One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis
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Lecture 09 - Factors affecting the chemical shifts

In the last class, we started discussing about varieties of things about chemical shifts. I introduced to you about chemical shift, how do we calculate in PPM, what is the reference we use for different nuclei. I said for proton, carbon and silicon, tetramethyl silane is the reference, which is always used. Measure the resonating frequency of a particular peak from your sample with respect to the reference, which is set as 0 frequency divided this by the spectrometer frequency. The value you are going to get is nothing but the chemical shift expressed in parts per million. The advantage of expressing in parts per million is it removes field dependency that means you record the spectrum in any spectrometer, when you express its value in PPM, it remains same.
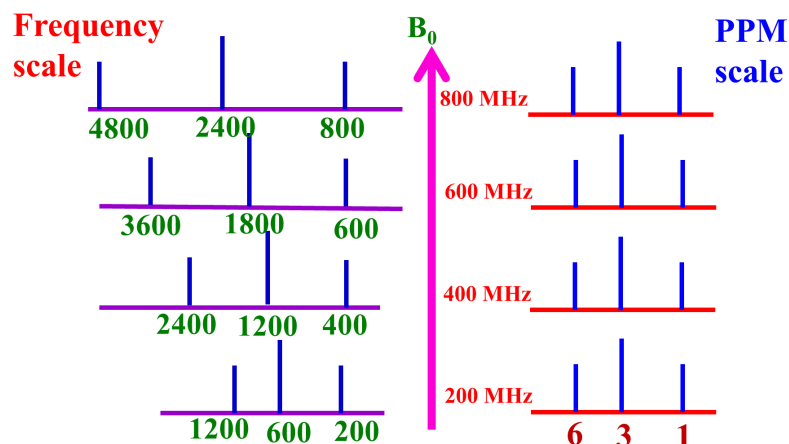
For example, if I say $CHCl_3$ proton peak comes at 7.2 PPM in 400 megahertz, whether you go to 600 megahertz, 800 megahertz, 1000 megahertz, its chemical shift is always 7.2 PPM, there is no change. And then, when you get the chemical shift in PPM for a particular spectrometer, we can convert into frequency. How do you convert into frequency? By multiplying the PPM value by the resonating frequency of a particular nuclei. For example, in a given spectrometer, different nuclei will have different resonating frequencies. That is what we have been discussing from the first class. Now, I know in 800 megahertz, nitrogen comes at 80 megahertz, 10 times lower gamma. What we can do is, if I know the resonating frequency or chemical shift of nitrogen 15 in a particular peak, let us say 100 PPM, if I have to express in frequency, simply I have to multiply this value by 80 .

If I know, let us say 8000 is the frequency for nitrogen 15 in 80 megahertz, in 800 megahertz spectrometer, its resonating frequency is 8000 divided 80, which is 100 PPM. So, like that for any given nuclei, you know how to convert frequency to PPM and vice versa. And I also mentioned about the concept of high field and low field. When you go from left to right in the spectrometer, I mean the spectrum scale, left to right is always going to the high field, lower frequency, higher shielding. So, this is what the concept we said. When you go from right to left, this concept gets reversed, which is less shielded, higher frequency and then lower PPM.

