One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture – 13
NMR Spectrum and Chemical Equivalence

Welcome back we were discussing in the last 2 classes about the interaction parameters that contribute to the NMR spectrum. And we discussed chemical shifts, its origin and understood something about shielding, shielding factor and Lamb's formula etcetera. The chemical shift is a really a big topic, lot more we can discuss, but still we have not come to the point where we know how to utilize this as a parameter for the analysis of NMR spectrum. So we will continue further with the discussion of chemical shifts.

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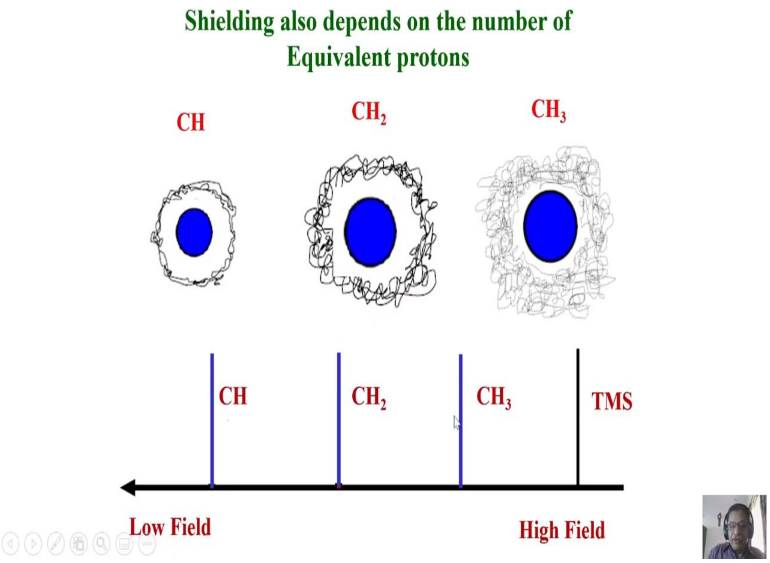

Shielding also depends on the number of Equivalent protons

I remember in the last class I said, when I took CH and CH3, I said CH3 is more shielded than CH. And that is the reason I said CH3 comes at high field than this CH proton, the reason was I said the nucleus of CH3 sees more electron density surrounding this one, because it is more shielded compared to CH proton. Now, I just want to take an example what happens if there are more number of equivalent protons like this, different types of proton with different number of protons present like this. For example, CH, CH2 and CH3. Of course logic is simple.

We discussed in last class where I said CH3 is more shielded, comes to high field because it sees a different field, more shielded than this one. Now I take in between another group called CH2 what is the logical conclusion? where this peak should come? With the extended logic, CH has 1 proton let us say it comes here, CH3 comes more shielded little high field here, then CH2 has to come somewhere in between, because this charge density or distribution of charge around this nucleus for CH2 is in between that of CH and CH3. As a consequence if we look at the NMR spectrum of the molecule containing CH, CH2 and CH3, of course forget about other parameters, I am just for the purpose of explanation, I am taking an example CH3 should come here, then CH2 and then CH, that should be the case. Of course the peaks are not of the same height. I made it a crude diagram, just I have drawn 3 peaks to say that they come at different fields. That is all. We are not worrying about the intensity, that is topic which we will discuss later.

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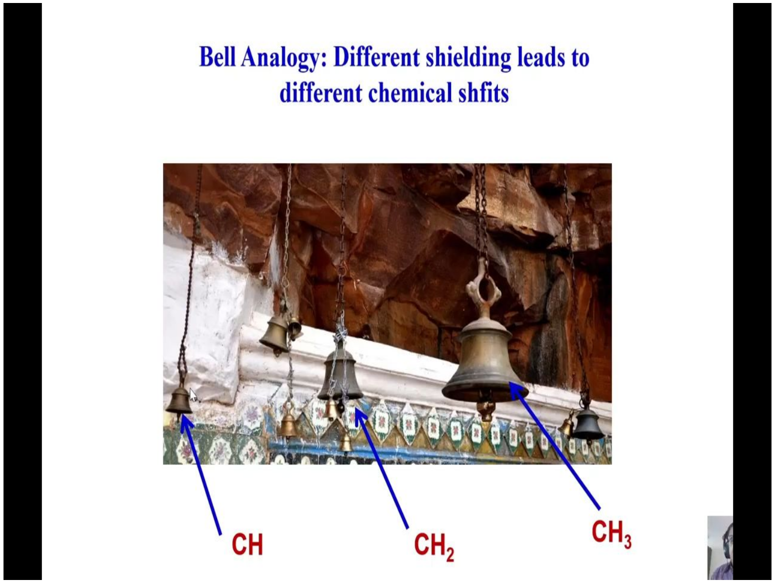

Bell Analogy: Different shielding leads to different chemical shfits

So to say, very simple bell analogy, looks at these things. Very beautifully you can understand from this, this is the bell. You consider this as the charge distribution surrounding this nucleus. This is a nuclear spin, it is much more compared to this bell. This is the center of the bell. consider this as the nucleus and this is the charge distribution, right, come back to this one, this is even smaller than this. This also has a nucleus and charge distribution.

