

## **Interpretative Spectroscopy**

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### **Lecture 05**

#### **Introduction to the concept of Chemical Shifts in NMR spectra**

#### **Chemical Shifts for different type of protons**

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. So, in my last lecture, I was discussing about chemical shifts, and how a chemical signal we get in NMR for a molecule, which is denoted as chemical shift and what are the implications and why we call it as chemical shift and what all the information signals give, all those things we discussed. Let us continue from where I had stopped. In my last lecture, I did mention about some of the chemical shift values for different types of protons in organic molecules. If you can see here, in methyl groups in alkane resonate at 0.9 ppm, whereas methylene groups resonate at 1.3 and methyne group CH shows chemical shift at 1.4 and when methyl group is next to a carbonyl group it comes around 2.1 and next when acetylene carbon bond hydrogen resonates at 2.5 ppm and then when CH<sub>2</sub> is next to halogens or oxygen the chemical shift comes around 3 to 4 ppm and then in alkenes the chemical shift due to H comes around 5 to 6 ppm and similarly methyl groups comes at 1.7 and aromatic region in phenol comes around 7.2 or even benzene for that matter and in case of toluene methyl groups resonate at 2.3 ppm and aldehydic hydrogen comes around 9 to 10. And then acidic carboxylic acid H comes around 10 to 12 ppm, and in alkyl alcohols OH groups comes at 2 to 5, whereas in case of aromatic alcohols or phenols it comes around 4 to 7 ppm. In case of amines H on nitrogen resonates in the region 1.5 to 4 or it can go further depending upon the type of substituents we have and also the nature of the molecule. Here I have given different nuclei having nuclear spin I equals half and also I have considered hydrogen with instrument frequency 100 megahertz (MHz) and you can see what is the corresponding frequency for different nuclei, all having nuclear spin value of I equals half ( $I = 1/2$ ) and

also I have given natural abundance here H is 99.9% and it is 100 MHz and the standard we are using is tetramethylsilane in case of  $^{13}\text{C}$  also we use tetramethylsilane then if you compare the frequency this is one fourth of it and similarly when you look into  $^{19}\text{F}$  its abundance is 100% we don't have any other nuclei other than  $^{19}\text{F}$  so here the frequency corresponding to 100 MHz in proton is 94 and similarly you can see here for  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{77}\text{Se}$ ,  $^{103}\text{Rh}$ ,  $^{117}\text{Sn}$  as well as  $^{119}\text{Sn}$  and  $^{129}\text{Xe}$ ,  $^{183}\text{W}$ ,  $^{195}\text{Pt}$  and  $^{199}\text{Hg}$ . So, for all these corresponding frequencies are given here and this gives you approximate ratio from that one you can calculate, if the frequency is known for hydrogen, you can calculate the corresponding frequency for other nuclei and also, I have given the standard references for some of these nuclei. So, before I proceed further, let me try to make familiar with the equation I showed you. That equation is; you just recall  $h\nu = 2\pi\hbar\omega$  this is nothing but  $\omega$ . For  $\omega$  it is  $2\pi\nu$ , if you substitute for this one here, this will be equal to  $\gamma h B_0$ . So now this  $h$  will cancel so then what we left is  $\nu = \gamma B_0 / 2\pi$  so this is the equation we are going to use in NMR extensively. So, let us try to understand the utility of this equation in calculating the precision frequency or Larmor frequency for different nuclei placed in a magnetic field of different magnetic field strength so now one such problem is here you can see here.

Calculate the radio frequency necessary for the transition of  $^{11}\text{B}$  nucleus at a magnetic field of 10 tesla (10T).

So, use this equation, of course here what is required is you need to know this gyromagnetic ratio that is given here and also 10 tesla is given simply use this equation here so  $\nu = \gamma B_0 / 2\pi$ . Let me write here:  $8.584 \times 10^7$ , into 10 over  $2 \times 22/7$  [ $\nu = (8.584 \times 10^7 \times 10) / 2 \times (22/7)$ ]. So now if I simplify, this one will become  $8.584 \times 10^8 \times 7/44$ . On simplifying this one, what we get is 136.5 megahertz (MHz). So, this is the radio frequency necessary for the transition of  $^{11}\text{B}$  when it is placed in a magnetic field of 10 tesla (10T). So, you should be able to calculate this one of course  $136.5 \times 10^6$  hertz (Hz), it becomes 136.5 megahertz (MHz).

