Molecular Spectroscopy: A Physical Chemist's perspective

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Lecture No. – 32

Representations Reducible and Irreducible

Knowledge is supreme.

Okay. yes, wait. Alright. So far we have arrived at the transformation matrices for two operations. One is identity. One is reflection. Next we are going to discuss the matrix for rotation and from there we'll go and talk about something called your reducible and irreducible representations. We will see what that means.

So the question is can we not have an operation in some other plane if I have translated it right? So yes you can so what you could do is you use this [Indiscernible] [00:01:10] planes one is this, one is this, and one is this. You could think of operation reflection or any other plane but the question is does the plane have to go through origin. yes it does. Otherwise it will not be a symmetry operation. The origin is the center of the molecule. So if you put it anywhere else then that can never be a symmetry operation. We are talking about symmetry operations here. But what you could do as an exercise is that think of a different plane. So this is X-axis. This is Y-axis think of this plane and see how they'll change and then you will reach some interesting – why don't we do it. I was not planning to do it but let's do it now. Okay now I'll draw it in this way. This is X. this is Y. Let us talk about this plane. Set 45 degrees. If you perform a reflection with respect to this plane then what happens? XYZ first of all it goes to Z the way I have drawn it. So Z does not change. Z remains Z. What about X? What about Y? X becomes Y and Y becomes X. what is the matrix now? 010100001.

Now I hope the difference between the matrices we got earlier and the one that we have drawn now are obvious to you. What is a major difference between this and this? The first one is a diagonal matrix. This is not a diagonal matrix. So here you have non-zero of diagonal elements as well. I was planning to discuss this a little later but since we have reached here let us discuss it right now.

What is the meaning of a diagonal matrix? What is the meaning of a non-diagonal matrix in this case? So a diagonal matrix means X remains X. It can change sign or it can remain itself. So very simple symmetric anti-symmetric relationship holds. Y remains Y or becomes minus Y nothing else is possible. Z remains Z or becomes minus Z. Nothing else is possible. The moment you have this what is the meaning of this term? X has become Y, Y has become Z. Now you have interchange of coordinates. That is what it means. If you have a non zero of diagonal elements that means that you have contribution from a different coordinate in the transform coordinate of the particular one. That is a meaning of nonzero of diagonal elements and that is what we see in a little more detail when we discuss a rotation. Let's talk about rotation.

Let's for the sake of convenience see I do it in some coordinate system you should be able to transform from any coordinate system to any other one. That is just a matter of mathematical exercise. So what we will do is we'll try and find the coordinate system that is easiest, more convenient for us that's all. Now let us say that we are talking about rotation Cn and just as a method of convenience let us say that this Cn is along Z direction.

Now what will happen? For a matter of convenience again I will write x1 y1 z1 and x2 y2 z2 where x1 y1 z1 are coordinates of the point that we start with. We are working with the position vector and let us say I am rotated by an angle theta. Any angle theta. It is not necessary that rotation of theta will take me from first coordinate to fourth coordinate. I could have gone here. I could have gone here. All I am doing is a clockwise rotation and we'll just keep this as an acute angle but exactly similar discussion will follow if the angle is not acute. You can work it out yourself if you want. Let us say we are rotating by an angle theta. What is theta then? This is Cn axis and rotation is theta so theta is 360 degrees by n. So theta is not just any angle. Now also let us say that this angle is alpha. In that case what is x1? X1 is the X-coordinate of the point in its initial position. Initial point. What is x1? Angle between the position vector and X-axis is theta, sorry alpha. What is x1? Okay r cos alpha. I'll just stop to write that arrow. It's okay. what is y1? What is y1? So you have to give me the answer otherwise I'll write whatever comes to my mind. R sine alpha. What is x2? If this angle is theta, this angle is alpha. This of course is theta minus alpha, isn't it? What is x2? First of all the way I have drawn it is x2 positive or negative, positive. Is y2 positive or negative? Negative. Let's remember that. What is x2? Length does not change that's because I've rotated lengths are not change. Length is r. This angle is theta minus alpha. So what is x2? Yes Divya x2 is the X- coordinate of the transform point. X1 y1 denote the initial coordinates the question was what is x2. X2 y2 denote the coordinates of the transform point or transform coordinates.