Very simple comparison to the spectrum I showed before. This is CH3 more shielded with 3 protons comes at high field, then come CH2 and then CH in the same order. It is a fantastic analogy to say how different shielding leads to different chemical shifts.

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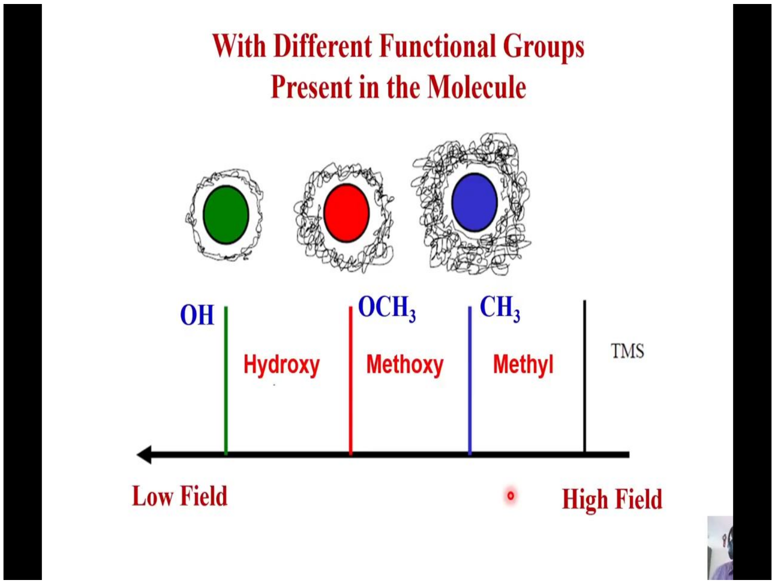

With Different Functional Groups Present in the Molecule

With different functional groups present in the molecule also we have different shieldings, as a consequence, the peaks come at different fields. Resonate different fields. Look at the CH3 which we discussed, it comes here. Now instead of CH2, I will take a OCH3 group, a methoxy group. What do you expect? But I take a methoxy group. There is an oxygen attached to CH3 group, it is a electro negative atom, it withdraws electrons from this CH3 protons.

As a consequence what happens? Shielding reduces so same CH3 proton, without any electro negative atom, let us say it comes here. Now moment you put an oxygen here, when you make it OCH3 group the peak shifts to the down field, it comes here. Now I take a single CH proton it was somewhere here, instead of that I will take OH. The same analogy like here. Oxygen is electro negative withdraws electrons from this proton.

As a consequence what happens to OH peak? it comes down field. So in a molecule 3 different functional groups are present, for example CH3, OCH3 and OH, the logical conclusion is CH3 should come here, then OCH3 and OH, when you go from high field to low field. This order it follows. It is only a crude example I am giving, it may happen because of the neighboring groups which move here and there. I am not worried about that. I am just telling you as a simple example what happens to different functional groups when different electro negative atoms are attached to it.

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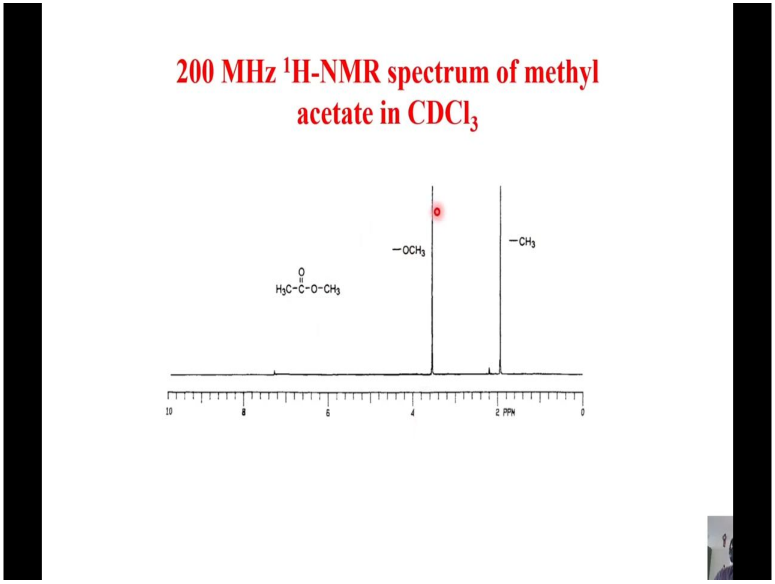

200 MHz ^{1}H-NMR spectrum of methyl acetate in $CDCl_3$

So now it, this is a easy way to understand. And look at the peak, I have taken NMR spectrum like this. This is simple molecule. Both peaks are present here, there are 2 peaks. Why? Look at this molecule. There are 2 different types of CH3 groups, both are CH3 mind you, this is also CH3, this also CH3. But this is attached to a C double bond OCH3, this is is only OCH3, methoxy, but interestingly this CH3 is not directly attached to oxygen. So this CH3 comes here.

Whereas as I said in the previous example the CH3 group to attach to this oxygen, because it withdraws electron comes down field. Look at the peak heights, both are same. But this comes down field, whereas this comes high field. So when you want to analyze the spectrum, as you go ahead, I will tell you as we go further, I will tell you, you have to consider the height of the peaks also. I took a special example of this because both these are CH3 groups containing equal number of protons.

