One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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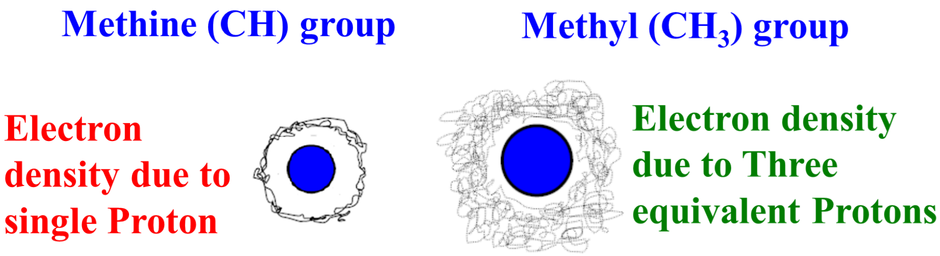
Lecture 07 - Chemical Shifts

Welcome all of you. In the last class, I started introducing about the internal interaction parameters. We discussed four different types of internal interaction parameters, chemical shifts, scalar couplings, dipolar couplings. And for nuclei with spins greater than half we also have quadrupolar interactions. We are dealing with spin half nuclei, quadrupolar coupling we do not have to consider. Also, there was a minute difference, which I told you. All the NMR interactions are magnetic interactions, except quadrupolar interaction, which is an electric interaction.

Since, you are dealing with spin half nuclei, we do not have to worry about quadrupolar interaction. Further, these internal interactions if you have to worry about and if you consider in the solution state, dipolar coupling we can remove it, because that gets averaged out. Every interaction parameter in NMR is anisotropic and in the solution state, all anisotropic interactions get averaged out. We do not have to worry about it and what we are going to be dealing with is only our isotropic chemical shifts and J couplings, the scalar couplings.

We did not discuss scalar coupling which we will come to that later. But in the chemical shifts, I said how it comes when you put the sample in a magnetic field because the current is induced by the external magnetic field. The circulating current in turn induces magnetic field, and I said induced magnetic field is very small. External magnetic field is of the order of several Tesla, but induced magnetic field is 0.00000X Gaus, with some value, a very small negligible value. But it adds to the external magnetic field. The field seen by the nucleus is not just the external magnetic field, but also the field induced due to surrounding electrons at the side of the nucleus spins.

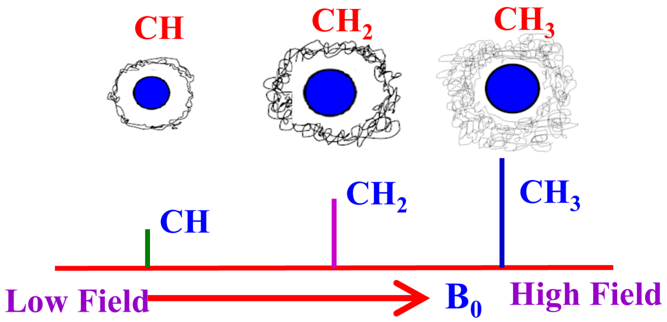
As a consequence, there is a shift in the resonant position. The resonance frequency is not just 400 MHz, but 400 MHz plus some value. And this causes a shift in the resonance position, which we call it as chemical shifts. And we took the example of a hypothetical molecule with different functional groups that have different chart distributions. As for example, if it is a C-H bond, it is elliptical. For any other bond like O-H or some other bonds, charge distribution is having different shapes. As a consequence, the field induced at the site of the nucleus is different. So, in any given molecule, at the different sites of the nucleus, if the charge distributions are different, then we are going to get different peaks in NMR. That is what we understood. And I also said the nuclear spins do not get involved in chemical reactions, but they give information about the chemistry of the molecules because the electronic charge distribution at the different nuclear sites are different. They give rise to different peaks in NMR. If you analyze and interpret the NMR spectrum, you can get about the chemistry of the molecule. You can understand the chemistry of the molecule. So, this is a very, very important thing. So, this is what we understood. Today, we will try to go further and see how different electron densities affect the chemical shifts.