Let us look into one more example so that you will become more familiar. The other two problems I have shown here are: if the radio frequency of approximately 200 megahertz (MHz) is required for the transition of  $^{31}\text{P}$  nucleus and 400 megahertz (MHz) required for the transition of  $^1\text{H}$  nucleus. Calculate the applied magnetic field strength in gauss as well as in Tesla. So, you should remember 10,000 Gauss equal to 1 Tesla (10,000 gauss = 1T) that also I have given here. So, let us do this one now: Again, here use the same equation  $\nu = \gamma \times 2 \pi \times B_0$ . So now we have to find out  $B_0$  in case of 200 megahertz (MHz) for phosphorus NMR. 200 megahertz (MHz) can be converted into 200 hertz (Hz). For phosphorus, gyromagnetic ratio is given.

Here, 10.840 into 10 raise to 7 into B-naught ( $B_0$ ) and now again 2 into 22 by 7 [ $200 \times 10^6 = (10.840 \times 10^7 \times B_0) / 2 \times (22/7)$ ]. On simplifying this one, it will become 200 into 22 into 2 into 10 raise to 6 equals 10.840 into 7 into 10 raise to 7 B-naught ( $200 \times 44 \times 10^6 = 10.840 \times 7 \times 10^7 \times B_0$ ). If you simplify this one what you get is 115,000 Gauss. This is nothing but 11.5 Tesla (T). So, this is the magnetic field and this corresponds to 500 megahertz (MHz) instrument. Okay, this corresponds to 500 megahertz (MHz) instrument, so this corresponds to 500 megahertz (MHz) instrument. I have given earlier this table of conversion of magnetic field strength and the corresponding frequency. You can just check from that data, it comes approximately 115,000 Gauss that is nothing but 11.5 Tesla (T) this corresponds to 500 megahertz instrument and if the 400 megahertz (MHz) instrument  $^{31}\text{P}$  nuclear require about 161.2 megahertz (MHz) radio frequency.

Now let us look into the second one which is 400 megahertz (MHz) for  $^1\text{H}$  so it is the same you can do it again. Use the same equation gamma into  $B_0$  over  $2 \pi$  ( $\nu = \gamma B_0 / 2\pi$ ) so this is 400. So simply I can write it here. 44 equals gamma is given here, for proton this is 26.753 into 10 raise to 7 and then this 7 whatever was there it goes here so this is nothing but 2 into 22 by 7 so 7 comes here and 2 is going here, so that is what I have written here ( $400 \times 44 = 26.753 \times 10^7 \times 7 \times B_0$ ). Now B-naught ( $B_0$ ) can be calculated from this one 400 into 44 divided by 26.753 into 7 so this will give: into 10 to the power of minus 7 [ $B_0 = (400 \times 44) / (26.753 \times 7) \times 10^{-7}$ ]. So then when you convert into megahertz what you get is approximately 9.39 Tesla (T) or that is equal to 9.4 Tesla (T). so that means basically 94,000 Gauss, so this is the magnetic field strength for this one

Let us move on to further discussion. Now let us look into the aromatic protons, for example if you take a benzene molecule and subject to the NMR what would happen to its chemical shift? We all know that the chemical shift range is 7 to 8 and why that happens, you can see clearly here and of course here also we should look for all possible orientations of benzene molecule in a magnetic field strength of  $B_0$  and then if you take average of all of them you can consider only two possible orientations. One is perpendicular, one is parallel and here I have considered perpendicular one. In this one, the circulating electron density would generate a magnetic field or induced magnetic field generated because of circulation of electron density in the benzene molecule under the influence of  $B_0$  is aligned with the magnetic field  $B_0$ . You can see the direction shown here. This is aligned with the magnetic field, as a result what happens, the net magnetic field experienced by the protons in aromatic molecules would be going to high frequency shift so that is the reason we call it as deshielding. Then how about the parallel one; so parallel one you can consider here; little circulation of electron density and hence whatever the magnetic field generated can be totally ignored or neglected so that means not much contribution is coming from the parallel orientation the bulk of the influence of electron density that generates induced magnetic field comes from the perpendicular orientation that is responsible for pushing the protons into deshielded region of chemical shift range 7 to 8 ppm. So now let us look into vinyl protons. Again, vinyl protons, I have considered the perpendicular one and in the parallel orientation same thing is observed what I had described in case of aromatic molecules. So, in this perpendicular one what would happen? Again, induced magnetic field is acting in this direction, that is reinforcing the applied magnetic field as a result, the net magnetic field experienced by vinyl protons is much more compared to the protons in the absence of induced magnetic field. As a result, the net effect is deshielding, they appear in the range of 5 to 6 ppm, and again in this case also perpendicular orientation has little circulation of electron density and hence there is not significant magnetic field developed. Because of this effect and hence that can be ignored. So now let us consider aldehydic proton. Again, in this case also we can ignore the parallel orientation, where the induced field magnitude is negligible so we have to focus on again the perpendicular