So they have the same heights, but substituent has different effect on one of the CH3 and brings it to down.

So now let me introduce a term called chemical equivalence, the term which is very important.

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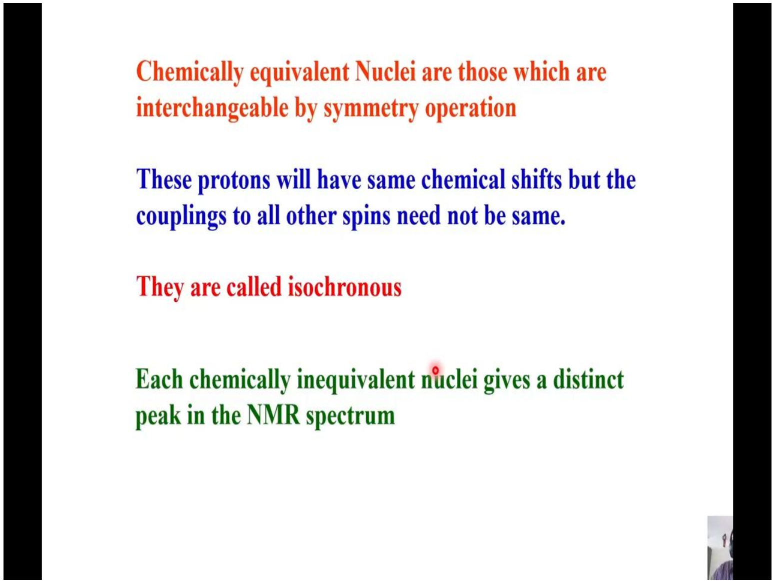

Chemically equivalent Nuclei are those which are interchangeable by symmetry operation

These protons will have same chemical shifts but the couplings to all other spins need not be same.

They are called isochronous

Each chemically inequivalent nuclei gives a distinct peak in the NMR spectrum

Chemically equivalent nuclei are those which are interchangeable by symmetry operation. I do not need to explain this. The molecule has symmetry whether it is a C2V symmetry or whether it has a inversion symmetry, depending upon the type of symmetry it has, we can say whether the protons have the same chemical environment. Chemically equivalent means they should have the same chemical environment.

We can find out by simple symmetry operation. Just write down the symmetry axis or symmetry plane or symmetry point whatever it is, and you can find out which are the protons that are chemically equivalent. And such protons which are chemically equivalent will have the same chemical shifts. But the coupling to all other spins need not be the same. What is the coupling? I have not even introduced about scalar coupling. I only gave some introduction when I introduced interaction parameters. We will come to that later. But remember coupling may be different but so long as they are chemical equivalent, they are called isochronous nuclei. They are called isochronous. So each chemically inequivalent nuclei gives a distinct peak in the NMR. Remember in the previous example OCH3 and CH3, these 2 are different groups.

Because the chemical environments are different, they are chemically inequivalent spins. And those 2 CH3 gave two distinct peaks. Similarly, in a molecule if there are n number of chemically inequivalent protons, you will get n number of chemical shifts. You understand!! Let us say there are 6 different chemical shifts, six functional groups in a molecule.; I am not taking into account the couplings, you must get 6 distinct peaks.

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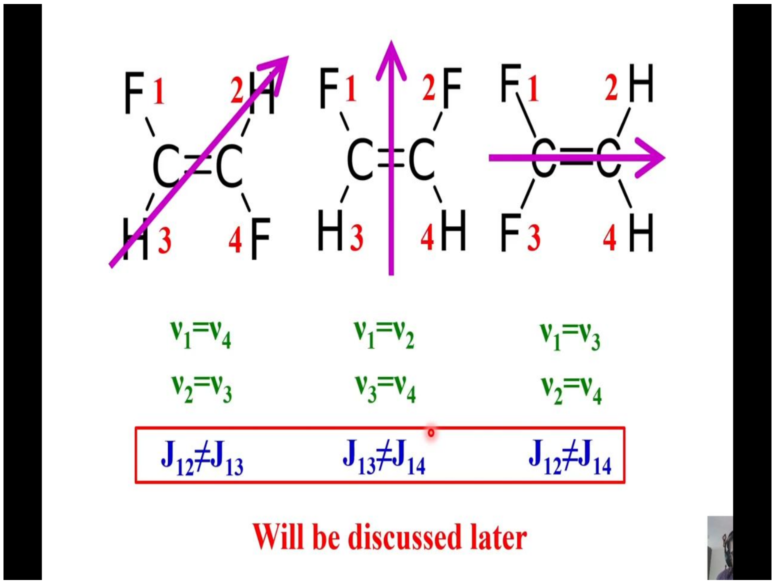

$\nu_1=\nu_4$ $\nu_1=\nu_2$ $\nu_1=\nu_3$

$\nu_2=\nu_3$ $\nu_3=\nu_4$ $\nu_2=\nu_4$

$J_{12}\neq J_{13}$ $J_{13}\neq J_{14}$ $J_{12}\neq J_{14}$

Will be discussed later

Now let us look at chemical equivalence by looking at some of the molecules like this. Take a simple molecule like this, which I think, 1 2 difluoroethylene. Now where is the symmetry axis for this molecule. Just look at this one, this is a symmetry axis. Of course you can write like this also there is no problem because of the symmetry axis what is going to happen here is; the fluorine 1 and fluorine 4 are equivalent, chemically equivalent.

