Interpretative Spectroscopy

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Lecture 06

N+1 Rule and Pascal's Triangle

Hello everyone, once again I welcome you all to MSB lecture series on Interpretative Spectroscopy. In my last lecture I was discussing about spin-spin splitting, so that means often when we run NMR spectrum for a molecule we see not a single line and single line consists of many lines with different heights that means different intensity, why that happens? So, I started discussion on that one, let me continue from where I had stopped. As I mentioned another useful property that allows NMR spectra to give structural information is called spin-spin coupling which is very important and it is very vital in understanding and diagnosing the molecule while elucidating its structure which is caused by spin-spin coupling between NMR active nuclei. You should remember, NMR active nuclei that all are not chemically identical. Different spin states interact through chemical bonds in a molecule to give rise to this coupling. That means if you have two carbon atoms, two carbon atoms are connected by a bond or two in that case protons present on both the carbon atoms interact provided they are in different chemical environments. In NMR spectra, this effect is shown through peak splitting that can give direct information concerning the connectivity of atoms in a molecule. Not only that, and also, they can precisely tell you how many equivalent protons are there on the carbon, and the adjacent carbon atom.

Nuclei which share the same chemical shift do not split the peaks in an NMR spectrum. This is very important. Nuclei which share the same chemical shift do not cause splitting peaks in an NMR spectrum. In general, neighboring NMR active nuclei, three or fewer bonds away give this coupling.

In special cases, even if they are four to five bonds away, they can still interact and influence in splitting the signal. The splitting is described by the relationship wherein the neighboring nuclei results in N plus one (n + 1) peaks that means if you have N number of proton atoms on adjacent carbon atom that leads to the splitting of the adjacent one by N plus one peaks (n + 1). If CH_2 is there, then it will make the neighboring one into three (1 x 3). If CH_3 is there, then the neighboring appears as four, something like that and that information directly comes from Pascal triangle for a particular I value. So, you should remember Pascal triangle will varies with I values.

For I equal to half, we have a different Pascal triangle, I equal to one, we have a different Pascal triangle and we have to use a totally different Pascal triangle when I equal to three by two or five by two. However, being adjacent to a strongly electronegative group such as oxygen that can prevent spin-spin coupling between two neighboring groups where we have protons. For example, a doublet would have two peaks with intensity ratio of one is to one while a quartet would have four peaks with a relative intensity of one is to three is to three is to one (1:3:3:1) or if you have a triplet the relative intensity will be one is to two is to one (1:2:1). So, the magnitude of the observed spin-spin splitting depends on many factors and is given by the coupling constant *J* which is in units of hertz (Hz). So, when we see this triplet (t) quartet (q) or doublet (d) the spacing between the two lines we call as coupling constant *J*. It is always represented in units of hertz (Hz).

Also, we get information about peak intensity. The size of the peaks in the NMR spectra can give information concerning the number of nuclei that give rise to that peak. So, this is done by measuring the peak area using integration that information again comes from NMR spectra. Even without using integration the size of different peaks can still give relative information about the number of nuclei, even if you do not have that integration simply by looking into the height of the peaks. We should be able to judge but sometime it can be misleading and we should not just go by the height. Sometime what happens if the peak broader, the height is small that can occupy more larger area and still that can be having considerable peak height. One should be very careful about that one, and it is

better to integrate rather than looking into the height to decide the intensity. For example, a singlet associated with three hydrogen atoms would be about three times larger than a singlet associated with a single hydrogen atom. What are the limitations of NMR then? Despite its ability there are several limitations that can make NMR analysis difficult or impossible. In certain situations, one such is that the desired isotope and element that is needed for NMR analysis may have little or no natural abundance. For example, I am interested in a particular isotope of a nuclei which is NMR active but that may be in very insignificant quantity in the natural resources. That means, for example if you consider the natural abundance of NMR active ^{13}C, with I equals half (I = 1/2) is about 1.1 percent, whereas the rest is 12 carbon ^{12}C which is NMR inactive, because I value is 0 (I = 0). Still 1.1 percent is quite sufficient to plot ^{13}C NMR and look into NMR spectrum. It can still help to great extent in elucidating the structure and getting lot of information. However, in case of oxygen, the active isotope for NMR is 17 oxygen (^{17}O) which is only 0.035 percent naturally abundant. This means that there are certain elements that can never be measured through NMR. So, no matter how much quantity we take, it is very difficult to identify and run ^{17}O NMR spectra for a molecule where we have insignificant quantity of ^{17}O isotope. In case if you want to run ^{17}O NMR it has to be enriched.

