as well. The condition for a transition moment integral to be non-zero is that the triple product, the two wave functions and dipole moment must belong to the totally symmetric representation. I can modify that a little more by saying that any one of the components of the dipole moment where I can be x or y or z because dipole moment can be in any direction. You have to resolve it into x, y and z. what is the symmetry of mu x in any point group? To which symmetric species will mu x belong? Mu x is along x direction. Sorry. No. This is a general question. You need to understand the question. And as I said it is an easy question as always. So give me an easy answer. What will be the symmetry to which symmetry species or to which irreducible representation will mu x belong in any point group? Yes. Well same symmetry species as x. simple answer in simple words. Is that point made?

Similarly so what we are trying to say is that this triple product we can write as something like psi two x psi one. If psi two x psi one belongs to the totally symmetric representation then the transition moment integral will be non-zero or if psi two y psi one or if psi two z psi one belongs to this totally symmetric representation. That is the condition for the transition moment integral with non-zero. Do you agree with this?

Now we need to worry about when we are talking about vibration of wave functions what is the symmetry of the vibrational wave functions? That's what we need to think. Now when we talk about vibration what is the transition, let's say we are talking about a simple harmony oscillator. What is the only transition that we care about? Simple harmonic oscillator. V equal to zero to v equal to one. Well the fundamental transition in the terminology that we have used so V equal to zero to v equal to one that is what is important. So here what are the wave functions that are important? The wave functions that are important are psi v equal to zero, and psi v equal to one. So if you are talking about vibrantional transitions then this is what we need to consider. What is the symmetry of psi v equal to zero, what is the symmetry of psi v equal to one? Of course everybody remembers what the wave functions look like. They look pretty much like well qualitatively they look similar to but not exactly the same as the wave functions of particle in a box. So but we will go a little bit deeper into it. Who can tell me what is the generic form for wave function of a simple harmonic oscillator? What is psi v? I will start. Psi v is equal to Nv multiplied by E to the power minus alpha x square by two and what is alpha? For our purpose for now alpha is a constant. We don't care. It's the constant multiplied by Hv. What is Hv. Hermite polynomial. Yes Hermite polynomial of X – if we are writing psi v and x better write Xi [Indiscernible] [00:15:43] normal modes so instead of x let us write Xi. Xi square by two Hv in Xi. Actually it is Xi multiplied by a constant but Xi will work. So this is the constant we don't have to worry. What kind of a plot will this be? E to the power minus alpha Xi square by two if I plot this against Xi it is Gaussian function. It's totally symmetric. No matter what you do to it it will not change. So totally symmetric. We don't have to worry about this part. The only thing we have to worry about is what is the symmetry of the Hermite polynomial and we only have to talk about two Hermite polynomials for V equal to zero and v equal to one. Who can tell me what is Hv equal to zero of Xi? It is one. So the wave function is basically a constant with respect to Xi. Well not constant you have this e to the power minus Xi square by two as well that is why the wave function looks like this. What is Hv equal to one of Xi? Since I have a poorer memory than you guys I do not remember the coefficient. All I remember that it is some constant c multiplied by Xi. Now see.

So what is this? So if can I write like this? Psi zero of Xi what will be the symmetry of psi zero of Xi? It is totally symmetric. Are we clear about that? Are we clear that for V equal to zero the wave function is totally symmetric? So this is totally symmetric. What about psi one Xi? What is the symmetry of the V equal to one wave function? V equal to one wave function is such symmetric part totally symmetric part multiplied by Xi. So what is the symmetry of psi one? Yeah? Anti-symmetric. Don't forget we are talking about a situation where you have many symmetry operations. It can be symmetric with respect to one, can be anti-symmetric with respect to one. So the generic – what would be the more generic answer? More general answer? Yes. Well what is – well even that is not a generic answer.

No. Who said that. Hand? Symmetry of Xi. You are right. That was the answer I was looking for. Whatever is the symmetry of Xi that is the symmetry of V equal to one wave function. There is no specific answer. It maybe totally symmetric. Maybe E dashed maybe double dash whatever I don't know. But at this point I can say same symmetry as Xi. And now I come back to this problem. What do I need to determine? I need to determine whether this triple product is totally symmetric or see when I am talking triple products usually you will not get one dimensional representation. When are you going to get a one dimensional representation? If all three belong to one dimensional representation because then it will be one multiplied by minus one multiplied by minus one or minus one multiplied by one multiplied by one something like that. But suppose one of these belongs to more than one dimensional representation then the product is going to be reducible representation. So what we are saying is this triple product must contain a totally symmetric representation. Yes. If it's one dimensional, if everything is one dimensional here then you understand easily. Suppose it is not one dimensional. Suppose this belongs to a two dimensional representation. This belongs to a three dimensional representation. This belongs to one dimensional representation. Then product will be two into three psi but then usually five dimensional representations are not even there in most of the point [Indiscernible] [00:20:31] so it will be a reducible representation not an irreducible representation. I think we will understand it better once we start doing the examples.