So resonating frequency for this fluorine and this fluorine, both are same, they come at the same chemical shift. So $\nu 1 = \nu 4$. Similarly look at protons, $\nu 2 = \nu 3$, because of the symmetry operation. So proton 2 and proton 3 come at the same chemical shift position, so they give single peak, these 2 fluorine's give single peak in the fluorine spectrum; these 2 protons give single peak in the protons spectrum. You understand how symmetry simplifies the spectrum.

Otherwise, let us say we attach some x here, something else, or here I will attach another functional group, then there is no symmetry. So in this proton spectrum we have 2 different peaks. Similarly in the fluorine spectrum we have 2 different peaks. In this example because of symmetry this proton and this proton are equivalent and this fluorine and this fluorine are equivalent.

And what about other interaction parameters. We will come to that later. Now look at this molecule the same difluoroethylene, but now the position of the fluorine is shifted here. Here it was trans move now it is cis, these 2 fluorines are in cis configuration, these 2 are in trans configuration. Now where is the symmetry axis? here you see the symmetry axis. What does it mean? In this molecule also fluorine 1 and fluorine 2 are equivalent. Similarly proton 3 is chemically equivalent with proton 4. So fluorine NMR gives you only one peak for these 2 fluorines. Similarly proton NMR will give you only one peak for these 2 protons because of chemical equivalence.

What about this molecule, now again I have shifted the position of the fluorine. Now both the fluorines are attached to a single carbon, again difluoroethylene.

Now do you have a symmetry for this molecule? Yes, if you look at the molecule carefully, this is a symmetry axis. Now, look at the chemical equivalence. Fluorine 1 again is equal to fluorine 3 chemicals shift of 1 and 3 are same. It gives a single peak again in the fluorine NMR. What about protons? look at it, for protons also $\nu 2 = \nu 4$. Again there is symmetry and these 2 are equivalent, so you get single peak for this, even in the proton NMR.

So these are the 3 different difluoro substituted ethylenes, where the substituent position is varied. All the 3 molecules have symmetry axis. As a consequence, both fluorine's are chemically equivalent and both protons are chemically equivalent in all the 3 different molecules. So if I take proton NMR, all the 3 molecules will give only one peak, if I take fluorine NMR all the 3 molecules will give a single peak. Now this is another parameter which I will discuss may be later.

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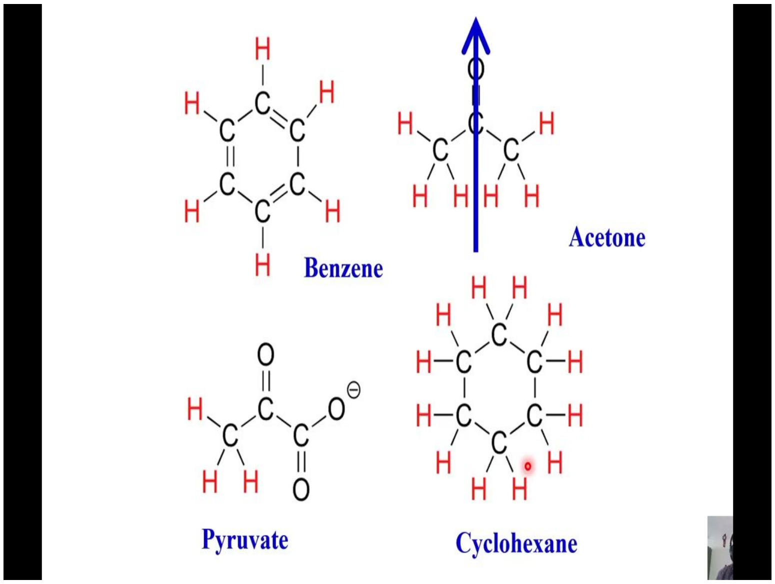

Now let us look at this molecule. What is it? Benzene. What about the symmetry of benzene? it has a D6h symmetry. This is a symmetry axis here, passing through the plane of the ring. Now all the 6 protons of benzene are chemically equivalent, this proton, this proton, this proton whatever the numbering you do, all are same, it means benzene will give only one peak in the proton NMR.

There is something interesting also you can see, look at this carbon here. Are they equivalent? Yes, benzene has a resonance structure. If you look at these things all these 6 carbons are also equivalent and I am not talking about heteronuclear NMR at the moment, it takes some more classes to come to you. But at the moment I tell you, from the symmetry consideration, all 6 carbons are equivalent, chemically equivalent.