So another problem is that some elements have an extremely low magnetic moment (μ), that means the sensitivity is very very low. The sensitivity of NMR machines is based on the magnetic moment of the specific element, but if the magnetic moment is too low, it is very difficult to obtain NMR spectra with enough peak intensity to properly analyze. So, these are the limitations of NMR. One is less abundance and another one is the low magnetic moment value. What is the basis for spin coupling? Well already I discussed some of those in a couple of slides earlier but let me go back again and repeat some of these facts so that understanding would be much better. NMR signals arise when nuclei absorb a certain radio frequency and are excited from one spin state to another one if the energy we are supplying is equal to the Larmor frequency. Then flipping of this one takes and that we call it as nuclear transition and the exact frequency of electromagnetic radiation that the nucleus absorbs depends on the magnetic environment around the nucleus. That means whether the given nucleus is shielded or deshielded also should be

considered. This magnetic environment is controlled mostly by the applied field but is also affected by the magnetic moments of nearby nuclei. So, nuclei can be in one of many spin states giving rise to several possible magnetic environments for the observed nucleus to resonate. This causes the NMR signal for a nucleus to show up as a multiplet or multiplets rather than a single peak. Because of the interference of magnetic field generated by neighboring nuclei what happens the signals will be split into multiplets 1, 2, 3 or 4 depending upon the magnitude of the field and also number of such nuclei that are generating induced magnetic field. In NMR experiments, only nuclei with I equal to non-zero ($I \neq 0$) will show up in NMR spectrum. Again, I am telling you so when I equals 0 ($I = 0$) there is only one possible spin state and hence nucleus cannot flip between states and it cannot flip since the NMR signal is based on the absorption of radio frequency and the nuclear transition from one spin state to another one, plus half to minus half or 1 to minus 1 ($I = \pm 1/2$ to ± 1). Nucleus with I equal to 0 ($I = 0$) neither show up NMR nor cause splitting of other NMR signals, because they have one possible magnetic moment. This simplifies NMR spectra, in fact this also comes very handy in simplifying the NMR spectra, in particular, for organic and organometallic compounds greatly since the majority of carbon atoms are 12 carbon (^{12}C) which have I equal to 0 value ($I = 0$).

So, I have given a typical spectrum here, for chloroethane (C_2H_5Cl) and you can see here, we have a triplet of 1 is to 2 is to 1 (t, 1:2:1) intensity and we have a quartet of 1 is to 3 is to 3 is to 1 intensity (q, 1:3:3:1) for this methylene protons and a triplet for methyl protons (CH_3) how we get triplet here and how we get quartet here. I will show you after a couple of slides. So now for a nucleus to cause splitting it must be close enough to the nucleus being observed to affect its magnetic environment. For example, if a particular group of protons present on a particular group are influencing the splitting, they should be on the adjacent carbon atom or at least they should not be beyond 3 or 4 bonds that is what it means. The splitting technically occurs through bonds and often we can also come across through-space coupling also that I would take up at the end. So here the splitting technically occurs through bonds, not through space. So as a general rule, only nucleus separated by 3 or 4 bonds can split each other. However even if a nucleus is close enough to another, it may not cause splitting. For splitting to occur the nuclei must also be non-equivalent as I mentioned in case of ethane (C_2H_6), we have two CH_3 groups and

both the CH_3 groups are not splitting each other because both are chemically equivalent that means there must be some non-equivalence split the neighboring signals.