These are the concepts which we discussed. Now, we will go further and understand a bit more about chemical shift for different nuclei, what are the factors which governs chemical shifts, etc. Those things we will try to understand today. And the chemical shift and its field dependence, that is what we will understand. Of course, chemical shift is field dependent and the spectral dispersion is better with higher and higher magnetic field. That means, higher and higher frequency spectrometer if you go, the spectral dispersion becomes better. That means, the peaks start spreading more and more. Let us say, there are two peaks which are close by like this, in some frequency let us say, 100 megahertz spectrometer. If you go to 1000 megahertz, it will become like this, well separated. This is an advantage, that means, as you go to higher and higher the resonating frequency, for the chemical shift what happens, there is a spreading, The frequency starts spreading, more and more dispersion, becomes better and better. Let us see, what happens to the chemical shift scale.
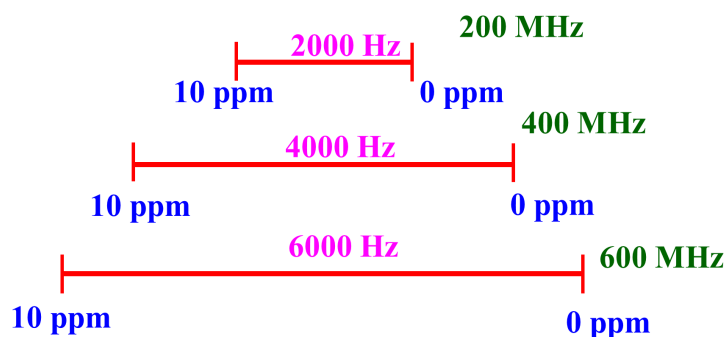
In a 200 megahertz chemical shift range of proton is 0 to 10 ppm, if I consider the total frequency, it is 2000 hertz. We already know how to convert. The 10 ppm in 200 megahertz is 2000 hertz. If I go to a 400 megahertz spectrometer, same 0 to 10 ppm range is 4000 hertz, see the dispersion became better now. Go to 600 megahertz, the same 0 to 10 ppm becomes 6000 hertz. What is happening? The spectrum which gets crowded at lower frequency, start becoming better and better, gets dispersion more and more as you go to higher and higher frequencyThis is the reason, the chemical shift, when you express in frequency, it keeps becoming more and more spread, becomes better and better dispersed, that pertains to better and better resolution. Thus your analysis become much better as you go to higher frequency spectrometer, because of better resolution. And we will consider the chemical shift in frequency in ppm scales, that is what we have been discussing. In ppm scale, it would not change, but in frequency scale it changes. I will show you like this.

Frequency scale

4800	2400	800
3600	1800	600
2400	1200	400
1200	600	200

B₀

800 MHz
600 MHz
400 MHz
200 MHz

PPM scale

6 3 1

For example, in a ppm scale, let us say I have 3 peaks and in a 200 megahertz spectrometer, they are coming at 1 ppm, 3 ppm and 6 ppm, 3 peaks are there. Record it at 400 megahertz, chemical shifts remains same, 1, 3 and 6ppm. It would not change. Go to 600 megahertz, same. Go to 800 megahertz. In ppm scale, it remains unaltered. When expressed in ppm, it always comes at the same ppm in any spectrometer.

Go to now to a frequency scale. In 200 megahertz, 1 ppm is 200 Hz, 3 ppm is 600 Hz, 6 ppm is 1200 Hz. Go to 400 megahertz, see the spreading is becoming better. Now, 1 ppm in 400 Hz, this 3 ppm is 1200 Hz and 6 ppm is 2400 Hertz. Go to 600 MHz, even become better, 800 even better. See this is the dispersion. For chemical shift a field dependency is there. When expressed in frequency and when you go to higher and higher magnetic field, you see better and better dispersion. When expressed in frequency scale, there is lot of field dependency.

Functional Group	Chemical Shift in ppm		
	@ 400 MHz	@ 600 MHz	@ 800 MHz
X	2	2	2
Y	4.5	4.5	4.5
Z	7	7	7

Just to show you in the number, let us say, I am given some molecule, which has different functional groups like this, x, y and z. I want to measure their chemical shifts in ppm. At 400 megahertz, it comes at ppm. The functional group x could be CH3 or whatever it is. Then, at 600 MHz also it is same, 800 MHz also same. You go to another functional group, instead of CH3, let us say, some other CH group, which comes at 4.5 ppm at 400 MHz. It remains the same and all the spectrometers. Functional group, let us say, OH or NH is there, comes at 7 ppm. It also remains same in all the 3 spectrometers.

Functional Group	Chemical Shift in Frequency (Hz)		
	@ 400 MHz	@ 600 MHz	@ 800 MHz
X	800	1200	1600
Y	1800	2700	3600
Z	2800	4200	5600

On the other hand, I am expressing the same functional groups in frequencies at 400 megahertz, it is at 800 Hz, at 600 megahertz it is 1200 Hz and at 800 megahertz it is 1600 Hz. Like that, for different functional groups, the frequencies are different. This is the table you should remember always. Again, I gave this example to make sure that chemical shift in expression in ppm remains invariant with respect to the spectrometer frequency.