So if I go to carbon 13 NMR then also I will get a single peak. OK, that is benzene. Let us look at 1 or 2 more examples. Go to acetone, is there a symmetry axis here? Yes, along this axis, the structure is written like this, but there is a fast rotation going on about CC axis, along this axis. and there is a fast rotation going on about this axis. So that these 2, this CH3 group and this CH3 group are equivalent. These 3 protons of the methyl group are also chemically equivalent, they are not different. In addition to that, this methyl group is also chemically equivalent with this methyl group. So, this acetone molecule has 6 different protons, 6 protons, but because of the symmetry consideration, if we take the proton NMR, all the 6 protons are symmetric, and gives rise to a single peak. You understand, acetone gives at single peak. Of course, what about the carbon here? Very interesting. All protons are same, or equivalent and they will give a single peak. But carbons are not same. This carbon is chemically equivalent with this carbon because of symmetry consideration, but what about this carbon? This is different from these 2. So if I look at the carbon 13 NMR we get 2 peaks for carbon, one for this and one for this, I am sorry one for this. These 2 carbons are same and this is different, we get 2 peaks. Proton NMR gives a single peak.

Now come to this molecule pyruvate, this has no symmetry consideration at all. As far as the proton NMR is concerned or carbon 13, whichever the nuclei consider, but all the 3 protons of the methyl group are identical, because of the fast rotation of the methyl group about this CC axis and you will get only 1 peak for proton, but if you look at the carbons of this molecule because, there is no symmetry at all. This molecule lacks any type of symmetry, of course plane of symmetry may be there, but then because of that, this carbon, this carbon and this carbon, all the 3 carbons are chemically non equivalent. As a consequence, in carbon 13 NMR you still get 3 peaks. But in proton NMR you get only 1 peak. Remember.

But this fantastic molecule, cyclohexane. Now let us see, is there any symmetry for this molecule? Fantastic. Symmetry is there, all protons are equivalent, all carbons are chemically equivalent. If I look for a proton NMR we get a single peak, if we look for a carbon 13 NMR we still get a single peak, remember. This is because of symmetry operation.

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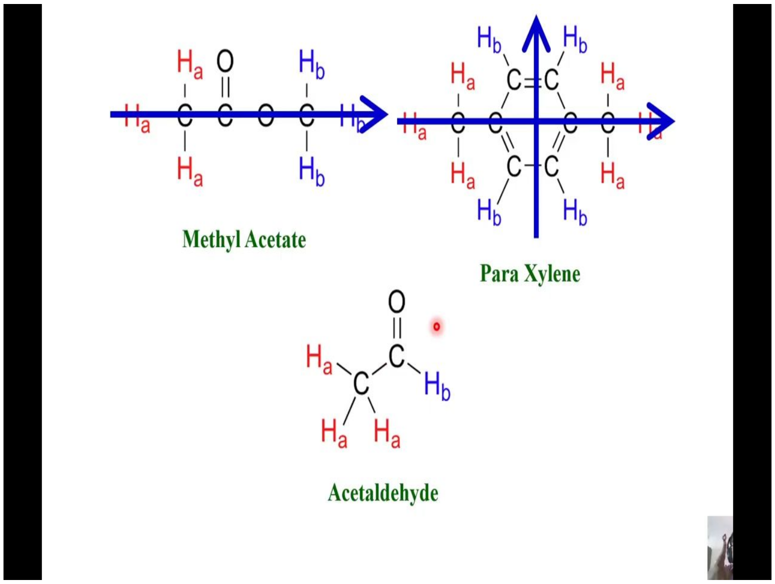

Methyl Acetate

Para Xylene

Acetaldehyde

Now look at this molecule methyl acetate, here there are 2 CH3 groups, but remember this CO is attached to this CH3. Only oxygen is attached to this CH3. As a consequence, the protons marked with red color and the protons marked with blue color are not the same. So these 3 protons will be equivalent, they are equivalent. these 3 protons of CH3 will be equivalent. But between them this CH3 is different from this CH3, they are not chemically equivalent.

So the methyl acetate, if you look for proton NMR, you get 2 different types of peaks. That is what we saw. Remember in one of the spectra I showed 2 CH3 peaks. One was attached to CO coming down field and this CH3 was high field, you saw that methyl acetate. I showed you the spectrum of this.

Now it is a para xylene really interesting. All the 3 types of xylene you take ortho, meta and para all of them have symmetry. Now what is a symmetry axis here? This is the symmetry axis. Now what does it mean? Of course there is another symmetry axis also for this, this side; it has C2V symmetry. Now because of that you look at it, these 3 protons, CH3 protons are equivalent with these 3 protons, there are 6 protons chemical equivalent. All the protons of this methyl, all the protons of this methyl are equivalent, and both the methyl groups are equivalent. So we will get one peak for methyl protons.

What about these 4 protons? this proton is chemically equivalent with this, this is chemically equivalent with this, you should go along this symmetry axis, this is equivalent to this and this is equivalent to this. So all the 4 protons of para xylene are also chemically equivalent.
The ring protons are also equivalent. That means these 4 protons will give you only a single peak. Do you understand? the para xylene because of its symmetry give you only 2 peaks. One peak for CH3 and other peak for methyl protons.

Of course, what about the carbon here, you should understand. How many peaks we get for carbon. Remember this carbon is equivalent to this carbon, we get only one peak this are equivalent. what about these 6 carbons, but this carbon and this carbon ipso carbons are not equivalent. They are different from the remaining 4 ring carbons. This is equivalent to this.

