One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture No 33
Analysis of ^{1}H NMR Spectra Examples

Welcome back, in the last couple of classes we discussed varieties of NMR parameters, like chemical shift, scalar coupling, coupling strengths and multiplicity pattern and also I introduced to you the Pople nomenclature, where strong and weak coupling spins can be defined by the roman alphabets. For example, two weakly coupled spin system, if it is there, we refer to as AX spin system. If we have strongly coupled we denote this with AB, similarly for more coupled spin system, like 3 or 4 we represented them, by different Pople nomenclatures and also we discuss about what happens to a Pople nomenclature when there are chemically equivalent nuclei; when there are more spins present, groups of equivalent spin present like CH2 groups, CH3 groups, etc. ; how to represent them by Pople nomenclature.

I took one or two examples of analysis such spectra like; AX, AB, A2, AMX and quickly we saw some of the analysis of the spectra of AA'X, AX2 etc. Like the there are lot of things we can discuss, lots of spin systems can be analyzed. In fact this can be a subject of discussion by itself. So what I will do is to continue today with the real analysis of the 1H NMR spectra with typical examples.

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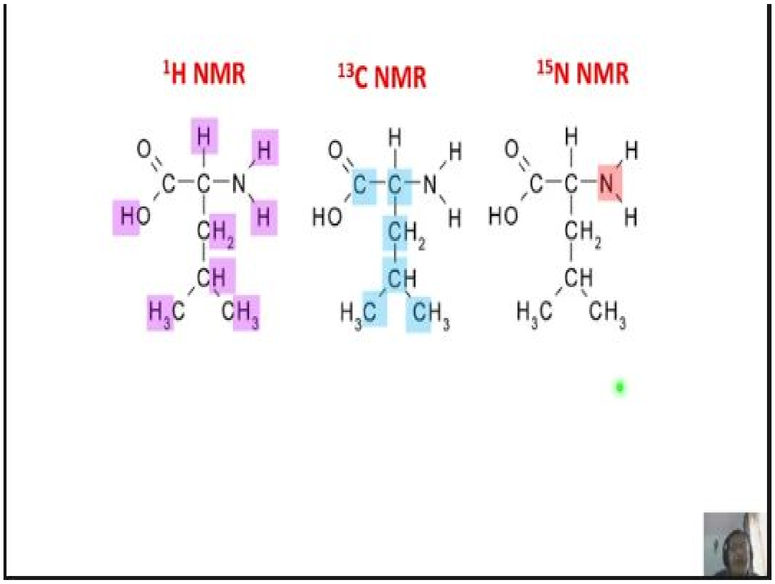

^{1}H NMR ^{13}C NMR ^{15}N NMR

Now momentum I say 1H NMR, what can I get from that? Supposing if I ahve a molecule like this, if I take a proton NMR spectrum; I can get the information of the chemical shifts of all these protons, there are coupling interactions etcetera. So, I will be getting more information about total structure of this molecule; proton positions, who are their nearest neighbors’ etcetera, I can do.

If I want to get the carbon 13 skeleton or carbon 13 information of this molecule, I have to do the carbon 13 NMR. So if I take carbon 13 NMR, I will get information about these carbons in this molecule. If you also see carefully, this molecule also has nitrogen. I can take nitrogen 15 NMR and get information about nitrogen present in the system. Although you can look at very carefully this one more NMR active nuclei like this 17O, this also can be studied, if one is interested in oxygen, then we can get information about oxygen 17 of the molecule.

So essentially depending upon the molecule of your interest, and the type of NMR active nuclei present how many different NMR active nuclei that are present, you can study that type of NMR spectrum; start the analysis by assignment of the peask, get the structural information. First you get spectral information like chemical shifts, coupling constants, etc. and I will tell you as we go ahead later you can use this information to get the structure, conformation and dynamics of these molecules.

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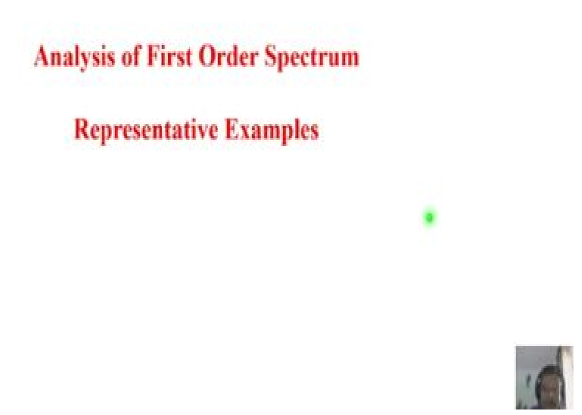

Analysis of First Order Spectrum

Representative Examples

Now I am going to take, as far as the analysis is concerned, the first order spectrum with some representative examples. Some of them are representative.