And of course, when you measure the chemical shift for any given molecule, for every functional group, over several years, several decades, lot of research has been done and peoplehave identified ranges of chemical shifts for different functional groups. For example, it is like a finger printing of the molecule for a particular functional group. If I say, there is one particular peak coming in this region, this corresponds to CH3. If a peak is coming may be somewhere here, I can say it is because of benzene, somewhere it is here, CH2 group is there or somewhere here I can say some other functional group is there. Like that, more or less it has been tabulated. Over the years, different functional groups, where it comes in a scale of 0 to 10 ppm or 12 ppm have been by and large demarcated. It is like telling different frequencies of a different radio. For example, there is a frequency here which comes at Mysore, this comes at Darwad, this comes at Bangalore, different radio frequencies. Similarly, the range of frequencies for functional groups are constant, but it is not a dogma, it can vary. By and large it is only a guideline for you to start the analysis. Ranges are known more or less. Of course, with respect to your molecule, depending upon the functional groups surrounding a given functional group, what other groups are nearby, how the charge density is distributed at the site of

the nucleus, your chemical shifts can slightly vary. But you can use this as a starting point for the analysis.

Then you go to NMR spectrum in the solution state. The solute of interest, normally it is dissolved in a solvent, a deuterated solvent, which is always used. We always have to use a deuterated solvent, so that you have to fix the field, for locking. So, that the field will not drift. If the field starts changing, your resonating frequency keeps changing. This, of course, I have discussed in one of the classes, in the previous courses, the field frequency lock, etcetera. By using this deuterated solvent at a particular frequency, where deuterium resonates in a given spectrometer, I can fix the field from drifting by electronics. Then, field will not move. Then, I can record the spectrum of proton and others, because deuterium frequency will not interfere at the proton resonating frequency. That is what we can do. So, we take the samples in NMR tubes like this, dissolve in some deuterated solvents in which your molecules dissolves, or D2O or whatever it is, and then you can record the spectrum. So, deuterated solvents normally used are acetic acid, acetone, acetonitrile, chloroform, benzene. All these are commonly used solvents and each of them have a certain resonating frequency for the protons of the solvent, because remember it is not 100 percent deuterated solvent. There is always a certain percentage of protonated solvent present. For example, if I have acetic acid, it is not 100 percent deuterated, little bit of protonated compound will be there. Then, it gives rise to CH3 and COOH peaks. CH3 group comes here, and COOH groups comes at 11.6. For example, if I take benzene, it can come at 7.2. Chloroform comes around 7.25. Like that, for different solvents by and large, we know where it comes, proton peak of that deuterated solvent, where it comes. And then, similarly for carbon-13 also, we have a range of chemical shifts. Incidentally, what happens is, the most of the solvents generally will absorb moisture from the atmosphere. There will be a residual water peak. Here where it comes also I have written. For example, if I have benzene, the residual water peak comes at 0.4 ppm. If I have dimethyl sulfoxide, DMSO as a solvent, residual water peak comes at 3.3 ppm. Like that, by and large, this information is available in this table, so that we know where the solvent peak is there, where the impurity peak or residual water peak is there. Apart from that, we can start interpreting the spectrum of your molecule.

These are the chemical shift ranges of the protons. For example, over the years, this has been tabulated. As I told you. If I have a peak from 0 to 2 ppm, I can conclude it must be CH3 group. If I have a peak here, somewhere here, I can say aromatic NH is there. If I say I am going to get a peak around 7 ppm, it will be aromatic, benzene or phenyl group must be there. I can say this is methylene region, this is a methane proton, this is methyl region. Like that, more or less ranges have been classified. Please note there is a range here. It is not a fixed value. This is also a guideline. For example, a CH3 peak, which is here, can come here also depending upon the environment, where it is situated in a molecule. So, these are all the guidelines we have for different nuclei. For example,

carbon 13, we have range of chemical shifts for different functional groups present in the molecule. Same thing for fluorine also. So, all these things have been tabulated over the years.

Research has been done and we know where these chemical shifts come for different nuclei. And you can start looking at a fluorine spectrum. If you take, if you have a CF3 group, generally it should come from minus -5o to minus 75 ppm. Start looking at a peak there. Then, this could be the starting point to say there may be a CF3 group present. Like that, we have to start analyzing the spectrum. That is a starting point. All these things are the starting points for the interpretation of the NMR spectrum. Now, we will say these are all the guidelines. How did you arrive at these guidelines? What are the factors which contribute to the shielding or to the chemical shifts? There are several factors.

