Circular Dichroism and Mossbauer and Spectroscopy for Chemists
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Lecture – 2
**Symmetry and Molecular properties**

Welcome to this new segment of CD Spectroscopy and Mossbauer
Spectroscopy for chemist. Previously, we have discussed what is
chirality? And what is symmetry? And we look through and we found in
nature, we have various examples of symmetry and chirality remaining
there. And when we are talking about the symmetry we found there are
three different major portions or segments of symmetry.

Bilateral, radial and also spherical and we have also found chirality
is one of the important aspect of this symmetry. The the chirality is a
important aspect because it has a huge role to play in biology. It
helps it to do the molecular recognition. Whereas the chirality which
means a particular object whose mirror image is not super impossible on
each other is a key role to play when it comes to the proteins,
carbohydrates or nucleic acids.

And that is why we are very much interested to know about chirality and
we have also discussed that there are certain drug molecules whose
properties are also dependent on its chirality. One form of the
enantiomer can be a life saving drug, whereas the other one looks very
much similar to it other than one or two chiral centers can be lethal
to us. So, that is why a knowledge about chirality is very important.

So now, we have to connect a molecular structure chirality with certain
properties by which we can differentiate a chiral molecule. So, before
jump into that let us know about how this molecular structure and its
properties are connected.

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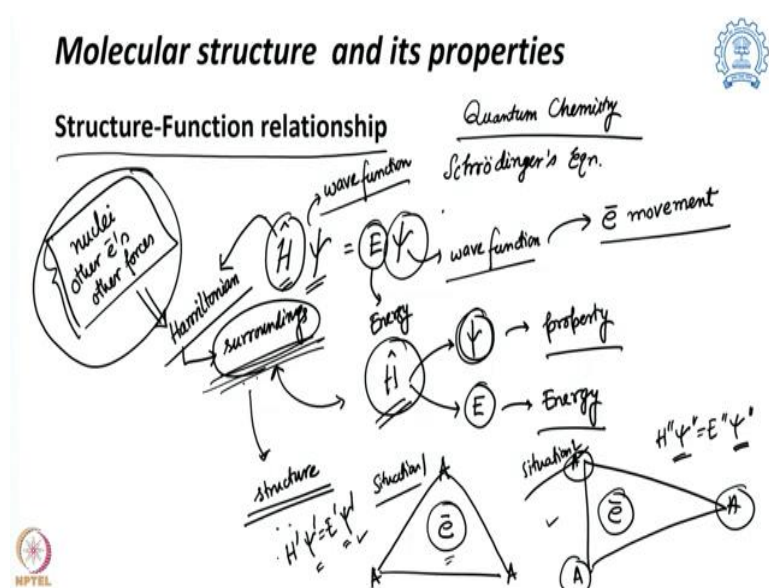
And for that we are looking into this structure function relationship
and to understand how a structure of a molecule is controlling its

properties. We are going to take a little bit of help from quantum chemistry. So, in quantum chemistry we have various equations comes to our mind but one of the most important equation that comes is the Schrodinger equation. And what is a Schrodinger equation? A Schrodinger equation is this particular system, $H\psi = E\psi$.

We all know this equation but what are the meaning of this equation? So, this term H which is known as the Hamiltonian is nothing but a system which actually defines our surrounding will come into that a little bit later. This ψ is known as the wave function & E is quite obviously the energy and the psi is wave function back again. So, when we draw this particular thing, what is this particular wave function means? Wave function means, typically when you are talking about an electronic system.

How the electron is moving the electron movement. If I want to define that with a Mathematical expression, that is the wave function psi(ψ). Now, this electron movement is controlled it cannot put anywhere as it want it is controlled by what? It is controlled by the nuclei. It is controlled by other electrons and other forces around it. And all those things control how the electron should move.

And if I can define the presence of nuclei other electrons or other forces around this system of the electron. This is nothing but this Hamiltonian that you have written over there. So, this factor H, Hamiltonian operator, nothing but defines how my electron is surrounded by different particular segments or factors which can control the movement of the electron. And that is known as the Hamiltonian operator.

Now, with this, you can define that this surrounding has a lot to say because if I change the Hamiltonian factor, it affects directly its energy. It also, controls how the psi(ψ) would look like. So, this Hamiltonian factor actually has a direct role to play on the psi, a direct role to play on the energy. So, that means by psi(ψ) I am controlling the property by E, I am controlling the energy.

So, with these two factors, the Hamiltonian is controlling that and it is controlled by the presence of the surrounding and the surrounding is nothing but the description of its structure. Just imagine I am talking about an electron where there are three nuclei in a regular triangle shape, versus the same electron a shape like this. You can say the situation 1 vs situation 2, is not exactly the same situation 1 the electron will behave differently compared to the electron in the situation 2.

