Principles and Applications of NMR spectroscopy

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Module 4
Lecture No 16

Today we will look at analysis we will continue with the analysis of 1d NMR spectrum. in the last class we saw that given a structure of the molecule how do we interpret the spectrum? Today we will see that we will not have the structure to start with. We will have only the formula. we only know the contents of a carbon. How much many carbon, how many hydrogens and so on. So we will have to then when we are 1d NMR spectrum.

So now then our task will to find out the structure hich is compatible to the formula as well as compatible with the spectrum? And we will be only using the proton NMR spectrum as our uuh starting point, we will not have any other data with us. Typically when organic chemists analyze NMR data, for a new molecule they will also have the IR spectrum, the mass spectrum. As well as some idea of the structure. But let us see how we can analyze the data without knowing the structure that all.

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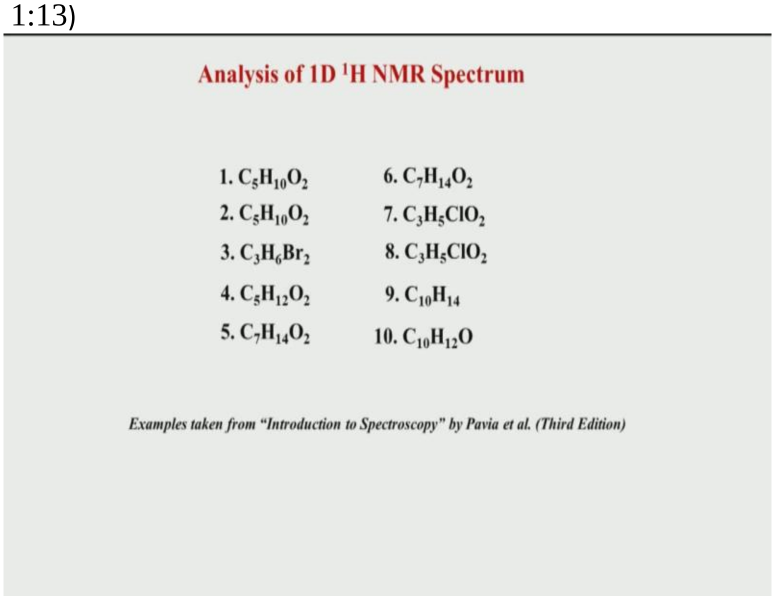

So these are the ten com.s which we will go through one by one. Because this will reveal different intricacies, different types of data possible. And all of these example have been taken from this book called introduction to spectroscopy by Pavia where actual spectrum actually has been shown. But we are not going to see actual spectra here. We will only look at the, the typically the schematic drawing of the spectrum. So let us start with a first com..

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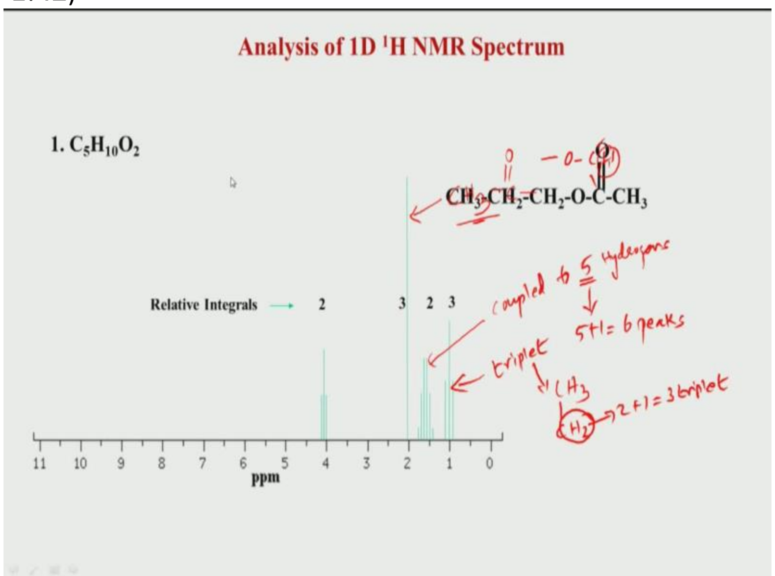

So this is the, the spectrum given to us, so we know this case this is the formula. This is what is the molecule which has been obtained by some other means. It could be through the chemical analysis and so on. So now this is a spectrum given to us. And our we want to figure out what is the structure which will be compatible with this formula as well as with this spectrum. So as we discussed in the last class the first thing you will have to see is the number of hydrogens. So if you see here four peaks main peaks of course remember the small peak are the multiplet of J values because of J coupling, that is the whole structure together is consider as one peak.

