Molecular Spectroscopy: A Physical Chemist's perspective

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Lecture No. – 44

Normal Modes : Internal Motion IR and Raman Activity

Knowledge is supreme.

so now that we have learned how to mechanically arrive at the symmetries of normal modes we want to see to what extend without getting into the quantum mechanics to what extent we can talk about what kind of internal motion, internal motion means bond stretching and bending. We want to see what kind of internal motions give rise to what kind of symmetry and since this is a spectroscopy course we also want to know which of these vibrations are IR active which of these vibrations are Raman active, which are inactive. That is the recurring theme of this course anyway. We want to know which transitions take place which transition don't. Let us see how far we get to that in the remaining 20 minutes or so that we have.

All right. See how do I go about it? When we did the discussion of water we could figure out the normal modes quite easily. So now let us go one step back. Let us look at the stretch individual stretches let us use them as basis elements and let us see what kind of reducible representations we get. Let us use the bends as the basis and let us see what kind of reducible representations we get and then we are going to tally with this and let's see where that takes us.

So what I'll need to do is I'll need to write these E 2C3 3C2 Sigma h 2S3 3 Sigma. Have I written everything? Yeah. So we are dealing with this molecule say BF3. Let me call these bond lengths bonds L1, L2, L3 and let me call these angles theta1, theta2, theta3. So what is gamma L1, L2, L3 can we figure that out? So I am now taking each bond as a coordinate. So when it stretches it's plus, plus L1 plus L2 plus L3. When it compresses it is minus L1 minus L2 minus L3.

So what will be the character for E? What is the character for E? There are three coordinates. Three coordinates. One for each. Remember what is the matrix 1 0 0 0 1 0 0 0 1. So character is 3. Remember character of E is equal to the dimensionality of the representation.

What about C3? When I apply C3 what is the character? Okay let's work out the matrix then. This is C3. Where does L1 go? What does L1 become if I apply C3? L2. What does L2 become? L3. What does L3 become? L1. L1 becomes L2. L2 becomes L3. L3 becomes L1. Simple. What will the matrix be in that case? Yeah first row. Second. Third. What is the character? 0 and this is something we learned already, isn't it? Rolling stone gathers no mass. So once again the coordinates that move from their position do not contribute to the character. That's all we need to remember.

So even without working out the matrix we can actually work out the characters. So this is zero. What about C2? Let us say apply C2 this C2. How many coordinates don't move from their position? 1. Now this is one coordinate. So you are saying two because you are thinking of atom. Now don't forget the each bond is so L1, L2 and L3 are going to interchange. L1 remains in its own place. So what will be the character? 1. What about Sigma h? What will be the character for Sigma h? 3. Nothing moves. S3, 0 because again they move from their places. See you're getting the hang of it. What about Sigma B? 1. Excellent 3 0 1 3 0 1 okay. so if you use the formula you'll see that it breaks down into A1 dash plus E dash. I'm just giving you the answer to save time but what you could do is you could verify this answer quickly. You have the character table in front of you add A1 dash and E dash and see whether you get 3 0 1 3 0 1 or not.

Now if I try to make gamma theta1, theta2, theta3 I want to use these three and now when I say theta1, theta2, theta3 what is important to remember is that all these are in plane bends. What will the characters be for Gamma theta1, theta2, theta3? What is the character of E? 3. What is the character of C3? Theta1 becomes theta2, theta2 becomes theta3, theta3 becomes theta1. 0. What about C2? 1 or minus 1? 1 or minus 1? I understand why you are saying 1 because if I apply this theta1 and theta3 interchange and theta2 does it remain theta2 doesn't become minus theta2? It remains theta2 why because this is theta2 this is minus theta2 it does not matter that the two bonds have interchanged. Don't forget what is the coordinates. It's very important to understand what the coordinate is. When the bond opens up then it is plus when the bond closes it is minus or the other way around depending on how you depend -- how you define it. So just because you have rotated it doesn't mean that what was going out will start coming in. It will still keep going out. So character is 1. Sigma h what is the character? 3. S3. S3, 0 and Sigma V. Sigma V theta1 and theta2, 3 interchange theta2 is plus theta 2 or minus theta2 what does it? Still plus. So again 3 0 1 3 0 1 is what you get and again it breaks down into I can write gamma theta1, theta2, theta3 is equal to again A1dash plus E dash. Is there any other kind of coordinate we can think of? So far we have only talked about stretch of the bond and we have talked about in-plane bending. We can think of doming motion. We talked about doming motion in some context I don't remember what. No. Yes. We discussed what a dome is so dome is. so doming motion means what kind of a motion will it be let me draw it plus minus minus minus this is one kind of motion. One. The 3 pendant atom - so I'm going to use the term pendant atom quite often so this is a central atom and these are the pendent atoms. I hope you know the meaning of pendant. Pendant means something that hangs. You wear a necklace and then you put a locket in it that locket is called pendant. So that is a meaning of pendant. So this is one kind of vibrational motion we can think. This is doming motion. What will be so if this is called Xi6 what will minus Xi6 be? This is one of the phases? What is the opposite phase? This plus phase I am defining as the central atom coming towards you. The pendant atom going away from you. What will the minus phase be? Just reversal of directions. Is it right? Right.