orientation. In case of perpendicular orientation again this group is attached to electronegative oxygen atom. Again, in this case also, the induced field generated because of this, ring current produced is aligned with the applied magnetic field. Here you can see: applied magnetic field as a result, the net effect is deshielding or shifting the signal to high frequency and it appears in the range of 9 to 10 ppm and same analogy holds good in case of acetylenic protons also. Here the parallel one is what dominates here, and in this case, because of the alignment of hydrogen protons in this way, the induced field that we are seeing is opposing the applied field. As a result, what happens, the net shielding in case of acetylenic proton and hence the chemical shift appears in the region of 2.5 ppm and then if you consider the perpendicular orientation, again here in case of perpendicular orientation, there is no significant contribution from  $B_i$  developed. Here, it can be ignored only the parallel one is what matters here so once if you know, it is very easy to understand why in a given molecule, nuclei are shielded or deshielded or appear in high frequency region or low frequency region, what would happen to the OH and NH protons. Chemical shifts of OH and NH depends on concentration. In concentrated solutions, hydrogen bonding deshield the protons. So signal is around 3.5 for NH and 4.5 for OH so that means if considerable hydrogen bonding is there that results in deshielding of the protons involved in hydrogen bonding and hence the chemical shift due to NH protons or OH protons would shift respectively, to 3.5 ppm and 4.5 ppm. That means hydrogen bonding is there. For molecules in solution, and one should be able to diagnose and tell approximately to what extent the hydrogen bonding is there by just simply looking into the chemical shifts of such molecules. Another reason for broadening of this OH and NH peaks in NMR is because of proton exchange between the molecules. Now let us look into carboxylic acid, acetic acid is considered and  $\delta_{11}$  ( $\delta_{11}$ ) for OH comes here this is for OH, whereas for  $\text{CH}_3$  it comes around 2.1 here. here considerable deshielding is observed for carboxylic proton and appears at 11 ppm. Now look into another molecule here, we have three different type of protons are there. So, one is next to carbonyl group, another one is next to oxygen and another methylene group is in between two carbonyl groups and the corresponding chemical shifts I have shown. This one comes around 2.25 so this is here and then this is 3.41 so this is here and then this one is here and again what you should notice is equivalent hydrogen have the same

chemical shift. That means all hydrogen present on this carbon show single resonance and similarly all hydrogen present on this carbon show single resonance and all hydrogen present on this methyl group also show single resonance. You should remember we will come back to looking into why they are equivalent and whether there can be some nonequivalence and hence we can see some interaction of the hydrogen atoms present on the same carbon atom.

So now let us look into the importance of intensity of signals. You can see here in this molecule, we have two type of hydrogen atoms: I have designated H with blue color and red color. here this is one methyl group is there and this carbon we have three methyl groups are there and then if you just look into the signals by simply looking into the intensity you should be able to tell which signal is for which group so this one shows chemical shift here and this one shows chemical shift here and if you just measure the intensity it is almost three times if this is say this quantity is there and this is about three times here you can see here three times one two three so that means basically the intensity what we see can also tell you about how many such groups are there and how many protons are there so that understanding the structure and elucidation of the structure becomes rather easy. Now I have simplified here in the graph you can measure and you can see the intensity here and then you can show here and up to here if you go it can clearly tell you about here nine protons are there and here three protons are there that means it is one is to three ratio is there that could be clearly seen from this one so that means intensity looking into the intensity is very very important in identifying similar type of groups in the molecule. So, the area under each peak is proportional to the number of protons. So, this is shown by integral trace this is what we call it as integral trace usually you can get this information directly from NMR spectrum. Now let us consider this molecule here, three protons are here, two protons are there and here one is there and then we have here six and that means basically one, two, three, four, these two are one and this is two this is three and this is four.