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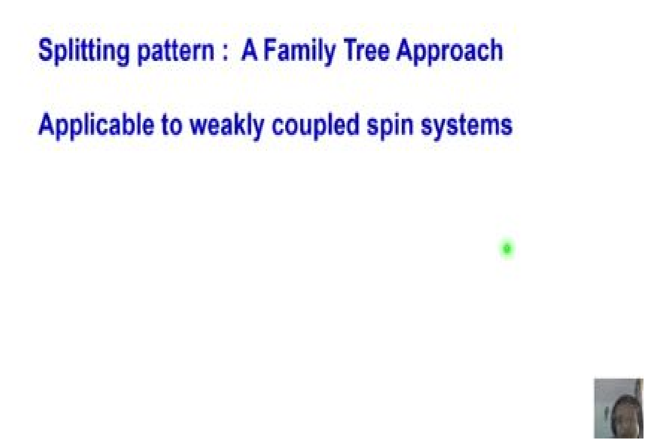

Splitting pattern : A Family Tree Approach

Applicable to weakly coupled spin systems

First, of course, I analyzed by family tree approach and we discussed this at the end of the scalar couplings; where it was applicable to the weakly coupled spin system.

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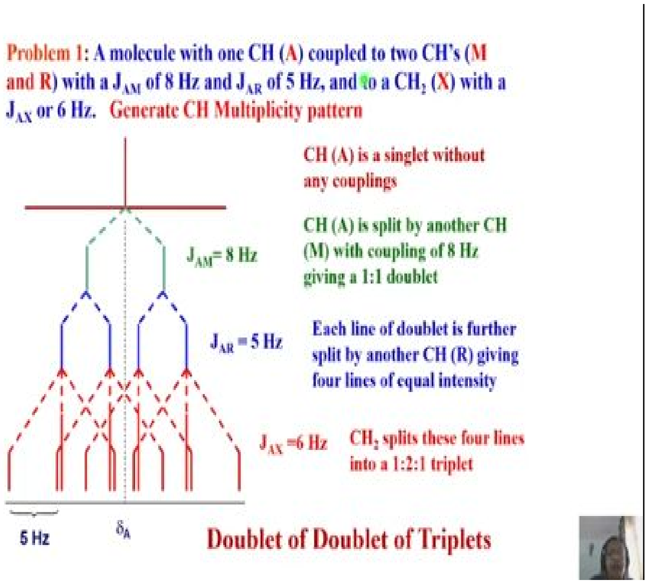

Problem 1: A molecule with one CH (A) coupled to two CH's (M and R) with a J_{AM} of 8 Hz and J_{AR} of 5 Hz, and to a CH_2 (X) with a J_{AX} or 6 Hz. Generate CH Multiplicity pattern

CH (A) is a singlet without any couplings

CH (A) is split by another CH (M) with coupling of 8 Hz giving a 1:1 doublet

Each line of doublet is further split by another CH (R) giving four lines of equal intensity

CH_2 splits these four lines into a 1:2:1 triplet

Doublet of Doublet of Triplets

We are looking at this proton CH which is coupled to two other protons, we discussed this problem; and we understood; we generated the multiplicity pattern for this proton. Let us say this proton is coupled to two other protons CH, one with a coupling of 8 Hertz other with the coupling strength of 5 Hertz and to the CH2 group with a coupling strength of 6 Hertz. Remember exactly the same problem was discussed and we generated multiplicity pattern.

The CH proton split is into a doublet because of this CH. One of the CH's and each of those split further into a doublet because of another CH and each of lines of this doublet of doublet splits is into a triplet because of coupling to CH2 group. Essentially the totally the spectrum of spectrum of CH, as far as the CH group is concerned, the multiplicity pattern is like doublet of doublet of triplets. Of course, in a given molecule I took the example for this.

Of course, you can also take the example for the multiplicity pattern how it comes for CH2 group; how it comes for this CH, etc. you can work out all those things later. So right now, I do not think that is a matter of too much of importance for us because this already you have learnt.