So here is one peak, one three and four peaks. So there are four peaks in this molecule which immediately tells us the, there are four different types of the hydrogen uh which you would expect in this molecule. And the next thing is to look at the J coupling. Uh you can see in the J coupling we are having a triplet here. This is basically a sextet that is there are six peaks. and this is a singlet and this is a triplet again.

So if you count the number of hydrogens in this is a integral. So if you see the integration is relative integration is shown here. See consider the two + three + five + seven + three ten which ten is the exactly the number which is here. So everything is matching well, we have the number of proton which we have corresponds to number proton in the molecule. And also the number of types of hydrogen is now four.

So the next task is to figure out what molecular structure will fit this particular spectrum. So we are doing the reverse approach that given a spectrum what could be the structure which matches this spectrum. So now let us see when you say that, when you that there is. First of all you can see the, this region remember always the methyl peaks comes in this particular region but in this what is happening? and remember thus one more.

If you remember this, we saw the general ranges of chemical shifts in the last class where we saw that if you oxygen attached to a carbon and carbon attached to hydrogen. And that hydrogen it is now will come down field shifted because of the oxygen. And this typically means that this particular peak could be coming from an OCH kind of a moiety. So uh we will right this down when we to derive the structure.

So basically we are having a kind of a OCH type of a moiety. Therefore this hydrogen will come down field shifted at around 4 ppm. and then we see this particular peak which showing a singlet and it is a three. So most likely this is an isolated CH3. That is why it is having three hydrogens. And it is not coupled to anybody so that means it is attached, not to attach to any coupled to any protons. So what that means is that most likely this is coupled now to a. This is attached to carbon, and this carbon does not have any hydrogens.

Because if it had any hydrogens in that case scenario it would have then coupled to that hydrogen. And this would not have been a singlet. The fact that this peak is a singlet means that it is attached to a CO. Therefore this C this CH3 is not having any hydrogen to couple with. So this is basically the way to interpret this particular peak which is showing a singlet the tall peak. And it is having integration three.

So three corresponds to three hydrogens. So now we are look we have looked at we can see that there are two things now. There is this particular functional group. And there is also COHCH here, which is shown in the right side. So now remains, the remaining two and three. This two basically means there are six peaks. So there are, this hydrogens whatever with this two hydrogen here so this two hydrogens coupled to five hydrogens because only five will give you five + one equal to six peaks.

So basically what this means is this particular hydrogen then which is showing a sextet which is one two six peak here basically it means it is coupled to five hydrogens. Only because if it is then is coupled to five according to five + one rule you will get you expect six peaks. And then this one is a triplet. So triplet so what this means there are three hydrogens now which are coupled to a this is basically three hydrogen means CH3. And it could be coupled to a CH2.

And because of this two, two + one equal to three triplet. So what has happened is this particular CH3 this particular CH3 what you see so will now we have we will explain this in more detail. So this particular CH3 peak because there are three hydrogens it showing the integration value of three. And it could be coupled to a CH2. I mean attached to a CH2. Because of it there is coupling between this two three and two between this methyl to methylene.

And because there are two hydrogens this methyl will now show a triplet. And that is what you see a triplet here. And this sextet is coming because of a hydrogen which is coupled to five hydrogens. And we expect this kind of a moiety. So if you put all this together. If you put all this together the structure which will satisfy this particular molecule is this shown here. So you see we have a CH3 CH2 CH2 co CH3. So basically yaa there is slight correction the C is carbonyl this C is attached to oxygen.