$$\sigma = \sigma^{dia} + \sigma^{para} + \sigma^{I}$$

Basically, it has been divided into three parts. One is diamagnetic contribution, other is paramagnetic contribution and the third is from the neighboring groups. The diamagnetic contribution comes mainly because of the electrons immediately surrounding the nucleus; that is S orbitals which opposes the main magnetic field B_0. And paramagnetic component part comes because of electrons in P orbitals or other bonds. It adds to the main magnetic field. Remember, the main magnetic field part opposes the main magnetic field. Paramagnetic component adds to that and this generally has a little contribution in proton. It has a contribution to other nuclei. And also it is because of the neighboring group. Neighboring group where it is situated, what is that neighboring group? Whether it is electron donating group or electron withdrawing group, based on all these factors which can add or subtract. All these many factors will be there. There is not one single number. The neighboring groups, what it is contributing, how it is contributing, whether it adds to the shielding or deshielding, based on that we can arrive at the chemical shift values. These are all the factors which contribute for the total shielding at the site of the given nucleus. These are the factors which affect chemical shifts. One is the steric factor which we all know, the steric effect. Resonance effect which is there when the resonance is going on, where it is coming, whether you are sitting here or here, based on that you know whether it is shielded or deshielded. Conjugation, the hyperconjugation, heavy atom effect, that can also give rise to shielding or shifting of the peak either to high field or low field. There is a delocalization in the aromatics. If there is a substitution here, whether it is a proton donating group, electron donating group or electron withdrawing group, based on that we can also arrive at chemical shifts. This is because of delocalization in aromatics. There is also ring current effect which is going on, if I have a phenyl ring. Anisotropic effect because every bond is inherently anisotropic. How the charge is distributed generally from the center of the bond to the end. There is you can

draw a cone like this especially for CH groups, CH2 groups and CH3 groups. And depending upon whether the proton is situated here or here it is shielded.

For example, in the ethylene groups like this, if it is situated here and here it is deshielded. Like that all these factors are there. Lot of information is available in the books. These are all the factors. Many of them contribute for the shielding or deshielding. We will take one or two examples. See it is impossible to cover everything. Numerous examples are there. Numerous factors are there which contribute for the chemical shift, but one or two examples we will take it.

What is the effect of electronegativity? That we will understand. Higher the electronegativity, lower is the resonating frequency. That is what I said. Now, we consider methane. Methane is CH4. If I take the spectrum of methane, its electronegativity in the Millikan scale is 2.1 and its proton resonating frequency is 0.23 ppm. That is the chemical shift of methane is 0.23 ppm. In some books say 0.24 does not matter. Around this value is the chemical shift of methane. Now, I am going to do knock off one of the protons and put an iodine here. Iodine is electronegative. Then its electron density is 2.5 and already from 0.23 it moved to 1.98 ppm. So, that means, you move towards the lower field. And if instead of iodine, I put bromine. It is more electronegative than iodine. Already you see the chemical shift moved further down field. Instead of bromine, I put chlorine further down field and I put fluorine instead of chlorine. Then you see it comes at 4.3 ppm. Look at it 0.23 ppm was the chemical shift of methane. Just by replacing one of the hydrogen by different electronegative atom, I can move this peak from left to right and to some other value. This is the effect of electronegativity on the chemical shift.

|	$H\text{-}CH_3$	$H\text{-}CH_2I$	$H\text{-}CH_2Br$	$H\text{-}CH_2Cl$	$H\text{-}CH_2F$
E	2.1	2.5	2.8	3.0	4.0
δ	0.23	1.98	2.45	2.84	4.13