To see how these factors affect real NMR spectra, consider the spectrum for chloroethane: there are two groups of peaks in the spectrum as I mentioned a triplet and a quartet. These arise from the two different types of I equals non-zero nuclei in the molecule. Yes, the protons on the methyl (CH_3) and methylene (CH_2) groups and the multiplet corresponding to CH_3 proton appears with a relative integration, the peak area comes here is 3 one for each proton and is split by the two methyl protons n equal to 2 ($n = 2$) which results in N plus 1 ($n + 1 = 2 + 1 = 3$) peaks that is 3 which is a triplet (t). So, the multiplet corresponding to CH_2 protons has an integration of one for each proton and is split by 3 methyl protons N equals 3 which results from n plus 1 ($n +1 = 3+1 = 4$), that is 4 peaks which is a quartet and each group of nucleus splits the other. So, in this way, they are coupled, that means both are coupled here and if you measure the spacing between the lines here, and the lines here, that is similar. This the spacing what we call between the two lines in a chemical shift as coupling constant and is represented in Hertz (Hz). To see how these factors, affect real NMR spectra, again

To see how these factors, affect real NMR spectra, consider the spectrum for chloroethane. There are two groups of peaks in the spectrum, a triplet and a quartet. These arise from the two different types of $I \neq 0$ nuclei in the molecule, the protons on the methyl and methylene groups. The multiplet corresponding to the CH_3 protons has a relative integration (peak area) of three (one for each proton) and is split by the two methylene protons ($n = 2$), which results in $n + 1$ peaks, i.e., 3 which is a triplet. The multiplet corresponding to the CH_2 protons has an integration of two (one for each proton) and is split by the three methyl protons ($n = 3$) which results in $n + 1$ peaks, i.e., 4 which is a quartet. Each group of nuclei splits the other, so in this way, they are *coupled*.

So now let us consider now 1,1,2-tribromoethane. Here the protons on adjacent carbon are non-equivalent. So why this doublet (d) and a triplet (t). This one shows a triplet (t)

whereas these two show a doublet (d) here. So how that happens, let us look into it and then values are given here we can see 4.26, 4.26, these two are showing a doublet, whereas a triplet is centered at 6.51. For this one we give only one value the middle one. If we have 5 peaks, you know the middle one, If, we are taking about 6 peaks, value between 3 and 4 is taken as chemical shift and here chemical shift is 6.51. So now we have to see why this is doublet and why this is a triplet. Let us first look into this H_a signal. H_a so first this is split by these two into triplet we have two protons here and the magnetic field generated by both the protons can be aligned with the magnetic field this is more towards the deshielded region and then in this case what happens one can be upward one can be downward this is one possibility, so we can also have this kind of orientation. If you represent this one and two and one and two one and two both are upwards and one is up and two is down and now one can be down and two can be up this is another possibility and then we cannot have any other possibilities now the third one will be something like this one and two so that means now if you just see these two are degenerate so this is one set and this is two set and this is one set so this is how the signal due to H H_a appears as a triplet. This is for H_a so now let us look into H_b. We have to see H_b signal, so these two will be split based on the magnetic field generated with this one, so now one can be something like this only one is there or one can be something like this only two possibilities are there. As a result, what happens either this one can influence its chemical shift as a result what happens it will come little bit deshielded and this one will be little bit shielded so we get two peaks two lines of equal intensity. So, this is how the splitting can be seen and overall one can write something like this and this spacings are identical, so this we call as J and if you see; one, two, three so this we call it as three J_{HH} ($^3J_{HH}$) coupling, okay. Even if you want to be more precise you can say that one is a superscript and this is subscript and this should be in italic this is how the coupling constant is presented. So, this is how a typical coupling constant is represented so now what is this n plus one rule ($n + 1$). So if a signal is split by n equivalent protons, it splits into n plus one peaks ($n + 1$), that means the relative peak intensities of symmetric multiples of first order and this Pascal triangle that predicts number of peaks with I equals half (I = 1/2), it is very unique for this one and also this holds good only for first order spectrum that means if I say first order spectrum that means something else can