Not to this oxygens. So there is this got shifted. So basically it is a CH3 COO CH2 CH2 CH3. So what is basically it means that this CH3 is showing this singlet this tall singlet here. This C double bond O remember this has got shifted this has to come here. C double bond O is a ester group. And because of the ester group this oxygen is attached to this carbon and because of that this CH2 gets downfield shifted ok. This is the one which comes around here.

And this you see there are two hydrogens in this. And therefore so the molecule which satisfy now we have looked at the different peaks here. The molecule which will best satisfy all these conditions will be this. So now let us look at how this can be interpreted. So this is a CH3 peak which is an isolated peak which is not coupled to not hydrogens, so that is why you would expect a triplet here. So this is what we looked at.

And because it is attached to carbonyl group its value the CH3 peak which typically comes between zero to two comes at the downfield part because remember if you look back at the slide where we looked at the chemical shift dependence on the carbonyl group of the proton because of this electro negative group CO this CH3 peak which normally should come somewhere between zero to two comes at the edges of that. And it comes at little bit down field value. Now if you proceed to this part this oxygens is attached to this carbon.

And therefore this hydrogen is basically very much down field shifted around four ppm. And because it is now coupled this hydrogen is coupled to this particular two hydrogen this will show a triplet. And that is why you see a triplet here. And the integration says that there two hydrogen present here. Now if you go to this hydrogen now there are three hydrogen on one side and two on the other side so this hydrogens which are chemically equivalent this two protons will expect three + two + one six peaks that is sextet.

And that is what is shown here. And that is what we said that this particular peak is coming from a proton which is attached to five hydro coupled to five hydrogen and you can see there is a coupling to five hydrogens here. And finally what we are left with is this methyl peak which basically now is the peak which is showing here, this triplet here.

And this is coupled to CH2 that is two protons and that is what we saw here that there is a CH3 which is coupled to two protons. And therefore it is showing a triplet this is the triplet. So this is how we basically find out the structure based on the NMR spectrum that given the coupling pattern and integral we can reduce the structure, if the formula is if this given to us.

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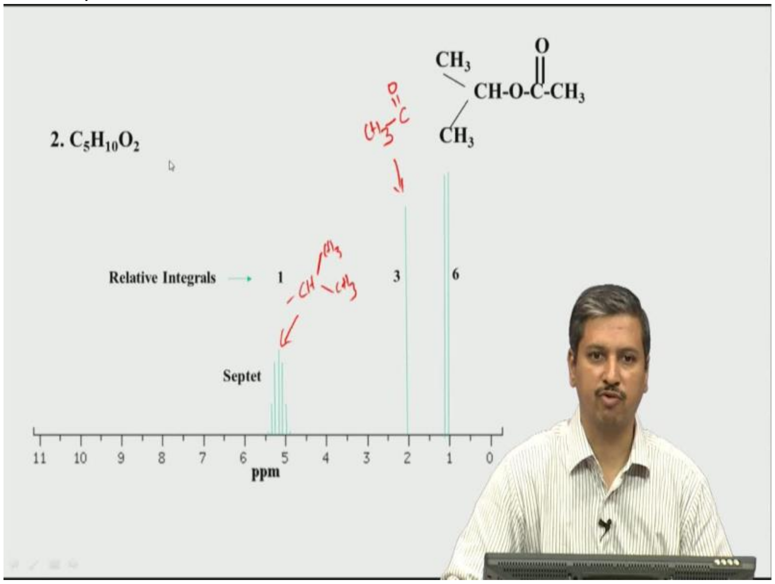

So let us look at the second example now. in this case we can again see there are ten hydrogens so if you look at the integral six + three nine. Nine + one is ten. So ten hydrogens are matching with this particular formula. Now let us analyze the chemical shift wise you see there is septet here seven peaks multiplet. So if you remember Pascal or n + one rule what it means is any proton the single proton which is having a septet basically means it is coupled to six hydrogens.