So these 2 carbons are equivalent but these 2 are not equivalent with the remaining ring carbons. These 2 and these 2 are same; this and this are same. So we have 3 different types of carbons in para xylene, we get 3 peaks in carbon 13 NMR.

Look at acetaldehyde. There are only 2 different groups. 3 protons of one CH3 group, 1 proton of CH group. There are 2 different types of peaks for proton. Similarly, there are 2 different carbons, acetaldehyde gives 2 proton signals and 2 carbon signals because of chemical non equivalence of this molecule. There is no symmetry here at all.

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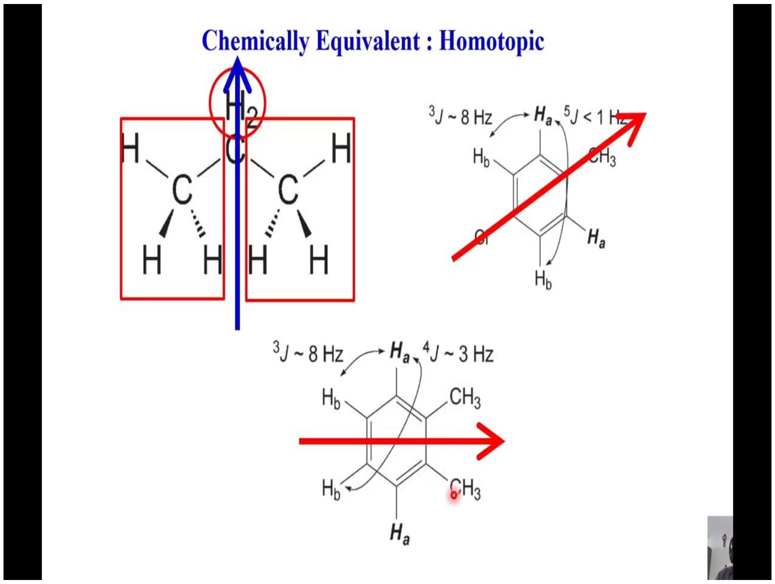

Chemically Equivalent : Homotopic

So now continuing with the chemical equivalent homotopic. Another example, I want to give you look at this molecule, this molecule, there is a symmetry axis along this, and this CH3 is equal to this CH3; whereas this CH2 is different. So what does it mean? We get 2 different types of peaks for protons and these 4, 2 methyl protons gives a single peak, this CH2 give a single peak. What about the carbons? exactly same.

This carbon is chemically equivalent with this carbon and both these carbons are inequivalent with this carbon. So again there are 2 types of carbons. we get 2 peaks in the carbon 13 NMR. OK, like this, you can look at varieties of molecules, and this is a molecule where the chlorine is in the fourth position, here there is a CH3, now there is a symmetry axis along this, and this proton is equal to this and this proton is equal to this.

Look at this molecule. Now, we have taken CH3 here and CH3 here. There is a symmetry axis along this. Now what happens? This proton is chemically equivalent with this proton and gives a single peak. This proton and this proton are same, because the environment for this is different. This side is different the side is different, so all the remaining ring protons are not same, whereas this proton and this proton have the same environment, on either side. So they are equivalent. Similarly this proton b and this proton b are equivalent. So there are 3 different types of protons here, one for CH3, one for this proton Ha, one for this proton Hb.

Similarly look for the carbon here, how many chemically inequivalent carbons you can think of? 1 carbon for 2 methyl protons equivalent, what about theis carbons? It is different, they are not equal to the other carbon. So, this is another carbon, these 2 are equivalent, what about this carbon and this carbon, they are different. What about this and this. So these 2 carbons are equivalent and different from these 2 carbons which are equivalent, and different from these 2 carbons which are equivalent, and different from these 2 carbons which are equivalent. So how many chemical inequivalent carbons are in this molecule? There are 4 different types of carbons.

Remember, these 2 gives 1 type of carbon, these 2 gives are another type of carbon, these 2 gives another chemical equivalent carbon and these 2 gives another chemical in equivalent carbon. So this molecule had 3 different protons and 4 different chemically equivalent carbons.

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Chemically Equivalent

So this is the fantastic diagram to show what the chemical equivalence is. I showed you for the chemical shift, different types of bells, where the charge distributions were different at the site of the nucleus. But here see all are same, identical, it is a perfect example of chemical equivalence of this type and also of this type. These type may different, but all these become 1 type of protons or carbons, and all these becomes another type. This is an example for chemical equivalence.

