Principles and Applications of NMR spectroscopy
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Module 4
Lecture No 17

So we will continue in this class with analysis of 1D proton spectrum uhh. We looked at some five examples of how a given a spectrum and only the molecular composition we can figure out try to figure out the possible structure which fits the spectrum. of course if more data available to us like IR and carbon spectrum it will be the useful and but in absence of that also we can get the fair ideaof what the spectrum could be. So we will continue with thus that in this class. So let us start from this example number six.

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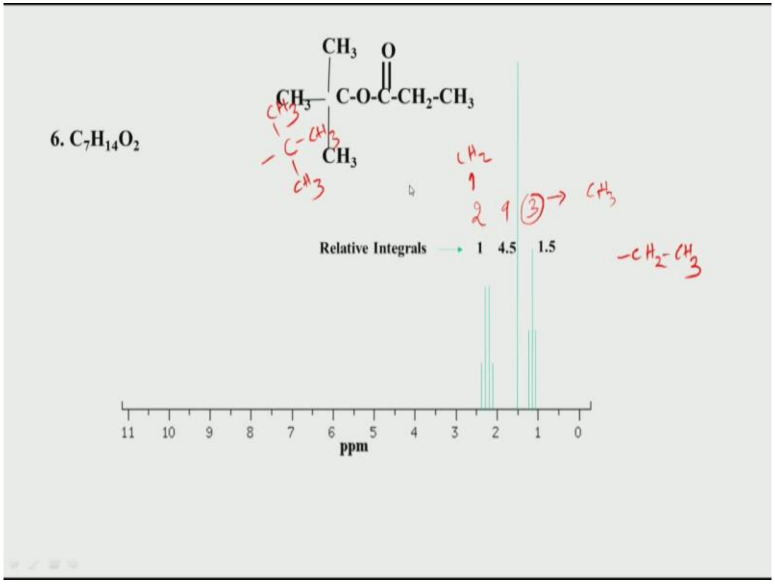

6. $C_7H_{14}O_2$

Relative Integrals → 1 4.5 1.5

So here this is the molecular formula or the composition given to us. So there are fourteen hydrogens and two oxygens, seven carbons. And this is the spectrum. So if you look at now this relative intensity it is very interesting that they know it is basically giving a fractional integral and this is essentially there are triplet singlet and a quartet. Now the question is how do we interpret this integral which is fractional?

So remember again as we discussed saw in the last class in NMR all you get is what is called relative integrations. Unless you take a reference and then compute, calculate quantify you will get the absolute value but if you look at only within this spectra within this molecule, it is only a relative value which you will get. So then one has to take a judgment on how to analyse this. So but I expect let us say 14 protons ok. But if you add up this 4 . 5 + 1 . 5 + 1, it adds up to seven.

So what it means is if I want to get 14 I have to multiply all of this with 2. If I multiply by 2, I will get 2 here, 9 here and 3 here. So that means there are 3 protons in this, 9 protons in this this tall peak and there are 2 protons in this. So that is how we have to basically interpret. So now if you look at it further now what is happing is we don't see any peak down field shifted around 4 5 ppm.

What it means is that I don't have any hydrogen. See remember if in the previous class in slides we saw that if a hydrogen is attached to carbon which is attached to oxygen directly OCH kind of a system then that H comes somewhere between 4 and 5. But that is not what we see here, all of them are in this upfield shifted. So that means they are there is no OCH in this particular case.

So this 9 protons has to be basically 3 methyl protons because CH3 CH3 CH3 only then you get 9. And it looks like that is all this 9 protons are chemically equivalent. Therefore they all are coming at the same place they are equal same chemical shift value and they are actually 9 peaks because 9 in 3 into 3 is 9.

And they seem to be singlet which means they are not coupled to any hydrogens. So if they were coupled to any other hydrogen you would expect to see multiplex like this. But because there is a singlet it means these is three CH3, which are kind of isolated means they are not coupled not any hydrogens. So what is that which can comes to our mind which will satisfy this particular condition and that is basically like this.