That is what we will discuss today. For example, I consider a methyl group, methane group, C-H group. Let us see how the electron density will be there at the site of each nucleus. Methine group has a single proton, only one proton. Hypothetically, we have written the charge distribution at the site is like this, and the effective field seen by the nucleus is more than the static magnetic field. So, B_{effect} is more than B_0. It is not same because shielded by the electrons surrounding that. Go to methyl group. There are three protons. Electron density due to three equivalent protons are there. That is much different now. The effective field seen by the nucleus is more than the static field here. $B_{effective}$ is more than B0. But remember, I am considering CH proton here, and CH3 proton here. Methyl group has three protons, CH3. So, each of them has different effective fields. Effective field for CH proton is different and more than that of B0. The effective field at methyl proton B_{effect} is also more than that of B0. But between these two, $B_{effective}$ of the methyl is more than $B_{effective}$ of methine. Why? Because this has three protons, the methine group has only proton, $B_{effective}$ due to one proton. So, $B_{effective}$ of methyl proton is more than that of the $B_{effective}$ of the methine proton. So, that means the methyl protons are more shielded than methine proton. Understand the concept.

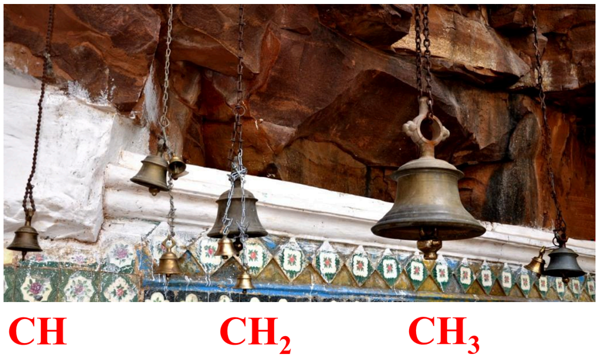
If I consider the methine, methine proton is more shielded than B0. Methyl proton is more shielded than B0. Effective field between these two are different. But when you compare the methine proton with the methyl proton, methyl protons are more shielded than methine proton, because $B_{effective}$ of methyl is more than that of the methine proton. So, as a consequence the effective field seen by the methyl proton is more than the methine proton. As a consequence CH_3 protons resonate at higher field than CH proton, because of three protons shielding is more, and it comes at higher field. So, shielding also depends upon number of equivalent protons.

Now, consider another example. Instead of only this and this, methine and methyl, we also bring in CH2 protons.

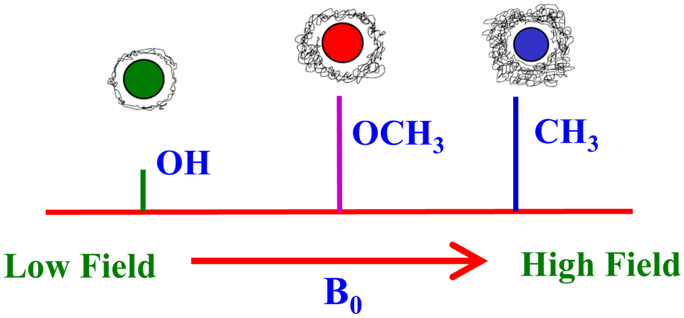


The methyl, methane and methine all the three. Now, the charge density at the site is different. Here it is only one proton, written charge distribution has some shape. Here for two protons, it is slightly different and more. But more than this, here for three protons, it is different. But more than this and this. So, that means, this is more shielded than this, this is more shielded than thi,s and this is more shielded than these two. As a consequence CH3 protons is more shielded comes at the \ high field region.

If I consider the magnetic field direction B0 field, B0 field iplus induced field is more for this, B0 plus induced field of CH2 is here it is less than this, but more than this. If you come to CH it is less compared to this and this. So, there are three peaks; one of these, is more shielded comes at high field here, to the right side, because I am increasing the magnetic field direction from left to right. That is the convention in NMR, the field always increases when you go from left to right. So, more shielded comes to the right. Then CH2 is less shielded then CH, which is less shielded than these two. This is how the NMR spectrum comes. If I have three functional groups only, we have three peaks CH3, the one which comes at the high field is more shielded CH3 with three protons, Then next to that is CH2. Then next to that is CH. You understood this is how we see the peaks in NMR. Just to give you the comparison if you look at the Bell analogy; fantastic, seen in one of the temples; beautiful Bell analogy.