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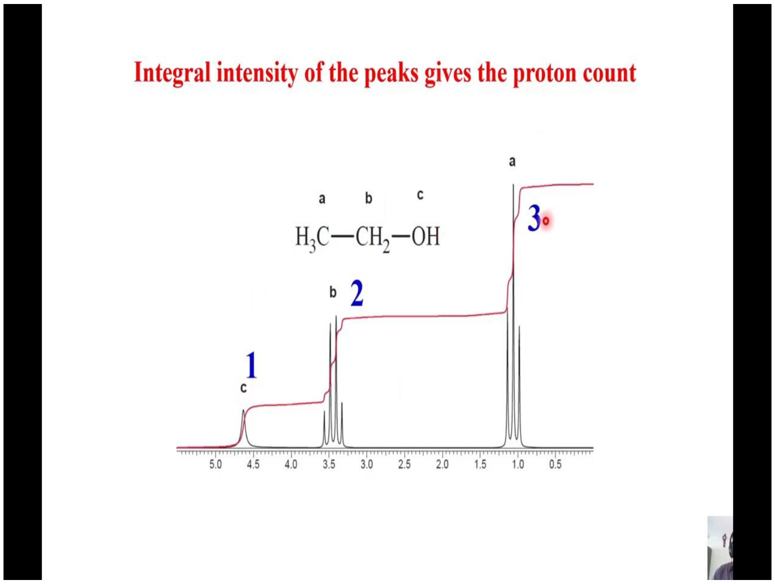

Integral intensity of the peaks gives the proton count

Now, in the NMR spectrum of a proton if I take, you can observe very interesting things. Let us look at the spectrum of ethyl alcohol. CH3, CH2, OH, you all know it is ethyl alcohol. There is one proton coming here, one proton coming here, one proton coming here. Do not worry about the multiplicity, I will discuss that when I explain scalar couplings. At the moment assume there is 1 proton here, 1 proton here and 1 proton here. Because these 3 different types of protons all of them are chemically inequivalent.

Remember all of them are chemically inequivalent and we got 3 different types of peaks. And this CH3 as we have been discussing, it is highly shielded, because of these 3 protons. It comes high field, this CH2 comes next. This OH proton is directly attached to this oxygen, directly bonded to this oxygen. So it pulls electrons from this proton, an electron withdrawing group, electronegative group. So it comes here.

So now if you carefully look at the intensity of the peaks, see this height and this height and this height are in the ratio of 1 : 2 : 3. I am not talking about the height, I am talking about the area it will be broad here. Why OK peak is broad is for a different reason, and I will explain to you later. But take the area of this, area of this group. There are 3 groups of protons with intensity ratio pertains to 1 : 2 : 3, interesting right !

Look at the intensity, it is 1: 2 :3 3. But look at the number of protons in each of these group, CH3 has 3 protons, intensity is 3, I said this is CH2 it has 2 protons and the intensity is 2, this is 1 proton, intensity is 1. That means if I take the integral area of all these groups of the molecule, each of these peaks corresponding to each of these groups. If I take the integral area, what does the area will tell you? When you compare with another single proton or other group of the same molecule, you can find out the number of protons present. So each peak integral area gives you the protons count for the peak. So the intensity is 3 here, integral area is 3, the proton count is 3 compared to 2, here proton count is 2, and this is proton count 1. But remember there must be something relative. If I give you, or if I don't give you any of these things, you will not be able to say, they must be relative, I know this is a single proton of OH, because of this I can compare.

This is twice the intensity I can compare this as twice the intensity. If I give you only this 1 peak, I do not give the numbers and I do not give this region of the spectrum you do not know, whether it is 3 or 5 or 10, you will not say. You do not know how many protons are there in this group.

So, there must be a relative comparison. You must find another peak which you are sure of the number of protons that are present in that group. Related to that you will measure the areas of other peaks and number of protons which are present in that group. You are understanding my point?

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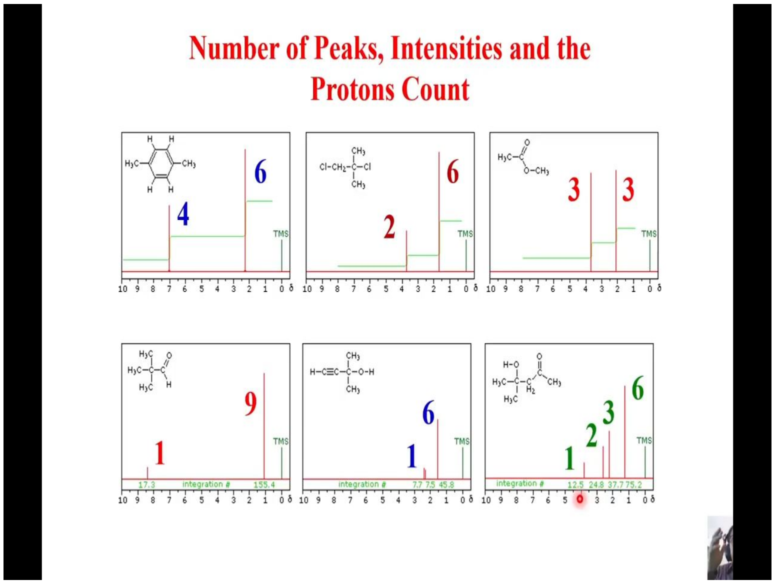

Number of Peaks, Intensities and the Protons Count

Now we will make a simple exercise. What is the exercise, the number or peaks based on the intensities and the number of protons that are possible in each of them. Look at it very carefully. I will find out the number of peaks in the spectrum, measure the intensity and I can count the number of protons. So now look at this one, this is a molecule with a perfect symmetry here, there are 2 CH3 present on either side, in para position, and these are 4. And we discussed this type of molecule already earlier.