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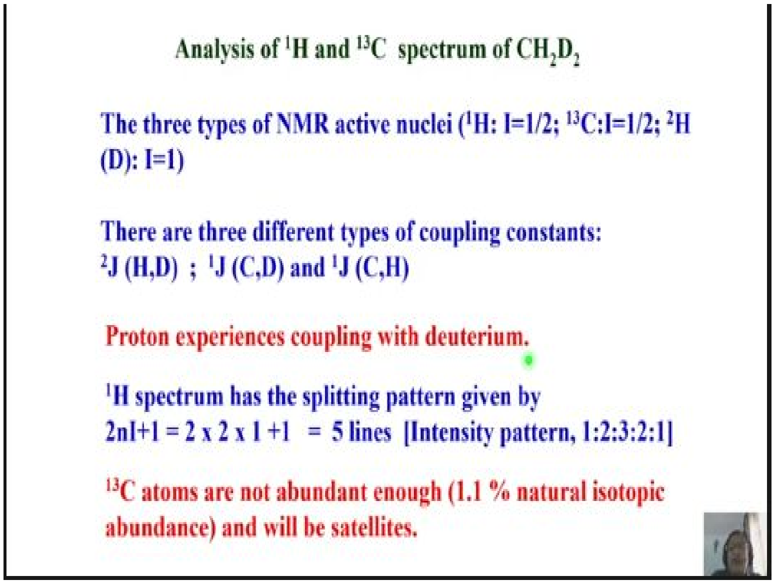

Analysis of ^{1}H and ^{13}C spectrum of CH_2D_2

The three types of NMR active nuclei (^{1}H: I=1/2; ^{13}C:I=1/2; ^{2}H (D): I=1)

There are three different types of coupling constants:
^{2}J (H,D) ; ^{1}J (C,D) and ^{1}J (C,H)

Proton experiences coupling with deuterium.

^{1}H spectrum has the splitting pattern given by
2nI+1 = 2 x 2 x 1 +1 = 5 lines [Intensity pattern, 1:2:3:2:1]

^{13}C atoms are not abundant enough (1.1 % natural isotopic abundance) and will be satellites.

Now, we will go into the analysis of spectrum, Okay, let us look at now the analysis of Proton and carbon 13 spectrum of a simple molecule like CH2D2.

Now with the knowledge we have gained, in the last few classes we have discussed a lot of things, you must be in a position to analyze the spectrum of this molecule. I do not give you the spectrum; you can generate a spectrum. We can find out what type of spectrum we should expect for this molecule.

I am now looking at proton spectrum, H2 of this molecule. But I will also give you information deuterium is spin 1 and carbon 13 natural abundance is 1% that is spin half. This information is sufficient for us to generate the spectrum; for proton spectrum of this molecule and also carbon 13 spectrum. We are studying this molecule in the natural abundance of carbon 13; remember it is not a labeled system. Carbon 13 is in it is natural abundance and we are trying to analyze the spectrum.

Let us get the proton spectrum. This information is given there are three types of nuclei possible in this molecule, there are three different NMR active nuclei. Carbon 13; proton and deuterium There can be CH coupling, there can be HD coupling and there can be CD coupling. All three are possible, all are one bond couplings, of course; actually is this also should be one D.

Now, let us look at the proton spectrum of this. Proton experiences coupling with the deuterium. We are not bothered about carbon 13 as you know, why? Because, its natural abundance is 1%. You look at major component, major isotope of carbon 12 attached, carbon 12 has magnetic moment zero, this one. So that will not couple to proton. Now how many peaks I expect for proton? Remember, this proton will be coupled to deuterium.

What is deuterium spin? Spin one, use the same family tree approach to this one, this deuterium, 2 deuterium's which are magnetically equivalent, will spit this proton or these two protons because of J coupling. Now if you put 2nI+1 what are going to get is; Put two there are two nuclei here two into two; spin of deuterium is one; plus one; so totally you are going to get five lines pattern.

But what is intensity pattern? Of course you can work out very easily; like there is a Pascal triangle which I gave for spin half nuclei, there is also a Pascal triangle for spin one nuclei, spin 3/2 nuclei etc. Now without going into that, I will tell you how the intensity pattern of this proton is split because of this two deuterium, equivalent deuterium will be 1, 2, 3, 2, 1 multiplet. Of course, carbon 13 as I said 1%, it will not split. That is the spectrum of proton compared to deuterium.

Now I look for the Carbon 13 spectrum, what type of spectrum we are going to get for carbon? Of course we discuss more about carbon NMR in next one or two classes. In depth, I will tell you a lot about carbon 13 NMR. At the moment let us consider that we know something. Similar to analysis of proton spectrum, we can generate carbon 13 NMR spectrum, just by looking at this splitting pattern.