It could be a C which is attached to this three hydro three methyls. And therefore none of these methyls are therefore coupled to any protons. So if you look at this particular case you will see here that these three hydrogen are isolated because this C does not have any hydrogen. The nearest hydrogen could be somewhere here but that is very far away. So therefore these three hydrogens these three methyls are chemically equivalent ok.

And they are not coupled to any hydrogens so they expected we expected to get a singlet which is corresponding to nine nine, why nine? because we have multiplied this by two now to get 2 is to 9 is to 3. So this is one particular answer one answer for this origin of this peak. Now we have seen a quartet and a triplet ok. So typically if you multiply this by 2 you get 3. So what is basically has happened we have rescaled this integral.

So we have rescaled this, we call it 2, 9, 3. So now what it means is whenever you see three, it basically means this is CH3 and this is a CH2 because two hydrogens. Now this CH3 if it is coupled to this CH2 so suppose let us say I have this kind of a moiety then in that case what will happen is that this CH2 this CH2 is now coupled to this CH3. So this two protons will expect to get a quartet and that is what is here.

And similarly this CH3 when it is coupled to two protons you expect to get a triplet and that is what is this peak. So you see whenever you see a triplet and a quartet you typically expect that to be this particular system. And because this is coming in this zone between 0 to 2, 2 . 5 therefore it not directly attached, there is no oxygen here direct oxygen ok. But there is definitely electro negative system because this CH2 seems to be down field shifted somewhere around 2 . 5.

Normally this CH2 comes around 1 1 2 ppm. But because of something here that is showing up a 2 . 5. So what that could be, that could be a carbonyl. So if you have a carbonyl group and that carbonyl group will basically give you because of that this CH2 will get shifted and it will come at down field system. So we get a carbonyl and a CH2 CH3 moiety on one side and there is this one also present in the molecule.

So now if you join this together this is the structure what you would expect. You would expect this particular structure where there is a three CH3s attached to this carbon and this oxygen is attached, this carbon attached to this oxygen. And then this carbonyl CH2 CH3 is present. So this is what we discussed that it this CH2 remember this carbonyl you could say why don't we flip it to the other side? That means this O comes this side.

But then if that is so then this OCH2 would have come somewhere at 4 to 5 ppm. But that not what we are seeing here. Therefore this oxygen is this side and not on the other side. And therefore this is what we get. So now if you have a carbon spectrum again you could have figured out, because you have seen a quaternary. This is a quaternary carbon and that would have got down field shifted because of direct attaching to oxygen.

But even without that we can see that we can fit the structure to this spectrum. So this is an example.

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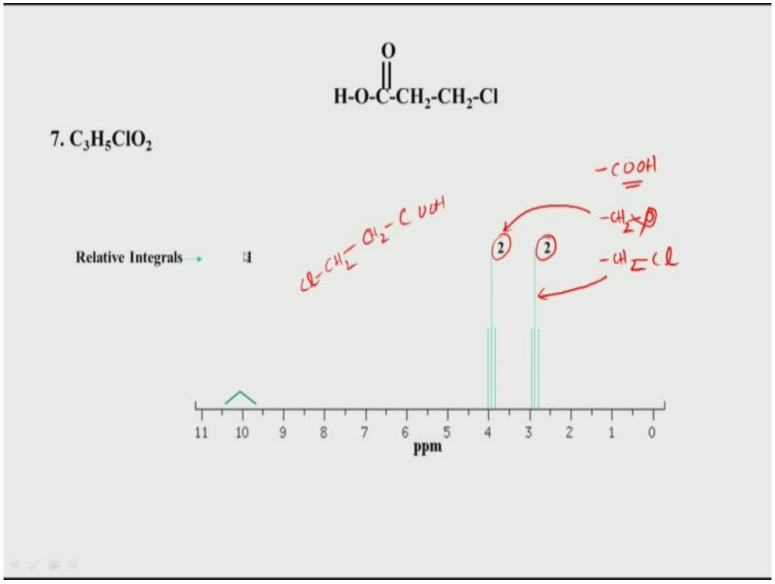

$H\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}Cl$

7. $C_3H_5ClO_2$

Relative Integrals → 1

Let us look at the next one where now we have an halogen in addition to two oxygens. So now here what is interesting is we are seeing a very down filed shifted peak at that the integral for that is one. So what it means is, it means it is an carboxylate the acid proton COOH. Again this you have to refer to that slide where we saw the carboxylate protons and aldehyde proton come very down field shifted.