So because of chemical equivalent this CH3 and this CH3 are same. It is giving a single peak, these 4 protons, again because of C2V symmetry, are same. This gives another peak, so there are only 2 peaks here. Supposing I do not know which proton comes where, can I say which is a CH3, which is aromatic ring protons? Easily you can say that now, because of 2 CH3 are equivalent, this should have intensity 6 compared to these 4 protons which has intensity 4. The intensity ratio must be 2:3. In which case we can say this corresponds to ring protons, and this corresponds to CH3 protons.

This is another way of assignment looking at the intensity, you can also do that. So 4:6, so this is are ring protons and these are CH3 protons, you understand. So 2 : 3 intensity.

Look at this molecule. There are 3 different types of protons, 3 groups CH3, CH3 and CH2, because of the symmetry here, along this axis, this CH3 and this CH3 are identical, chemically equivalent, and this is different. So when these 2 overlap what is the intensity? 3 protons plus 3 protons, the CH3 equals to 6 intensity, the CH2 must be 2 intensity. If you look at it CH2 and CH3, the intensity ratio is 1 : 3. We can easily identify.

Come back to this molecule, which we saw already, acetamide. We saw that you know, CH3 and OCH3 both are equivalent, this CH3, this is CH3, but they are not chemically equivalent, so the have 1:1 intensity ratio, both are CH3 protons. Now go to next set of molecules, just to understand, very quickly.

What about this molecule? look at it very carefully. Is there a symmetry along this axis? No, because this side we have proton and this is oxygen. So these 2 are not same. But anyway, this structure is written in such a way, the spectrum is obtained theoretically in such a way all the 3 CH3 groups are equivalent, and the CH is separate. So that means, in this molecule there are 10 protons, 9 of which are equivalent because 3 CH3 and only one is different. So what you should expect? 2 peaks. But the intensity ratio is 1: 9.

We understood that right, now go to this molecule, there is a symmetry along this axis. Now because of this there are only 2 types of protons, because of symmetry this proton and this proton are same.

Now we will take the last example of this molecule which has no symmetry at all. Now how many types of protons are present here 1, 2, 3, 4 and 5. You should get different types of protons. Maybe one of them is not seen here, OH, because it is broadened out. Dont worry. So you should get peaks with intensity ratio, 1, 2, 3 and 6. In this case it so happens, maybe structure is written like this, these 2 CH3 are equivalent, I am sorry I did not know the structure. So there are 4 peaks here OH is also here, OH is 1 peak, it is a theoretical plot, a stick plot.

So this is OH, I mean you theoretically although there is no symmetry it made to be equal, there are 2 CH3 are overlapped here, intensity is 6 then, 1 CH3 here intensity is 3, this is CH2 intensity is 2, OH has intensity 1. This is how you can see the number of peaks, count the number of peaks measure their areas, it will give the proton count, you understood.

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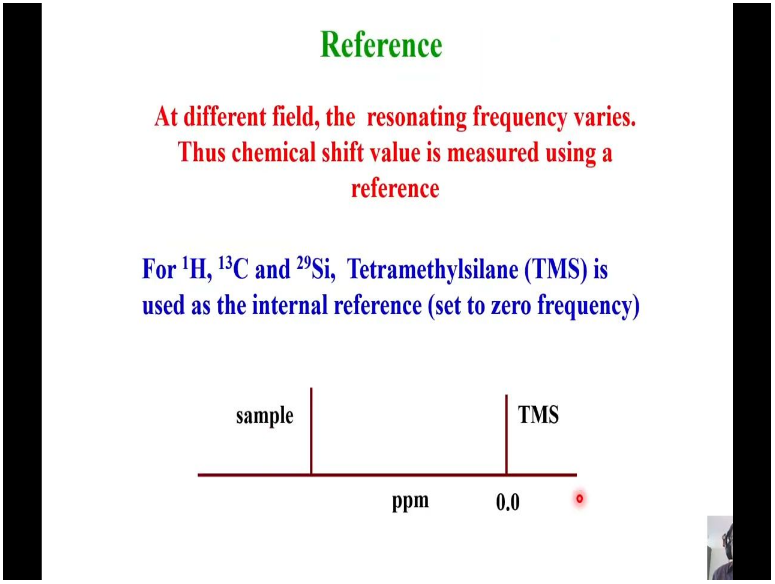

Reference

At different field, the resonating frequency varies. Thus chemical shift value is measured using a reference

For ^{1}H, ^{13}C and ^{29}Si, Tetramethylsilane (TMS) is used as the internal reference (set to zero frequency)

And next we will talk more about the references, how do you measure the chemical shift? What is the unit of measurement of chemical shift? and what happens to the chemical shift for different groups, everything, we will discuss later. But for today I am going to stop here. I hope you are all with me. I gave you some idea about the chemical shift, about the especially symmetry operation, counting of the protons with the peak positions, peak height, everything. It is a very interesting topic. You should know more about chemical shift, because this is the basis for your analysis of NMR spectra. We will come back later. I stop here.