And that is because the nuclei over here are in different position. The other associated electrons are in different distance compared to this one in the situation 1. And that is why the behaviour will be different because of this psi(ψ) and E will be different. Because, the surrounding or the structure is defined which can be defined by this H the Hamiltonian factor. So, we can say the situation 1 is that $H'\psi?' = E'\psi?'$ whereas for the situation 2 can be $H''\psi'' = E''\psi''$.

And accordingly, the energy and the wave function will also change. So because these are actually going to be different. The property will be different, the energy will be different and that is how the structure of a molecule controls what will be the behaviour of the electron.

Specially, the electrons sitting on the valence bond and as you know valance bond electron controls the most important properties.

The acid based properties, the redox properties, the other important properties like electro negativity and all the periodic properties and that is why the surrounding on the structure has a big role to play over there. So, now we understand what is the effect of structure and function? Does it really affect that much?
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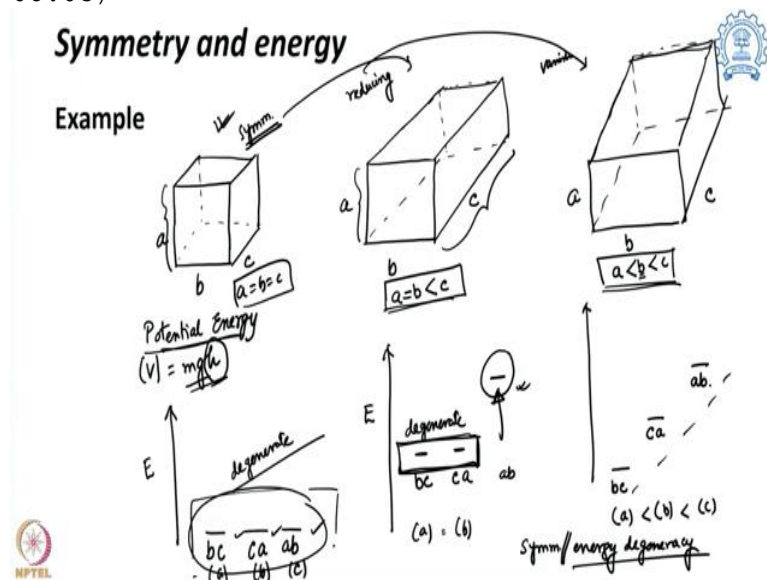
So, for that we will take an example and we will take an example of a very simple system. We will start a cube. You start with the cube, they have the three sides. So, let us say I am naming them a, b and c. And now, if I put this cube on each of the different faces because it has 6 faces 2 ab's, 2 bc's and 2 c's and if I put them on a particular phase, what will be their energy the potential energy that I am going to measure.

And as you know potential energy (v)= mgh, say the mass and g remains same. So, the factor will be h. So, if I put this particular system on the face of bc as it is, the energy will be dependent on only on this a. So, the energy of bc will be somewhere around here, now if I want to do and change the phase which is sitting on the base. So, if it is a ab phase, the height will be c but because c and a are same. So, the ca will also have the same energy.

Same thing, if we do for the ab phase, the system will have the energy height of c. So, heights will be over here a, over here b, over here c and because all of them are same over here in this case, a=b=c. This energy will be all same or in other words we can say they will remain degenerate. Ok So now, say I am taking a case number 2, where I am taking the similar system, where the a and b remain the same but I am changing the c.

I am making it a bit longer. This is my c over here, a=b, but they are less than c and c is much more higher. So, now, if I want to plot the energy then what will happen? Now I can put them in three different phases. I can put them in bc and put them in ca we can put them in ab. Now bc will be this phase as it is written. The height is a, so, the

energy will be some around here, ca if I put that on the ca phase, the height will be b and a or b are same over here.

So, their energy will be also same. But when I put that in a b phase the height will be c. The c has much more higher height so, the energy will be higher, So, previously all three are same because a=b=c over here I break the symmetry. I make it less symmetric a equal to b but not equal to c or less than c and for that one of them got out. The rest of them remain symmetric or degenerate but this one goes higher in range. It breaks the degeneracy.

Now, take an example, the third case where it is such a case where I am breaking the symmetry further. So, this is a, a, this is b, this is c and it is such a way a is less than b is less than c. So, all of them are now different. Now, what will happen? The energy will be dependent on which of them is actually higher in energy. So because you are measuring a potential energy over here, height is the important factor.

So, c will be the height when I am talking about the phase ab. Then will come the b which will be the height when I put the system on the cf case and a will be the height when I put in the bc case. So, this is a, this is b, this is c and as we said is less than those so, that is why the highest energy will see on the ab then ca then bc and over here you can see, there is no degeneracy at all.