When you look for the carbon 13 NMR, remember, you are not now worried about 12C isotopomer, you are directly looking for carbon 13 isotopmer. When I am looking for proton you have to say that there are 99% of the molecule with carbon 12 and 1% of the molecule carbon 13 isotopomer. But now you are directly looking at carbon 13, there is no question of looking for satellites; and all those things like I said earlier. So what are you going to get here?

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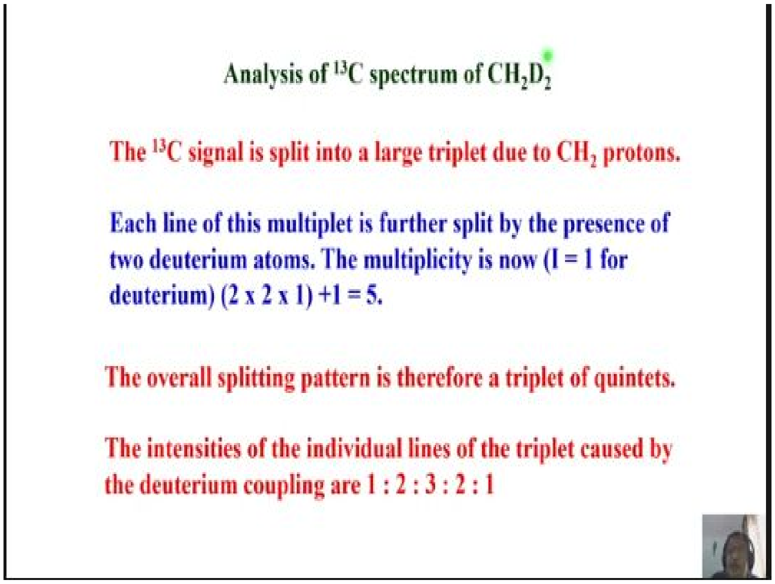

Analysis of ^{13}C spectrum of CH_2D_2

The ^{13}C signal is split into a large triplet due to CH_2 protons.

Each line of this multiplet is further split by the presence of two deuterium atoms. The multiplicity is now (I = 1 for deuterium) (2 x 2 x 1) +1 = 5.

The overall splitting pattern is therefore a triplet of quintets.

The intensities of the individual lines of the triplet caused by the deuterium coupling are 1 : 2 : 3 : 2 : 1

The carbon 13 is split by proton; two equivalent protons, it will become a triplet. Again remember 2nI+1 rule apply; This, direct detection of carbon 13, though in natural abundance, is split by protons into a triplet. This we have observed already; so it is going to be triplet. But now deuterium is also coupled. This is not simple triplet here; then what is going to happen? Each line of this split, carbon 13 triplet, is split into 5 lines of deuterium.

Why it split into 5 lines? I told you in the previous example of proton. Like it split proton into five lines these two equivalents deuterium also split carbon 13 into five line pattern. So how many lines you are going to get. You get triplet for carbon, due to proton coupling, and each line of this triplet is split into a pentet like 1, 2, 3, 2, 1 intensity. So you get 15 lines for carbon 13.

One group of lines 1, 2, 3, 2, 1, and other one and another one, but to remind you, the central peak has double the intensity because carbon 13 is split by 1: 2 : 1 triplet by proton. That pattern remains the same; but each one of this triplet is further split into 5 lines, that is all. So totally you are going to get 15 lines for this Carbon 13, very interesting right? It is a simple molecule remember?

Now I can also ask a question; what happens if I see deuterium. Let us take the example; I will looked at the proton spectrum, I looked at the Carbon 13 spectrum; now I am going to look at deuterium spectrum, what do I get? Now carbon 13 is in natural abundance here. Assume that its abundance is small and it is not going to split this deuterium. So what are you going to get? This is split by two equivalent protons ,into a triplet; it will become a triplet that is all.

It will become a triplet. Now all the three nuclei we can study here; and we can generate the multiplicity pattern. This is how we can analyze spectrum of even a small molecule with several nuclei present.