Now six hydrogens can be only possible if there are two methyl group CH3, CH3. So what it basically means is that we have a like this a spin system. This particular peak is coming probably because there is a CH which is one hydrogen coupled to two CH3s. So only then three, three + three six + one seven, you expect seven peaks for this. So basically this is an isopropyl moiety. So this is how we can interpret a given molecule.

So you can see that in basically you have an isopropyl moiety always remember you will expect to get seven peaks seven J peaks, J coupling peaks because of this n + one rule, six + one is seven. So this is what it could be in the molecule. If you look at this particular peak here it shows three again remember three proton means has to be CH3. So there is a methyl group here. And there is six here, mean again two methyl groups. And these two methyl group probably could be this two methyl groups.

Ok so these two six peaks together corresponds to this two peaks. This C, this isolated methyl is not coupled to any hydrogen and therefore it is a singlet. So again remember according to previous slide we saw that this probably comes from something like this one, this particular peak could be an isolated CH3 which is now having no hydrogen as coupling so it could be a CO. Ok so therefore this CH3 is an isolated case isolated hydrogen methyl group and therefore it does not show any coupling.

So now we can now add up all this together and come up with a probable structure. And looking one more where we can see is that this hydrogen he is now coming at 5 ppm, which means this hydrogen probably there is an oxygen here. Only if there is an oxygen here only then can this hydrogen become so much down field. So therefore there is an oxygen here and there is carbonyl here. So if you add this together what happens this is the structure.

So this is the structure of the com. which we corresponds to this formula. So you will see there are five carbons here, ten hydrogen here. And two oxygen groups according to this. So if you had a IR spectrum with you. IR spectrum would also give an indication of an ester group because of the vibrational frequencies of ester. If you have a carbon spectrum, carbon spectrum also will be also very useful here. But right now we are as we said we are relying only on the hydrogen.

When we include the carbon spectrum later on you will see that it becomes more easier to interpret because a carbonyl frequency in NMR for a ester group is much different what you get from a ketone group. Or what you expect from aldehyde. So based on the carbonyl peak also you can figure out whether ester group is present or it is a carboxylate groups and so on. So this is one second example where you see that a given molecular formula. And the spectrum you should be able to deduce the possible structure of the molecule.

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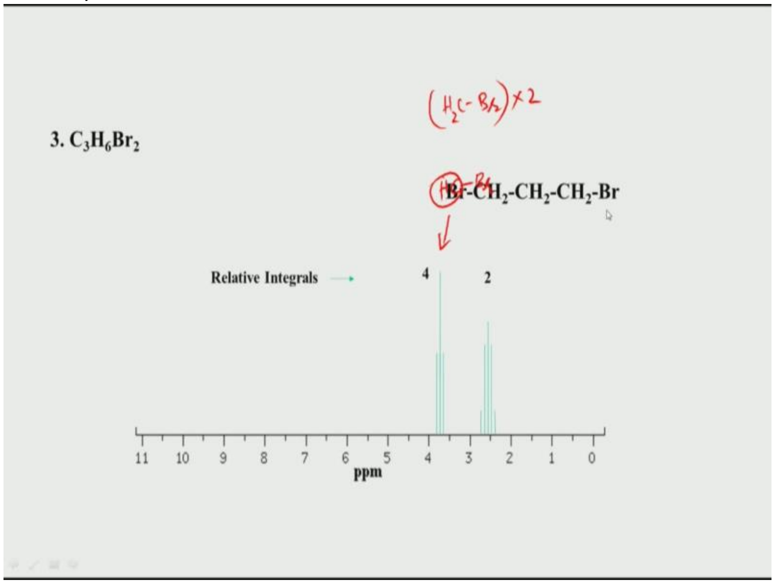

So let us go to the next example, so the previous two slides previous two examples were actually structural isomers. So they were isomers of each other. So in this case now we have a halogen com.. So now let us look at this molecular spectrum here. So here what do we see? We see a triplet an a pen quintet. So these are the five peaks here. So you can see one is to four is to six is to four is to one roughly in that particular ratio.

And area if we take the area the peak what it says is that this should be two corresponding to two hydrogens. And this is corresponding to four hydrogen. So if you add these two, four + two, you basically gets this six hydrogens which is satisfying this particular formula. So now let us see what happens.