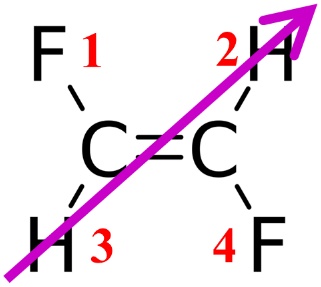
We could see they have put three different Bells. Look at this Bell, this is a nucleus, and the charge distribution. I consider this Bell at the center as the nucleus, this is the charge distribution. This is much larger; three protons shielding is more. Come to the CH2; this smaller Bell. This is the nucleus and charge distribution is much smaller than this. Go to this Bell; even smaller than this. This chart distribution is much smaller than these two. Fantastic analogy, it is a Bell analogy where the shielding comes because of the different charge distribution of three protons, two protons and one proton for methyl, methane and methine groups are different. So, now we will go further we considered only CH CH2 and CH3. What happebs? in a given molecule it is not only these types of protons present, there could be different functional groups, they could be OH, it could be OCH3, it could be CH3, does not matter.

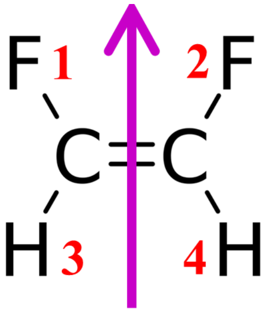


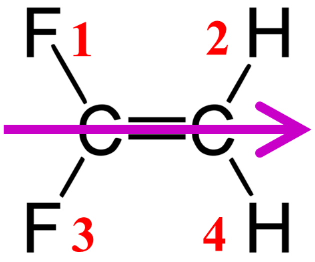
We saw that CH3 comes at the high field. Let us consider the methoxy group, for CH3 add a oxygen group it becomes methoxy. Now oxygen you see is electron withdrawing group, it is an electro negative group. So, it deshields the CH3 to some extent. Instead of coming here, it comes to the left side. From high field it moves to the low field side. I said low field to high field when you go from left to right. So, instead of coming to the right it moves slightly to the left because of OCH3, the addition of oxygen. That means oxygen OCH3 group is deshielded compared to CH3. Let us go to OH group. This is the OH group where a single proton, but directly attached to oxygen, deshields it, withdraws electrons on this. More deshielded, when you have more electrons, more and more deshielded. So, what is going to happen? it is even deshielded. It comes even more low field compared to CH3 and OCH3. The OH is here; this is the hypothetical graph I am giving you. Of course, in a given molecule OH may be surrounded by something else, it may come here, the OH can go anywhere in the spectrum. I am just giving you a comparison between these three. When compared to OCH3 and CH3; OH is coming to the down field that is low field. Ghat is what I am telling you, that is the concept I wanted to tell you.

And with this I will introduce a term called chemical equivalence. A given molecule may have a symmetry, because of symmetry there will be chemical equivalence. When you have chemical equivalence you will not get more number of peaks. The chemical equivalence brings brings down the number of observable peaks in the NMR spectrum. The number of peaks gets reduced. Look at this one, all are chemical equivalent nuclei, which are interchangeable by symmetry operations. They have the same chemical shifts. But I have not introduced the term coupling, but I will introduce later. But a coupling to all other spins that means, the interaction of this to other spins could be different, coupling may be same, but the chemical environment will be same. They are called chemically equivalent spins. They are interchangeable by symmetry operation. And remember in the NMR only chemically inequivalent spins; or only chemically equivalent nuclei give distinct peaks. When they are chemically equivalent, they will overlap and give rise to the same peak, peak will not be different. But if they are chemically inequivalent that means, the charge distribution at the site of the nuclei are different, then they give rise to distinct peaks in NMR. Please understand, chemically inequivalent nuclei give distinct peaks in NMR.

Now look at this Bell analogy all these bells are identical. And you can see all of them have the same shape. Of course, when you take the photo from left to right, it appears they are different. But they are all of the same size, and shape. They are all chemically equivalent. If you take such type of molecules, if you look at this, they are chemically equivalent and give rise to a single peak in NMR. Similarly, here they give rise to a single peak because all of them are chemically equivalent. So, remember only chemically inequivalent spins gives rise to distinct peaks in NMR. Alright, let us consider the molecules like this.