Typically the carboxylate protons come to around 10 to 11 and that is what basically you are seeing here. you are seeing that there is a carboxylate proton here that is one proton. And then there is this these are 2, 2 each and that corresponds to five. And that is what we are seeing five here. So now you can see there is an four here uhh. So that means there is an attachment to a CH OCH group is present.

Only if there is a OCH group remember we expect to see a peak here somewhere between 4 to 5 ppm. So there is an OCH group. But then the next one, there is a chlorine and that also is a electro negative atom. So therefore there is a hydrogen which is attached a chlorine and that is also getting down field shifted. So what could be the structure which will satisfy this particular case?

So this could be like this. So we probably have a acid group. So let us build the structure probable. So this is has an acid group. And this has a CH2, there are two CH2 because both are proton, both are two hydrogens. But one is attached to oxygen and therefore it comes down field shifted. And one probably one probably is attached to Cl and it comes here. So if you look at this but there are two oxygens here.

There are two hydrogen but so it cannot be this possibility is ruled out because we already have taken care of these two hydrogen. So then what could be the structure which will satisfy this? This will basically has to be something like branch chain situation where we have this one. Let me draw this again. On this particular case, so basically there is a COOH. And there should be one CH2 and then there should be another CH2 attached to Cl.

So if you have this kind a situation then this particular molecule now this particular CH2 will be triplet because of this hydrogen and this CH2 will be triplet because of this hydrogen and this one may be down field shifted because of this and this also is down field shifted because of this. So if this is the case, yes so this is the structure of the molecule what we see, this is the answer. And we see this matches with the spectrum. So this CH2 which is attached to Cl is basically down field shifted here coming at this position and that CH2 which is attached to COOH is coming at 3 ppm because there is no oxygen.

Remember again if you look at the slide we look at if you have a CH2 Cl or C C attached to oxygen or halogen or C attached to nitrogen then you expect a down field shift of this proton. But here it is attached to oxygen it is attached to carbonyl not to directly to the oxygen. And carbonyl shifts not so much as down field in as you expect from Cl.

So this is what is the structure matching with this spectrum ok. So the main important point is that the peak is absorbed which corresponds to a carboxylate group.

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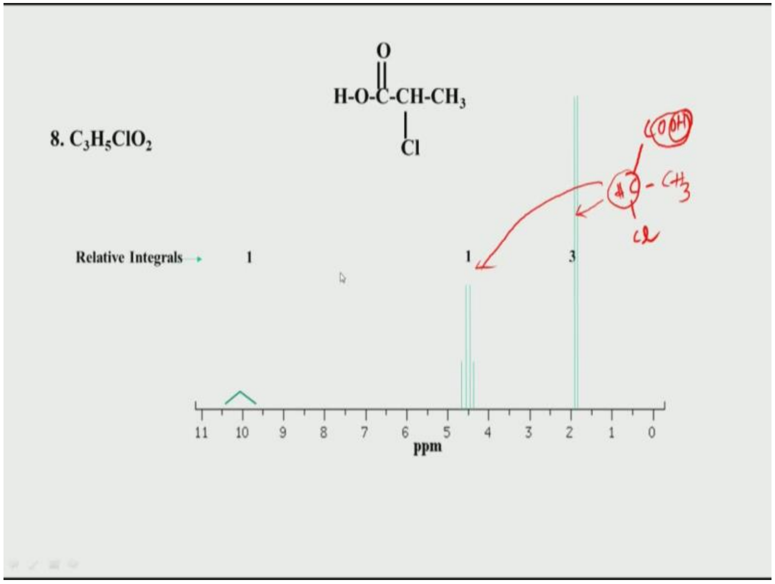

So let us look at the next example again here. This seems to be the same molecular formula as we saw in the previous slide. So that means it is a structural isomers of the com.. So in NMR the structural isomer can be distinguished by looking at a J multi plate pattern which you know if you use if you use IR spectroscopy a kind of difficult to figure out whether there is a branch chain because as far as the functional groups are concern if they are same IR spectroscopy cannot distinguish so much.