So I started with this. I have done a rotation by an angle theta. I've come here. Tip of my finger is the point. So coordinates of the tip of my finger here are x1 y1 x2 y2. But maybe we can get Z out of the way before that. What is z2? Z2 is equal to z1. I might as well write that. So this one will be definitely 0 0 1. When I do a rotation with respect to Z what I get is Z coordinate remains unchanged so this last row is going to be 0 0 1. What about X2 if this angle is theta minus alpha? Help me. I will write the thing I know r. Length doesn't change. r. Then what do I write? cos theta minus alpha and y2 is r sine theta minus alpha what I will do is I will just put a minus sign here.

Now not very difficult to expand this. What is cos theta minus alpha? Tell me. Cos theta cos alpha minus plus very good sine theta sine alpha.

Now see what is r cos alpha? X1. So X1 cos theta. What is who's going to our write r here? What is r sine alpha? Yeah Y1 sine theta. So I have my first equation X2 is equal to X1 cos theta plus Y1 sine theta second equation actually because they already written Z2 equal to Z1. Is this clear? Now can I write the first line here? First row. Can I fill that in? So what is X1 sorry what is X2. X1 cos theta plus Y1 sine theta plus 0 into Z1. So I've got two rows already. I'll now fill in the second same way. Y2 equal to minus r sine theta minus alpha so minus r. What is sine theta minus alpha? Help me. Sine theta cos alpha minus but there's already a minus here plus r so. So yeah sine alpha cost theta is okay. Again r cos alpha is X1 and r sine alpha is Y1. So I got minus X1 sine theta plus Y1 cos theta. What will the second line be then? Minus sine theta cos theta 0. So this here is your transformation matrix for rotation by angle theta. Point to note Z here is the unsocial coordinate. It does not mix with X or Y. Z remains itself. However, the action of Cn is to mix X and Y. This is something that we need to understand very clearly. Do you understand this? See what was the action of this reflection? Identity anyway leaves everything the same. When we did the reflection here there was no mixing of coordinates. X either remained X or became minus X. Same with Y. Same with Z. Here however, when you rotate it is not very difficult to see that mixing of coordinates takes place. The transform X coordinate cannot be represented just as something multiplied by X. There is a contribution of the original Y coordinate also. Same is true for the transformed Y coordinates. So what Cn does is in differentiates, it kind of classifies your three coordinates into two classes. One XY other Z. Z remains by itself doesn't mix with anything. Z and Y mix with each other. Of course if your axis of rotation was X instead of Z then X would have remained the unique coordinate Yand Z would have mixed. This is the first thing that we need to understand.

So when we talk about an axis of rotation we denote them as Cn. So suppose the axis of symmetry such that you have to rotate by 180 degrees. We call it C2 axis. Where do I get this number 2? It is 360 by 2. 180 is 360 by 2. If I rotate by 120 we call it C3 axis. Where do I get the number 3 360 divided by 3. Understood? Okay. Any other question at this point? No?

Then let us do something let us recall what we had said about the planes of symmetry of C2v and C3v. Remember C2v and C3v? In case of water it's a C2v molecule the planes are like this. One plane is Sigma V one plane is Sigma V dashed. What had we said they are non-equivalent planes. Their actions are different. They – another way of putting it is they long to two different classes. The word class has its origin from the formal group theoretical treatment. We don't have to go there. For us it is enough if you understand that equivalent symmetry operations belong to the same class. What about ammonia C3v? The three planes are the equivalent. One, two, more flexibility is required. Three. One, two, three. What is the axis? Do you see what is this axis that is at the juncture of the three planes? C3 axis. What does the C3 axis due to the planes? They can – it can interchange the planes. You can just imagine the third plane. So that is another way in which you can define equivalent symmetry operations. Symmetry operations that can be converted from one to the other are equivalent.