So if you have again remember if you have a, bromine attached to a hydrogen because of the shielding that is called inductive effect this hydrogen any at hydrogen attached to carbon which attached to a bromine will be down filed shifted. So if you recollect again the slide where we saw the general ranges of chemical shifts values we see that a CCl, CBr or CI halogen com. typically comes somewhere between 3 to 4 ppm for that proton which is attached to that carbon so that probably what is happening here that this is there is hydrogen which is attached to carbon which attached to a bromine.

So basically what it means is that this particular peak this particular peak is probably coming from S proton. Which is attached to a bromine this hydrogen. So now we have four hydrogens like this. So four hydrogen basically what it means that we have basically a CH2br this whole thing two times ok. So if you have that type of a system then we would expect a four peaks we will expect a four we expect four because two into two is four.

And therefore this and Br there are two Br is coming twice here also in the molecular formula so therefore that it could be that this Br is they are repeated two times and the CH2 this the whole moiety is repeated two times. So that is why we are getting this four peaks. But then there is a triplet here. This is triplet. So what it means is this CH2 has to be coupled to another two hydrogens this hydrogen. Only then you expect according to N + one rule that this will be triplet.

So that mean what we expect in this molecule is that this whole unit is coupled to a CH2. And if that is so and then that CH2 could be this because there are two hydrogens. Therefore the CH2 which is coupled to this four hydrogens could be that. But then it has to have a quintet. A quintet means four coupling, four protons. Because four + one is five. And five is a quintet.

So that means a CH2 we are looking for. Which is coupled to this hydrogen has to be now in between this two. Because only then on either side it will have two hydrogens and therefore it will give a five. So let us look at the structure which is shown here. So this is what the structure is, this is CH2Br and this unit is appearing two times here also and here also so that that is what it shown.

That is what I mentioned here into two. And in the middle in the centre there is a CH2 group. And that CH2 group is this peak. How do we find out? We can say look at this, which coupled to this hydrogen on one side. And these two is coupled to this hydrogen another side. So two and two four. Four + one rule N + one rule gives five and five what we see here. So that corresponds to two and that integral also says three are two hydrogens which is two here.

Now coming to here these two and these two are equivalent because there is a symmetry. If you draw a line here an axis of symmetry, which separates this two that means this two are equivalent. So this CH2 same as this CH2. So therefore you expect same peak for this both this hydrogen and this hydrogen and two + two is four. And therefore the integral is four as far as J coupling is concerned both of thes hydrogens are coupled to the centre hydrogen, two hydrogens.

So therefore both of this will show a triplet because they are coupled to each of the, each of them is coupled to this hydrogen these two hydrogens, so therefore there is triplet. And that is what you see here, you get a triplet from the, the adjust. So we can see this is how we can interpret the presence of the coupling based on the coupling and the integration.

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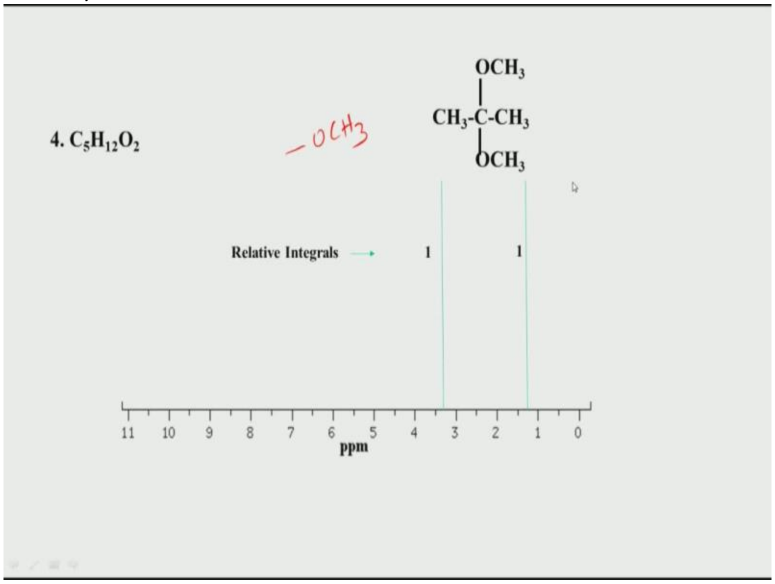