This is the inductive effect which is seen because the inductive effect is transmitted through bonds in a molecule like for example, nitro propane.
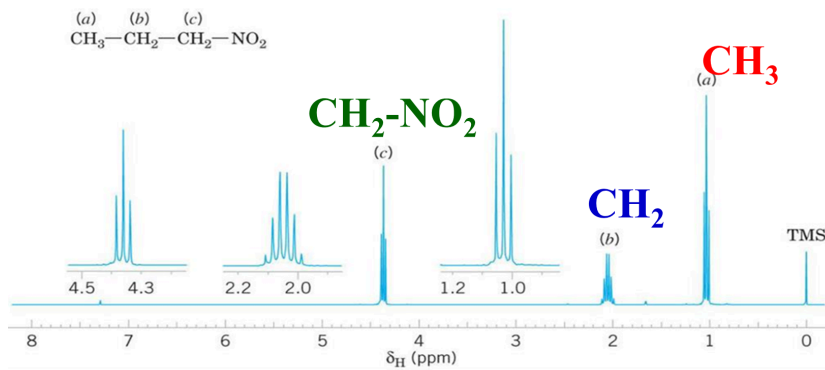
Nitro ropane has three different chemically inequivalent groups. One is CH3, CH2 and CH2NO2. There are three groups. CH3 comes at the high field, that is more shielded. That is what I said in the last class or before the last class. CH3 is more shielded than CH2 and CH2 will come here, But this CH2 comes even down field because it is attached to NO2 group. As a consequence, it comes even further down field. This CH2 attached is between CH3 and CH2. This is CH3 and this CH2 attached to NO2. Very easily with the knowledge of functional group whether the electronegative group is there and how the inductive effect is there, how this transmitted through bonds, I can start making the assignment. This is with certain knowledge of chemistry. This is what it is. And if I have different groups, the inductive effect can be seen. The OH, SH, NH2, all these groups may have an inductive effect. I have a molecule. I showed you instead of replacing one of the protons in the methane by a electronegative atom,

$$0.24 \qquad 0.80 \qquad 0.91$$
$$\text{H-CH}_3 \qquad \text{H-CH}_2\text{-CH}_3 \qquad \text{H-CH}_2\text{-CH}_2\text{-CH}_3$$

I will do one thing. I keep on lengthening the molecule. Remove one of the hydrogen, put CH3 group, remove another in between put another CH2. I keep on lengthening the molecule, proton of methane which comes at 0.23 or 0.24 ppm. Now, as soon as I added one more CH2 group, it comes at 0.8 ppm. It moves down field. I lengthen the molecule by adding one more CH2. It moved even further down field. So, the lengthening the carbon chain also decreases the shielding. So, when we decrease the shielding, the peak moves towards down field and deshielding becomes more and more with more number of electronegative atoms.

$$\text{CHCl}_3 \quad \text{CH}_2\text{Cl}_2 \quad \text{CH}_3\text{Cl}$$
$$7.27 \qquad 5.30 \qquad 3.05 \qquad \text{ppm}$$
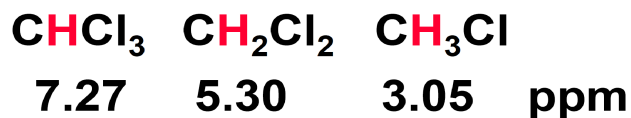
If the electronegative atoms are more at a particular site, then deshielding is higher. I take the example of CHCl3 chloroform. It comes at 7.27 ppm. There are three chlorine atoms here. Instead of CHCl3, I make CH2Cl2. There are two chlorine atoms. It already move to the high field. Instead of CH2Cl2, I make it CH3Cl. Now, there is only one chlorine atom. It moved to the further up field 3.05 ppm. So, the deshielding effect also depends upon not only lengthening the chain, but also on number of electronegative atoms, which

are there at the part -CH$_2$-Br   -CH$_2$-CH$_2$Br   -CH$_2$-CH$_2$CH$_2$Br   with the increase
in the distance from   **3.30**   **1.69**   **1.25**   **ppm**

There is directly attached bromine to the CH2 group. It comes at 3.3 ppm. I lengthen the molecule, add a CH2 in between. The effect of this bromine on this CH2 is much less. So, it moves to the high field. Add one more CH2 group. The effect of this Br on this CH2 is even much less. So, it moves to even higher field. So, the deshielding effect decreases with increase in the distance from the electronegative atom. Also there are few other factors, which generally contribute for the chemical shift, they are, mesomeric effect which depends upon electron withdrawing group or the electrondonating group, which is present.

Take for example, this molecule. It is ethylene. Here, all the protons are equivalent. There is a perfect symmetry here. As a consequence, all the four protons are equivalent. It gives rise to a single peak at 5.29 ppm. What I do is, I knock off one of the protons and put CO-CH3 group. And CO-CH3 is an electron withdrawing group. When it withdraws the electron, remember what is going to happen. These two protons move to the down field. This ppm value increased and move to the higher frequency side, down field. So, this is what happens. It is because of mesomeric effect. On the other hand, instead of putting this group CO-CH3, I can put OCH3. What is OCH3? It is not electron withdrawing. It is an electron donating group. It donates electrons. As a consequence, what happens? See, it moves to the higher field. Now, it is not deshielding, it is more shielded. So, it most goes to the high field region. This is what happens depending upon whether you have electron donating group or an electron withdrawing group. These are called mesomeric effects. They also contribute significantly for the chemical shifts.