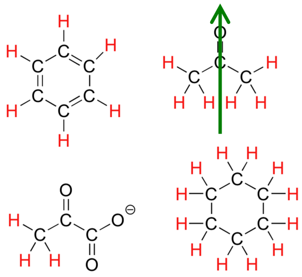


What about this molecule? it is difluoroethylene. Is there a symmetry for this molecule? If I write the symmetry axis, you see there is a symmetry axis like this. What does it mean? The 2 fluorines are chemically equivalent. The 2 protons are chemically equivalent. If I see the proton NMR, the protons 2 and 3 are identical having a same chemical environment, and the charge distribution at the site of these 2 protons are identical. There is no distinction. So, they give rise to a single peak, although there are 2 protons. Thus because of the same chemical environment it gives rise to single peak.

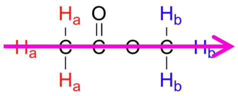
Now if I go to the fluorine NMR, there is also possible to say fluorine resonance. Then this one, this and this, 1 and 4 are identical. So, we like protons these fluorines also have \same chemical environment. So, if I see fluorine NMR, this and this gives rise to single peak. For this molecule, remember if I take proton NMR you get single peak, if I take fluorine NMR also you will get single peak, because of chemical equivalence. Of course, there is another parameter called coupling, which I will introduce, may be to next class or after subsequent classes. The coupling between proton 1 and 2, and 1 and 3 are not same. This coupling and this coupling between fluorine are not same. Similarly this coupling and this coupling are not same. They are different. The couplings may be different, but the chemical environment is same, because they are chemically equivalent.

Let us go to a molecule like this. In this molecule let us see what is going to happen. is there a symmetry? of course, there is a symmetry axis here. What does it mean? the same molecule, now the fluorine substitution position is different. Again because of symmetry remember the fluorine chemical shifts of 1 and 2 is same. The chemical shifts of 3 and 4 is same. The coupling may be different, coupling between 1 3 and 1 4 may not be same. But if I take proton NMR these two protons give rise to a single peak. If I go to fluorine NMR these two fluorines will give rise to a single peak.

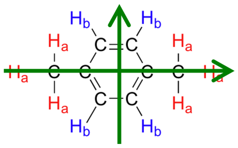
Now, let us go to a different molecule. Again same difluoro substituted ethylene. Now the symmetry axis is different. This is the symmetry axis. Sgain the fluorine 1 and fluorine 3 have this same chemical environment. Here 1 and 3 have the same chemical environment give rise to a single peak. The protons 2 and 4 have the same chemical environment and give rise to a single peak. Again the coupling 1 2 and 1 4 may be different; they are not same. Nevertheless in all the difluoro substituted ethylenes, fluorine NMR give single peak, proton NMR gives rise to single peak for proton because of chemical equivalence. They are all called chemically equivalent spins.



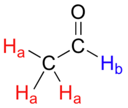
Consider a molecule like this, benzene. Here there are 6 protons, all the 6 protons have the same chemical environment They are chemically equivalent. So, if you take the spectrum of benzene, proton NMR, you get single peak. What about the carbon? Look at the carbon the chemical environment, it is also same. If you take carbon NMR, that also gives you single peak, of course, with a decoupling. Everything we will see later. So, benzene proton NMR gives a single peak. What about the acetone? there is a symmetry axis here. The CH3 groups, and 3 protons of the methyl group are chemical equivalent. And also these 3 protons and these 3 protons are again equivalent. So, if you take the acetone spectrum, proton NMR, you are going to get a single peak. Come to a molecule like this you have only one CH3 group, you get a single peak. Go to cyclohexane, very interesting molecule. There are 12 protons, and interestingly all the 12 protons are chemically equivalent. If you take the proton NMR of this, you get single peak. If you take the carbon NMR of this you get a single peak. These are all chemically equivalent nuclei.