Similarly if you look at mass spec, mass spec of course will give you the same mass for both the systems. So regular mass spectrum, its spectrum will also will not be able to help in deciding whether isomer or not. So NMR is that way unique a nice technique where we can deduce as differentiate two structural isomers from each other.

So let us now look at this example. So again here we have a carboxylate acid group. That is why it a proton is single proton and coming very much downfield shifted. Now there is here instead of two triplets what we saw there is now a quartet and a doublet. So again remember this is CH3, so what it means? It means it is a methyl group CH3 methyl group and that is seems to be coupled to one hydrogen because only then you get a doublet ok.

And that one hydrogen is coupled in turn to this three. Remember if A is coupled to B, B is also coupled to A. So A one proton is also coupled to another proton, that proton is also coupled to this. So if one proton coupled to methyl group N + one rule means you should get a quartet and that is what you see ok. And look at the chemical shift value this coming between 4 and 5. So that means it could be directly attached to oxygen or it is attached to a halogen CCl or CC.

Remember halogen CCl or CCO or C N all have down field shifted values. So most likely if you now put all this together before we see the final answer let us try to work out what could be the structure. So basically now this says that I I expect a CH3 here. That is why I get three peaks three integral. But this is doublet, that means it is attached to CH only one hydrogens ok.

And this this CH is now coming down field shifted. Therefore it should be attached to a oxygen or a chlorine which is what we expect from the molecule. And further this is probably an acidic group here because only then you can explain that is OH COOH COOH peak coming at 12p, 10ppm. So let us see whether that is a correct answer. And if you see the structure this is what we see, this is exactly what is it shown here.

So you can see that this CH is now doublet quartet because it is coupled to three hydrogens that what we saw here. And this CH3 is coupled to only one. So this CH3 is a doublet and because of this attachment to this chlorine down it is down field shifted. Not only that it is this hydrogen is also attached to this carbon which is attached to carbonyl. CO double bond O and another O.

So therefore this CH, this particular hydrogen is down field shifted because of two electro negative groups, one is chlorine and another is this carboxylate group. And if you see look at this here even it is also down field shifted. Remember again methyl peaks are between zero to two. And if it is at the edge of this, that is around 2 ppm what it mean it is kind of mathoxy group or it could be not a methoxy sorry it could be a CH3 attached to carbonyl.

Or it could be CH3 attached to some more electro negative atom. But what is happening is this is because of this chlorine. There is electro negative inductive effect. So if you recollect the inductive effect even though the CH3 is not directly attached to chlorine there is a suppression by two bonds. And that also is enough to create a little bit de shielding of this hydrogens and that is what is causing this thing to come down filed shifted.

So to getting together you can see that the structural formula this satisfies our spectrum. So now in the next two examples uhh, we will look at aromatic group. So we have till now not analyse the aromatic systems. This are all been aliphatic with different functional groups. Now let us see what happens in the case of aromatic uhh.

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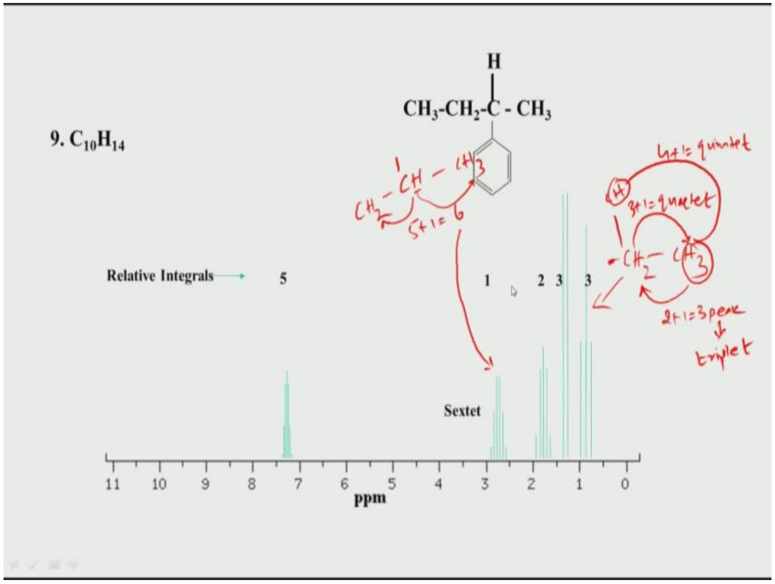