Now I want to make one more point that you know already the C3 axis better draw on the board because otherwise again I'll need a 360 degree rotating shoulder. So see what I'm trying to say is this I'm talking about

the C3 axis? Where is the C3 axis here? Look here forget the time. This is the C3 axis. Let us say I have three atoms ABC these are the three hydrogen atoms of ammonia. I can do a C3 operation like this. C3 axis ABC 3 hydrogen atoms C3 takes it A goes to B, B goes to C, C goes to A. ABC. I can do it again. I can do another C3. Then what will happen? C comes here. A comes here. B comes there. So this first operation is called C3. Second operation you can think you can go you have gone from here to here directly this is called C3 square. This rotation by 120 degrees rotation by your 240 degrees. There's another way of thinking of it. This is clockwise rotation and if I do an anti-clockwise rotation C3 minus then also you get. The crux of the matter is associated with the C3 axis. You have two operations C3 plus, C3 minus or C3 and C3 square in whichever way you want to put it. And these operations actually belong to the same class.

Do you agree that C3 and C3 square belong to the same class? Same kind of operation. They belong to the same class. What I'd like you to do is I will give you the answer but you work it out yourself. This here is the transformation matrix for Cn class. We have taken a clockwise rotation. I asked you to work out the transformation matrix for an anti-clockwise rotation. You'll get something like this. For Cn minus the matrix will be cos theta minus sine theta 0, no sorry plus sine theta cos theta 0 0 0 1 just you don't have to believe me on this. Work it out yourself you'll get this and while you do it I'd encourage you to work out different kinds of angles. Don't stop in making this an acute angle. Make it an obtuse angle. You'll get the same answer.

And this leads to us leads us to an important conclusion. Do you know what is the character of a matrix case it is something like this sum over aii you add the diagonal elements. What is the sum here? 2 cos theta plus 1. What is the diagonal here? Again 2 cos theta plus 1. This is a manifestation not proof. This is a manifestation of a very important principle that for symmetry operations of the same class values of character are the same. Chi is the notation that we are going to use for character or diagonal. So why do we call this character of all things? We could have just called it a trace or a sum of diagonal elements or something like that. Why character? Let's wait we see that these are actually unique properties that are going to allow us to perform a systematic treatment of symmetry in molecules and in spectroscopy. So the name character is actually justified. They are unique properties of these operations. We elaborate upon that a little later. For now it is enough if you know that this sum is called a character and as long as you one well understood that we have demonstrated not proved that for symmetry operations of same class characters are the same. Now so what we have arrived at is transformation matrices for identity reflection and rotation.

Now what we want to do is this so what is this we are giving numbers so and we said that these are characters, these are markers of symmetry operations. Now I have a basis and I have several symmetry operations in a point group. These are sort of like we can say the grade score even though I don't believe in it but generally we use grades to decide whether a student is good or not. So when you do that is it enough to take up any random course and look at the grade of the student? No right because I can get a in 1 and a in everything else or the other way round. So that is why we have this concept of Spi and Cpi, isn't it? What we do there is of where they are necessary. So don't don't get personal about Spi and Cpi but we are just demonstrating – we are doing have a philosophical discussion here. There's no personal business. So when you want to assess some student quantitatively then it is not enough to look at the performance in one course or one semester. That is why you do this Cpi business. Same is true for the symmetry operations. You want to know how a basis transforms it is not enough if you look at only reflection, only rotation, or something else, only inversion. What you want to do is you want to look at – get a holistic picture and you want to develop an idea of how the function behaves as a result of each and every symmetry operation and the collective information that we get from all these matrices is called a representation. So a representation is somewhat analogous to your SPI or CPI. We will do it very quickly with one example and then we'll come back next day and we'll elaborate upon it. Water C2v molecule. I'll just draw it once this is what we are talking about a C2v molecule. This is your C2 axis let us define this as Z. This here is X. This is Y. This is Z. What we'll do is we'll use the basis XYZ for this system and we'll see what kind of transformation matrices we get. So far so good.