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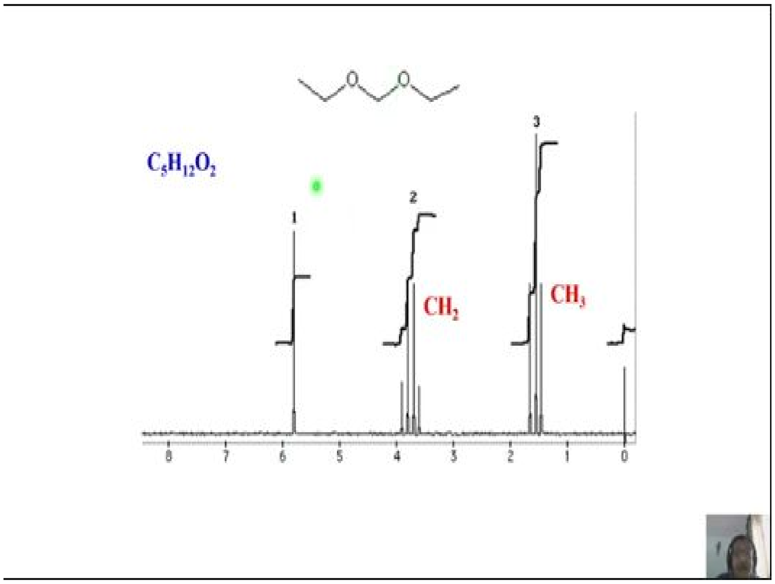

Now we start with a simple example. This is a very famous spectrum, which you will see in most of the textbooks. What could be this spectrum, what could be the molecule which gives a spectrum like this; if I ask this question by giving this spectrum, look at it you have a triplet. You have a quartet and a singlet. Common sense tells me this triplet when it is coming with intensity of 1:2:1, I will say this must be attached to a CH2 group. As a consequence CH2 splits this peak, this proton, whatever it is, into a triplet. Similarly, when I say there is a quartet of intensity 1:3:3:1, this proton must be attached to a CH3, which splits this proton in to a quartet, you understand? This is split into a triplet because of CH2; this is split into a quartet because of CH3. This is a proton which is not split by any other protons, it gives rise a singlet.

So you can find out the intensity also, this is integral intensity values, this is one, two and three, This also tells me the number of protons present in this group is one, number of protons present this group is two, and the number of protons present in this group is three, Am I right? It is true but I am not telling it is absolute number. It could be more it could be a multiple, for example, 2, 4, 6 is also allowed, ratio of the multiplicity of this three groups of peaks are 1:2:3.

You consider like that, consider the ratio of this proton to this proton to this proton, is 1 : 2 : 3, because it can be CH_2 to this can be some four protons, this can be six protons, it is possible. Now what is the first guess for this molecule, for this type of spectrum. Of course CH_3-CH_2-OH you could think of that, where CH_3 is split into a triplet, because of CH_2, CH_2 is split into a quartet because of CH_3, OH is not split by either of them, that is what we expect right. So it is quite likely this could be the spectrum of ethyl alcohol.

I have not given you the molecular formula or the molecular structure also. let us see now molecular formula is not C_2H_5OH; it is $C_5H_{12}O_2$. Spectrum looks identical to ethyl alcohol spectrum, but the molecular formula is different. So the analysis is correct, there is a CH_3 group there is a CH_2 group and some uncoupled proton, need not be OH, it could be CH or something is there.

So how do you now tell me what is the structure of this molecule? So one thing, in this case I will give you the structure. This is structure of the molecule. Look at this structure, now there is a perfect symmetry along this axis. So this is CH_3 group. This is CH_3 group. This is CH_2. This is CH_2 and this is CH_2. Now this CH_3, is the terminal CH_3, this and this are identical; there is a chemical equivalence because of symmetry.

So essentially molecule has only three groups of protons; one, two and three, that is all. So this one; now there is a coupling between them there is a single chemical bond here; because of that this CH_3 is split into a triplet because of the CH_2, correct? it is understandable and this CH_2 is split to the quartet because of this CH_3, that is correct. What about this CH_2? It is separated by two or three bonds it is not experiencing coupling with this CH_2 or this CH_3. So the CH_2 uncoupled to any of these groups is a single peak. But now intensity ratios 1 :2 : 3.

If I take this proton as number two, there are two protons. This is 2 + 2, 4 protons, this is 3 + 3, 6 protons. It agrees with the intensity ratio it is 1 : 2 : 3. This is not a single proton but it is a CH2 protons, in which case the uncoupled CH2, then you can get intensity ratio perfectly as 1 : 2 : 3.

So, we could analyze this spectrum and you can interpret it for a particular molecule if you know the formula, and if you know its structure also. So this is very easy to interpret, this is for CH2 group, that one.