So there are different ways to figure out. So this is the molecular formula which we are going to look at composition. Now first thing is how do you know this aromatic ring here? Remember in chemistry there are rules which can tell you whether there is an aromatic system what is known as index of hydrogen efficiency. So that we will not go into this course.

Or you can use what is called rule of thirteen. These are the rules which typically chemist will use to figure out then the number of Pi bonds that is unsaturation, the degree of unsaturation and so on so there is one way to find out, if there is aromatic benzene ring present. Another way is in FM NMR you can look at this spectrum here. What will happen is you will get a little complicated peaks pattern somewhere between 7 to 8 ppm.

So this remember we saw this belongs to aromatic amino acid sorry aromatic groups function groups. But you may also get amides here. But here we don't see any nitrogen ans oxygen. So that means there is no amide possibility. So typically you see a bunch of peaks remember the word bunch of peaks coming clustering around 7 to 8 ppm immediately it it denotes signifies a presence of a aromatic ring.

So what we do normally is we don’t analyze the aromatic pattern. The reason being the that aromatic pattern there are two things, one is there is coupling, long range coupling present. So hydrogens are not only coupled to the three bond hydrogens which is what we typically we use when we analyse this type of data.

But it is also coupled to a long range five bonds away and so on. And there is these are strong coupling in the sense there are chemical difference between them is very small and the coupling is bigger than that so we have what is called strong coupling scenario. And therefore because of that the peak pattern what you see here in aromatic ring is not straight forward to interpret compare to what you see here.

So therefore what typically we do is, we bunch all the aromatics together and then get a common integral value for that. And that and also the presence of peaks at this is already tells us there is an aromatic system + the integral under the integral this together will give me the total integration value relative. And that is tells me that there are five proton. So essentially it means there is a phenyl ring the benzene the phenyl group.

And that is why there are five hydrogens. So that is what we interpret, how we interpret this side. And now coming back to here this is again the standard interpretation what we have been doing. So what we have here is a triplet, a doublet and here is a quintet and there is a sextet. Now sextet is six protons, so six protons can be six sorry five protons, five protons will give you a sestet. So what it means again remember a sextet can possibly come, a sextet can possibly come if you have a CH which is sandwich between H2 and a CH3.

Becaue only then this hydrogen is coupled to this and this five. So five + one six peaks. That is what you would expect for a sextet ok. So we will see this is how we can think about and then if you look at this methyl there are now there are two methyl groups here. Again remember always between 0 to 2 typically the methyls will come and therefore the methyl is there is remember there is no oxygen is here.

So there is no electro negative atom here. So that is why you don’t see any peak in this 4 to 5 ppm ok. So therefore this is all coming in this side. So they are all aliphatic spin systems, aliphatic protons and here you can see there is a triplet here. There is a methyl which that means it is attached to a CH2. Only if a methyl is attached to CH2 you expect the methyl to be a triplet.

So that means this could a particularly if you think about it this could probably be a CH3 attached to a CH2. That is so this will give two + one equal to three peaks. And this particular hydrogen is coupled to three. So three + one this will be quartet quartet. And this this will be a triplet.

So you see that is how we can think about it. And therefore this quartet and triplet which we are expecting could be this quartet. sorry this is a quintet here. So there is no quartet so that means this particular possibility all there. So this is a CH3 which is attached to a CH2 but the CH2 is now attached to some another hydrogens.