What are the operations that are there? E, C2 which is Z, Sigma V the way I have drawn it which one is Sigma V very – the way I have drawn it the molecular plane is zx plane. So SV is zx X-axis is on the board. Y-axis is perpendicular to the board. Sigma V ZX and Sigma V dash then will be YZ. What we want to do is we want to draw we want to work out the transformation matrices for each of these symmetry operations using XYZ as basis. So far so good. Can I start? First one will write without even discussing. It is done. When we apply C2 what happens usually you would expect a mixture of x and y but this is a special case because your axis is C2 axis, 180-degree rotation. So what happens is each axis becomes negative of itself as long as you are talking about X and Y and Z remains the same. Agreed. So -1 0 0 0 - 1 0 0 0 1. Are we comfortable with C2? What happens when I apply zx? We have discussed already. The axes that are on the plane will not change sign and the axis that is perpendicular to the plane will change sign. So Y will change sign others remain the same and there is no mixing. So 1 0 0 0-10 001 and I might as well write that one that is yz so X will change sign Y and Z will remain the same. -100 010 001 what we do is generally we call the molecular plane Sigma V and we call the perpendicular plane Sigma P dashed. It is just a convention nothing else. As long as you understand zx and yz you are good. The reason why we put that dashed is that they are not equivalent planes. So if I write both as Sigma V we might make the mistake of thinking they are equivalent they are not. That is why we put a dashed on that Sigma V. What do they have to do? Yes. Yes. They do. Okay. So what he is asking is this two matrices have the same trace. So how is it that they are not equivalent. That reminds me of this clichéd story that everybody has heard somebody went as a witness in a case where a hen was stolen and the judge asked how big was the hen the guy said this big and the judge of course blew up and then when the judge got really angry and all the other guy said I wait for my second hand. So now the second hand remember what I said I said that symmetry operation is belonging to the same class have the same trace, same character. I did not say that converse is true. So that is my second hand in this hen stealing case. Are we comfortable with the matrices? Now we will arrive at representations.

So first of all see what has happened in the basis that we chose XY and Z the basis is such that no symmetry operation causes a mixing of the basis element. See the matrices are such that the basis elements do not mix with each other and they either remain the same or change signs. So they're either symmetric or anti-symmetric. So what I can do is now I will erase all these zeros. This is called the method of block factorization of matrices. What I can do in these matrices is that I can draw these lines. Same kind of pattern that you used to draw in tic-tac-toe and what I find is that I have been able to block factorize. If I take all the one-one elements they are non-zero. 1 -1 1 -1. I take that two-two elements 1 -1 -1 1. I take the three-three 1 1 1 1. All other elements are 0. This method is called block factorization. You divide all the transformation matrices in the same way so as to leave out the zero elements to the maximum extent possible. Very qualitatively this is the block factorization. So what I will do is I will even erase these.

Now see think about X. How does X transform with each symmetry operation. It is symmetric with respect to E, anti-symmetric with respect to C2. Symmetric with respect to Sigma V ZX, anti-symmetric with respect to Sigma V – YZ. Instead of saying it in English what I can say is that for X I have the combination 1 -1 1 – 1. For Y it is 1 -1 -1 1 symmetric, anti-symmetric, anti-symmetric, symmetric. For Z it is 1 1 1 1 symmetric all the way. So now this is a representation. In fact if I look at the matrices the entire matrices that was also a representation. You look at all the matrices that are there transformation matrices collectively they form a matrix representation. What we have learned is how we can reduce a representation to smaller dimensionalities. So what I am now saying is that for X it is 1, what was it here, -1 1 -1 I don't need this anymore. For Y it is. For Z I remember it's 1 1 1 1. For X it is 1 - what 1 -1 I didn't realize you are trying to help me sorry. Thanks 1 -1 -1 1. Excellent. So now see this 1 -1 1 -1 is the representation for X. 1 -1 -1 1 is the representation for Y. 1 1 1 1 is the representation for Z. Those of you who have worked with character tables would perhaps recognize that this looks exactly like those rows that are there in character table. Actually we have arrived there. So there is one out of these representations which is special and that is the one with Z. All characters are 1. What is the meaning of all characters being 1? It is totally symmetric. So this representation is called the totally symmetric representation. No matter what you do the function does not change. It remains symmetric these are not totally symmetric representation. What we learn next week is how to give what are called Mulliken nomenclatures to these things.

So here what we have been able to see is if you use XYZ as basis then you end up with three 1 dimensional representations. What is the meaning of dimensionality? How many basis elements are there for that particular representation. You end up with three 1 dimensional representations XY and Z are completely separable in this point drop at least. Next day what we'll do is we'll use the atoms as basis and we'll see what kind of representations we get. Until then.