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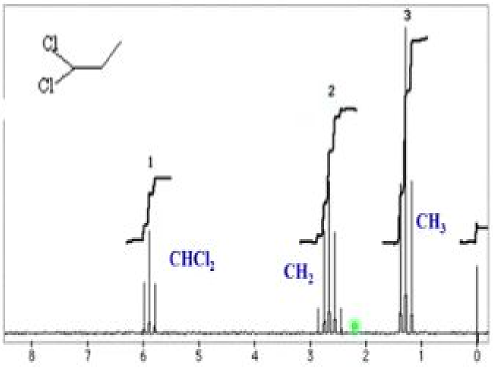
$C_3H_6Cl_2$



Now similar spectrum is there, I will give you another Molecule and molecular formula is also given C3H6Cl2. Now tell me how do you interpret this spectrum? Remember, just carefully look at this spectrum, this is a triplet, this is 1, 2, 3, 4, 5; 5 line pattern is a pentet. Remember I told you when do we get the pentet when we interpreted the multiplicity pattern and the scalar couplings, that is why I introduce lots of multiplicity patterns for you. So that looking at this spectrum, you know what it is. So we get a multiplicity pattern it is pentet here; and there is one group, which is a triplet. But again intensity ratio is 1 : 2 : 3. Interesting, this also looks like a ethyl alcohol spectrum but and unfortunately it is not ethyl alcohol, because it is formula given is different. Now how do you understand this? this is one proton, two protons and three protons? And this is the formula if you write, see what is happening here.

This is CH3 group. This CH3 is split into a triplet because of CH2; here two protons; two equivalent protons are present here, CH2 group. This will split this CH3 into a triplet, correct? And in this there are three protons, terminal CH3, intensity is three. What about this one? This is CH2 group, it is coupled to CH3. As a consequence it will split this CH2 into a quartet use the 2nI+1 rule, it is a quartet, 1,3,3,1 quartet. But that is not all, this CH2 is also coupled to the CH proton. What does it mean? What will happen now? If you look at this quartet each line of this quartet is further split into a doublet because of the CH proton. So what will happen you are not going to get only four lines, a quartet of intensity 1,3,3,1 you are going to get 8 lines, 8 eight lines in such a way, 1,3,3,1 ratio is still maintained; a doublet and a doublet into a doublet of intensity 1 : 1, 3 :3, 3 : 3, 1 : 1.

But in reality there is going to be a overlap. It is not distinctly different couplings, if the couplings are very much different, it would have got that distinctly different pattern a small doublet a big doublet,big doublet and the small doublet of same ratio 1 : 3: 3 : 1. But now there is a overlap of peaks. As a consequence a quarte, each line of the quarter is split into a doublet, which is overlapped and gives a pentet pattern.

Please recollect what I said about the pentet, multiplicity pattern, so it is a pentet pattern. What about this CH? This CH is experiencing coupling with CH2. What will happen? then it will become a triplet but now intensity ratio agrees. It is one proton, it is CH; two protons CH2, you say CH3, three protons here. So intensity ratio agrees, multiplicity pattern also agrees, now you know how to interpret. Sometimes very simple molecule, it can be complicated when you look at the spectrum, you will be wondering, what is the CH3 coming? then immediately you say CH attached to CH2, you know, what is this pentet ? you must understand immediately there must be a proton coupled to two types of protons, that is how you should start your analysis. I hope you agree with me, you are all with me.

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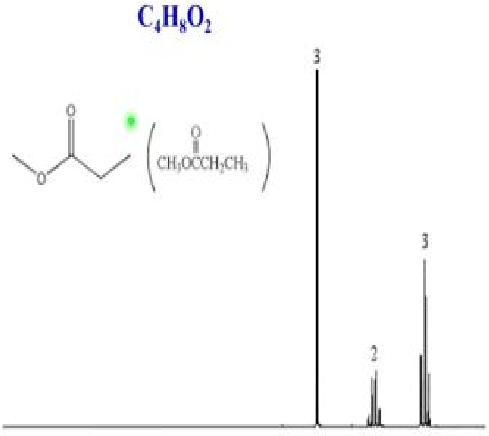

Now I will take this molecule another molecule. Formula is also given C4H8O2 again triplet quartet and a singlet. But now the intensity ratios are different. This is three, two, three. One first conclusion you can draw now by looking at this spectrum is, there must be CH3 coupled to CH2 like in the previous example, so it is a triplet. Then this CH2 is coupled to CH3; it must be a quartet, and what about this one? why it is three intensity? and also no splitting here.

Let us see the molecular formula. This is the molecular formula, very interesting right? Now, this is a CH3 protons, this is CH3 group, is split by CH2 in to a triplet; this is split into a quartet because of this here; so these two are understandable. Now, immediately look at this intensity and also it comes down field in the chemical shift, this is far away, coming down field. Then you must understand 3 protons if they are present in a single line, must be a CH3 group, that too without splitting, only 1 peak of the intensity 3, without any splitting means it must be a CH3 group.