What does this rule boil down to? This part we have shown is totally symmetric. So we are left with these two, isn't it? And this part what is it? Psi v equal to one. We have said it is the same symmetry as Xi. So the problem boils down to what is the symmetry of Xi multiplied by X or Y or Z, isn't it? So the condition boils down to this product, direct product, this is called the direct product when you multiply two. Xi x or Xi y or Xi z these must contain the totally symmetric representation. Is the problem defined? Yeah. So this is the condition for IR activity that direct product of the normal mode of vibration and one of the [Indiscernible] [00:22:00] coordinates must contain the totally symmetric representation. Before we take the examples we will simplify it a little more. This is our condition then.

So what we will do is we will quickly derive another small working role that will make our life a little simpler. So we are talking about a product. So let us say I am talking about a product AB. A is Xi and B is x or y or z. what is Chi AB? This is something we have done earlier. What is a character of a product? Sum or product? Product of the characters. Product. Xi of A multiplied by X of B. What do we require? We require that this character I think I am not – I have suddenly started writing in a different convention than what we have used so far. I think that is a problem. So I will write like this. Sorry. I will write like this. Sorry.

XiAB or R. this is the convention we have been using, isn't it? Inside brackets we always wrote the symmetry operation. So Xi AB of R that is the character of the function which is the direct product of A and B that is equal to Xi A R multiplied by Xi B R. so what doe this condition boil down to? If it is totally symmetric then and let us work with one dimensional representation. It is easy to understand. Just believe me that it can be carried on two dimensional representations as well. So if you are talking about one dimensional representations what are the characters, what are the values the characters can take? Plus one or minus one. Now if this AB belongs to a totally symmetric representation what should be the character of Chi AB for any R? Totally symmetric representation, what is the character no matter what the operation is? Plus one. Right or wrong? Totally symmetric representation means something that does not change as a result of any symmetry operation.

So no matter what R is this should be equal to one. Now we are working with one dimensional representation. So Chi A of R what are the possible values? Plus one or minus one. What about Chi B of R? Plus one or minus one. So what are the possible combinations? 1 1 -1 -1 1 -1 -1 1. In these two cases of course the product is not plus 1. For the product to be plus 1 both the characters have to be plus one or both characters have to be minus one. Are we clear so far? Now I am going to make the general statement. The general statement is a direct product contains the totally symmetric representation if and only if the two functions of whose product we are taking the two functions belong to the same irreducible representation. Do we agree do we not agree? I take a direct product so let us talk about one dimensional representation for now, if the direct product has to be totally symmetric then it is imparitive that both the functions participating in the product belong to the same symmetry species. Do we agree with that? We can demonstrate with our old friend C2v character table. Good thing about C2v is everything is one dimensional. Now see convince yourselves suppose I have A2 and B2. What are the characters? One into one is one. But then one into minus one is minus one. So it cannot be totally symmetric. But if it is A2 and A2 one into one is one. One into one is one. Minus one into minus one is one. Minus one into minus one is one. Same is true for B2. If both the functions belong to B2. One into one, minus one into minus one, minus one into minus one, one into one. If there is a question please ask now. The point I am trying to make is that a direct product contains a totally symmetric representation if and only if the two functions belong to the same irreducible representation. Once we are convinced about this we will make the statement about IR activity. If there is a question this is the time to ask.

Do you have a question? Any question? Yes. I said that product of yeah I said that product of X with Xi where Xi is the normal mode or Y with Xi or with of Z with Xi one of these direct products must contain the totally symmetric representation. That is what I said. Not necessary. All cannot. If this is the case what have we shown that they have to belong to the same symmetry species. You look at the character table that is given here. X belongs to B1, Y belongs to B2, Z belongs to A1. So all three simultaneously cannot satisfy it. But at least one of the components of dipole moment should contribute to the transition. That what we are saying. It is impossible usually unless XYZ belong to the same symmetry species it is impossible that all will be non-zero. And we are going to make a statement about that as well.

Do you have a question? So the statement that I wanted to make is that the normal mode must have the same symmetry as either X or Y or Z in order to be IR active. Are we clear. Okay. So in that case we come back and we proceed from here.