So, basically, you look at it. There is a generic chemical shift range. If I consider the phenyl group, benzene group. Generally, it comes in the region of 7 to 8 ppm. That is the generic region for the phenyl groups. If you attach electron poor group at the ortho position, electron poor group, for example, nitrogen or CO like that; or the electron rich group like containing O or N. Then what happens? The ortho protons moves down field in this case and the para proton will move towards this side. Similarly, see, this is ortho and para, this should be meta, I think. Similarly, if I have this one, it changes; depending upon which is the functional group that you have, whether it is electron donating or electron withdrawing. Especially the effect is seen on the ortho position and in the para position.

Meta position has a different effect. I can show you by an example like this. This is a benzene. Let us say it is coming at 7.3. It should be 7.27 or 7.28. Some people have different values, does not matter, small change. Instead of proton here, I put a CH3 group. Then, it becomes a toluene. Toluene has methyl group, which is an electron donating group. Look at it, which was 7.3 here. All these protons, have moved to 7.06. Especially, you see the effect is seen in ortho and para positions, but in meta position the effect is slightly lower. This is because of mesomeric effect again. Instead of CH3, if I put NH2 what happens? The NH2 is the electron withdrawing group. Now, what is happening? Look at it. The chemical shift was 7.3. It moves to the high field, compared to benzene. Put nitro group instead of NH2. It is strongly electron withdrawing group. Then, aromatic ring will be electron-poor relative benzene and the aromatic protons are deshielded here. This is what happens. If I put methoxy, methoxy is another thing. It is strongly electron donating group. Look at it. Ortho and especially, para protons move to high field compared to normal benzene generic value. These are all less affected especially, meta. Only ortho and para are more significantly affected.

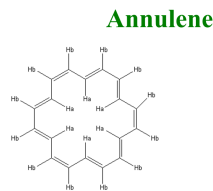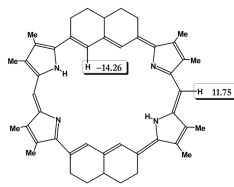**Benzonitrile. ^{1}H NMR: $\delta_{ortho} > \delta_{para} > \delta_{meta}$**

Benzaldehyde. ^{1}H NMR: $\delta_{ortho} > \delta_{para} > \delta_{meta}$

Aniline (EDG). ^{1}H NMR: $\delta_{meta} > \delta_{para} > \delta_{ortho}$

The proton chemical shift trends in few mono substituted benzenes. If you look at it, I take benzonitrile, benzaldehyde and aniline. If I take chemical shift of ortho protonzs they come at higher field, the chemical shift is larger for this, than this, than this. If I take benzaldehyde, delta of ortho protons is larger than para, than meta. If I take electron withdrawing group like aniline, the meta proton delta is more than para and ortho. This is all about the substituted benzenes; some trends about the chemical shifts, especially, ortho and para positions and the meta positions. This is what we need to understand.
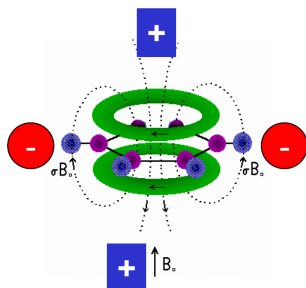
One more important effect is the ring current effect in aromatics. Especially, if I consider benzene or phenyl groups, the ring current will be there. Electrons will be circulating like this. As a consequence, it produces a field perpendicular to the plane of the ring like this. This is the B_0 position.   See, then what will happen? The proton situated above and below the plane are always shielded. Proton in the plane of the ring are deshielded. It is all because of ring current effect. The charges starts going like this. So, as a consequence, what happens? Here, it gets added up above and below the plane of the benzene ring, but

in the plane of the ring, always gets deshielded. happens, like this. The the plane of the ring are above and below are This is the reason why

Annulene

in its plane, it This is what protons sitting on deshielded, lying always shielded. all the protons of

benzene are coming between 7 to 8 PPM.

We also have effect of magnetic anisotropy. Look at this type of molecule. There is a magnetic anisotropy coming into the picture. The protons which are inside of this ring comes at minus 14 PPM. It is highly shielded and whereas, the peripheral protons are highly deshielded. Same thing, if you look at annulene, the protons which are inside this ring are shielded and it comes at -2.99 ppm.