But since it is coming to the down field, you must think it is attached to a electronegative group, and generally methoxy groups come in this region. As a consequence, you can immediately say it is a OCH3 group. So this is very easily interpret this spectrum, this is CH3 group this is CH2 and this must be OCH3. Simple spectrum we should know now how to interpret. We can interpret this one, also now we will not go into this; this is also not difficult we will not go into this.

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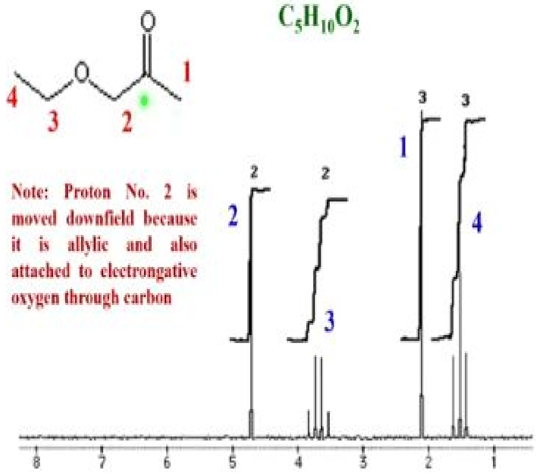

$C_5H_{10}O_2$

Note: Proton No. 2 is moved downfield because it is allylic and also attached to electrongative oxygen through carbon

Let us take this molecule, something interesting is there. Now I am giving you the molecular formula C5H10O2 and spectrum is very simple. Look at this spectrum, very simple. There is one CH3 group or whatever it is, one single peak of intensity three. There is one group of multiplicity with intensity 3, there is one multiplet of intensity 2, and 1 singlet with intensity two. Now we have to generate the molecular structure, for this to get the structure, and then make the assignment of the peaks.

As usual CH3 and CH2 must be there, that is the first guess; because it is a triplet and this is a quartet for this must be CH2 and this must be CH3; intensity ratio agrees 2 : 3. But how do you account for single peak with three and two intensities? Are we in the right track? We do not know. Let us look at this structure now; very interesting again. What is happening here, this is a terminal proton, a terminal CH3 here and it is coupled to CH2 here.

As a consequence this is a triplet and this CH2 is a quartet, so intensity ratio also perfectly agrees. And if you look at this molecule, we have a CH2 group here, which is in between this and this, separated by O here and double bond O, and these two protons, the CH2 protons do not experience any coupling with this group or this group. So what happen this remains a singlet and it is a CH2 protons as a consequence it gives a singlet of intensity 2.

So, this can be accounted for CH2 protons. As I said in the previous case, there is a OCH3 group it is not OCH3, C double bond O CH3 is there. This CH3 is not coupled to anything and remains a singlet, of intensity three. very clear right? So analysis becomes very simple now; you make this as proton two, I have number the protons here, you can assign the peaks with the same numbering, this is the proton 1 uncoupled and do not couple to anything, and this is proton 2 do not couple to anything, this is proton 2.

The CH2 is coupled to CH3, this is CH3 coupled to CH2; as a consequence there is multiplication. So very simple analysis, this is the way we can go ahead and start analyzing the spectrum very easily. Now why this proton 2 has moved to down field, this another important question we can answer, because you have discussed a lot about chemical shifts, when you attach the electro negative atom, what happens and everything.

Remember proton 2 is moved down field because it is allylic proton and also attached to electronegative oxygen through carbon. As a consequence this proton moves very much down.

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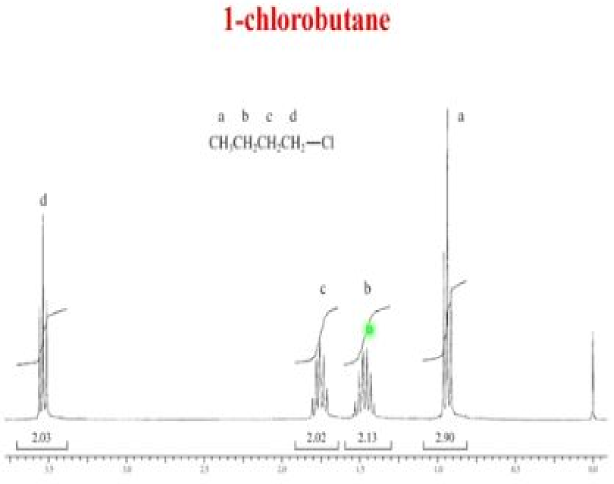
1-chlorobutane

Now, this is a spectrum taken from the book of Pavia, fourth edition; Let us see how do you interpret this spectrum? This molecule is 1-chlorobutane, that is chlorine attached to one position. Now as a consequence what happens, there is no symmetry here, if it would have been

CH3 then there would have symmetry in the molecule. Now just because you are knocked off a proton and attached chlorine ere, the symmetry is broken.