Methyl Acetate



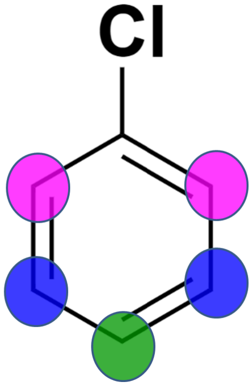
Para Xylene



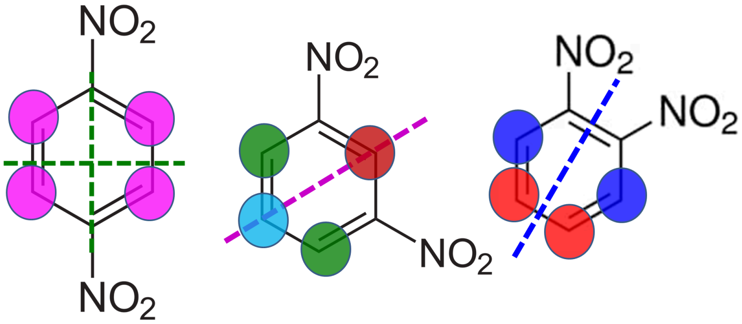
Acetaldehyde

If you go further, for the methyl acetate these 3 protons and these 3 protons are different. This CH3 and this CH3 are not same. There is no symmetry for this molecule chemically they are inequivalent, As a consequence this CH3 will give give one peak, and this CH3 will give one peak. Go to paraxylene, now you can write a symmetry axis for this like this and this, because of that these 3 protons of methyl and these 3 protons of methyl are same. The two methyl groups are identical, chemically equivalent gives us a single peak, There are 2 methyl groups in the paraxylene, but gives us a single peak. Go to these 4 protons. The 4 protons of the phenyl group here are identical because of the symmetry operation, that gives such a single peak. So, if I take the proton NMR spectrum of xylene these two CH3 groups gives us a single peak. The 4 protons of the phenyl group gives such a single peak, only get 2 peaks in spite of the fact the molecule have 2 CH3 and 4 CH protons. Go to acetaldehyde. In acetaldehyde you have only CH3 proton and CH proton. They are different there is no symmetry. So, acetaldehyde gives you 2 peaks 1 for CH3, and 1 for CH. So, you have understood now, how the chemical equivalence may helps in reducing the spectral complexity. More the symmetry in the molecule more the chemical equivalence, less the number of peaks, less complexity of the spectrum. Ghis helps you in easy interpretation. So, remember chemical equivalence, if it is there in the molecule, the number of peaks that you are going to see get drastically reduced.

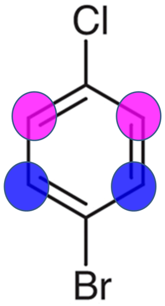
Let us look at this thing. See most of the time when you are dealing with the organic molecules, invariably in many of the molecules always, all need not be aliphatic, you come across phenyl groups present in the molecules. Let us consider the chemical equivalence in mono substituted benzene. I look for chlorobenzene, the monochlorobenzene.

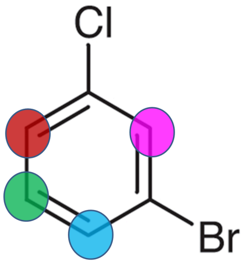


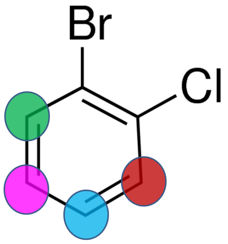
Now, where is the symmetry here? There is a symmetry axis; the symmetry axis comes along this. So, as a consequence these 2 protons are same; they give rise to single peak, worry about the multiplicity due to couplings later. These 2 protons are chemically equivalent, gives rise to single peak; and this is different. So, there are 3 different types of protons here, chemically in equivalent protons. This is what you are going to see if you look for the mono substituted benzene.