So we will look at the second next example which is here. Now this is a very interesting situation here. What is happening the is look at this case. This is C5 H12 O2. But here there are twelve hydrogens. But here we see only one and one. So if you add them up. It is only two hydrogens. So how can that be? So remember that is why very important the word what is written here is, relative integrals.

Relative integrals means it is relative to each other, they are equal. It does not tell you the number of hydrogens. So that is the biggest one of the one not biggest, I would say drawback in NMR is that it gives always relative, relative to each other. So if I take this as a reference I means in term of the height of the peak this height is same, area is same so I would say this is equal. But it does not tell me the resolute number of proton.

So there is a big is only if I had a another reference here. Let us say TMS which has twelve hydrogens. So if TMS peak if I know, that it corresponds to some X hydrogens relative to that this could have given me more correct picture. But that is what we don’t have. So now what we have to look at is how do we interpret this particular case. So we see there are twelve hydrogens.

So it could be the that there are six hydrogens here in this under this peak, this peak corresponds to six hydrogens. And this peak also corresponds to this hydrogens. So if that is so then it will match with our formula that six and six together is twelve hydrogens. And both are one is to one means they are equal six and six and therefore that adds up to twelve. So that is the most likely the scenario because we are only getting two.

So we can’t expect two hydrogens, this is six this whole peak corresponds to six proton. And this whole peaks corresponds to six protons. So now if there are six protons three six here how can six protons come under one peak? It automatically means there are two CH3 groups two methyl groups. They corresponds to one particular peak here. And there are another two methyl groups corresponding to this.

So that is how we have to interpret. Because there are six hydrogen, if I take here six hydrogen has to come from two protons. Similarly six hydrogens here. Sorry two methyl, similarly six hydrogens here has to come from two methyls. Now there are two oxygens remaining here. So how do we interpret here that two oxygen? So what it basically means now look at this value it is somewhat down field shifted.

So if this is a methyl peak remember methyl peak inside it always come between zero to two. If it is not attached the carbon of methyl is not attached to any oxygen. But if the carbon of the methyl is attached to an oxygen then it is comes here, that is called a methoxy. So a methoxy group is like this, a methoxy group is OCH3, this is methoxy.

So only if there is a methoxy group can the metyle come at downfield shifted and that is what we are seeing. We are seeing this is basically coming from a methoxy group. So that means they are two methoxy groups in my sample because two methoxy groups will corresponds to six hydrogens and that is what is coming from here. That means the remaining two are only CH3 because the oxygens if i put two, then it is already taking care of this oxygen.

So therefore putting all this together this is the structure which is most likely matching with this particular spectrum. So you can see there are two methoxy groups here, there are two methoxy and there are two isolated methyl groups. And this methyl is not coupled to this methyl because protons because there are very far away ok. and similarly this methyl is also equally far away. So this is very symmetrical structure. And because of the symmetry in the structure the two these two are equivalent these two methyls. And they together corresponds to this peak.

And this OHC OCH3 methoxy group OCH3 they are again six protons and they corresponds to this peak. And this is called a quaternary carbon and it does not have any hydrogens. So therefore you don't see any peak in the proton. But if you go to carbon spectrum, in a carbon you may be able to see peak for this. But remember that we are not looking at right now. We are only trying to get the structure based on hydrogen. So this is how we can interpret the hydrogen spectrum based on this.