Now how many groups of protons are present here, there are four different groups of protons here. CH3, CH2, CH2, CH2; and I remember I took the example when there is a electronegative atom is attached how the chemical shift moves. One which is directly attached to the electro negative atom, this withdraws electrons here. As a consequence, this get deshielded I told you, so this has to come down field.

Look at the spectrum there is only one group of protons, one group of peaks, which is coming down field. This triplet must be for CH2. Of course this CH3 protons comes here. Why it is triplet, you can look at the molecule now, it is attached to CH2. As a consequence, this proton D has to be a triplet, correct, very well. We understood. This is a triplet. So this is attached. What is the next one? Remember the terminal CH3, it is easy to make the assignment.

Look at the CH3 here, always CH3 comes in the high field region. This CH3 because it is coming here, look at the intensity given here, this is nearly three intensity, so this must be a CH3 peak. Looking at intensity also we can say this CH3 group. Further why it is a triplet because it is attached to proton B which is CH2, because CH2 splits this CH3 into a triplet, very clear. Now we have to understand B and C, this is slightly tricky.

Please understand, I do not have to explain looking at the pattern, we should say which is B and C. Both are two intensity right? Both are 2 intensity. If I do not tell you which is B and C, look at the multiplicity pattern you can say, you know, why? Look at this proton B this proton experiences coupling with CH3 group and CH2 groups. What will happen then? This CH2 will become a quartet, because of CH3, right? 1 : 3 : 3: 1 intensity quartet, but each line of the quartet is split in to triplet because of this CH2 protons.

In both the cases you have to apply 2nI+1 rule, so what will happen 1, 3, 3, 1 quartet, each line of the quartet is split into a triplet. What did I say for this one? It is quartet of triplets, depending upon the coupling strength which coupling is larger, if this coupling is larger; it is triplets of quartet. So it depends whatever you want, since we do not know the coupling. But the interesting situation, what happens here is, as a consequence of several overlaps here look at this pattern here, this is more complex than the other one, this must be the proton attached to CH3 and CH2 very easily you can assign this to B.

Look at this group now, this group of multiplicity. This also has proton 2 intensity wise, You assigned this, you assigned this, and you assigned this. Then this must be the one leftover. True, well then what is the multiplicity? why it is coming? Remember this CH2 experiences the coupling with this CH2 and also this CH2, so what is a pattern? because of coupling with these CH2, it is a triplet, and each line of the triplet is split further into a triplet, because of this CH2.

As a consequence, you see some of the lines are overlapping, you get a pentet. This is what, we generated the pentet pattern, you know? Remember, when I was explaining the multiplicity. I generated sextet, pentet, septet, various peaks I generated. This is the reason why I spend the extensive time on that to make you people understand. So now you can look at it this has to be the CH2 this one, which is split into triplet of triplets; this is quartet of triplet, this is a triplet and a triplet.

So intensity clearly agrees 2 intensity, 2 intensity, 2 intensity and 3 intensity very nicely you can interpret this spectrum. You can also use your knowledge of chemical shift with electronegative substituent, you say this comes down and CH3 comes up. Only confusion was between CH2 which is which, that you look at the multiplicity pattern. Very simple molecule, you see so much of information, you can get.

You can use knowledge of chemical shift CH3 comes, here and CH2 attach the problem comes down field and the multiplicity pattern and intensity pattern you can utilize,e area of the peak and also for assigning B and C use the, pattern you get, like this pentet, if it is more complex depending upon how the splitting arises, as how the multiplicity comes because of coupling with neighbors, you can even make the assignment.

So all the information which I gave you about chemicals shift, coupling, multiplicity patterns everything could be utilized here to analyze the spectrum. The simple molecule I gave, you were able to analyse. I hope. What I am going to do is, I will stop with this analysis today, we come back tomorrow and continue with the interpretation of more complex molecules. In the next one class are two class I spend more time in analysis.

So that you get to feel for analysis, finally you will get a molecule of your interests, you synthesize in chemistry lab come back and take this spectrum of an unknown molecule. The molecular structure is known, spectrum is known, you can interpret, but you must be in the position to analyze interpret the spectrum of unknown molecule which is interesting. So we have to know how to interpret this spectrum and get the structure. So we will try to get into more and more analysis, couple of more spectra in the next 1or 2 classes.