And that hydrogen is probably so that means this particular peak this particular carbon is attached to a HCH. So then 1 + 3, 4 so this is 4 + 1, quintet. And that could be probably this quintet here so what we are seeing ok. So that could be the quintet here. So we have basically a spins system like this CH3, CH2, CH.

Now remember we saw drew here CH, CH3, CH2. So that means this CH could be a part of this CH2, CH, CH3 ok. And where do we fit the aromatic ring? An aromatic ring probably is coming basically from attached to this CH2. Because that is a only way we will have valencies left ok? Because if this if I put a phenyl ring here then I can have a phenyl ring a CH2, a CH, CH3 and to this CH here is attached a CH2 CH3.

So if you put this structure all together this is what you get. So you see this CH is attached uhh. So basically this proton is getting me a quintet. So basically it has a CH. So it is attached to CH2 CH3 what is what we saw ok. But this CH2 is attached to this CH3. So therefore this CH2 is basically this here what we saw here. That this CH2 is having a 3 and 1, 4. So 4 + 1, 5. So 5 means quintet, so this CH2 is this quintet here ok. This is this mapping.

And this CH3 is expected to show a triplet, because of these two. And this CH3 and this CH3 here. And this CH3 now is attached to couple to one proton. So we expect a doublet and that is a doublet here. And finally this known CH is now coupled to 2 and 3, 5 + one, 6. That is what we saw here and that is a sextet.

So this is basically coming from here. Now because it is attached to aromatic group aromatic ring is also causes de shielding. Remember we saw that and because of the de shielding that hydrogen is coming around 3 ppm. Regularly it should come around between 2, 1 to 2 or 2 . 5. But normally it is comes, it is coming little bit down field shifted because of this aromatic ring.

So this is how the structure matches with the given spectrum ok.

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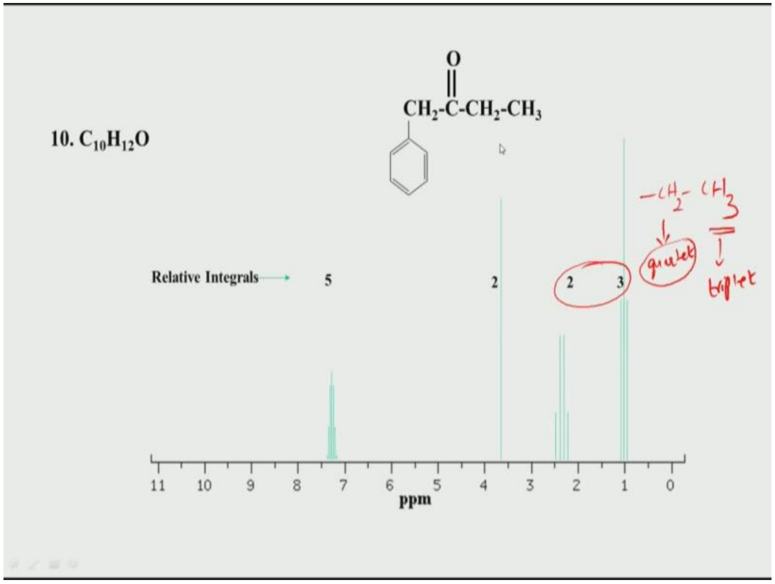

10. $C_{10}H_{12}O$

Let us look at another example where again we have an aromatic spin system aromatic group. How did we figure out there is aromatic group is basically based on again the bunch of peaks appearing around 7 ppm ok. So here you see the bunch of peaks and we don’t go into the detail analyses here. but what we will see is basically count the number relative proton. So there are 5 protons 2, 2 and 3.

So if you add them up it attaches to about 12 protons. And 12 protons is what we get here we expect. But now there is an oxygen group here. Earlier that was not there and that probably is causing this downfield shift of this ok. So what basically happening is that there is a CH2 because there is two now, this is not a methyl.