Four type of groups are here and we should have four signals of course one is here one is here one is here one is here and just by looking into the intensity, we should be able to

tell these two will be corresponding to this one and now  $\text{CH}_2\text{CH}_3$  is there  $\text{CH}_3$  will be coming to this one and then  $\text{CH}_2$  will be coming to this one so simply by intensity you should be able to tell and then values are there so you can clearly see now where exactly these signals are located and this is the integration. So far, whatever we saw, we saw only single signal do we see always one signal no matter how many protons are there, how many nuclei are there that is not the case. Now let us look into this term, that is spin-spin splitting. So non-equivalent hydrogen on adjacent carbons have magnetic fields that may align with or oppose the external field; you should remember when we are subjecting a molecule to the magnetic field under NMR conditions. If you are focusing on, let us consider an ethanol molecule, here so when I am focusing on this methyl group and of course here methyl group; what happens, circulation of electron density also induces a magnetic field and that can be aligned or oppose the magnetic field based on that one we get a chemical shift at some reason so but on the other hand when these protons are precessing you know the neighboring would not keep, they will also be precessing as a result what happens, the induced magnetic field they generate can also influence on the chemical shift of this one and to what extent they influence depends on whether they are aligned with the magnetic field or opposing the magnetic field so that means the neighboring protons can split the adjacent protons and adjacent carbon atom depending upon how many such protons are there and how they are aligned or how they are behaving in the magnetic field so this would lead to the term called spin-spin splitting. As a result, signals would be seen as multiplets so that means this magnetic coupling causes the protons to absorb slightly down field when the external field is reinforced and slightly up field when the external field is opposite. That means the magnetic field they generated can be something like this or can be something like this. If they are something like this, you can see signals are more deshielded and if they have something like this shielded so this is how they can influence and that means all possibilities should be considered so signal is split. So now another useful property, that means now I am giving some more details about spin-spin splitting so another useful property that allows NMR spectra to give structural information is called spin-spin coupling, which is caused by spin coupling between NMR active nuclei that are not chemically identical. If they are chemically identical, what would happen, you will see only one signal, for example, if we

take ethane molecule  $2\text{CH}_3$  are there. They are chemically equivalent and you will see only one signal but if you take  $\text{CH}_3\text{CH}_2\text{OH}$  or something  $\text{CH}_3\text{CH}_2\text{Cl}$ , then the neighboring ones are different so then you can see interaction between them and that what we call it as spin-spin coupling. So different spin states interact through chemical bonds in a molecule to give rise to this coupling which occurs when a nucleus being examined is disturbed or influenced by a nearby nuclear spin. So, in NMR spectra, this effect is shown through peak splitting that can give direct information concerning the connectivity of atoms in a molecule, which shares the same chemical shift do not form splitting peaks in an NMR spectrum, so this is very important. In general, neighboring NMR active nuclei, three or fewer bonds away leads to this splitting. This splitting is described by the relationship wherein neighboring nuclei results in  $n + 1$  peaks ( $n + 1$ ), and the area distribution can also be seen from the Pascal triangle. So being adjacent to a strong electronegative group such as oxygen, can prevent spin-spin coupling so that means in between two methyl groups you have oxygen that can prevent the interaction of these two groups. For example, a doublet would have two peaks with intensity ratio of 1 is to 1 (1:1), while a quartet would have four peaks of relative intensities 1 is to 3 is to 3 is to 1 (1:3:3:1). This information comes from Pascal triangle. The magnitude of the observed splitting depends on many factors and is given by coupling constant  $J$  which is in units of hertz.

So, let us discuss more facts and look into more examples to understand in a better way the spin-spin coupling in my next lecture until then have an excellent time reading about spectroscopy. Thank you.