also be there yes that is called second order spectrum. Second order will be totally different so that I shall discuss after completing about first order spectrum and looking into more examples. So, in a typical first order spectrum, and if the I value is half (I = 1/2), then we can use very effectively this Pascal triangle for example. When number of equivalent protons causing splitting is zero if you have nothing then only singlet will be observed, because n plus one n is zero ($n + 1 = 0 + 1 = 1$). So only one will be there and if only one is there, then we will see n plus one equals to two lines ($n + 1 = 1 + 1 = 2$). will be there in one is to one ratio (1:1), and if you have two neighboring protons are there, they cause this one into a triplet. Then intensity will be one is to two is to one (1:2:1), and then if three are there, we get a quartet that is one is to three is to three is to one (1:3:3:1) and then if four are there quintet, we get one is to four is to six is to four is to one ratio (1:4:6:4:1) and then if five are there then n plus one will be sextet we get six lines the relative intensities are one is to five is to ten is to ten is to five is to one (1:5:10:10:5:1) and, then if six lines are there, we get a septet then intensity ratio will be one is to six is to fifteen is to twenty is to fifteen is to six and one (1:6:15:20:15:6:1). So, this is how if you name one, second one can be written. There is no need to remember this one next one you can write one four six four one you can write here and next one is one five and then ten and then ten and five one you should be able to write so now it is one is there one six is there and then fifteen is there and then this is twenty and then again fifteen is there and six is there so you can keep on writing like that so once we know up to here in extrapolating that one and writing for higher number of lines should be very easy using this Pascal triangle. Pascal triangle is for I equal to half value (I = 1/2). Similarly when I equal to one (I = 1), it changes and now, if you see for example, we have zero you know nuclei which are influencing, still we get n plus one we get one peak and then when we have one we get three peaks because n plus one here we have to use two n i plus one two n i plus one we should use i is the value two into if say one is there and then this is one plus one i value is one i value what we are considering is one you get three lines ok this is what is there and if two are there two into two plus one so we get five this is how you can calculate and if three are there three into two plus one so we get seven lines so you should be able to calculate so it five eleven and six thirteen and this is the corresponding intensity ratio for number of peaks it goes like this so this is this

Pascal triangle holds good for those nuclei which have I equal to one value (I = 1). I have written another Pascal triangle for I equal to three by two (I = 3/2). For example, if you are using say eleven boron ^{11}B ok I equals three by two (I = 3/2) and if you come across any spectrum and if you have more number of lines, we can conveniently use this Pascal triangle to calculate the relative intensities so here again if you simply take zero so here what happens two n I plus one (2nI + 1). So, zero means it becomes only one. If you have one, then two into one into three by two plus one (2 x 1 x 3/2 + 1 = 4). So, we get four lines here. What would happen if two are there, two into two into three by two plus one, so it becomes seven lines (2 x 2 x 3/2 + 1 = 7). and similarly if you go for three, here three into two into three by two plus one (2 x 3 x 3/2 + 1 = 10). So, we will get three into three nine plus one ten lines, so ten will be there and similarly you can go for four, we get thirteen (2 x 4 x 3/2 + 1 = 13). That means if four equivalent nuclei with I equal to three by two (I = 3/2) are splitting, then thirteen lines will be there and the corresponding intensity will be this one shown here. We have some rough idea about coupling constants. What we have to understand is equivalent protons do not split each other so that means, if you consider a CH_3CH_2OH, and these are equivalent protons. They do not couple each other, that means if I expand them, we write like this. These are all geminal, that means when they are equivalent geminal coupling is not observed in first order spectrum. The protons bonded to the same carbon atom will split each other if they are not equivalent due to unsymmetrical nature of the molecule due to some reason. If the two hydrogen atoms present on a carbon are non-equivalent because of unsymmetry present in the molecule or molecule is differently substituted on both the ends. In that case geminal coupling can be observed. In that case we come across second order spectrum. Protons on adjacent carbon atoms normally will couple provided they are not chemically equivalent. They normally do not couple if separated by four or more bonds or show very weak coupling. Let us discuss more interesting aspects about coupling constant in my next lecture until then have a good time thank you. Thank you.