All of them are different and you can kind of say previously where the system is very much symmetric. I actually have all of them in the degenerate level. Now I slowly changing the symmetry. So, I am reducing the symmetry over there what happens I break only one part and two of them remain degenerate but one of them is going out of degeneracy over here and on the last hand when we actually totally vanish the symmetry.

All of them are different and similarly, it is reflected on their energy. All of them are different so, over here you can see symmetry and energy degeneracy is kind of holding hand and showing us their effect. So, if I want a very symmetric system I would end up with a very energy degenerate system whereas, if I take asymmetric system, my energy degeneracy will be breaking down.

And this energy degeneracy and exactly what is the energy that will define the reactivity of a molecule. And that is why symmetry and energy are very crucial point where we have to take a close look onto.
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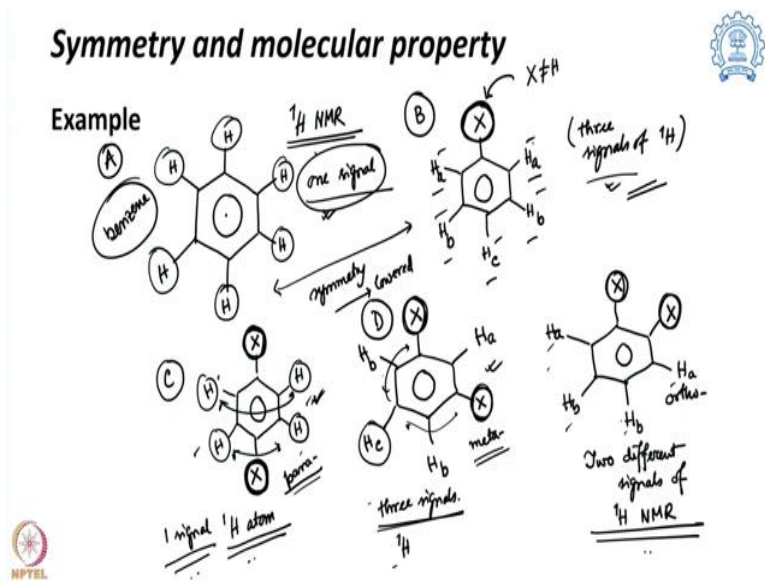
Symmetry Definition

So, with that now we move to the definition of symmetry. So, we are talking about symmetry a long time we have also loosely defined what we mean by symmetry when you are talking about the natural system talking about the bilateral symmetry talking about the radial symmetry spherical symmetry. But, if I want to define symmetry, what is actually symmetry? And if I take this oxford dictionary and over there try to find what is written there about symmetry.

And this is the system we are going to find I am just writing it mutual relation of the parts of an object, in respect to magnitude, position, relative measurement and arrangement of parts. So, over there this is very important mutual relation that means I am going to change of the molecule in between such that one part of that whole object or molecule is going to be magnitude electrically.

That means by the measurement the position, the relative measurement and arrangement will be very much similar in relation and if you are seeing this, we say we are having a symmetry. So, that is, we actually try to define. So, in the previous slide, we actually just saw that see. If I go back so, you can see over there, we saw that yes, we are actually having these different symmetries and as we are going down, we are changing the energy.

So, similarly over here that is the definition of symmetry. So, now we understand what is the definition of symmetry? We understand yes, the shape and symmetry can affect the energy but how does it coming to a chemical molecule?

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Symmetry and molecular property

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So, for that we will take an another example. The example will take one of the very common molecule that if all aware of is benzene. So, this is the benzene molecule I draw so so, the example will be taking benzene is quite common molecule and this actually has six hydrogens around it. And now, if I try to follow up the symmetry of this molecule by doing and 1 H NMR spectroscopy how many signals we are going to get in 1 H NMR? We are going to get only one signal.

Why one signal? Because of this particular symmetry of this molecule, you actually have all the hydrogens are actually mutually very

symmetric to each other. So, that means this molecule the hydrogen although they are different, they are not going to show that difference in an environment when you are doing this proton animal spectroscopy. They are going to be very much symmetric and that is why we are going to get only one signal because this structure defines is symmetry.

Now, take a variation of this same benzene molecule but over here, what we are doing. We are putting an X say instead of all hydrogen, now I break down the symmetry by putting an system X over here. And due to the presence of the X the previous symmetry is now gone. So, if we talk about the symmetry, symmetry is actually lowered as we put this X molecule over here X is anything but Hydrogen. So then, how many proton signals I am going to have.

As we learn these two protons like H a will be very similar, these two protons will be similar, this proton will be different. So, these are nothing but the ortho protons, metaprotons and paraproton. So, all together, I am expecting three different signals of proton in proton NMR and that is coming because the symmetry is now going down. So, just by introducing one extra group other than Hydrogen I can get difference start difference in signal.