So there is a isolated CH2, which is attached to an oxygen. Ok and that is what is interesting that there is a isolated group and what is a particular case here you see a (quart) triplet and a quartet. So what could be happing is that now again if you analyze this data we have seen this coming many times that whenever we have this kind of a thing a you have a triplet and a quartet so it could be again something like this, something like this. That there is a CH2, CH and this is basically giving me a triplet and this is giving me a quartet.

But if that is so then I should not have anything here. No hydrogens should be present here. If there is hydrogen present here that will give rise to uh another de splitting but that is not the case. So that means there is no hydrogens there. So what could be? And then we here we have one here we have a phenyl ring, so we have a phenyl ring here. And there is a singlet which is coming basically because of a methylene group.

Because a methylene group only can have a two peaks you cannot expect a methyl group to have two peaks. and therefore what so let us see how we can put it together. I basically something like this. So here we can see that there is single oxygen. And because there is no direct oxygen attached this particular peak is not down field shifted.

So this is what is shown here. So this is two is an isolated CH2. Isolated because the nearest hydrogen to this coupling is this side is here and this side is here, the ortho proton. And all of themes are five bonds away. This is five bond away and this is more than around five or six point. So therefore we don’t expect any coupling. So this is an isolated CH2 methylene group. And that what is what is showing a singlet and it is down field shifted.

It is coming around 3 . 7, 3 . 8 because it is attached to CO on one side which is not very strongly electro negative like a direct oxygen. But definitely a more electron withdrawing because of this oxygen is here. And also the electron withdrawing or de shielding factor coming because of the benzene ring. So both of this together make this proton become down field shifted.

On this side, this is what we saw there is a CH2 and CH3 and that is what standard. Remember I said that it whenever you see a triplet methyl and a quartet somewhere in 2 ppm automatically it means if this is a group present. But this group is not attached to oxygen. That means it has to be attached to something else. But if it is attached to hydrogen, I mean a carbon containing hydrogen then you will not expect a quartet because this hydrogens is there was present that hydrogen would add to this.

So 3 + 1, 4 + so you would expect a quintet for this. So where if you have getting a quartet for this which means that there is no hydrogen coupled to this hydrogen this side. So that is only possible if there is a group like this. And if it is not an oxygen, it is a carbonyl group because a ketone group, because that will not down field shift this so much. So it comes around 2 . 5 ppm. So based on this consideration carbonyl group we can say that this CH2 is attached to CO and because based on a chemical shift.

And this side is basically this. So this is molecule which we can see. Now one thing is if we had again a carbon spectrum with us we would have actually looked at the carbonyl peak in NMR spectrum. And that actually gives you a very nice peak at around depending on the functional group around 180 to 200 ppm, 170 to 200. So there is a wide range of distribution. And depending upon whether it is an ester group or say (carbok) is a ketone group or if say carboxylate group or its aldehyde and so on based on that the carbonyl frequency is very specific and that will value. So this kind of brings to the end of this class. And we have look at basically 10 exam of how we can analyze a proton spectrum given only the, the composition and not the structure and how we can get the structure read the structure but remember this is a this an way exercise for you to understand how we can use this spectrum. But we don’t in really to practical in a real research we just rely on proton spectrum, we also use carbon 1 D spectrum.

We use IR spectrum. We use mass spectrums and so on, all this together are used. Remember how, why do we need a mass spectrum? Mass spectrum is useful because we can get the information of the unsaturation, degree of unsaturations. There is this famous rule of thirteen which is used to reduce the index of hydrogen efficiency or a basically getting the unsaturation. So that is useful. Then you know whether there is a ethylene bond.

Remember we have not looked at any pi bond analysis currently in this proton spectrum. We will take up the pi bond cases when we come to the carbon experiment. And in the in the so now what we will do in the next class we will go to start with a carbon 13 NMR where we will look at 1 D carbon 13 NMR. Again we will go through the process as we did for proton looking at what are the factors which affect the chemical shifts, what are the coupling patterns and so on.

Once we understand a how carbon spectrum is recorded and what kind of data we expected we can then combine with proton NMR. Again to look at some more examples of how to solve a structures, given only carbon and proton NMR. And then we will go on to 2D NMR.