Let us look for chemical equivalence in symmetrically disubstituted benzene. The symmetrically disubstituted could be ortho substitution, meta substitution. Go for this para disubstituted benzene, symmetrically. There is symmetry axis here, and here. As a consequence all the 4 protons are chemically equivalent. So, if you take symmetrically para disubstituted benzene, the proton NMR spectrum gives you a single peak. What about the carbon 13? of course, that is the different question. Rhese 4 carbons are same, but this carbon and this carbon are different. So, if you take carbon 13 NMR, you get 2 peaks. One peak for these 4 carbons; and 1 peak for these 2 carbon. So In the same way of course, in the previous example we have this carbon is different, these 2 carbons are same, these 2 carbon are same, this carbon is same. So, in a mono substituted benzene we get 4 peaks in carbon 13 NMR, 3 peaks in proton NMR. So, now, we understood for para disubstituted, symmetrically disubstituted benzene, we have a single peak for proton; of course, 2 peaks for carbon. For meta disubstituted symmetrically, this is symmetry axis. These 2 protons are identical because of symmetry, they are symmetrical and equivalent, this is different this is different. So, how many peaks you get for symmetrically meta disubstituted benzene? We get 3 peaks. Let us look at symmetrically ortho disubstituted benzene now. Rhese 2 protons are identical; these 2 protons are identical. These 2 give rise to 1 peak, these 2 gives rise to 1 peak. We are going to get 2 different peaks for symmetrically ortho disubstituted benzene.

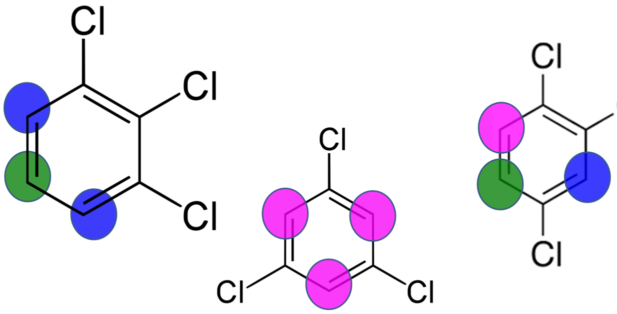




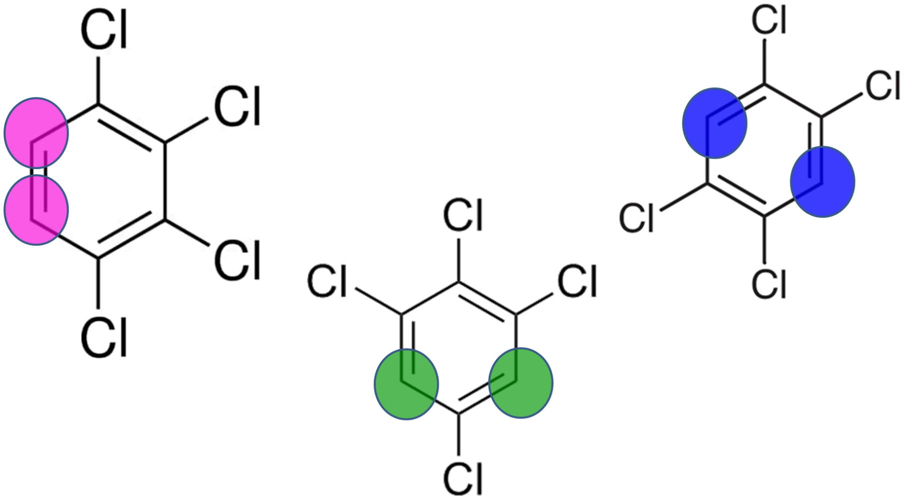


Now, asymmetrically disubstituted benzene we will take. The previous example was of symmetrically disubstituted. If you go to asymmetrically disubstituted, take the example of a molecule like this. This one is chlorine, this is bromine. There is no symmetric substitution; they are different. As a consequence chemical environment at the site of these 2 protons are different; and the chemical environment at the site of these 2 protons are different. In the previous example for the symmetrically para disubstituted benzene, we get single peak. But here it is asymmetrically disubstituted, these 2 protons are same; and these 2 protons are same. You get 2 peaks; 2 chemical environments. These 2 protons are have different chemical environments; and these 2 protons have chemical environments. So, we get 1 peak for these 2 protons and one peak for these two protons.

What about asymmetrical meta-disubstitution? Now, there is no symmetry at all. Where is the symmetry? There is no symmetry. All the four protons are completely different. I have put different colors. So, this proton is different chemically, this is different, this is different, this is different. All the four protons gives rise to four different chemical shifts. They are chemically in equivalent. So, we get four peaks for asymmetrically meta-disubstituted benzene. What about asymmetrically ortho-disubstituted benzene? Very simple. Here also. All the four are different. There is no symmetry. So, we get four peaks for this. Very interesting. Now go for this. This is symmetrically trisubstituted.