I told you there are few examples where peaks can go even beyond TMS, more shielded. This is what happens. Protons which are inside goes to very very high field beyond TMS up to minus 3 ppm. Whereas, the peripheral protons are deshielded, comes at 9.2 PPM, more downfield. This goes more high field. These are all the effects which we can see.

Single Bond

Double Bond

Triple Bond
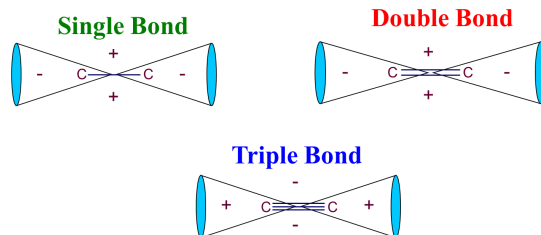
If you consider, for example, CH group, CH2 group and CH3 group, acetylene group or ethylene group, for the charge distribution, we can see a sort of a cone. Inherently, all these bonds are anisotropic. From the center of the bond, if you start drawing how the charge is distributed, you can draw a cone. For example, if I have a C single bond C molecule in ethylene groups like this, especially aliphatic and the protons which are situated in the cone are deshielded. Protons which are situated outside this cone are shielded. This is an example when you have a molecule with a C-C single bond like this. If I see double bond C, double bond C, again same. We have two cones like this from the center of the bond. Protons situated inside the cone are deshielded, above and below are shielded. On the other hand, look at a triple bond like acetylene. Acetylene you take an example. Here in this cone, protons are shielded converse of this single bond and double bond. Within the cone, if the protons are situated, they are shielded and the above and below this triple bond, the protons are deshielded. This is something strange. This is a thing which is observed especially when you have acetylene proton. If you look at the acetylene proton, which actually is more shielded.

This is what I just wanted to tell you lot of examples I gave about the chemical shifts. Too many things we can discuss. Lot of things are there. It is an ocean; NMR spectroscopy is a big ocean. There is no end for it. We can start discussing even chemical shift alone for several hours. Lot of example, lot of molecules we can take and what are the effects of different substituents and different regions, we can discuss a lot. But there is no reason to go further. I have given you the basic idea about how we can get the chemical shift in this class and we discussed a lot about varieties of factors which affect chemical shifts, starting from let us say diamagnetic contribution, paramagnetic contribution, contribution is coming because of the neighboring group. And I also told you about how do we convert PPM to frequency, frequency to PPM. What will \ happen for the field dependence of the chemical shift at different magnetic field? When the expressdc in ppm, it remains same. When expressed in frequency, they change linearly. They have field dependence that we observed. As a consequence, at higher and higher frequency, that is, if you go to high frequency spectrometer, there is a dispersion in the chemical shift. That is what also we saw and we took several examples of the factors which contributes to the chemical shift, especially both for shielding and deshielding. We took the example of molecule containing different halogens. What happens with the electronegativity changes from iodine, chlorine, bromine and fluorine. How the peak starts shifting to the down field, etc. We took the example of an electron donating group and the mesomeric effect, also with electron withdrawing group. We saw the effects of that. How peaks will move to high field or low field depending upon whether you have a electron donating group or withdrawing group. Similarly, if we have aromatics, especially the delocalization in the aromatics causes some effect. Then, the more effect is seen on the ortho proton and the para-proton than on the meta-proton. Whatever the effect we see for ortho and meta-proton for electron donating group, if it is present, converse is the

case if it is the electron withdrawing group, more effect will be seen and the meta than on the para. And then, we took the example of some of the cones like single bond, double bond, triple bond. How the charge distribution is expressed as a cone like this when you draw the charge distribution and especially when you have acetylene group like this, I said it is different from single bond and double bond like this; protons which are situated within the cone get deshielded and outside the cone gets shielded converse is the case with the acetylene group. So, these are the general examples and I said about magnetic anisotropy, I also took the examples of aniline, and others. Sometimes, you can get an sample where it is so shielded, the peak can go beyond TMS to some value. So, so many factors contribute to chemical shifts. By experience, we should know what are the factors which are contributing in a given molecule and we can start interpreting and analyze the spectrum. So, this is all about chemical shift. In the next class, we will discuss more about another interaction parameter which is scalar coupling. So, I will stop at this point. Thank you very much.