And that is showing that now the environment around the hydrogens are different and they are going to behave differently. So, their behaviour is directly connected to the structure which is can be defined by the symmetry terms. The next one we can have another portion of proton and on the benzene and over here we are putting we are putting two X around it. So, these are one, this is the second. So, these are the two different X molecules here.

And now if I want to define it, how many hydrogen atoms you can find? We are going to get only one hydrogen atoms why? Because all these Hydrogen's are similar in nature. So, they are all symmetric. Because they are ortho to one X and the meta to other and it is true for all these hydrogens and that is why we are going to get only one signal. So, again the change of the symmetry you can say from one to two.

I am getting more symmetric and as the symmetry changes my signal is actually varying. Now say I am taking this two X but putting that not in the para position like this. However, I put them in the meta position over there how many hydrogen signals you are going to get. So, obviously the first one will be this one which is ortho to both the X groups so, that will be different. This one will be the other one H b which is para to one of the X and ortho to the other.

And this H c which is also, unique because this is meta position to both the X's. So, over here we are also getting three signals and you can say this molecule is actually have different symmetry lower symmetry compared to this one and as we are changing the symmetry, we are changing the number of proton signals also. And the last one with bisubstituted benzene I can have, that they are in ortho position and over here how many signals we are going to get.

So, over here this will be hydrogen ortho to one and meta to other same for this one. So, one type and this one is para two one and meta to other similar for this. So, over there I am going to get two different signals of proton NMR and that is what we are going to get for this

particular molecule. So, you can see from the starting from the benzene in the beginning which is very much symmetric.

I have only one signal. This is case a, in case b we actually mono substituted the benzene and over there we introduce a bit of asymmetry. The symmetry is going down and it is very much well signalled by this three different signature peaks in proton number. Then case number c, where you have a bi-substituted one, where the para substituted quite symmetric and that is why we get only one protons.

This is case d, where we actually have again a bi-substituted but meta one which is actually have a little bit lower symmetry and we are going to get three signals. When you put them in the ortho position we get also two signals. And you can see that symmetry has a direct role to play how many hydrogen signals I am getting and hydrogen signal in NMR defines how many different environments, chemical environment these protons are facing.

So, with that it is showing that the symmetry is directly controlling the electronic environment of the molecule which we can say nothing but the property of the molecule and that is what is actually coming over here. Now, we define the symmetry, we define that yes, it changes its energy, it changes its symmetry along with the molecular properties. And we also have a definition of symmetry with respect to the definition from English.

But, how to define symmetry with Mathematics? That is one of the most important thing that we have to cover and that we will be covering in the next segment.

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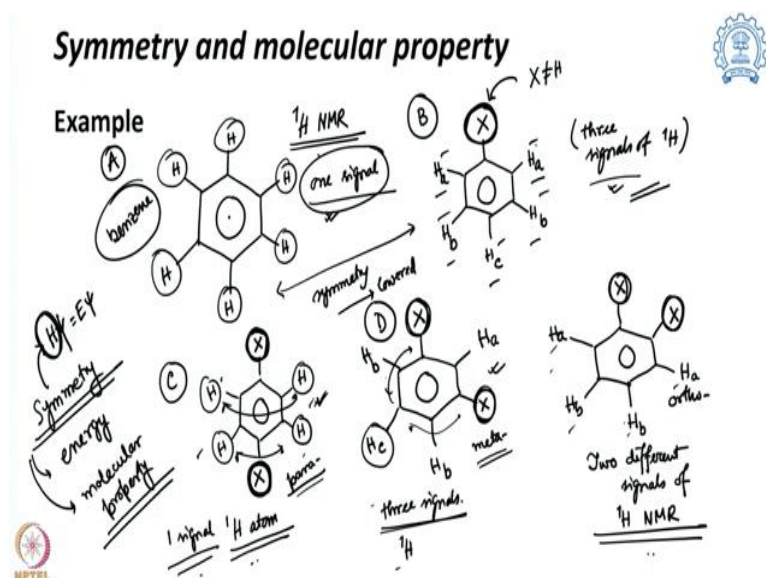
So, before going there we would like to just conclude in the beginning section that the symmetry is important aspect and that controls its energy and that controls is molecular property and all of them can be also defined by the Schrodinger equation $H\psi = E\psi$ where this H is nothing but an operator which actually reflects the definition of a surrounding. That means the symmetry around the molecule.

So, with that we would like to conclude over there for this segment, where we have defined how the symmetry and molecular property are

interconnected and by following the symmetry how we can define the different properties or the structural effects on the energy on different molecules. In the next segment, we are going to follow little bit of Mathematics to combine them properly. So, that we like to conclude over here. Thank you. Thank you very much.