Of course, these three are CH3 protons. All of them give rise to single peak, But, look at these phenyl group here. This is different and this and this are different. They give different peaks. They are chemically inequivalent. This gives a different peak, these two gives one peak, this gives one peak. Of course, CH3 gives rise to one peak, I am not worried about that. Only I am worried about the phenyl group. This gives one peak, these two and this gives one peak. What about symmetrically disubstituted benzene like this? All the three chlorines are in the 1, 3, 5 trisubstituted; trichlorosubstituted benzene. Now, you can see all the three protons are chemically equivalent. So, what will happen? If I take the proton NMR spectrum of 1, 3, 5 trichlorobenzene, you get only single peak. There is another possibility. You can have a trisubstitution with a different substitution like this. There is no symmetry here for this. There is no symmetry. So, as a consequence, we get different peaks. Look at this one. Tetra substituted, beautiful.



You have a symmetry here. These two are same, these two are same, these two protons are same. Look at this one. There is a possibility here. This is also tetra substitution, and now the is a symmetry axis here.

This and this are same, this and this are same and this and this are different. Look at this one. We have tetra substitution, but these two protons are identical and CH3 groups of course, this CF3 and this CF3 are identical. Look at the examples I have given in the phenyl substitution; depending upon the mono substitution, disubstitution, symmetrical asymmetric, trisubstitution, symmetrical asymmetric, tetra substitution, we have different chemical environments. So, as a consequence, we understood how many peaks we are going to get in mono substituted benzene, symmetrically disubstituted ortho, meta and para, symmetrically trisubstituted, how many peaks we are going to get.

So, this is a beauty of this thing. So, chemical equivalence we understood and different examples I gave you, because we come across phenyl groups in molecules, not only we come across aliphatic groups. I took the example of acetone. I took the example of cyclohexane. I took the example of pure benzene without any substitution. All six protons are equivalent. So, we understood a lot about chemical equivalence. So, what we discussed with the chemical shifts today, we understood lot about chemical equivalence. We understood, how many peaks we are going to get for different chemically equivalent groups. I told you only chemically inequivalent groups gives rise to distinct peaks in NMR. If there is a chemical equivalence, the peaks overlap and gives rise to reduced number of peaks.

There are two groups which are chemical equivalent, it gives rise a single peak. If there are three groups which are chemically inequivalent, still all of them will overlap and give rise to single peak. So, we understood what is the chemical equivalence, how the peaks will come, took number of examples of this. So, we discussed lot about chemical shifts and how the chemical shift arises, how the different functional groups are responsible for it. We took the example of groups CH3, CH2, and CH. CH3 is more shielded than CH2. CHw is more shielded than CH group. Then, as a consequence, we saw CH3 comes at high field, then CH2, then CH. Instead of CH3, if you put OCH3 and OH, OCH3 is less shielded than CH3. The CH3 comes at high field region, then OCH3, then OH. So, lots of examples we took. So, summarize we understood today, the chemical equivalence, how many peaks we get when there is chemical equivalence in a molecule, when it is shielded or deshielded, where the peaks come, took number of example of CH3, CH2, CH, OCH3, OH, NH, etcetera. All these groups depending upon whether it is shielded or deshielded, depending upon number of protons which are present, whether there is a symmetry in the molecule or not, the number of peaks we are going to get and where it comes whether it is shielded or deshielded matters.

This is what we understood. So, I am going to stop here today. So, we have understood lot about chemical equivalence, number of peaks we are going to see based on the chemical equivalence and shielding, how many peaks we get, whether it is shielded, whether it moves to the high field or low field, that is what we understood. So, with this, we will stop here today. We continue further about chemical shifts, the reasons for this, how we get and everything based on the symmetry operations, how many chemical shifts are there, how many chemical equivalent groups are there, everything. We will continue further and understand the factors that affect the chemical shifts. We will discuss that in the next class. So, I am going to stop here today. Thank you very much. I hope I have given lot of information about chemical shifts already. So, we will ontinue further and discuss lot of things in the next class. So, thank you very much.