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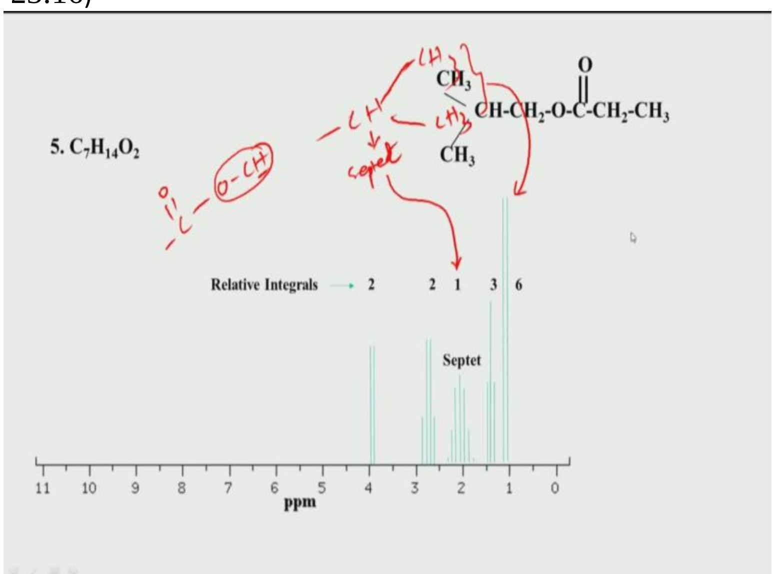

So we will look at the next example which is now this particular molecule. Now here it seems we are looking at the integral if you see and the spectrum it seems to add up properly. So there is nine + two, nine + one ten, welve and fourteen, so this is seems to fine matching well with thus one. Now let us see there are different and how many types of hydrogens are present? 1,2,3,4 and 5. So there are 5 types of hydrogen in this molecule.

And this molecule seems to be now having a five seven hydrogen, five hydrogen. Now if you look at this particular start from here there is the doublet is integral is six, relative integral is six. And if you look at this, there is one hydrogen which is a septet. So this we encountered in the a few some example a few slides back where we saw a septet there. So remember the septet we set is isopropyl group.

So what basically is this septet this septet is coming from isopropyl group. Only then this will give a septet. So this most likely is this particular peak which is showing to one proton similarly this two could be most slightly this because two CH3s are now this each of the CH3 what we are seeing can be a giving will give a doublet. So if you see this, each of this CH3, CH3 is coupled to this hydrogen. And therefore this CH3 will be a doublet what we are seeing here, this doublet.

And this septet is coming from this hydrogen. Now if you look at CH3 and remaining is 3 and 2. And again remember there is a downfield shifted proton and corresponding to two which means it is most likely attached to a oxygen directly. So OCH kind of a moiety. OCH we saw earlier can come from the ester group which is having like this. So basically it is OCH and there could be a CH2 something like this.

So here this CH this CH comes at a downfield shifted because of the oxygen attached to this to this particular. ok so this is basically this particular peak where there a two hydrogens. So I have written only one here. But there is two and it continues further. So if you put all this together this is the structure possible for this particular molecule because you can see here that we have now CH3 CH3 that is a and this CH isopropyl group.

And therefore this hydrogen where the arrow is here, that is giving the septet. And that is one proton and these two CH3s are the two doublets which we saw here earlier. So this is matches with that particular case. So remember always a septet if you see in your spectrum it automatically means an isopropyl group is most likely present. Of course this is not the final confirmation. One has to first build a structure and then figure out but a most likely the 90% of the time it could be because of this particular moiety and therefore you are getting a septet.

But if you expect this moiety then you should also expect the a doublet which is here like a proton which is of intensity six. Then you have a CH2 which is attached to oxygen and because of this this CH2 comes down field and because this CH2 this hydrogen is coupled only to one this hydrogen and therefore it is having a doublet ok. Now we will go to this particular case here CH2 CH3 here.

This CH3 is showing a triplet and this CH2 is showing a quartet. So in this manner we can see that there are seven hydrogens now 1,2,3,4,5,6,7. And there are basically two oxygens and the seventh fourteen proton ok. So in this way we can interpret this molecular structure.

We will further take it up in the next class more complicated molecular structure we will continue this. So we have looked at five examples. We will see five more examples and then we can actually get an idea of how this proton spectrum is analyses in absence of other data which has carbon spectrum or mass spectrum or IR spectrum.