So what do I call it. I call it drama dome as I'm making up the names. I can write whatever I want. It doesn't matter. What will be the character for E? One. Not four, one because it's one kind of motion. The whole thing together is one motion. So dimensionality is one. Don't forget this is + Xi6 this is minus Xi6. This is one kind of motion. What is the character of C3? Think of this. This is C3 apply C3 does it remain Xi6 does it become minus Xi6. It remains Xi6 so character this plus one.

What is the character of C2? Don't forget where C2 is. This is C2. Is the character plus one? Is it minus one? For C6 is the character plus one? Is it minus one?

Lend me your pen, please. Lend me your pen please. This is plus, this is C2. If I apply C2 it becomes like this. This is plus, plus Xi6 C2 means it will go behind. Is that right? So it becomes minus Xi6 character is minus one. Who's pen is which? Okay. Thanks. Are we convinced that it's minus one. Minus one. Sigma h what is the character? Minus one. S3? turn doesn't change then reflect with respect to Sigma h. Minus one. Sigma V. Sigma V plus one or minus one. Plus one. 11-1-1-11is it there. Yes. Is it there in the character table? It will be there and that is the one that is not taken. Don't forget. So your gamma dome where do I write, is equal to A2 double dash.

See another way of thinking is this only this doming motion would be anti symmetric with respect to Sigma h. In plane straight in plane bend they would always be symmetric with respect to Sigma h. So just by looking at it you can say that this doming motion has to be A2 double dash because out of the symmetries that I have got only A2 double dash is anti-symmetric with respect to Sigma h. So far so good.

What have we been able to say? We have been able to say that this A2 double dash is pure doming motion and this A1 dash and A2 double dash, A1 dash and E dash seems to be mixture of in plane stretches and bend but now we have a problem. What do we get if we add all of them we get 2A1 dash plus 2E dash plus A2 double dash. So no problem with E dash. No problem with A2 double dash. There is a problem with A1 dash. We have – so see we need 6 coordinates. In fact we have ended up creating 7. So there is one coordinate extra. That coordinate that shows up when you do this simple-minded analysis is called a redundant coordinate. Where is that redundant coordinate hiding? Can you tell me where that redundant coordinate is hiding/ one of this coordinates should be discarded. Which one? Yeah. And well I'll give you a hint one of the A1 dash coordinate should be discarded because the number of E dash coordinates have tallied. The number of A2 double dash coordinate has tallied. There is one extra A1 dash. A1 dash don't forget is totally symmetric representation. We have somehow created a fictitious coordinate, a fictitious totally symmetric coordinate.

So you have to eliminate it now. Where is that coordinate hiding? Of course you got A2 dash from this stretches and the bends. So let us think a little bit. What would be the symmetric stretch? Everything expanding together that can happen no issue. But what could be the symmetric bend in this case? Theta1 increasing. Theta2 increasing. Theta3 increasing. Is that ever possible? No right because theta1 plus theta2 plus theta3 if it is in plane has to be 360 degrees. So if theta1 and theta2 increase theta3 cannot increase. So the whole issue is that we have taken theta1, theta2 theta3 to be three independent coordinates whereas they're actually not. Actually theta3 is dependent on theta1 and theta2. So what we do is we happily delete one A1 dash from here. So what do we end with? We end with one A1 dashe vibration which is a pure symmetric stretch. No contribution of any bending in A1 dash. We end up with two sets of E dashed coordinates which are in plane motion comprising of stretch as well as bend and we have this doming motion which has A2 double dash dimension. All right and now I hope our discussion is sounding a little more like what you do in organic spectroscopy or inorganic spectroscopy where they talk about stretches and scissoring motion and all that. That discussion comes from this.